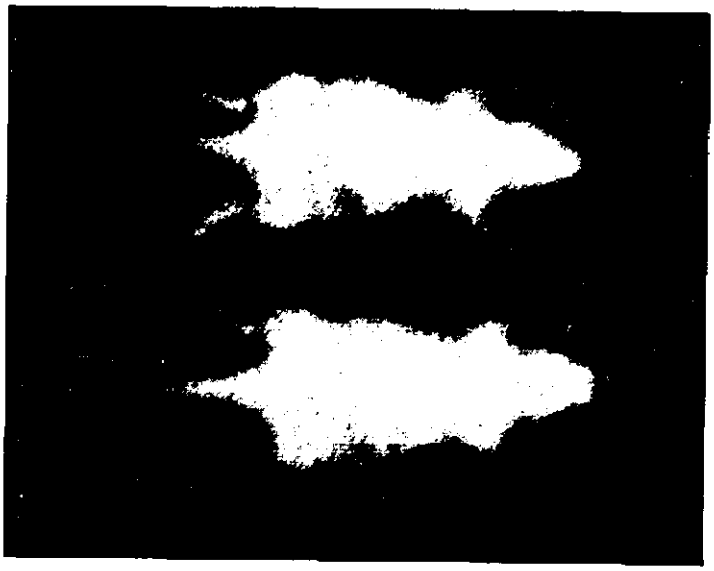
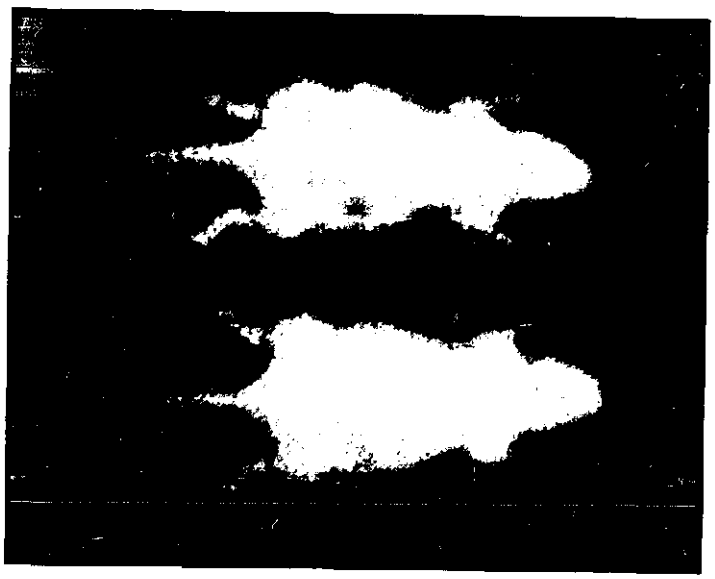
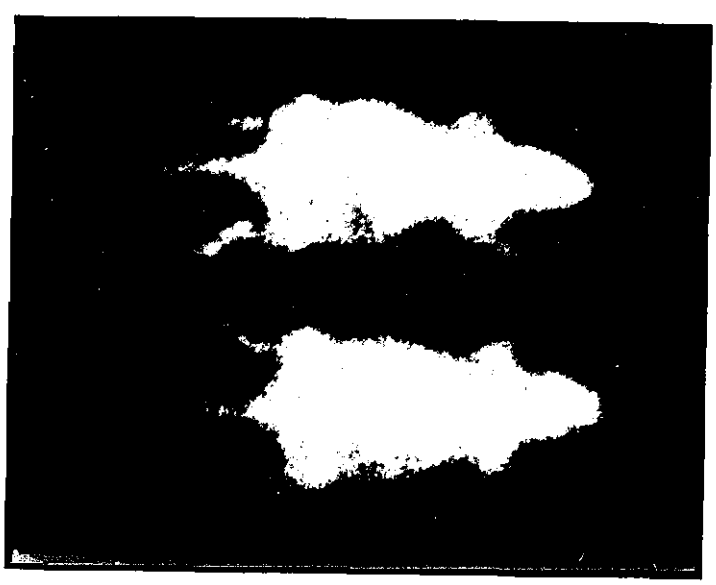
1

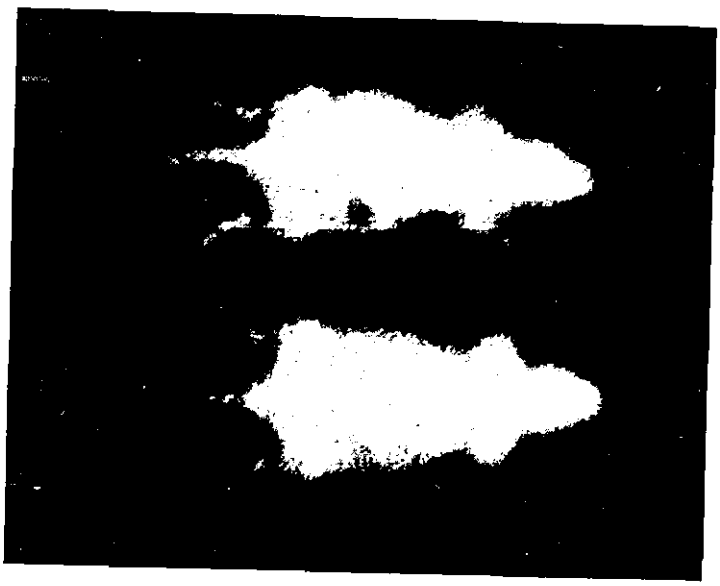
2

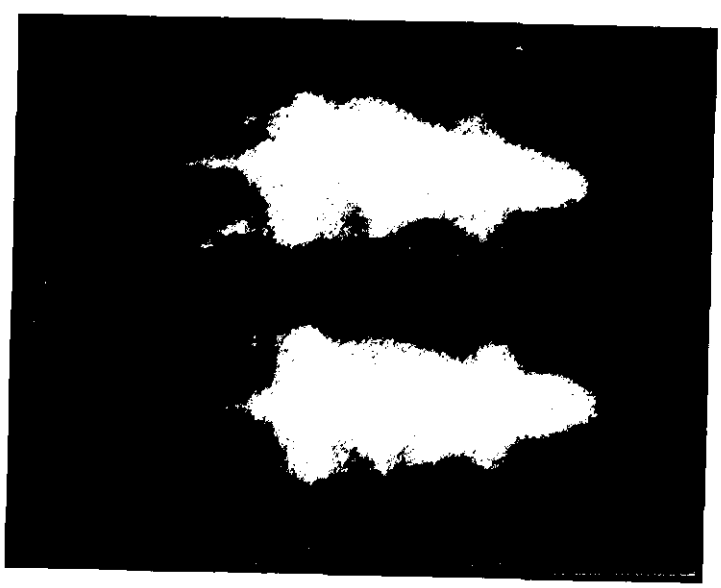
3











3.4. Crystal structure determination of the tetrachloro(methanol)nitrosyltechnetium(II) anion.

The anion $[Tc(NO)Cl_4(CH_3OH)]^-$ has a distorted octahedral geometry with the four chlorine atoms lying in an equatorial plane and the other two ligands in axial directions. The nitrosyl group is bonded almost linearly to the technetium and the co-ordinated methanol trans to it was found to be hydrogen bonded to a methanol of solvation.

Two forms of bright green crystals were grown from the methanol/diethylether mixture, rectangular plates and needles. A single crystal, (0.63 x 0.39 x 0.13mm), of the rectangular plate form was mounted about a.

Formula: $[(C_4H_9)_4N][Tc(NO)Cl_4(CH_3OH)]$;

Formula weight: M_r=545.3;

Space group: monoclinic, $P2_1/n$;

Cell dimensions: a=11.350(10), b=11.450(5), c=22.154(10)Å;

Cell volume: U=2878.85Å^3;

Z=4;

Density: D_m=not measured, D_x=1.256 gcm^{-3};

Radiation: λ(MoKα)=0.7107Å;

μ=8.0cm^{-1};

F(000)=932;

T=293K;

R=0.051 for 2282 observed reflexions with I>3σ(I);

Stoë Weissenberg diffractometer, $\sin\theta/\lambda < 0.6 Å^{-1}$;

lattice parameters by maximising fit of axial row reflexions in the range sin θ/λ 0.2 to 0.5;

3797 reflexions measured, 2283 with $I > 3\sigma(I)$;

h 0 → 8, k 0 → 13, l -26 → +26;

standard check reflexions on each layer with no significant changes;

no absorption corrections applied;

Tc positions found by Patterson and other atoms by successive difference-Fourier methods, refined by full-matrix least squares on F to R=0.051, wR=0.051;

all atoms anisotropic, unit weighting (based on weight analysis and rapid convergence of refinement),

15 H atoms located by difference map and not refined;

remaining H atoms omitted;

max Δ/σ=0.009,

$\Delta\rho$ excursions +0.3 to $-0.6 eÅ^{-3}$;

Final atomic coordinates are given in Table 3.4. bond lengths and angles in Tables 3.5. and 3.6. respectively. H atom coordinates are given in Table 3.7. and the anisotropic thermal parameters in Table 3.8.

The numbering schemes of the atoms of the anion and cation are shown in Figures 3.5. and 3.6. respectively. A view of the unit cell is shown in Figure 3.7. Observed and calculated structure factors are given in Appendix I

Table 3.4.

Final positional parameters ($X10^4$) and isotropic thermal parameters ($Å^2$) for $[(C_4H_9)_4N][Tc(NO)Cl_4(CH_3OH)]$.

$B_{eq}=8\pi^2(1/3)(\Sigma u_{ii})$

	x	y	z	B_{eq}
Tc	318(1)	1095(1)	-1537(0)	4.9(1)
Cl(1)	10667(3)	582(2)	1188(1)	6.4(2)
Cl(2)	8638(3)	-2826(2)	1751(1)	6.0(2)
Cl(3)	7865(3)	-175(2)	1319(2)	7.8(2)
Cl(4)	11470(3)	-2110(2)	1632(2)	7.3(2)
N(1)	9770(9)	-628(8)	2260(5)	7.0(6)
O(1)	9901(13)	-269(9)	2752(5)	13.2(8)
O(2)	9679(6)	-1595(7)	612(3)	6.5(4)
N(2)	5107(7)	1074(6)	7476(3)	4.7(4)
C(1)	6014(9)	1196(8)	6982(4)	5.4(5)
C(2)	5861(10)	341(9)	6466(5)	6.4(7)
C(3)	6927(13)	462(11)	6042(6)	9.0(9)
C(4)	6785(15)	-284(12)	5477(6)	8.0(10)
C(5)	3861(9)	1131(8)	7240(4)	5.0(5)
C(6)	3514(10)	2234(9)	6900(5)	6.4(7)
C(7)	2256(10)	2100(10)	6597(5)	6.7(7)
C(8)	2185(14)	1181(13)	6104(6)	9.9(9)
C(9)	5387(9)	2074(8)	7913(5)	5.0(6)
C(10)	4670(11)	2110(9)	8478(5)	6.2(6)
C(11)	5117(12)	3144(10)	8861(5)	7.4(7)
C(12)	4464(15)	3197(13)	9464(6)	10.0(10)
C(13)	5197(10)	-121(8)	7783(4)	5.1(5)
C(14)	6445(10)	-401(9)	8042(5)	6.6(7)
C(15)	6362(12)	-1591(10)	8370(7)	8.0(8)
C(16)	5710(14)	-1548(14)	8952(7)	10.2(10)
C(17)	8886(15)	-2302(12)	269(6)	10.2(10)
C(18)	2406(14)	3844(15)	4917(6)	10.1(10)
O(3)	8577(9)	1315(8)	119(4)	8.9(6)

Table 3.5.

Bond Distances for $[(C_4H_9)_4N][Tc(NO)Cl_4(CH_3OH)]$.

Anion

	Å
Tc-Cl(1)	2.363(3)
Tc-Cl(2)	2.364(3)
Tc-Cl(3)	2.355(3)
Tc-Cl(4)	2.344(3)
Tc-N(1)	1.689(11)
Tc-O(2)	2.128(7)
N(1)-O(1)	1.171(15)
O(2)-C(17)	1.417(17)

Cation

N(2)-C(1)	1.53(1)
C(1)-C(2)	1.51(1)
C(2)-C(3)	1.56(2)
C(3)-C(4)	1.52(2)
N(2)-C(5)	1.50(1)
C(5)-C(6)	1.52(1)
C(6)-C(7)	1.57(2)
C(7)-C(8)	1.52(2)
N(2)-C(9)	1.53(1)
C(9)-C(10)	1.51(2)
C(10)-C(11)	1.54(2)
C(11)-C(12)	1.54(2)
N(2)-C(13)	1.53(1)
C(13)-C(14)	1.55(2)
C(14)-C(15)	1.55(2)
C(15)-C(16)	1.50(2)

Solvent

C(18)-O(3)	1.403(19)Å

Table 3.6.

Bond Angles for $[(C_4H_9)_4N][Tc(NO)Cl_4(CH_3OH)]$.

Anion

O(1)-N(1)-Tc	175.5(10)
Cl(1)-Tc-Cl(2)	172.5(1)
Cl(1)-Tc-Cl(3)	89.4(1)
Cl(1)-Tc-Cl(4)	90.9(1)
Cl(1)-Tc-N(1)	92.1(3)
Cl(1)-Tc-O(2)	83.8(2)
Cl(2)-Tc-Cl(3)	88.6(1)
Cl(2)-Tc-Cl(4)	90.2(1)
Cl(2)-Tc-N(1)	95.3(3)
Cl(2)-Tc-O(2)	88.8(2)
Cl(3)-Tc-Cl(4)	172.8(2)
Cl(3)-Tc-N(1)	94.7(4)
Cl(3)-Tc-O(2)	86.8(2)
Cl(4)-Tc-N(1)	92.4(3)
Cl(4)-Tc-O(2)	86.1(2)
N(1)-Tc-O(2)	175.6(4)

Cation

C(1)-N(2)-C(5)	113.2(7)
C(1)-N(2)-C(9)	104.6(7)
C(1)-N(2)-C(13)	111.2(7)
C(5)-N(2)-C(9)	111.6(7)
C(5)-N(2)-C(13)	104.2(7)
C(9)-N(2)-C(13)	112.2(7)
N(2)-C(1)-C(2)	114.6(8)
C(1)-C(2)-C(3)	108.8(9)
C(2)-C(3)-C(4)	112.3(11)
N(2)-C(5)-C(6)	116.1(8)
C(5)-C(6)-C(7)	110.6(9)
C(6)-C(7)-C(8)	114.0(11)
N(2)-C(9)-C(10)	115.9(8)
C(9)-C(10)-C(11)	107.5(9)
C(10)-C(11)-C(12)	110.4(10)
N(2)-C(13)-C(14)	113.6(8)
C(13)-C(14)-C(15)	106.8(11)
C(14)-C(15)-C(16)	114.3(11)

Table 3.7.

Final positional parameters ($X10^4$) and isotropic thermal parameters ($Å^2$) for the hydrogen atoms of $[(C_4H_9)_4N][Tc(NO)Cl_4(CH_3OH)]$.

$B=8\pi^2u$

	x	y	z	B
H(1)O(2)	10571	-1398	387	7.3
H(1)	5857	2002	6871	5.9
H(3)	5037	418	6196	7.3
H(5)	7124	1187	5839	9.1
H(10)	3777	470	6954	5.9
H(11)	3182	1040	7664	5.9
H(13)	4058	2216	6565	9.9
H(14)	1780	1650	7033	9.9
H(19)	5249	2854	7633	6.0
H(20)	6347	1916	8060	6.0
H(22)	4726	1254	8793	7.1
H(28)	4778	-9	8186	6.0
H(29)	4849	-617	7442	6.2
H(33)	5655	-2202	8178	8.2
H(40)C(18)	7465	981	-561	10.8

Table 3.8.

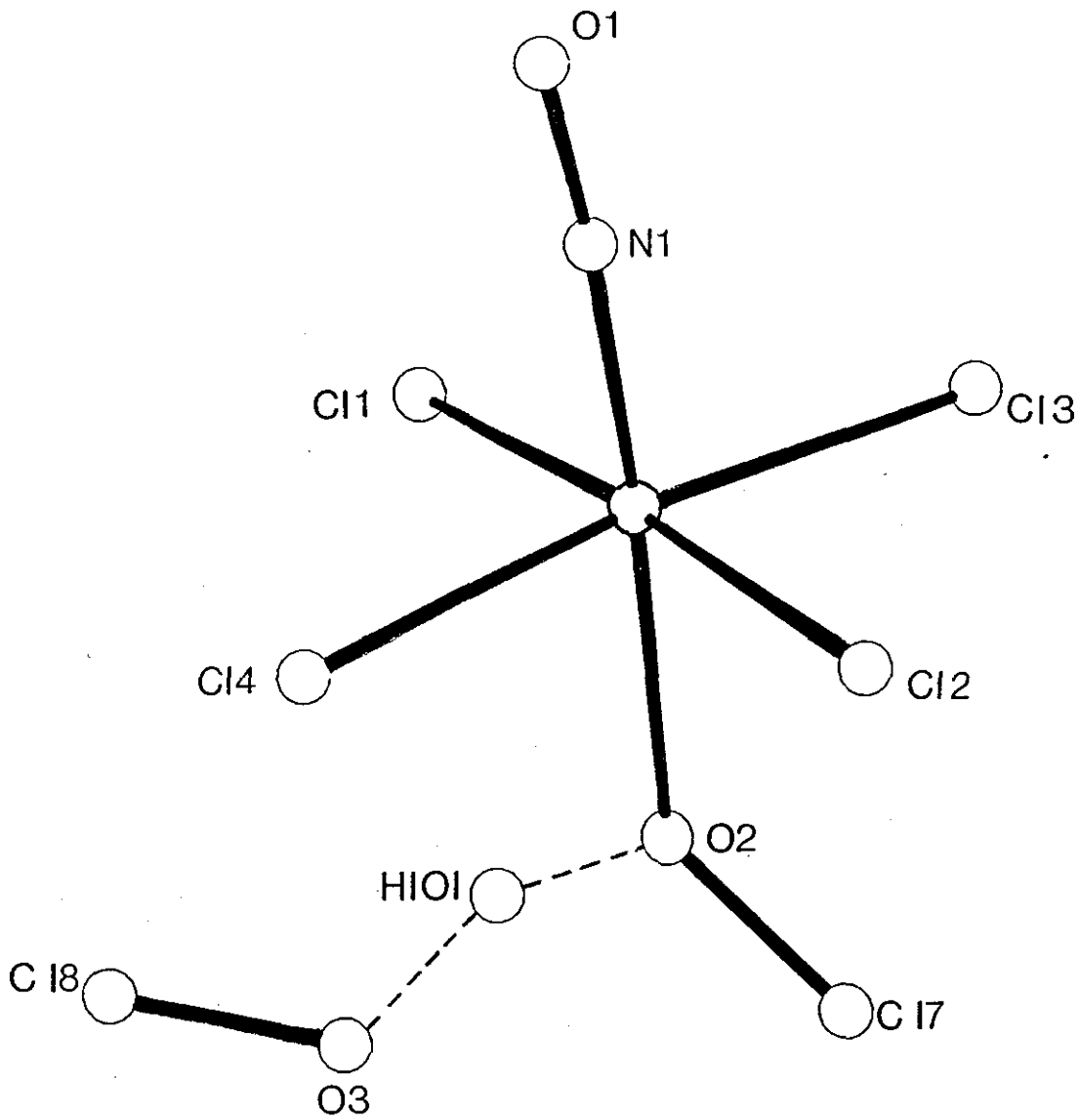
Anisotropic thermal parameters* ($X10^3$, $Å^2$) for $[(C_4H_9)_4N][Tc(NO)Cl_4(CH_3OH)]$.

