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A STUDY OF SOME QUINOXALINE AND HALO-PYRIDINE COMPLEXES OF TRANSITION-METALS.

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November, 1967.

PART 2.

Chapters VII - XI.

Investigation of the Quinoxaline

Complexes and Conclusions.

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CHAPTER VII

SOME PROPERTIES OF THE 1:4-DIAZINES

& THEIR

REPORTED COMPLEXES

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468-473 The diazines have been known for some time Their aromatic 474,475 nature (see figure 7.0) has been confirmed but they have been little studied until the recent discovery of their chemotherapeutic 216,476-479 derivatives 185,480 Pyrazine and Quinoxaline are weak bases (see table 7.1), which 48ሰ are usually monoacidic They are potentially bidentate ligands, although the 1:4 arrangement of aza-atoms restricts such co-ordination to a bridging, rather than a chelating type. The molecules, being 220 M -electron-deficient, are more susceptible to nucleophilic, 480,481 than to electrophilic, attack On the basis of such reactivity, 480,481 the order of π -acceptor character Q > pyz > py and Q > A > Quin > py. is 220 482 These amines are easily reduced , and the order Q 7 4C1py 7 2Brpy of reduction potentials (E₀) probably reflects that of their π -acceptor 486. 483,484 Table 7.2 lists the known polarographic half-wave natures 485 (E_1) of these molecules, in decreasing order. reduction potentials The position of other ligands relative to this order may be roughly 228 interpolated, since it is known than halo-substituents generally raise, but alkyl- and aryl- substituents lower, reduction potentials.

487,488

It has been shown that mutually perpendicular \mathfrak{M} -systems do partially conjugate. This, and a slight twisting of the phenyl rings (towards the plane of the quinoxaline nucleus) permitted sterically, should make Dpq a poorer \mathfrak{M} -acceptor than Q. By analogy with 2- \mathcal{Q} py 185 184 (see table 7.1) the partial conjugation is expected to lead to a







b

Figure 7.0

Table 7.1

Base strength (pKa) of the quinoxalines, and some related molecules, at room temperature.

Compound	рКа	Compound	<u>pKa</u>
ру	5.32	4-NO ₂ py	1.39
Quin	4.89	3-NO ₂ Quin	1.03
2-Фру	4.48	2 Mq	0.95
ТМр	3.55	3-NO ₂ py	0.92
2,6-IMp	1.90	Pyz	0.65
2,5-IMp	1.85	Q	0.56
2-Мр	1.45		

Table 7.2

Reduction Potentials (volts) for some Heteroaromatic Molecules. The values are given for neutral or basic conditions and at room temperature.

Molecule	E _o	E1
4NO ₂ py		-0.28
P	-0.13	-0.36
Q	-0.64	-0.66
Dinq	-0.71	
A	-1.1	-0.79
Tmp		-0.98
4CNpy		-1.32
4C1py	-1.25	
2Brpy	-1.36	
2CNpy		-1.70
ру		-1.75
Anthracene		-1.90
Napth ålene		-2.46

slightly lower pKa value for Dpq relative to that of Q.

The T-7 T* electronic absorption bands of the diazines 220 are found at lower frequencies than those of their mono-azalogues. This is consistent with the reduction potentials in suggesting that the diazines are the better TT-acceptors. Table 7.3 lists the frequencies of the 'tails' of the electronic bands of the amines studied here (by reflectance (Dmq,Dpq, P and T), or in C Cl₄(0.2M) solution). This absorption is exceptional for Mq in extending well into the visible region.

The Complexes of Pyrazine

495 Lever, Lewis and Nyholm have reported the complexes of 496 168 497. substituted pyrazines with Cu(I) Ni(II) and Co(II) These complexes are briefly surveyed below, and listed in table 7.4 with their proposed stereochemistries.

Copper (I) complexes

The appearance of infrared bands at 1248 cm^{-1} , or 1075 cm^{-1} for 497the complexes of Mp or 2:5-Dmp, was used as an empirical criterion for the presence of monodentate amines. Thes e bands are probably due 498to the \mathcal{V}_{9a} or \mathcal{V}_1 vibrations which occur at 1232 cm⁻¹, or 1015 cm⁻¹ 496in the Raman spectrum of pyrazine. This criterion indentified the Cu(I) complexes as binuclear species involving bidentate amines.

Table 7.3

Absorption maxima (kK) for some heterocyclic amines.

Amine	Band maxima	ν* <u>1</u> 2
Q	6.Ontv; 8.8vw	~25.6
2-Mq	6.Ov; 15.4sh	~17.7
2:3+Dmq	5.7sh;6.Om;7.2w;8.6b,w;24.4sh	-26.7
2:3-Dpq	6.On;7.Ovw,b;8.8w	-25.6
Р	6.Om;6.9vw;7.2vw;8.9w;19.Osh,b;24.2vs;25.6sh	~22.2
Т	6.1m;7.3vw,b;9.1w	>28.6
2-Clpy	6.Ow	>28.6
2-Brpy	6.0w;21.0w	>28.6
3-Brpy	6.0w;25.0vw	>28.6
4-Clpy	6.0w;7.2vw;8.8vw;27.8sh.m	>28.6

* $v_{\frac{1}{2}}$ denotes the approximate frequency at which the $\pi \rightarrow \pi$ * band reaches half of its maximum intensity (measured as absorbance). The relative values of $v_{\frac{1}{2}}$ indicate the extent to which the band extends into the visible region.

Table 7.4

Stereochemistry of the complexes of Pyrazine.

Copper (I): Linear

		Cu ₂ I ₂ (pyz)	Cu ₂ (CN) ₂ (pyz)
Cu ₂ C1 ₂ Mp			Cu ₂ (CN) ₂ Mp
Cu ₂ C1 ₂ (2:5-Dmp)	CuBr ₂ (2:5-Dmp)		Cu ₂ (CN) ₂ (2:5Dmp)
Cu ₂ Cl ₂ (2:6-Dmp)	CuBr ₂ (2:6-Dmp)		
	Cu ₂ Br ₂ (Tmp)		Cu ₂ (CN) ₂ (Tmp)
Copper (II) : O	ztahedral_		
CuCl ₂ (pyz)			
<u>Nickel (II) : 0</u>	ztahedral		
NiCl ₂ (pyz) ₂	NiBr ₂ (pyz) ₂	NiI ₂ (pyz) ₂	Ni(NCS)2(pyz)2
NiCl2 ^{Mp} 4		`	
NiCl2 ^{Mp5}	NiBr2Mp5	$\text{NiI}_{2}^{\text{Mp}}$ 5	$Ni(NCS)_2^{Mp}$
		$NiI_2^{Mp}2$	$Ni(NCS)_2Mp_2$
NiCl ₂ Mp	NiBr2Mp		
Ni: Cl ₂ (2:5-Dmp)			
			Ni(NCS)2(2:6-Dmp)4
NiCl ₂ (2:6-Dmp) ₂	NiBr ₂ (2:6-Dmp) ₂		Ni(NCS)2(2:6-Dmp)2
Squa	re-Coplanar		
	NiBr ₂ (2:5-Dmp)	Nil ₂ (2:5-Dm	p)
		Nil ₂ (2:6-Dm	p)
		Nil ₂ (Tmp) ₂	

Table 7.4 cont.....

 $\frac{\text{Cobalt (II)}}{\text{CoCl}_{2}(\text{pyz})_{2}} : \frac{\text{CoBr}_{2}(\text{pyz})_{2}}{\text{CoBr}_{2}(\text{pyz})_{2}} : \frac{\text{CoI}_{2}(\text{pyz})_{2}}{\text{CoCl}_{2}(\text{pyz})}$ $\frac{\text{CoCl}_{2}^{M}\text{p}_{4}}{\text{Co}(\text{NCS})_{2}^{M}\text{p}_{5}}$ $\frac{\text{CoCl}_{2}(2:5;\text{Dmp})}{\text{CoCl}_{2}(2:5;\text{Dmp})}$ $\frac{\text{CoBr}_{2}(2:6-\text{Dmp})_{2}}{\text{CoBr}_{2}(2:6-\text{Dmp})_{2}}$

 $CoI_2(2:6-Dmp)_2$

* denotes dimeric structures.

496 Linear, monomeric structures (see figure 7.1) were proposed for these complexes on the basis that the C-N stretching frequencies 432,499 of the cyanides were too low to result from bridging anions.

500,501 Other complexes of d¹⁰ ions with pyrazines have been reported 502 and the crystal structure of AgNO (pyz) determined . This is based 3 upon both pyrazine- and nitrato-bridges.

Copper (II) Complexes

496 Lever, et al, have mentioned unstable complexes of the pyrazines 503with Cu(II). CuCl₂(pyz) has been reported by Reimann and Gordon and, on the basis of a single d-d band at 14kK, a polymeric octahedral 504structure suggested. This is similar to that proposed for CuCl₂Q (figure 7.6).

Nickel (II) complexes

395 168 and spectral properties were used Magnetic to assign octahedral or square-planar structures to these complexes. The bis-octahedral 187 of NiCl₂py species were thought to have similar structures to that (figure 3.2), the pyrazines being monodentate. Similar structures were for the octahedral mono-complexes in which NiX, chains were proposed bridged by bidentate amine molecules (see figure 7.2). The other octahedral complexes were monomeric, the pentakis-species involving four co-ordinated and one clathrated Mpmolecules.



Nil⁷₂ (Tmp) was a square-planar monomer (c.f. figure 3.3), but the remaining four-co-ordinate complexes consisted of chains involving bidentate amine molecules. Such a structure (see figure 7.3) has been 505 confirmed for NiBr₂(2:5-Dmp). The higher \mathcal{M} -acceptor character of the pyrazines relative to the pyridines was thought to lead to a preference of the former ligands for a square-planar configuration (in 189,190 which optimum \mathcal{M} -orbital overlap is achieved), and the latter for

152,198 The spectra of the octahedral complexes have been discussed and found to indicate more metal-ligand M-bonding than in the complexes of pyridines. Longer Ni-N bonds in the complexes of the sterically hindered ligands were suggested as the cause of the lower Dq values of these complexes relative to those of unhindered amines. Low Dq values were also found for those complexes which involved bridging amine molecules. This could be due to the effective cancellation of opposing dipole moments induced on the amines; or to the low M-acceptor nature of a molecule towards a second metal ion, when it is already accepting electrons from one metal ion.

497,506,507

Cobalt (II) Complexes

167 The spectral and magnetic data indicated tetrahedral or octahedral structures for these complexes. All the octahedral complexes 186 were polymeric, the bis-species having & -CoCl_py2-type structures



Figure 7.4

(figure 3.2), and the mono-species having additional amine bridges (c.f. figure 7.2).

The bis-tetrahedral complex $\operatorname{Col}_2(2:6\operatorname{Dmp})_2$ was monomeric (c.f. figure 3.3). The tetrahedral mono-complexes were probably halogen-bridge dimers (see figure 7.4), with the exception of $\operatorname{Col}_2(2:5\operatorname{Dmp})_2$ for which a polymeric structure (see figure 7.5) was proposed, with 508 amine bridges. Nelson, et al, have reported a tetrahedral isomer of $\operatorname{Cocl}_2(2:5\operatorname{Dmp})$ which appears to have this polymeric structure. A binuclear, amine-bridged structure was proposed for the tetrahedral complex $\operatorname{Cocl}_2(2:5\operatorname{Dmp})_{3/2}$.

Several octahedral-tetrahedral equilibria were studied in solution and found to involve solvent molecules.

Preliminary Studies of Quinoxaline Complexes

An initial survey with solutions of quinoxaline and of metal salts showed that complexes could be obtained with Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Cu(I), Ag(I) and Hg(II); but not easily with Fe(III), Zn(II), Tl(I) or Mg(II).

The complexes of copper (II) with unsubstituted quinoxaline were 504 reported by Underhill. Octahedral CuCl₂Q and CuBr₂Q were thought 495 to consist of polymeric sheets (see figure 7.6) like those of NiBr₂Mp (see figure 7.2), while Cu(OAc)₂Q had a binuclear structure like that⁵⁰⁹



Figure 7.5



Figure 7.6

of Cu(OAc), H₂O. Sulphato- and nitrato- complexes were also prepared. The complexes of Nickel (II) with unsubstituted quinoxaline have also 510.511 and their spectral and magnetic properties discussed. been reported 495 Polymeric octahedral structures, like that of NiBr, Mp (figure 7.2) were proposed for NiCl₂Q and NiBr₂Q. NiI₂Q was considered to be a square-Nil₂(Tmp)₂ (c.f. figure 3.3). These complexes, planar monymer like and those of Cu(II), Cu(I), and Co(II) are more fully discussed in Chapters 11,9,8 and 10. Figures 7.7 and 7.8 show other possible 183,197,275 structures for the MX L complexes. The first has been proposed for NiCl py, while the second is a variant of NiBr2Mp (figure 7.2) obtained by interleafing chains running in two perpendicular directions. Work on the complexes of Cr(III) and Mn(II) was abandoned because only impure complexes could be obtained. Complexes approximating to MnCl,Q and MnCl,Mq, were prepared from ethanolic solution ; while CrCl₃.6H₂C and excess Quinoxaline gave, from an acetone solution, a black residue of uncertain composition.

Infrared Spectra of the Quinoxalines

512

Katritzky's treatment of the vibrations of quinoxaline, along 513 with the work of Perkampus, have not alone been adequate to permit an 514,515 assignment of all the observed infrared bands. However, it is known 516,517 518-522 that the spectrum is related to those of quinoline naphthalene 498,523,524 525,527 pyrazine and pyridine , and this has allowed tentative





assignments to be made for the infrared bands of Q, Mq, Dmq and Dpq. These are given in tables 8.1 and 9.5. The notation used is 518 based upon that given for naphthalene. Quinoxaline has C symmetry (see Appendix A5), but the point groups of its derivatives depend on the exact orientation of the substituents.

<u>Chapter</u> 8

THE COMPLEXES OF COPPER (1) WITH QUINOXALINES

The complexes of copper (II) with the pyrazines often underwent spontaneous reduction to the binuclear copper (I) compounds ^{495, 496}. This behaviour was not observed (see chapter 9)for the copper (II) complexes with quinoxalines, and it was therefore decided to attempt to prepare the copper (I) species by other means. Further interest in these complexes arose from the possibility that their infrared spectra would be characteristic of the bidentate amines.

Most of the complexes listed in table 8.1 were prepared by direct synthesis from the amines and copper (I) halides. Attempts to prepare $\operatorname{Cu}_{22}^{C1}_{Q}$ by this method gave mixtures of yellow, orange and brown products. A titration of Cu Cl in aqueous NaCl with an aqueous solution of quinoxaline gave a series of differently coloured precipitates at stoicheiometries corresponding to $\operatorname{Cu}_{n}^{C1}_{n}_{Q}$ (n=1,2,3,6). Similar colour changes were observed with CuBr in aqueous K Br. It was only possible to isolate Cu Cl Q by this method, and this complex may be compared with Cu Cl py⁵²⁹ and the unstable ⁴⁹⁶Cu Cl(pyz). Pure Cu Cl_2Q and Cu₂ (CN)₂ Q were obtained by reduction of the copper (II) complexes. No pure products could be obtained from Diphenylquinoxaline.

The complexes all have the same stoicheiometry as their pyrazine analogues 496 . They are all diamagnetic and exhibit no d-d bands in their visible spectra, consistent with their d¹⁰ configuration. All are insoluble in water, in contrast to the

- 138 -

Infrared spectra (400-1700 cm^{-1}) of the complexes of copper(I) with the quinoxalines.

<u>Cu2C12Q</u>	<u>Cu₂Br₂Q</u>	<u>Cu2120</u>	<u>Cu2 (CN)20</u>	<u>Q</u>	QHC1	Vib ⁿ . No.
410vs	417s	417vs	414m	394s	40 1 m	36
430m	427m	427m	427m	402vs	493mw	24
		518m		535vw	524m	48
		633m	628w	603mw	603vs	35
			731mw	726mw(sh)	731m	11
769vs	757vs	757vs	756vs	756vs	759vs	27
	77 8m	·	790w	783vw	772vs	39
866m	868vs	870vs	863ms	867s	867 vs	- 23
	962s	962vs		953s	940m	22
	968m	968vs	967m		921sh	
1062s	1051vs	1049vs	1050s	1025vs	1042s	46
				1099w	1080m	37
1146s	1138s	1137s	1131mw	112 8m	1130m	34
	1207vs	1205vs	1214m	1204	1216vs	45
				1209)		
1361vs	1363vs	1362s	1360ms	1356mw(sh)	1342m	4
1378m	1373s	1373s		1370m	1380vs	32
1390vs	1385m	1387m	1390ms			
	1423m	1420s	1420m(sh)	1416mw	1403w	18
				1463mw	14 6 0s,b	17
1500vs	1500vs	1499vs	1500s	1495s	1480s	44
1532s						

Table 8.1 cont....

<u>Cu₂C1₂O</u>	<u>Cu₂Br₂Q</u>	<u>Cu₂I₂Q</u>	Cu ₂ (CN) ₂ 0	Q	QHC1	Vib ^{n.} No.
	1583mv	1581m			1570mv	1522s	3
1610m					1608)	1617s	16
					1622) ^W		
Mq	Eu2C12Ma	<u>Cu2</u>	Br ₂ Mq	<u>Cı</u>	1212Mq	<u>Vibⁿ.</u>	No.
410s	424vs	42	3vs	2	123ms	36	
448m						24	
		518	Sm				
609ms		628	ms	6	30mv	35	
699m		73	3w(sh)	7	734w	12	
759vs	760vs	76	lvs	7	763vs	27	
792(sh)	788mw					39	
884s				S	394mw	23	
911ms	905mv	90	7ntw	ç	908m	10	
967vs	962mw	95	9m	9	060ms	22	
1009s	988mw	98	4mw	ç	985m	(Me	rock)
1034ms	1039mw]	L035m	46	
1123]	1128 m	11	30ms	-	1130s	34	
1130) ^{vs}							
1204vs	1202m	12	O2ms		1208s	45	
121 3 sh						(Me	rock)
1293vs	1292mw				1295m	33	
	1307mw				1307ms	19	
1371)	1366ms	13	62ms	-	1369s	4	
1378	1382m	13	80ms		1380ms	32	

TABLE 8.1 cont....

Mq	<u>CuCl₂Mq</u>	Cu	2Br2Ma	<u>Cu212Mq</u>	<u>Vibⁿ No</u> .
14 12s	1406ntv			1406ms	18
1437m				1432ms	17
	1475ms	14	76s	1476ms	•
1493vs	1493s	14	93s	1492vs	44 .
				1499s	
1563s	1540m	15	43ms	1547s	3
<u>Cu2C12Dmq</u>	<u>Cu2Br2Dmq</u>	<u>Cu2I2Dmq</u>	Dmq	Dmq IIC1	<u>Vibⁿ· No</u> .
444s	442s	442s	428w	417mw	24
		522mw		491m	48
	628m	630s	614m	607vs	35
			670m	672vw	12
	732m	722ms	722w(sh)) 723s	11
769vs	774vs	762s	762vs	775vs	27
			789 vw(sł	1) 793vs	39
836s	838s	84 1 m	820mm	832s	23
	·		906m	900s	10
959m	962s	959m	978m)	981vw	22 Morrock
1004ms	1009s	997s	990m	1022m	46
				1073s	37
1142 m	1142s	1139vs	1137mw	1150s	34
1180s	1180s	1177s	1165m	117 2m	26
1199m	1206s	1201s	1212m	1230) 1232) s	45
	1220m	1215s			(Me rock)

Table 8.1 cont....

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Cu2C12Dmq	Cu2Br2Dmq	$\underline{Cu_2I_2}\underline{Dmq}$	Dma	Dma HC1	<u>Vibⁿ No</u> .
	1312m		1258mw		5
1332m	1334s	1336m	1328 1328 mw 1337	1309m 1332w	33
		1352s	1363mw	1358w	4
			1373	1375	
1379s	1382 v s	1376vs	1379. ^W	1377) m	32
1397s	1400vs	1408vs	1400mw	1421(sh)	18
	1408s				
	1432m			1466)	
1461m	1465mw		1437mv	1460 1471 vs	17
1490s	1490vs	1489 v s	1491mw	1498m	44
1552s	1556m		1565mw	1580mv	3
	1572mv		1603vw	1610mv	16

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chloro- and bromo- pyrazine complexes which dissociated 496 when washed with water. The greater stability of the quinoxaline complexes is unlikely to be associated with basicity, since the two amines have approximately the same pka values (see table 7.1), and may be due to stronger π -bonding (see table 7.2: assuming that the relative orders of amine-reduction-potentials are the similar for the free, and the complexed, molecules).

INFRARED SPECTRA

Cyanide Bands

The C-N stretching vibration of the cyano-complex is observed (see figure 8.1) as a single peak with maxima at 2107, 2118, and 2127 cm^{-1} .

Bridging cyanide ligands exhibit $\mathcal{P}_{\rm CN}$ bands in a range close to the value 530 of 2172 cm⁻¹ for Cu CN. The range of terminal cyanide frequencies is lower; 432,499 for example at 530 2125 cm⁻¹ for K Cu (CN)₂ and 2094, 2081 and 2075 cm⁻¹ for K₃Cu (CN)₄. 531,532 . The cyanide frequency of Cu₂ (CN)₂Q is very similar to those (2103-2132 cm⁻¹) of Cu₂(CN)₂L 496 (L=pyz,Mp, 2:5-Dmp 2:6-Dmp), falling within the range for terminal cyano-groups. The splitting of the peak into three components has also been observed for K₃ Cu (CN)₄, 531,532 K₄ Co (CN)₅S₂O₃ 499 and Co (en)₃ Co(CN)₅OH 499 and has been attributed to site symmetry.



This evidence, and the stoicheiometry of the complexes, suggest that $Cu_2 (CN)_2Q$ and, by inference, the other complexes have the linear, binuclear structure (see figure 7.1) proposed⁴⁹⁶ for their pyrazine analogues.

No \mathcal{P}_{Gu-C} bands could be observed above 400 cm⁻¹ (See table 8.1) and this is in accord with the value⁵³¹ of 364 cm⁻¹ for this frequency in K₃Cu (CN)₄.

Amine Bands

It is seen from table 8.1, and the typical spectra illustrated in figure 8.1, that the bands in the 400-1700 cm⁻¹ region are changed little on coordination. A tentative assignment is given, as explained in chapter 7. The spectra are all very similar, justifying the suggestion that they all have the same structure.

The monoprotonated salts Q H Cl and Dmq H Cl belong to the C_s point group rather than having the C_{2V} symmetry of their parent amines. The \mathcal{V}_{11} , \mathcal{V}_{37} and \mathcal{V}_{39} vibrations⁵¹⁸ transform as A₂ in C_{2V} symmetry, but as A'' in the C_s group (see Appendix A.5), and should be infrared-inactive in the former case, but active in the latter case. Table 8.1 confirms that these modes are weak or absent for Q and Dmq but appear moderately strongly for the hydrochbrides. Further the A₂ vibrations are generally weak in the complexes of Q and Dmq, suggesting that these ligands are bidentate and so retain their C_{2V} symmetry. Generally the amine vibrations increase in frequency when coordinated, following an anion dependence: Cl > Br > l > CN. Table 8.2 gives the mean band shifts due to coordination. These shifts also show the amine dependence: $Q>D > M_q$. The data is consistent with the relative Cu-N bond strengths, as explained later.

THERMAL DECOMPOSITION

The complexes decompose before melting, and thermogravimetric analyses show that the initial loss of amine is followed by oxidation to Cu O. The intermediate steps corresponding to the Copper (I) halides are evident in the typical thermograms given in figures 8.2 and 8.3. Table 8.3 compares the percentage weights remaining (W_r) , which are observed and calculated for the Cu X stages. Agreement is evident to within experimental error. These intermediates were confirmed as the Copper (I) halides (for the decomposition of the quinoxaline complexes) by recording their X-ray powder photographs. The positions of the lines observed in these photographs are given as lattice d-spacings in table 8.4, and agree well with those listed for the copper (I) halides have been shown⁷⁹ to decompose in the same way, to leave the anhydrous metal halides.

Mean infrared shifts (cm^{-1}) due to co-ordination, decomposition temperatures (^oC) and frequencies (kK) of charge-transfer onst for the complexes of quinoxalines with copper(I)

Complex	$\delta_{\mathbf{r}}^{\star}$	T _m	ν _o
Cu ₂ C1 ₂ Q	+13.1	280	15.7
Cu ₂ Br ₂ Q	+ 9.4	270	17.5
Cu ₂ I ₂ Q	+ 8.8	260	16.9
Cu ₂ (CN) ₂ Q	+ 7.9	220	18.2
Cu_2Cl_2Mq	- 2.0	255	16.0
Cu ₂ Br ₂ Mq	- 2.4	220	16.4
$Cu_2 I_2^Mq$	- 0.8	155	16.5
Cu2C12Dmq	+ 3.6	275	16.1
Cu2Br2Dmq	+ 6.2	250	17.5
Cu ₂ I ₂ Dmq	+ 3.2	245	16.5

* δ_r denotes the mean shift (cm⁻¹) of the amine vibrations due to co-ordination.





Thermal data for the complexes of copper(I) with the quinoxalines

<u>Complex</u>	<u>T</u> i(^o C)	<u>T</u> _c (^o C)	Found ^W r	(%) <u>Calculated</u>
Cu ₂ C1 ₂ Q	220	300	61.8	60.3
Cu ₂ Br ₂ Q	190	300	68.8	68.8
Cu ₂ I ₂ Q	200	280	75.2	74.5
Cu ₂ (CN) ₂ Q	160	235	57.5	57.9
Cu ₂ Cl ₂ Mq	100	350	57.8	57.9
$\mathrm{Cu}_{2}\mathrm{Br}_{2}\mathrm{Mq}$	100	290	67.0	66.6
$Cu_2 I_2^{Mq}$	90	180	73.5	72.5
Cu2Cl2Dmq	240	340	57.8	55.6
Cu2Br2Dmq	190	280	65.5	64.5
Cu ₂ I ₂ Dmq	200	260	71.8	70.7

* Percentage weight remaining after the loss of organic ligand

Diffraction lines (dA) observed for the intermediates from the decomposition of copper(I) complexes. Reported lines for copper(I) halides are given for comparison.

Résidue	A.S.T.M.	Residue	<u>A.S.T.M.</u>	Residue	<u>A.S.T.M.</u>
$\frac{110m}{Cu_2Cl_2Q}$	$CuCl(6-0344)^*$	<u>Cu₂Br₂Q</u>	<u>LOF</u> CuBr(6-0292)	$\frac{110m}{Cu_2I_2Q}$	<u>LOF</u> Cul (6-0246)
(3.2)**	3.127	3.35	3,285	3.6	3.493
(2.77)	(2.710)	2.03	2.012	3.1	3.025
(2.58)		1.73	1.716	2.18	2.139
(2.37)		1.43	1,423	1.84	1.824
1.94	1.915	1.315	1.306	(1.77)	1.747
1.65	1.633	1.17	1,1615	1.53	1.5127
1.365	1.354	1.10	1.0951	1.395	1.3881
1.25	1.243			(1.37)	1.3529
1.115	1.1054			1.24	1.2351
1.045	1.0422			1.17	1.1 644
0.96	0.9574			1.075	1.0696
(0.918)	0.9154			(1.02)	1.0228
				·	1.0084
(0,858)	0.8564			0.960	0.9568
				(0.926)	0.9228
				(0.914)	0.9121
				(0.876)	0.8733
				0.849	0.8473
				(0.841)	0.8391
				0.810	0.8086

* A.S.T.M. reference code

** brackets denote weak lines
The complexes of Q and Dmq are generally stable up to ~200°C but those of Mq start to decompose at $\sim 100°$ C. Tables 8.2 and 8.3 list the temperatures at which the loss of amine begins (T_i), reaches a maximum (T_m) and is complete (T_c). The thermal stabilities (T_m) follow the orders: $Cl^- > Br^- > I^- > CN^-$ and Q > Dmq > Mq. These trends probably reflect the relative Cu-N bond strengths⁸⁰. Thus, they are consistent with the infrared shift data, since strong Cu-N σ -bonds will cause⁸⁹ 'tightening' of the amine ring vibrations. The reason for this particular order of amine dependence, for the Cu-N σ -bond strengths, is not understood. The order of anion-dependence is presumably due to the influence of polarisability via the electroneutrality principle (see chapter 1).

CHARGE TRANSFER ABSORPTION

Table 8.2 gives the frequency (\mathcal{Y}_{o}) of the onset of the strong electronic bands in the U.V. region. The position of \mathcal{P}_{o} is arbitrarily taken as that of the inflexion in the curve, and only has relative significance. These bands 'tail' into the visible region, providing the source of the bright colours of the complexes.

The ligand Mart* transitions, listed in table 7.3, are

not expected to vary greatly in frequency, and cannot generally account for the present bands, which must be ascribed to chargetransfer processes. Table 8.2 shows that the frequencies are higher for the bromide complexes than for their chbride analogues. The reverse order is observed for the copper (II) complexes (see chapters 4 and 9), and attributed to $Cu \rightarrow L$ and X \checkmark Cu transfer. The present bands may be due to L \Rightarrow Cu or Cu >X transfer. The halogen dependence would then be consistent, for the former process, with the Cu-N σ -bond strength order (indicated by TGA and IR data); or, for the latter process, with easy transfer to electronegative halogens. The higher electronegativity of Cu(I) with respect to Cu(II) (first and second copper ionisation potentials are 15.45 ev and 12.55 ev)^{467, 86} suggests that the chargetransfer may be associated with the L \rightarrow Cu σ -bond, since the

than for those of Cu(II).

The iodides have values of $\hat{\boldsymbol{v}}_{o}$ between those of their chloride and bromide analogues. This may be due to the L+Cu transfer being $\frac{descured}{descured}$ by the lower X+Cu bands. The anomalous behaviour of the Mq complexes may be due to the proximity of the ligand absorption (see table 7.3) for this amine.

absorption is observed at lower energy for the Cu(I) complexes

X-RAY DATA

Powder photographs were taken of most of the complexes, and the lattice d-spacings are collected in table 8.5. The patterns are all similar, but do not indicate strict isomorphism.

DISCUSSION

The low \mathcal{V}_{CN} bands and the stoicheiometry strongly suggest that these complexes have the same linear, binuclear structure (see figure 7.1) as the pyrazine species 496 . The infrared data is consistent with the presence of bidentate amine coordination.

Molecular models show that hindrance between the 8-H atom and Cu atom is such as to prohibit the coordination of any of these ligands unless the Van der Waal's radius of copper is effectively less than ~ 1.4 Å. That complexes have been prepared indicates that this condition is fulfilled. With such an upper limit on the copper radius, models show further that the nature of the substituents in the 2- or 3- positions does not affect the feasibility of coordination. The linear structure leads to no dependance of steric hindrance on the anion present.

Linear structures⁵³³ are uncommon for copper (I) compounds, which mostly exhibit tetrahedral coordination^{534-545,547}. Orgel has, however, explained⁵⁴⁶ how they can arise by the

Table 8.5

d-spacings (A) measured from the X-ray powder photographs of the copper(I) complexes with quinoxalines.

<u>Cu2(CN)2</u> Q	$\underline{\mathrm{Cu}}_{2}\underline{\mathrm{I}}_{2}\underline{\mathrm{Q}}$	<u>Cu₂Br₂Q</u>	<u>Cu2C12Q</u>	<u>Cu₂C1₂Mq</u>	$\underline{Cu_2Cl_2Dmq}$	<u>Cu2Br2Dmq</u>	$\underline{Cu_2I_2Dm}$
			9.0				
			8.2*	<u>8.2</u> b	<u>8.7</u> b		
	7 . 7b		7.4				
			5.9				•
				4.8	4.9		
	4.5		4.3	4.3		·	
3.6			3.57	3.85	3.62		
<u>3.25</u> b	3.52	3.35	3.40	3.35	3.45		
	3.4			3.15b	3.2	3.1	3.2
						2.95	2.97
	3.05	2.95	2.6	2.8b	2.75	2.82	2.8
	2.92	2.75	2.53	2.55	2.55	2.66	2.6
	2.76	2.55					
2.58b	2.66	2.5	2.48	2.35b	2.37	2.45	2.42
2.48	2.34						
2.39	2.3	v			2.28	2.35	2.3b
2.29b	2.12	2.23b	2.02b	1.92	2.0	2.19	2.22
2.2							
2.13		2.12				2.12	2.09
2.02	2.03	2.03				2.05	2.06
1.96	<u>1.97</u> b	1.97	1.9	1.86	1.97	1.96	1.95
1.92	1.88	1.87				1.88	

Table 8.5 cont....

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$\underline{\operatorname{Cu}_2(\operatorname{CN})_2\mathrm{O}}$	$\underline{Cu_2I_2Q}$	$\underline{Cu_2Br_2Q}$	<u>Cu₂C1₂Q</u>	$\underline{Cu_2C1_2Mq}$	$\underline{\mathrm{Cu}_{2}\mathrm{Cl}_{2}\mathrm{Dmq}}$	$\underline{Cu_2Br_2Dmq}$	$\underline{Cu_2 I_2 D}$
1.85	1.84	1.81				1.82	
1.76		1.78					
1.71	1.74	1.72				1.71	1.74
1.54b	1.52	1.65				<u>1.57</u>	1.48
		1.59					
		1.54					
		1.51					
		1.39					

* Underlined values appear strongly.

formation of a hybrid $(1/\sqrt{2})$ $(dz^2 - S)$ orbital. This orbital is localised in the xy plane and electrons placed in it, instead of in d_z^2 , are effectively withdrawn from the z-axis regions. This permits ligands to approach, with reduced coulombic repulsion, along the z-axis.

EXPERIMENTAL

Thermal decompositions were studied on a Stanton Thermal Balance, working at a chart speed of 3 in / hr. and a rate of temperature rise of $2/3^{\circ}$ /min. Q and Mq were obtained from Koch-light, while Dmq and Dpq were prepared by condensation reactions⁵²⁸.

Other practical details have been described earlier. Carbon , hydrogen and nitrogen analyses were performed by Mr. P. Borda.

All compounds were dried at $20^{\circ}/25$ mm.

DICHLORO (QUINOXALINE) DICOPPER (I)

Quinoxaline (1.5 g., 1 mol.) and copper (II) chloride dihydrate (3.9g., 2 mol.) were dissolved in water (150 ml), 50% hypo-phosphorous acid (8 ml.) was added, and the mixture kept at 90° for 1 hour. The initial yellow precipitate rapidly turned to dark brown flakes of the product (2.4g., 63%), which were filtered off and washed with water. (Found: C,29.6; H, 2.0; Cl 22.1; Cu 38.8. $C_8H_6Cl_2Cu_2N_2$ requires C,29.3; H, 1.8; Cl,21.6; Cu, 38.7%).

DIBROMO (QUINOXALINE) DICOPPER (I)

Copper (I) bromide (4.4g., 2 mol.) was dissolved in an acidified (2 drops, $5N H_2SO_4$), cold saturated solution of potassium bromide (110 ml.), and the solution was added slowly to a stirred solution of quinoxaline (2.0 g., 1 mol.) in water (100 ml.). The initial yellow precipitate turned into the orange product (5.9 g., 92%) during the addition. The product was filtered off and washed with dilute potassium bromide solution and water. (Found: C, 23.4,; H, 1.6; Br, 39.0; Cu,30.5; $C_8H_6Br_2Cu_2N_2$ requires C, 23.0; H,1.5; Br,38.3; Cu,30.5%) DI-IODO (QUINOXALINE) DICOPPER (I)

This complex was similarly prepared (Found: C,19.2; H,1.5; Cu,24.7; I, 49.5. C₈H₆Cu₂I₂N₂ requires: C, 18.8; H,1.2; Cu, 24.9; I, 49.7%).