	U11	U22	U33	U23	U13	U12
Tc	63(1)	44(1)	79(1)	-1(1)	-1(1)	-1(1)
Cl(1)	73(2)	58(2)	112(2)	10(2)	5(2)	-10(1)
Cl(2)	73(2)	49(1)	107(2)	12(1)	-4(2)	-2(1)
Cl(3)	68(2)	64(2)	163(3)	31(2)	17(2)	10(2)
Cl(4)	63(2)	64(2)	150(3)	4(2)	-24(2)	1(1)
N(1)	112(9)	66(6)	96(8)	-2(6)	15(6)	-25(6)
O(1)	286(17)	121(8)	97(8)	-34(7)	25(9)	-76(9)
O(2)	60(6)	106(6)	81(5)	-12(4)	-1(4)	-19(4)
N(2)	52(6)	45(4)	81(5)	-3(4)	-6(4)	-1(4)
C(1)	72(8)	47(5)	86(7)	-1(5)	19(6)	-4(5)
C(2)	78(10)	75(7)	89(8)	4(6)	3(6)	-1(6)
C(3)	154(14)	86(9)	101(10)	13(8)	61(10)	-13(9)
C(4)	169(16)	105(10)	99(10)	-4(9)	29(10)	14(10)
C(5)	60(9)	58(6)	72(6)	4(5)	-8(5)	-5(5)
C(6)	71(9)	62(7)	109(9)	19(6)	-9(7)	-3(6)
C(7)	64(10)	82(8)	109(9)	28(7)	-17(7)	-10(6)
C(8)	144(15)	109(11)	122(11)	-19(10)	-52(10)	-1(10)
C(9)	56(8)	50(6)	86(8)	2(5)	-11(6)	-1(5)
C(10)	86(10)	65(7)	84(8)	-13(6)	5(6)	-5(6)
C(11)	117(12)	80(8)	84(8)	-15(7)	1(7)	4(7)
C(12)	154(15)	125(12)	101(11)	-29(9)	10(9)	-5(10)
C(13)	80(9)	44(5)	70(7)	7(5)	-10(6)	-6(5)
C(14)	72(9)	61(7)	120(10)	30(6)	-20(7)	2(6)
C(15)	100(12)	62(7)	143(12)	25(8)	-28(9)	-6(7)
C(16)	128(14)	146(14)	114(11)	37(10)	-4(10)	-8(10)
C(17)	159(15)	121(11)	109(11)	-21(9)	-26(10)	-70(11)
C(18)	94(13)	190(16)	101(10)	-10(11)	-8(8)	10(11)
O(3)	99(8)	146(8)	94(6)	10(6)	14(5)	12(6)

* The form of the anisotropic thermal parameter is given by

$$\exp\{-2\pi^2(U_{11}a^{*2}h^2+.....2U_{23}b^*c^*kl+....)\}$$

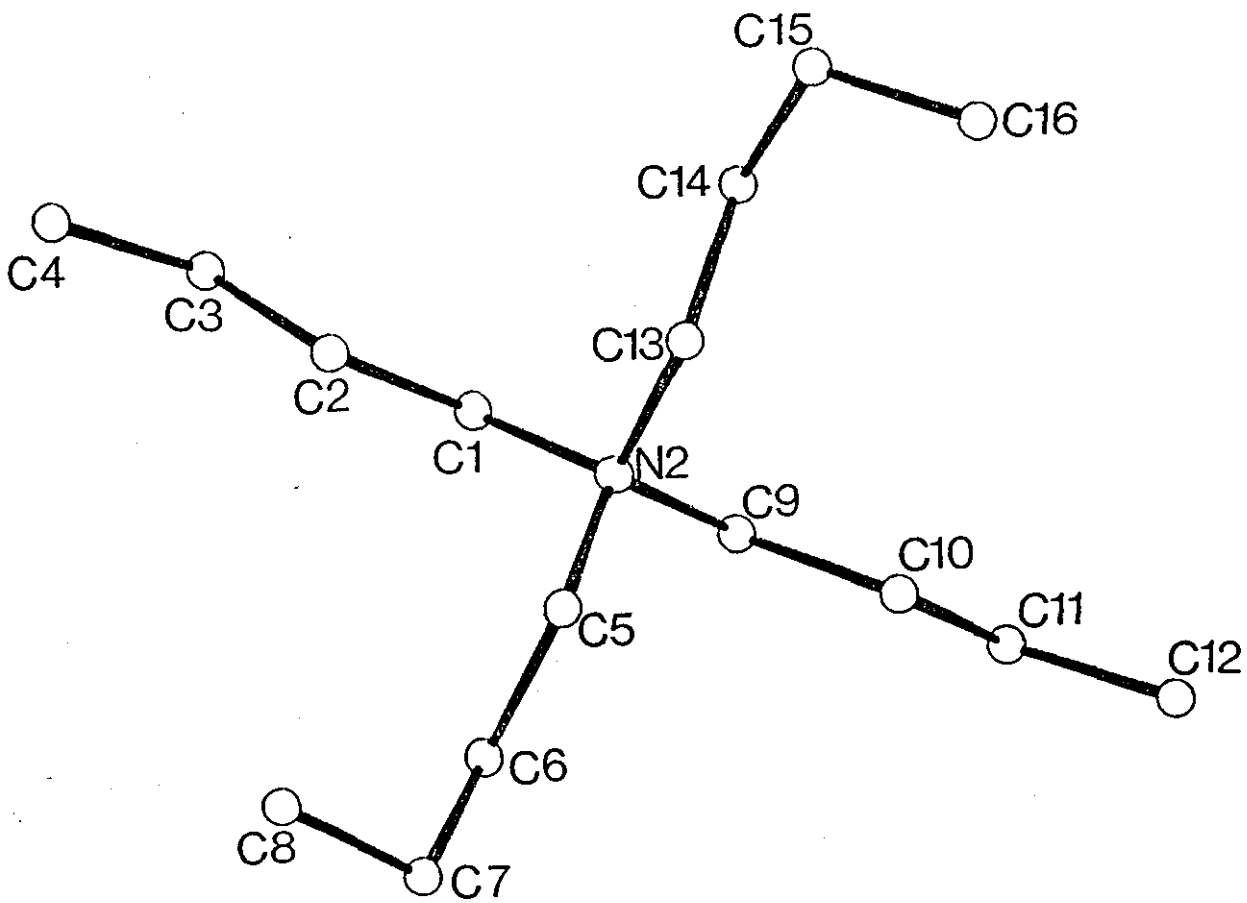
Figure 3.5.



Molecular structure and atom numbering for the tetrachloro(methanol)nitrosyltechnetium(II) anion and solvated methanol showing hydrogen bonding.

Figure 3.6.

Molecular structure and atom numbering for the tetrabutylammonium cation



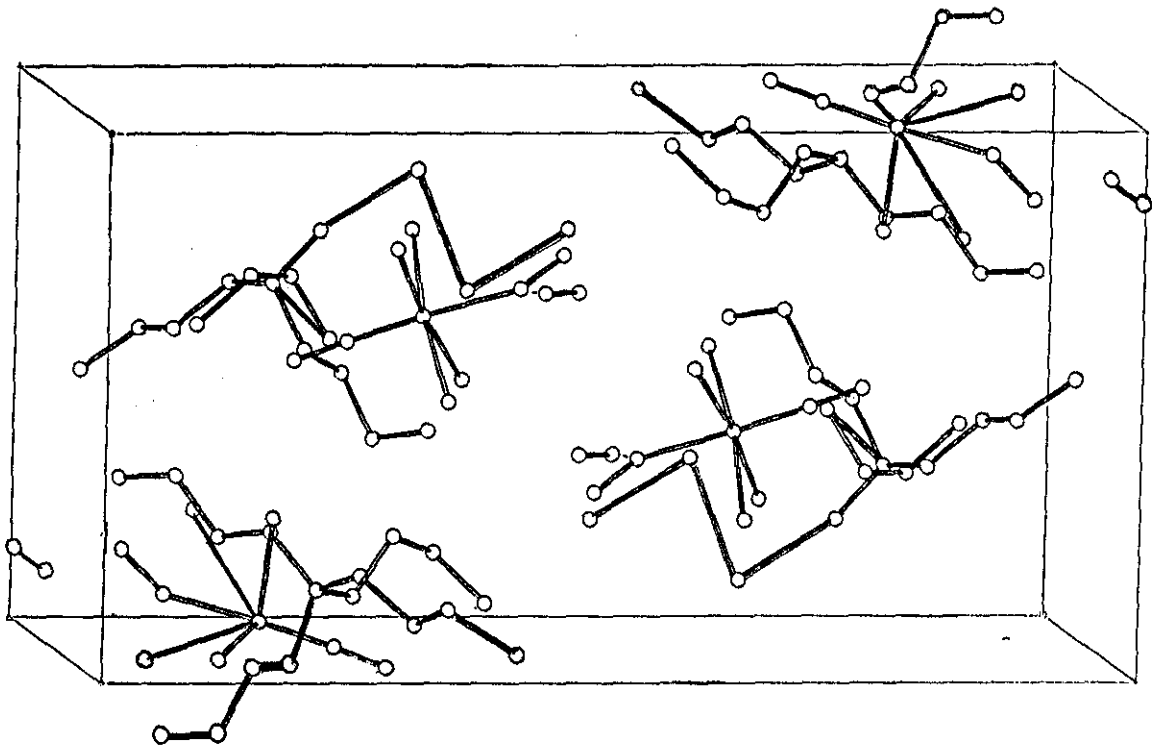


Figure 3.7.

A view of the unit cell contents of the tetrabutylammonium salt of the tetrachloro(methanol)nitrosyltechnetium(II) anion.

3.5. Discussion.

The reaction of $[^{99}Tc/^{99m}Tc][TcO_4]^-$ with HCl gives $[TcCl_6]^{2-}$ when the reaction is heated for a prolonged period (158). The yellow ammonium salt may be isolated from the ^{99}Tc reaction solution. $[^{99}TcCl_6]^{2-}$ disproportionates in the absence of large chloride excess to TcO_2 and $[TcO_4]^-$. On this paper chromatography system with saline eluant there is evidently sufficient chloride for the complex to remain intact at least on a ^{99m}Tc scale (Table 3.1). With the organic eluant decomposition to $[TcO_4]^-$ may occur but no TcO_2 was observed. Reaction of $[^{99}TcCl_6]^{2-}$ with NH_2OH gives quantitatively $[Tc(NO)Cl_4]^-$. This is similar to the results reported by Armstrong and Taube (30). The same complex is also formed when $[^{99}TcOCl_4]^-$ is reacted with NH_2OH in methanol. From the solution a green solid was obtained and after recrystallisation from methanol/diethylether green crystals were obtained which had infra red absorptions at 1805cm^{-1} [v(NO)] and 326cm^{-1} [v(Tc-Cl)]. This concurs with the reported absorptions for $[Tc(NO)Cl_4]^-$. The single crystal X-ray determination indicates that in the crystalline form there is a methanol ligand trans to the NO group. The nature of a sixth ligand trans to the NO with the four chlorides in an equatorial plane which may be chloride, water or alcohol depending on the solution conditions is unimportant since it will be labile and so in vivo will be readily replaced (157).

It seems likely that in the final ^{99m}Tc injection solution the methanol will be displaced and possibly replaced by water.

On a no carrier added ^{99m}Tc scale the reaction proceeds in a similar manner. The R_f values obtained are identical to the carrier added ^{99}Tc preparation except at the $[TcCl_6]^{2-}$ stage. To check that one species was formed HPLC was performed and showed only a single species which is only weakly retained on the reversed phase column. There is no evidence of any other species in the solution and only minimal losses of radioactivity on the column.

Electrophoretic measurements proved impossible for $[TcCl_6]^{2-}$ due to decomposition but $[^{99m}Tc/^{99}Tc][Tc(NO)Cl_4]^-$ moved as an anion with a mobility half that of TcO_4^- and in all preparations only one species was observed.

The animal biological distribution data for $[^{99m}TcNOCl_4]^-$ is given in Table 3.2. and dissections were carried out at 2 and 60 minutes. Gamma camera scintigraphs were taken at 0, 10, 20, 30 and 60 minutes post injection (Figure 3.4). Both the images and the dissection data show that while there is some renal clearance the majority of the material remains in the muscle and carcass. There is evidence in all the animals studied of some specific accumulation of activity in the leg joints although whether or not this is of any significance is not clear. After 60 minutes there is also considerable blood retention and there

is comparatively little change in the biological distribution during the period of the experiment. These comments also are applicable to the $[Tc(NO)Br_4]^-$ biodistribution data (Table 3.3) which shows that the majority of the complex remains in the muscle and carcass, with a high percentage also in the blood. The tetrabromide complex is known to be five coordinate with no ligand trans to the nitrosyl (65,66) but there appears to be little difference in biological activity in these two complexes.

Protein binding experiments revealed that 90% of the complex is associated with the initial plasma fraction with the remainder in the cellular pellet. 92% of the activity is bound to plasma after partition. These results are as expected, since the gamma camera study reveals extensive blood and muscle activity even after 1 hour post injection. Lability of the ligand trans to the nitrosyl and the other chloride ligands presumably lead to rapid ligand exchange with the large number of possible ligating moieties in the plasma proteins.

The exact structure of the $[Tc(NO)X_{4-5}]^{1-or2-}$ complexes has been a matter of some discussion. The ESR data for the complexes where X = Br or I suggests that the species are 5 coordinate with no ligand trans to the nitrosyl (65,66). Since the data for X = Cl is difficult to assign to either 5 or 6 coordinated species (70,27) it was decided to undertake a structure determination. In addition this has confirmed the identity of a species prepared by the same methods for both ^{99}Tc and ^{99m}Tc.

The X-ray data of the monoclinic crystal shows that the tetrachloro(methanol)nitrosyltechnetium(II) anion has a distorted octahedral geometry with the nitrosyl and coordinated methanol mutually trans and the four chlorines in an equatorial plane with the technetium 0.15Å above towards the nitrosyl.

The bond angles of 172.5(1)° (Cl(1)-Tc-Cl(2)) and 172.8(2)° (Cl(3)-Tc-Cl(4)) reflect this. In other Tc(NO) complexes, namely $[Tc(NO)(NH_3)_4(H_2O)]^{2+}$ (69) and $Tc(NO)Br_2(CNCMe_3)_3$ (68) similar distortions have been observed. The Tc-N-O bond angle of 175.5(10)° confirms that the ligand should be considered as NO^+ rather than NO^-. The Tc-N bond length of 1.689(11)Å appears shorter than in the two complexes above which are 1.716(4)Å and 1.726(15)Å respectively but this may not be statistically significant while the N-O bond is intermediate between the other two, 1.203(6)Å and 1.136(17)Å. The Tc-O bond is probably elongated, due to the trans effect of the nitrosyl, although a lack of suitable other technetium complexes prohibits a quantitative assessment of the effect. However a long axial bond has been observed in the analogous rhenium complex (159). The contact distance of 2.610(2)Å for O(2)-O(3) is attributed to hydrogen bonding between coordinated and solvated methanols.

In conclusion while this formulation is rather involved from the radiopharmaceutical point of view the complex may be made in a form amenable to intravenous injection and may therefore find use as a precursor to a series of novel radiopharmaceuticals through ligand exchange reactions.

CHAPTER 4

SYNTHESIS, CHARACTERISATION AND BIOLOGICAL STUDIES OF THE CATION $[Tc(I)(NO)(NH_3)_4(H_2O)]^{2+}$ AND RELATED COMPOUNDS

4.1. Introduction.

The cation trans-aquonitrosyltetraaminetechnetium(I), $[Tc(NO)(NH_3)_4(H_2O)]^{2+}$, has been well characterised by Taube (30) following the work by Eakins (44). The compound is found to be stabilised by the π-acid character of the NO group, the nitrosyl group being inert to nucleophilic attack while the ammonia ligands, although themselves not susceptible to ligand exchange, may be replaced in a modified synthesis. Hence, this compound would appear to be an ideal model for a range of novel potential radiopharmaceuticals with the technetium nitrosyl core but enabling variation of charge, lipophilicity, size and shape of the complex.

Here a modified synthesis of $[Tc(NO)(NH_3)_4(H_2O)]^{2+}$ is described from $[Tc(NO)Cl_4]^-$ as prepared in the preceding chapter and its identity confirmed by crystal structure determination. In addition a range of compounds of the general formula $[Tc(NO)(RNH_2)_4(H_2O)]^{2+}$ is prepared and the biological activity of some of the compounds is studied.

4.2. Synthesis of the trans-aquonitrosyltetraaminetechnetium(I) cation.

4.2.1. Synthesis of no carrier added $[^{99m}Tc(NO)(NH_3)_4(H_2O)]^{2+}$

To 1 ml of generator eluant was added 1 ml of concentrated HCl. The mixture was heated in a pressure cooker for 30 minutes. The product of the reaction is sodium hexachlorotechnetate. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine hydrochloride (1ml, 2.3M) and heated for a further 30 minutes. The resulting solution contains the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). By neutralising the solution to pH 7.5 with 5M NH_4OH the complex $[Tc(NO)(NH_3)_4(H_2O)]^{2+}$ is formed. To ensure reaction the solutions were heated for 15 minutes on a waterbath.

After each stage of the reaction the product formation was monitored by the standard chromatographic procedures described earlier.

4.2.2. Preparation of the complex for biological studies.

It was not possible to inject the complex as formulated above because of the high concentration of chloride ions in the solution. These were removed by shaking the solution with an ion exchange resin (Amberlite IRA-67). The product was then passed though a Millipore filter before use in the biological studies.

4.2.3. Synthesis of carrier added $[^{99}Tc(NO)(NH_3)_4(H_2O)]Cl_2$.

An aqueous solution of the green $[Tc(NO)Cl_4]^-$ anion was prepared as described earlier (3.2.3). The complex was not isolated as the tetrabutylammonium salt but instead the solution was neutralised using 5M NH_4OH as for the no carrier added preparation. A purple solution formed. The product crystallised as hexagonal plates on slow evaporation of the solution after the addition of ethanol.

4.2.4 Synthesis of the no carrier added derivatives of the formula $[Tc(NO)(RNH_2)_4(H_2O)]^{2+}$

Derivatives of the type $[Tc(NO)L_4(H_2O)]^{2+}$ are formed by neutralisation of the tetrachloronitrosyltechnetium(II) anion solution with solutions of other amines (RNH_2) to pH 7.5. (R = methyl-, ethyl- etc).

4.2.5. Analogous no carrier added complexes

Complexes of the type $[Tc(NO)L_2(H_2O)]^{2+}$ where L is a derivative of ethylenediamine (en) may be prepared by neutralising the tetrachloronitrosyltechnetium(II) anion solution with the diamine to pH 7.5. The reaction mixture was heated for 15 minutes on a waterbath to ensure reaction.

4.3. Results.

4.3.1. Paper chromatography.

Paper chromatography results are summarised in Table 4.1. for the amine derivatives and Table 4.2. for the diamine derivatives.

4.3.2. Electrophoresis.

All of the compounds were found to move as cations under the standard electrophoretic conditions

Results for the diamine derivatives are given in Table 4.3.

4.3.3. Infra-red spectrum.

Absorption at $1795cm^{-1}$ for $\nu(NO)$ in the complex $[Tc(NO)(NH_3)_4(H_2O)]Cl_2$.