DICHLORO- (2- METHYLQUINOXALINE) DICOPPER (I)

This complex was also obtained as above, but with the addition of the 2-methylquinoxaline to the solution of Copper (I) chloride. (Found: C, 31.7; H, 2.5; Cl, 20.8; Cu, 36.4. $C_9 H_8 Cl_2 Cu_2 N_2$ requires C, 31.6; H, 2.4; Cl, 20.7; Cu, 37.1%) <u>DIBROMO - (2- METHYLQUINOXALINE) DICOPPER (I)</u>

This complex was similarly prepared, but without the presence of acid (Found: C, 25.6; H, 1.9; Br, 37.0; Cu, 29.0. $C_9H_8Br_2Cu_2N_2$ requires C, 25.1; H, 1.9; Br, 37.1; Cu, 29.5%), as was <u>di-bodo (2-methylquinoxaline) dicopper (I)</u> (Found: C, 20.7;

H, 1.7; Cu, 24.0; I, 48.0. C₉H₈Cu₂I₂N₂ requires C, 20.6; H, 1.5; Cu, 24.2; I, 48.3%)

DICHLORO- (2:3 -dimethylquinoxaline) DICOPPER (1)

This was similarly prepared in 50% aqueous ethanol. The impure red product was dissolved in boiling water (200 ml.) by adding concentrated hydrochloric acid. The resulting brown solution was neutralised with dilute ammonia and then slightly acidified with dilute hydrochloric acid while still hot. The pure, red product which precipitated as the solution cooled was filtered off and washed with water (Found: C, 33.9; H, 3.0; Cl, 20.0; Cu, 36.0; $-C_{10}H_{10}Cl_2Cu_2N_2$ requires C, 33.7; H, 2.8; Cl, 19.9; Cu, 35.7%)

DIBROMO - (2:3 DIMETHYLQUINOXALINE) DICOPPER (I)

This complex was also obtained as above, but with the addition of the copper solution to the solution of 2:3 dimethylquinoxaline. No acid was used in the initial reaction, and dilute sulphuric acid was used in the purification (Found: C, 27.0; H, 2.2; Br, 36.2; Cu, 28.9. $C_{10}H_{10}Br_2Cu_2N_2$ requires C, 27.0; H, 2.3; Br, 35.9; Cu, 28.5%).

DI-IODO - (2:3 DIMETHYLQUINOXALINE) DICOPPER (I)

This complex was similarly prepared but without reprecipitation (Found: C, 23.0; H, 2.1; Cu, 23.6; I, 46.8. $C_{10}H_{10}Cu_2I_2N_2$ requires C, 22.3; H, 1.9; Cu, 23.6; I, 47.1%)

DICYANO (QUINOXALINE) DICOPPER (I)

Quinoxaline (0.9 g., 1 mol.), potassium cyanide (1.8 g., 4 mol.), and hydroxylamine hydrochloride (2.0 g.) were dissolved in water (20 ml.) and the mixture was slowly added to a solution of copper (II) chloride dihydrate (2.2 g., 2 mol.) in water (20 ml.) A yellow-brown complex was formed initially and converted into the orange product (1.5 g., 75%) on boiling the solution for 30 mins. This was filtered off and washed with ethanol, dilute sodium chloride solution, dilute potassium cyanide solution and water. (Found: C, 38.9; H, 2.3; Cu, 40.8; N, 18.1. $C_{10}H_6Cu_2N_4$ requires C, 38.8; H, 2.0; Cu, 41.1; N, 18.1%).

QUINOXALINIUM MONOCHLORIDES

The hydrochlorides of quinoxaline and 2:3dimethylquinoxaline (and also 2:3-diphenylquinoxaline) were prepared by adding a few drops of concentrated hydrochloric acid to a solution of the amine in acetone. The pale precipitates were washed several times with acetone.

2:3 DIMETHYLQUINOXALINE

o-Phenylenediamine (43.2 g., 1 mol.), biacetyl (35.0 ml., 1 mol.), glacial acetic acid (100 ml.), and water (700 ml.) were refluxed together for 3 hours. Yellow-brown needles of the product were deposited when the mixture cooled to room temperature. These were filtered off and the filtrate added, with stirring, to water (3000 ml.). The filtrate was neutralised with sodium hydroxide and more product was obtained on leaving the mixture for 24 hours. The product was refluxed with decolourising charcoal, in alcohol, for one hour. The resulting solution was filtered, and the pure product (21 g., 33%) crystallised as yellow needles, m.p. 105.5 - 106° C, from the filtrate. (Found: C, 76.1; H, 6.5; N, 17.9. C $_{10}$ H $_{10}$ N $_{2}$ requires C, 75.9; H, 6.4; N, 17.7%).

2:3 - DIPHENYLQUINOXALINE

o-Phenylenediamine (21.6 g., 1 mol.), benzil (42.0 g., 1 mol.) and glacial acetic acid (500 ml.) were refluxed together for 3 hours. The cold reaction mixture was added slowly, with stirring, to water (1500 ml.), whereupon the white product precipitated. This was purified, as above, to give needles, m.p. $124-125^{\circ}C$ (48 g., 85%). (Found: C, 85.2; H, 5.0; N, 10.0. $C_{20}H_{14}N_2$ requires C, 85.1; H, 5.0; N, 9.9%). Chapter 9

COPPER (II) COMPLEXES WITH SUBSTITUTED QUINOXALINES

The Copper (II) complexes with pyrazines were found ⁴⁹⁶ to be unstable, but Underhill reported ⁵⁰⁴ stable complexes of this ion with quinoxaline. The factors affecting this type of complex were therefore investigated. As the instability of some of the pyrazine complexes was ascribed ⁵⁰⁴ to steric hindrance, this factor was studied by preparing a number of complexes of quinoxaline substituted in the 2and 3- positions.

The complexes listed in the upper part of table 9.1 were prepared and their room-temperature magnetic moments were found to lie in the range (1.7 - 2.0 B.M.) generally observed¹³¹ for Copper (II) compounds. The low moment (1.55 B.M.) of $\widehat{\text{Cu Br}_2}$ Dmq may be compared with the low values reported^{19,420} for some other complexes of Cu Br₂, and may be due to an exchange mechanism.

All these complexes were stable, and the only evidence obtained for spontaneous reduction was the isolation of brown diamagnetic crystals from acetone solutions of $Cu Br_2$ and Dmq. However, this reduction appears 548-558 to be more characteristic of Cu Br_2 and acetone than of Dmq; and in the absence of the amine, Cu Br and bromoacetone can be isolated. Analysis of the brown crystals indicated that the ligand involved was probably a product of an attack on Dmq by bromoacetone. The Copper (II) complex $Cu Br_2$ Dmq was obtained from ethanolic solution.

No evidence was found for the existence of complexes/of quinoxaline with CuI_2 or Cu (NCS)₂, nor of the substituted quinoxalines with CuSO_4 or Cu (OAc)₂. This may be contrasted with the preparation⁵⁰⁴ of CuSO_4 Q and Cu(OAc)_2 Q. It was not possible to isolate pure Cu(CN)_2 Q or $\text{Cu(NO}_3)_2$ Dpq₂

Table 9.1

Electronic spectral data (kK) and room temperature magnetic moments (B.M.) for the copper(II) complexes with quinoxalines.

Complex	^µ eff	Band Maxima	<u></u> *
CuCl ₂ Mq2	1.84	14.7(.5)	4.9
CuBr ₂ Mq ₂	1.75	16.1(.4), 10.5(b,w,sh)	3.6
Cu(NO ₃) ₂ Mq	1.96	17.2(.4), 13,8(sh), 11.1(vw,sh)	4.6
Cu(NO ₃) ₂ Mq ₂	1.88	17.2(.4), 14,3(sh), 11.1(vw,sh)	5.1
$Cu(NO_3)_2Mq_3$	1.72	16.7(.7), 13.5(sh), 11.1(vw,sh)	6.1
CuCl ₂ Dmq	1.73	21.3(b,w,sh), 18.7(sh), 14.2(.4)	4.7
CuBr ₂ Dmq	1.55	14.9(.5), 10.0(w,b,sh)	3.2
Cu(NO ₃) ₂ Dmq	1.86	17.5(.5), 13.9(sh)	4.7
CuC12Dpq2	1.89	20.0(vw,sh), 18.7, 14.3(.5), 10.0(b,sh)	5.7
CuBr ₂ Dpq ₂	1.84	14.9(.3), 10.5(b,w,sh)	3.0

CuCl ₂ Q	14.3(1.1)	4.6
CuBr ₂ Q	14.0(1.3)	4.0
Cu(NO ₃) ₂ Q	18.0(1.2), 14.3(vw,sh)	5.2

Cu(NO ₃) ₂ py ₂	15.9(.4), 13.5(.4), 11.1(sh)
Cu(NO ₃) ₂ (Mepy) ₂	16.1(b)
Cu(NO ₃) ₂ Quin ₂	-16,1(b)

* Estimated since the higher frequency part of the line shape is obscured by charge transfer bands.

Electronic Absorption Spectra

The d-d band maxima of these and some related complexes, are collected in table 9.1, while the spectra of the chloro-complexes are illustrated in figure 9.1.

Halo-complexes

The chloro-complexes may be divided into two groups on the basis of their reflectance spectra:

- a) CuCl₂Q and CuCl₂Mq₂ have very similar spectra to that
 (c.f. figure 4.1) of CuCl₂py₂, exhibiting a single band
 close to 14.5 kK.
- b) CuCl₂Dmq and CuCl₂Dpq₂ exhibit two d-d peaks like those (see figure 4.1) of CuCl₂ (2Brpy)₂. The bands (~14.3 kK and ~18.7 kK) have a mean frequency higher than that of CuCl₂py₂.

As earlier found (see chapter 4) for the halopyridine complexes, the low frequency of the charge-transfer bands of the bromides partially obscures the d-d bands. The spectra otherwise appear to be very similar to those of the corresponding chlorides. The higher frequencies of the d-d bands for the bromides, relative to the chlorides, was ascribed in chapter 4 to increased Cu-N π -bonding, or to shorter Cu-N bonds in the former complexes.

The high frequency of the bands for all these complexes precludes(as discussed in chapter 4) the possibility of tetrahedral



or trigonal-bipyramidal structures. Only the quinoxaline complexes exhibit comparable high-intensity d-d spectra to those reported⁴⁴⁶ by Waters for cis-configurations. However, the bands of the quinoxaline complexes probably have too high frequencies to result from cis-chromophores. No explanation can yet be given for the high intensities of these spectra.

All the complexes must be at least as tetragonal as $CuCl_2py_2$, to account for the high d-d frequencies. This criterion restricts the possible structures to (see chapter 4):

i) a six-coordinate structure like that of CuCl₂py₂,

- ii) a five-coordinate, square-pyramidal structure like that of CuCl₂(2-Mepy)₂,
- iii) a four-coordinate, square-planar structure like that proposed for CuCl₂Quin₂.

The similarities in the spectra, noted above, suggest that the complexes of Q and Mq may have octahedral structures based on that of $CuCl_2py_2$, and that those of Dmq and Dpq may be square-coplanar. The spectra of the first group of complexes may be assigned in the same way as given (in chapter 4) for $CuCl_2py_2$. The spectra of the square-coplanar complexes may be assigned like that of $CuCl_2(2Brpy)_2$. The feasibility of these assignments confirms the suggested structures. These tentative assignments are given in table 9.2 with the estimated values of 10Dq. As expected, 10Dq is very similar for all these complexes. The high value for CuBr_2Mq_2 is not understood. The high tetragonalities indicated by \mathcal{N}_1 for the complexes of Dmq and Dpq are in accord with the square-planar structures proposed for them.

The charge-transfer bands have been attributed (in chapter 4) to $Cu \rightarrow L$ and $X \rightarrow Cu$ processes. Both should occur at comparatively low energies if the amine (L) can easily accept π -electrons. The observed order of \mathcal{P}_{0} (as defined in the previous chapter) is Q < Dpq < Dmq < Mq, and this can be understood as roughly the reverse of the π -acceptor order (see chapter 7).

Nitrato-complexes

All the reflectance spectra of the nitrato complexes are similar to that of $Cu(NO_3)_2py_2$, for which an octahedral structure has been proposed.²⁶⁷ Since no structures are known for this type of complex, the spectra assignments, indicated in table 9.2, are made very tentatively. The values of 10Dq appear to be slightly higher than those of the halides, which is consistent with the higher position of the nitrate group in the spectrochemical series²³. The origin of a weak 11.1 kK shoulder, which appears in the spectra of many of these complexes, is unknown.

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Tab1e 9.2

Tentative assignments of the reflectance spectra (kK) of the complexes of copper(II) with quinoxalines.

<u>Complex</u>	<u>~</u> 1	<u>~</u> 2	<u>~</u> 3	10Dq
CuC1 ² Q	14.3	14.3	14.3	7.1
CuBr ₂ Q	14.0	14.0	14.0	7.0
$CuC1_2Mq_2$	14.7	14.7	14.7	7.3
$\mathrm{CuBr}_{2}^{\mathrm{Mq}}$	17.2	17.2	17.2	8.6
CuCl ₂ Dmq	18.7	18.7	14.2	6.3
CuBr ₂ Dmq	18.5*	18.5*	14.9	6.8*
CuC12Dpq2	18.7	18.7	14.3	6.4
$CuBr_2Dpq_2$	18.5ush	18.5ush	14.9	6.8
Cu(NO ₃) ₂ Q	18.0	14.3	18.0	7.8
Cu(NO ₃) ₂ Mq	17.2	13.8	17.2	7.5
$Cu(NO_3)_2Mq_2$	17.2	14.3	17.2	7.6
$Cu(NO_3)_2Mq_3$	16.7	13.5	16.7	7.3
Cu(NO3)2Dmq	17.5	1 3. 9	17.5	7.5
Cu(NO ₃) ₂ py ₂	15.9	13.5	15.9	7.1

* Estimated from the similarity of the spectrum to that of $CuBr_2Dpq_2$

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It is not known whether $Cu(NO_3)_2 py_2$ has a polymeric anion-bridged structure, or whether it is monomeric with chelating nitrato-groups. The change²⁶⁷ in the spectrum on dissolving the complex in chloroform may be due to dissociation of the former structure.

The spectrum of $Cu(NO_3)_2Mq_3$ is somewhat different, consisting of a very broad band like that of $Cu(NO_3)_2(IQuin)_2$, for which a cisoctahedral structure has been proposed³⁵⁹ (with chelating nitratogroups). The infrared data (see later) confirms that at least one of the Mq molecules is not coordinated. This situation is similar to that of $Cu(NO_3)_2py_6$ in which two py molecules are not coordinated.²⁶⁷

The spectra also exhibit an intense band near 31.5 kK which is due^{559, 560} to the $n \rightarrow r^{\dagger}$ transition of the nitrato-group. Smith has studied^{559, 560} this band in fused salts, finding an environmental dependence of the frequency. Addison has recently extended⁵⁶¹ this work to the study of coordinated nitrato-groups. Because of the complication of this region of the spectrum by ligand bands (see table 7.3), no obvious trends are revealed by the present spectra.

Far-Infrared Spectra

Table 9.3 gives the vibration frequencies of these complexes in the 60-380cm.⁻¹ region, and tentative assignments which are mostly due to Adams and Morris⁵⁶². The spectra of the Dmq complexes are shown in figure 9.2. The assignments have been treated cautiously since they

Table 9.3

Far-infrared frequencies (cm⁻¹) in the solid state for the copper(II) complexes of quinoxalines.

Compound	^v Cu-X	^v Cu-N	^δ Cu–X	^π Cu-X	<u>~40</u>	<u>v28</u>	<u>v25</u>	Other bands
Q						205sh	184s	
CuC1 ₂ Q	324vs	220m	180vs	98m	246s	19 5 0 sl	h 172ıs h	147m, 129m 8
CuBr ₂ Q	255s	211w	138m		244sh	193w	172s	141 u sh
Mq					276vs,	188vs	137m	274w
CuC12Mq2	320s	208sh	217m	90 . 5m	2955h 286m, 300sh	17 3m	13 8m	107sh
$^{\text{CuBr}_2^{\text{Mq}}2}$	252s	200s	239m		294s, 305sh	181m	132m	102s
Dmq					278s, 320m		166s	
CuC1_Dmq	368vs	214s	156s	88m	315s		178w	110v , 13!
CuBr ₂ Dmq	278vs	220s	105m		315s		176w	112sh,13
Dpq					307m, 332m	192s		97w,36
CuCl ₂ Dpq ₂	337s	217s	144sh		298 u sh, 315m	202m		345ush 115w, 194sh,
CuBr2Dpq2	269s	220s	98m		298w, 317m	201m		349m, 110w, 188m, 165m,
								139m.



depend⁵⁶² on a number of assumptions:

- that the corresponding chloride and bromide complexes are isomorphous, so that halogen-sensitive bands may be identified with certainty;
- ii) that the Cu-N, Cu-X and ligand vibrations are independent;
- iii) that no lattice modes are present above 60 cm.⁻¹;
 - iv) that bands do not overlap;
 - v) that coordination does not split the ligand vibrations or activate modes not observed in the spectra of the free amines.
 - vi) Comparisons of the bands of several complexes are only validif it is certain that the compared frequencies are due to thesame vibration mode for all the complexes.

The following considerations are conditional upon these assumptions. Copper-halogen frequencies

Only one Cu-X stretching vibration is observed for all of these complexes. This is consistent with, either the six-coordinate, or the four-coordinate structures proposed above; but precludes a five-coordinate structure of the $\operatorname{CuCl}_2(\operatorname{2Mepy})_2$ -type (figure 4.2), or any cis-, tetrahedral or trigonal-bipyramidal configurations. Since all of these latter stereochemistries are accentric, the asymmetric and symmetric stretching frequencies are both allowed (see Appendix A5) in the infrared spectrum.

It has been demonstrated in chapter 4 that the long Cu-X bonds in the six-coordinate structures will probably stretch in a manner which is equivalent to a deformation of the short Cu-X bonds. Adams has suggested 353 that this vibration ($\boldsymbol{\delta}_{\text{Cu-X}}$) should increase and $\boldsymbol{\mathcal{V}}_{\text{Cu-X}}$ should decrease in frequency as the long Cu-X bonds shorten and tetragonality decreases. The correlation between $\boldsymbol{\mathcal{V}}_{\text{Cu-X}}$ and tetragonality was confirmed in chapter 4.

On the basis of both criteria the Dmq and Dpq complexes are shown to be more tetragonal than those of Q and Mq. The high frequency of \mathcal{P}_{Cu-X} (368 cm⁻¹) for CuCl₂Dmq may be compared with that (362 cm⁻¹ - see chapter 4) of CuCl₂P, and is the highest yet recorded³⁵³. Square-planar structures may, therefore, be proposed for the complexes of Dmq and Dpq and octahedral, polymeric structures suggested for the complexes of Q and Mq.

Although relatively low ($\sim 320 \text{ cm}^{-1}$) the $\mathcal{V}_{\text{Cu-X}}$ bands of the CuCl₂Q and CuCl₂Mq₂ are higher than that (287 cm⁻¹) of CuCl₂py₂. This effect is also exhibited by CuCl₂(4-NO₂py)₂ ($\mathcal{V}_{\text{Cu-Cl}} = 313 \text{ cm}^{-1}$) and was ascribed in chapter 4 to considerable Cu-N π -bonding. Such an explanation agrees with the larger π -acceptor character (see chapter 7) of the quinoxalines.

Copper-nitrogen bands.

Only one \mathcal{V}_{Cu-N} band is observed for these complexes, in agreement with the proposed structures. These frequencies are all close to 210 cm⁻¹, if the band at ~ 245 cm⁻¹ in the quinoxaline complexes is accepted as the amine \mathcal{V}_{40} ring vibration (observed at 285 cm⁻¹ and 267 cm⁻¹ respectively, in the Raman spectra of naphthalene⁵¹⁹ and -quinoline⁵¹⁷) rather than \mathcal{V}_{Cu-N} . These bands are at lower frequency than (157 cm⁻¹) that of CuCl₂Quin₂, presumably due to the lower basicity of the amines²⁷⁰ (table 7.1 and chapter 4). The bands are at slightly higher frequencies in the chloride complexes of Q and Mq than in the bromides; the reverse being true of the complexes of Dmq and Dpq. If this difference is significant it may be due to easier Cu-N \mathcal{T} -bonding in the square-planar complexes, and to the influence of anion polarisability on \mathcal{T} -bonding (see chapter 1).

Near-Infrared Spectra (375-1700 cm.⁻¹).

Nitrate bands (Table 9.4)

All the nitrato-complexes, unlike the halo-complexes but like $Cu(NO_3)_2Q$ and $Cu(NO_3)_2py_2$, exhibit absorption bands in the ranges of 798 - 806, 1014 - 1020, 1277 - 1296 and 1496 - 1513 cm.⁻¹. All except $Cu(NO_3)_2Mq_3$, have a further band in the 711 - 712 cm.⁻¹ range. As described in Appendix A5, these bands are characteristic of coordinated nitrato-groups and may be assigned respectively, to the \mathcal{V}_6 , $\mathcal{V}_2 \mathcal{V}_1$, \mathcal{V}_4 and \mathcal{V}_5 vibrations. A further vibration (\mathcal{V}_3) is obscured by an amine band (\mathcal{V}_{27}).

Field and Hardy have concluded 563 that near-infrared vibration frequencies cannot be used to distinguish between monodentate- and bidentate- nitrato groups, because both belong to the C_{2v} point group. Far-infrared M-O stretching frequencies have been found 564 to be more informative on this matter, but this data was not available.

Tab1e 9.4

Infrared absorption bands (cm^{-1}) due to the nitrate group in the copper(II) complexes of quinoxalines.

Complex	<u>~</u> 5	<u>~</u> 6	<u>v</u> 2	<u><u>v</u>1</u>	<u>~</u> 4
Cu(NO ₃) ₂ Mq	711mw	803s	1020vs	1296vs	1500vs*
$Cu(NO_3)_2Mq_2$	712w	801s	1019vs	1280vs	1496vs*
$Cu(NO_3)_2Mq_3$		806m	1018s	1277vs	1502vs*
Cu(NO3)2Dmq	712w	798vs	1014vs	1279) 1289) s	1513vs*
Cu(NO ₃) 2Q	708mw	800vs	1008 1028	1285) 1300) vs	1502vs*
Cu(NO ₃) ₂ py ₂		804m	1024m	1268 1282	1468 1477

* Ligand bands which are broadened in the nitrate complexes relative to the halides.

ŧ

Amine bands

The spectra of the complexes are simply related to those of the free amines, allowing the tentative assignments, given in table 9.5, to be made as discussed in chapter 8. The complex $\operatorname{Cu}(\operatorname{NO}_3)_2\operatorname{Mq}_3$ is exceptional, in that the \mathcal{V}_{36} , \mathcal{V}_{35} , \mathcal{V}_{27} , \mathcal{V}_{22} , \mathcal{P}_{45} and \mathcal{P}_{33} vibrations give rise to one set of bands close to that of $\operatorname{Cu}(\operatorname{NO}_3)_2\operatorname{Mq}_2$, and to a further set close to the frequencies of the free amine. This suggests that the tris-complex contains some coordinated, and some free, Mq molecules.

The spectra of the Dpq complexes were very similar to that of DpqHCl, suggesting (see the previous chapter) that this amine is monodentate in its complexes. The criteria, suggested in chapter 8, for monodentate Q and Dmq yield inconclusive results when applied to the Copper(II) complexes. A search was made for other empirical criteria of monodentate character, by comparing the spectra of the hydrochlorides and the complexes of Cu(I), CU(II) and Ni(II). A strong band in the 603 - 635 cm.⁻¹ region (due to \mathcal{V}_{35}) was often exhibited by the monodentate Q complexes. The appearance of bands near 465cm.⁻¹, 1018cm.⁻¹ (\mathcal{V}_{46}) and the strengthening of the \mathcal{V}_{35} and \mathcal{V}_{39} bands may be characteristic of monodentate Dmq. Monodentate Mq usually gave rise to new bands near 472cm.⁻¹ (\mathcal{V}_{24}), 540cm.⁻¹ (\mathcal{V}_{48}) and 891cm.⁻¹ (\mathcal{V}_{23}), and to a splitting of the \mathcal{V}_{34} band near 1130cm.⁻¹.

<u>Table 9.5(a)</u>

Infrared absorption frequencies(cm⁻¹) for the copper(II) complexes of quinoxalines. Nitrate bands are excluded.

<u>CuCl</u> 2Q	<u>CuBr2Q</u>	<u>Cu(NO₃)₂Q</u>	2	<u>Vibration</u> Number
422m	4 17 m	423s	394s	36
430m	429m	432ms	402s	24
540mv	539nav	537mav	535vw	48
547mw	543w	547m		
645mw	643nav	6 54m	603nav	35
		667mw	663vw	
			726nw,sh	11
756vs	752s	744vs	756vs	27
785m	780mw	*	783vw	39
876vs	875ms	863s	867s	23
		955mw	917vw	
973s	973m	981ms	953s	22
1066vs	1062ms	1057vs	1025vs	46
1100m	1095mw	1090mv	1099w	37
1140)	11387	1146)	112 8m	34
1147 VS	1145] ^{ms}	1150 s		
1213)	1213ms	1214)	1204)	45
1218 vs		1218 s	1209 mw	
1286m	1290mv	*	1267vw	5
1352mw	1352m	1362	1356mw,sh	4
1375w		, 1372 ^{ms}	137 0m	32

Table 9.5 (a) cont....

<u>CuCl₂Q</u>	<u>CuBr₂Q</u>	<u>Cu(NO₃)₂Q</u>	<u>Q</u>	Vibration Number
	1405) 1421)	~	1416r.w	18
1466s	1470ms	1476	1463s	17
1503s	1507ms	*	1495s	44

* Obscured by nitrate bands.

Table 9.5(b)

Table 9.5(<u>b)</u>					Wibn
<u>CuC12Mq</u> 2	CuBr ₂ Mq ₂	<u>Cu(NO₃)₂Mq</u>	<u>Cu(NO₃) 2^{Mq}2</u>	$Cu(NO_3)_2Mq_3$	Mq	<u>No</u> .
433s	434vs	427m	434ms	411ms	410s	36
				430s		
473m	472s		472m	452m	448m	24
				473ms		
				510m		
537mw	540m	540	539mw	537m	534w	48
		546) ^{mv}				
623ms	623vs	620vw,b	623m	615m	609ms	35
				624s		
646nw		64Qmw	644m	6 4 8m	648mw	
727m	732s	726wyb,sh	728vw _s sh		699m	12
757)	763vs	748vs	752s,sh	757s	759vs	27
767) vs			762vs			
				776s		
774m,sh	781ms	*	790ms	792mv	792sh	39
891ms	893mw	898m	898ms	898m	884s	23

Table 9.5(b) cont....

<u>CuCl₂Mq₂</u>	<u>CuBr₂Mq₂</u>	<u>Cu(NO₃) 2^{Mq}</u>	<u>Cu(NO3) 2Ma</u> 2	<u>Cu(NO₃)₂Mq₂</u>	Mq	<u>Vibn.</u> No.
908ms	911m	917w,sh		917w,b	911ms	10
953mw,sh		952vw,sh		939w,b		
964ms	960mw				967vs	22
978s	98 Om	994s,sh	981s	969ms		
				985ms		
1011mv	1013w	*	*	*	1009s	(Me rocl
1030ms	1033b,vw	*	1034m , sh	1038mw,sh	1034ms	46
1130	1132)	1139s	1138s	1132ms	1123	34
1140 ^s	1141) ^m		1147s	1148vw	1130)	5
1209s	1207m	1203s	1213vs	1205s,sh)	1204vs	45
				1212s J		
1220s		1230ms			1213sh	(Me ro
1278m	1278vw				1272sh	
1294ms	1298vw	*	*	1298ms	1293vs	33
1307ms	1310w	1321s	1318mw	1315ms	1334mw	19
1368s	1368ms	1342m	1368mw	1372s	1317	4
1377ms,sh		1380ms	1380mw	1383ms	1378)	32
				1410)		
1412m	1411w	1422	1417mw	1414 W	1412s	18
		1439 sh		1410		
1474ms		1467s,b,sh	1470s,b,sh	L	1437m	17
1500s	1498ms	*	*	*	1493vs	44
1550)	1552w		156Om	1558m	1563s	3
1560 (1563w		1572m	1567m,sh		

Table 9.5(b) cont....

.

CuC12Mq2	<u>CuBr₂Mq₂</u>	<u>Cu(NO₃) 2Mq</u>	<u>Cu(NO₃)₂Mq₂</u>	<u>Cu(NO₃)₂Mq₃</u>	Mq	<u>Vibn.</u> No.
1584m			1592w	1594mw	1579m	31
1614m			1613vw	1617mw	1612mv	16

.

Table 9.5(c)

CuCl2Dmq	CuBr2Dmq	Cu(NO ₃) ₂ Dmq	Dmq	Vibration Number
444m	444m	449vs	428m	24
547w	548mw	542m		48
635ms	635m	638s	614m	35
682ms	687m	679s	670m	12
729ms	723mw	725vw	722w(sh)	11
748 vs	745s	760vs	762vs	27
7 93w	788nw	*	789vw(sh)	39
838m	840m	843s	820mw	23
913m	913w	916m	906m	10
			978nav 🛛	22
997m	998m	*	990m /	46
				37
1143vs	1143s	1143vs	1137mw	34
1172	1170ms	1179s	1165 m	2 6
1178				
1214s	1214m	1208s	1212m	45
1266s	1266m	*	1258mw	5
			1320)	:
1319m	1317m		1328 mv	33
			1337	

Table 9.5(c) cont....

CuC12Dmq	<u>CuBr2Dma</u>	<u>Cu(NO3) 2 Dmq</u>	Dmq	Vibration Number
1343s	1347ms	1350s	1348w	
1361s	1363ms	1370w	1363mw	4
1373s	1376ms	1378)	1373)	32
		1383 ^{w, sn}	1379)	
1405sh	1406w 👌	1411m	1400mw	18
1466s	1466w_	1459sh	1437mm	17
1491m	1491ms	*	1491mw	44
1510				
1513 ^{Inw}	1516mw,sh			
			1565mw	3
			1603vw	16

Table 9.5(d)

<u>CuBr₂Dpq₂</u>	Dpq	DpaHC1	Vibration Number
439w	427mv		24
498mw	491mv	488w	9
513mv			
		539)	
547ms	541vs	544	48
558mv		560w	
565m	566s	566m	21
571m			
607ms	600vs	601	
633m	610m	609	35
672mv,b	621mw	618w	
	<u>CuBr₂Dpq₂</u> 439w 498mw 513mw 547ms 547ms 558mv 565m 571m 607ms 633m 672mv,b	CuBr 2Dpq2 Dpq 439w 427mw 498mw 491mw 513mw 491mw 513mw 541vs 547ms 541vs 558mw 566s 571m 560vs 607ms 600vs 633m 610m 672mw,b 621mw	CuBr 2Dpq Dpq DpaHC1 439w 427mw 488w 498mw 491mw 488w 513mw 539 mw 547ms 541vs 539 547ms 541vs 560w 558mw 566s 566m 571m 560v 566m 571m 560vs 560m 607ms 600vs 601 633m 610m 609 672mv,b 621mv 618w

Table 9.5(d) cont....

CuCl_Dpq_	CuBr2Dpq2	Dpq	DpqHC1	Vibration Number
693 v s	692	698 v s	703vs	(Phenyl)
	696 S			
730mw	732w	7 29m	731m	11
761	756s	761s	760s	8
770	768s	768vs	770vs	27
			788m	39
917m	919mw	928m	930w	10
982ms	985m	979s	978m	22
1028ms	1028m	1024m	1026m	46
1063ms	1066m	1060s	1060m	(Pheny1)
1071sh		1078m	1079m	37
1131ms	1133m	1130w	1130w	(Pheny1)
1142mw	1144 mw	114 3m	1145s	34
1219m	1218mw	1221		45
1227ms	1228m	1228	1230s	
1259mw	1261w	125Om	1249w	5
			1333m	
1351s	1357s	1350vs	1347s	4
1400niw	1404ms	1396m	1397m	32
1443s	1446ms	1441s	1445s	18
	1477b,m	1473sh	1453m b	17
1482m	1486ms	1479m	1471s	(Pheny1)
1497mw	1501m	1495m	1500m	44
15 43w	1548mw	1549sh	1542m	3

Table 9.5(d) cont....

CuC12Dpq2	CuBr2Dpg2	Dpq	DpqHC1	Vibration Number
1561w	1567mw	1557m	1559m	(Pheny1)
1599vw	1580w,sh	1574w	1598w	31
1676mw	1627w	1651m		(Pheny1)

Powder X-ray diffraction data

X- ray powder photographs were recorded for the complexes and the measured d-spacings are listed in table 9.6. No strict isomorphism is indicated, ⁵⁶⁵ but the complexes of the same amine have very similar patterns, allowing for slightly different lattices in the order: Br $> NO_3 > Cl^-$.

Thermal Decomposition Studies

As figure 9.3 shows, very few of these complexes decompose in a simple manner. No attempt has been made to isolate or analyse the intermediates corresponding to the many points of inflexion on the curves. However, table 9.7 shows that some intermediates agree well with the proposed formulae, on the basis of the observed and calculated values of W_r .

The table also gives details as to whether the initial reaction appears to involve fission of copper-amine or of copper-amine bonds, and the temperatures (T_m) at which the fission of copper-amine bands first reaches a maximum rate. If the order in which the bonds are first broken reflects the relative strengths of the copper-amine and copper-amion bands then the order of bond strengths is generally: Cu-Br < Cu-N < Cu-O < Cu-Cl. A reversal of the apparent bond strengths of the Cu-Br and Cu-Cl bonds in the Mq complexes is not understood, but may be correlated with the very high long-bond Cu-Br stretching frequency ($\mathcal{V}_{Cu-Br} = 239$ cm.⁻¹) for CuBr₂Mq₂.

Table 9.6

Main lines (d-spacings in \Re) in the X-ray powder photographs of the copper(II) complexes of quinoxalines.

<u>CuCl₂Q</u>	<u>CuBr2Q</u>	<u>Cu(NO₃) 2Q</u>	CuCl2Mq2	<u>CuBr2Mq2</u>		
				10.5		
				7.7s		
				6.7		
		•		6.0		
				5.3b,s		
			4.6b	4.2vs,b		
3,55			3.45b	3.45s,b		
3.35						
3.13			3.1	3.07s		
2.82				2.9		
2.63s	2.75	2.95	2.68s	2 .73 s		
			2.53s	2.51s		
2.3s	2.43	2.59	2.4	2.35vs		
		2.40				
		2.38	· · ·			
		2.32				
2.21s	2.2b,s-	2.25s,b	2.13	2.23s		
		2.16				
1.89s	2.03	2.02s	2.08	2.13		
1.80	1.86	1.96	1.87	1.97		
	1.84	1.89				
	1.80	1.85				
1.74s	1.74s.b	1.75s	1 74b	1 72		
Table	9.6	cont.				
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10010	~ • · ·	COLLER	۰	٠	٠	

<u>CuC1₂Q</u>	<u>CuBr₂Q</u>	<u>Cu(NO₃) 20</u>	<u>CuCl2Mq2</u>	<u>CuBr₂Mq₂</u>
1.65b	1.64	1.72		
		1.70		
1.44	1.54	1.68		
		1.64		
-		1.59		
	1.45	1.47		
		1.42		
1.36	1.36s	1.39		
	1.30b	1.31		

CuC12Dmq	Cu(NO ₃) 2 Dmq	CuCl2Dpq2	CuBr2Dpg2
7.5		8.2	
6.7vs,b	6.9vs,b	6.0	
	6.5		
	6.2		
5.4s	5.2	5.5	
4.3vs,b	4.3vs	4.3	
	3.85	3.9	
3.65	3.55vs	3.7	3.6
	3.35	3.4	3.45
3.2	3.13vs		3.15
2.9vs		2.95s	2.95b
		2.8	
2.64s		2.7	2.72
2.58		2.57s	2.55s,b

Table 9.6 cont....

CuC12Dma	Cu(NO3) 2 Dmg	CuCl_Dpq_	<u>CuBr2Dpq</u> 2
2.41s		2.49	
2 . 33s	2 . 3s	2.38	2.4b
2.2	2 . 23s	2.235	2.23s,b
2 . 12s	2.13	2.12	2.08
2.02s	2.07	1.96	1.98
1.88		1.9	1.92s,b
1.82			1.85
			1.76
1.72	1.73		1.70
1.65			1.66
			1.61
1.58			1.57
1.52			1.52
			1.49
1.44			1.43
	,		

•



Table 9.7

Thermal data for the copper(II) complexes of quinoxalines.

<u>Complex</u>	a) _{T'} m	b) _{T'(°C})	c) Product	d) _W	r(%)
				Found	Calculated
CuC1 ₂ Q	285*	300	CuCl ₂ Q 1/2	76.5	75.2
CuBr ₂ Q	235†	190	CuBr _{3/2} Q	89.7	88.7
Cu(NO ₃) ₂ Q	255*	260	Cu(NO ₃) ₂	58.0	59.0
$CuCl_2Mq_2$	485†				
$\mathrm{CuBr}_{2}\mathrm{Mq}_{2}$	420*	440	CuBr ₂ Mq	70.9	71.8
Cu(NO3) 2 ^{Mq}	215*	•			
$Cu(NO_3)_2 Mq_2$	125*				
$Cu(NO_3)_2Mq_3$	120*	130	$Cu(NO_3)_2^{MQ_3/2}$	65.1	65.2
CuCl ₂ Dmq	?	260	CuCl _{3/2} Dmq	67.7	67.0
CuBr ₂ Dmq	?	550	CuBr	38.0	37.6
Cu(NO ₃) ₂ Dmq	215*	260	CuNO3	36.8	36.3
CuCl ₂ Dpq ₂	315*	340	CuCl ₂	20.1	19.2
CuBr ₂ Dpq ₂	280*	310	CuBr ₂	28.9	28.4

Notes:

- a) T^{*}_m is the temperature at which the rate of fission of Cu-N bonds first reaches a maximum
- * denotes that Cu-N bond fission is involved in the initial decomposition reaction.
- + denotes that Cu-X or Cu-O bond fission is involved in the initial decomposition reaction.
- b) T' is the temperature at which the intermediate listed is formed.
- c) Only those intermediates are listed for which there is good agreement of W_r data.
- d) Wr is listed for these intermediates.

The T_m values in table 9.7 reveal that the stabilities to copper-nitrogen bond fission are generally in the orders: Mq>Dpq > Q > Dmq and Cl > Br for the halo-complexes. These cannot necessarily be interpreted as the order of Cu-N bond strengths (therefore no correlation with infrared frequencies is possible) for the following reasons:

a) The complicated nature of the decomposition reactions of Copper (II) complexes has been attributed ⁸⁰ by Bowman and Rogers to the prevalence of redox processes.

b) The fission of Cu-N bonds is not always the initial reaction, and in such cases the structure of the intermediate in which the Cu-N bonds break may bear no relationship to the starting complex.

c) Many thermodynamic factors may contribute to stability:

i) If decomposition proceeds via $Cu \times_2$ species, which involve chain structures, then the octahedral complexes already contain such chains, but the square planar complexes do not.

ii) If decomposition proceeds via Cu_2X_2L species, which involve bidentate amines, then the Q and Dmq complexes already contain such amines but those of Mq and Dpq do not.

iii) The bidentate ligands may involve an entropy factor analogous to the "chelate effect".

iv) Hydrogen bonds may be involved in the Mq and Dpq complexes, which have non-coordinated nitrogen atoms.

v) Unknown values for Lattice energies and latent heats of evaporation will be involved.

d) Kinetic factors may be important; for example Dpq may be a bulky leaving-group.

The factors a) and c(ii) are illustrated by the easy decomposition of most of the complexes with bidentate amines, via the species $CuBr_{3/2}Q$, $CuCl_{3/2}Dmq_{1/2}$ (table 9.7), Cu_2Br_2Q and $CuBr_{3/2}Dmq_{1/2}$ (more tenuous evidence). These intermediates may be formulated as the Copper (I) complexes CuBrL, Cu_2Cl_2L' , Cu_2Br_2Q and Cu_2Br_2L'' ; where L, L' and L'' are halogenated amines (c.f. the diamagnetic complex involving bromoacetone and Dmq, mentioned above). The existence of such halo-amines is supported by the observation that the decomposition of these intermediates involves simmultaneous loss of halogen and amine. <u>Studies of Molecular Models</u>.

In order to study the importance of steric hindrance scale molecular models were built from polystyrene, using the dimensions of table 9.8. For the reasons put forward in chapter 8, a value of 1.4 Å was assumed for the Van der Waals' radius of copper. This value is not critical for a valid comparison of the differences between the complexing abilities of the amines studied. These differences were investigated by attempting to "co-ordinate" the model amines to a model of the CuCl₂ chain present ¹⁸⁶ in CuCl₂py₂, and also to copper atoms involved in five-co-ordinate and square-planor stereochemistries. Six-coordination.

If Pauling's value³⁹¹ (1.8 Å) for the Van der Waals' radius of chlorine (ionic) was used, then none of the amines could coordinate to the CuCl₂ chain because of hindrance (see figure 9.4) between the

Table 9.8

Molecular parameters (Å) used in making models.

Distance	Value Taken	Reference
Normal Cu-Cl bond	2.28	186
Long Cu-C1 bond	3.05	186
Cu-N bond	2.02	186
C-C bond in aromatic rings	1.395	566
C-N	1.352	566
С-н	1.084	566
C-H bond in methyl groups	1,101	566
C(ring)-C(methy1) bond	1.52	5 66
C(ring)-C(pheny1)bond	1.50	566
Cl covalent radius	0.99	391
H Van der Waal's radius	1.0*	
N	1.5	392
C1	1.4**	390
Cu	1.4**	
Aromatic half-thickness	1.7	391

* Value used in Stuart organic models.

** See text.



Figure 9.4

chlorine atoms and the 8-H atom or the 2:3- substituents. However, if Sanderson's value 390 (1.4 Å; appropriate for covalent 567 chlorine) was used, then it was possible to coordinate, at normal Cu-N bond lengths (~ 2.0 Å), the Q and Mq molecules but not Dmq or Dpq. Further, Mq could coordinate at the unhindered 4-N position but not at the hindered 1-N atom. The optimum orientation for coordination was achieved when the amine rings were perpendicular to the chain axis.

The experimental evidence suggests that Q and Mq do coordinate the CuCl₂ chain. Thus the effective Van der Waals' chlorine radius in these compounds appears to be less than 1.8 Å, consistent with some degree of covalent bonding. It was found in chapter 4 that $CuCl_2Quin_2$ was probably a square-planar monomer. If this is due to steric hindrance, the six-coordinate nature of $CuCl_2Q$ may be related to a higher degree of covalent bonding in the quinoxaline complex. This would be consistent with the higher π - acceptor capacity of Q, which is evident from the frequencies of charge-transfer-onset $(\mathcal{P}_{Q} = 25 \text{kK}$ for the $CuCl_2Quin_2$; $\mathcal{P}_{Q} = 21 \text{kK}$ for $CuCl_2Q)$.

No models were built of the bromo-complexes, but it seemed likely that the longer 390 bromine Van der Waals' radius would be compensated by longer 237 Cu-X and Cu-Cu bonds, and so the effects of steric hindrance would be similar to those in the chloro-complexes. Even longer Cu-Cu distances were expected 568 in the nitrato-complexes, and consequently, little steric hindrance of polymeric six-coordination would occur.

Five-coordination.

Stoicheiometry only permits the chloro-complexes of Q and Dmq to achieve five-coordination via chloride bridges. Models show that trigonal-bipyramidal or square-pyramidal structures are possible.

Both types of structure are also possible for the complexes of Mq, either with or without chloride bridges. For Dpq, however, models show that five-coordinate structures are only possible with chloride bridges (c.f. figure 4.2). Structures with bidentate Dpq are sterically impossible because the molecules orient themselves in such a way that either a chlorine atom touches the 8-H atom, or a phenyl group touches the quinoxaline nucleus of another amine molecule (see figure 9.4).

Five-coordinate structures appear to be **lmprobable**e for the bromo-complexes.

Four-coordination.

Models show that there is no hindrance of square-planar coordination because the amine rings can orient themselves in a plane perpendicular to that of the halogen atoms (c.f. NiBr₂Dmp in figure 7.3).

Discussion.

The evidence from the study of reflectance spectra, far-infrared spectra and molecular models is consistent, and suggests the following structures:

Halo-complexes.

Infrared spectra and X-ray powder patterns suggest that the corresponding chloro- and bromo- complexes have similar structures.

a) The evidence, taken with the stoicheiometry, suggests that the complexes of Dpq have square planar monomeric structures (c.f. figure 3.3). Their monomeric nature is confirmed by the observation of clear melting points (Cl⁻: 264-8°C; Br⁻: 254-6°C) for these compounds; but not for any of the other complexes, in agreement with their polymeric structures.

b) The Dmq complexes exhibit reflectance spectra which are very similar to the Dpq complexes. The square-planar nature of the former compounds is confirmed by the far-infrared data and the studies of models. The stoicheiometry of these complexes suggests that they have polymeric structures, like that 505 (figure 7.3) of NiBr₂ (2:5 Dmp), with amine bridges. The alternative square-planar, halogen-bridged dimeric structure (c.f., the similar 569 units in CuCl₂MeCN) is excluded since only one \mathcal{P}_{Cu-Cl} bond is observed, at high frequency, and since the optical d-d band is observed at high frequency.

c) The evidence suggests that the complexes of Mq have structures very similar to that ¹⁸⁶(figure 3.1) of CuCl₂py₂; and the models indicate that coordination occurs probably via the 4-N atom.

d) The present consideration confirms Underhill's suggestion⁵⁰⁴ that the quinoxaline complexes have structures (figure 7.6) based

on that ¹⁸⁶(figure 3.1) of CuCl₂py₂, but in which the CuCl₂ chains are bridged by bidentate amine molecules. An alternative structure like that of NiCl₂py (figure 7.7), is excluded because the d-d transition is observed at a high frequency; while the three-dimensional variant (figure 7.8) is excluded on steric grounds, since the Cu-Cu distances within the CuCl₂ chains are too short to accommodate the quinoxaline molecules between the chains.

Nitrato-complexes.

It has been suggested that all the complexes have polymeric octahedral structures with anion bridges (and also amine bridges in all except the bis- and tris- Mq complexes). The structures may be similar to that 570 of Cu (NO₃)₂ (MeNO₂), with the addition of a further ligand to the chromophore.

The complexes described here show that 2-substituents (on a ligand) may have a very specific steric effect on their structures. The facility with which copper (II) halides form these complexes is probably due to the tetragonal distortion present 103 in these complexes, which will reduce steric effects due to the 2-substituent. The increased stability, relative to the pyrazine complexes, 495,496,503 is probably due to the greater **m**-acceptor character of the quinoxalines. Experimental.

Reflectance spectra were obtained by Dr.B.J.Hathaway at Hull University. Mr. P. Borda performed the carbon, hydrogen and nitrogen analysis. Far-infrared spectra were recorded by Dr. D.M.Adams and

Mr.D.M.Morris, at Leicester University, using nujol mulls supported on Rigidex plates and a Research and Industrial Instruments Co., FS-520 Interferometer. Cosine Fourier transforms were computed to a resolution of 5 cm⁻¹ on an Elliott 803 computer. Other details have been described previously. All compounds were dried at 20°/25mm. Dichloro bis-(2-methylquinoxaline) copper (II).

2-Methylquinoxaline (2.1 g., 2 mol.) was added to a stirred solution of copper (II) chloride dihydrate (1.25 g., 1 mol.) in ethanol (20 ml.). The green product (2.4 g., 78%) was filtered off and washed with ethanol and ether (Found: C, 51.1; H, 4.0; Cl, 16.9; Cu, 15.4. $C_{18}H_{16}Cl_2CuN_4$ requires C, 51.1; H, 3.8; Cl, 16.8; Cu, 15.0%). Dibromobis-(2-methylquinoxaline) copper (II).

A solution of copper (II) bromide (1.4 g., 1 mol.) in ethanol (15 ml.) was added, with stirring, to 2-methylquinoxaline (2.0 g., excess). The dark brown product (2.8 g., 87%) was filtered off and washed with ethanol and ether (Found: C, 41.8; H, 3.5; Br, 31.4; Cu, 12.6. $C_{18}H_{16}Br_2CuN_4$ requires C, 42.2; H, 3.2; Br, 312; Cu, 12.4%). Dinitrato-(2-methylquinoxaline) copper (II).

2-Methylquinoxaline (1 g., excess) was added to a stirred solution of copper (II) nitrate trihydrate (1.5 g.) in ethanol (7 ml.). Ether (15 ml.) was added, and the pale blue product (1.8 g., 87%) slowly precipitated, then was filtered off and washed with ether (Found: C, 32.7; H, 2.6; Cu, 19.6; N, 17.1. $C_9H_8CuN_4O_6$ requires C, 32.6; H, 2.4; Cu, 19.2; N, 16.9%).

Dinitrato tris-(2-methylquinoxaline) copper (II).

A solution of copper (II) nitrate trihydrate (l g.) in acetone (10 ml.) was filtered and added, with stirring, to 2-methylquinoxaline (1.5 g., 3 mol.). The medium blue product (1.3., 60%) was filtered off, and washed with a little acetone (Found: C, 52.3; H, 3.9; Cu, 10.4; N, 18.1. $C_{27}H_{24}CuN_8O_6$ requires C, 52.3; H, 3.9; Cu, 10.3; N, 18.1%). Dinitrato bis-(2-methylquinoxaline) copper (II).

This compound was prepared by the same method but with only 2 mol. of 2-methylquinoxaline (Found: C, 45.3; H, 3.5; Cu, 13.5; N, 18.0. $C_{18}H_{16}CuN_{6}O_{6}$ requires C, 45.4; H, 3.4; Cu, 13.4; N, 17.7%). Dichloro-(2:3-dimethylquinoxaline) copper (II).

A solution of copper (II) chloride dihydrate (2.5 g., 1 mol.) in acetone (150 ml.) was filtered and added slowly to a vigorously stirred solution of 2:3-dimethylquinoxaline (2.5 g., excess) in acetone (50 ml.). The solution was cooled in ice, and the yellow-green product (4.0 g., 93%) filtered off and washed with acetone and ether (Found: C, 41.2; H, 3.4; Cl, 24.4; Cu, 21.7; N, 9.9; $C_{10}H_{10}Cl_2CuN_2$ requires C, 41.0; H, 3.4; Cl, 24.2; Cu, 21.7; N, 9.6%).

Dichloro bis-(2:3-diphenylquinoxaline) copper (II).

This compound was prepared as above (Found: C, 68.8; H, 4.1; Cl, 10.1; Cu, 9.1. C₄₀H₂₈Cl₂CuN₄ requires C, 68.7; H, 4.0; Cl, 10.1; Cu, 9.1%).

Dibromo-(2:3-dimethylquinoxaline) copper (II).

A solution of 2:3-dimethylquinoxaline (l g., l mol.) in ethanol (30 ml.) was added to a stirred solution of copper (II) bromide

(1.4 g., 1 mol.) in ethanol (80 ml.). The brown product (1.4 g., 58%) was filtered off and washed with ethanol and ether (Found: C, 31.7; H, 2.8; Br, 41.6; Cu, 16.2. $C_{10}H_{10}Br_2CuN_2$ requires C, 31.5; H, 2.6; Br, 41.9; Cu, 16.6%).

Dinitrato-(2:3-dimethylquinoxaline) copper (II).

A solution of 2:3-dimethylquinoxaline (2.5 g., 1 mol.) in acetone (50 ml.) was slowly added to a filtered solution of copper (II) nitrate trihydrate (4.1 g., excess) in acetone (150 ml.) at 0°C. The pale blue product (3.2 g., 59%) slowly precipitated and was filtered off and washed with acetone (Found: C, 35.1; H, 3.2; Cu, 18.5; N, 16.2. $C_{10}H_{10}CuN_{4}O_{6}$ requires C, 34.7; H, 2.9; Cu, 18.4; N, 16.2%). <u>Dibromo bis-(2:3-diphenylquinoxaline) copper (II).</u>

Copper (II) bromide (0.8 g., 1 mol.) and 2:3-diphenylquinoxaline (2.1 g., 2 mol.) were stirred together at 150-170°C for 20 minutes. Benzene (10 ml.) was added, with stirring, and when the mixture had cooled to room temperature the yellow-brown product (1.3 g., 46%) was filtered off and washed with ethanol, water, and then a mixture of ethanol and ether. (Found: C, 60.8; H, 3.7; Br, 20.6; Cu, 8.0. $C_{40}H_{28}Br_2CuN_4$ requires C, 61.0; H, 3.6; Br, 20.3; Cu, 8.1%). Chapter 10

THE COMPLEXES OF COBALT (II) SALTS WITH QUINOXALINES

The importance of steric factors and of ligand basicity and polarisability has been demonstrated in Chapter 5 for the substituted pyridine complexes of Co(II). Lever, et al, have found ⁴⁹⁷ evidence of the operation of these effects in the Co(II) complexes of the pyrazines. Steric effects in complexes involving bidentate ligands have already been studied in the Copper (II) complexes of quinoxalines, and it was of interest to investigate the Cobalt (II) complexes of these ligands.

Complexes were prepared having either CoX_2L or CoX_2L_2 stoicheiometry, as shown in Table 10.1. In each ease the monoquinoxaline complexes were obtained by thermal treatment of the bis-complexes. Thermogravimetric analysis of CoI_2Q_2 , however, revealed no evidence for the existence of CoI_2Q_2 . Attempts to prepare CoI_2Mq , $Co(NO_3)_2Mq$ and $Co(NO_3)_2Dmq$ yielded only impure products. No evidence was obtained for the existence of any complexes with Dpq. None of the ligands yielded sulphate or acetate complexes, but there was some evidence for thiocyanate complexes containing Cobalt (II).

Diffuse Reflectance Spectra.

Table 10.1 collects the electronic band maxima of these complexes, while some of the spectra are illustrated in Figure 10.1.

Tetrahedral Complexes.

Intense, split bands near 7kK (\mathcal{D}_2) and 16kK (\mathcal{D}_3) have been shown ^{191, 452, 571} to be characteristic of the spectra of tetrahedral

Table 10.1

Electronic spectra (kK) and room:temperature magnetic moments (B.M.) of Cobalt(II) complexes with quinoxaline.

Complex	$\frac{\mu_{eff}}{\mu_{eff}}$	Band Maxima
CoC1 ₂ Q	5.31	19.0(42,sh), 17.1(.54), 14.8, 13.1, 6.6(.27), 6.0(sh)
CoC1 ₂ Q ₂	4.55	17.2(.75), 16.4(.88), 15.6(.74,sh), 8.6(.47), 6.4(.65)
CoBr ₂ Q	4.58	16.3(1.03,sh), 15.3(1.28), 8.2(.65,sh), 6.8(1.04), 5.7(1.1
CoBr ₂ Q ₂	4.61	16.8(.88), 15.5(1.06), 8.4(.61), 6.3(.72)
CoI ₂ Q ₂	4.60	15.7(1.06,sh), 14.7(1.20), 8.2(.71), 6.1(.74),9.4(.16)
Co (NO ₃) 2Q	4.95	22.8(.39), 21.0(.33), 20.2(.32), 18.9(.29),17.2,15.9 (.25)
Co (NO ₃) 20, 2HO	5.14	21.4(.45),19.9(.50),18.8(.51),16.1(.24,sh),8.4(.26)
Co (NO3) 202. 240	-	21.0(.55),20.0(.56),15.4(sh),8.2(.23)
CoC1 ₂ Mq	5.07	16.8(.83), 15.7(sh), 7.6(b,sh),6.6(.37,b),5.1(.40)
CoC12 ^{Mq} 3/2	5.12	19.2(.49,sh),16.8(.51),15.7(.49),7.9,6.7(20,b)4.5(b)
CoBr ₂ ^M q	4.97	16.8(1.08,sh),16.0(sh),15.5(1.22),8.9(.24),7.0(.44)6.1(.4 4.8(.68,
CoCl ₂ Dmq	4.90	15.9(.77),14.9(.86),14.4(.87),7.9(b,sh),6.0(.66,b) 5.2(.68,b)5.1(.94,b),4.5(.91,b)
CoBr ₂ Dmq	4.83	15.5(1.10,sh),14.9(1.34),14.1(1.47),8.0(.16,sh),5.7(.88,b
Col_Dmq	4.56	14.1(sh,b),12.7(1.24),7.8(.18,b),4.8(.82,vb)



Co(II) complexes. The bis-quinoxaline complexes and those of Dmq, along with CoBr₂Mq and CoBr₂Q, have electronic spectra clearly showing these features and are thus concluded to have tetrahedral structures.

The \mathcal{D}_2 band has three components $(A_2 + B_1 + B_2)$: as expected ¹⁹³ for a CoX_2L_2 chromophore of C_{2v} , C_s or C_1 symmetry) in all these spectra, except for those of the bis-quinoxaline complexes. At room-temperature these have two components, but the broader lower energy peak splits at -180°C. The higher energy side of the \mathcal{D}_3 band of $CoBr_2Mq$ is partly obscured by the tail of a ligand electronic band which extends down to 15kK (see Chapter 7).

As before, the centres of gravity of the \mathcal{D}_3 and \mathcal{D}_2 systems have been estimated visually and used to calculate the Dq and B' values given in Table 10.2. Both the bis-quinoxaline and the Dmq complexes show the orders of Dq and B' (Cl⁻ > Br > I⁻) expected ^{23, 149} from the positions of the anions in the spectrochemical and nephelauxetic series. The Dmq complexes all have significantly lower Dq values than the quinoxaline series. This may be a result of steric hindrance, or of the presence of bridging Dmq ligands. 167, 198 The effect could also reflect differences between Q and Dmq in these

Table 10.2

Calculated ligand field parameters (kK) for Cobalt(II) complexes with quinoxalines.

Complex	Stereochem.	Obser	ved Frequ	encies	Cal	culate	d parameters
		<u><u>v</u>1</u>	<u>v</u> 2	<u>v</u> 3	Dq	<u>B'</u>	$\frac{\lambda'}{2}$
CoCl ₂ Q	0 _h	6.6		17.1	.75	.76	14.1
CoC1 ₂ Q ₂	т _d		7.1	16.4	.41	.75	13
CoBr ₂ Q	T _d		6.0	15.3	.35	.73	12
CoBr ₂ Q ₂	т _d		7.0	16.1	.41	.73	15
CoI2Q2	T _d		6.5	15.2	.37	.70	13
Co(NO ₃) ₂ Q.2H ₂ O	0 _h	8.4		19.9	.95	.84	17.9
$Co(NO_3)_2Q_2.2H_2O_3$	o _h	8.2		20.6	.94	.90	· 17.6
CoC1 ₂ Mq	0 _h	6.6		16.8	.75	.74	14.1
CoC12 ^{Mq} 3/2	0 _h	6.7		16.8	.76	.73	14.3
CoBr ₂ Mq	т _d		7.0	15.5	.41	.68	24
CoC12Dmq	T _d		5.2	14.9	.30	.75	17
CoBr ₂ Dmq	т _d		5.1	14.4	.29	.72	15
Col Dmq	T d		4.8	12.7	.27	.62	09

complexes, with regard to their mono-, or bi-, dentate character. $CoBr_2Mq$ has a Dq value equal to that of $CoBr_2Q_2$, as would be expected if the former complex contained bidentate, and the latter monodentate amine.

All these values of Dq and B' are close to those calculated in chapter 5 for the tetrahedral halopyridine series. Little comparison of these values is possible with data ⁴⁹⁷ from the tetrahedral complexes of the pyrazines, since only \mathcal{P}_3 was generally recorded for the latter. However, the solution-spectra of the pyrazine complexes are very similar to those of the quinoxalines in the \mathcal{P}_3 region. Both \mathcal{P}_2 and \mathcal{P}_3 have been recorded ¹⁶⁷ for CoI₂ (2:6 - Dmp)₂, this data yielding Dq = 0.39kK and B' = 0.64kK. In this case, Dq is near the values for iodides found in this chapter and in chapter 5, while B' is slightly lower than that found for either the quinoxaline, or the halopyridine series of complexes.

Octahedral Complexes.

The spectra of the complexes $CoCl_2Q$, $Co(NO_3)_2Q$, $Co(NO_3)_2Q.2H_2O$ and $Co(NO_3)_2Q_2.2H_2O$ exhibit the relatively weak bands at 7kK and 15-20kK which are characteristic 205,206,371,571 of octahedral Co(II) species. The low energy band is assigned to \mathcal{P} , and, unlike the halopyridine complexes, shows no splitting (CoCl_2Q has a shoulder at 6kK which is a ligand infrared overtone common to all these

compounds). The infrared overtones, or the electronic \mathcal{P}_3 system, may obscure a component of \mathcal{P}_1 .

The band system near 18kK is assigned to \mathcal{V}_3 , though it may be complicated by the presence of close doublet terms.⁵⁷¹ The centre of gravity of this system was taken as \mathcal{V}_3 , allowing Dq and B' to be calculated. These values are given in table 10.2. \mathcal{V}_2 is predicted to lie near a shoulder observed at 14.8kK for Co Cl₂Q, but within the \mathcal{V}_3 systems of the nitrates. An alternative assignment, including the 15kK shoulder as a \mathcal{V}_1 component, gave meaningless calculated parameters. No satisfactory assignment was possible for Co(NO₃)₂Q. This may be due to the proximity of the intense nitrate $n \rightarrow \pi^*$ band.⁵⁶¹

The spectra of these complexes are very similar to those of the pyrazine species, though a detailed comparison is possible only with $\operatorname{CoBr}_2(2:6-\operatorname{Dmp})_2$. In this case the spectrum ⁴⁹⁷ is sufficiently simple to allow assignments of $\mathcal{P}_2 = 15.6$ kK and $\mathcal{P}_3 = 18.2$ kK, giving values of Dq = 0.83kK and B[†] = 0.80kK which are in the range of the quinoxaline complexes.

The tetrahedral and octahedral complexes of quinoxaline may be compared if allowance is made for the lower ligand fields in the former species. When this is done the octahedral complexes are found to have slightly lower Dq, and higher B^{*}, values than the tetrahedral complexes. This may be due to steric hindrance and bridging in the former molecules, or to greater C6 - N \Im -bonding in the latter species.

The nitrates are a special problem since there are few complexes with which to compare them. It has been suggested 266 that $Co(NO_3)_2py_3$ may contain mono-, and bi-, dentate nitrato-groups, and its spectrum has maxima in the same range as the quinoxaline series.

Remaining Complexes.

The spectra of $CoCl_2Mq$ and $CoCl_2Mq_{3/2}$ are not clearly characteristic of either of the common stereochemistries, since they exhibit a relatively strong, broad band at 16.8kK. These complexes are probably octahedral, since the broadness and intensity may be attributed to a ligand electronic band (see chapter 7). The relatively weak 7kK bands confirm this stereochemistry.

The spectra of these two complexes are very similar (apart from an overall higher intensity for $CoCl_2Mq$), and this would be expected if both contained the same $CoCl_4N_2$ chromophore. The ligand field parameters, calculated on the basis of octahedral structures, are close to the values for $CoCl_2Q$ (see table 10.2).

Magnetic Susceptibilities.

The room-temperature magnetic moments, given in table 10.1, confirm (see chapters 1 and 5) that all the bis-quinoxaline complexes, $\operatorname{CoBr}_2 \mathbb{Q}$ and $\operatorname{CoI}_2 \operatorname{Dmq}$ have tetrahedral structures while $\operatorname{CoCl}_2 \mathbb{Q}$, $\operatorname{CoCl}_2 \operatorname{Mq}$, $\operatorname{CoCl}_2 \operatorname{Mq}_{3/2}$ and $\operatorname{Co}(\operatorname{NO}_3)_2 \mathbb{Q}_2 \mathbb{H}_2 \mathbb{O}$ are octahedral. Repeated determinations of the magnetic moments of $\operatorname{CoBr}_2 \operatorname{Mq}$, CoCl_2 Dmq , $\operatorname{CoBr}_2 \operatorname{Dmq}$ and $\operatorname{Co}(\operatorname{NO}_3)_2 \mathbb{Q}$ gave values between the usual ranges ¹⁹ for tetrahedral, and octahedral, complexes. These complexes are assigned structures (tetrahedral, except for the nitrate) on the basis of their reflectance spectra. However, when this is done and a T.I.P. correction applied to the tetrahedral complexes, values of λ ' (given in table 10.2) may be obtained from equation 1.14.

The high moments of the Dmq complexes may be attributed to their relatively low Dq values. A good correlation is evident for the Dmq complexes and for $\operatorname{CoBr}_2 \operatorname{Q}_2$ and $\operatorname{CoI}_2 \operatorname{Q}_2$, between the trends in B' and λ '; in agreement with the work of Jørgensen ¹⁴⁹ and Owen.⁴⁶ They found that both parameters were related to the extent of covalency in the metal-ligand bonding. The high moment of $\operatorname{CoBr}_2 \operatorname{Mq}$ cannot be explained on this basis.

The low moment of the octahedral complex $Co(NO_3)_2Q$, may be due to the presence of a large distortion.¹⁹ No attempt has been made

here to seek significance in the actual values of the octahedral moments, since it has already been noted 572 that they reveal no obvious regularities.

Infrared Spectra.

Table 10.3 collects the absorption maxima (and their tentative assignments) of the complexes in the infrared region; with the exception of the bands due to the nitrate group, which are listed in table 10.4.

Nitrate Bands.

All the nitrate-complexes exhibit bands in the regions 696-716, 799-825, 1035-1048, 1289-1312 and 1502-1521 cm⁻¹, which have previously (see Chapter 9 and Appendix A5) been assigned to the \mathcal{P}_5 , \mathcal{P}_6 , \mathcal{P}_2 , \mathcal{P}_1 and \mathcal{P}_4 vibrations of the co-ordinated nitrate group.¹⁰⁰ The positions of the bands are very similar to those of the Cu (II) complexes, also to those reported for $Co(NO_3)_2(py)_3$.

The presence of water in the two complexes formulated as hydrates is confirmed by the broad O-H bands near 1650 and 3300 $\rm cm^{-1}$, also by the appearance of an overtone near 5.1 kK in their reflectance spectra.

Amine Bands.

In Chapter 5 it was noted that the amine infrared bands were often split in tetrahedral complexes. Split bands for quinoxalines are most prevalent in the bis-complexes, the Dmg

Table 10.3

Infi	rared s	pectra (3	75-1700cm	-1) of the	cobalt ((II) com	plexes	with quine	oxalines.	Bands due	e to the
<u>Vib</u> <u>No</u> .	<u>Q</u>	<u>CoCl₂Q</u>	<u>CoBr₂Q</u>	$\frac{\text{CoCl}_2 Q_2}{2}$	CoBr ₂ Q ₂	Comple Col ₂	$\frac{x}{Q_2}$	0(NO3)2Q	<u>Co (NO3)</u>	2 ^{Q•2H20}	$Co(NO_3)_2Q_2.2H_2O_3$
36 24	394s 402s	420 426	416m 427m	394 407 415 420sh	414m,b	41	3m	422ms	400 407	m,b	
		503mw	508mw	510mw	505mw						
48	535vw	523sh 532m	517mw 526mw	525 535 mw,b	537mw	53	3mw	528 538 ^m			NOT
			562mv	557mw	556mw	56	2mw	562mv	562m	īv	
35	603mw	622mw	625mw	625mv	625mw	62	5mw	626m			
					645mw	64	3mw	642mw			
	66 3v w	667mw	673mw					665mw			
		707m	700]		710sh	70	9m	708m	*		
		71.8mw	709) mw		722sh	72	3sh		722s	;h	*
11 27 39	726mw,s 7 5 6vs 783vw	sh 737ms 750s	739ms 758ms 763sh	731s,b 750m 762sh	7397 759 ms,b 766	73 73 75	07 77 9ms	739 748]s 768mw	733s 748s 762s	;,b sh sh	740sh 762sh 775vs,b
23	867s	842s	851sh 857m 863sh	850) 862] ^{mb}	846sh 863 869 (m 872)	85 86	1] 2] ^m ,b	839mw 857ms	843n 863n	IW IV	850sh

.

	Tab1	le 10.3	cont				Complex			
	<u>Vib</u> <u>No</u> .	<u>d</u>	CoCl ₂ Q	<u>CoBr₂Q</u>	<u>CoC1₂Q2 C</u>	oBr ₂ Q ₂	<u>Col</u> 2Q2	<u>Co(NO₃) 2Q</u>	$\dot{Co(NO_3)}_2 Q_{\bullet} 2H_2 O$	$Co(NO_3)_2O_2 \cdot 2H$
		917vw	890 m w 936sh , b	920mw	890nw 918sh	89 0 mw 918sh	890mw 920sh	. •	886m,b 917sh	886s 898ms
		057-	0(0)		934) 948 ms,b	935sh 953sh	939m	950sh		
	22	9535	960s	962 (970) ^m	962)	960ms J 970sh	960ms 972sh	971ms	903s,b	973 980) ^{ms}
			997nw		1002mav	1000mw	994mw	1006m		1008w
			1022mw		1026mv		1020mw	1020mv	1020ms,b	
•	46	1025 vs	s 1042sh	1042m	1042m	1045ms	1042m	*	*	*
	37	1099w	1062ms 1098mw	1060m 1088mw	1062 1079 mw,b	1075mw	1062m 1083m,b	1091mw	1077m	1058ms
				1113mw	1132mw	1130)	1129mv			
·	34	1128 m	1147ms	1149m 1164mw	1159) 1170 ms	1134 m, 5 1161	1158) 1168 m,b 1181	1146ms 1170mw	1152 1168] ms,b	1138ms 1152ms
	45	∫1204] 1209] ⁿ	^W 1212ms	1212m	1210m	1214m	1201 1213 mw	1204m 1217mv	1207m	1208ms
	5	1267vi	1290)	1239mw 1263mw 1280mw	1280mw	1242) 1250 sh,b 1263 1280	1248mw		1241sh	
			1301 sh, 1310	b 1302sh,	b,m					

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Vib.	<u>Q</u>	<u>CoC1₂Q</u>	<u>CoBr₂Q</u>	<u>CoC1202</u>	<u>CoBr₂Q₂</u>	<u>CoI20</u> 2	$Co(NO_3)_2Q$	$C_0(NO_3)_2Q.2H_2O$	$Co(NO_3)_2O_2 \cdot 2H_2C$
<u>110</u> .		1310 sh,t	þ	1311 m	1307) 1317] ^m	1305) 1317] ^m ,b	*	*	*
4	1356	mwşh 1351m	1328mw 1370sh,	b 1360mw	1341 1356) ^m	1352mw	1358) 1366(m		NOT
32	137 0	m 1385) 1397) ^m	13987 1419 ^m ,	1384mw	1382mw	1387m 1404 1413 m	1374) 1407sh 1426ms b	1420)	RECORDED
18	1416	nw 1428m,b	14195	1432 m,b		1419	1420m3,0	1420 ms,b	
17	1463	s 1488sh	1489sh	1470 ^{J mw}	1474ms	1475 ms	144731	1472mv	ļ
44	1495	s 1512s	1500m	1501ms	1497ms	1498m	1491s	1488ms	*
3	1570	mw 1542m	1512m 1544 1555] ^{mw}	7	1538) 1555) ^{mw}	1522) 1538) ^m	*	*	
16 Э	1608 1622	w ^{1601m}	1587) 1595) mw	ī	1580mw 1610mw	1593mw			
ا 1–0°	H							1628] 1669 ^{]m} ,b	1660m,b

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cont. . . .

Table 10.3 cont....

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$\frac{\text{Vib}}{\text{No}}$.	Mq	<u>CoCl₂Mq</u>	<u>CoCl₂Mq3/2</u>	<u>CoBr₂Mq</u>
		415sh	405mw	400ms
36	410s	423m,b	42 2m	419s
		455mw	451mw	450mw
24	448m	465mw	460mw	470m
		503mw	502mw	
		518mw	514mw	
48	534w	541mw	532 537	532mw
		590mw	588mw	
35	6 09ms	600mw	615mw,b	619mv
	648mw		640mw	642mw
12 27	699m 759vs	720sh 733s	714 vs 724	710 719 ^m 732ms
		752sh		750s
39	792sh	764sh	770sh	770sh
·		841 858) ^m	845mv	848 864 m,b
23	884s	890m	888m,b	887m
10	911ms	935 945) ^m	944mw	936m
22	967vs	970ms,b	963) 975) mw	971ms,b
(Me- rock)	1009s		1018mw	1036mw
46	1034ms	1081 1094	1085m,b	

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Table 10.3 cont....

<u>Vib</u> . No.	Mq	<u>CoC12^{Mq}</u>	CoCl ₂ Mq3/2	<u>CoBr₂Mq</u>
34	$\begin{pmatrix} 1123\\ 1130 \end{pmatrix} vs$	1155) 1170 ms	1150mw 1175mw	1154} 1166] ^m
45	1204vs	1199mw	1197mv	1200m
(Me Rock	1213sh			
	1272sh	1280mw		1277mw
33	1293vs	1310m,b	1305ms,b	1305m
	1334mw	1340sh	1349mw	1353mw
4	1371 s	1365mw,b	1373m	1367mw
52 18 17	1378) 1412s 1437m	1398) 1412 m,b 1440)	1409 1420} ^m	1410 1425 ms,b 1430
44	1493vs	1499m	14942 1502 J ^m	1494 1502) ^{ms}
		1525mv	1537mw	1531sh
3	1563s	1557mw	1548mv	1549) 1559) ^m
31 16	1579m 1612mw	1582]m,b		1591mw
<u>Vib</u> . <u>No</u> .	Dmq	CoC12Dmq	CoBr ₂ Dmq	Col_Dmq
		425mw	425mw	
24	428m	47 6m	472mw	NOT
			512	RECORDED
9,13		517	517 527	
48		567mw	569mw	
35	614m	607s	606ms	
		624mw	621mw	V

Vib. No.	Dmq	CoC12Dmq	CoBr ₂ Dnq	$\underline{\text{Col}}_2 \underline{\text{Dmq}}$
12	670m	662) 667) ^{mw}	655) 663) mw	663sh 677s,b
		710sh	709m	
		721sh	720m	720m
11	722w(sh)	734ms	733ms	740sh
27	762vs	753s	762ms,b	770s,b
23	820mv	82Om	822m	82 7 m
		843mw	840mw	840sh
		891m	888mv	
10	906m	930m	915m,b	908mv
22	978mw	965) 971] ^m	961) 972) ^m	965sh
(Me Rock)	990m	99 7 m	998m	1002ms,b
46		10 1 9m	1029mw	1020sh
37		1080mw	1075m,b	
			1111 1125] ^m	1120sh
34	1137mw	1145ms	dd41ms	1145m
26	1165 m	1158) 1165 ms 1170	1159sh 1167ms	1178mw
45	1212m	1210m 1220ms	1213sh 1222ms	1215sh 1226s
33	1320 1328 mw 1337	1300m	1301 1317 ms,b	1300sh 1316sh
4	1363mw	1380ms	1375m	138Om

Table 10.3 cont....