Table 4.1

Paper chromatography results for amine derivatives of

$[^{99m}Tc(NO)(RNH_2)_4(H_2O)]^{2+}$

Complex R=	R_f in butan-2-one	R_f in saline
H	0.02	0.96
methyl-	0.05	0.81
ethyl-	0.05	0.83
n-propyl-	0.04	0.80
n-butyl-	0.04	0.80
t-butyl-	0.02	0.84
n-pentyl-	0.06	0.75
n-hexyl-	0.06	0.66
n-heptyl	0.05	0.68
n-octyl-	0.06	0.48
1-methylheptyl-	0.07	0.48
dimethyl-	0.02	0.77
benzyl-	0.03	0.68

Standard deviations have not been calculated for these mean R_f values of several experiments.

Table 4.2

Paper chromatography results for diamine derivatives of $[^{99m}Tc(NO)(NH_3)_4(H_2O)]^{2+}$

Complex	R_f in butan-2-one	R_f in saline
ethylenediamine	0.05	0.89
triethylenetetramine	0.04	0.88
N,N-dimethylethylenediamine	0.03	0.85
N,N,N'-trimethylethylenediamine	0.03	0.80
N,N,N',N',tetramethylen	0.02	0.84
cyclohexane-1,2-diamine	0.02	0.83
N,N'-dimethylethylenediamine	0.00	0.93
N,N-dimethyl-N'-ethylen	0.02	0.80

Standard deviations have not been calculated for these mean R_f values of several experiments.

Table 4.3

Electrophoretic movement of the diamine derivatives of

$[^{99m}Tc(NO)(NH_3)_4(H_2O)]^{2+}$

Complex	Distance moved in 1 hour (cm)	Volts/ cm
ethylenediamine	0.60	1.82
triethylenetetramine	0.92	1.82
N,N-dimethylethylenediamine	0.40	1.82
N,N,N'-trimethylethylenediamine	0.20	1.82
N,N,N',N',tetramethylen	0.20	1.82
cyclohexane-1,2-diamine	0.23	1.82
N,N'-dimethylethylenediamine	0.33	1.82
N,N-dimethyl-N'-ethylen	0.16	1.82

4.3.4. Octanol/saline partition experiments.

The results for $[^{99m}Tc(NO)(RNH_2)_4(H_2O)]^{2+}$ are given in Table 4.4.

Table 4.4.

Octanol/saline partition experiments - % activity in organic layer

Complex R =	% activity in organic layer mean (S.D.)
methyl-	0.62 (8)
ethyl-	0.83 (27)
n-propyl-	1.91 (11)
n-butyl-	2.81 (16)
t-butyl-	5.82 (-)
n-pentyl-	6.68 (-)
n-hexyl-	7.95 (-)
n-heptyl-	10.25 (15)
n-octyl-	10.66 (12)

4.3.5 Biodistribution studies.

The animal biodistribution data for $[^{99m}Tc(NO)(NH_3)_4(H_2O)]^{2+}$, $[^{99m}Tc(NO)(ethylNH_2)_4(H_2O)]^{2+}$, $[^{99m}Tc(NO)(n\text{-}butylNH_2)_4(H_2O)]^{2+}$ and $[^{99m}Tc(NO)(t\text{-}butylNH_2)_4(H_2O)]^{2+}$ are given in Tables 4.5., 4.6., 4.7. and 4.8. respectively.

Gamma camera scintiphotographs of $[^{99m}Tc(NO)(NH_3)_4(H_2O)]^{2+}$, $^{99m}Tc(NO)(n\text{-}butylNH_2)_4(H_2O)]^{2+}$ and $[^{99m}Tc(NO)(t\text{-}butylNH_2)_4(H_2O)]^{2+}$ are shown in Figures 4.1., 4.2. and 4.3. respectively.

Table 4.5.

Animal biodistribution data for $[^{99m}Tc(NO)(NH_3)_4(H_2O)]^{2+}$

% injected dose/organ

	2 min sacrifice		60 min sacrifice	
	mean	S.D.*	mean	S.D.*
Muscle	28.87	2.87	13.60	3.94
Blood	17.61	0.92	5.79	1.07
Kidneys	4.09	0.92	5.47	2.31
Bladder	0.29	0.15	34.24	17.21
Lung	1.56	0.23	0.66	0.25
Liver	4.52	0.74	5.06	0.86
Spleen	0.23	0.05	0.13	0.04
Stomach	0.91	0.14	0.60	0.28
S.intestine	3.89	0.64	3.14	0.59
L.intestine	2.27	0.63	1.38	0.65
Heart	0.44	0.08	0.19	0.03
Thyroid	0.17	0.03	0.08	0.03
Brain	0.07	0.02	0.03	0.00
Carcass	35.08	2.36	29.64	7.82
Injection site	3.28	0.70	2.86	1.15
Counts/gram ratio				
Heart/blood	0.36	0.03	0.46	0.02
Heart/muscle	1.61	0.17	1.50	0.22
Heart/liver	0.89	0.50	0.38	0.02
Brain/blood	0.03	0.00	0.03	0.00
Brain/muscle	0.13	0.00	2.86	1.15

= standard deviation of three animals

Table 4.6.

Animal biodistribution data for $[^{99m}Tc(NO)(ethylNH_2)_4(H_2O)]^{2+}$

% injected dose/organ

	2 min sacrifice		60 min
	mean	S.D#	sacrifice*
Muscle	30.15	0.51	9.81
Blood	18.04	0.48	7.04
Kidneys	3.35	0.55	3.29
Bladder	0.15	0.04	45.75
Lung	1.70	0.00	0.81
Liver	5.16	0.13	5.13
Spleen	0.24	0.02	0.20
Stomach	1.21	0.01	0.78
S.intestine	2.79	0.11	3.12
L.intestine	3.02	0.31	1.14
Heart	0.64	0.09	0.17
Thyroid	0.18	0.00	0.05
Brain	0.10	0.03	0.02
Carcass	33.30	0.52	22.70
Injection site	3.19	0.37	2.52
Counts/gram ratio			
Heart/blood	0.42	0.04	0.24
Heart/muscle	1.83	0.10	1.26
Heart/liver	1.20	0.05	0.28
Brain/blood	0.03	0.01	0.02
Brain/muscle	0.16	0.05	0.13

= standard deviation of three animals

* = results for one animal only

Table 4.7.

Animal biodistribution data for $[^{99m}Tc(NO)(n\text{-butylNH}_2)_4(H_2O)]^{2+}$

% injected dose/organ

	2 min sacrifice		60 min sacrifice	
	mean	S.D#	mean	S.D.#
Muscle	25.77	0.67	12.94	2.65
Blood	15.94	0.48	6.41	1.55
Kidneys	6.61	1.68	5.99	3.81
Bladder	0.20	0.08	30.68	14.67
Lung	1.85	0.07	0.80	0.30
Liver	9.55	1.31	12.36	1.35
Spleen	0.25	0.04	0.13	0.02
Stomach	0.96	0.08	0.46	0.08
S.intestine	3.90	0.66	4.84	0.05
L.intestine	2.79	0.41	1.37	0.16
Heart	0.44	0.04	0.20	0.03
Thyroid	0.15	0.01	0.06	0.01
Brain	0.08	0.03	0.02	0.00
Carcass	31.52	2.18	23.74	4.91
Injection site	2.45	0.15	2.98	1.65
Counts/gram ratio				
Heart/blood	0.42	0.02	0.57	0.06
Heart/muscle	2.12	0.62	1.53	0.02
Heart/liver	1.43	0.07	0.64	0.06
Brain/blood	0.03	0.00	0.04	0.00
Brain/muscle	0.13	0.05	0.10	0.01

= standard deviation of three animals

Table 4.8.

Animal biodistribution data for $[^{99m}Tc(NO)(t\text{-butylNH}_2)_4(H_2O)]^{2+}$

% injected dose/organ

	2 min sacrifice		60 min sacrifice	
	mean	S.D#	mean	S.D.#
Muscle	26.45	1.22	12.24	4.62
Blood	16.62	4.69	4.36	1.35
Kidneys	5.35	2.14	4.39	1.54
Bladder	0.23	0.09	41.95	19.41
Lung	1.80	0.41	0.63	0.21
Liver	4.29	1.16	3.27	1.10
Spleen	0.26	0.04	0.14	0.06
Stomach	1.13	0.02	0.53	0.19
S.intestine	4.49	0.98	2.86	1.17
L.intestine	3.28	0.37	1.36	0.41
Heart	0.64	0.18	0.19	0.08
Thyroid	0.18	0.02	0.06	0.03
Brain	0.08	0.03	0.02	0.00
Carcass	32.19	5.73	28.02	8.86
Injection site	3.38	1.01	3.34	2.06
Counts/gram ratio				
Heart/blood	0.39	0.01	0.45	0.02
Heart/muscle	1.79	0.09	1.66	0.11
Heart/liver	0.54	0.04	0.18	0.03
Brain/blood	0.03	0.00	0.03	0.00
Brain/muscle	0.14	0.04	0.10	0.02

= standard deviation of three animals

Figure 4.1.

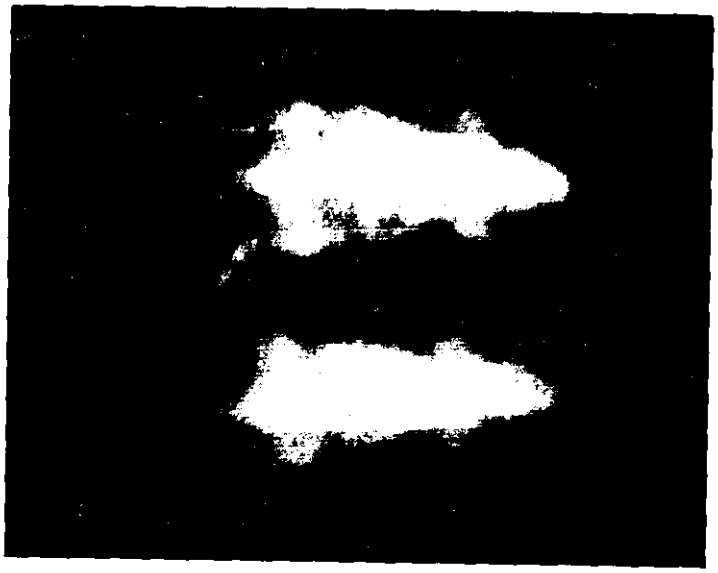
Gamma camera images of $[^{99m}Tc(NO)(NH_3)_4(H_2O)]^{2+}$

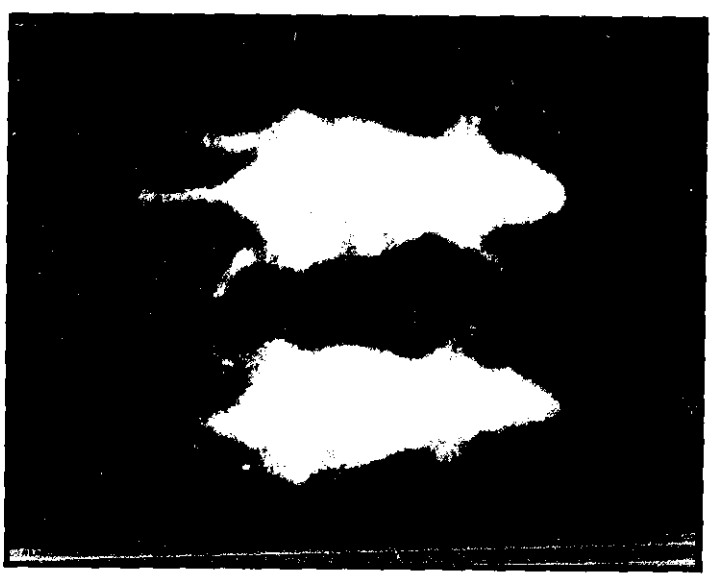
Time post injection	Image No.
0 min.	1
10 min.	2
20 min.	3
30 min.	4
60 min.	5

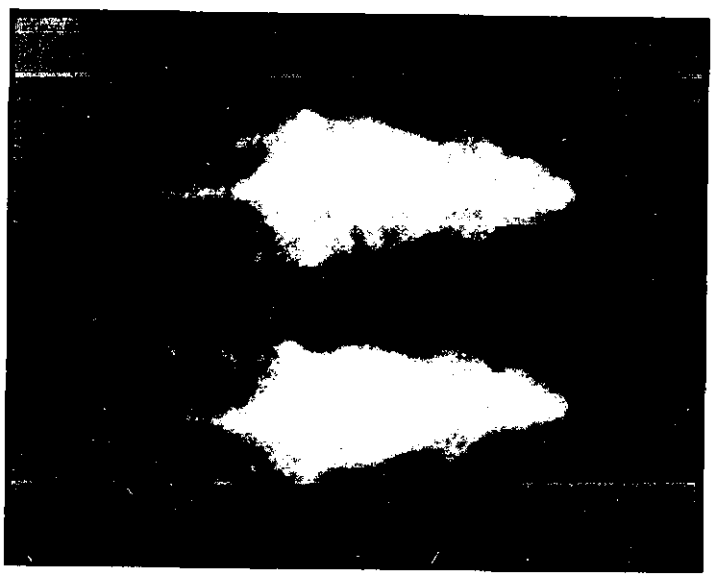
1

2

3







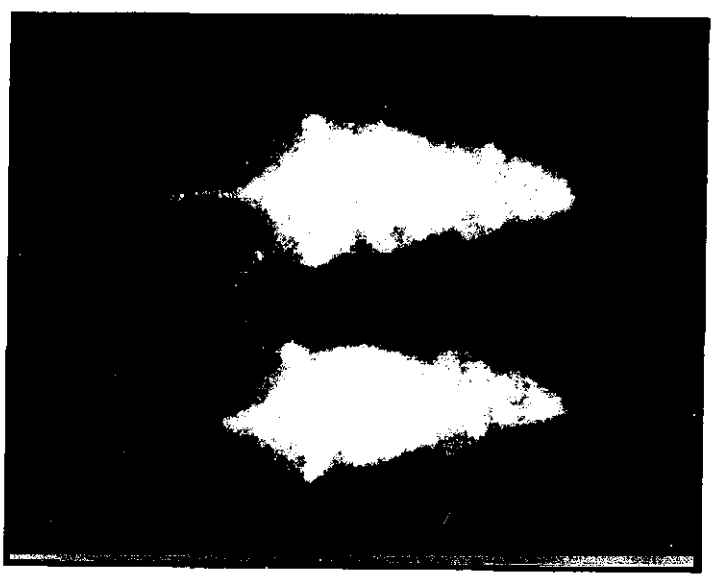


Figure 4.2.

Gamma camera images of $[^{99m}Tc(NO)(n\text{-butyl}NH_2)_4(H_2O)]^{2+}$

Time post injection	Image No.
0 min.	1
10 min.	2
20 min.	3
30 min.	4
45 min.	5
60 min.	6

1

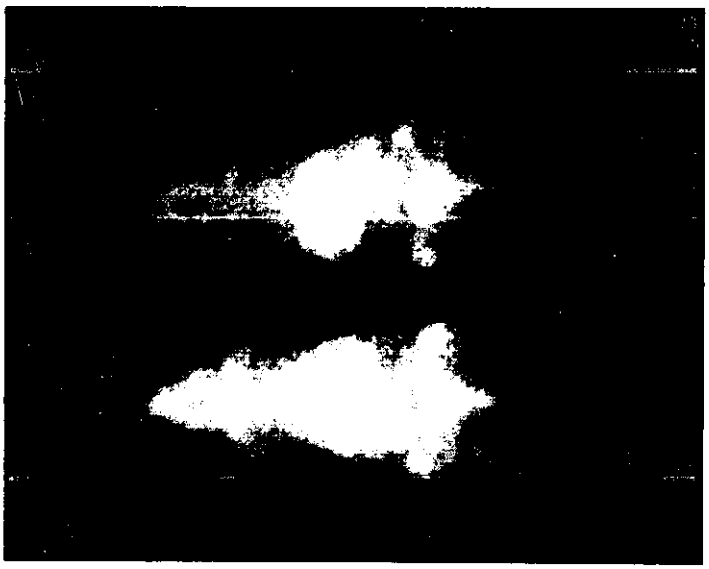
2

3

6

5

4



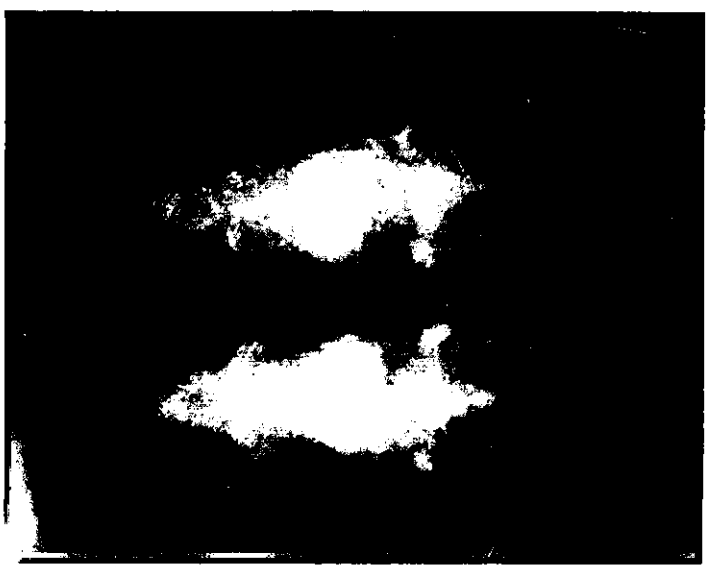


Figure 4.3.

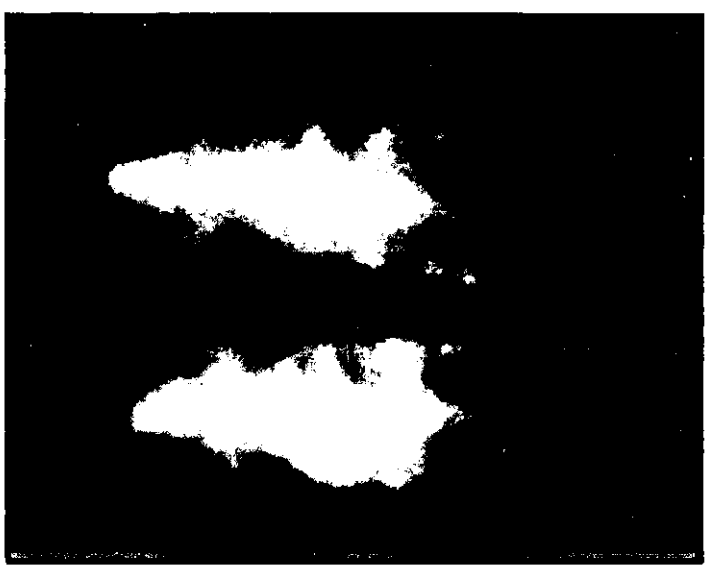
Gamma camera images of $[^{99m}Tc(NO)(t\text{-butyl}NH_2)_4(H_2O)]^{2+}$

Time post injection	Image No.
0 min.	1
10 min.	2
20 min.	3
30 min.	4
60 min.	5

1

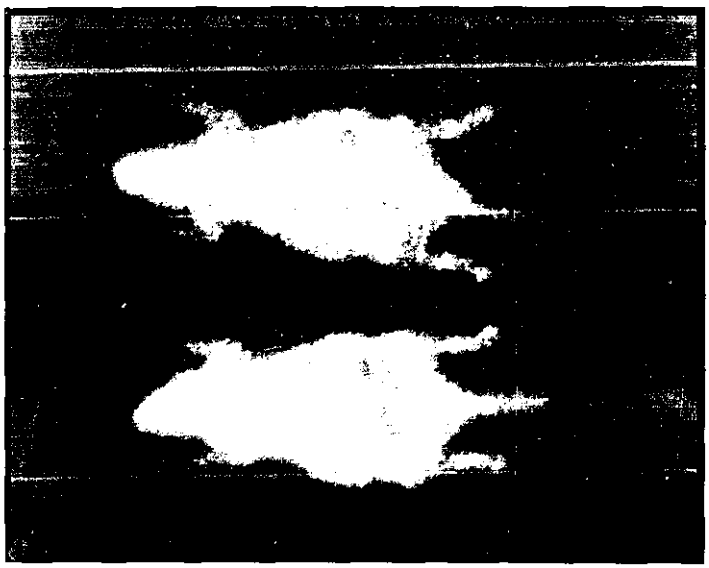
2

3



5

4



4.4. Crystal structure determination of the trans-aquonitrosyltetraaminetechnetium (I) cation.

The crystal structure determination of the above compound has already been reported by Radonovich and Hoard (69) on the crystals prepared by Taube (30). In order to confirm that the complex produced by the alternative synthesis described above (4.2.3.) was in fact the trans-aquonitrosyltetraaminetechnetium (I) cation it was decided to undertake a structure determination.