<u>Vib</u> . <u>No</u> .	Dmq	CoC12Dmq	CoBr ₂ Dmq	<u>Col</u> 2Dmq
		1405mw	1402mw	1402w
18	1400mw		1413) 1428) ^{ms} ,b	
17	1437mw	1439mw	1450ms	1455mw
44	1491mw	1473vs 1494mw	1484) 1492 1502 ms,b	1490mw
		1520ms	1514	1514mw
3	1565mv	15 7 9mw	1571mw	
16	1603vw	1611mw	1608mw	1608sh
	1640vw	1640mw	1637m	1635mw,b

Notes:

* Denotes regions obscured by nitrate bands.

Table 10.4

Infrared absorption peaks (cm⁻¹) due to the nitrate group in the Cobalt(II) complexes of quinoxalines.

Complex	<u>ν</u> 5	<u><u><u>v</u>6</u></u>	<u>~</u> 2	<u><u>v</u>1</u>	$\frac{v_4}{4}$
Co (NO ₃) ₂ Q	696m	799ms	1048m,b	1289 1309 ^{}ms} ,b*	1510 1521 ^{}s*}
Co(NO3)20.2H20	712sh	810mw	1035ms,b	1312ms,b*	1502ms,b*
$Co(NO_3)_2 Q_2 \cdot 2H_2 O$	716sh	815 _{}m} 825 ^{}m}	1040vs	1290 1310 ^{}vs,b*}	1508vs*

* Ligand bands which are broadened in the nitrates compared, with the halides.

complexes and CoBr_2 Q, which are confirmed as tetrahedral species.

These splittings are probably caused by coupling between two amine molecules co-ordinated to the same metal ion, giving a symmetric and an asymmetric combination for each frequency (see Appendix A.5). Only one component will be observed unless the complex belongs to an acentric point group, such as the tetrahedral group. However, octahedral complexes may be acentric, due to a cis-configuration or the orientations of the quinoxaline nuclei; but only if two amine molecules are co-ordinated to the metal ion will they give rise to split infrared bands. This may account for the few bands which are observed to split in the spectra of CoCl₂Q and the nitrato-complexes. Activation of A₂ fundamentals or overtones is an alternative mechanism for producing new bands, but this would lead to a more random distribution than is evident.

Infrared band splittings are not necessarily indicative of any stereochemistry for the Mq complexes, since the one methyl substituent confers very low symmetry upon them.

The complexes of Dmq exhibit the \mathcal{P}_{46} vibration, a band at 470 cm⁻¹ and strengthening of the \mathcal{P}_{35} and \mathcal{P}_{11} bands. These features were suggested in Chapter 9 to be associated with monodentate co-ordination. However, the similar criteria suggested for Q and Mq do not apply to the Co (II) complexes, possibly because of the low molecular symmetry.

The observed infrared shifts due to co-ordination do not appear to be as systematic as found for the halopyridine complexes. This may be due to the occurrence, in the same series of complexes, of effects due both to differences of stereochemistry and to differences in mono-, or bi-, dentate ligand character. For the larger and more weakly basic quinoxaline ligands the Co-N bonds may not be greatly stronger for tetrahedral, than for octahedral, Any effect of Co-N σ -bond strength on the ring species. frequencies, might be overwhelmed by the greater backdonation to antibonding orbitals, in the tetrahedral complexes of quinoxalines, compared with those of halopyridines (see Chapter 7). This is observed, and (unlike the halopyridine complexes) the octahedral complexes CoCl₂Q and CoCl₂Mq show larger co-ordination-shifts than the tetrahedral CoCl_Q_ and CoCl_Dmq molecules.

The bromides generally show lower frequencies than the chlorides, but the differences are somewhat greater for the CoX_2Q and CoX_2Mq complexes, than for CoX_2Q_2 and CoX_2Dmq . This is due to a difference in stereochemistry between the chloride and bromide complexes of the former group.

Discussion.

The stereochemistries of the complexes have been assigned, as shown in table 10.2, on the basis of their reflectance spectra and usually confirmed by magnetic and infrared data. The structures
possible within these stereochemistries will now be discussed.

The CoX Q complexes.

The structures of these tetrahedral complexes depend on whether the amine molecules are mono-, or bi-, dentate. The parameters of the electronic spectra are very similar to those of the bis-halopyridine complexes, suggesting monomeric structures (c.f. Figure 3.4) with monodentate quinoxaline molecules. This is confirmed by the occurrence of pairs of amine infrared bands rather than of triplets or quartets.

The CoX_L complexes.

The tetrahedral complexes $\operatorname{CoBr}_2\mathbb{Q}$ and $\operatorname{CoBr}_2\mathbb{M}q$ have similar spectral parameters to those of $\operatorname{CoBr}_2\mathbb{Q}_2$, suggesting that both are polymeric (Figure 7.5) with bidentate amine molecules, rather than dimeric (Figure 7.4). This is confirmed in the quinoxaline case by the observation of split amine infrared bands.

The complexes of Dmq are all tetrahedral and their lower range of Dq values suggests that the co-ordination sphere contains only one amine molecule. This would be consistent with dimeric structures (Figure 7.4) containing monodentate Dmq. The infrared criteria for monodentate character supports this structure, but the split amine infrared bands do not. Far-infrared data, which might resolve this ambiguity, was not available.

The octahedral complexes $CoCl_2Q$ and $CoCl_2Mq$ probably have polymeric structures (c.f. Figure 7.2), containing bidentate, rather than monodentate 7^8 , 7^9 (c.f. Figure 7.7), amine molecules. This

The nitrato-complexes.

All these are octahedral, and contain co-ordinated nitratogroups only. The low electronic intensities suggest trans-The similar spectra for all these complexes configurations. indicates that they all may contain the CoO_hN_p chromophore, which very approximate calculations (using the rules of average environment) have tentatively suggested for the hydrates. The hydrates probably contain monodentate nitrato-groups, Co(NO3)2Q2.2H20 being monomeric and Co(NO₃)₂Q.2H₂O having bridging amine molecules. Co(NO3)2Q would also contain bidentate quinoxaline, six-co-ordination being achieved with bidentate nitrato-groups. It is uncertain whether the anions have bridging or chelate character in this complex. Factors influencing the structures of the halides.

The CoX₂L species have been arranged in table 10.5 to show how the change from octahedral to tetrahedral structures is influenced by the anion and the amine present. These effects can be explained just as were the similar effects shown by the Co(II) halopyridine complexes. The anion-dependence is probably due to polarisability,

Table 10.5

Stereochemistries of the CoX_2L complexes.

Increasing T_d tendency due to ligand basicity and steric hindrance.

Increasing T_d tendency due to anion polarisabilit

		*		
	CoCl ₂ Q	CoC12 ^{Mq}	CoC12Dmq	
37	CoBr ₂ Q	CoBr ₂ Mq	CoBr ₂ Dmq	
y .			CoI2Dmq	
•				

* The box encloses the octahedral complexes. The rest are tetrahedral.

though the same structures would be predicted if the iodide ion caused steric hindrance of the formation of octahedral polymers. The polarisability factor also accounts for the octahedral structures 497 of CoCl₂Mp, CoCl₂(2:5-Dmp), CoCl₂(2:6-Dmp)₂ and for the tetrahedral structures 497 of CoBr₂Mp, CoI₂Mp, CoBr₂(2:5-Dmp), CoI₂(2:5-Dmp) and CoI₂(2:6-Dmp)₂.

The amine-dependence of the structures probably reflects the influence both of ligand-basicity and of steric hindrance, though γ -acceptor character may also be involved (see Chapter 7). In the pyrazine complexes the steric, basic and electrophilic effects enhance When compared with those of pyridine, steric effects are each other. probably negligible in both series, but the lower basicity and higher $\boldsymbol{\Upsilon}$ -acceptor character of the diazine lead to octahedral structures for all three halides; whereas only &-CoCl₂py₂ is octahedral ¹⁸⁶ among the complexes of the monoazine. For the CoX_2Q_2 complexes the basicity and *M-*bonding effects should also be conducive to octahedral structures, and thus the observed tetrahedral structures may indicate the presence of a steric or a thermodynamic effect. A steric effect, alone, would not explain why CoCl_Q and CoCl_Mq are octahedral, as are CoCl_Mp and CoCl_ (2:5-Dmp). 497 All four of these complexes contain bidentate amines, and this suggests that an unfavourable steric effect may be overcome thermodynamically, perhaps by the favourable entropy term or extensive delocalisation introduced by the presence of bridging ligands.

The failure to prepare complexes of Dpq with Co(II) cannot be

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a purely steric effect, since Cu(II) does form such derivatives. However, steric effects would limit any Co(II) complexes to tetrahedral stereochemistries. In this case the lower basicity and poorer T-acceptor properties (see Chapter 7) of Dpq, relative to those of Q, may be insufficient to overcome unfavourable factors such as the tetrahedral C.F.S.E. Further, as shown in Chapter 5, Co(II) less readily forms complexes in which backdonation is inhibited, than does Cu(II).

Experimental.

The diffuse reflectance spectra were recorded at the temperature of liquid nitrogen by Dr. B. J. Hathaway at the University of Hull. Mr. J. Plenderlieff measured the infrared spectra and Messrs. P. Borda and R. White performed the microanalyses. The preparation of $CoCl_2.2H_2O$ and $CoBr_2$ have been described in Chapter 5, and other details have also been given previously.

All compounds were dried at 20°C/25mm.

Cobalt (II) nitrate dihydrate.

Cobalt (II) nitrate hexahydrate was heated at 60°C in a vacuum oven overnight.

Dichlorobis (quinoxaline) cobalt (II).

Cobalt (II) chloride dihydrate (1.5g; 1 mol.) was mixed with quinoxaline (4g; excess) and stirred for 45 minutes at 120°C. Dry

benzene (20ml) was added, and the mixture allowed to cool. The blue product (3:4g; 97%) was washed with benzene, and dried at 50° C in a vacuum oven for 24 hours. (Found: C,49.4; H,3.2; Co,15.3; Cl,18.7. $C_{16}H_{12}Cl_2CoN_4$ requires C,49.3; H,3.1; Co,15.1; Cl,18.2%).

Dichloro (quinoxaline) cobalt (II).

The above bis-complex was heated overnight at 150°C to give the grey product. (Found: Cl,27.4; Co,22.8. C₈H₆Cl₂CoN₂ requires Cl,27.3; Co,22.7%).

Dibromobis (quinoxaline) cobalt (II).

A solution of cobalt (II) bromide hexahydrate (3.3g, 1 mol.) in acetone (35 ml) was added, with stirring, to a solution of quinoxaline (3.0g; excess) in acetone (2 ml). On scratching the walls of the vessel the bright blue-green product (2.0g. 41%) precipitated. This was filtered off and washed three times with acetone, and then with ether. (Found: C,40.6; H,2.8; Br,33.3; Co,12.3. $C_{16}H_{12}Br_2CoN_4$ requires C,40.1; H,2.5; Br,33.4; Co,12.3%).

Dibromo (quinoxaline) cobalt (II).

The above bis-complex was heated overnight at 150° C to give the pale green product. (Found: C,27.1; H,2.6; Br,45.5; Co,16.7. $C_8H_6Br_2CoN_2$ requires C,27.5; H,1.7; Br,45.8; Co,16.9%).

Di iodo bis (quinoxaline) cobalt (II).

A filtered solution of cobalt (II) iodide dihydrate (3.0g; 1 mol)

in acetone (6ml) was added, with stirring, to a solution of quinoxaline (2.24g; 2 mol.) in acetone (3ml). The bright green precipitate of the product (3.8g; 77%) formed on adding ether (15ml) and then allowing to stand for 30 minutes. This was filtered off and washed once with a little acetone and then with ether. (Found: C,33.4; H,2.2; I,44.6; Co,10.3. $C_{16}H_{12}I_2CoN_4$ requires C,33.5; H,2.1; I,44.3; Co,10.3%).

Dinitrato bis (quinoxaline) Cobalt_(II) dihydrate.

This pink complex was prepared by a similar method to that used for dibromobis (quinoxaline) cobalt (II). (Found: Co,12.1. $C_{16}H_{16}CoN_6O_8$ requires Co,12.3%).

Dinitrato (quinoxaline) Cobalt (II) dihydrate.

This was prepared in an identical fashion to dichlorobis (quinoxaline) cobalt (II). (Found: N,15.1; Co,16.9. $C_8H_{10}CoN_4O_8$ requires N,16.0; Co,16.9%).

Dinitrato (quinoxaline) Cobalt (II).

The above pink dihydrate was heated for 24 hours at 100° C, after which the grey product was left. (Found: C,30.5; H,2.3; N,17.7; Co,18.8. C₈H₆CoN₄O₆ requires C,30.7; H,1.9; N,17.9; Co,18.8%).

Dichloro (2-methyl quinoxaline) Cobalt (II).

2-Methyl quinoxaline (0.5g, 1 mol.) was added to a solution

of cobalt (II) chloride dihydrate (0.6g, 1 mol.) in acetone (10ml), and the solvent evaporated off. The dark blue-grey product (1.0g; 100%) was dried in a vacuum oven at 50° C. (Found: Co,21.5; Cl,25.8. C₉H₈Cl₂CoN₂ requires Co,21.5; Cl,25.9%).

Tetra chloro tris (2-methyl quinoxaline) di cobalt (II).

A mixture of cobalt (II) chloride dihydrate (1.0g; 1 mol) and 2-methylquinoxaline (2.5g; excess) was stirred, at 110° C, for 10 minutes. Benzene (20 ml) was added, and the mixture allowed to cool. The grey product (1.5g; 72%) was filtered off and washed with benzene, acetone and ether. (Found: C,47.2; H,3.8; N,12.3; Co,17.1; Cl,20.1. $C_{27}H_{24}Cl_4Co_2N_6$ requires C,46.8; H,3.5; N,12.1; Co,17.0; Cl,20.5%).

Dibromo (2-Methyl quinoxaline) Cobalt (II).

Cobalt (II) bromide (1.5g; 1 mol.) was stirred with 2-methyl quinoxaline (1.0g; excess), at 60° C, for 10 minutes. Benzene (20ml) was added, and the mixture allowed to cool. The crude dark bluegreen product (2.1g; 84%) was filtered off, washed with benzene and a little acetone, and purified by heating overnight, at 90° C, in an oven. (Found: Br,44.2; Co,16.5. $C_9H_8Br_2CoN_2$ requires Br,44.0; Co,16.2%).

Dichloro (2:3-Dimethyl quinoxaline) Cobalt (II).

2:3-Dimethylquinoxaline (1.4g; 1 mol) and cobalt (II) chloride hexahydrate (1g; 1 mol) were mixed in acetone (20ml) solution, and the solvent evaporated off. The crude, pale blue product (1.1g; 91%) was washed on a sinter crucible with benzene, acetone and ether, and purified by heating for 6 hours, at 90° C, in an oven. (Found: Cl,24.2; Co,20.6; $C_{10}H_{10}Cl_2CoN_2$ requires Cl,24.6; Co,20.5%).

Dibromo (2:3-Dimethyl quinoxaline) Cobalt (II).

A solution of cobalt (II) bromide hexahydrate (1.5g; 1 mol) in acetone (2 ml) was added, with stirring, to a solution of 2:3-dimethylquinoxaline (1.4g; excess) in acetone (15 ml). Addition of ether (20ml) gave a blue precipitate which was filtered off, washed with ether and heated at 100°C for two hours, to give the grey-green product (1.2g; 69%). (Found: Br, 42.7; Co,15.5. $C_{10}H_{10}Br_2CoN_2$ requires Br,42.4; Co,15.6%).

Di iodo (2:3-Dimethyl quinoxaline) Cobalt (II).

Cobalt (II) iodide dihydrate (2g; 1 mol.) was stirred with 2:3-dimethylquinoxaline (1g; 1 mol.), at 110° C, for 15 minutes. Benzene (20ml) was added, and the mixture allowed to cool. The crude yellow-brown product (1.2g; 44%) was filtered off, washed with benzene and ether and purified by heating overnight in an oven at 80° C. (Found: I,54.1; Co,12.5. $C_{10}H_{10}I_2CoN_2$ requires I,53.9; Co,12.5%).

Chapter 11

THE COMPLEXES OF NICKEL (II) SALTS WITH QUINOXALINES

Structural effects due to steric hindrance have been observed in the alkyl-pyrazine complexes of Nickel (II).^{168,198,495} This chapter describes a study of the nickel (II) complexes of substituted quinoxalines, and compares them with earlier work ^{510,511} on quinoxaline itself.

Table 11.1 lists the complexes which have been prepared with the 2-methylquinoxaline and 2:3-dimethylquinoxaline ligands. No complexes containing Dpq could be prepared, nor could Dmq complexes with NiCl₂, NiBr₂ or Ni(NO₃)₂ be obtained.

Diffuse Reflectance Spectra.

The spectra are detailed in table ll.l and some are illustrated in figure ll.l. All the complexes exhibit strong bands above 31kK which are probably due to charge-transfer or to ligand absorption. In addition, the tails of the strong ligand U.V. absorption bands of Mq and Dmq extend considerably into the visible region (see chapter 7) and confuse the identification of d-d bands above 17kK. A sharp, weak absorption appears near 7.2kK in the spectra of the quinoxaline complexes and confuses the measurement of broad d-d maxima near 7kK. This may be due to an amine infrared overtone. The d-d bands are discussed below.

Octahedral Complexes.

The spectra of the chlorides, bromides and nitrates show two well-defined bands of moderate intensity near 7kK and 12kK, along with some less pronounced peaks in the 17-27kK region. These features are very similar to those of the halopyridine complexes

Diffuse Reflectance maxima (kK) and room temperature magnetic moments

(B.M.) for th	ne complex	es of nickel (II) with quinoxalines.
<u>Complex</u>	^μ eff	Band Maxima
NiC12 ^{Mq}	3.34	22.7(.32),19.9(.22),18.9(.21),13.0(sh),12.0(.22), 7.5(.25), 6.8(sh)
NiBr Mq 2	3.17	21.1(.32),18.2(b,vw,sh),17.0w,15.4(.16),12.0(.14) 10.7(sh),7.3(.12),6.7(.13)
$Ni(NO_3)_2Mq$	3.22	22.2(sh),20.0(vb,sh,w),11.8(.24),10.5(sh),6.8(.24)
$^{\text{NII}}2^{Mq}2$	0.96	32.3(1.59),27.3(1.41),24.3(.1.44),16.4(.71),11.1(sh,w), 8.9(.07b)
NiI_2Dmq_2	0.77	33.0(1.73),28.2(sh),24.4(1.48),14.9(.50)
NiCl ₂ Q	3.23	25.2(vb,vw,sh),19.2(vw),13.0(sh),11.8(.14),7.4(.18)
NiBr ₂ Q	3.23	24.7(b,w,sh),22.0(sh),18.9(w,sh),12.2(.16),11.2(.14), 7.0(.18)
$Ni(NO_3)_2Q$	3.13	24.7(vb,w,sh),22.5(b,w,sh),17.5(.10),13.9(.03),8.7(.21
NiI ₂ Q2	-0.0	34.5(1.66),26.6(1.52),22.5(1.24),16.0(.62),11.2(1.0,b)



of Nickel (II), suggesting that they have octahedral structures.

In agreement with Smart⁵¹⁰ and Lever,⁵¹¹ the 7kK and 12kK bands are ascribed respectively to the \mathcal{P}_1 and \mathcal{P}_2 transitions in octahedral pseudo-symmetry. The amine and charge-transfer absorption complicate the assignment of \mathcal{P}_3 . The parameters, given in table 11.2, were calculated from \mathcal{P}_1 and \mathcal{P}_2 . The selection of values for \mathcal{P}_1 and \mathcal{P}_2 was difficult, due to the splitting of the former band in the Mq complexes and the latter band in all the complexes. As discussed in chapter 6, this could be a genuine tetragonal splitting, or the shoulders might be caused by spin-forbidded transitions. The former assignment gives the more reasonable values of Dq and B', implying that the tetragonal component of the crystal field is larger than in the halopyridine complexes.

The values calculated for Dq and B' conform to the usual spectrochemical and nephelauxetic series 23,149 for the anions, and suggest that Mq may give rise to stronger σ -bands than does Q (in agreement with the order of basicities). The assignments are confirmed by the similarity of the ligand field parameters for analogous Ni(II) and Co(II) complexes, (in agreement with the adjacent position of the metal ions in the spectrochemical and nephelauxetic series). Both Dq and B' are lower for the Co(II) and Ni(II) complexes of the quinoxalines, than for those of the halopyridines. This is presumably due to the lower basicity of the quinoxalines and to a greater covalency¹⁴⁹ (consistent with \mathfrak{M} -acceptor, rather than σ -donor, properties) in their complexes.

Calculated ligand field parameters (kK) for the octahedral complexes of nickel(II) with quinoxalines.

<u>Complex</u>	Observed 1	Frequencies	Calcul	lated	Parame	ters
	<u>v1</u>	<u>v2</u>	Dq	<u>B</u> *	<u>v</u> 3	<u>λ</u> *
NiCl ₂ Q	7.4	12.2	.74	.74	21.1	20
NiBr ₂ Q	7.0	11.5	.70	.68	19.7	19
NiCl ₂ Mq	7.5	12.3	.75	.72	21.0	28
NiBr ₂ Mq	7.1	11.6	.71	.66	19.6	16
Ni(NO3)2Mq	6.8	11.4	•68	•80	21.0	18

Table 11.2 also gives values of \mathcal{P}_3 predicted from \mathcal{P}_1 and \mathcal{P}_2 . These are in the 19.6 - 21.1kK region where several peaks are observed. No fully acceptable assignment was possible for Ni(NO₃)₂Q.

Square-Planar Complexes.

The spectra of all the iodides are very weak below 12kK, but exhibit a number of strong peaks in the 20 - 33 kK region and a moderately strong band near 15.5 kK. High intensity in the 14 - 23 kK region is characteristic of tetrahedral, square-coplanar or fivecoordinate complexes. The absence of a moderately strong peak near 10kK eliminates the possibility that the complexes are tetrahedral 190,192,193,199,200 or five-coordinate ^{412,419,453,456}, and suggests (in agreement with Smart and Lever, et al) that they have square-planar structures. Very similar spectra have been recorded for square-planar nickel (II) complexes.^{161,192,198,573,574,575}

Various authors have discussed the spectra of square-planar complexes.^{113,161,573-576} It is generally agreed that the ground-state is ${}^{1}A_{g}$ and that the stronger bands involve singlet excited states, while the weaker bands correspond to triplet excited states. Other details are in dispute and as a result, little information is available from these spectra.

Smart was able, approximately, to fit ⁵¹⁰ the spectra of NiI₂Q₂ and of the pyrazine complexes to the energy-level diagram given¹¹³ by Maki for four-coordinate, trans-planar symmetry (with R=1.5 and μ_1 =1). The best agreement for the quinoxaline complex was obtained with μ_2 =1.6. (R is the radial part of the wave function and μ_1 and μ_2 are the point-dipole moments of the two types of ligand present). In this case the ll.2, 16.0, 22.5 and 34.5kK bands may be assigned to transitions involving the ${}^{3}B_{1g}$ (or ${}^{3}A_{g}$), ${}^{1}B_{3g}$, ${}^{1}B_{1g}$, ${}^{1}A_{g}$ and ${}^{1}B_{2g}$ excited states, respectively. Such an assignment was given 192 by Goodgame and Goodgame for the very similar spectrum of NiI₂Quin₂.

If this assignment is correct it is possible to predict how the energy levels should diverge or converge as \mathcal{N}_2 varies. In this way the relative order of \mathcal{N}_2 values may be seen to be Q < Mq < Dmq, a series increasing in Dq. It may be tentatively suggested that Dq follows the amine basicity order in the iodide complexes as well as in the chloride and bromide series.

Magnetic Measurements.

As table 11.1 shows, the chlorides, bromides and nitrates all have high-spin moments within the same range (3.13 - 3.35 B.M.) as that of the octahedral halopyridine complexes. The range of the 'values of λ ' (derived from equation 1.14, and given in table 11.2) is somewhat lower than that for the halopyridine complexes, in agreement ¹⁴⁹ with the higher covalency shown by the B' values.

The low-spin moments of the iodides are consistent with the singlet ground-state generally found ^{19,161,168,576,577} in square-planar complexes. The complexes of Mq and Dmq have moments somewhat greater than zero, but this is not unusual and has been attributed ^{176,576} to the thermal population of a low-lying triplet state. Ni(3Mepy)₄ (ClO₄)₂ has a ¹⁷⁶ moment as high as 1.05 B.M. Maki's diagrams do include¹¹³ low triplet states.

Infrared Spectra.

Table 11.4 lists the amine infrared bands, and table 11.5 gives the bands due to the nitrate groups. A tentative assignment is also given to Smart's data 510 on the complexes of unsubstituted quinoxaline. Nitrate Bands.

The complexes exhibit bands near 795, 1015, 1280 and 1490 cm^{-1} , and such features have been shown (in chapters 9 and 10) to be characteristic of coordinated nitrato-groups.

Amine Bands.

The infrared spectra of the octahedral complexes of the same amine are practically identical, but the iodides have more complicated spectra. The 2_{35} band, for example, is observed in the spectra of all the iodides but of none of the other halides. The data on these complexes has been used, in chapter 9, as part of a survey on which the proposed criteria for monodentate characters were based.

Thermal Decomposition Data.

Smart has given⁵¹⁰ T.G.A. curves for the complexes of unsubstituted quinoxaline. Figure 11.2 shows the results for the complexes of Mq, while table 11.6 compares the observed and calculated values of W_r for some proposed intermediates. Agreement is poor but probably within the experimental error. NiCl₂Q, NiBr₂Q and NiCl₂Mq appear initially to lose their amine molecules, but NiI₂Q₂ and NiI₂Mq₂ decompose to NiO in one stage. The temperatures for the maximum rates of these processes are given in table 11.6. The other

Infrared spectra (cm⁻¹) of the nickel(II) complexes of quinoxalines.

<u>Vib</u> . <u>No</u> .	Q	NiCl2Q	<u>NiBr2Q</u>	<u>Ni(NO3)20</u>	$\underline{\text{NiI}_2\text{Q}_2}$
36	394s	41 2m	416m		
24	402s	428ms	428m	425vs	433ms
48	535vw	536mw	536mw	538) 543) ^m	532) 537 m 544
35	603mw			648mw	642) ^s
12	663vw	5 67mw	667mw		
11	726w,sh	721m	724m	730m	
27	756vs	746vs	746vs	743s	756vs
					778m
39	783vw				786m
23	867s	846m 853ms	844ms) 855s J	864ms	861ms}
22	953s	966]	965s		962mw
		970) ^{ms}	974m_	977m	980mw
		1028mw		1026m	
46	1025vs	1050m	1050m	1052m	1049s
37	1099w	1060m	1.075m		1090m
34	1128 m	1131 1148 m	1135m 1146m	1145sh 1150m	1132s 1140m
45	1204 1209 mw	1203mw 1215m	1202mw 1217ms	1208m 1219mw	1203ms 1221mw
5	1267vw			1252m,b	1268mw
		1298mw	1298m.b	*	1290mv

Table 11.4 cont....

<u>Vib</u> . <u>No</u> .	<u>Q</u>	<u>NiCl2Q</u>	<u>NiBr₂Q</u>	<u>Ni(NO3)2Q</u>	<u>Nil₂Q2</u>
4	1356mw,sh	136Om	1357ms		1361ms
32	1370m	1380mv	1380mw	1378ms	1380mw
18	1416nw	,		1432m	1423mw
17	1463s	1479m,b	1464mw,b	1460mw,b	1473vs,b
44	1495s	1508 ? 1514) ^{ms}	1508 1515]ms	1523vs	1497s
3 .	1570mw				1580m
16	16062 1622) ^w	1625m	162Om,b	1606mw	1609mw
<u>Vib</u> . <u>NO</u> .	Mq	<u>NiCl₂Mq</u>	<u>NiBr₂Mq</u>	<u>Ni(NO3)2^{Mq}</u>	<u>NiI2Ma</u> 2
					388m,b
		410m			
36	410s	425ms	425m,b	427ms,b	438m
24	448m	467m	472mw	46 8mw	477m
					510m,b
48	534w				543ms
					596 604 m,b
35	609ms				620ms
·	648mw	631mw	632mw	631 645 mw,b	641mw
12	699m	710sh		708sh	707m
		721sh	718sh	721sh	720sh
11 27	759vs	749s,b 763sh	732) 745 s,b 757)	736sh 748s,b	732sh 750 760

Table 11.4 cont....

<u>Vib.</u> <u>No</u> .	Mq	<u>NiCl2Mq</u>	<u>NiBr₂Mq</u>	<u>Ni(NO3)2^{Mq}</u>	<u>Nil2Mq</u> 2
39	792sh	786mw		*	78Om
38		848mw	847m,b	850mv	860mw
23	884s	890) 898] ^m	891m	889m	892s
10	911ms	939sh	94 1 sh	938mw	932mw
22	967vs	973ms,b	971ms,b	970m,b	972ms
(Me rock)	1009s				1008m
46	1034ms	1027m,b	1032m,b	*	1028sh
37		1067mw	10 7 5m,b		1070m
34	1123) 1130] vs	1158) 1168) ^m	1152 1167 ^{ms} , b	1130m	1121ms 1133s
$\begin{pmatrix} 45\\ Me\\ Rock \end{pmatrix}$	1204vs 1213sh	1202mw 1220mw	1206) 1220) ^m , ^b	1206m	1205ms
33 19	1272sh 1293vs	1282) 1291 m,b 1312	1282mv 1300) 1310) ^m	* 1304) 1314) ^m	1270mw 1300ms,b
	1334mw	1332mw			
4 32	1371) 1378) ^s	1376ms	1361) 1376) ^m	1353m	1364m
18 17	1412s 1437m	1401mw	1391mw 1442mw	1387m 1427mw	1405 1431) ^m ,b
44	1493vs	1510m,b	14 9 4ms	a)	1495ms
3 31	1563s 1579m	1556) 1566) ^{mw}	1555m,b	1563sh 1580m	155 <i>3</i> m 1571m
16	1612mw	1607 1613 ^m ,b	1611mw	1601) 1611 (m,b 1625)	1610mw

1649) 1656)^m ,

<u>Vib. No</u> . 24	228m	$\frac{\text{Nil}_{2}\text{Dmq}_{2}}{450\text{m}}$ 2
		465m
48		546ms
35	614m	625s
12	670m	660m
11	722w,sh	710m
27	762vs	756vs
39	789vw,sh	77 4m
23	820mw	830ms
vС-Ме		854m
10	906m	911mw
22	978mw 2	970mw
(Me rock)	990m _	1001ms
46		1018m
34	1137mw	1129s
26	1165 m	1170s
45	1212 m	1201mw
[~] 5	1258mw	1261 m
33	1320	1312m
	1328 JINY 1337	1330sh
	1348w	1340s
4	1363mw	1360ms
32	1373w	1371 m
18	1400mw	1397m

Table 11.4 cont....

Vib. No.	Dmq	$\underline{\text{NiI}}_2 \underline{\text{Dmq}}_2$
17	1437mw	1421m
		1483s
44	1491mw	1495s
3	1565mw	1570ms
16	1603vw	1610mw
43		1720mw

Note: * Denotes regions obscured by nitrate bands.

Infrared Bands due to the nitrate group in the Nickel(II) complexes of Quinoxalines

Complex	<u>~</u> 6	$\frac{v}{2}$	<u>~1</u>	<u>~4</u>
Ni(NO3)2 ^{Mq}	793ms	1015ms	1274ms	1483vs [*]
Ni(NO3)2Q	799ms	1012m	1289s	1495vs [*]

* Ligand bands which are broadened in the spectra of the nitrate complexes.



Comparison of observed, and calculated, percentage original weight remaining, at various stages, in the thermal decomposition of the nickel(II) complexes of quinoxalines.

			Percentage or remain	riginal weight Ing
Initial Complex	Product	<u>т (^ос)</u>	Observed	Calculated
NiCl ₂ Mq	NiCl ₂	160	55.1	47.4
,	NiO	490	31.7	27.4
NiBr ₂ Mq	$\mathrm{NiBr}_{2}^{\mathrm{Mq}_{\frac{1}{2}}}$	130	87.2	80.2
	NiBr ₂	220	66.3	60.5
	NiO	510	25.3	20.5
Ni(NO3)2 ^{Mq}	$Ni(NO_3)_2Mq_1$	160	80.3	77.9
	$Ni(NO_3)_2$	510	53.0	55.8
	NiO	535	29.6	22.9
NiI2 ^{Mq} 2	NiO	190	16.2	12.5
Nil ₂ Dmq ₂	Nil ₂ Dmq	200	75,9	74.8
	NiI ₂	240	44.8	49.7
	NiO	280	16.6	11.9

complexes appear to decompose by more complicated routes.

The initial reaction in these processes is always a loss of organic ligand, although anion loss is sometimes simultaneous. The reactions like those of Co(II), but unlike those of Cu(II), are not complicated by redox processes. Bowman and Rogers found⁸⁰ this to be the case with the pyridine complexes.

The T_m values for initial amine loss are compared in table 11.7 for the complexes of Ni (II), Co (II) and Cu (II). These figures reveal that:

i) For the same anion and amine, the stabilities depend on the cation, in the order Cu^{2+} Ni²⁺ Co^{2+} . This is the same order as that found⁸⁰ for the pyridine complexes, and correlates with the Irving-Williams stability⁸⁶ order. Cu⁺ may be fitted into this series between Ni and Co (see chapter 8).

ii) For the same metal and anion, the quinoxaline complexes are more stable than those of methylquinoxaline. If this reflects M-N bond strength it may be the result of steric hindrance in the Mq complexes or of greater π -bonding (see chapter 7) in those of Q.

iii) For the same metal and amine, the chlorides are more stable than the bromides. Presumably this is due to the anion polarisabilities¹⁸¹ and the electroneutrality principle, or to greater steric hindrance in the bromides.

The nickel iodide complexes do not show these features. They are morstable than the analogous chlorides, and the stabilities depend on the amine, in the order $Dmq \ge Mq \ge Q$. The absence of steric hindrance

Temperature (Tm) for the maximum rate of initial organic ligand loss from the complexes of quinoxalines.

Complex	$\underline{T}_{m}(^{O}C)$	Complex	T _m (^O C)
NiCl_Q	260	NiCl ₂ Mq	160
NiBr ₂ Q	210	NiBr ₂ Mq	130
CoC12Q2	190	^{CoC1} 2 ^{Mq} 3/2	170
CoBr ₂ Q ₂	160		
CuC12Q	300		
CuBr ₂ Q	235		

in the square-planar complexes could explain both of these features. X-ray Data.

As table 11.8 shows, the powder photographs of the quinoxaline complexes do not indicate isomorphism. This is consistent with the proposed structures if the way in which the structural units pack together differs in the various complexes.

Discussion.

The reflectance spectra and magnetism of the complexes suggest that the iodides have square-planar stemochemistries and that the rest of the complexes are octahedral. Many features of the infrared spectra and thermal data can be understood on this basis.

The stoicheimetry of the octahedral halo-complexes indicates that the most likely structures involve anion-bridging and either bidentate 495 (c.f. figure 7.2), or monodentate 202,275 (c.f. figure 7.7) amines. Support for the former structure comes from the relatively low intensities of the d-d bands (which are nearer 197 to those of centrosymmetric NiCl₂py₂ than to those of acentric NiCl₂py) and from the relatively high values of Dq for the complexes. The values of Dq for NiCl₂Q and NiCl₂Mq are closer to that of NiCl₂Quin₂ (0.80kK) than to that of NiCl₂Quin (0.66kK).

The nitrato complexes are also probably polymeric with bridging amine molecules and bidentate anions. It is not clear whether the nitrato-groups have bridging or chelate character; though the structures suggested 359 for Ni (NO₃)₂Quin₂, Ni(NO₃)₂(IQuin)₂, Ni(NO₃)₂(2Mepy)₂ and other²⁰⁰ bis-amine complexes support the latter bonding mode.

d spacings (Å) from X-ray powder photographs of the nickel([]) complexes of quinoxalines. Strong lines are underlined.