The cation has an octahedral geometry with the almost linear Tc-NO linkage trans to the coordinated water while the four amine groups lie in the equatorial plane and, as prepared, crystallises as the dichloride salt.

Slow evaporation of the aqueous purple solution resulted in the formation of hexagonal plate shaped crystals which appeared to be suitable for crystal structure determination. A single crystal, (0.19 x 0.19 x 0.07mm) was selected and mounted about a.

Cell dimensions calculated from Weissenberg photographs and refined on the diffractometer were comparable with those already reported and confirmed the structure to be solved. Rather than locating the technetium and chlorine atoms by the Patterson method, the reported coordinates were used immediately in least squares refinement calculations. These coordinates were revised by subsequent refinements and the coordinates of the other atoms

determined. A reliability factor of R=0.02 was achieved (literature R=0.042)

The crystal data are summarised below:

Formula: $[Tc(NO)(NH_3)_4(H_2O)]Cl_2$;

Space group: monoclinic, $P2_1/m$;

Cell dimensions: a=6.86, b=10.62, c=6.63Å, β=93.99°;

Cell volume: 482.03Å^3;

Z=2;

Density: D_m not measured, D_x=1.969 gcm^{-3};

Radiation: λ(MoKα)=0.7107Å;

μ=18.58cm^{-1};

F(000)=283.98;

T=273K;

R=0.020 for 1202 observed reflexions with I>3σ(I) out of 1329 measured reflexions;

standard check reflexions on each layer with no significant changes;

no absorption correction applied;

T_{min}= 0.7019, T_{max}= 0.8778;

All atoms anisotropic, unit weighting (based on weight analysis);

8 H atoms located by difference map and refined, remaining H atoms omitted.

Final atomic coordinates are given in Table 4.9., bond lengths and angles in Table 4.10. H atom coordinates are given in Table 4.11. and the anisotropic thermal parameters in Table 4.12.

The numbering scheme of the atoms of the cation is shown in Figure 4.4. A view of the contents of the unit cell is given in Figure 4.5.

Observed and calculated structure factors are given in Appendix II

Table 4.9.

Final positional parameters ($X10^4$) and isotropic thermal parameters ($Å^2$) for trans-$[Tc(NO)(NH_3)_4(H_2O)]Cl_2$

$B_{eq}=8\pi^2(1/3)(\Sigma U_{ii})$

	x	y	z	B_{eq}
Tc	2173(0)	2500(0)	1773(0)	1.7(0)
Cl(1)	2700(1)	-207(1)	6981(1)	2.7(3)
N(1)	2307(4)	463(2)	1948(4)	2.6(1)
N(2)	4186(5)	2500(0)	-602(6)	2.7(1)
N(3)	639(5)	2500(0)	4496(5)	2.8(1)
N(4)	142(5)	2500(0)	114(5)	2.1(1)
O(1)	4741(5)	2500(0)	3855(5)	2.0(1)
O(2)	-1256(4)	2500(0)	-1073(5)	3.3(1)

Table 4.10.

Principal bond distances and angles for trans-$[Tc(NO)(NH_3)_4(H_2O)]Cl_2$

Bond Lengths

	Å
Tc-O(1)	2.161(3)
Tc-N(1)	2.168(2)
Tc-N(2)	2.165(4)
Tc-N(3)	2.149(3)
Tc-N(4)	1.174(3)
N(4)-O(2)	1.197(4)

Bond Angles

	°
O(2)-N(4)-Tc	178.8(3)
O(1)-Tc-N(4)	179.8(1)
O(1)-Tc-N(1)	86.3(1)
O(1)-Tc-N(2)	86.1(1)
O(1)-Tc-N(3)	83.7(1)
O(1)-Tc-N(1)	86.3(1)
N(1)-Tc-N(4)	93.7(1)
N(1)-Tc-N(2)	90.7(1)
N(1)-Tc-N(3)	88.7(1)
N(1)-Tc-N(1)	172.4(1)
N(4)-Tc-N(2)	93.7(1)
N(4)-Tc-N(3)	96.6(1)
N(2)-Tc-N(3)	169.7(1)

Table 4.11.

Final positional parameters (X10^4) for the hydrogen atoms of $[Tc(NO)(NH_3)_4(H_2O)]Cl_2$

	x	y	z
H1N1	2421	-10	670
H2N1	3340	256	2709
H3N1	1311	40	2610
H1N2	5479	2500	-360
H1N3	4109	1832	-1252
H1N3	2052	2500	5397
H2N3	-555	2062	4406

Table 4.12.

Anisotropic thermal parameters* (X10^3, $Å^2$) for $[Tc(NO)(NH_3)_4(H_2O)]Cl_2$

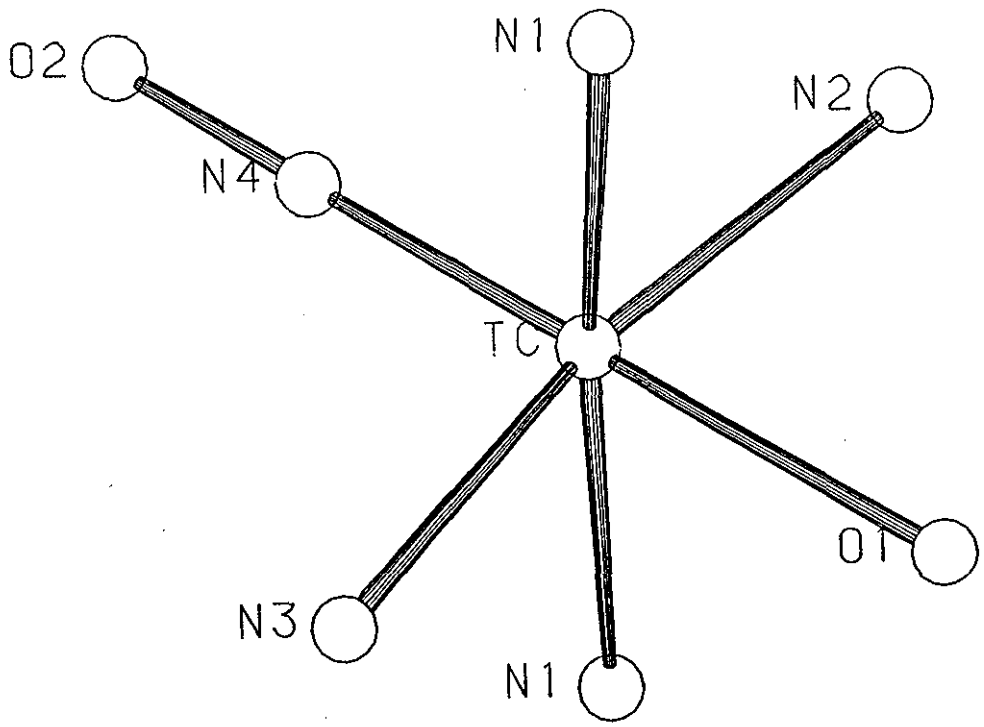
	U11	U22	U33	U23	U13	U12
Tc	21(0)	19(0)	28(0)	0(0)	1(0)	0(0)
Cl(1)	34(1)	32(1)	38(1)	-2(0)	2(0)	1(0)
N(1)	38(1)	21(1)	40(1)	1(1)	-12(1)	0(0)
N(2)	28(2)	33(2)	44(2)	0(0)	9(1)	0(0)
N(3)	29(2)	45(2)	34(2)	0(0)	6(1)	0(0)
N(4)	25(2)	24(2)	33(2)	0(0)	2(1)	0(0)
O(1)	28(2)	27(1)	50(20	0(0)	-9(1)	0(0)
O(2)	29(2)	53(2)	44(2)	0(0)	-12(1)	0(0)

* The form of the anisotropic thermal parameter is given by

$\exp(-2\pi^2(U_{11}a^*H^2+.....2U_{23}b^*c^*kl+.....))$

Figure 4.4.

Molecular structure and atom numbering for the trans-aquonitrosyltetraaminetechnetium(I) cation



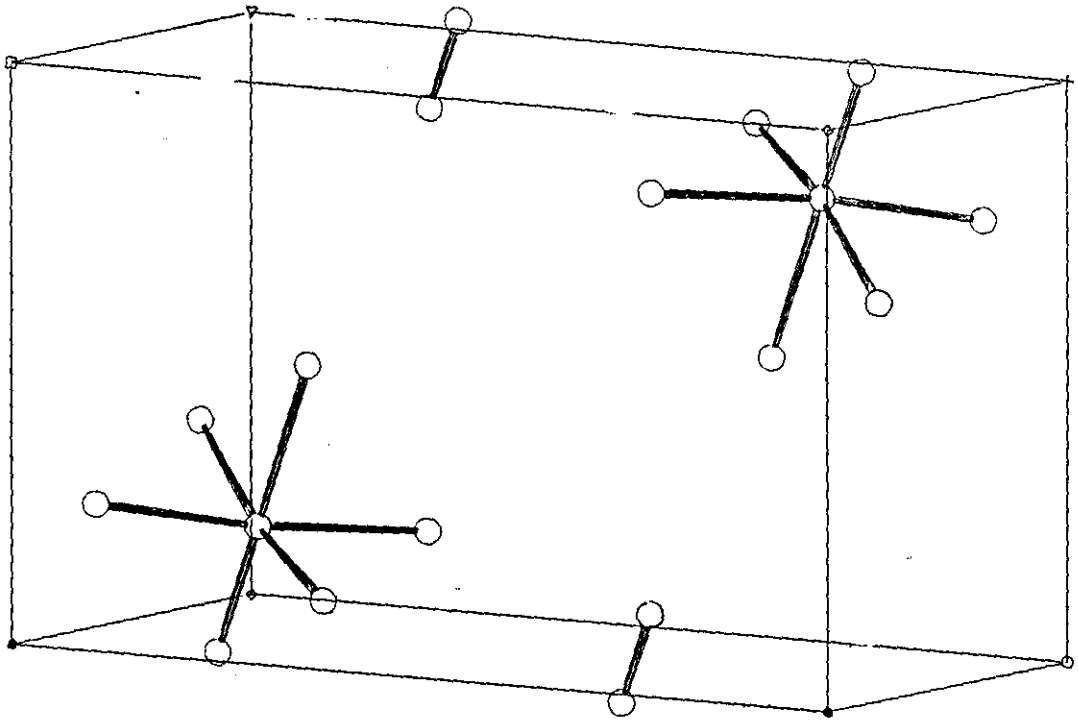


Figure 4.5.

A view of the unit cell contents of

trans-aquonitrosyltetraaminetechnetium(I) dichloride

4.5. Discussion.

Paper chromatography results show that by increasing the length of the amine chain, more lipophilic complexes were produced - the R_f in saline decreases with increasing carbon chain length. For all neutralisation products, no movement was seen when the paper chromatograms were developed in butan-2-one. As expected, this lipophilic trend is also seen in the octanol/saline experiments.

Biodistribution data for $[Tc(NO)(NH_3)_4(H_2O)]^{2+}$ are given in Table 4.4. and the gamma camera images in Figure 4.1. Both the images and the dissection data show renal clearance (34% after 60 minutes) with the majority of the remaining activity in the muscles and carcass. There is some clearance through the liver but this is not significant. Heart uptake is not significant either.

Biodistribution data for $[Tc(NO)(ethylNH_2)_4(H_2O)]^{2+}$ are given in Table 4.5. Initially there is very high blood and muscle uptake with the lungs and liver quite low. After 60 minutes this has decreased significantly through mainly renal clearance with little hepatobiliary system clearance. Again heart retention is poor.

Biodistribution data for $[Tc(NO)(n\text{-}butylNH_2)_4(H_2O)]^{2+}$ are given in Table 4.6. and gamma camera images are shown in Figure 4.2. This compound shows significantly more liver clearance than the analogous samples described above with similar high initial blood and muscle uptake. A large proportion of the activity remains in

the carcass at sixty minutes with mostly renal clearance of the complex.

Biodistribution data for $[Tc(NO)(t\text{-butyl}NH_2)_4(H_2O)]^{2+}$ are given in Table 4.7. and gamma camera pictures are shown in Figure 4.3. Again, rapid urinary excretion of this complex, although little liver clearance is apparent, unlike the n-butyl analogue. There also appears to be some bone uptake of this complex, the backbone being clearly visible.

These results are not unexpected given the similarity of the complexes and whilst it can be demonstrated that even small variations in the basic tetraamine complex produces different biological activity none of the complexes demonstrate the heart uptake sought.

The structure determination of the trans-aquonitrosyltetraamintechnetium dichloride crystal provided confirmation of the effectiveness of the preparation method. The Tc-N-O linkage is almost linear (178.8(3)°) and essentially the complex conforms to C_{4v} geometry. The extent of π bonding in the complex is reflected by the combination of a short Tc-N bond (1.714(3)Å) and longer N-O bond (1.197(4)Å). Together with the observed infra red absorption of $\nu(NO)$ at $1795cm^{-1}$ this would confirm NO^+. The $Tc-OH_2$ and $Tc-NH_3$ represent σ bonding with Tc-O at 2.161(3)Å and averaged $Tc-NH_3$ of 2.163(8)Å. The amine ligands in the equatorial plane are bent slightly away from the

nitrosyl and toward the coordinated water and this could well be as a result of the extent of the π bonding of the Tc-NO linkage.

CHAPTER 5

SYNTHESIS, CHARACTERISATION AND BIOLOGICAL STUDIES OF THE TRICHLORONITROSYL(ACETYLACETONATO)-TECHNETIUM(II) ANION

5.1. Introduction.

The reaction of $[Tc(NO)Cl_4]^-$ with acetylacetone was found to give the complex $[Tc(NO)(acac)Cl_3]^-$ which was isolated as its tetraphenylarsonium salt. This complex has been fully characterised by X-ray crystallography and FAB$^-$ mass spectrometry. The former shows that one of the oxygens of the acac is trans- to the nitrosyl which is essentially linear, although disorder in the crystal prohibits accurate measurements of the bond angle. The latter shows facile loss of a single chlorine which suggests that ligand exchange of this may also be facile. The ESR spectrum at room temperature shows the expected 10 lines due to splitting by the technetium. At -196°C the spectrum may be modelled as having three g values, g_x = 2.0107, g_y = 2.02225 and g_z = 1.9460.

5.2. Synthesis of the trichloronitrosyl (acetylacetonato)technetium(II) anion.

5.2.1. Synthesis of no carrier added $[^{99m}Tc(NO)(acac)Cl_3]^-$.

To generator eluant (1 ml) was added concentrated HCl (1ml). The mixture was heated for 30 minutes. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylaminedihydrogensulphate (1ml, 2.3M) and heated for a further 30 minutes. The resulting solution containing the species $[Tc(NO)Cl_5]^{2-}$ was cooled and acetylacetone (0.5ml, 5mM) added. Further heating for 30 minutes produced the $[Tc(NO)(acac)Cl_3]^-$ cation which was extracted into dichloromethane (5ml). Evaporation of the dichloromethane solution followed by redissolution in methanol:water (50:50) yielded the complex in a form suitable for HPLC.

The reaction was monitored at each stage by the standard chromatographic methods.

5.2.2. Synthesis of carrier added $[^{99}Tc(NO)(acac)Cl_3]^-$.

To an aqueous solution of ammonium pertechnetate (1ml., 0.15mM) was added concentrated hydrochloric acid (1ml) and the mixture heated for 30 minutes. The product of the reaction is $[TcCl_6]^{2-}$ as the yellow ammonium salt. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine

in water (1ml, 2.3M), and heated for a further 30 minutes. The resulting green solution contains the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). To this solution was added acetylacetone (0.5ml, 5mM) and the solution heated under pressure for a further 30 minutes. The product was extracted from the resulting red solution into dichloromethane (10ml) leaving the unreacted $[Tc(NO)Cl_4X]^-$ in the aqueous phase. Evaporation of the dichloromethane layer gave a red oily residue which was redissolved in methanol:water (80:20) (5ml). Addition of tetraphenylarsonium chloride (0.02g in 1ml of methanol) followed by evaporation of the solution to a low volume gave a red precipitate. Recrystallisation of this red solid from methanol/water gave kite shaped plates suitable for X-ray analysis.

5.2.3. Preparation of the complex for biological studies.

6.2mg of the carrier added $[^{99}Tc(NO)(acac)Cl_3][(C_6H_5)_4As]$ complex was dissolved in ethanol:water (50:50, 2ml).

5.3. Results.

5.3.1. Paper chromatography.

For the no carrier added complex.

	R_f in butan-2-one	R_f in saline
$[Tc(NO)(acac)Cl_3]^-$	0.03(2)	0.80(4)

5.3.2. Electrophoresis.

Both the carrier added and no carrier added complexes decomposed under electrophoretic conditions.

5.3.3. HPLC.

For the no carrier added complex, retention time on system X (Amersham) 4.0 minutes.

5.3.4. Infra-red spectrum.

(KBr Disc) Absorptions at 1770cm^{-1} for ν(NO) and 320cm^{-1} for ν(Tc-Cl). Other absorptions as expected for co-ordinated acetylacetone.

1770(s), 1570(m), 1520(m), 1480(m), 1435(m), 1365(m), 1275(m), 1180(m), 1160(m), 1080(m), 1020(w), 995(m), 930(w), 895(m), 845(w), 785(w), 740(s), 685(s), 475(sh), 450(m), 320(m)cm^{-1}.

5.3.5. Analysis.

Found (calculated for $C_{29}H_{27}NO_3Cl_3TcAs$)

C 48.81(48.50); H 3.79(3.76); N 1.89(1.95)

5.3.6. FAB- mass spectrum.

The FAB$^-$ mass spectrum has a major ion at $^M/_z$=333

with other lower mass ions at $^M/_z$ = 298,

$^M/_z$ = 269,

$^M/_z$ = 262,

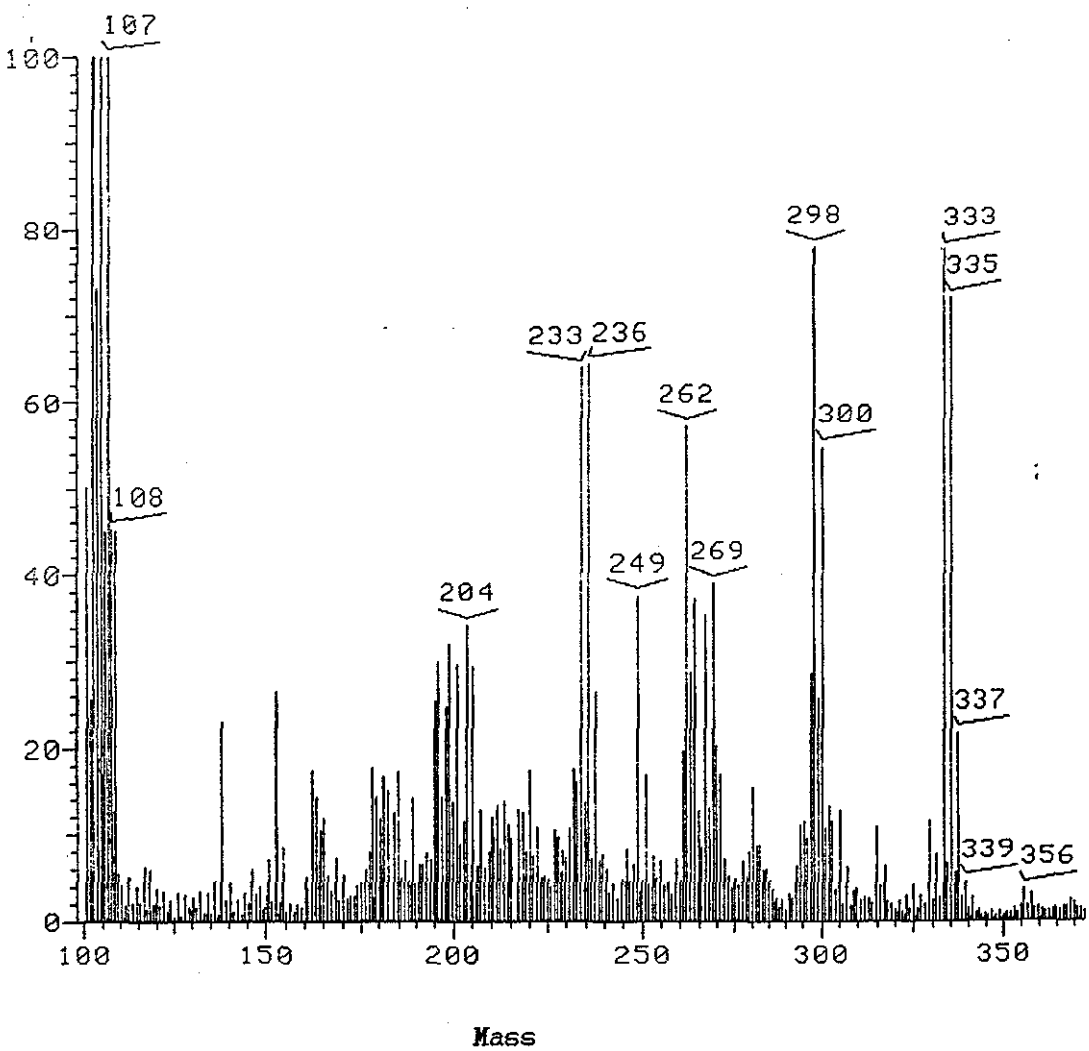
$^M/_z$ = 233,

$^M/_z$ = 204.

The FAB mass spectrum is shown in Figure 5.1.

Figure 5.1.

FAB⁻ mass spectrum of $[Tc(NO)(acac)Cl_2]^-$



5.3.7. Electron Spin Resonance spectra.

The ESR spectra of the complex in ethanol were recorded at ambient temperature (Figure 5.2.) and -195°C (Figure 5.3.). The $g_{av} = 2.12$ and $a_{av} = 135$ gauss were measured directly. Since the complex has a low symmetry the frozen solution gave a complex spectrum which could only be resolved into its component parameters using the POWDER simulation program.

The results are summarised in Table 5.1.

The ESR spectra at ambient temperature and at -196°C are shown in Figures 5.2. and 5.3. The simulated spectrum from the POWDER program is shown in Figure 5.4.

5.3.8. Biodistribution studies.

The animal biodistribution data for $[^{99}Tc(NO)(acac)Cl_3]^-$ is given in Table 5.2.

Table 5.1.

ESR Parameters for [Tc(NO)(acac)Cl$_2$]$^-$

Parameter	Value
$\langle g \rangle$	2.12
$\langle a \rangle$	94.0G
g_x	2.0107*
g_y	2.02225*
g_z	1.9460*
a_x	105.4G*
a_y	105.4G*
a_z	258.4G*

* values from the POWDER simulation program.

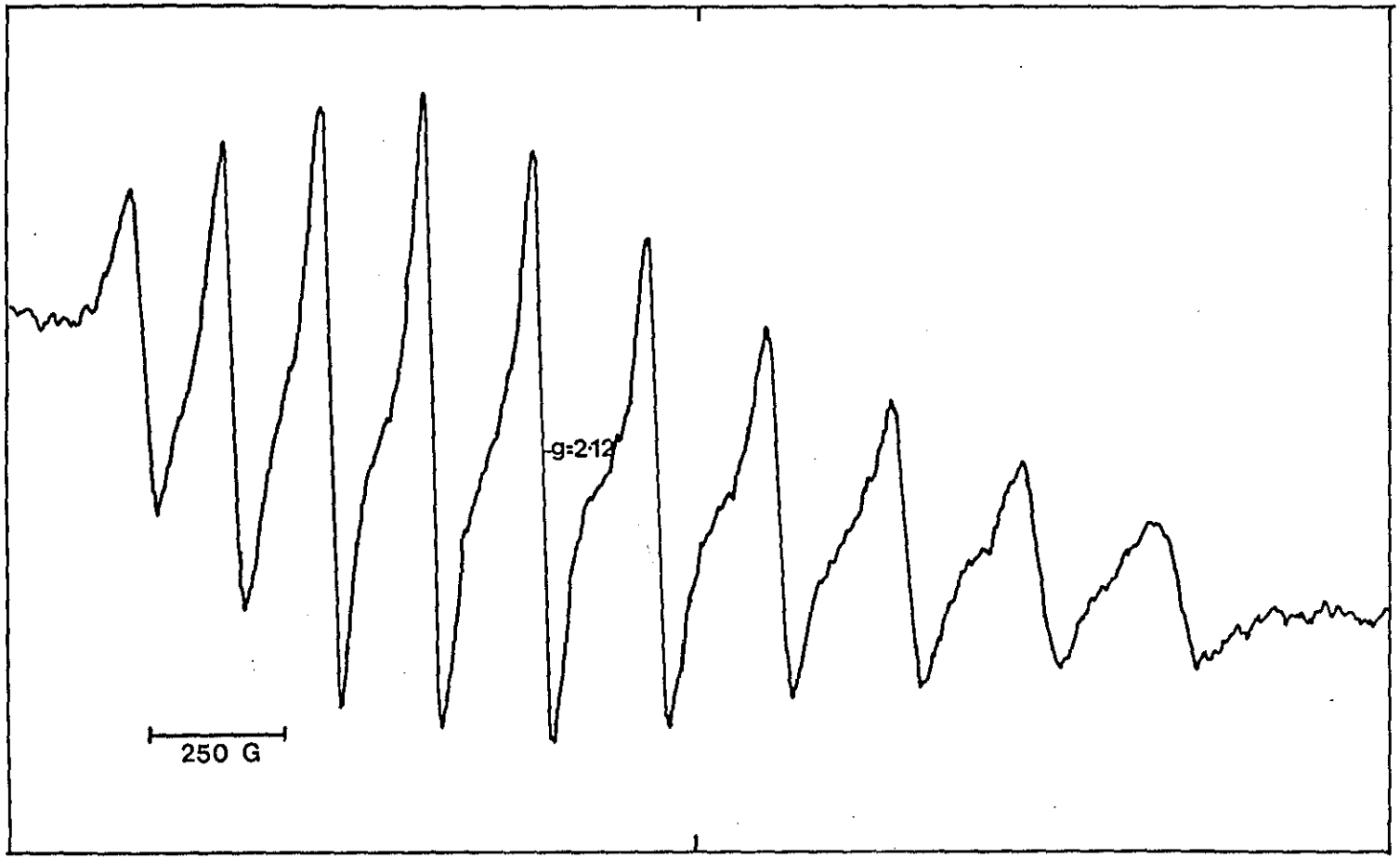


Figure 5.2. The ESR spectrum of an ethanolic solution of $[Tc(NO)(acac)Cl_4]^-$ at ambient temperature.

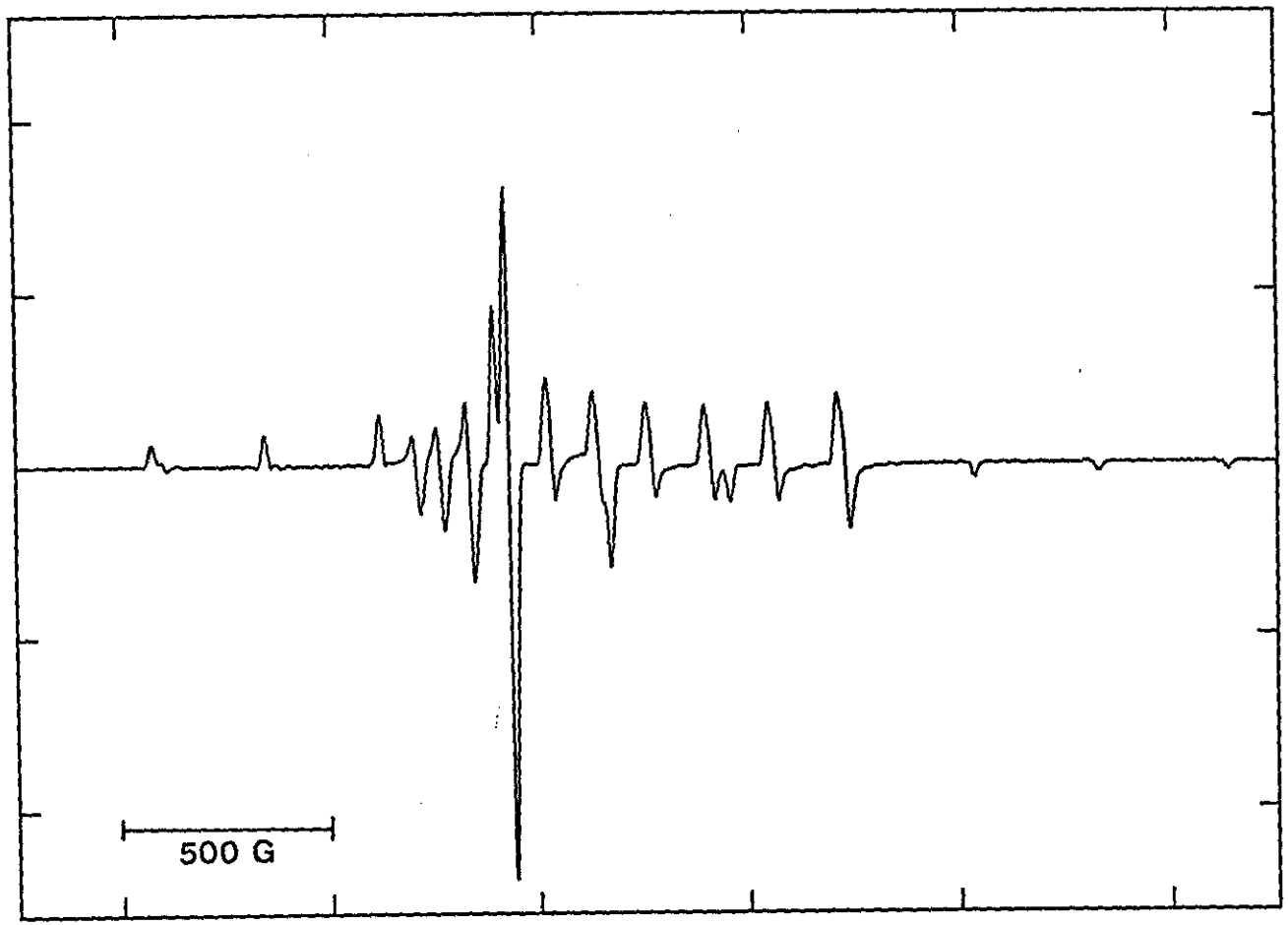


Figure 5.3. The ESR spectrum of an ethanolic solution of $[Tc(NO)(acac)Cl_3]^-$ at -196°C

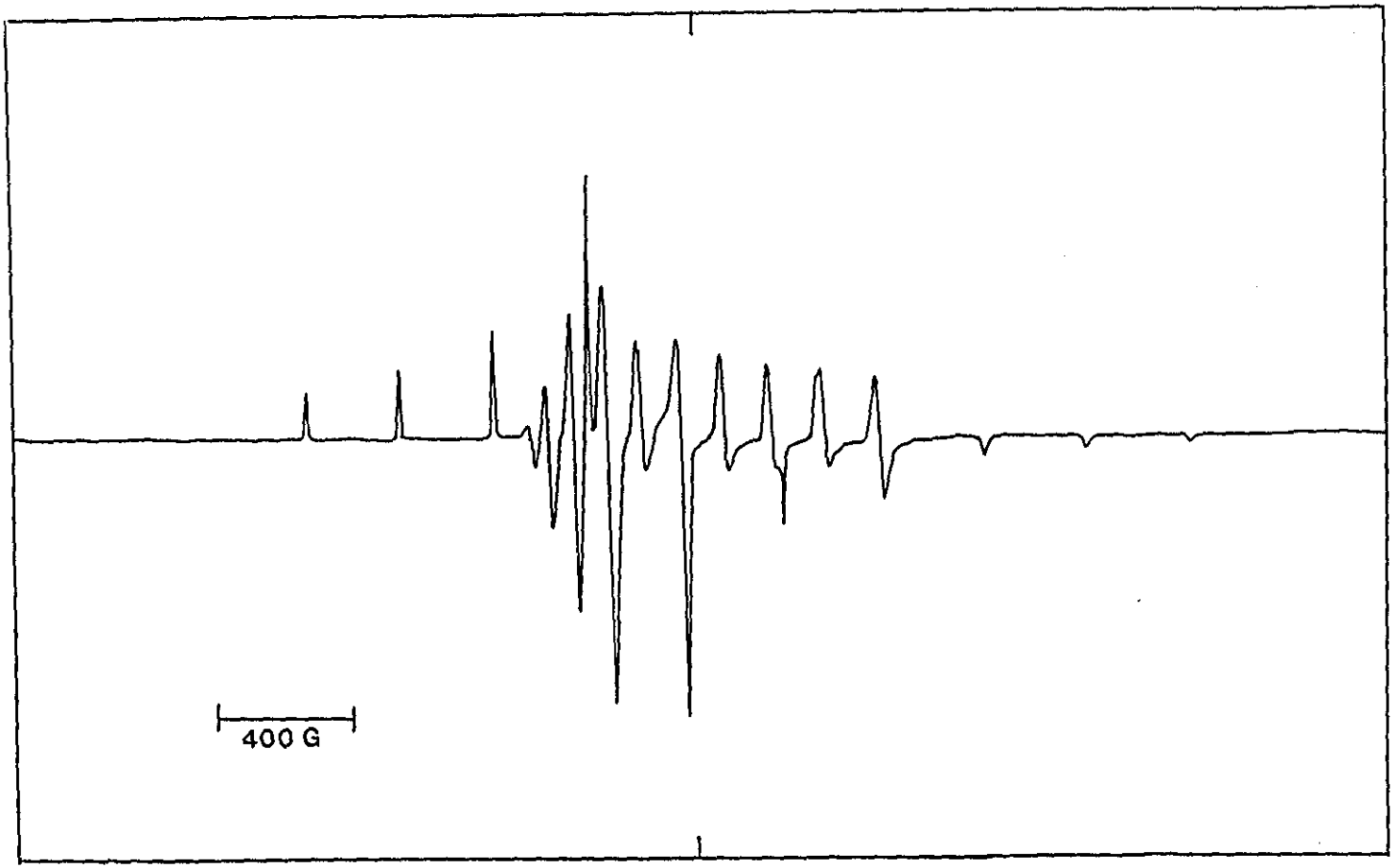


Figure 5.4. The simulated ESR spectrum from the POWDER program of $[Tc(NO)(acac)Cl_4]^-$

Table 5.2.

Animal biodistribution data for $[^{99}Tc(NO)(acac)Cl_2]^-$

% injected dose/organ

	2 min. sacrifice		60 min. sacrifice	
	mean	S.D.#	mean	S.D.#
Muscle	27.62	3.24	14.38	0.03
Blood	3.57	0.00	2.03	0.08
Kidney	0.76	0.14	1.07	0.47
Bladder	0.83	0.35	12.48	1.91
Lung	0.73	0.03	0.53	0.13
Liver	3.16	0.64	8.27	0.72
Spleen	0.27	0.00	0.21	0.00
Heart	0.57	0.07	0.23	0.02
Brain	0.10	0.00	0.05	0.00
Tail	0.91	0.19	0.59	0.36
Carcass and gut	62.10	4.44	60.74	3.21
Counts/gram ratios				
Heart/blood	2.36	2.04	2.06	1.47
Heart/muscle	1.99	2.22	2.07	1.60
Heart/liver	1.96	2.61	0.41	0.37
Heart/lung	1.13	1.11	0.63	0.84

= standard deviation of two animals

5.4. Crystal structure determination of the tetraphenylarsonium salt of the trichloronitrosyl (acetylacetonato)technetium(II) anion.

The anion $[Tc(NO)Cl_3(acac)]^-$ has a distorted octahedral geometry with three chlorine atoms, a bidentate acac ligand and the nitrosyl trans to either of the equivalent oxygens. The other trans position is occupied by a chlorine atom resulting in a disordered structure.

The analysis of the data proved a non routine problem because of the disorder. As chlorine and nitrosyl have a similar number of electrons differentiation was not possible from a Fourier map. However, the positions of the individual atoms were eventually determined through careful analysis of difference maps and the atoms refined isotropically with occupancy factors of 0.5.

This refinement showed that the chlorine and nitrosyl ligands opposite the oxygen atoms of the acac group were disordered with random reversal. Attempts to refine the structure in space group P1 rather than $P\bar{1}$ showed the same disorder. Full matrix least squares refinement was carried out with bonds of the disordered nitrosyl fixed at conventional values (Tc-N 1.69 and N-O 1.17Å).

Red crystals grown from methanol/water mixture proved suitable for crystal structure determination. A kite shaped plate crystal (0.31 x 0.19 x 0.08mm) was mounted about a.