Complex	<u>d</u>
NiCl ₂ Q	8.0, 5,8, 5.2, 3.7, 3.45, 2.8, 1.82
NiBr ₂ Q	8.5, 4.7, 3.6, 2.95, 2.6
$Ni(NO_3)_2Q$	<u>6.2(b), 4.4, 4.1, 3.55, 3.4, 3.05, 2.32</u>
NiI ₂ Q2	5.8, 5.3, <u>4.4</u> , <u>4.1(b)</u> , <u>3.65</u> , 3.25, 2.6, 2.38, 2.1, 1.91

The stoicheimetry of the square-planar complexes suggests that they are monomeric, as do the similarity of their electronic spectra to those of Nil₂Quin₂¹⁹² and NiBr₂ (2:5-Dmp)¹⁹⁸. As discussed earlier in connection with the pyridine complexes octahedral structures are preferred, except in the case of the iodides whose anion polarisability is too high. The only octahedral chloro- and bromocomplexes isolated were those containing the bidentate ligands Q and Mq. No octahedral complexes of Dmg and Dpg could be obtained. This suggests a delicate balance of factors, such as steric hindrance and the entropy term for bridging ligands. Steric hindrance may be greater in the complexes of Dmq and Dpq, than in those of 2:5-Dmp¹⁶⁸, Bidentate bonding may, therefore, be prevented in the Mg and Q. former complexes, but allowed in the latter complexes. The complexes of Dmg and Dpg would then lack the entropy term associated with bridging ligands.

That NiBr₂Q and NiBr₂Mq are octahedral, whereas CoBr₂Q and CoBr₂Mq are tetrahedral, could be connected with the contribution from the Crystal Field Stabilisation Energy (see chapter 1), although this is usually a small term.

The pyrazines 495,505,168 and quinoxalines form square-planar Ni (II) complexes, rather than tetrahedral species, when fourcoordination is necessary. It has been suggested 330 that this results from the optimisation of Υ -bonding overlap integrals for planar complexes. This factor should become more important as M-N Υ -bonding increases, that is in the complexes of poor σ -donors

and good π -acceptors (diazines), rather than those of better σ -donors and poorer π -acceptors (monoazines).^{189,190,200,274} The results obtained with the quinoxalines support this contention. <u>Experimental</u>.

All compounds were dried at 50°C/25mm. Other details have been previously described.

Dibromo (2-Methylquinoxaline) Nickel (II).

A mixture of nickel (II) bromide hexahydrate (1.6 g., 1 mol.) and 2-Methylquinoxaline (1 g. excess) was stirred together, at 110°C, for 15 minutes. Benzene (20 ml.) was added, and the mixture allowed to cool. The grey-pink product (1.8 g., 100%) was filtered off, and washed with benzene. (Found: N, 7.2; Br, 44.0; Ni, 16.0. C₀H₈Br₂NIN₂ requires N, 7.7; Br, 44.1; Ni, 16.2%). Dichloro (2-Methylquinoxaline) Nickel (II) was similarly prepared as a cream-grey powder (Found: Cl, 25.6; Ni, 20.9. C_qH₈Cl₂NiN₂ requires Cl, 25.9; Ni, 21.4%), as was brown Dinitrato (2-Methyl-<u>quinoxaline) Nickel (II)</u> (Found: Ni, 17.9; C₉H₈NiN₄O₆ requires Ni, 18.0%), light-brown Di Iodo bis(2-Methylquinoxaline) Nickel (II) (Found: N, 10.4; I, 43.2; Ni, 9.7. C₁₈H₁₆I₂NiN₄ requires N, 9.3; I, 42.2; Ni, 9.8%) and dirty-yellow Di Iodo bis(2:3-Dimethylquinoxaline) <u>Nickel (II)</u> (Found: N, 11.3; I, 41.2; Ni, 9.4. C₂₀H₂₀I₂NiN₄ requires N, 8.9; I, 40.4; Ni, 9.3%).

GENERAL CONCLUSIONS AND SCOPE FOR FUTURE WORK

The structural, spectral and magnetic properties of the Cobalt (II), Nickel (II) and Copper (II) complexes of the halopyridines and quinoxalines have been interpreted in terms of a combination of steric, electronic and thermodynamic effects. In the absence of substantial steric hindrance, high ligand basicity and high anion polarisability the complexes were found to exhibit polymeric, octahedral structures similar to that 186 (figure 3.2) of \ll - CoCl₂py₂. In the presence of one, or more, of these effects four-coordinate stereochemistry generally occurs.

The influence of steric hindrance is evident in the structures of all the series of complexes. The clearest example was found in the Copper (II) complexes of quinoxalines. Quinoxaline, 2-Methylquinoxaline, 2:3-Dimethylquinoxaline and 2:3-Diphenylquinoxaline present a series of ligands which increasingly restrict the formation of polymeric, octahedral structures. This results in a progression from a polymeric, octahedral structure to a square-planar monomer for the series of complexes of these amines. Increasing tetragonality was also observed in the Copper (II) complexes of 1:2:4-Triazole, pyridine, 2-chloropyridine, 2-Methylpyridine, 2-Bromopyridine and Phenazine. The four-coordinate structures of the Cobalt (II) complexes of the 2-halopyridines are clearly consequences of steric hindrance.

Other factors appear to modify the influence of steric hindrance on structures. A smaller degree of covalent bonding was suggested in CuCl_Quin than in CuCl_Q, and was considered to lead to a larger

chlorine Van der Waal's radius; and a resulting square-planar structure for the former complex, compared with the octahedral structure of the latter complex.

The effect of amine basicity on the stereochemistry of the complexes is shown most clearly by those of Cobalt (II) halides with substituted pyridines. For both the chloride and the bromide complexes octahedral structures were found for the ligands of low basicity, whilst those of high basicity gave tetrahedral complexes. This behaviour can be explained in terms of Pauling's electroneutrality principle.

The weak Metal-nitrogen σ -bonds, resulting from low basicity, are usually compensated by strengthening of π -bonding. No such compensation occurs for the poor (relative to quinoxaline) π -electronacceptor 2:3-Diphenylquinoxaline and this, combined with steric hindrance, results in the existence of few complexes of this amine.

The evidence for these conclusions depends mainly on the correct assignment of the electronic spectra of the complexes. More accurate data is desirable in order to confirm the proposed structures and also the interpretation of the calculated Dq and B' parameters. Such data could be provided by the polarised spectra of crystals, by low-temperature spectra, by gaussian analyses, and subsequently by a more detailed application of the crystal-field, and molecularorbital theories.

The infrared spectra of Triazole, Phenazine and the quinoxalines have been tentatively assigned and this treatment could be confirmed

by studies of dichroism, and the effects of deuteration.

The strength of the metal-nitrogen bonds was shown, by thermal data on the complexes of the quinoxalines and by infrared shift data on those of the halopyridines, to follow the Irving-Williams stability order.⁸⁶

Many effects have been attributed to the influence of metalnitrogen M-bonding. Among these are the occurrence of square-planar structures for the Nil, complexes, and the variations of thermal stability, infrared shifts, charge-transfer bands and ligand field parameters. However, there is no direct evidence for substantial **T**-bonding. This is, perhaps, an area in which much further work is required. The NMR studies of azine ions 578,579 could be extended to the complexes of these ligands. Some work has already been reported^{72,580}, in which the proton contact shifts have been related to metal-ligand π -bonding. However, it has been demonstrated 581that delocalisation of the metal electrons onto the ligand can occur without metal-ligand **W**-bonding. In view of this it may be better to use NMR methods to measure the barrier to free rotation about the metal-nitrogen bonds. Other approaches to \mathbf{m} -bonding could involve polarography, a study of the effects of substitution⁵⁸³ on the energy levels of coordinated azines 416 and studies of the intensities of infrared bands due to substituents 584.

Steric effects and the influence of bridging ligands could be further studied by the preparation of complexes of 4-nitroquinoline and its derivatives. The nitro- group should¹⁸⁴ give this amine similar
electronic properties to those of quinoxaline. The influence of steric effects could also be studied by the preparation of complexes of 5- and 5:8- substituted quinoxalines.

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Appendix A.l.

Calculation of Ligand Field and Racah parameters for octahedral

$$d^3$$
 and d^8 ions, and tetrahedral d^2 and d^7 ions.

i) Calculation from \mathcal{Y}_2 and \mathcal{Y}_3 only.

Inspection of figure 1.4 shows that:

$$\mathcal{V}_{1} = \mathbb{E}(\mathbb{T}_{2}) - \mathbb{E}(\mathbb{A}_{2}) = 10Dq$$

$$\mathcal{V}_{2} = \mathbb{E}'(\mathbb{T}_{1}\mathbb{F}) - \mathbb{E}(\mathbb{A}_{2}) = \mathbb{E}'(\mathbb{T}_{1}\mathbb{F}) + 12Dq$$

$$\mathcal{V}_{3} = \mathbb{E}'(\mathbb{T}_{1}\mathbb{P}) - \mathbb{E}(\mathbb{A}_{2}) = \mathbb{E}'(\mathbb{T}_{1}\mathbb{P}) + 12Dq$$

$$A.1.1$$

The secular equation is 23 (energies relative to the ^{3}F state): 15B'-E = -4Da = 0

$$\begin{array}{c} 1 \\ 1 \\ -4 \\ Dq \\ 6 \\ Dq - 0 \end{array} \\ \hline \\ or: \\ E^{2} - E(15B' + 6 \\ Dq) + 90B' \\ Dq - 16 \\ Dq^{2} = 0 \\ A.1.2 \\ \hline \\ which has the roots: \\ E_{+} = E'(T_{1}P) = \widehat{\mathcal{V}}_{3} - 12 \\ Dq \\ E_{-} = E'(T_{1}F) = \widehat{\mathcal{V}}_{2} - 12 \\ Dq \\ \end{array}$$

The sum rule for these roots gives:

$$\hat{\nu}_{3} + \hat{\nu}_{2} = 15B' + 30Dq \dots A.1.3$$

while the product rule and equation A.1.3 give:

 $340Dq^{2} - 18Dq (\mathcal{V}_{3} + \mathcal{V}_{2}) + \mathcal{V}_{2}\mathcal{V}_{3} = 0 \quad \dots \quad A.1.4$ and hence: $Dq_{23+} = (1/340) \left[9(\mathcal{V}_{3} + \mathcal{V}_{2}) + (81\mathcal{V}_{2}^{2} - 178\mathcal{V}_{2}\mathcal{V}_{3} + 81\mathcal{V}_{3}^{2})^{\frac{1}{2}} \right]$ A.1.5

At the weak field limit, (Dq=O) A.1.4 becomes $\mathcal{V}_2 \mathcal{V}_3 = 0$; i.e. $\mathcal{Y}_2 = 0$ or $\mathcal{Y}_3 = 0$.

 \mathcal{V}_2 is the meaningful solution of this equation, since figure 2.1 shows that \mathcal{V}_3 is never zero. Equation A.1.5 only gives Dq = 0 at $\mathcal{V}_2 = 0$ for the negative value of the square root, which must be the meaningful value. ii) Calculation from \mathcal{V}_1 and \mathcal{V}_2 only.

Equating E'(T₁F) from equation A.1.1 to the lower root of
equation A.1.2 gives:

$$\gamma_2$$
-12Dq = E'(T₁F) = $(\frac{1}{2}) \left[(6Dq+15B') - (225(B')^2 - 180B'Dq+100Dq^2)^{\frac{1}{2}} \right]$
with Dq = $\gamma_1/10$, from equation 1.5, this gives:
B'₁₂ = $(2\gamma_1 - \gamma_2)$ ($\gamma_1 - \gamma_2$) / $3(5\gamma_2 - 9\gamma_1)$ A.1.6
iii) Calculation from γ_1 and γ_3 only.
Figure 1.4 shows that:
 γ_2 = 15B'+ $3\gamma_1 - \gamma_3$.

This expression and equation A.1.6 then lead to:

$$B_{13} = (\mathcal{V}_{3} - \mathcal{V}_{1}) (\mathcal{V}_{3} - 2\mathcal{V}_{1}) / 3(5\mathcal{V}_{3} - 9\mathcal{V}_{1}) \dots A.1.7$$

Appendix A.2.

Computer programmes used for the

calculation of ligand field parameters.

The following two programmes were devised for use with a Ferranti Argus 100 computer. They are written in the autocode language.

a) For the d^2 and d^7 octahedral and the d^3 and d^8 tetrahedral complexes.

Programme

Remarks

Ν

270CTA 38 TETRA L.F., B.PARAMETERS Prints heading JV1 STOP TEXT DQ(23-) B(123) P(2) DQ(23+)) DQ(23-) B(23+) B(23-) V(IP) B(12) V(3P)) Prints column headings Reads in \mathcal{V}_1 , \mathcal{V}_2 , \mathcal{V}_3 1) V10 = TAPE 3 V1 = 18 x V11 V1 = V1/340Format for Dq=18 $\mathcal{V}_2/340$ Goes to 2) if $\mathcal{V}_1 = 0$ PRINT V1, 3081 \rightarrow 2, V10 = 0 Vl = Vll - VlOV1 = V1/10Format for $Dq_{123} \mathcal{V}_{z} = 0$ Goes to 3) if PRINT V1, 4081 →3, V12 = 0 $V1 = 3 \times V10$ Vl = Vll - VlV1 = V1 + V12V1 = V1/15Format for B¹123 PRINT V1, 4081 $Vl = Vl0 \times Vl0$ $V1 = 17 \times V1$ $V2 = V10 \times V11$ $V2 = 16 \times V2$ $V3 = V11 \times V11$ $V3 = 4 \times V3$ $V4 = V10 \times V12$ $V4 = 9 \times V4$ $V5 = V11 \times V12$ $V5 = 4 \times V5$ V5 = V5 + V1V5 = V5 - V2

V5 = V5 + V3V5 = V5 - V4V5 = V5/1000000PRINT V5, 4063 \rightarrow 4 2) PRINT VIO, 4081 PRINT VIO, 4081 PRINT V10, 4063 4) $V1 = V12 \times V12$ $Vl = 81 \times Vl$ $V2 = V11 \times V12$ $V2 = 16 \times V2$ V2 = V1 + V2V3 = V11 x V11 $V3 = 16 \times V3$ V3 = V2 - V3 \rightarrow 5, 0>V3 V3 = SQRTV3 $V4 = 2 \times V11$ V4 = V4 - V12 $V5 = 9 \times V4$ V6 = V5 + V3V6 = V6/340PRINT V6, 4081 V7 = V5 - V3V7 = V7/340PRINT V7, 4081 V8 = V4/15 $V1 = 2 \times V6$ V9 = V1 - V8PRINT V9, 4081 $V7 = 2 \times V7$ V9 = V7 - V8PRINT V9, 4081 $V6 = 10 \times V6$ V6 = V11 - V6PRINT V6, 3101 **→** 6 5) Vl = 1PRINT V1, 4081 PRINT V1, 4081 PRINT VI, 4081 PRINT V1, 4081 PRINT V1, 3101 6) \rightarrow 7, V10 = 0 ->8

Format for P2

- Allows 3 spaces under
-) DQ(2), DQ(123) and P(2) columns
-) (by printing 3 zeroes).

Goes to 5) if the argument is negative under square root of Dq₂₃₊

Format for Dq₂₃₊

Format for Dq₂₃₋

Format for B'23+

Format for B¹23-

Format for predicted \mathcal{V}_{1}

) If the argument of the square) root in Dq₂₃ is negative "1") is printed²³⁺ under the DQ(23+),) DQ(23-), B(23+), B(23-) and) V(IP) columns. Goes to 7) if **P**₁ = 0 Goes to 8), otherwise. xxvii

3) PRINT V12, 4081) PRINT V12, 4063) PRINT V12, 4081)	Prints zeroes under B(123), P(2), DQ(23+), DQ(23-), B(23+), B(23-) and V(1P) columns if $\mathcal{V}_3 = 0$
$ \begin{array}{l} \text{PRIM} \forall 12, \ \text{SIOI} \\ \text{8)} \forall 2 = 2 \times \forall 10 \\ \forall 2 = \forall 11 - \forall 2 \\ \forall 2 = \forall 2 \times \forall 10 \\ \forall 3 = 9 \times \forall 10 \\ \forall 4 = 4 \times \forall 11 \\ \forall 4 = \forall 3 - \forall 4 \\ \forall 4 = 3 \times \forall 4 \\ \forall 4 = \forall 2/\forall 4 \\ \end{array} $	
PRINT $V4$, 4081 $V4 = 15 \times V4$ $V5 = 3 \times V10$ V5 = V5 + V4 V5 = V5 - V11	Format for B'12
PRINT $\sqrt{5}$, 4101 7) TEXT $\rightarrow 1$ ($\rightarrow 0$)	Format for predicted \mathcal{V}_3 Finished row with spaces. Reads in next set of \mathcal{V}_1 , \mathcal{V}_2 , \mathcal{V}_3 values.
b) For the d^3 and d^8 octahedral and the complexes.	the d ² and d ⁷ tetrahedral
Programme	Remarks
N 380CTA 27 TETRA L.F., B.PARAMETERS JV1 STOP TEXT	Prints heading
B(123) P(3) DQ(23+) DQ(23-) B(23+) B(2 B(12) V(3P)	Prints column headings
<pre>1) V10 = TAPE 3 → 2, V10 = 0 → 3, V12 = 0 V1 = 3 x V10 V1 = V11 - V1 V1 = V1 + V12 V1 = V1/15</pre>	Reads in $\mathcal{V}_1, \mathcal{V}_2, \mathcal{V}_3$ Goes to 2) if $\mathcal{J}_1 = 0$ Goes to 3) if $\mathcal{J}_3 = 0$
PRINT V1, 3081 V1 = V10 x V10 V1 = 17 x V1	Format for B'123

,

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I	$V2 = V10 \times V11$ $V2 = 9 \times V2$ $V3 = V10 \times V12$ $V3 = 9 \times V3$ $V4 = V11 \times V12$ $V4 = 5 \times V4$ V4 = V1 + V4 V4 = V4 - V2 V4 = V4 - V3 V4 = V4 - V4 V4 = V4 +	
2)	PRINT V10, 3081 PRINT V10, 4063 V2 = V11 x V11 V2 = 81 x V2 V3 = V11 x V12 V3 = 178 x V3 V4 = V12 x V12 V4 = 81 x V4 V4 = V4 + V2 V4 = V4 - V3 \rightarrow 5, 0 > V4	
	V4 = SQRT V4 V5 = V11 + V12 V6 = 9 x V5 V7 = V6 + V4 V7 = V7/340 PRINT V7, 4081 V8 = V6 - V4 V8 = V8/340 PRINT V8, 4081 V9 = V5/15 V7 = 2 x V7 V7 = V9 - V7 PRINT V7, 4081 V8 = 2 x V8 V8 = V9 - V8 PRINT V8, 4081 $\rightarrow 6$	
5)	V1 = 1 PRINT V1, 4081 PRINT V1, 4081 PRINT V1, 4081 PRINT V1, 4081	
5)	\rightarrow 7, V10 = 0 \rightarrow 8	

- Format for P3 Prints zeroes under B(123) and P(3) if $\mathcal{V}_1 = 0$)
-)

Goes to 5) if the argument is negative under the square root in Dq23+

Format for Dq₂₃₊

Format for Dq.

Format for B'23+

Format for B'23-

) Prints "1" under DQ(23+),) DQ(23-), B(23+) and B(23-) if) argument of square root in Dq₂₃ is negative. Goes-to 7) if $\boldsymbol{\mathcal{P}}_1 = 0$ Goes to 8), otherwise.)

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3)	PRINT V12, 3081
	PRINT V12, 4063
	PRINT V12. 4081
	PRINT V12, 4081
	PRINT V12, 4081
	PPINE V12 4081
8)	$W_{2} = W_{10} = W_{11}$
0)	$V_{2} = V_{10} \times V_{11}$
	$v_2 = 5 \times v_2$
	$V_{2} = V_{11} \times V_{11}$
	$V_3 = V_2 - V_3$
	$V4 = V10 \times V10$
	$V4 = 2 \times V4$
	V4 = V3 - V4
	$V5 = 9 \times V10$
	$V6 = 5 \times V11$
	V6 = V5 - V6
	$V6 = 3 \times V6$
	V6 = V4/V6
	PRINT V6. 4081
	$V6 = 15 \times V6$
	$V7 = 3 \times V10$
	V7 = V7 + V6
	$V_7 - V_7 - V_{11}$
	$\mathbf{PRTNP} \mathbf{V7} 410$
7)	
()	(-20)
	<u>\</u> ¬ y ∪)

Prints zeroes under B(123),
 P(3), DQ(23+), DQ(23-), B(23+)
 and B(23-) if D₃ = 0
)

Format for B¹12

Format for predicted \mathcal{P}_1 , \mathcal{P}_2 , \mathcal{P}_3 Reads in next set \mathcal{P}_1 , \mathcal{P}_2 , \mathcal{P}_3

Units of cm^{-1} were used in these programmes, except that P was in kK^2 . Unmeasured frequencies were given the value of zero in the input data. In these cases zeroes appeared in the results when the parameters could not be calculated.

Appendix A3

Reported frequencies and calculated ligand field parameters.

Table A3 a) Data for the d^2 and d^7 octahedral and the d^3 and d^8 tetrahedral complexes. All units are kK except those of P_2 (kK²).

Complex	<u>~1</u>	<u>v</u> 2	<u>v</u> 3	<u>P</u> 2	<u>Dq</u> 123	<u>Dq</u> 23+	<u>Dq</u> 13+	<u>B</u> ¹ 23	<u>B</u> *23+	<u>B'</u> 13+	<u>B</u> ¹ 2	Ref.	
V ³⁺ /&-A1 ₂ 0 ₃	17.4	34.5	25.2	-165.99	1.710	1.792	1.868	.500	.665	.605	093	21	
VF ₆ ³⁻	14.8	-	23.0	-	-	-	1.605	-	-	.630	-	24	
Co(H ₂ O) ₆ ²⁺	8.35	17.85	20.0	0.01	.950	.950	.950	.853	.853	.853	.854	18	
Co(H ₂ O) ²⁺	8.2	16.0	19.4	-122,24	.780	.854	-	.720	.869	-	112	23	
Co(H ₂ O) ₆ ²⁺	8.2	16.0	21.55	-143,31	.780	.858	-	.863	1.019	-	112	23	ŭ
Copy ₆ ²⁺	8.479	-	19.8	-	-	-	.962	-	-	.831	. –	210	Я
CoCl ₂ py ₂	8.584	***	17.39	-	-	-	.961	. –	_	.655	-	210	
$Co(NH_3)_6^{2+}$	9.0	18.5	21.1	-65.70	.950	.985	-	.840	.911	-	.214	23	
$\cos en_3^{2+}$	9.4	18.7	21.7	-124,26	.930	. 997	-	.813	.947	-	032	23	
Co enta ²⁻	9.1	16.3	19.9	-235.08	.720	.871		.593	.894	-	345	23	
Co enta ²⁻	9.1	16.3	20.6	-246.77	.720	.872	-	.640	.943	-	345	23	
Co enta ²⁻	9,1	16.3	21.5	-261.80	.720	.873	-	.700	1.006	-	345	23	
KCoF ₃	7.15	15.2	19.2	-13.80	.805	.813		.863	.879		.604	206	
CoCl ₂	6.6	13.3	17.25	-63.35	•670	.712	. –	.717	.801		.035	206	

Complex	<u>~</u> 1	<u>۷</u> 2	<u>_v</u> 3	<u>P</u> 2	<u>Dq</u> 123	<u>Da</u> 23+	<u>Dq</u> 13+	<u>B</u> 123	<u>B'</u> 23+	<u>B'</u> 13+	<u>B'</u> 12	Ref.
CoBr ₂	6.2	12.0	16.4	-88.84	.580	•644	-	.653	.781	-	106	206
$Co(NCS)_2 dpa_2$	9.9	18.7	20.5	-190.30	.880	.994	-	.633	. 862	-	254	213
Co(26DPNO) ₂ Br ₂	9.259	16,129	18.868	-246 .44	.687	.860	-	.481	.827	-	392	212
Co(246TPNO)2Br2	9.434	12.195	19.231	-427 6 2	.276	.657	-	.208	.970 .	-	581	212
$Co(26DPNO)_2(SCN)_2$	9.709	12,903	19.231	-423,83	.319	•694	-	.200	.950		589	212
$Co(246TPNO)_2(SCN)_2$	9.804	12.121	19.23	-44413	.232	.653	-	.129	•972	-	615	212
$Co(26DPNO)_2(NO_3)_2$	9.756	12.121	20.0	-472.71	.236	.654	-	.190	1.025	-	611	212
Co(246TPNO)2(NO3)2	9.302	11.765	18.692	-411.59	.246	.634	-	.170	.946	-	578	212
Copy ₄ C1 ₂	-	16 .129	19 2 31	-	-	.861	-		.853	-	-	78
Co(Brid 4C12	-	15.873	19.048	-		.847	-	_	.848	-	-	78
Co(γpic) ₄ Cl ₂	-	15.873	19 J 48	-	-	.847	-	-	. 848	-	-	78
Co(spic) ₄ Br ₂	-	17.24	19.048	-	-	.917	-	-	.805	-	-	78
Co(ypic) ₄ Br ₂	-	17.241	19,231	-	-	.917	-	-	. 818	-	-	78
Copy412	-	17 ,241	20.0	-	-	.919	-	-	.872	-	-	78
Co(βpic) ₄ I ₂	-	16.949	20.0	-	-	.904	-	-	.881		-	78
Co(ypic) ₄ I ₂	-	17.241	18.519) _	-	.916	-	-	.767	-	-	78

	Complex	<u>~1</u>	<u>~</u> 2	$\frac{\nu_3}{2}$	<u><u>p</u>2</u>	<u>Dq</u> 123	<u>Dq</u> 23+	<u>Dq</u> 13+	<u>B'</u> 123	<u>B</u> +23+	<u>B'</u> 13+	<u>B'</u> 12	Re:
	Co(ypic)Br ₂	-	15.152	18.868	-	-	.810	. '	-	.857	-	-	7
	Co(2,6-L)Br2	-	16,129	18,182	-	-	.859	-	-	.779	-	-	7
	CoBr ₂	-	14.925	17.857	-	-	.796	-	-	.793	-	-	7
	Co(Tc) ₂ (H ₂ O) ₂	8.7	17,5	-	-	.880	-	-	-	-	-	.035	58
	Co(ATc)_fL_O)	8.7	17.0	-	-	.830	-	-	-	-	-	113	58
Col	(DTc) ₂ (H ₂ 0) ₂	8.7	18.2	-	-	.950	-	-	-	. .	-	.422	58
Co(Cl ₂ py ₂	8.584	15.873	18.762	-177.85	.729	.847	-	•592	.828	-	269	21
Co(Cl ₂ py ₂	8.584	17,391	18.762	-70.43	.881	.924	-	.693	•780	-	.083	21
Co(21 ₂ (3Brpy) ₂	8.889	16.393	18.868	-185.56	.750	.873	-	•573	.819	-	284	Th wo
Co	Cl ₂ (3Brpy) ₂	6.452	16.393	18.868	231.91	.994	.873	-	1.060	.819	-	-1.000	11
Co	Cl ₂ (3Brpy) ₂	8.889	17.699	18.8 6 8	-94.64	.881	•940	-	.660	.778	-	025	ti
Col	C1 ₂ (3Brpy) ₂	6.452	17.699	18.868	373.75	1.125	.940	-	1.147	.778	-	810	11
Coł	Br ₂ (3Brpy) ₂	8.163	15.221	18.315	-158.94	.706	.812	-	.603	.816	-	239	ŦI
Col	Br ₂ (3Brpy) ₂	8.163	16.807	18.315	-46.71	.864	.893	-	.709	.767	-	210	11
Co(Cl ₂ (4Clpy) ₂	8.696	16.129	18.868	-177.40	.743	.860	-	.594	.827	-	266	ŧ
Col	Cl ₂ (4Clpy) ₂	6.250	16,129	18.868	247.70	.988	.860	-	1.083	.827	-	915	1 1
Co(C1 ₂ (4C1py) ₂	8.696	16.667	18.868	-141.07	.797	. 8 87	-	.630	.810	-	181	1 1

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Complex	<u>~1</u>	<u>⊸</u> 2	<u>~</u> 3	<u>P</u> 2	<u>Dq</u> 123	<u>Dq</u> 23+	<u>Dq</u> 13+	<u>B</u> ¹ 23	<u>B</u> *23+	<u>B'</u> 13+	<u>B'</u> 12	R
$CoCl_2(4Clpy)_2$	8,696	15.6 2 5	18.868	-209.32	.693	.834	-	.560	.843	-	-,325	11 W(
CoCl ₂ Q	6.269	17.123	19.011	352.87	1.085	.911	- '	1.155	.806	-	794	1
CoCl2Q	61269	17.123	30.864	495 495	1.085	.926	-	1.945	1.627	•••	794	1
CoC1 ₂ Q	6.269	13.986	17.123	39.52	.772	.747	-	.820	.771	-	6.343	١
Co(NO ₃)Q	9.434	15.873	-	-	.644	-	-	-	-	-	440	۲
$Co(NO_3)_2Q.2H_2O$	8.439	16.129	19.881	-153.88	.769	.862	-	.713	.898	-	184	ł
Co(NO3)20.2H20	8.439	19.342	21.368	125.78	1.090	1.029	-	1.026	.903	-	-4.891	t
$Co(NO_3)_2Q.2H_2O$	8.439	18.797	20.619	63.35	1.036	1,013	-	1.540	1.494	-	7.075	t
Co(NO3)20.2H20	8.439	18.797	19.881	70.78	1.036	.998	-	.891	.815	-	7.075	۲
$Co(NO_3)_2Q.2H_2O$	8.439	19.881	28.369	208.65	1.144	1,068		1.529	1.376	-	-2.364	t
$Co(NO_3)_2Q.2H_2O$	8.439	19.881	31.847	221.08	1.144	1.072	-	1.761	1.616	-	-2.364	Ŧ
$Co(NO_{32}Q_{2} \cdot 2H_{2}O)$	8.230	20.0	21.053	242.70	1.177	1.061	-	1.091	.86 0	-	-1. 63 8	1
$Co(NO_3)_2Q_2 \cdot H_2O_2$	8.230	20.619	30.769	395.57	1.239	1,109	-	1.780	1.520	-	-1.357	t
Co (ND3)2 Q . 2H2 0	8.230	20.619	32 .8 95	413.44	1.239	1,111	-	1.922	1.667	-	-1.357	+
CoC1 ₂ Mq	6.580	16.807	18.018	240.79	1.023	.893	-	1.006	.746	-	999	Ŧ
CoC12 ^{Mq}	7.570	16.807	18.018	52.17	.924	.893	-	.808	•746	-	-4.663	t
CoC1 ₂ Mq	6.580	15.748	16.807	133.48	.917	. 836	-	.854	.693	-	-1.505	t

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Complex	<u>~</u> 1	<u>~</u> 2	<u>~</u> 3	<u>P</u> 2	$\underline{\text{Dq}}_{123}$	<u>Dq</u> 23+	<u>Dq</u> 13+	<u>B'</u> 123	<u>B</u> *23+	<u>B'</u> 13+	<u>B'</u> 12	Ref.
CoC12 ^{Mq}	7.570	15.748	16.807	-27.57	.818	.836	-	.656	.693		.299	This work
CoC12 ^{Mq}	6.580	15.748	18.018	138.05	.917	.839	-	.935	.77 9	-	-1.505	**
CoCl ₂ Mq	6.570	15.748	18.018	-33.79	.818	.839	-	•737	.779	-	.299	**
$CoC1_2Mq_{3/2}$	6.667	15.748	16.807	117.99	.908	.836	-	.837	.693	-	-1.795	11
CoCl ₂ Mq _{3/2}	6.667	16.260	19.231	175.56	.959	.867	***	1.033	.849	-	-1.291	**
CoCl ₂ Mq _{3/2}	6.667	17.391	-	-	1.072	-	-	-	-	-	943	**
CoCl ₂ (3Brpy) ₂	8.889	-	17.7	-	-	-	.993	-	-	.657	-	11
CoCl ₂ (4Clpy) ₂	8.696	-	16.67	-	-	-	.968	-		.597	-	**
CoBr ₂ (3Brpy) ₂	8.163	-	16.81	-	-	-	.915	-	-	.642	-	**
CoBr ₂ (4C1py) ₂	7.605	-	14.81	-	-	-	.848		-	.539	-	11
ശവ ₂ റ	6.270	-	17.98	-	-		.724	-	-	.845	-	**
CoCl ₂ Mq	6.579	-	17.09	-	-	-	.754	-	-	.765		**
CoCl ₂ Mq	7.576	-	17.09	-	-	-	.857	-	-	.701		11
CoCl ₂ Mq	7.042	-	17.09	-	-	-	.802	-	-	•735	-	**
$\operatorname{CoCl}_{2}^{\operatorname{Mq}_{3/2}}$	6.667	-	17.39	-	-	-	.764		-	.780	-	**
CoCl ₂ Mq _{3/2}	7,905	-	17.39		-	-	.892	-	-	.700	-	tt

Table A3 a) cont....

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	Complex	<u>~1</u>	<u>~</u> 2	<u>~</u> 3	<u>P</u> 2	<u>Dq</u> 123	<u>Dq</u> 23+	<u>Dq</u> 13+	<u>B</u> *123	<u>B'</u> 23+	<u>B'</u> 13+	<u>B</u> 12	<u>Ref</u>
-	^{CoC1} 2 ^{Mq} 3/2	7.233	-	17.39	-	-	-	.823	-	-	.744	-	Thisworl
	CoBr ₂ Mq	7.017	-	15.75	**	-	-	•794	-	-	.643		11
	CoBr ₂ Mq	8,889	-	15.75	-	-	-	•980	-		.518	-	11
	CoBr ₂ Mq	7.843	-	15.75	-	-	-	.877	-	-	.589	-	TŤ
	$Co(NO_3)_2Q_2 \cdot 2H_2O$	8.230	-	20,62		-	-	.940	-	-	.904	-	11
	$Co(NO_3)_2Q.2H_2O$	8.439	-	20.12	-	-	-	.960	-	-	.856	-	11
	Ni ²⁺ /CdS	4.20	8.2	12.5	-44.70	.400	.441	.486	•540	.623	.597	056	23
	Ni ²⁺ /CdS	4.20	8.0	12.3	-53.06	.380	.431	-	.513	.615	-	097	24
	Ni ²⁺ /CdS	4.20	8.0	12.6	-54.80	.380	.431	-	.533	. 635	-	097	24
	Ni ²⁺ /CdS	4.20	8.0	13.5	-60.02	.380	.432	-	.593	.697	-	- 097	24
	$\text{NiCl}_4^2 \text{Me}(\Phi_3 P)_2^N$	iC1 ₄ -	7.407	14.61 ^{a)}	-	-	.402	-	-	.789	-	-	199
	$Ni(\Phi_3PO)_2Br_2/Me_2$	2 ^{Co}	7.250	15.58	-	-	.394	-	-	.860	-	-	199
	$Ni(\Phi_3PO)_2I_2/\Phi Cl$		7.078	15.10	-	. –	.384	-	-	.832	-	-	199
	Ni(ϕ_3 PO) ₂ I ₂ Me ₂ Co	0	7.255	14.01	-	-	.393	-	-	.753	-	-	199
	$Ni(\Phi_3AsO)_2Br_2/\Phi$	C1	7.654	15.26 ^{a)}	-	-	.415	-	-	.827	-		199
	NiBr ₂ Quin ₂		10.0	16.4	-	-	•539	-	-	.839	-	-	192
	NiC12 Mp5		9.2	15.62	-	-	. 497	_		808	-	-	198

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Complex	<u>~</u> 1	<u>۷</u> 2	<u>~</u> 3	<u>P</u> 2	<u>Dq</u> 123	<u>Dq</u> 23+	<u>Dq</u> 13+	<u>B'</u> 123	<u>B'</u> 23+	<u>B</u> ¹ 13+	<u>B'</u> 12	Ref.
NiBr2Mp5	-	8.6	15.47	-	-	.465	-	-	.815	-	-	198
Nil2 ^{Mp} 5	-	8.1	15.4	-	-	.439	-	-	.824	-	-	198
NiCl ₄ ²⁻	-	7.4	14.2	-	-	.401	-	-	.762	-		23
NiCl ₄ ²⁻	-	7.4	15.2	-	•	.402	-	-	.830	***	**	23
NiCl ₄ ²⁻	-	7.4	16.0	-	-	.402	-	-	.884	-	-	23
NiCl ₄ ²⁻	-	7.4	15.3		-	.402	-	-	.837	-	-	24
NiCl ₄ ²⁻		7.4	16.7	- ·	-	.402	-	-	.931		-	24
NiBr ₄ ²⁻	-	7.0	13.3	-	-	.379	-	-	.712	-	-	23
NiBr ₄ ²⁻	-	7.0	14.2	-	-	.380	-	-	.773	-	-	23
Ni ²⁺ /ZnO	-	8.4	16.2	-	-	.455	-	-	.870	-	-	24
Ni(2,3-L) ₂ Cl ₂	-	10.235	17.035	-	-	.552	-	-	.876	-	-	200
Ni(2,3-L) ₂ Cl ₂	-	10.13	18.083	-	-	.548	-	-	.950	-	-	200
Ni(2,4-L) ₂ Cl ₂	Ĩ	10.31	17.15	-	-	.556	-	-	.882	-	-	200
Ni(2,4-L) ₂ Cl ₂		10.15	18.18	-	-	.549	-	-	.956	-	-	200
Ni(2,5-L) ₂ Cl ₂	-	10,205	18.18	-	-	•552	-	-	.955	-	-	200
Ni(2,3-L) ₂ Br ₂	-	10.05	16.53	-	-	.542		-	.846	-	-	200
Ni(2,3-L) ₂ Br ₂	-	10.0	17.48	-	-	.540	-	-	.913	-	-	200

Table A3 a) cont....