The crystal structure data are as follows:

Formula: $[(C_6H_5)_4As][Tc(NO)Cl_3(C_5H_7O_2)]$;

Formula weight: M_r=717.5;

Space group: triclinic, $P\bar{1}$;

Cell dimensions: a=10.261(4), b=11.261(10), c=13.686(10)Å, α=101.7(5), β=91.9(5), γ=97.3(5)°;

Cell volume: U=1532.93Å^3;

Z=2;

Density: D_m=not measured, D_x=1.554gcm^{-3};

Radiation: λ(MoKα)=0.71069Å;

μ=18.17cm^{-1};

F(000)=717.87;

T=293K;

R=0.076 for 2008 observed reflexions with I>3σ(I).;

Stoë Weissenberg diffractometer, sinθ/λ<0.6Å^{-1};

lattice parameters by maximising fit of axial row reflexions in range sinθ/λ 0.1 to 0.4;

3958 reflexions measured, 2008 with I>3σ(I);

h 0 → 8, k -12 → +12, l -15 → +15;

standard check reflexions on each layer with no significant changes;

absorption correction applied, t_{min}=0.717, t_{max}=0.866;

Tc and As positions found by Patterson and other atoms by successive difference-Fourier methods, refined by full-matrix least squares on F to R=0.076, wR=0.079;
overall scale factor and inter-layer scale factors refined;
all atoms anisotropic except disordered and H, unit weighting (based on weight analysis and rapid convergence of refinement);
20 H atoms in calculated positions, remaining H atoms omitted;
max Δ/σ=-0.378, $\Delta\rho$ excursions +0.9 to -1.0eÅ^{-3};

Final atomic coordinates are given in Table 5.3., bond lengths and angles in Tables 5.4. and 5.5. respectively, atomic coordinates for the hydrogen atoms are given in Table 5.6. and anisotropic thermal parameters in Table 5.7.

The numbering scheme of the atoms of the anion is shown in Figure 5.5. N(3), O(3) and N(4), O(4) refer to the disordered nitrosyls and Cl(3) and Cl(4) to their respective chlorines. The numbering scheme of atoms of the cation is given in Figure 5.6.

Observed and calculated structure factors (x10) are given in Appendix III.

Table 5.3.

Final positional parameters ($X10^4$) and isotropic thermal parameters ($Å^2$) for $[(C_6H_5)_4As][Tc(NO)(acac)Cl_3]$

$B_{eq}=8\Pi^2(^1/_3)(\Sigma u_{ii})$
* isotropic thermal parameter=$8\Pi^2u$ (atoms at half occupancy)

	x	y	z	B_{eq}
Tc	10910(2)	3166(2)	1944(1)	5.3(1)
As	4414(2)	8117(2)	2911(1)	4.9(1)
Cl(1)	9884(7)	4871(5)	1685(5)	7.4(4)
Cl(2)	11782(8)	1329(6)	2007(6)	9.8(5)
Cl(3)	13046(21)	4221(16)	2402(12)	5.6*
Cl(4)	10390(16)	3426(14)	3584(10)	6.8*
O(1)	11335(15)	2912(13)	458(9)	6.2(7)
O(2)	9089(13)	2101(11)	1514(10)	5.0(7)
C(1)	11178(26)	2289(23)	-1293(15)	7.3(11)
C(2)	10600(22)	2280(18)	-280(15)	5.2(9)
C(3)	9407(28)	1592(19)	-222(16)	6.8(11)
C(4)	8684(23)	1520(18)	633(16)	5.7(6)
C(5)	7475(26)	641(21)	567(20)	7.4(12)
C(6)	15818(22)	2590(17)	8487(13)	4.8(9)
C(7)	16921(19)	3403(19)	8863(14)	4.7(9)
C(8)	17053(28)	3944(20)	9861(18)	6.9(11)
C(9)	16003(28)	3649(22)	10447(16)	6.8(11)
C(10)	14839(28)	2829(22)	10094(17)	7.1(12)
C(11)	14771(23)	2276(20)	9089(16)	5.8(11)
C(12)	12712(23)	8147(19)	3459(14)	5.1(10)
C(13)	12028(26)	7085(20)	3663(15)	5.8(11)
C(14)	10790(25)	7126(21)	3970(16)	5.6(18)
C(15)	10155(35)	8130(30)	4095(18)	9.2(13)
C(16)	10885(28)	9202(22)	3882(18)	6.8(12)
C(17)	12172(28)	9182(24)	3555(16)	6.5(11)
C(18)	15405(19)	9714(16)	3064(13)	4.0(9)
C(19)	14900(22)	10588(20)	2615(15)	5.8(10)
C(20)	15544(26)	11752(20)	2750(19)	4.3(12)
C(21)	16790(26)	11991(19)	3231(19)	6.5(11)
C(22)	17319(26)	11094(23)	3692(18)	4.6(11)
C(23)	16618(25)	9971(17)	3592(16)	5.5(10)
C(24)	14608(29)	2846(19)	6431(14)	6.9(10)
C(25)	13784(19)	3637(20)	7016(16)	4.7(10)
C(26)	13046(30)	4310(21)	6546(18)	7.7(11)
C(27)	13024(26)	4169(24)	5530(20)	7.0(11)
C(28)	13717(32)	3409(27)	4961(17)	8.3(12)
C(29)	14510(26)	2724(24)	5421(16)	7.3(11)
N(3)	12425(24)	4076(31)	2282(27)	5.2*
O(3)	13594(27)	4332(37)	2436(30)	7.3*
N(4)	10442(54)	3377(51)	3144(21)	10.6*
O(4)	9805(30)	3793(29)	3780(22)	6.6*

Table 5.4.

Bond Distances for $[(C_6H_5)_4As][Tc(NO)(acac)Cl_3]$

Anion

	Å
Tc-Cl(1)	2.385(7)
Tc-Cl(2)	2.372(8)
Tc-Cl(3)	2.36(2)
Tc-Cl(4)	2.29(1)
Tc-N(3)	1.74(3)
Tc-N(4)	1.71(3)
N(3)-O(3)	1.20(4)
N(4)-O(4)	1.16(5)
Tc-O(1)	2.06(1)
Tc-O(2)	2.08(1)
O(1)-C(2)	1.27(2)
O(2)-C(4)	1.28(2)
C(1)-C(2)	1.53(3)
C(2)-C(3)	1.38(3)
C(3)-C(4)	1.42(3)
C(4)-C(5)	1.47(3)

Cation

As-C(6)	1.91(2)
As-C(12)	1.93(2)
As-C(18)	1.92(2)
As-C(24)	1.90(4)
C(6)-C(7)	1.37(3)
C(7)-C(8)	1.37(3)
C(8)-C(9)	1.44(4)
C(9)-C(10)	1.43(3)
C(10)-C(11)	1.39(3)
C(6)-C(11)	1.43(3)
C(12)-C(13)	1.39(3)
C(13)-C(14)	1.35(4)
C(14)-C(15)	1.36(4)
C(15)-C(16)	1.42(4)
C(16)-C(17)	1.41(4)
C(12)-C(17)	1.34(4)
C(18)-C(19)	1.40(3)
C(19)-C(20)	1.36(3)
C(20)-C(21)	1.39(4)
C(21)-C(22)	1.45(4)
C(22)-C(23)	1.35(3)
C(18)-C(23)	1.39(3)
C(24)-C(25)	1.45(3)
C(25)-C(26)	1.37(4)
C(26)-C(27)	1.37(4)
C(27)-C(28)	1.33(4)
C(28)-C(29)	1.41(4)
C(24)-C(29)	1.36(3)
average C-C	1.39(3)

Table 5.5.

Bond angles for $[(C_6H_5)_4As][Tc(NO)(acac)Cl_3]$

Anion

Tc-N(3)-O(3)	158.6(33)
Tc-N(4)-O(4)	152.1(47)
Cl(1)-Tc-Cl(2)	172.6(2)
Cl(1)-Tc-Cl(3)	97.5(5)
Cl(1)-Tc-Cl(4)	93.0(5)
Cl(1)-Tc-O(1)	86.8(5)
Cl(1)-Tc-O(2)	86.9(4)
Cl(1)-Tc-N(3)	92.1(12)
Cl(1)-Tc-N(4)	90.6(20)
Cl(2)-Tc-Cl(3)	87.8(5)
Cl(2)-Tc-Cl(4)	92.0(5)
Cl(2)-Tc-O(1)	88.1(5)
Cl(2)-Tc-O(2)	87.7(4)
Cl(2)-Tc-N(3)	93.3(12)
Cl(2)-Tc-N(4)	94.2(20)
Cl(3)-Tc-O(1)	89.8(6)
Cl(3)-Tc-O(2)	175.3(6)
Cl(3)-Tc-N(4)	93.8(17)
Cl(4)-Tc-O(1)	178.7(6)
Cl(4)-Tc-O(2)	89.7(5)
Cl(4)-Tc-N(3)	91.2(12)
O(1)-Tc-O(2)	89.0(5)
O(1)-Tc-N(3)	90.1(13)
O(1)-Tc-N(4)	175.8(19)
O(2)-Tc-N(3)	178.6(14)
O(2)-Tc-N(4)	87.6(17)
Tc-O(1)-C(2)	126.3(14)
Tc-O(2)-C(4)	126.9(14)
C(1)-C(2)-C(3)	120.3(18)
C(2)-C(3)-C(4)	128.4(19)
C(3)-C(4)-C(5)	120.8(19)

Cation

C(12)-As-C(18)	113.1(8)
C(12)-As-C(6)	108.9(9)
C(12)-As-C(24)	108.7(11)
C(18)-As-C(6)	107.8(8)
C(18)-As-C(24)	108.4(9)
C(6)-As-C(24)	109.9(9)
C(7)-C(6)-C(11)	123.0(16)
C(6)-C(7)-C(8)	119.9(20)
C(7)-C(8)-C(9)	118.0(21)
C(8)-C(9)-C(10)	122.8(20)
C(9)-C(10)-C(11)	117.0(23)
C(10)-C(11)-C(6)	119.3(19)
C(13)-C(12)-C(17)	121.6(23)
C(12)-C(13)-C(14)	118.0(23)
C(13)-C(14)-C(15)	125.0(25)
C(14)-C(15)-C(16)	115.5(29)
C(15)-C(16)-C(17)	120.6(26)
C(16)-C(17)-C(12)	119.3(24)
C(19)-C(18)-C(23)	121.4(17)
C(18)-C(19)-C(20)	120.8(20)
C(19)-C(20)-C(21)	117.5(23)
C(20)-C(21)-C(22)	121.4(21)
C(21)-C(22)-C(23)	119.0(23)
C(22)-C(23)-C(18)	119.3(22)
C(25)-C(24)-C(29)	117.5(24)
C(24)-C(25)-C(26)	119.1(21)
C(25)-C(26)-C(27)	120.0(24)
C(26)-C(27)-C(28)	122.7(28)
C(27)-C(28)-C(29)	118.8(23)
C(28)-C(29)-C(24)	121.6(24)
average C-C-C	120.0(22)

Table 5.6.

Final positional parameters ($X10^4$) and isotropic thermal parameters ($Å^2$) for the hydrogen atoms of $[(C_6H_5)_4As][Tc(NO)(acac)Cl_2]$

$B=8\pi^2u$

	x	y	z	B
H(7)	17680	3618	8374	4.6
H(8)	17924	4563	10178	6.5
H(9)	16091	4087	11230	6.5
H(10)	14058	2645	10574	6.8
H(11)	13936	1614	8762	5.6
H(13)	12468	6254	3579	6.1
H(14)	10270	6297	4126	6.5
H(15)	9162	8116	4341	8.3
H(16)	10447	10035	3977	7.3
H(17)	12713	9996	3385	6.4
H(19)	13988	10336	2159	5.8
H(20)	15101	12461	2493	7.3
H(21)	17378	12867	3266	6.1
H(22)	18258	11318	4113	7.4
H(23)	16998	9281	3921	5.2
H(25)	13751	3695	7811	5.4
H(26)	12478	4953	6979	6.9
H(27)	12421	4700	5179	6.8
H(28)	13673	3316	4157	7.6
H(29)	15053	2084	4963	5.8

Table 5.7.

Anisotropic thermal parameters* ($X10^3$, $Å^2$) for
$[(C_6H_5)_4As][Tc(NO)(acac)Cl_3]$

	U11	U22	U33	U23	U13	U12
Tc	97(3)	58(1)	48(1)	6(1)	-6(1)	-21(1)
As	92(3)	54(1)	39(1)	8(1)	-3(1)	-17(1)
Cl(1)	122(6)	67(4)	92(4)	2(3)	-22(4)	-8(4)
Cl(2)	158(8)	62(4)	149(7)	29(4)	-49(5)	-8(4)
O(1)	114(12)	76(9)	47(8)	8(7)	-3(8)	-33(8)
O(2)	52(9)	62(8)	76(9)	1(7)	15(7)	-24(7)
C(1)	122(17)	112(15)	44(11)	23(11)	14(11)	-6(13)
C(2)	84(15)	58(11)	55(11)	-1(9)	-4(11)	-17(11)
C(3)	144(18)	55(12)	58(12)	2(10)	-3(13)	-8(13)
C(4)	100(16)	59(12)	59(12)	4(10)	-16(12)	-36(11)
C(5)	100(16)	63(13)	118(16)	-7(12)	-16(13)	-30(12)
C(6)	86(15)	54(11)	42(10)	4(8)	-20(10)	-13(10)
C(7)	44(12)	83(13)	51(10)	2(10)	7(9)	-13(10)
C(8)	125(17)	63(13)	74(13)	3(11)	-19(13)	-11(12)
C(9)	115(17)	89(14)	55(12)	2(11)	15(12)	21(14)
C(10)	130(17)	90(14)	57(12)	1(11)	-9(12)	-35(13)
C(11)	72(15)	78(13)	69(12)	3(11)	18(11)	-6(11)
C(12)	97(15)	50(11)	46(10)	13(9)	-13(10)	-18(12)
C(13)	75(16)	84(14)	63(12)	1(11)	11(11)	-30(12)
C(14)	63(16)	71(13)	80(13)	-9(11)	12(12)	-24(12)
C(15)	188(20)	110(17)	52(12)	-12(13)	-29(14)	-29(17)
C(16)	91(17)	75(14)	92(14)	12(12)	1(13)	12(13)
C(17)	92(17)	92(15)	62(12)	25(11)	2(12)	-12(13)
C(18)	50(13)	51(11)	51(10)	7(9)	2(8)	-19(9)
C(19)	74(14)	79(13)	69(12)	30(11)	-14(10)	-2(11)
C(20)	90(16)	63(12)	115(15)	40(11)	12(13)	-22(12)
C(21)	76(16)	52(12)	118(15)	-9(12)	62(13)	-13(11)
C(22)	106(16)	69(13)	85(14)	3(11)	-19(12)	-18(13)
C(23)	106(16)	35(10)	67(12)	2(9)	-8(11)	-7(11)
C(24)	181(18)	53(12)	29(9)	7(9)	-13(12)	-26(13)
C(25)	17(12)	80(13)	81(13)	21(11)	10(10)	-16(10)
C(26)	161(19)	63(13)	67(13)	11(11)	-9(14)	-3(14)
C(27)	93(16)	90(14)	84(14)	37(12)	-3(13)	-1(13)
C(28)	142(18)	122(16)	51(12)	31(12)	-4(13)	31(15)
C(29)	118(17)	111(15)	49(11)	22(11)	20(12)	37(14)

* The form of the anisotropic thermal parameter is given by
$\exp\{-2\Pi^2(U_{11}a^{*2}h^2+.....2U_{23}b^*c^*kl+....)\}$

Figure 5.5.

Molecular structure and atom numbering for the trichloronitrosyl (acetylacetonato)technetium(II) anion showing one of the disordered arrangements where N(3), O(3) and Cl(4) are the disordered atoms.

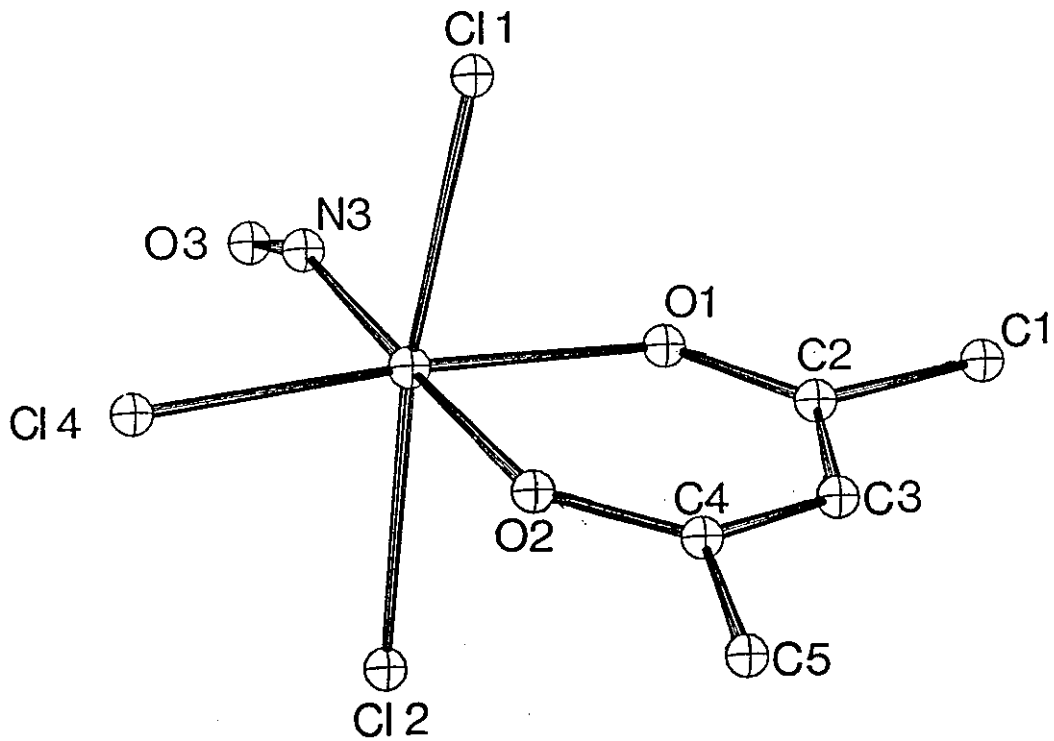
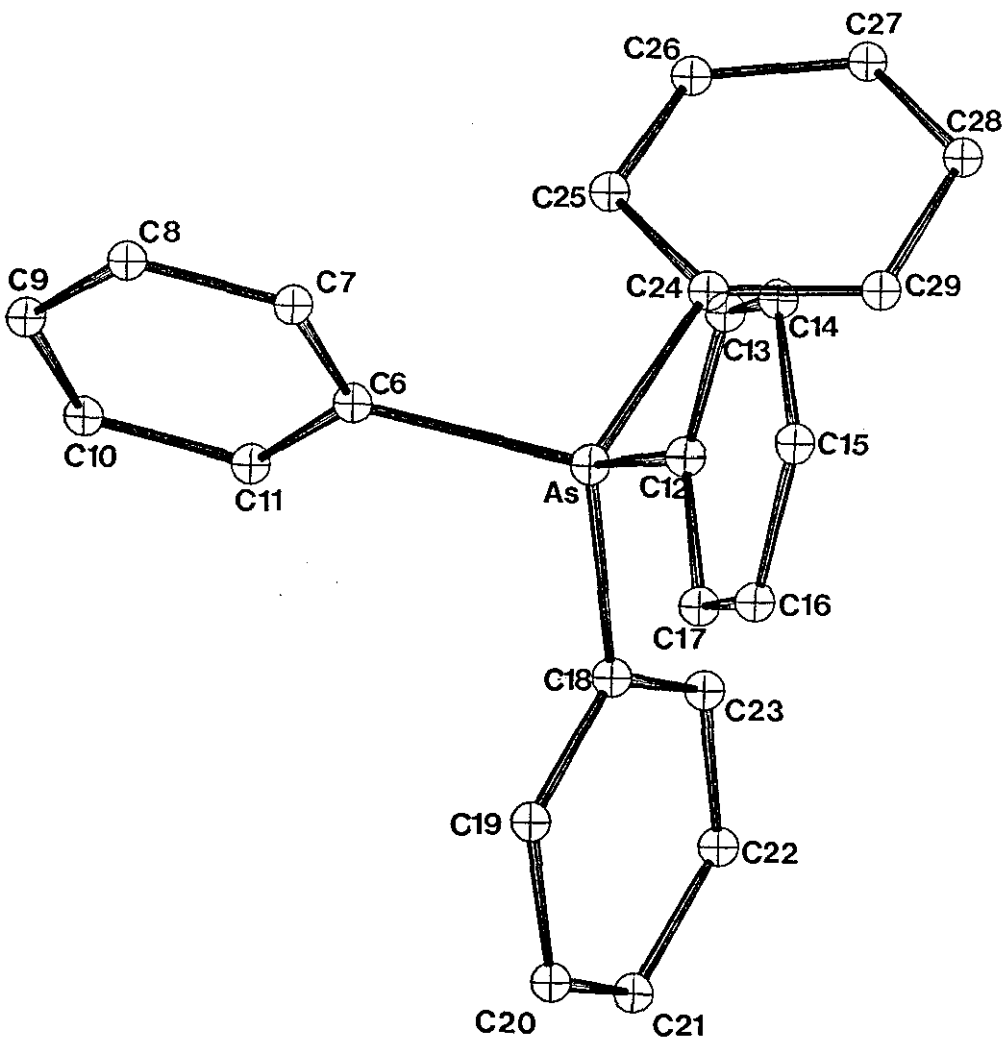


Figure 5.6.