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Complex	<u>v</u> 1	<u>~</u> 2	<u>∼</u> 3	<u>P</u> 2	<u>Dq</u> 123	<u>Dq</u> 23+	<u>Dq</u> 13+	<u>B'</u> 123	<u>B'</u> 23+	<u>B'</u> 13+	<u>B'</u> 12	Ref.
Ni(2,4-L) ₂ Br ₂	-	10.245	16.64	-	-	.553	-	-	.848		-	200
Ni(2,4-L) ₂ Br ₂	-	10.03	17.7	-	-	•542	-	-	.927	-	-	200
Ni(2,5-L) ₂ Br ₂	-	10.1	17.605	-	-	.546	_	-	.919	-	-	200
Ni(DMAÄP)C12	. –	13.3	22.6	-	-	.718	-	-	1,170	-	-	201
Ni(DÄAÄP)C12	-	10.8	19.5	- `	-	• 584	-	-	1.028	-	-	201
Ni (PAÄP) Cl ₂	-	13.8	23.2	-	-	.745	-	-	1.197	-	-	201
Ni (PAÄP)Br ₂	-	13.2	22.1	-	. –	.713	-	-	1.138		-	201
Nipy2I2	-	9.85	17.1	-	-	.532	-	. –	.891	-	-	190
Ni(βpic) ₂ I ₂		9.9	17.0	-		• 535	-	-	.883	-	-	190
Ni(ypic) ₂ I ₂	-	10.0	16.95	-	-	• 540	-	-	.877	-	-	190
Ni(3,4-L) ₂ I ₂	-	9.9	16.95	-	-	• 535	-	-	.879	-	-	190
Ni(3,5-L) ₂ I ₂	-	9.9	16.95		-	.535	-	-	.879	-	- .	190
NiI ₂ (2Clpy)	-	7.353	16.667	-	-	.400	-	. 🕳	.930	-	-	This worl
Nil ₂ (2Brpy)	-	7.220	16.0		-	.392	-	-	.889	-	-	11

Notes:

a) Bari centre of a complicated band.

Table A3 b)

Data for the d³ and d⁸ octahedral and d² and d⁷ tetrahedral complexes. All units are kK except those of P_3 (kK²).

Complex	<u>v</u> 1	<u>~</u> 2	<u>~</u> 3	<u>P</u> 3	\underline{Dq}_{23}^{a}	<u>B'</u> 23	<u>B'</u> 12	<u>B'</u> 13	<u>B</u> ¹ 123	R
V(H ₂ 0) ₆ ²⁺	12,35	18.5	27.9	16.27	b)	-	.681		.623	•
VS04.7H20	12.0	18.2	27.8	9.80	b)	-	.705	.646	.667	20
V ³⁺ /CsA1C1 ₄	-	9.4	15.0	. –	•596	.434		-	-	2:
Cr(H ₂ O) ₆ ³⁺	17.4	24.6	37.8	24.48	b)	-	.729	-	.680	
**	17.4	24.5	38.0	14.42	b)	-	.715	· –	.687	
Cr(H ₂ O) ₅ F ²⁺	16.8	24.0	37.6	-3.84	1.699	.708	.738	•754	.747	:
$cis-Cr(H_2O)_4F_2^+$	16.4	23.9	36.8	10,60	b)	-	.792	-	.767	:
trans- "	16.3	22.7	37.0	-41.76	1.745	.491	. 636	-	.720	2:
13 11	16.3	25.5	37.0	65.48	b)	-	1.134	-	.907	2:
Cr(H ₂ 0) ₅ C1 ²⁺	16.5	23.25	-	-	-	-	.680	-		2:
Cr(H ₂ O) ₄ Cl ₂ *	15.75	22.2	36.8	-61.39	1.752	•429	. 650	-	.783	2:
Cr ³⁺ /MgO	22.7	29.7	46.0	125.41	b)	-	.656	-	.507	2(
17	22.7	29.7	48.3	-2.92	2.274	.652	•656	.665	.660	2(
11	16.2	22.7	29.7	192.51	b)	-	.651	-	.253	2:
Cr ₂ 0 ₃	16.6	21.6	-	-	-	. –	•467	-	-	2
11	16.8	23.0	29.5	252.58	b)	-	.605	-	.140	2:
Cr ³⁺ /Al ₂ 0 ₃	18,15	25.73	39.1	40,41	b)	- ,	.770	-	.692	2.
11	18.1	24.40	39.1	-4.58	1.820	.593	.606	-	.613	2:
KCr(SO4) 2.12H2 0	17.5	24.7	38.0	24.0	b}	-	•727	-	•680	2:
CrUrea ₆ 3+	16.1	22.6	34.4	34.47	b)	-	.652	-	.580	2:
Crpy ₃ Cl ₃	15.9	22.2	-	-	-	. –	.628	-	-	2:

<u>Complex</u>	<u>~</u> 1	<u>ب</u> 2	<u>~</u> 3	<u>P</u> 3	<u>Dq</u> 23 ^{a)}	<u>B</u> 'a) 23	<u>B'</u> 12	<u>B'</u> 13	<u>B'</u> 123	R
$\operatorname{CoCl}_4^{2-}$	-	5.9	14.75	-	.340	. 697	-	-	-	1!
tt .		5.6	14.7		.321	.710	-	-	-	1!
H.	—	5.26	14.7	-	.301	.729	-	-	-	1!
**	-	5.25	14.7	-	.300	.729	-	-	-	19
II .	-	5.7	14.6	-	.328	.698	-	-	-	19
tt	-	5.65	14.6		.325	.701	-	-	-	1!
CoC1 ₄ ²⁻	-	5.22	14.7	-	.298	.731	-	<u>1</u>	-	19
	-	5.58	14.8	. –	•320	.718	-	_ ·	-	19
$\operatorname{CoBr}_4^{2-}$	· •	5.75	14.0	-	•332	.653	-	=	-	19
11	-	5.78	14.0	-	.333	.652	-	-	-	19
*1	-	5.08)	14.3	-	.286	.715	-	-	-	19
11	-	c)	14.0	-	.299	.683	-	-	-	19
11	-	4.88	·14.2	-	.279	.715	-	-	-	19
11	-	5.08	13.8	-	.291	. 677	-		-	19
CoI ₄ ²⁻	-	5.62	13.2	-	.325	.605	-	-	-	19
, 11	-	4.93	13.2		.283	.643	-	-	-	19
11	-	5.70	13.8	-	.329	.642	-	-	-	19
11	-	4.70	13.2	-	.269	.656	-	-	-	19
11	-	4.54	13.5	-	.259	.685	-	-	-	19
11	-	4.70	13.0	-	.269	.642	-	-	-	19
$Co(NCS)_4^{2-}$	-	7.80	16.3	-	•456	. 694	-		-	1
HgCo(NCS)	-	8.30	16.7	-	.488	.691	_		-	20
CoCl ₂ Cdpa ₂	c) 4.25	7.87	16.1	28.15	.489	.676	531	_	•763	2]
CoBr ₂ dpa ₂	4.45)	8.30	16.5	23.74	.461	.675	691		•748	2]

N.

Complex	<u>~</u> 1	<u>۷</u> 2	<u>~</u> 3	<u>P</u> 3	<u>Dq</u> 23 ^{a)}	<u>B</u> , a) 23	<u>B'</u> 12	<u>B'</u> 13	<u>B'</u> 123	Re
CoI2dpa2	4.18)	7.63	15.4	23.47	•448	.639	554	.676	.715	21
CoBr ₂ py ₂	-	6.803	15.873	-	•394	•724	-	-	-	21
CoCl ₂ (2Clpy) ₂	-	7.168	16.393	-	.415	•740	-	-	-	39
CoBr ₂ (2Clpy) ₂	-	7.017	15 .674	-	.407	. 698	-	-	-	39
CoI2(2Clpy)2	-	6.689	14 , 97 0	-	•388	.667	-	-	-	39
CoCl ₂ (2Brpy) ₂	-	7.273	15.748	-	•424	.687	-	-	- 1 W	hi vor
CoBr ₂ (2Brpy) ₂	-	6.969	15,504	-	•405	.688	-	-	-	**
11	-	7.017	Б 504	-	•408	•685	-		-	11
CoC1 ₂ (3Brpy) ₂ / MeNO ₂	c) 3.88	c] 12.4	16.4	267.03	b)	_	.487	-	1.144	t "
**	3.88 ⁾	c) 12.4	16.6	272.44	b)	-	.487	-	1.157	7 11
CoBr ₂ (3Brpy) ₂ / CH ₂ CI ₂	c) 4.02	c) 6.4	15:7	-22.45	• 369	.735	.311	-	.669	11
88	4.02	6.4	16.0	-23.70	.368	•756	.311	-	•689	11
ft	c) 4.02	7.8	16.0	37.64	. 457	.672	107	-	.783	11
11	c) 4.02	c) 7.8	15.7	36.80	•458	•650	107	-	.763	11
CoI ₂ (3Brpy) ₂ / CH ₂ CI ₂	c) 4.02	c) 6.4	14.6	-17.85	.371	•658	.311	-	•596	11.
TI	c) 4.02	6.4	15.2	-20.36	.370	.700	.311	-	.636	11
11	c) 4.02	c) 7.6	15.2	27.42	•447	.626	288	-	.716	**
11	c) 4.02	c) 7.6	14.6	26.33	•450	•280	288	-	.676	**
CoI ₂ (3Brpy) ₂	-	6.993	15.267	-	•407	.670	-	-	-	11
CoBr ₂ (4C1py) ₂	-	5.168	14,493	-	.296	•720	-	-	-	11
11	-	7.605	14.4B	-	.451	.571	-	-	-	11
CoBr ₂ (4C1py) ₄	-	5.208	15,038	-	•297	•755		-	-	11

	Complex	<u>v</u> 1	<u>۷</u> 2	<u>v</u> 3	<u>P</u> 3	<u>Dq</u> 23	<u>B'</u> 23	<u>B'</u> 12	<u>B'</u> 13	<u>B'</u> 123	Rei
	CoI ₂ (4C1py) ₂	-	4.630	14.493	*** .	.264	.748	-	-	-	Thi woi
	CoCl ₂ Q ₂	-	6.410	16.393	-	.368	.783	-	-	-	11
	11	-	7.067	16.393	- .	.409	•746	-	-	-	11
	CoBr ₂ Q ₂	-	6.329	16.051	- .	•364	.764	-	-	-	**
	11		6.993	16.051	_	.405	.726	-	-		**
	CoI ₂ Q ₂	-	6.493	14.706	-	.377	.660	-	-	-	**
	**	-	6.452	15.198	-	.373	.697	-	-	-	11
	11	6.116	5 8,230	14.706	21.44	.495	.540	.203	-	.306	**
	CoBr ₂ Q	-	6.042	15.337	-	.347	.730	-	-	-	11
	11	-	6.780	15.337	-	•393	.688	_	-	-	**
	CoC1 ₂ Mq	-	6.580	16.807	-	.378	.803	-	-	-	Ħ
	CoBr ₂ Mq	-	7.017	15.504	-	.408	.685	-	-	-	11
	CoC12Dmq	-	5.168	14.925	-	.295	.749	-	-	-	11
	CoBr ₂ Dmq	-	5.063	14.388	- .	•289	.718	-	-	-	11
	$\text{Col}_2 \text{Dmq}$	4.76	2 7 843	12.739	2.96	.490	.391	.474	-	.420	77
	**	-	4.762	12.739	-	.273	.621	-	-	-	**
	NiCl (3Etpy) ₂	-	13.42	23.58	-	.810	.846	-	-	-	152
	NiBr ₂ (3Etpy) ₂	-	12.97	23.00	-	.781	.835		_	-	11
	NiCl ₂ (IQuin)	2 - 2	13.91	24.1	-	.844	.846	-	-	-	11
	NiBr ₂ (IQuin)	2 - :	13.64	23.42	-	.830	.811	-	-	-	**
÷	$\text{NiCl}_2(\text{PNH}_2)_2$	- :	13.76	23.26	-	.842	.783	-	-		11
	$\operatorname{NiBr}_{2}(\operatorname{ANH}_{2})_{2}$	-	13.23	22.47		.808	.763	-	-	-	11
	NiCl ₂ (m-Tol)	2 - 3	13.79	23,26	-	.845	.780	1 00	-	-	11

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Complex	<u>~</u> 1	<u>۷</u> 2	<u>~</u> 3	<u>P</u> 3 D	Dq ₂₃ a)	<u>B'</u> 23	<u>B'</u> 12	<u>B'</u> 13	<u>B'</u> 123	Ref.
NiBr ₂ (m-Tol)) ₂ -	13.25	22.47	-	.810	.761	-	-	-	152
NiCl ₂ (p-Tol)) ₂ -	13.81	23.31	-	.846	.783	-	_	-	11
NiBr ₂ (p-Tol)) ₂ -	13.26	22.57	-	.809	.770	-	-	-	11
NiCl ₂ Quin ₂	-	13.15	22.70	-	.799	.793	-	-	-	11
$MiCl_2Q_2$. 7. 58	13.04	23.64	15.78	.781	.883	1.278	-	.929	**
$NiBr_2Q_2(y)$	7.22	12.30	21.00	13.85	.7 50	.720	1.041	-	.776	11
NiCl ₂ Quin	6.4	11.1 2	2.1	12.65	.658	.830	1.268	-	.867	197
NiBr ₂ Quin	6.25	10.8 2	20.0	11.56	.644	.766	1.146	-	.803	197
NiCl ₃ (MeN)	6.6	11.2	21.2	3.16	.665	.830	.902	.835	.840	197
$Ni(N_3)_2 py_4$	9.8	16.21	25.84	18.20	1.029	.745	1.013	-	.843	153
Ni(N ₃) ₂ (ppic)	4 ⁹ •79	16.08	25.77	13.85	1,016	.758	•952	-	.832	11
Ni(N ₃) ₂ (ypic)	9.8	16.23	25.71	19.94	1,038	.720	1.024	-	.836	11
Ni(NCO) ₂ py ₄	4 10.05	16.61	26.81	16.27	1,043	.808	1.031	-	.885	**
Ni(NCO) (Spic)	$D_{4}^{D.01}$	16 .5 6	26.67	17.09	1.042	•798	1.036	-	.880	Ħ
Ni(NCO) ₂ (ypic)	10,04	16.61	26.67	17.79	1,048	•790	1.040	-	.877	
Ni(NCS) 2py4	10 . 45	16.9	22.2	54.99	b)	-	.900	-	.517	11
Ni(NCS) (Bpic) ₄	10.40	16.9	c) 22.5	52.13	5 b)	-	.929	-	•547	11
Ni(NCS) (Ypic)	10,45	17.06	22.5	55.07	b)		.967	-	.547	**
Ni(NCS) ₂ (IQuin) ₄	1050	17.15	22.5	56.70) b)	-	.975	-	•543	11
Ni (NCS) 2py4	10,58	17.24	22.7	56.57	• Ъ)	-	. 965	-	•547	**
Ni(NCSe) ₂ (^{gpic)} 4	10.54	17.18	c) 22.7	55.47	у Ъ)	-	.963	-	.551	**

Complex	<u>~</u> 1	<u><u>v</u>2</u>	<u>~</u> 3	<u>P</u> 3	\underline{Dq}_{23}^{a}	$\underline{B'}_{23}^{a)}$	<u>B</u> *12	<u>B</u> •13	<u>B'</u> 123	<u>Ref</u> .
Ni(NCSe) 2 (ypic) 4	10.58	17.24	22 .7	56.57	b)		•9 6 5	. –	.547	153
NiCl ₂ Mp	-	13.15	23.0		.795	.819	-	-	-	198
NiBr ₂ Mp	-	13.4	23.0	-	.815	•796	-	-	-	**
NiC12(2,6 Dmp) ₂ -	13.5	23.8	**	.814	.858	-	-	-	11
NiBr ₂ (2,6Dmp) ₂ -	13.5	23.2	-	.821	.804	-	-	-	11
Ni(2,5Dmp)C	1 ₂ -	13.0	22.75	5	.78 6	.811	v 	-	-	**
Ni(NCS)2(py)10,4	1 6. 65		-	•••	-	.835	-	-	11
NiCl ₂ (py,)2	10,5	16.15	-	-	-	-	.664	-	-	11
$\operatorname{NiBr}_2(\operatorname{py}_z)_2$	10.4	15.75		-	-	-	.606	-	-	11
$NiI_2(py_z)_2$	10.6	15.6	-		-	-	•536	-	-	11
$Ni(NCS)_2Mp_2$	10.4	16.0	-	-	-	-	. 659	-	-	11
$Ni(NCS)_2Mp_5$	10.5	16.65	-	-	-	-	.793	-	-	**
NiCl2 ^{Mp5}	10.0	15.75		-	-	-	•724	-	-	11
$^{\rm NiBr}2^{\rm Mp}5$	10.0	15.8	-	-	. 🖷 🕔	-	•738	-		198
NiI2 ^{Mp} 5	11.4	15.8	-	-	-	-	.435	-	-	11
Ni(NCS) (2,6Dmp) ₄	10.4	16.65	-	-	-	-	.835	-	-	11
Ni(NCS) ₂ (2,6Dmp) ₂	10.4	16.15		-	-	-	. 694	-	-	11
$Ni(H_20)_6^{2+}$	8.5	14.0	26.0	-11.7	5.834	.998	•846	-	. 967	16
	8.5	13.5	25.3	-32.2	0.803	.981	.648	-	.887	150
**	8.5	13.8	18.4	34.5	5 b)	. - .	•734	** *	.447	24
11	8.5	15.4	25.3	62.8	0.956	.801	-7.360	-	1.013	55
$Ni(NH_3)_6^{2+}$	10.6	16.7	27.4	-9.1	2 1.037	.865	.769	.835	.820	16

	Table A3 b)	cont.	•••								
	Complex	<u>~</u> 1	<u>v</u> 2	<u>~</u> 3	<u>P</u> 3	Dq123	<u>B</u> •a) 23	<u>B'</u> 12	<u>B'</u> 13	<u>B'</u> 123	Ref
	$Ni(NH_3)_6^{2+}$	10.7	17.5	28.2	12.92	1.100	.846	1.004	-	•907	24
Sec.		10.75	17.5	28.2	10.59	1.100	•846	.973	-	.897	24
	NiEn ₃ ²⁺	11.2	18.3	29.0	18.14	1.170	.814	1.043	-	.913	16
	TT	11.2	18.35	29.0	20.35	1.177	.802	1.067	-	.917	55
	NiEnta ²⁻	10.1	17.0	26.2	34.29	b)		1.247	-	. 860	11
-	Ni(NH ₃) Enta ³ 2-	10.2	17.2	26.9	33.70	1.124	.692	1.287	-	.900	11
	Ni(En)Enta ²⁻	10.05	17.3	27.1	45.21	1.126	.707	1.713	-	.950	11
	Ni(NH ₃) Tetr e n	11.1	18.7	28 : 6	43.40	b) [.]		1.385	-	.933	p
	NiBn ²⁺	10.95	18.0	28.6	19.91	1.147	.812	1.072	-	.917	11
	NiO	8.8	13.9	23.9	-16.23	.845	.829	.648		.760	23
	Ni ²⁺ /MgO	8.6	13.8	24.5	-16.60	.831	. 891	.702	-	.833	23
	11	8.6	13.5	24.6	-31.12	.808	.925	.610	-	.820	24
	NiCl ₂	-	12.9	22.1	-	.786	.762	-	-	- 1.5	23
	NiBr ₂	-	12.1	20.7	- .	.737	.712	-	-	-	23
	KNI F ₃	-	12.5	23.7		.742	.930	-	-	-	23
	pyHNiBr3	-	11.2	19.9	-	.674	•725	-		-	23
	pyHNiCl3	-	11.2	21.3	-	.664	.838	-	-	-	23
	NiCl ₂ Py4	10.9	16.0	25.8	-16.81	1.006	.775	•545	-	•607	27.
	$\operatorname{Nipy}_4(\operatorname{CD}_4)_2$	10.1	16.6	27.0	11.93	1.037	•83 3	.987	-	.887	17
	Ni(C10 ₄) ₂ (3Mpy) ₄	10.1	16.5	26.9	8.36	1.029	•835	.940	-	.873	17 1
	$\frac{\text{Ni}(C10_4)_2}{(4Mpy)_4}$	10.1	16.6	27.0	11.93	1.037	.833	.987	-	.887	17
	Ni(NO ₃) ₂ (2Mpy) ₄	8.868	15.53	24.88	43.63	•981	.731	2.266	-	•920	35
						,					

	Complex	<u>-~</u> 1	<u>۷</u> 2	<u>~</u> 3	<u>P</u> 3	$\frac{Dq_{123}}{Dq_{123}}$	$\frac{B'^{a}}{23}$	<u>B'</u> 12	<u>B'</u> 13	<u>B</u> [†] 123	Re
	Ni(NH ₃) ₂ Br ₂	-	13.12	23.8	-	.786	.890	-	-	-	18
	NiBp3(C104)2	12.9	20.0	27.6	62.61	b)	-	.853	-	•593	58
ч.,	NiBr ₂ (ΦNH_2) 4	10.638	14.925	23.81	-7.90	.947	.688	.430	-	•455	58
·.,	Ni(Bipy) ₃ ²⁺	12.65	19.2	-	-	-	-	.746	-	-	41
	Ni/MgTiO ₃	-	12.0	22.2	-	.715	.849	-	-	-	24
	RbNiBr ₃	-	11.5	202	-	.695	.724	-	-	-	24
	Niphen ₃ ²⁺	12.7	19.3	-	-	-	-	.754	-	-	24
	Ni py ₃ (NO ₃) ₂	-	16.393	26.667	-	1.024	.823	-	-	-	26
	Ni(N ₃) ₂ (IQui	n) _9,81	716.31		-	-	-	1.011	-	-	15
	Ni(NCO) (IQUin)	10.08	16.64	-	-	_	-	1.023	-	-	15
	NiCl ₂ Quin ₂	-	13.16	22.73	-	•799	.794	-	-	-	20
	NiCl ₂ Quin	-	11.15	21.14	-	.662	4829	-	-	-	20
	NiBr ₂ Quin	-	11.36	20.0	-	.686	.719	-	-	-	20
	$\text{NiCl}_{2}\text{py}_{2}$	-	14.1	24.1	-	.859	.828	-		-	20
	NiC12	-	13.0	22.17	-	.793	.759	-	-	-	20
	NiBr ₂	-	12.2	20.83	-	.744	. 714	-	-	-	20
	$\operatorname{NiT}_{c_2}(H_2O)_2$	9.1	15.4	-	-	-	-	1.200	-	-	58
	NiATC2 (H2O)2	9.1	15.6	-	-	-	-	1.444	-	-	58
	NiDTc (H ₂ 0) ₂	9.1	15.3	-	- .	. -	-	1.110	-	-	58
·:	NiCl ₂ py2	-	13 .9 9	24.1	-	.850	.839	-	-	-	18
ŝ	Ni(Bpic) ₂ C1 ₂	-	14.18	24.27	-	.864	.836	-	-	-	18
	Ni(ypic) ₂ C1 ₂	-	13.95	23.98	-	.848	.832	-	-	-	18
	Nipy2Br2	-	13.85	23.53	-	. 846	.800		-		18

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	Complex	<u>~</u> 1	<u>~</u> 2	<u>~</u> 3	<u>P</u> 3	<u>Dq</u> 123	<u>B</u> ²³	<u>B'</u> 12	<u>B'</u> 13	<u>B'</u> 123	Re:
2	Ni(spic)2Br2	-	13.33	23.42	-	.805	•840	-	-	-	18:
	Ni(ypic) ₂ Br ₂	-	13.76	23.42	-	.840	•799	-	-	-	11
ŧ.	$Ni(NH_3)_2Cl_2$	-	13.6	24.8	- .	.813	.933	-	-	-	tt
	Ni(spic)Br ₂	-	11.63	20.53	-	.701	.741	-	-	-	11
	$Nipy_4C1_2$	-	15.8	25.64	-	.988	.786	-	-	-	11
	Ni(spic) ₄ Cl ₂	-	15.75	25.3	-	.993	.750		-	-	11
	Ni(ypic) ₄ Cl ₂		15.9	25.64		.999	.771	-	-	-	11
	$Nipy_4Br_2$	-	15.62	25.3	-	.978	.771	-	-	-	11
•	Ni(Bpic) ₄ Br ₂	-	15.8	25.3	-	.999	.742	-	-	-	91
,	Ni(ypic) ₄ Br ₂	-	15.8	25.3	-	.999	.742	-	-	-	11
	Ni(3pic) ₂ Br ₂	-	13.3	23.2	-	.805	.823	-	-	-	274
	Ni(2pic)Cl ₂	-	10.2	21.0	-	.598	.885	-	-	-	27/
	Ni(3pic)Br ₂	-	11.7	20.6	-	.706	.741	-	-	-	274
	Ni(O-tol) ₂ Cl	2	13.699	22.989	-	.841	.763		-	-	203
	Ni(m-tol) ₂ Cl	2 -	13.793	23.256	-	.845	.779	-	-	-	20:
	Ni(m-tol) ₂ Br	2 -	13.158	22.727	-	.799	.794	-	-	-	203
	Ni(p-tol); Cl ₂ .6H ₂ 0	-	14.286	23.81	-	.880	.779	-	-	-	203
	Ni(p-tol) ₂ Cl	2 -	13.699	23.256	-	.837	.789	-	-	-	203
	Ni(p-to1) ₂ Br	2 -	13.158	22.727	-	.799	.794	-	-	-	11
	Ni(2.5xy1) ₂ C	1 ₂ - '	13.514	22.727		.829	. 758	***	-	-	11
	Ni(3,4xy1) ₂ C	¹ 2 ⁻	13.699	23.256		.837	.789	- .	-	-	11
	Ni(3,4xy1) ₂ B	r ₂ -	13.158	22.727	- .	.799	•794		-	-	**
	Ni(3,4xy1) ₆ I	2 ^{10,98}	9 15 6 2 5	-	-	.	-	.472	-	-	71

Complex	<u>v</u> 1	<u>.</u> 2	<u>.</u> v3	<u>P</u> 3	<u>Dq</u> 23	<u>B</u> ,b) 23	<u>B'</u> 12	<u>B'</u> 13	<u>B'</u> 123	Ref
NiCl ₂ py4	-	15 .8 98	25.641	-	.999	.771	-	-	-	587
NiCl ₂ py2	-	14.085	24.096	-	.858	.829	-	-	-	11
Ni(4NH2)2CI	¹ 2 -	13.699	23.256	-	.837	.789	-	-	-	**
Ni((NH2) 2B	°2 [—]	13.158	23.256	-	.793	.841	-	-	-	11
Ni(4NH ₂)4 ¹ 2	2 10.989	14.925	-				.381		-	11
Ni(@NH2)2 ¹ 2	2 -	11.905	23.81	-	.700	•980	-	-	-	**
$Ni(\Phi NH_2)_2$ $Cl_2(Et Oldstart)$	1) ₂ -	14.493	23.81	-	.900	•754	-	-	-	11
Ni(ϕ NH ₂) ₂ Br ₂ (EtOH)	2	13.889	23.256	•	.854	.769	 .	-	-	**
NiCl2py2	8.23	13,793	24.213	6.20	.833	. 867	•969	-	.888	210
NiBr2py4	8.0	15.504	25.189	110,75	.969	.775 ·	225	-	1.113	11
NiCl ₂ (3Brp)	7) ₂ 8.511	14.085	24.096	3.77	.858	.829	•884	-	.843	This work
NiBr ₂ (3Brp)	7.968/	µ3. 333	22.989	7.15	.810	.801	.922	-	.828	11
NiI ₂ (3Brpy)	27.752	9.852	26.667	-212.65	.564	1.306	.193	-	.884	11
**	7.752	13.072	26.667	-7.97	.770	1.115	.978	-	1.099 .	11
NiCl ₂ (4Clp)	7) ₂ 8.511	14.085	24.096	3.77	.858	.829	.884	-	.843	11
NiBr ₂ (4C1py) ₂	8.163	13.699	23.810	7.98	.830	.840	.975	-	.868	11
NiCl ₂ Q	7.194	12.422	18.519	26.72	b)		1.300	- ,	.624	51 C
ft	7.194	12.422	31.746	-8.15	.714	1.516	1.300	-	1.506	**
NiBr ₂ Q	6.969	12,195	21.978	22.38	.731	.815	1.739	-	. 884	tt
11	5.16	12.12	22.25	204.84	•724	.844	.295	-	1.259	511
**	7.81	12.12	22.25 -	-30.58	•724	844	.519	- .	.729	11
Ni(NO3)2Q	8.696	13.889	22,989	-4.20	.859	.741	•688	-	.719	51 C

Complex	<u>~</u> 1	<u>~</u> 2	<u>~</u> 3	<u>P</u> 3	<u>Dq</u> 23	$\frac{B^{1}}{23}$	<u>B'</u> 12	<u>B'</u> 13	<u>B'</u> 123	Ref
Ni(NO ₃) ₂ Q	8.696	13.889	30.030	-66.30	.809	1.309	.688		1.189	510
tt .	8.696	13.889	17.544	43.82	b)	-	.688	-	.356	11
Ni(NO ₃) ₂ Q (H ₂ O)	8.333	15.152	32.258	68.72	•884	1.392	-4.510	-	1.494	11
**	8.333	15.152	23.529	62.06	b)	_ ·	-4.510	-	.912	**
NiCl ₂ Mq	7.246	12.658	22.779	23.27	.759	.843	1.720	-	.913	This work
11	7.246	12.658	25.641	17.76	•743	1.067	1.720	· _	1.104	11
11	7.246	12.658	31.348	6.78	.729	1.475	1.720	-	1.484	**
NiBr ₂ Mq	6.897	12.048	21.097	22.14	.728	. 753	1.635	-	.830	Ħ
Ni(NO3)2Mq	6.849	11.779	22.222	10.34	.700	.868	1.148	-	.897	11
Nipy ₆ ²⁺	9.479	15.570	26.150	4.08	.956	. 870	.922	-	.886	21 C

Notes:-

- a) D_{q23+} and B'₂₃₊ are given for Cr³⁺ complexes. Dq₂₃₋ and B'₂₃₋ are given in all other cases.
- b) $Dq_{23\pm}$ cannot be evaluated because the argument of the square root is negative.
- c) Of doubtful accuracy.

Y is the yellow isomer.

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Appendix A.4.

The correction of spectral data for the effects of spin-orbit

coupling in Octahedral Nickel (II) Complexes.

Figure 1.5 shows that the ¹E(D) state does not cross ${}^{3}T_{lg}(P)$. Therefore there is no interaction for which to correct the value of \mathcal{P}_{3} . The correction of \mathcal{P}_{1} and \mathcal{P}_{2} values is considered below, using two methods.

Method A.

Correction of \mathcal{P}_1 .

Jørgensen suggests ¹²¹ that the interaction between the ${}^{3}T_{2g}$ and ¹E(D) states depresses the former by an energy $K_{1}^{2}/(E_{a}-E_{b})$ and raises the latter by the same amount. $(E_{a}-E_{b})$ is the energy interval between the ¹E(D) and ${}^{3}T_{2g}$ levels, and $2K_{1}$ is its minimum value, given ¹²¹ as $\sim 1kK$.

Hence, the energy increment due to the interaction is given by:

$$K_1^2/(E_a-E_b) = \sigma_1 - \vartheta_1 = \vartheta_4 - \sigma_4 \dots A.4.1$$

where (see figure 1.5):

 $E_a - E_b = \sigma_4 - \sigma_1$ A.4.2

More detailed calculations have shown that no accuracy is lost by replacing ($\sigma_4 - \sigma_1$) by ($\mathcal{P}_4 - \mathcal{P}_1$). In this case equations A.4.1 and A.4.2 yield:

$$\sigma_{1} = \vartheta_{1} + \kappa_{1}^{2} / (\vartheta_{4} - \vartheta_{1})$$

$$\sigma_{4} = \vartheta_{4} - \kappa_{1}^{2} / (\vartheta_{4} - \vartheta_{1})$$

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Correction of \mathcal{P}_2 .

The energy difference (E_c-E_a) between the ${}^{3}T_{lg}(F)$ and ${}^{1}E(D)$ states may be replaced by $(\mathcal{V}_{2}-\mathcal{V}_{4})$. Very similar arguments to those above then lead to:

$$\sigma_{2} = \vartheta_{2} - \kappa_{2}^{2} / (\vartheta_{2} - \vartheta_{4})$$

$$\sigma_{4} = \vartheta_{4} + \kappa_{2}^{2} / (\vartheta_{2} - \vartheta_{4})$$

$$(\vartheta_{2} - \vartheta_{4})$$

 K_2 has been given ¹²¹ as approximately 0.8 kK. Method B.

The interaction between two states, of energies E_1 and E_2 , is given by the secular equation:

$$\begin{vmatrix} E_1 - E & W \\ W & E_2 - E \end{vmatrix} = 0 \dots A.4.5$$

W has been given ¹²¹ by JAgensen for the ${}^{3}F_{2} - {}^{1}D_{2}$ interaction, as - (2 $\sqrt{5}/5$) $\mathbf{\xi}_{3d}$ = - 0.976kK (using the free-ion value for $\mathbf{\xi}_{3d}$). Actual values may be numerically less than this because of the reduction 149 of the spin-orbit coupling constant in complexes. The solutions of equation A.4.5 are the (E') energies (relative to that of the ${}^{3}F$ term) of the states after the interaction, in terms of the original energies (E_{1} and E_{2}).

Correction of $\boldsymbol{\mathcal{V}}_{1}$.

The energies of the ¹E(D) and ³T_{2g} states before interaction are:¹⁵⁰ $E(^{1}E) = E_{1} = 8B' + 2C - 12Dq$) $E(^{3}T_{2g}) = E_{2} = -2Dq$)

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Substitution of these expressions into equation A.4.5 gives, on expansion: $E^2-E(8B' \pm 2C-14Dq) - 2Dq (8B' + 2C) + 24Dq^2 - W^2 = 0 \dots A.4.6$

Further

$$E^{1}({}^{3}T_{2}) = \mathcal{V}_{1} - 12Dq)$$

$$E^{1}({}^{1}E) = \mathcal{V}_{4} - 12Dq)$$

$$Dq = \sigma_{1}/10)$$

$$BB'+2C = \sigma_{4})$$

Putting the solutions of equation A.4.6 into equation A.4.7 gives:

$$\boldsymbol{\sigma}_{4} = \boldsymbol{\gamma}_{1} + \boldsymbol{\gamma}_{4} - \boldsymbol{\sigma}_{1} \qquad)$$

$$\boldsymbol{\gamma}_{4} - \boldsymbol{\gamma}_{1} = \left[(\boldsymbol{\sigma}_{4} - \boldsymbol{\sigma}_{1})^{2} + 4W^{2} \boldsymbol{j}^{\frac{1}{2}} \right] \qquad (A.4.8).$$

Elimination of σ_4 between these two equations leads to:

$$(\boldsymbol{\vartheta}_{4^{+}}\boldsymbol{\vartheta}_{1} - 2\boldsymbol{\sigma}_{1})^{2} + 4\boldsymbol{W}^{2} = (\boldsymbol{\vartheta}_{4^{-}}\boldsymbol{\vartheta}_{1})^{2}$$

which has solutions:

$$\sigma_{1} = (\frac{1}{2}) \left\{ (\vartheta_{4^{+}} \vartheta_{1}) \pm [(\vartheta_{4^{-}} \vartheta_{1})^{2} - 4W^{2}]^{\frac{1}{2}} \right\}. A.4.9.$$

The meaningful solution has the negative square root, since otherwise $\sigma_1 \neq \mathcal{V}_1$ in the limit of no interaction (W=O). Correction of \mathcal{V}_2 .

In the case of the interaction between the ${}^{1}E(D)$ and ${}^{3}T_{lg}(F)$ states:

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Equations A.4.5 and A.4.10 then give, on expansion:

 $E^2 - E(\sigma_4 - \sigma_2/3) + (\sigma_2/3) (\sigma_4 - 2\sigma_2/3) - W^2 = 0 \dots A.4.11.$ Further:

Putting the roots of equation A.4.11 into A.4.12 gives:

$$\sigma_{4} = \vartheta_{4} + \vartheta_{2} - \sigma_{2}$$

and

 $\sigma_2 = \frac{1}{2} \left\{ (\mathcal{V}_4 + \mathcal{V}_2) + \left[(\mathcal{V}_2 - \mathcal{V}_4)^2 - 4W^2 \right]^2 \right\}.$ The sign must be positive to ensure that $\sigma_2 = \mathcal{V}_2$ when W = 0. Comparison of Methods of Correction.

The equations developed above were compared by calculating $P_{3\sigma}$ from the data ¹⁵⁰ of Bostrop and Jørgensen. Table A.4.1 gives the results. These demonstrate that minimisation of P_3 is best achieved by the use of method B, in the region where $\mathcal{V}_1 < \mathcal{V}_4 < \mathcal{V}_2$. In the cases when $\mathcal{V}_4 \sim \mathcal{V}_1$ and $\mathcal{V}_4 \sim \mathcal{V}_2$, it is better to use method A. Method B may be improved by using numerically lower values of the spin-orbit coupling constant. This is particularly evident in the case of Ni(H₂O)₆²⁺, for which it is impossible to calculate σ_2 unless W is reduced.

When $\mathcal{V}_4 < \mathcal{V}_1$ or $\mathcal{V}_4 > \mathcal{V}_2$ it is only necessary to correct the spin-allowed frequency most affected (\mathcal{V}_1 or \mathcal{V}_2 respectively).

Table A.4.1

A comparison of the methods of correcting the d-d frequencies of octahedral Nickel(II) complexes for the effects of intermediate coupling. All units are in kK except those (kK^2) of $P_{3\sigma}$.

Complex	Method	<u> </u>	<u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u><u></u></u>	<u> </u>	<u>~4</u>	<u></u> 23σ
Ni(tren)SO ₄ . H ₂ O	. 1	10.6	17.9	27.5	12.9	40.2
**	2	11.0	17.9	27.5	12,9	23.6
**	3	10.7	17.9	27.5	12.9	35.6
**	4	11.1	17.9	27.5	12.9	19.1
11	5	11.1	17.7	27.5	12.9	12.4
Ni(NO3)2py4	1	10.1	16.5	27.0	13.5	5.2
11	2	10.2	16.5	27.0	13.5	2.9
**	3	10.2	16.5	27.0	13.5	1.5
11	4	10.5	16.5	27.0	13.5	-7.6
†1	6	10.2	16.3	27.0	13.5	-7.0
11	5	10.5	16.1	27.0	13.5	22.3
Ni(H ₂ O) ₆ ²⁺	1	8.5	13.5	25.3	15.4	-32.2
11	2	8.5	14.3	25.3	15.4	7.8
11	3	8.5	13.5	25.3	15.4	-34.6
11	4	8.6	13.5	25.3	15.4	-40.3
**	7	8.5	13.8	25.3	15.4	-15.2
11	б	8.5	13.8	25.3	15.4	-17.7
Ni(SCN) ₂ py ₄	1	10.1	16.7	26.7	12.8	18.6
11	2	10.2	16.7	26.7	12.8	14.0
11	3	10.2	16.7	26.7	12.8	14.4

Table A.4.1 cont....

Complex	Method*	<u>_</u> 1	<u>_</u> 2	<u> </u>	<u>~</u> 4	$\frac{P}{3\sigma}$
Ni(SCN) ₂ py ₄	4	10.5	16.7	26.7	12.8	2.1
† †	6	10.2	16.5	26.7	12.8	7.8
**	5	10.5	16.4	26.7	12.8	-8.0
† 1	7	10.1	16.5	26.7	12.8	11.7
Ni(tren)SO4	1	10.0	17.2	26.9	12.9	44.4
tt	2	10.3	17.2	26.9	12.9	28.9
**	3	10.1	17.2	26.9	12.9	39.4
11	4	10.4	17.2	26.9	12.9	25.2
11	6	10.1	17.0	26.9	12.9	32.9
FT .	5	10.4	17.0	26.9	12.9	, 15.4
**	7	10.0	17.0	26.9	12.9	37.7
**	8	10.0	17.0	26.9	12.9	33.7

- * Key to numbering of methods:
 - 1) Uncorrected data
 - 2) Corrected by Bostrop and Jørgensen¹⁵⁰.
 - 3) v_1 corrected by method A.
 - 4) v_1 corrected by method B.
 - 5) v_1 and v_2 corrected by method B.
 - 6) v_1 and v_2 corrected by method A.
 - 7) v_2 corrected by method A.
 - 8) v_2 corrected by method B.

XXXV

Appendix A.5.

The Application of Group Theory to the

Treatment of Molecular Vibrations.

The use of group-theoretical principles will be illustrated by means of brief treatments of the vibrational modes of square-coplanar $MX_{2}L_{2}$ chromophores, of heteroaromatic amines, and of the nitrate ion.

a) The fundamental vibrations of square-planar MX2L2 monomers.

i) The Trans-configuration.

The complex will be assumed to have regular symmetry, and both types of ligand will be taken to be spherical. The molecule then belongs to the D_{2h} point group. The molecular plane will be defined as $\sigma(xy)$, with the x-axis taken along the M-X bonds. Atoms will be numbered from the positive axis in a clockwise direction as X_1 , L_2 , X_3 , L_4 and M_5 . The transformation matrices for the operation of each symmetry element on the cartesian vectors for each atom then have the characters given in table A.5.1.

The representation $\Gamma_{\rm QTR}$ consists of the sums of the columns, and contains the representations for all the nuclear displacements by vibration (Q), translation (T) and rotation (R). $\Gamma_{\rm TR}$ is the sum of those irreducible representations given by the D_{2h} character table ⁹⁶ (table A.5.2), which transform like the x, y, z, R_x, R_y and R_z vectors. Hence, $\Gamma_{\rm Q} = \Gamma_{\rm QTR} - \Gamma_{\rm TR}$.

If the character table for a particular group has the form given in table A.5.3 (where p_j is the number of symmetry elements

Table A.5.1

Characters for the operation of symmetry elements on the cartesian vectors for trans- MX_2L_2 .

Vector	Characters for the Symmetry Elements									
	Ē	<u>C₂(z)</u>	<u>C₂(y)</u>	<u>C₂ (x)</u>	i	<u> σ(xy)</u>	<u>σ(xz)</u>	<u>σ(yz)</u>		
x ₁	1	0	0	1	0	1	1	0		
у ₁	1	0	0	-1	0	1	-1	0		
^z 1	1	0	0	-1	0	-1	1	0		
x ₂	1	0	-1	0	0	1 ·	0	-1		
у ₂	1	0	1	0	0	1	0	1		
^z 2	1	0	-1	0	0	-1	0	1		
x ₃	1	0	0	1	0	1.	1	0		
y ₃	1	0	0	-1	0	1	-1	0		
z ₃	1	0	0	-1	0	-1	1	0		
x ₄	1	0	-1	0	0	1	0	-1		
У4	1	0	1	0	0	1	0	1		
^z 4	1	0	-1	0	0	-1	0	1		
x ₅	1	-1	-1	1	-1	1	1	-1		
У ₅ .	1	-1	1	-1	-1	1	-1	1		
^z 5	1	1	-1	-1	-1	-1	1	1		
r _{QTR}	15	-1	1 3	-3	-3	5	3	3		
r _{TR}	6	-2	-2	-2	0	0	0	0		
r_{Q}^{-}	9	1	-1	-1	-3	5	3	3		

\$

Table A.5.2

D _{2h}	<u> </u>	<u>C₂(z)</u>	<u>C₂(y)</u>	<u>C₂(x)</u>	<u>i</u>	<u>σ(xy)</u>	<u> σ(xz)</u>	<u>σ(yz)</u>		<u> </u>	
Ag	1	1	1	1	1	1	1	1		x^{2}, y^{2}, \dot{z}	
B _{lg}	1	1	-1	-1	1	1	-1	-1	Rz	xy	
B _{2g}	1	-1	1	-1	1	-1	1	-1	Ry	xz	
B _{3g}	1	-1	-1	1	1	-1	-1	1	R _x	yz	
Ą	1	1	1	1	-1	-1	-1	-1			
^B lu	1	1	-1	-1	-1	-1	. 1	1	z		
B _{2u}	1	-1	1	-1	-1	1	-1	1	у		
^B 3u	1	-1	-1	1	-1	1	1	-1	x		
b) The character table for the C_{2v} point group. ⁹⁶ $C_{2v} \models E = C_2(z) = \sigma_{v}(xz) = \sigma_{v}(yz) = 1$											
A ₁	1		1	1		1		z	x ² ,y	² ,z ²	
- A ₂	1		1	-1		-1		Rz	xy		
- B1	1		-1	1		-1		x,R _y	xz		
^B 2	1		-1	-1		1		y,R _x	yz		

a) The character table for the D_{2h} point group.⁹⁶

۰,
Table A.5.3

-	_{p1} s1	^p 2 ^S 2	^p j ^S j	p _m S _m		-
R ₁ R ₂ R _i R _n	C ₁₁ C ₂₁	$C_{12} C_{22} $	C _{1j} C _{2j} ' C' _{ij}	C _{1m} C _{2m} ' ' C'im ' ' ' C'nm	a)	b)

The generalised form of character tables.

- Notes: a) In this region of the table are found the symmetry properties of translation and rotation vectors.
 - b) This region of the table details the symmetry properties of the polarisability tensors.

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in class S_j , and R_i is an irreducible representation) then the representation:

 $\int = \chi_1 \quad \chi_2 \quad \chi_3 \quad \dots \quad \chi_j \quad \dots \quad \chi_m$ can be reduced ⁹⁶ to a sum:

 $\int = n_1 R_1 + n_2 R_2 + \dots + n_i R_i + \dots + n_n R_n$ of the irreducible representations $(n_i \text{ of } R_i)$, using the expression⁹⁶:

> $\Gamma_{M-X} = 20020220 = A_g + B_{3u}$ $\Gamma_{M-L} = 20200202 = A_g + B_{2u}$

These have been decomposed (using equation A.5.1), as shown, and the results are 96 the symmetries of the stretching vibrations. All the possible independent stretching vibrations are then constructed and, with the aid of the character table, those having A_g , B_{2u} and B_{3u} symmetries may be identified. These are the required stretching vibrations and are given in figure A.5.1a. The remaining vibrations in \int_Q^r are:

$$\int_{Q}^{1} = \int_{Q}^{1} - \int_{M-X}^{1} - \int_{M-L}^{1} = B_{1g} + 2B_{1u} + B_{2u} + B_{3u}.$$



These are the bending modes and have the forms shown in figure A.5.1b.

The character table reveals ⁹⁶ that only the B_{lu}, B_{2u} and B_{3u} modes are infrared active, since they transform like the x, y and z cartesian vectors. The infrared spectrum should therefore exhibit one \mathcal{V}_{M-X} mode (B_{3u}), one \mathcal{V}_{M-L} mode (B_{2u}), and four bending modes (2B_{1u}+B_{2u}+B_{3u}). The $S_{M-X}(B_{2u})$ and $S_{M-L}(B_{3u})$ deformations take place in the molecular plane (β), while the $\prod_{M-X}(B_{1u})$ and $\prod_{M-L}(B_{1u})$ modes consist of bending vibrations perpendicular to the molecular plane (χ).

More sophisticated techniques treat ⁹⁹ the internal coordinates of the system and applications of matrix theory^{588,589} allow the frequencies of the normal vibrations to be calculated.⁵⁹⁰

ii) The Cis-configuration.

This has C_{2v} symmetry (see table A.5.2 for the character table) and the molecular plane is defined as $\sigma_v(xz)$ with the $C_2(z)$ axis taken as the bisector of the M-X bonds. By similar methods to those given above it may be deduced that:

$$\Gamma_{Q} = 9 \ 1 \ 5 \ 1 = 4A_{1} + A_{2} + 3B_{1} + B_{2}$$

$$\Gamma_{M-X} = 2 \ 0 \ 2 \ 0 = A_{1} + B_{1}$$

$$\Gamma_{M-L} = 2 \ 0 \ 2 \ 0 = A_{1} + B_{1}$$

$$\Gamma_{Q}' = 5 \ 1 \ 1 = 2A_{1} + A_{2} + B_{1} + B_{2}$$

Figure A.5.2 illustrates the stretching and bending modes which have these symmetry properties. Only the A₂ vibration is infrared-inactive⁹⁶, and two \mathcal{P}_{M-X} (A₁+B₁) and two \mathcal{P}_{M-L} (A₁+B₁) stretching modes should appear in the infrared spectrum.

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iii) Lower symmetry.

If either of the ligands is not spherical then, rigorously, the MX_{2L_2} molecules belong to point groups of lower symmetry than D_{2h} or C_{2v} . Thus, if the trans-configuration contains ligands (L) which are heteroaromatic amines, and their ring-planes are inclined to the $\mathcal{O}_{(xy)}$ plane, C_2 symmetry results. In this case, all the vibrations become allowed in the infrared spectrum. However, because this is a small departure from what is still approximately D_{2h} symmetry, the new bands should be weaker than those allowed in the D_{2h} group. Table A.5.4 shows how the D_{2h} representations transform in lower point groups.

Clark and Williams have listed 59 the distributions of normal modes for other chromophores, in addition to MX_2L_2 .

b) The internal vibrations of heteroaromatic amines.

The vibration modes of the substituted pyridines and pyrazines are all based upon those of pyridine. These have been extensively discussed, 591,592,525,526. The vibrations of quinoline and quinoxaline are based on those of naphthalene, which have also been extensively studied, 518,519,522,593. Figure A.5.3 gives, for the purposes of illustration, the forms of the χ_{cc} vibrations of naphthalene. Quinoxaline is treated in more detail below.

Quinoxaline.

This amine belongs to the C_{2v} point group (table A.5.2). The $C_2(z)$ axis must be taken as the bisector of both aromatic rings, while the molecular plane may be defined as $\sigma_v'(yz)$. In this case, group

Table A.5.4

Symmetry of the D _{2h} normal modes in lower groups.													
D _{2h}	C _{2h} *(y)	^D 2	с ₂ (у)	C _{2h} (z)	C _{2h} (x)	^c _{2v} (y)	C _{2v} (z)	^C 2v ^(x)	C ₂ (x)	C ₂ (z)	Ci	C _j	с ₁
Ag	Ag	A	Α	Ag	A _g	A ₁	A ₁	A ₁	A	A	Ag	A †	A
^B 1g	Bg	^B 1	В	Ag	Bg	^B 1	A ₂	^B 1	В	А	Ag	A'' :	А
^B 2g	Ag	^B 2	A	$^{\mathrm{B}}g$	Bg	A ₂	^B 1	^B 2	В	В	Ag	A'	A
^B 3g	Bg	^B 3	В	Bg	Ag	^B 2	^B 2	A2	А	В	Ag	A ' '	A
Ą	A _u	А	А	Ąu	Au	A2	A2	A2	А	A ₋₁	Au	A' '	А
^B 1u	Bu	^B 1	В	Ąu	^B u	^B 2	A ₁	^B 2	В	. A	A _u	A	А
^B 2u	Au	^B 2	A	^B u	^B u	A ₁	^B 2	^B 1	В	В	Ąu	A* *	A
^B 3u	Bu	^B 3	В	^B u	Au	^B 1	^B 1	A ₁	A	В	Au	A '	A

* Axes included in the group symbol denote which axis of the original D_{2h} group has been taken as the principle axis in the lower symmetry.







Figure A.5.4

theory gives:

$$\begin{split} & \prod_{Q} = 42 \ 2 \ 0 \ 16 = 15A_1 + 7A_2 + 6B_1 + 14B_2 \\ & \prod_{Q} R_2 \text{ nucleus} = 24 \ 2 \ 0 \ 10 = 9A_1 + 4A_2 + 3B_1 + 8B_2 \\ & \prod_{C-C, C-N \text{ bonds}=} 11 - 3 - 3 \ 11 = 4A_1 + 7B_2 & \cdot \\ & \prod_{C-H \text{ bonds}} = 6 \ 0 \ 0 \ 6 = 3A_1 + 3B_2 \\ & \prod_{ring \text{ bending}} = 15 \ 5 \ 3 \ -1 = 5A_1 + 4A_2 + 3B_1 + B_2 \\ & \prod_{C-H \text{ bending}} = 12 \ 0 \ 0 \ 0 = 3A_1 + 3A_2 + 3B_1 + 3B_2 \end{split}$$

The infrared spectrum should exhibit ll ring-stretching, 6 in-plane ring bending, 3 out-of-plane ring bending, 6 \mathcal{V}_{C-H} , 6 $\boldsymbol{\beta}_{C-H}$ and 3 $\boldsymbol{\gamma}_{C-H}$ vibrations; since only the A_2 modes (4 $\boldsymbol{\gamma}_{cc}$ + 3 $\boldsymbol{\chi}_{CH}$) are infrared-forbidden.

c) The vibrations of the nitrate group.

The free nitrate ion has D_{3h} symmetry. Of the six vibration modes, two are doubly degenerate E' species. Only these two E' modes (\mathcal{V}_3 and \mathcal{V}_4) and the A_2 " (\mathcal{V}_2) species are infrared-active in the free ion.¹⁰⁰ These vibrations have the forms ¹⁰⁰ of figure A.5.4 and the frequencies ⁵⁶³ of table A.5.5.

A coordinated nitrato-group, whether monodentate or bidentate in character, belongs to the lower C_{2v} point group (table A.5.2). In this group, the \mathcal{V}_1 mode transforms with A_1 (\mathcal{V}_1) symmetry, and \mathcal{V}_2 with B_1 (\mathcal{V}_5) symmetry. The \mathcal{V}_3 and \mathcal{V}_4 vibrations lose their degeneracy, splitting into $A_1(\mathcal{V}_2) + B_2(\mathcal{V}_4)$ and $A_1(\mathcal{V}_3) + B_2(\mathcal{V}_6)$ species, respectively. All six modes are then active in the infrared region, with the typical frequencies 563 given in table A.5.5.

Table A.5.5

Frequencies (cm^{-1}) of the nitrate ion (a) and typical frequencies for the coordinated nitrato-group (b).



Hester and Grossman have performed calculations 594 which show that polarisation of the nitrate ion in an ionic lattice can also split the E' modes. Ambiguity therefore exists, regarding the interpretation of an observed splitting. However, from Hester and Grossman's diagrams it seems that only coordination can raise \mathcal{P}_6 to ~800 cm⁻¹, where it is observed in the complexes discussed in this work. Addison, et al, have suggested ⁵⁹⁵ that the patterns of Raman polarisation may be used to distinguish ionic, monodentate and bidentate nitrate groups.

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Bibliography.

Abbreviations used for Periodical Titles are the coden				
recommend	ed in "Coden for Periodical Titles" which is the ASTM			
Special T	echnical Publication No. 329-S-1 (1964). The coden are			
also list	ed on the inside cover pages of all issues of "Chemical			
Titles".	Relevant abbreviations are listed later in this work.			
1)	H. Bethe, ANPY, 1929 3 133.			
2)	J.H.Van Vleck. "The Theory of Magnetic and Electric			
	Susceptibilities", Oxford University Press, 1932.			
3)	J.H.Van Vleck. PHRV. 1932 41 208.			
4)	J.H.Van Vleck, W.G.Penney. PHMA. 1934 17 961.			
5)	J.H.Van Vleck. JCPS. 1935 <u>3</u> 803, 807.			
6)	J.H.Van Vleck, A.Sherman. RMPH. 1935 7 167.			
7)	J.H.Van Vleck. JPCH. 1937 41 67.			
8)	$J.H.Van Vleck. JCPS. 1939 \overline{7} 61.$			
9)	J.H.Van Vleck. JCPS. 1939 7 72.			
10)	R.Finkelstein, J.H.Van Vleck. JCPS. 1940 8 790.			
11)	H.A.Kramers. Proc.Acad.Sci.(Amsterdam). 1930 33 953.			
12)	R.Schlapp, W.G.Penney. PHRV. 1931 41 194; 1932 42 666.			
13)	J.B.Howard. JCPS. 1935 <u>3</u> 813.			
14)	0.Jordahl. PHRV. 1934 45 87.			
15)	C.J.Gorter. PHRV. 1932 42 437.			
16)	L.E.Orgel. JCPS. 1955 <u>23</u> 1004.			
17)	O.G.Holmes, D.S.McClure. JCPS. 1957 <u>26</u> 1686.			
18)	C.J.Ballhausen. "Introduction to Ligand Field Theory". McGraw-Hill, 1962.			
19)	B.N.Figgis, J.Lewis. Progr. Inorg. Chem. 1964 6 37.			
20)	B.N.Figgis. "Introduction to Ligand Fields". Interscience, 1966.			
21)	D.S.McClure. Solid State Physics. 1959 <u>9</u> 399.			
22) .	C.K.Jørgensen. "Orbitals in Atoms and Molecules". Academic Press, 1962.			
23)	C.K.Jørgensen. "Absorption Spectra and Chemical Bonding in			
	Complexes". Pergamon, 1962.			
24)	C.K.Jørgensen. Advan. Chem. Phys. 1963 <u>5</u> 33.			
25)	C.K.Jørgensen. Advan. Chem. Phys. 1965 8 47.			
26)	C.K.Jørgensen. Solid State Physics. 1962 13 375.			
27)	L.E.Orgel. "Introduction to Transition-Metal Chemistry".			
• ·	Methuen, 1960.			
28)	T.M.Dunn, D.S.McClure, R.G.Pearson. "Crystal Field Theory". Harper and Row. 1965.			
29)	J.S.Griffith. "The Theory of Transition-Metal Ions".			
	Cambridge University Press, 1964.			
30)	H.Watanabe. "Operator Methods in Ligand Field Theory". Prentice-Hall, 1966.			

. .

-

31) C.K.Jørgensen. Structure and Bonding. 1966 1 3. 32) E.J.Zavoisky. J.Phys. (U.S.S.R.) 1945 9 211. 33) P.W.Selwood. A.D.C.A. 1951 3 28. 34) D.E.O'Reilly. A.D.C.A. 1960 12 31. 35) M.Orchin: A.D.C.A. 1966 16 2. 36) R.J.P.Williams. FEPR. 1961 20 (3.2) 5. 37) G.L.Eichorn.FEPR. 1961 20 (3.2) 40. 38) P.Saltman. JCED. 1965 42 682. 39) L.E.Orgel in "Metals and Ensyme Activity". Crook, Cambridge University Press, 1958. 40) N.Bloembergen. PHRV. 1956 104 324. 41) R.W.G.Wyckoff. "Crystal Structures". Vols 1-5. Interscience, 1948-66. 42) A.F.Wells. "Structural Inorganic Chemistry". Oxford University Press. 1962. 43) A.J.C.Wilson. "Structure Reports". (1950-59) Vols 13-23. 44) E.KUnig. "Landolt-BUrnstein" New Series. 1966 II. 2. 45) B.Bleaney, K.W.H.Stevens. Repts. Progr. Phys. 1953 16 108. 46) K.D.Bowers, J.Owen. Repts. Progr. Phys. 1955 18 304. 47). J.Ferguson. Revs. Pure. Appl. Chem. 1964 14 1. 48) G.Kortum, W.Braun, G.Hertzog. Angew. Chemie (International). 1963 2 333. 49) R.J.H.Clark. JCED. 1964 41 488. W.W.Wendlandt, H.G.Hecht. "Reflectance Spectroscopy". 50) Interscience, 1966. 51) D.B.Sowerby, L.F.Audrieth. JCED. 1960 37 134. 52) C.N.Kenny in "Developments in Inorganic Polymer Chemistry". M.F.Lappert, G.J.Leigh. Elsevier, 1962. 53) K.V.Martin. JACS. 1958 80 233. 54) C.S.Marvel, N.Tarköy. JACS. 1958 80 832. 55) W.Manch, W.C.Fernelius. JCED. 1961 38 193. 56) J.Lewis, Sci. Progr. 1963 51 450. 57) R.L.Carlin. Transition Metal Chemistry. 1965 1 1. 58) R.J.H.Clark. SPAC. 1965 21 955. 59) R.J.H.Clark, C.S.Williams. INOC. 1965 4 350. 60) R.J.H.Clark, T.M.Dunn. JCS. 1963 1198. 61) B.R.McGarvey. Transition Metal Chemistry. 1966 3 89. 62) A.Carrington, H.C.Longuet-Higgins. QURE. 1960 14 427. 63) R.L.Mössbauer. SCIE. 1962 137 731. 64) A.J.F.Boyle, H.E.Hall. Repts. Progr. Phys. 1962 25 441. 65) H.Frauenfelder. "The Mössbauer Effect". Benjamin, 1962. 66) J.W.Smith. Sci. Progr. 1966 54 103. 67) P.R.Brady, J.F.Duncan, K.F.Mok. PRLA. 1965 287 343. 68) N.N.Greenwood. CHMB. 1967 <u>3</u> 56. 69) E.Fluck. Advan. Inorg. Radiochem. 1964 6 435. 70) J.F.Duncan, R.M.Golding. QURE. 1965 19 36. 71) E.L.Muetterties, W.D.Phillips. Advan. Inorg. Radiochem. 1962 4 231 72) B.B.Wayland, R.S.Drago. JACS. 1966 88 4597. 73) M.Inoue, M.Kubo. INOC. 1966 5 70. 74) F.Woldbye. Technique Inorg. Chem. 1965 4 249.

75) R.D.Gillard. Progr. Inorg. Chem. 1966 7 215.

xlii

xliii

76) A.M.Sargeson in "Chelating Agents and Metal Chelates" F.P.Dwyer, D.P.Mellor, Academic Press, 1964. A.D.Liehr. Transition Metal Chemistry. 1966 2 166. 77) 78) J.R.Allan, D.H.Brown, R.H.Nuttall, D.W.A.Sharp. JINC. 1964 26 1895. 79) D.H.Brown, R.H.Nuttall, D.W.A.Sharp. JINC. 1964 26 1151. 80) P.B.Bowman, L.B.Rogers. JINC. 1966 28 2215. 81) W.W.Wendlandt. JINC. 1963 25 833. 82) C.Duval, "Inorganic Thermogravimetric Analysis". Elsevier, 1963. 83) T.Ozawa. BCSJ. 1966 39 2071. 84) R.C.MacKenzie, B.D.Mitchell. ANAL. 1962 87 420. W.W.Wendlandt. Technique Inorg. Chem. 1963 1 209. 85) 86) H.Irving, R.J.P.Williams. JCS. 1953 3192. 87) J.Bjerrum. CHRE. 1950 76 381. W.R.May, M.M.Jones. JINC. 1963 25 207. 88) 89) M.Goldstein, E.F.Mooney, A.Anderson, H.A.Gebbie. SPAC.1965 21 105. N.S.Gill, R.H.Nuttall, D.E.Scaife, D.W.A.Sharp. JINC. 1961 18 79. 90) E.V.Condon, G.H.Shortley. "Theory of Atomic Spectra". 91) Cambridge University Press. 1963. 92) J.N.Murrell, S.F.A.Kettle, J.M.Tedder. "Valence Theory". Wiley, 1965. 93) G.Racah. PHRV. 1942 61 186. 94) G.Racah. PHRV. 1942 62 438. 95) G.Racah. PHRV. 1943 63 367. 96) F.A.Cotton. "Chemical Applications of Group Theory". Interscience, 1963. D.Schonland. "Molecular Symmetry". Van Nostrand, 1965. 97) R.McWeeny. "Symmetry". Pergamon, 1963. 98) 99) E.B.Wilson, Jr., J.C.Decius, P.C.Cross. "Molecular Vibrations". McGraw-Hill, 1955. 100) K.Nakamoto. "Infrared Spectra of Inorganic and Coordination Compounds". Wiley, 1965. H.Kaminura, S.Koide. JUPS. 1961 16 436. 101) 102) H.A.Jahn, E.Teller. PRLA. 1937 A161 220. 103) L.E.Orgel, J.D.Dunitz. NATU. 1957 179 462. 104) A.D.Liehr. Progr. Inorg. Chem. 1962 3 281. 105) B.N.Figgis. JCS. 1965 4887. 106) J.Otsuka. JUPS. 1966 21 596. C.J.Ballhausen, C.K.Jørgensen. KDVS. 1955 29 (14) 1. 107) M.Flato. JMOS. 1965 17 300. 108) 109) M.Ciampolini. INOC. 1966 5 35. 110) M.J.Norgett, J.H.Thornley, L.M.Venanzi. JCSI. 1967 540. 111) A.L.Companion, M.A.K.Komorynsky. JCED. 1964 41 257. 112) H.B.Gray. Transition-Metal Chemistry. 1965 1 239. 113) G.Maki. JCPS. 1958 28 651. 114) Y.Tanabe, S.Sugano. JUPS. 1954 9 753. Y.Tanabe, S.Sugano. JUPS. 1954 9 766. 115) C.J.Ballhausen. KDVS. 1953 29 (8) 1. 116) C.J.Ballhausen. KDVS. 1954 29 (4) 1. 117)

xliv

118) A.D.Liehr, C.J.Ballhausen. APNY. 1959 2 134. 119) A.D.Liehr. JPCS. 1963 67 1314. R.Papparlardo. JMOS. 1961 6 554. 120) 121) C.K.Jørgensen. ACSA. 1955 9 1362. A.D.Liehr, C.J.Ballhausen. PHRV. 1957 106 1161. 122) 123) R.F.Fenske. JACS. 1967 <u>89</u> 252. 124) A.D.Liehr. Advan. Chem. Phys. 1963 5 241. 125) C.J.Ballahusen. Progr. Inorg. Chem. 1960 2 251. 126) N.Tahabe, N.Sato, J.Fujita. SPAC. 1966 22 577. I.Nakagawa, T.Shimanouchi. SPAC. 1966 22 759. 127) 128) F.A.Cotton, R.H.Soderberg. JACS. 1962 84 872. 129) S.Koide, T.Oguchi. Advan. Chem. Phys. 1963 5 189. 130) R.L.Carlin. JCED. 1966 43 521. B.N.Figgis, J.Lewis in "Modern Coordination Chemistry". 131) J.Lewis, R.G.Wilkins, Interscience, 1960. 132) B.N.Figgis, J.Lewis, Technique Inorg. Chem. 1965 4 137. 133) P.W.Selwood. "Magnetochemistry". Interscience, 1956. 134) P.George, D.S.McClure. Progr. Inorg. Chem. 1959 1 381. 135) F.A.Cotton. JCED. 1964 41 466. 136) J.Owen. Discuss. Farad. Soc. 1955 19 127. 137) J.Owen. PRLA. 1955 <u>227A</u> 183. 138) T.M.Dunn. JCS. 1959 623. 139) K.W.H.Stevens. PRLA. 1953 A219 542. 140) J.Owen, J.H.M.Thornley. Repts. Progr. Phys. 1966 29 675. 141) J.Owen. Discuss. Farad. Soc. 1958 26 53. 142) C.K.Jørgensen. Ibid. 110. 143) B.R.McGarvey, A.H.Maki. JCPS. 1958 29 35. 144) D.M.S.Bagguley, J.H.E.Griffiths. PRLA. 1950 A201 366. 145) M.Kubo, D.Nakamura. Advan. Inorg. Radiochem. 1966 8 257. 146) H.Basch, A.Viste, H.B.Gray. JCPS. 1966 44 10. 147) R.A.Howald, D.P.Keeton. SPAC. 1966 22 1211. 148) R.Englman. Advan. Chem. Phys. 1965 8 13. 149) C.K.Jørgensen. Progr. Inorg. Chem. 1962 4 73. 150) 0.Bostrop, C.K.Jørgensen. ACSA. 1957 11 1223. 151) C.K.Jørgensen. ACSA. 1956 10 887. 152) A.B.P.Lever, S.M.Nelson, T.M.Shepherd. INOC. 1965 4 810. 153) S.M.Nelson, T.M.Shepherd. INOC. 1965 4 813. 154) H.B.Gray. JCED. 1964 41 2. 155) R.F.Fenske. INOC. 1965 4 33. R.F.Fenske, K.G.Coulton, D.D.Radthe, C.C.Sweeney. INOC. 156) 1966 <u>5</u> 951. 157) L.E.Sutton. JCED. 1960 37 498. 158) A.D.Liehr. JCED. 1962 39 135. H.B.Gray, N.A.Beach. JACS. 1963 85 2922. 159) 160) F.A.Cotton, T.E.Haas. INOC. 1964 <u>3</u> 1004. 161) H.B.Gray, C.J.Ballhausen. JACS. 1965 85 260. 162) B.Roos. ACSA. 1966 <u>20</u> 1673. 163) F.A.Cotton. Revs. Pure. Appl. Chem. 1966 16 175. 164) C.J.Ballhausen, H.B.Gray. "Molecular Orbital Theory". Benjamin, 1964. 165) F.A.Cotton, C.B.Harris, J.J.Wise. INOC. 1967 6 909.

166) P.Day, C.K.Jørgensen. JCS. 1964 6226. 167) A.B.P.Lever, S.M.Nelson. JCSI. 1966 859. 168) A.B.P.Lever, J.Lewis, R.S.Nyholm. JCS. 1963 5042. 169) R.J.P.Williams. Discuss. Farad. Soc. 1958.26 123. 170) R.Bersohn, R.G.Shulman. JCFS. 1966 45 2298. 171) D.Kivelson, R.Neiman. JCPS. 1961 35 149. 172) H.Irving, J.J.R.F.Da Silva. Proc. Chem. Soc. 1962 250. 173) J.J.R.F. Da Silva, J.G.Calado. JINC. 1966 28 125. 174) A.Yingst, D.H.McDaniel. JINC. 1966 28 2919. 175) D.P.Graddon, E.C.Watton. AJCH. 1965 18 507. 176) W.E.Bull, L.E.Moore. JINC. 1965 27 1341. 177) J. de O.Cabral, H.C.A.King, S.M.Nelson, T.M.Shepherd, E.Körös. JCSI. 1966 1348. 178) R.S.Nyholm, D.P.Craig in ref.76. 179) C.K.Jørgensen. Structure and Bonding. 1966 1 233. 180) R.J.W. Le Fevre. Advan. Phys. Org. Chem. 1965 3 1. 181) H.C.A.King, E.Körös, S.M.Nelson. NATU. 1962 196 572. 182) H.C.A.King, E.Körös, S.M.Nelson. JCS. 1964 4832. 183) S.M.Nelson, T.M.Shepherd. JCS. 1965 3276. 184) J.Clark, D.D.Perrin. QURE. 1964 18 295. 185) D.D.Perrin. "Dissociation Constants of Organic Bases in Aqueous Solution". Butterworths, 1965. 186) J.D.Dunitz. ACCR. 1957 10 307. N.S.Gill, R.S.Nyholm, G.A.Barclay, P.J.Pauling. JINC. 187) 1961 18 88. 188) E.KUnig, H.L.Schläfer. ZPCF. 1960 26 371. 189) M.D.Glonek, C.Curran, J.V.Quagliano, JACS. 1962 84 2014. 190) W.Ludwig, G.Wittmann. HCAC. 1964 47 1265. J.Ferguson. JCPS. 1960 32 528. 191) 192) D.M.L.Goodgame, M.Goodgame. JCS. 1963 207. D.M.L.Goodgame, M.Goodgame. INOC. 1965 4 139. 193) 194) J.A.J.Jarvis. ACCR. 1962 15 964. 195) F.A.Cotton, D.M.L.Goodgame, M.Goodgame. JACS. 1961 83 4690. 196) A.B.P.Lever, S.M.Nelson. CCOM. 1965 168. 197) D.M.L.Goodgame, M.Goodgame, M.J.Weeks. JCS. 1964 5194. 198) A.B.P.Lever, J.Lewis, R.S.Nyholm. JCS. 1964 4761. 199) D.M.L.Goodgame, M.Goodgame, F.A.Cotton. JACS. 1961 83 4161. S.Buffagni, L.M.Vallarino, J.V.Quagliano. INOC. 1964 3 480. 200) E.Uhlig, J.Csaszar, M.Maaser. ZAAC. 1964 331 324. 201) 202) D.H.Brown, R.H.Nuttall, D.W.A.Sharp, JINC, 1964 26 1151. 203) I.S.Ahuja, D.H.Brown, R.H.Nuttall, D.W.A.Sharp. JINC. 1965 27 162 204) F.A.Cotton, M.Goodgame. JACS. 1961 83 1777. 205) G.W.Pratt, Jr., R.Coelho. PHRV. 1959, 116 281. 206) J.Ferguson, D.L.Wood, K.Knox. JCPS. 1963 39 881. 207) R.M.Bennett, O.G.Holmes. CJCH. 1960 38 2319. 208) R.Stahl-Brada, W.Low. PHRV. 1959 113 775. F.A.Cotton, D.M.L.Goodgame, M.Goodgame, A.Sacco. JACS. 1961 209) 83 4157. 210) A.E.Underhill. Unpublished work.