Molecular structure and atom numbering for the tetraphenylarsonium cation of $[(C_6H_5)_4As][Tc(NO)(acac)Cl_3]$



5.5. Discussion.

The preparation of acetylacetonato containing technetium complexes has been noted previously. Mazzi reacted $[TcX_6]^{2-}$ and $TcX_4(PPh_3)_2$ (X = Cl^-, Br^-) with acacH and isolated a series of species including $[TcCl_4(acac)]^-$ and other technetium(IV) containing species with mixtures of chloride, PPh_3 and acetylacetonato ligands (23). Interestingly the technetium(III) complex $TcX(acac)_2(PPh_3)$ and $TcX_2(acac)(PPh_3)_2$ were also isolated depending upon the conditions employed (97). Davison, Jones and coworkers isolated $Tc(acac)_3$ directly from pertechnetate reduction by sodium dithionite (111). However, $[Tc(NO)(acac)Cl_3]^-$ is the first example of a technetium (II) acetylacetonato complex where the lower oxidation state is being stabilised by the presence of the nitrosyl group.

The infra red spectrum of the complex has a strong absorption at $1770cm^{-1}$ typical of the $\nu(NO)$ stretching vibration for linear nitrosyls, which may be considered as NO^+. The similar absorption in $[Tc(NO)Cl_4X]^{n-}$ varies between $1805cm^{-1}$ and $1795cm^{-1}$ depending upon the nature of the trans ligand, X (160).

The X-ray data of the triclinic crystal shows that the trichloro(acetylacetonato)nitrosyltechnetium(II) anion has a distorted octahedral geometry with two chlorides mutually trans and the other chloride and the nitrosyl occupying disordered

positions trans to the chemically equivalent oxygens of the acetylacetonato ligand.

As described above (5.4.) the solving of the crystal structure was not staightforward due to the disordered arrangement. Final matrix least squares refinement was carried out with bonds of the disordered nitrosyl fixed at conventional values (Tc-N 1.69 and N-O 1.17Å). This refinement showed that the chlorine and nitrosyl, while occupying the same geometrical position are slightly axially displaced Cl(3)-Tc-O(2) 174.7(6)°, N(3)-Tc-O(2) 178.1(12)° and Cl(4)-Tc-O(3) 175.4(7)°, N(4)-Tc-O(3) 170.5(11)°.

The bond angles for Tc-N(3)-O(3) and Tc-N(4)-O(4) are 154.0(30) and 155(30)° respectively which is considerably different from that of $[Tc(NO)Cl_4(CH_3OH)]^-$ which has a bond angle of 175.5(10)°. The i.r. vibration ν(NO) of the former is at 1770cm^{-1} while that of the latter is 1805 cm^{-1}. Both may be considered as NO^+ instead of NO^-. The disorder and slight axial displacement of the two ligands result in some loss of accuracy in the bond lengths and angles and detailed discussion of these is therefore not appropriate.

The acac ligand bond distances and angles are comparable with those reported for other technetium complexes containing this ligand and the non-disordered chlorines have bond distances to the technetium which are unremarkable.

The FAB$^-$ mass spectrum of the complex (Figure 5.1.) has a major ion at $^m/_z$=333 due to [Tc(NO)(acac)Cl_3]$^-$ with the expected isotope pattern due to the 3 chlorine atoms. Fragmentation occurrs via the loss of 1 chlorine to $^m/_z$=298. The ions at $^m/_z$=269 and 262 correspond to [M-Cl-NO+H]$^-$ and [M-2Cl+H]$^-$ respectively. The other lower mass ions at 233 and 204 are due to [TcCl(acac)]$^-$ and [$TcCl_3$]$^-$. The facile loss of a single chlorine indicates that the parent complex may readily undergo exchange of this ligand while loss of the acac group may be difficult.

The electron spin resonance spectra of the complex recorded at ambient temperature is that expected with the signal split into 10 by the I=$^9/_2$ technetium nuclear spin (Figure 5.2.). The g_{av}=2.12 and a_{av}=135 gauss were measured directly. The complex has low symmetry and the frozen solution gave a complex spectrum (Figure 5.3.) which could only be resolved into its component parameters using the POWDER simulation program (Figure 5.4.).

Several other technetium(II) nitrosyl complexes have been prepared and their ESR spectra measured. Kirmse and coworkers (65,71) reported the spectrum of Tc(NO)Cl_3(PMe_2Ph)$_2$ which appears to have the two phosphines mutually trans. However it was assumed that their spectrum could be modelled as axially symmetric. The complexes [Tc(NO)X_5]$^{2-}$ (X = halide, NCS^-) were modelled in a similar fashion. The [Tc(NO)Cl_3(acac)]$^-$ is unusual since one of the oxygens of the acac ligand is trans to the nitrosyl and thus the spectrum cannot satisfactorily be modelled as axial.

The animal biodistribution data collected from the sampling of the carrier added complex showed only moderate heart uptake which washes out with time whilst liver uptake increases with time. Initially the blood and muscle activity levels are high but these clear. Significant urinary excretion takes place over the period of the distribution, but not as high as in the tetrachloro- and tetrabromonitrosyltechnetium(II) anions or the technetium(I) nitrosyltetraamine analogues.

CHAPTER 6

SYNTHESIS, CHARACTERISATION AND BIOLOGICAL STUDIES OF TWO TECHNETIUM(I)NITROSYL CATIONS - THE CHLORONITROSYL-BIS-(DPPE)TECHNETIUM(I) AND CHLORONITROSYL-BIS-(DIARS)TECHNETIUM(I) CATIONS

6.1. Introduction.

Work by Deutsch's group has already demonstrated that technetium (III) cations of the type $[TcL_2X_2]^+$, where L = ditertiary phosphines or diarsines and X = Cl or Br, yield excellent images of the myocardium in dogs (25). Unfortunately in humans the Tc(III) complexes undergo reduction in vivo to the neutral Tc(II) complexes which are not taken up by the heart. However, it has been found that the neutral complexes and particularly the bis-diars complex are able to cross the blood brain barrier which makes them potential brain perfusion agents.

In an attempt to produce similarly lipophilic technetium(I) cations containing the $[Tc-NO]^{2+}$ core $[Tc(NO)Cl_4]^-$ was reacted with dppe and diars. The complexes have been fully characterised by FAB^+ mass spectrometry and, in the case of the diars complex X-ray crystallography.

6.2. Synthesis of the chloronitrosyl-bis-(dppe)technetium (I) cation.

6.2.1. Synthesis of no carrier added $[^{99m}Tc(I)(NO)(dppe)_2Cl]^+$.

To 1 ml of generator eluant was added 1 ml of concentrated HCl. The mixture was heated in a pressure cooker for 30 minutes. The product of the reaction is sodium hexachlorotechnetate. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine sulphate (1ml, 2.3M) and heated for a further 30 minutes. The resulting solution contains the species $[Tc(NO)Cl_4X]^-$ ($X=Cl^-$, H_2O). To this solution was added dppe (30mg, 0.075mM) and ethanol (1.0 ml) and the mixture heated in the pressure cooker for 30 minutes.

The reaction was monitored at each stage using the standard chromatographic procedures described above.

6.2.2. Preparation of the no carrier added complex for biological studies.

As prepared above the complex is 85% radiochemically pure. The complex was adsorbed onto a millipore filter and eluted with 50:50 ethanol:water to give a pure complex free of starting materials.

6.2.3. Synthesis of carrier added $[^{99}Tc(I)(NO)(dppe)_2Cl]^+$.

6.2.3.a. Method 1.

To an aqueous solution of ammonium pertechnetate (1ml., 0.15mM) was added concentrated hydrochloric acid (1ml) and the mixture heated for 30 minutes. The product of the reaction is $[TcCl_6]^{2-}$ as the yellow ammonium salt. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine in water (1ml, 2.3M), and heated for a further 30 minutes. The resulting green solution contains the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). To this solution was added tetrabutylammonium chloride solution in water (1ml, 75%) followed by dichloromethane (10 ml). The anion can be quantitatively extracted as the tetrabutylammonium salt. The dichloromethane is evaporated off leaving a green solid. To this solid was added ethanol (20 ml) and dppe (120mg, 0.30mM) and the mixture refluxed under nitrogen for 4 hours during which time the solution became yellow in colour. The solvent was evaporated to a small volume (3ml) and an equal volume of dichloromethane added. A solution of sodium tetraphenylboron (250mg in 1ml 50:50 dichloromethane:ethanol) was added until a cream coloured precipitate was obtained from the yellow solution. The precipitate was removed by filtration, redissolved in dichloromethane and pale orange needles of $[Tc(NO)(dppe)_2Cl][(C_6H_5)_4B]$ recrystallised by slow evaporation of the solvent.

6.2.3.b Method 2.

To an aqueous solution of ammonium pertechnetate (1ml., 0.15mM) was added concentrated hydrochloric acid (1ml) and the mixture heated for 30 minutes. The product of the reaction is $[TcCl_6]^{2-}$ as the yellow ammonium salt. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine hydrochloride (1ml, 2.3M) and heated for a further 30 minutes. To 2ml of the resulting green solution containing the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O) was added dppe (60mg, 0.15mM) and ethanol (1.0 ml). The mixture was heated in a pressure cooker for 30 minutes. A yellow solid resulted which was suspended in the aqueous solution. This yellow product containing the cation $[Tc(NO)(dppe)_2Cl]^+$ can be extracted into dichloromethane, precipitated as above (6.2.3.a. method 1) with sodium tetraphenylboron and allowed to crystallise.

6.3. Synthesis of the chloronitrosyl-bis-(diars)technetium(I) cation

6.3.1. Synthesis of no carrier added $[^{99m}Tc(I)(NO)(diars)_2Cl]^+$.

To 1 ml of generator eluant was added 1 ml of concentrated HCl. The mixture was heated in a pressure cooker for 30 minutes. The product of the reaction is sodium hexachlorotechnetate. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine sulphate (1ml, 2.3M) and heated

for a further 30 minutes. The resulting solution contains the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). To this solution was added diars (0.05ml, 0.16mM) and ethanol (1.0ml). The mixture was heated for 30 minutes in the pressure cooker. The product was adsorbed onto a Millipore filter and eluted with 50:50 ethanol:water to give a pure product free of starting materials.

6.3.2. Synthesis of carrier added $[^{99}Tc(I)(NO)(diars)_2Cl]^+$.

6.3.2.a Method 1.

To an aqueous solution of ammonium pertechnetate (1ml., 0.15mM) was added concentrated hydrochloric acid (1ml) and the mixture heated for 30 minutes. The product of the reaction is $[TcCl_6]^{2-}$ as the yellow ammonium salt. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine in water (1ml, 2.3M), and heated for a further 30 minutes. The resulting green solution contains the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). To 2ml of this solution, deoxygenated with nitrogen, was added diars (0.05 ml, 0.16mM) and the mixture heated in the pressure cooker for 30 minutes. A yellow oil formed which extracted into dichloromethane. Evaporation of the solvent yields a yellow solid.

6.3.2.b. Method 2.

To an aqueous solution of ammonium pertechnetate (1ml., 0.15mM) was added concentrated hydrochloric acid (1ml) and the mixture heated for 30 minutes. The product of the reaction is $[TcCl_6]^{2-}$ as the yellow ammonium salt. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine in water (1ml, 2.3M), and heated for a further 30 minutes. The resulting green solution contains the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). Addition of tetrabutylammonium chloride solution (75% in water) allowed extraction of the $[Tc(NO)Cl_4X]^-$ into dichloromethane (5ml). This solution was deoxygenated with nitrogen and diars (0.2ml, 67mM) added. The solution became yellow-green on standing and yellow rhomboid shaped crystals formed on slow evaporation of the solvent.

6.3.3. Preparation of the carrier added complex for biological studies.

4.3mg of the crystalline solid was dissolved in 50:50 ethanol:water to give a solution which was used without further purification.

6.4. Results.

6.4.1. Paper chromatography.

For both carrier added and no carrier added complexes.

Complex	R_f in butan-2-one	R_f in saline
$[Tc(I)(NO)(dppe)_2Cl]^+$	0.73(2)	0.03(2)
$[Tc(I)(NO)(diars)_2Cl]^+$	0.69(3)	0.04(3)

6.4.2. Electrophoresis.

For carrier added and no carrier added preparations of both cations, the complex does not move under electrophoresis conditions presumably due to its insolubility.

6.4.3. HPLC.

For the no carrier added preparation of $[Tc(NO)(dppe)_2Cl]^+$.

Retention time on system X (Amersham) 10.7 minutes

Retention time on system X2 (Amersham) 12.6 minutes

For the carrier added and no carrier added preparations of $[Tc(I)(NO)(diars)_2Cl]^+$

Retention time on system X (Amersham) 7.3 minutes

6.4.4. Infra-red spectra.

For $[Tc(NO)(dppe)_2Cl]^+$

(KBr disc) Absorptions at 1775cm^{-1} for ν(NO), Tc-Cl low.

For $[Tc(I)(NO)(diars)_2Cl]^+$

(KBr disc) Absorption at 1720cm^{-1} for ν(NO).

6.4.5. Analysis.

For $[Tc(NO)(dppe)_2Cl]^+$

(calculated for $C_{76}H_{68}NOClTcBP_4$)

C 70.31(71.28); H 5.57(5.32); N 1.37(1.09)

For $[Tc(I)(NO)(diars)_2Cl]^+$

(calculated for $C_{36}H_{36}NOClTcAs_4$)

C 40.53(41.14); H 6.80(6.48); N 2.76(2.67)

6.4.6. FAB+ mass spectra

	$[Tc(NO)(dppe)_2Cl]^+$	$[Tc(I)(NO)(diars)_2Cl]^+$
Major ion ($^m/_z$)	960	736
Lower mass ions ($^m/_z$)	925	706
	562	450

The FAB mass spectra for $[Tc(NO)(dppe)_2Cl]^+$ and $[Tc(I)(NO)(diars)_2Cl]^+$ are given in Figures 6.1. and 6.2. respectively.

6.4.7. Biodistribution studies.

The biodistribution data for the no carrier added preparation of $[Tc(NO)(dppe)_2Cl]^+$ are given in Table 6.1.

The biodistribution data for the carrier added preparation of $[Tc(I)(NO)(diars)_2Cl]^+$ are given in Table 6.2.

6.4.8 ^1H NMR of the carrier added complexes.

The spectrum of the dppe complex shows broad, unresolved singlets at 2.95, 2.80, 2.50, and 1.70 ppm.

The spectrum of the diars complex shows multiplets at 8.20 and 7.80 ppm and poorly resolved multiplets at 1.95, 1.65, 1.40, and 1.05.

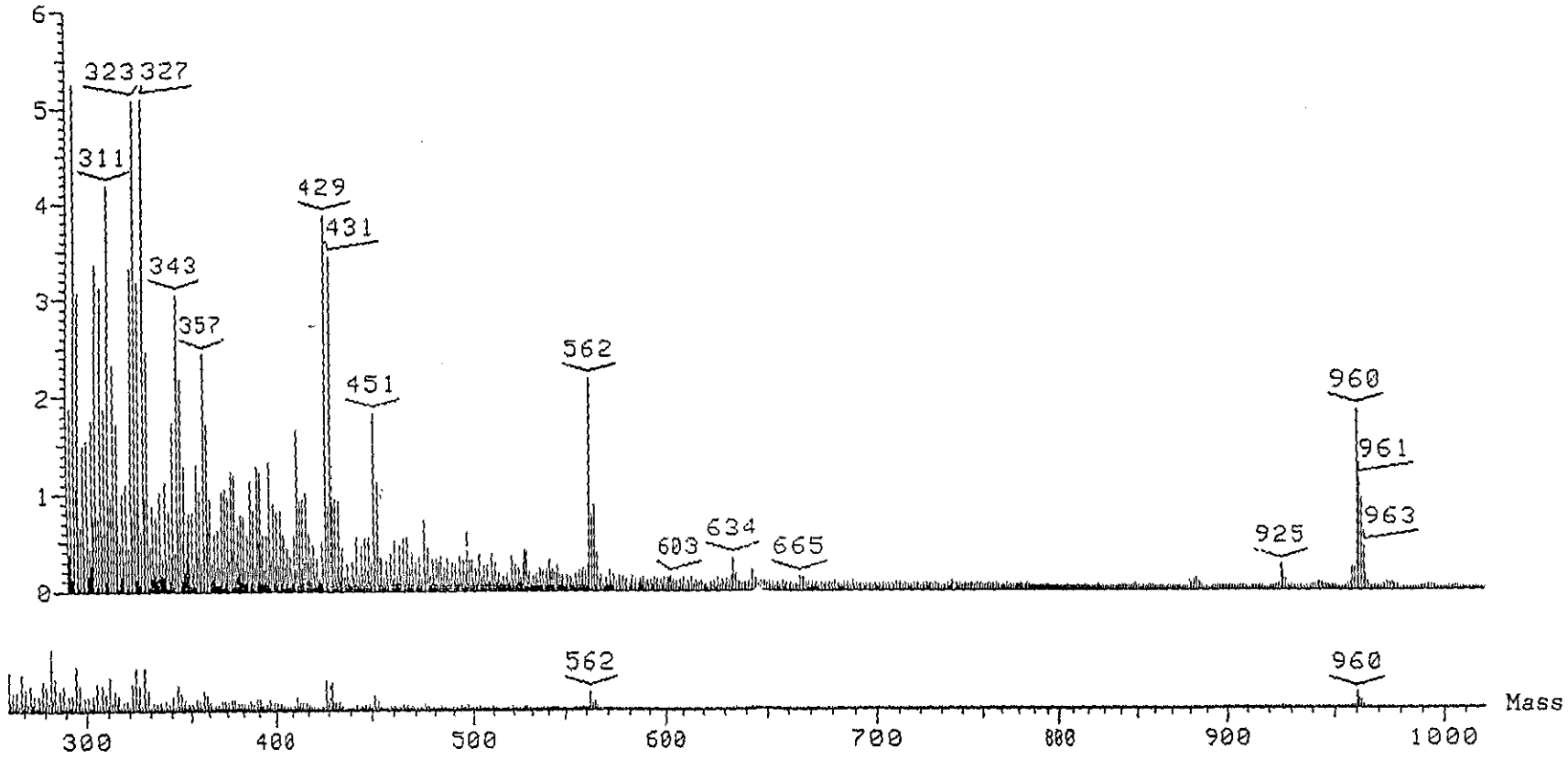


Figure 6.1. FAB+ mass spectrum of $[Tc(NO)(dppe)_2Cl]^+$

Figure 6.2.