211) A.G.Maddock. Quoted in a personal communication. 1967. H.N.Ramaswamy, H.B.Jonassen. INOC. 1965 4 1595. 212) M.Goodgame, P.J.Hayward. JCSI. 1966 632. 213) 214) D.M.Gruen, R.Gut. NATU. 1961 190 713. 215) N.Campbell. p.488 in "Chemistry of the Carbon Compounds". (ed) E.H.Rodd. Vol IVA. Elsevier. 1957. 216) R.M.Acheson. "Chemistry of Heterocyclic Compounds". Interscience, 1960. 217) MOCH. 1880 <u>1</u> 316. 218) T.Anderson. ACJL. 1851 80 44, 55. 219) W.Reppe. ACJL. 1956 606 128. 220) A.Albert. "Heterocyclic Chemistry". University of London Press. 1959. 221) J.R.Bailey. JACS. 1933 <u>55</u> <u>4141</u>; 1937 <u>59</u> 175. Laurent. ACJL. 1842 <u>41</u> 104. 222) Witt. CHBE. 1886 19 2791. 223) 224) J.A.Bladin. CHBE. 1885 18 1544. 225) E.Hoggarth; p.452 in Reference 215. 226) R.Criegee. Z.Angew. Chemie. 1938 51 519. 227) F.J.Welcher: p.l. in "Organic Analytical Reagents" Vol III. Van Nostrand. 228) M.G.Evans, J.De Heer. QURE. 1950 4 94. 229) Reference no.215 p.584. 230) D.E.Pearson: p.624 in "Heterocyclic Compounds". Vol 6. (ed) R.C.Elderfield. Wiley, 1957. 231) G.R.Ramage, J.K.Landquist: p.1371 in "The Chemistry of Carbon Compounds", Vol IVB.(ed)E.H.Rodd. Elsevier, 1959. 232) F.Dickens, H.McIlwain. BIJO. 1938 32 1615. 233) G.A.Swan, D.G.I.Felton. "The Phenazines". Interscience, 1957. 234) L.G.Sillen, A.E.Martell. "Stability Constants". Chem. Soc. Special Publication no.17., 1964. 235) T.W.Lang. CHBE. 1888, 21 1578. E.G.Cox, E.Sharrett, W.Wardlaw, K.C.Webster. JCS. 1936 129. 236) V.Kupčik, S.Durovič. Czech. J.Phys. 1960 10 182. 237) 238) Idem. NATU. 1959 184 1060. M.A.Porai-Koshits, G.N.Tishchenko. KRIS. 1959 4 216. 239) 240) F.Reitzenstein. ACJL. 1894 282 273. 241) E.G.Cox, A.J.Shorter, W.Wardlaw, W.J.Way. JCS. 1937 1556. 242) E.D.P.Barkworth, S.Sugden. NATU. 1937 139 374. 243) D.P.Mellor, B.S.Morris, J.Proc.Roy.Soc.N.S.W. 1938 71 536. 244) D.P.Mellor, C.D.Coryell. JACS. 1938 60 1786. 245) A.Di Paolini, E.Goria. GCIT. 1932 63 1048. 246) E.Sanero. Period. Miner. Roma. 1936 7 171. 247) J.A.Jarvis, A.F.Wells. ACCR. 1960 13 1027. 248) J.A.Jarvis. ACCR. 1962 15 964. 249) M.A.Porai-Koshits. Tr.Inst.Kristallogr.Akad.Nauk.SSSR. 1954 10 117. 250) A.S.Antsishkina, M.A.Porai-Koshits. KRIS. 1958 3 684.

xlvi

xlvii

251)	M.A.Porai-Koshits, A.S.Antsishkina. Izv. Sektora Ptatiny i Drug. Blagorodn. Metal. Inst. Obshch i Neorgan. Khim. Akad.
252)	Nauk. SSSR. 1999 29 19. M.A.Porai-Koshits, A.S.Antsishkina, L.M.Dickareva, E.K.Jukhov. ACCR. 1958 10 784.
253)	V.Duckworth: Aust.Cryst.Conf. 1966. Quoted in reference 358.
254)	F.Hanic. D.Stempelová, K.Hanicova, ACCR, 1964 17 633.
255)	S.Ooi, Q.Fernando. CCOM. 1967 532.
256)	M.A.Porai-Koshits, L.O.Atovmyan, G.N.Tishchenko. ZSTK. 1960 1 337.
257)	P.C.Jain, E.C.Lingafelter. JACS. 1967 89 724.
258)	M.R.Rosenthal, R.S.Drago. INOC. 1965 4 840.
259)	R.Varet. BSCF. 1891 5 843.
260)	J.R.Allan, D.H.Brown, R.H.Nuttall, D.W.A.Sharp. JCSI. 1966 1031.
261)	H.Elliott. Ph.D.Thesis. Hull 1965.
262)	A.V.Babaeva, I.B.Baranovskii, ZNOK, 1959 4 755.
263)	N.G.Mitra, P.C.Sinha, JICS, 1950 27 29.
264)	P.Pfeiffer, V.Pimmer, ZAAC, 1906 48 98.
265)	H.Abe. M.Ohtsuka, JUPS, 1956 11 896.
266)	R.V.Biagetti, H.M.Haendler, INOC, 1966 5 383.
267)	R.V.Biagetti, W.G.Bottier, H.M.Haendler, INOC, 1966 5 379.
268)	W.R.McWhinnie, JCS, 1964 2959.
269)	D.P.Graddon, R.Schulz, E.C.Watton, D.G.Weedon, NATU.
2000	1963 198 1299.
270)	C.W.Frank, L.B.Rogers, INOC, 1966 5 615.
271)	F.W.Lancaster, W.Gordy, JCPS, 1951 19 1181.
272)	D.H.Brown, R.H.Nuttall, J.McAvov, D.W.A.Sharp, JCST, 1966 892.
273)	W.Libus, T.Umuska, INOC, 1966 5 256.
274)	L.M.Vallarino, W.E.Hill, J.V.Quagliano, INOC, 1965 4 1598.
275)	D.H.Brown, R.H.Nuttall, D.W.A.Sharp, JINC, 1963 25 1067.
276)	J.R.Allan, D.H.Brown, R.H.Nuttall, D.W.A.Sharp, JINC.
2/07	1965. 27 1305.
277)	$G_{\rm Peyronel}$, A-Pignedoli, GCTT, 1962 92 745.
278)	K.T. Tomita, T.Nitta, BCSI, 1961 34 286.
279)	F.Hanic. ACAS. 1962 32 305.
280)	V.Kuncik, Proc. 7th Int.Conf.Goord.Chem. 1962.80.
281)	F_{Magzi} ACCB, 1955 8 137.
282)	$G_{\rm e}$ Gattow, J.Zermann, ACCR, 1958 11 866.
283)	E-Frasson, R.Bardi, S.Bezzi, ACCR, 1959 12 202.
284)	D-Hall, T.N. Vaters, JCS, 1960, 2644.
285)	G.A.Barclay C.H.T.Kennard, JCS, 1961 3289.
286)	H.C.Freeman, J.C.Schoone, J.G.Sine, ACCR, 1965 18 381.
287)	H.C. Freeman, J.T. Szymanski, ACCR, 1967 22 406.
288)	E.N.Baker, D.Hall, A.J.McKinnon, T.N.Waters, CCOM, 1967 134
289)	J.F.Blount, K.A.Frazer, H.C.Freeman, J.T.Szymanski.
	C.H.Wang, ACCR, 1967 22 396.
290)	D.E.Corbridge, E.G.Cox, JCS, 1956 594.
291)	M.Mori, Y.Saito, T.Watanabe, BCSJ, 1961 34 295.
292)	B.F.Hoskins, F.D. Whillans, CCOM, 1966 798.

1

xlviii

G.A.Barclay, B.F.Hoskins, C.H.L.Kennard. JCS. 1963 5691. 293) 294) J.Huang, J.Li, J.Lu. Acta.Chim.Sinica. 1966 32 162. F.Marumo, W.Nowacki. ZEKG. 1967 124 1. 295) E.N.Baker, G.R.Clark, D.Hall, T.N.Waters. JCSI. 1967 251. 296) E.Prince. ACCR. 1957 10 554. 297) 298) B.Morosin, E.C.Lingafelter. ACCR. 1960 13 807. 299) Idem. JPCH. 1961 65 50. J.G.Forrest, C.K. Prout, F.J.C. Rossotti. CCOM. 1966 658. 300) 301) K.Knox. JCPS. 1959 30 991. 302) F.Hanic. ACCR. 1958 11 610. 303) H.Montgomery, E.C.Lingafelter. ACCR. 1966 20 659. 304) N.V.Mani, S.Ramaseshan. ZEKG. 1961 115 97. 305) B.J.Hathaway. Personal communication. B.Bleaney, K.D.Bowers, R.S.Trenam. PRLA. 1955 A228 157. 306) 307) M.C.M.O'Brien. PRLA. 1964 A281 323. 308) B.J.Hathaway, H.Elliott, R.C.Slade. INOC. 1966 5 669. 309) N.W.Isaacs, C.H.L.Kennard, D.A.Wheeler. CCOM. 1967 587. F.Mazzi, M.Cola, G.Guisepetti. AANL. 1962 96 381. 310) 311) L.F.Dahl, Quoted in reference 395. 312) R.P.Linstead, J.M.Robertson. JCS. 1935 615; 1936 1736. E.C.Lingafelter, G.L.Simmons, B.Morosin, C.Scheringer, 313) C.Freiburg. ACCR. 1961 14 1222. 314) R.F.Bryan, P.M.Knopf. Proc.Chem.Soc. 1961 203. 315) A.C.Freeman, J.E.W.L.Smith, J.C.Taylor, ACCR. 1961 14 407. 316) T.I.Malinovskii. KRIS. 1957 2 723. J.A.Bertrand, D.L.Plymale. INOC. 1966 5 879. 317) 318) L.Sacconi, P.L.Orioli, M.Di Vaira. JACS. 1965 87 2059. 319) M.Di Vaira, P.L.Orioli. INOC. 1967 6 955. P.L.Orioli, M.Di Vaira, L.Sacconi. CCOM. 1965 103. 320) 321) M.Gerloch. JCSI. 1966 1317. I.G.Dance, M.Gerloch, J.Lewis, F.S.Stephens, F.Lions. 322) NATU. 1966 210 298. 323) F.A.Cotton, R.H.Holm. JACS. 1960 82 2979. P.Pauling. INOC. 1966 5 1498. 324) 325) J.M.Stewart, E.C.Lingafelter. ACCR. 1959 12 842. P.L.Orioli, M.Di Vaira, L.Sacconi. JACS. 1966 88 4383. 326) 327) M.Inoue, M.Kishita, M.Kubo. INOC. 1965 4 626. 328) B.R.James, M.Parris, R.J.P.Williams. JCS. 1961 4630. 329) N.H.Agnew, L.F.Larkworthy. JCS. 1965 4669. 330) M.Goodgame, M.J.Weeks. JCSI. 1966 1156. 331**)** S.F.Pavkovic, D.W.Meek. INOC. 1965 4 1091. 332) J.Ferguson, B.O.West. JCSI. 1966 1565. 333) L.Sacconi, G.Lombardo, P.Paoletti. JCS. 1958 848. 334) H.C.A.King, E.KBrBs, S.M.Nelson. JCS. 1963 5449. 335) R.A.Walton. JINC. 1966 28 2229. 336) J.Ferguson. JCPS. 1961 34 1609. A.H.Maki, B.R.McGarvey. JCPS. 1958 29 31, 35. 337) 338) S.K.Madan, M.Sulich. INOC. 1966 5 1662. C.K.Jørgensen. Coord. Chem. Revs. 1966 1 164. 339) R.J.H.Clark, C.S.Williams. SPAC. 1966 22 1081. 340)

xlix

341) N.Perakis, L.Capatos. J.Phys.Radium. 1936 7 391. 342) W.Klemm. ZAAC. 1931 201 32. 343) P.Ray, D.N.Sen, JICS. 1948 25 473. 344) J.A.McMillan, E.Smaller. JCPS. 1961 35 763. 345) N.N.Tikhomirova, K.I.Zamaraev. ZSTK. 1963 4 224. 346) B.Spacu, V.Voicu, I.Pascaru. JCPQ. 1963 60 368. 347) J.Ploquin. CHD. 1951 233 162. 348) F.W.Lancaster, W.Gordy. JCPS. 1951 19 1181; 1952 20 740. B.J.Malmström, T.Vännrgard. JMOB. 1960 2 118. 349) 350) W.J.Eilbeck, F.Holmes, A.E.Underhill. JCSI. 1967 757. 351) M.Goodgame, L.I.B.Haines. JCSI. 1966 174. 352) R.J.Clark, C.S.Williams. CHIN. 1964 1317. 353) D.M.Adams, P.J.Lock, JCSI. 1967 620. 354) P.C.H.Mitchell. JINC. 1961 21 382. 355) I.V.Mirgoshnichenko, G.M.Larin, E.G.Rukhadze, M.A.Litvinyuk. Russ. J.Inorg.Chem. 1966 <u>11</u> 180. 356) H.Rein, O.Ristau, F.Jung. ZPCL. 1962 221 197. 357) H.R.Gersman, J.D.Swalen. JCPS. 1962 <u>36</u> 3221. 358) N.S.Gill, H.J.Kingdon, AJCH. 1966 19 2197. 359) A.B.P.Lever. INOC. 1965 4 1042. 360) C.S.Williams, K.F.Fouché. ZENA. 1964 19A 363. 361) E.Cannillo, G.Guiseppetti. AANL. 1964 36 878. 362) H.Abe, K.Ono. JUPS. 1956 <u>11</u> 947. 363) W.R.McWhinnie. JINC. 1965 27 1063. 364) S.M.Nelson. Proc.Chem.Soc. 1961 372. 365) J.A.Friend, D.P.Mellor. J.Proc.Roy.Soc. N.S.W. 1947 81 154. A.S.Antsishkina, M.A.Porai-Koshits. KRIS. 1958 3 676. 366) 367) M.A.Porai-Koshits, A.S.Antsishkina. KRIS. 1958 3 686. 368) S.Datta. PHMA. 1934 <u>17</u> 585. 369) L.C.Jackson, H.K.Onnes. PRLA. 1923 A104 671. 370) S.M.Nelson, T.M.Shepherd. JCS. 1965 3284. 371) J.Ferguson. JCPS. 1960 32 533. 372) E.Hejmo, M.Ogorzalek. ROCH. 1960 34 1135. 373) D.P.Mellor, C.D.Coryell, JACS. 1938 60 1786. 374) E.D.P.Barkworth, S.Sugden. NATU. 1937 139 374. 375) H.Kobayashi, T.Haseda. JUPS. 1964 19 765. 376) H.Köhler, B.Seifert. ZECE. 1965 5 142. 377) A.V.Babaeva, I.B.Baranovskij, G.G.Afanaseva. DANK. 1962 143 587. 378) V.I.Belova, Y.K.Syrkin, Kh.V.Ikramov. ZNOK. 1961 6 830. 379) M.A.Porai-Koshits, E.K.Yukhno, A.S.Antsishkina, L.M.Dikareva. KRIS. 1957 2 371. 380) D.M.Goodgame, M.Goodgame, M.A.Hitchman, M.J.Weeks. JCSI. 1966, 1769. 381) S.Buffagni, L.M.Vallarino, J.V.Quagliano, INOC. 1964 3 671. 382) L.E.Moore, R.B.Gayhart, W.E.Bull. JINC. 1964 26 896. 383) H.Köhler, H.Hartung, B.Seifert. ZAAC. 1966 347 30. 384) I.Lifschitz, K.M.Dijkema. RTCP. 1941 60 581. 385) A.B.P.Lever. INOC. 1965 4 763.

386) V.I.Belova, A.A.Babaeva. ZNOC. 1959 4 1043. D.A.Rowley, R.S.Drago. INOC. 1967 <u>6</u> 1092. 387) R.N.Patel, D.V.R.Rao. ZAAC. 1967 351 68. 388) J.Vymetal, P.Tvaružek. ZAAC. 1967 351 100. 389) R.T.Sanderson."Chemical Periodicity" Reinhold. N.Y.1960. 390) 391) L.Pauling. "The Nature of the Chemical Bond". Cornell. 1960. 392) A. von Hippel. "Molecular Science and Engineering". Wiley, 1959. 393) D.J.Walker. Project Thesis. Loughborough College of Technology. 1965. W.R.McWhinnie. JINC. 1965 27 2573. 394) 395) T.S.Piper, R.L.Belford. MOPH. 1962 5 169. M.Goodgame, F.A.Cotton. JACS. 1962 84 1543. 396**)** 397) D.W.Smith. INOC. 1966 5 2236. 398) P.Day. Proc. Chem. Soc. 1964 18. A.Chakravorty, S.Basu. JINC. 1961 17 55. 399) 400) H.C.Allen, Jr., JCPS. 1966 45 553. 401) G.Basu, R.L.Belford, R.E.Dickerson. INOC. 1962 1 438. 402) G.Basu. JINC. 1967 29 1544. 403**)** B.Morosin, K.Lawson. JMOS. 1964 12 98. 404) F.A.Cotton, J.J.Wise. JACS. 1966 88 3451. F.A.Cotton, J.J.Wise. INOC. 1967 6 917. 405) 406) O.Schmitz-DuMont, H.Fendel, M.Hassanein, H.Weissenfield. MOCH. 1966 97 1660. 407) J.Ferguson. JCPS. 1964 40 3406. 408) J.Ferguson. JCPS. 1961 35 1612. H.A.Weakliem. JCPS. 1962 36 2117. 409) 410) R.A.Palmer, T.S.Piper. INOC. 1966 5 864. 411) W.E.Hatfield, H.D.Bedon, S.M.Horner. INOC. 1965 4 1181. 412) L.Sacconi. Coord.Chem.Revs. 1966 1 192. 413) R.J.H.Clark, C.S.Williams. JCSI. 1966 1425. 414) F.Hanic. ACCR. 1959 12 739. 415) K.K.Innes, J.P.Byrne, I.G.Ross. JMOS. 1967 22 125. 416) P.G.Perkins. JMOS. 1967 22 464. 417) C.K.Jørgensen. "Inorganic Complexes". Acad. Press., 1963. 418) Y.Komiyama, E.C.Lingafelter. ACCR. 1964 17 1145. 419) L.Sacconi, M.Ciampolini, G.P.Speroni. JACS. 1965 87 3102. 420) D.M.L.Goodgame, F.A.Cotton. JCS. 1961 2298. 421) J.Ferguson, R.L.Belford, T.S.Piper. JCPS. 1962 37 1569. 422) D.P.G.Graddon. JINC. 1960 14 161. 423) A.Abragam, M.H.L.Pryce. PRLA. 1951 A206 164. 424) B.J.Hathaway, D.E.Billing. Unpublished work. 425) R.L.Belford, M.Calvin, G.Belford. JCPS. 1957 26 1165. 426) C.K.Jørgensen. ACSA. 1954 8 1495. 427) I.Ruff. ACAS. 1965 45 13. 428) D.Papoušek, J.Pliva. CCCC. 1965 <u>30</u> 3007. 429) J.F.Corbett. SPAC. 1964 20 1665. 430) D.M.Adams, M.Goldstein, E.F.Mooney. TFSO. 1963 59 2228. 431) J.H.S.Green, W.Kynaston, H.M.Paisley. SPAC. 1963 19 549. 432) M.F.A.El-Sayed, R.K.Sheline. JINC. 1958 <u>6</u> 187.

1

433) J.H.S.Green, P.W.B.Barnard. JCS. 1963 640. 434) P.E.Gagnon, K.F.Keirstead, B.T.Newbold. CJCH. 1957 35 1423. 435) C.Stammer, A.Taurins. SPAC. 1963 19 1625. 436) N.Neto, F.Ambrosino, S.Califano. SPAC. 1964 20 1503. 437) L.Colombo. SPAC. 1964 20 547. 438) N.Abasbegović, N.Vukotić, L.Colombo. JCPS. 1964 41 2575. 439) S.Califano. JCPS. 1962 36 903. 440) W.Bruhn, R.Mecke. Z.Electrochem. 1961 65 543. 441) J.M.Lebas, M.J.Josien. Advan.Mol.Spec. 1962 2 849. 442) R.C.Lord, Jr., F.A.Miller. JCPS. 1942 10 328. 443) H.W.Thompson, R.B.Temple. TESO. 1945 41 27. 444) A.I.Vogel. "Quantitative Inorganic Analysis": Longmans, 1955. 445) P.Ros, G.C.A.Schuit. TCHA. 1966 4 1. 446) J.M.Waters, T.N.Waters. JCS. 1964 2489. 447) T.P.Cheeseman, D.Hall, T.N.Waters. JCSI. 1966 694. 448) J.Ferguson. JCPS. 1961 34 2206. 449) T.Tsumaki. BCSJ. 1938 13 583. 450) M.Goodgame. JCSI. 1966 63. 451) G.B.Bokii. T.I.Malinovskii, A.V.Ablov. KRIS. 1956 1 36. 452) J.Ferguson. JCPS. 1963 39 116. 453) M.Ciampolini, N.Nardi. INOC. 1966 5 41. 454) M.Ciampolini, G.P.Speroni. INCC. 1966 5 45. 455) L.Sacconi, I.Bertini. JACS. 1966 88 5180. 456) M.Ciampolini, N.Nardi, G.P.Speroni. Coord.Chem.Rev. 1966 1 222. 457) L.Sacconi, M.Ciampolini, G.P.Speroni. INOC. 1965 4 1116. 458) J.Lewis, R.S.Nyholm, G.A.Rodley. NATU. 1965 207 72. P.Pauling, G.B.Robertson, G.A.Rodley. NATU. 1965 207 73. 459) 460) P.R.H.Alderman, P.G.Owston, J.M.Rowe. JCS. 1962 668. 461) R.C.Stoufer, D.W.Smith, E.A.Clevinger, T.E.Norris. INOC. 1966 <u>5</u> 1167. 462) D.M.Adams, J.Chatt, J.M.Davidson, J.Gerratt. JCS. 1963 2189. 463) C.R.Hare, C.J.Ballhausen. JCPS. 1964 40 788. 464) A.Lopez-Castro, M.R.Truter. JCS. 1963 1309. 465) C.R.Hare, C.J.Ballhausen. JCPS. 1964 40 792. 466) M.A.Porai-Koshits, L.M.Dikareva. KRIS. 1959 4 650. 467) W.M.Latimer. "Oxidation Potentials". Prentice-Hall. N.Y.1952. 468) Laurent. ACJL. 1844 52 356. Hinsberg. CHBE. 1884 17 318. 469) 470) J.C.E.Simpson. "Condensed Pyridazine and Pyrazine Rings". Interscience, 1953. 471) Y.T.Pratt: p.377 in Reference 230. 472) Reference 231, p.1318. 473) Reference 231, p.1345. 474) Wleugel. CHBE. 1882 15 1050. S.Gabriel, A.Sonn. CHBE. 1907 40 4850. 475) 476) I.J.Krems, P.E.Spoeri. CHRE. 1947 40 279. 477) O.Gowran, P.E.Spoeri. JACS. 1945 67 514. 478) J.Weijland, M.Tishler, A.E.Erickson. JACS. 1944 66 1957. 479) J.Francis, J.K.Landquist, A.A.Levi, J.A.Silk, J.M.Thorp. BIJO. 1956 63 455.

480)	Y.T.Pratt: p.455 in reference 230.
481)	H.Gillman, J.Eish, T.Soddy, JACS, 1957 79 1245.
482)	J.Volke: p.217 in "Physical Methods of Heterocyclic
<u>.</u>	Chemistry", Vol. 1. (ed) A.R.Katritsky.
	Acad. Press., 1963.
483)	J. Hevrovsky, J. Kuta, "Principles of Polarography"
	Acad Press 1066
484)	T. Moitor "Polanographic Techniques" Intercaionae 1065
485)	G W H Choormant n 207 in Uldwanaag in Vetenoevelie Chomistand
	Vol 2. (ed) A.R.Katritsky. 1963.
486)	A.Streitweiser. "Molecular Orbital Theory for Organic
	Chemists". Wiley 1962.
487)	H.H.Jaffe, E.G.Spletzer. SPAC. 1967 23A 1923.
488)	H.H.Jaffé, O.Chalvet. JACS. 1963 85 1561.
489)	S.F.Mason: p.1 in reference 482, Vol 2. 1963.
490)	R.Zahradnik, J.Koutecky: p.69 in reference 485. Vol 5. 1965.
491)	J.Koutecky, R.Zahradnik, CCCC, 1963 28 2089.
492)	G.Conpens, C.Gillet, J.Nasielski, E.V.Donckt, SPAC, 1962 18 1441.
493)	G.Favini, T.Vandori, M.Simonetta, TCHA, 1965 3 418.
494)	S.G. Wait, $Jr. J.W. Wesley, IMOS, 1966 19 25.$
495)	A B P Lever J.Levis R.S. Nybolm NATH 1961 189 58
496)	Idem 109 1963 3156
407)	Idom JCS 1962 1235
408)	M Ito D Shimodo W Kunojshi M Misuchimo ICDS 1056 25 507
490)	D A Dours A Hoim W Wilmonth IINC 1061 21 37
7997 E00)	DE Mederal I B Vah K Ashler NAMU 1040 ET 70
500)	$R_{\bullet}r_{\bullet}Ir_{IIII}III = 1, IOII, R_{\bullet}ASHIEY_{\bullet} NATW_{\bullet} 1904 71 77.$
501)	D G Manuta, R.F. Trimble, JPCA, 1962 06 1069.
502)	R.G.V TAIKA, D.D.AMMA. INUU. 1900 <u>2</u> 1020.
5051	C.Reimann, G.Gordon, NATU, 1965 205 902.
504)	A.E. Undernill, JUS. 1965 4556.
5051	F.D.Ayres, P.Pauling, G.B.Robertson. 1NOC. 1964 3 1303.
506)	Freisen, A.B.P.Lever, J.Lewis, R.S.Nyholm. Unpublished results, auoted in reference 168.
507)	S.M.Nelson. Personal communication quoted in reference 168.
508)	S.M.Nelson, Proc.Symp.Coord.Chem.Tibany, Hungary, 1964.
509)	J.N.Van Niekerk, F.R.L.Schoening, ACCR, 1953 6 227.
510)	G.M.Smart. Project Thesis. Loughborough College of
<i>y</i>	Technology, 1964.
511)	A.B.P.J.ever. $JINC_{2}$ 1965 27 149.
512)	G.W.E.Cheeseman, A.B.Katritzky, B.J.Ridgewell, JCS, 1963 3764.
513)	H.H.Perkampus, A.Roders, ZENB, 1960 15B 1.
514)	A, R. Katritzky, GIRE, 1959 13 353.
515)	A R Katritzky A R Ambler in reference 482 Vol 2 n 161
516)	A R Katnitzky R & Jones, JCS. 1060 2042.
517)	C Kann In. P.A. Ecton A.I. Dana JACS 1050 &1 152
5181	P Chionhali A Bantalugga ANCE 3050 10 2/5
510)	C C Miture U I Reprotein CICU 2000 77 557
520) 5291	D = D = D = D = D = D = D = D = D = D =
5201	D.B.SCULLY, D.M.WILLIEN. JNUS. 1957 \pm 257.

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lii

521) Idem. SPAC. 1960 16 1409. 522) E.R.Lippincott, E.J.O'Reilly, Jr., JCPS, 1955 23 238. 523) D.B.Scully. SPAC. 1961 17 233. 524) R.C.Lord, A.L.Marston, F.A.Miller. SPAC. 1957 9 113. 525) L.Corrsin, B.J.Fox, R.C.Lord. JCPS. 1953 21 1170. J.K.Wilmshurst, H.J.Bernstein. CJCH. 1957 35 1183. 526) 527) F.A.Andersen, B.Bak, S.Brodersen, J.Rastrup-Andersen, JCPS, 1955 23 1047. 528) R.W.Bost, E.E.Towell. JACS. 1948 70 903. A.V.Malik. ZAAC. 1966 344 107. 529) 530) R.A.Penneman, L.H.Jones. JCPS. 1956 24 293. L.H.Jones. JCPS. 1958 29 463. 531) H.Poulet, J.P.Mathieu. SPAC. 1959 15 932. 532) G.Greenwood. PHMA. 1924 48 654. 533) 534) A.Ferrari, A.Broibanti, A.Tiripicchio. ACCR. 1966 21 605. 535) A.F.Wells. ZEKG. 1936 94 447. 536) S.Hoshina. JUPS. 1952 7 560. 537) M.R.Lorenz, J.S.Prener. ACCR. 1956 9 538. I.D.Brown, J.D.Dunitz. ACCR. 1960 13 28. 538) C.B.Knobler, Y.Okaya, R.Pepinsky. ZEKG. 1959 111 385. 539) J.A.Baglio. Dissertation Abstracts. 1967 27B 123. 540) B.Nyberg, P.Kierkegaard. ACSA. 1967.21 823. 541) 542) R.G.Vranka, E.L.Amma. JACS. 1966 88 4270. 543) C-I.Bränden. ACSA. 1967 21 1000. 544) D.T.Cromer, A.C.Larson, R.B.Roof, Jr., ACCR. 1966 20 279. 545) E.G.Cox, W.Wardlaw, K.C.Webster. JCS. 1936 775. 546) L.E.Orgel. "Introduction to Transition-Metal Chemistry". Methuen, 1960. 547) G.Guiseppetti, C.Tadini, Period. Mineral. Ital. 1966 35 431. 548) R.H.Barker, M.Kato, G.W.McLaughlin, H.B.Jonassen. BCSJ. 1966 39 1327. 549) D.C.Nonhebel. JCS. 1963 1216. 550) J.J.Kochi. JACS. 1955 77 5274. 551) A.W.Fort. JOCE. 1961 26 765. L.C.King, G.K.Ostrum. JOCE. 1964 29 3459. 552) P.B.Sollman, R.M.Dodson. JOCE. 1961 26 4180. 553) 554) K.B.Doifode. JOCE. 1962 27 2665. E.R.Glazier. JOCE. 1962 27 2937. 555) E.R.Glazier. JOCE. 1962 27 4397. 556) 557) E.M.Kosower, W.J.Cole, G-S.Wu, D.E.Cardy, G.Meisters. JOCE. 1963 28 630. 558) K.B.Doifode, M.G.Marathey. JOCE. 1964 29 2025. 559) G.P.Smith, C.R.Boston. Proc. 7ICCC. 1962 p.93. 560) D.W.James, C.R.Boston, G.P.Smith. JCPS. 1964 40 609. 561) C.C.Addison, D.Sutton. JCSI. 1966 1524. 562) D.M.Adams, D.M.Morris. Personal communication. 1965. 563) B.O.Field, C.J.Hardy. QURE. 1964 18 361. G.Topping. SPAC. 1965 21 1743.

- 564**)**
- D.S.Brown. Personal communication.1964. 565)

liii

566)	Chemical Society Special Publication no.11 "Tables of Interatomic Distances". 1958.
567)	S.B.Henricks. CHRE. 1930 7 43.
568)	S.C. Wallwork, W.E. Addison, JCS. 1965 2925.
569)	R.D.Willett, R.E.Rundle, JCPS, 1964 40 838.
570)	B.Duffin, S.C.Wallwork. ACCR, 1966 20 210.
571)	R.Pappalardo, D.L.Wood, R.C.Linares, Jr., JCPS. 1961 35 2041.
572)	F.A.Cotton, R.H.Holm. JACS. 1960 82 2983.
573)	J.Ferguson. JCPS. 1961 34 611.
574)	G.Maki, JCPS. 1958 29 1129.
575)	R.L.Belford, T.S.Piper. MOPH. 1962 5 251.
576)	C.J.Ballhausen, A.D.Liehr. JACS. 1959 81 538.
577)	M.T.Rogers. JACS. 1947 <u>69</u> 1506.
578)	C.A.McDowell, K.F.Paulus, J.R.Rowlands. Proc.Chem.Soc. 1962 60.
579)	P.J.Black, C.A.McDowell. MOPH. 1967 12 233.
580)	G.N.La Mar. MOPH. 1967 <u>12</u> 427.
581)	R.J.Fitzgerald, R.S.Drago. JACS. 1967 89 2879.
582)	R.G.Gilbert. Personal communication 1967.
583)	D.R.Williams. MOPH. 1967 12 41.
584)	D.G.Brewer, P.T.T.Wong. CJCH. 1966 44 1407.
585)	W.A.Baker, Jr., P.M.Brown. JACS. 1966 88 1314.
586)	A.B.P.Lever, J.Lewis, R.S.Nyholm. JCS. 1964 1187.
587)	I.S.Ahuja, D.H.Brown, R.H.Nuttall, D.W.A.Sharp. JINC. 1965 27 1105.
588)	E.B.Wilson, Jr. JCPS. 1941 9 76.
589)	J.C.Decius. JCPS. 1948 16 1025.
590)	T.Simanouti. JCPS. 1949 17 245, 734.
591)	E.B.Wilson. PHRV. 1934 45 706.
592)	F.A. Andersen, B.Bak, S.Brodersen, J.Rastrup-Andersen. JCPS. 1955 23 1047.
593)	A.L.McClellan, G.C.Pimentel, JCPS, 1955 23 245.
594)	R.E.Hester, W.E.L.Grossman. INOC. 1966 5 1308.
595)	C.C.Addison, D.W.Amos, D.Sutton, W.H.H.Hoyle. JCSI. 1967 808.
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Key to the Journal Coden used.

- Coden Usual abbreviation (Chemical Abstracts).
- AANL Atti. Accad. Nazl. Lincei, Rend., Classe Sci. Fis. Mat. Nat.
- ACAS Acta Chim. Acad. Sci. Hung.
- ACCR Acta Cryst.
- ACJL Ann. Chem.
- ACSA Acta Chem. Scand.
- ADCA Advan. Catalysis.
- AJCH Australian J. Chem.
- ANAL Analyst.
- ANCR Ann. Chim. (Rome).
- ANPY Ann. Physik.
- APNY Ann. Phys. (N.Y.).
- BCSJ Bull. Chem. Soc. Japan.
- BIJO Biochem. J.
- BSCF Bull. Soc. Chim. France.
- CCCC Collection Czech. Chem. Commun.
- CCOM Chem. Commun.
- CHBE Chem. Ber.
- CHD Compt. Rend.
- CHIN Chem. Ind. (London).
- CHMB Chem. Brit.
- CHRE Chem. Rev.
- CJCH Can. J. Chem.
- DANK Dokl. Akad. Nauk SSSR.

FEPR	Federation	Proc.	

- GCIT Gazz. Chim. Ital.
- HCAC Helv. Chim. Acta.
- INOC Inorg. Chem.
- JACS J. Am. Chem. Soc.
- JCED J. Chem. Educ.
- JCPQ J. Chim. Phys.
- JCPS J. Chem. Phys.
- JCS J. Chem. Soc.
- JCSI J. Chem. Soc., A. Inorg., Phys., Theoret.
- JICS J. Indian Chem. Soc.
- JINC J. Inorg. Nucl. Chem.
- JMOB J. Mol. Biol.
- JMOS J. Mol. Spectry.
- JOCE J. Org. Chem.
- JPCH J. Phys. Chem.
- JUPS J. Phys. Soc. Japan.
- KDVS Klg. Danske. Videnskab. Selskab, Mat.-Fys. Medd.
- KRIS Kristallogra fiya.
- MOCH Monatsh Chem.
- MOPH Mol. Phys.
- NATU Nature.
- NATW Naturwissenschaften.
- PHMA Phil. Mag.
- PHRV Phys. Rev.
- PRLA Proc. Roy. Soc. (London), Ser. A.

QURE Quart. Rev. (London).

- RMPH Rev. Mod. Phys.
- ROCH Roczniki Chem.
- RTCP Rec. Trav. Chim.
- SCIE Science.
- SPAC Spectrochim Acta. Part A.
- TCHA Theoret. Chim. Acta.
- TFSO Trans. Faraday Soc.
- ZAAC Z. Anorg. Allgem. Chem.
- ZECE Z. Chem.
- ZEKG Z. Krist.
- ZENA Z. Naturforsch., A.
- ZENB Z. Naturforsch., B.
- ZNOK Zh. Neorgan. Khim.
- ZPCF Z. Physik. Chem. (Frankfurt).
- ZPCL Z. Physik. Chem. (Leipzig).
- ZSTK Zh. Strukt. Khim.