FAB+ mass spectrum of $[Tc(NO)(diars)_2Cl]^+$.

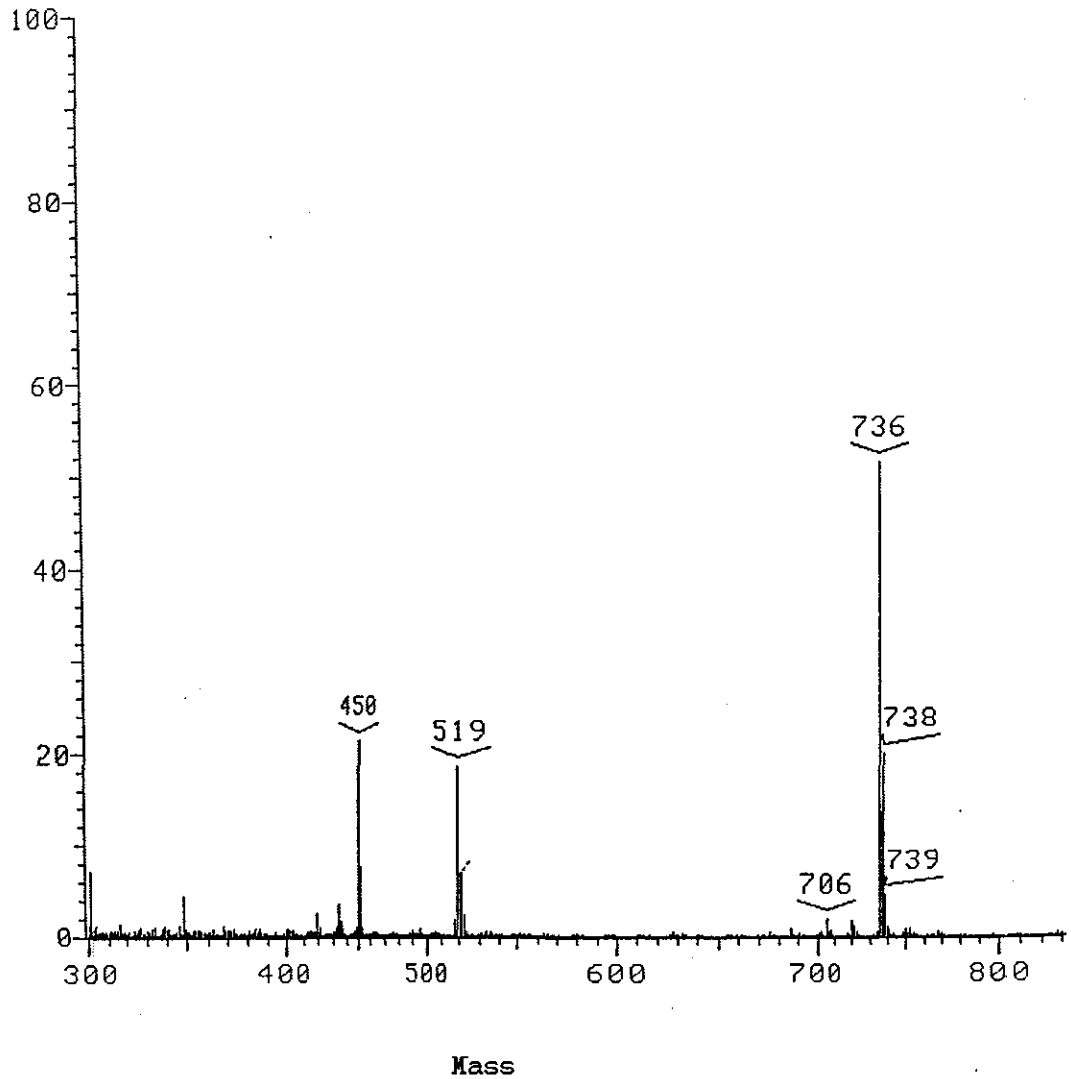


Table 6.1.

Animal biodistribution data for $[^{99m}Tc(NO)(dppe)_2Cl]^+$

% injected dose/organ

	2 min sacrifice		60 min sacrifice	
	mean	S.D.*	mean	S.D.*
Muscle	10.64	0.86	11.27	0.46
Blood	34.72	6.01	6.13	0.83
Kidneys	1.91	0.16	1.72	0.06
Bladder	0.07	0.00	0.79	0.08
Lung	6.04	0.31	3.41	0.26
Liver	41.67	2.51	53.76	1.08
Spleen	1.29	0.18	3.16	0.46
Stomach	0.48	0.18	0.54	0.10
S. intestine	1.58	0.45	10.63	0.25
L. intestine	1.09	0.21	0.83	0.16
Heart	0.63	0.11	0.47	0.03
Thyroid	0.09	0.05	0.05	0.01
Carcass	0.00	0.00	7.21	0.58
Injection site	11.79	15.54	2.34	0.45

Counts/gram ratio

Heart/blood	0.26	0.06	1.13	0.08
Heart/muscle	6.08	0.67	4.53	0.33
Heart/liver	0.17	0.03	0.10	0.00
Brain/blood	0.02	0.00	0.03	0.00
Brain/muscle	0.52	0.02	0.11	0.00

= standard deviation of three animals

Table 6.2.

Animal biodistribution data for $[^{99}Tc(NO)(diars)_2Cl]^+$

% injected dose/organ

	2 min sacrifice		60 min sacrifice	
	mean	S.D.#	mean	S.D.*
Muscle	25.54	4.81	30.99	7.65
Kidneys	8.80	1.74	3.38	2.60
Bladder	2.45	2.08	4.54	3.80
Lung	0.66	0.23	0.08	0.01
Liver	11.86	0.54	4.62	1.40
Spleen	0.91	0.12	0.71	0.24
Heart	1.33	0.00	1.14	0.25
Brain	0.06	0.09	0.07	0.01
Carcass and gut	48.48	4.12	55.81	6.37
Injection site	0.70	0.09	2.75	2.74
Counts/gram ratio				
Heart/muscle	6.35	0.83	5.41	3.38
Heart/liver	1.40	0.08	3.13	0.05
Heart/lung	2.68	0.40	19.42	5.18

= standard deviation of two animals

* = standard deviation of three animals

6.5. Crystal structure determinations.

6.5.1. Attempted crystal structure determination of the chloronitrosyl-bis-(dppe)technetium(I) cation.

A fine needle shaped crystal was selected for the structure determination. From the preliminary Weissenberg photographs it was found that the tetraphenylboron bis (bisdiphenylphosphinoethane)chloronitrosyltechnetium(I) $[(C_6H_5)_4B][Tc(NO)(C_{26}H_{24}P_4)_2Cl]$ crystal is monoclinic, space group $P2_1/a$, with cell dimensions of a=25.75, b=24.21, c=10.97Å, β=98.11°.

However early in the solution of the structure it became clear that because of the similarity, electronically, of P, Cl and NO that the structure was disordered. The technetium core was confirmed to be six co-ordinate but the ligands could not be resolved with the data collected from the crystal selected.

6.5.2. Crystal structure determination of chloronitrosyl-bis-(diars)technetium(I)chloride tetrabutylammonium chloride.

The chunky rhomboid shaped crystals appeared suitable for X-ray analysis and after preliminary observation under a polarising microscope were passed to Birmingham University for a structure determination.

The compound crystallises in the space group C2/c and it is found that the nitrosyl and chloride are again disordered. The technetium is confirmed to be six coordinate with the two diars ligands in the axial plane and the disordered nitrosyl and chlorine atoms trans to each other.

A summary of the crystal structure determination is described in Appendix IV.

6.6. Discussion.

The preparation and biological distribution of technetium complexes with diphosphine and diarsine ligands has been well explored by Deutsch and his coworkers. Reaction of the ligand (L) with either $[^{99}TcX_6]^{2-}$ (X = Cl or Br) or $[^{99m}TcO_4]^-$ leads to the series of complexes of the general formula $[Tc(III)L_2X_2]^+$. Where the ligand acts both as the reductant and chelating agent.

$[Tc(NO)Cl_4]^-$ reacts with dppe or diars in ethanolic solution to give $[Tc(I)(NO)(dppe)_2Cl]^+$ and $[Tc(I)(NO)(diars)_2Cl]^+$ respectively. Infra red spectra of the complexes show strong absorptions at $1775cm^{-1}$ for the dppe complex and $1720cm^{-1}$ for the diars complex which is typical of the $\nu(NO)$ stretching vibration in linear nitrosyls as seen in Table 1.3.

Confirmation of the linear nitrosyl is provided by the crystal structure of the diars complex which crystallises as

$[Tc(NO)(diars)_2Cl]Cl.[(C_4H_9)_4N]Cl$. Due to disorder of chlorine and nitrosyl in the crystal the solution was refined by calculating the position of the nitrogen and oxygen atoms relative to a chlorine atom with occupancy factors of 0.5.

Using this model, the Tc-N-O bond angle is virtually linear (179.9°) and because of this detailed discussion would not be appropriate. However, the average Tc-As distance of 2.492(12)Å is in close agreement with the comparable bonds in $[Tc(III)(diars)_2Cl_2]^+$ (2.512(2)) (106) and $[Tc(diars)_2Cl_4]^+$ (2.514(3)Å) (21). The Tc-Cl bond length of 2.411(13)Å is slightly longer than those in the above technetium(III) complexes. This would be expected of a ligand trans to the nitrosyl and particularly where the ligands in the equatorial plane are competing for electron density from the technetium with the nitrosyl. Both the Tc-N backbonding and the chelating effect of the two diars ligands will be stabilising the complex in oxidation state 1.

The As-Tc-As bond angle of 83.1(1)° is also comparable with those reported for the above complexes (82.4(1)° and 83.5(1)° respectively).

Ortep diagrams of the complex cation and of both cations as positioned in the unit cell are given in Figures 1. and 2. of Appendix IV together with bond lengths and angles in Tables 1. and 2. respectively.

As noted above a combination of disorder in the crystal and poor quality data prevented a structure determination on $[Tc(I)(NO)(dppe)_2Cl][(C_6H_5)_4B]$. However, during their parallel studies, Amersham International isolated and solved the crystal structure of the chloride salt (162) confirming, as expected, a slightly distorted octahedral geometry with the dppe ligands in the equatorial plane and the nitrosyl and chloride occupying the axial positions (Figure 6.3).

The FAB+ mass spectrum of $[Tc(I)(NO)(dppe)_2Cl]^+$ has a major ion at $^M/_z$=960 calculated for ($C_{52}H_{48}NOClTcP_4$) $^M/_z$=960 due to $[Tc(NO)(dppe)_2Cl]^+$. Fragmentation occurs via the loss of one chlorine to $^M/_z$=925. The ion at $^M/_z$=562 is due to the loss of a dppe ligand to give $[TcNO(dppe)Cl]^+$. It would appear therefore that loss of the chloride ligand is facile and would be amenable to ligand exchange which would not be unexpected due to the trans labilising effect of the nitrosyl.

The FAB+ mass spectrum of $[Tc(I)(NO)(diars)_2Cl]^+$ has a major ion at $^M/_z$=736 (calculated for $C_{20}H_{32}As_2NOClTc$ $^M/_z$=736). Fragmentation occurs via the loss of the nitrosyl to $^M/_z$=706 and the ion at $^M/_z$=450 is due to $[Tc(NO)(diars)Cl]^+$.

The ^1H NMR spectra of the complexes are complicated. The spectrum of the dppe complex shows broad unresolved singlets at 2.95, 2.80, 2.50 and 1.70 ppm. as the protons of the ligand are not equivalent due to the positioning of the phenyl groups.

The diars spectrum shows clearly the two types of proton of the phenyl groups. However the methyl groups are not clearly resolved and appear as four multiplets around 2 ppm.

The animal biodistribution data of the no carrier added $[Tc(NO)(dppe)_2Cl]^+$ cation shows that initially blood and liver values are very high although there does appear to be some heart uptake. This however could be largely due to blood pool. Over time the level of activity in the blood clears whilst liver activity increases and muscle uptake remains virtually the same. The lipophilic complex clears through the liver, hence the increase in activity in the small intestine and the heart/muscle ratio does improve over time.

The biodistribution of the carrier added $[Tc(NO)(diars)_2Cl]^+$ complex also shows interesting results. Initially high liver uptake clears significantly and muscle uptake remains constant over the 60 minutes. The heart/lung and heart/liver ratios improve over time and genuine heart uptake of this complex is again observed.

The presence of the Tc-NO moiety significantly alters the biodistribution of these complexes from their $[Tc(III)L_2X_2]^+$ equivalents as heart uptake and clearance from the blood and liver are not normally associated with these complexes.

In conclusion then lipophilic technetium(I) cations containing phosphine and arsine chelating ligands can be prepared from the ligand exchange reaction of $[Tc(NO)Cl_4]^-$. The biological distribution of these complexes is found to differ from their analogous complexes where the nitrosyl is replaced by chlorine.

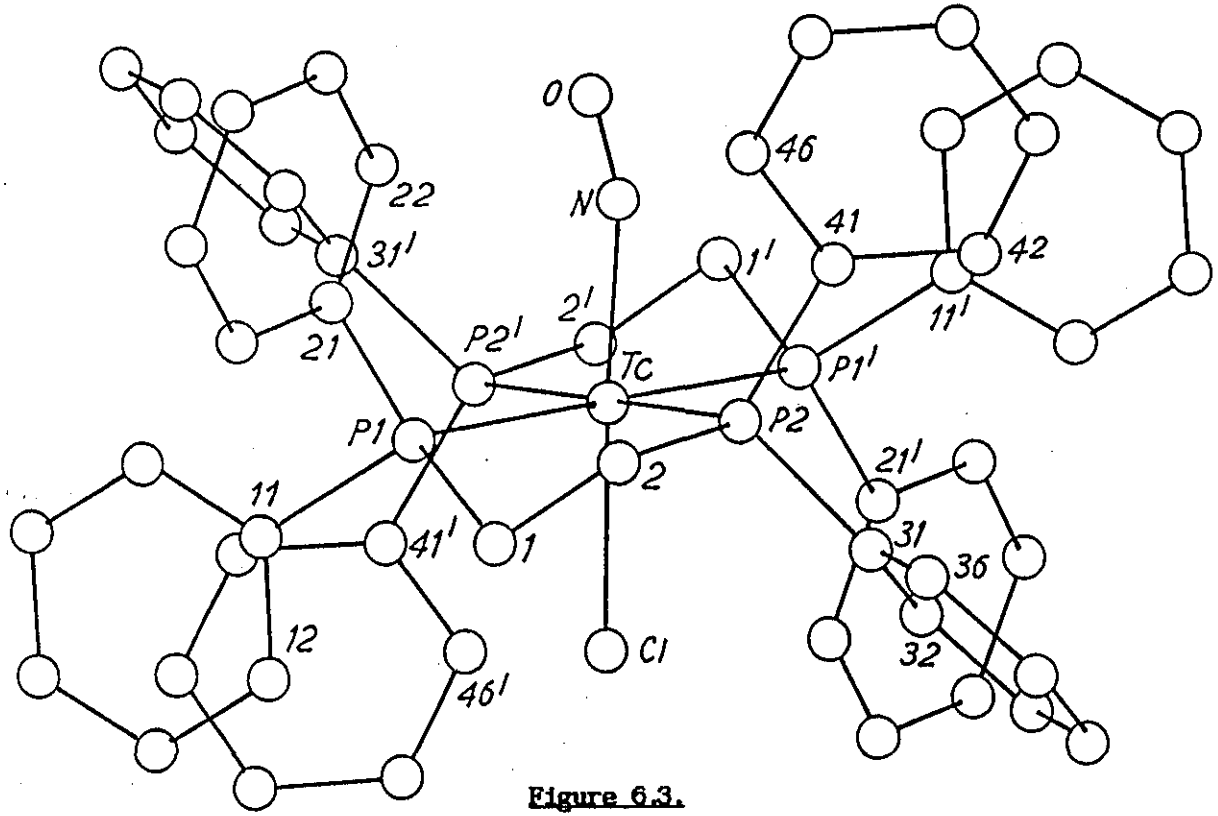


Figure 6.3.

The molecular structure of the $[Tc(I)(NO)(dppe)_2Cl]^+$ cation.

(Extracted from reference 163.)

CHAPTER 7

SYNTHESIS, CHARACTERISATION AND BIOLOGICAL STUDIES OF TECHNETIUM NITROSYL COMPLEXES OF 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDINE

7.1. Introduction.

As noted in chapter 1, until recently very few low valent technetium complexes containing phen or bipy had been reported. Taube has reported the only nitrosyl complexes $[Tc(NO)(NH_3)(phen)_2]^{2+}$ and $[Tc(NO)(NH_3)_2(phen)(H_2O)]^{2+}$(30) but that area of work was not expanded.

Depending on the reaction conditions the complexes $[Tc(NO)(phen)_2Cl]^+$, $[Tc(NO)(phen)Cl_3]$ and $[Tc(NO)(bipy)Cl_3]$ have been prepared where the technetium atom is in oxidation states (I), (II) and (II) respectively. The complexes have been characterised by mass spectrometry and the biological distribution of the neutral complexes studied

7.2. Synthesis of the complexes.

7.2.1. Synthesis of carrier added $[^{99}Tc(I)(NO)(phen)_2Cl]^+$.

To an aqueous solution of ammonium pertechnetate (1ml., 0.15mM) was added concentrated hydrochloric acid (1ml) and the mixture heated for 30 minutes. The product of the reaction is $[TcCl_6]^{2-}$ as the yellow ammonium salt. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine in water (1ml, 2.3M), and heated for a further 30 minutes. The resulting green solution contains the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). Addition of tetrabutylammonium chloride solution (75% in water) allowed extraction of the $[Tc(NO)Cl_4X]^-$ into dichloromethane (5ml). The dichloromethane was evaporated off to leave a green solid which was redissolved in methanol (10ml) and 1,10-phenanthroline (54mg, 3mM) added. The mixture was stirred until a dark green colour resulted. Slow evaporation of the solvent led to the formation of dark green crystals.

7.2.2. Synthesis of no carrier added $[^{99m}Tc(I)(NO)(phen)_2Cl]^+$.

To 1 ml of generator eluant was added 1 ml of concentrated HCl. The mixture was heated in a pressure cooker for 30 minutes. The product of the reaction is sodium hexachlorotechnetate. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine hydrochloride (1ml, 2.3M) and heated for a further 30 minutes. The resulting solution contains

the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). To this solution was added a solution of 1,10-phenanthroline (1ml, 80mM in 50:50 ethanol:water). The reaction proceeds at room temperature over 1.5 to 2 hours or after heating in the pressure cooker for 30 minutes.

7.2.3. Synthesis of carrier added $[^{99}Tc(II)(NO)(phen)Cl_3]$.

To an aqueous solution of ammonium pertechnetate (1ml., 0.15mM) was added concentrated hydrochloric acid (1ml) and the mixture heated for 30 minutes in a pressure cooker . The product of the reaction is $[TcCl_6]^{2-}$ as the yellow ammonium salt . The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine in water (1ml, 2.3M), and heated for a further 30 minutes in a pressure cooker. The resulting green solution contains the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). To 2ml of this solution was added 1,10-phenanthroline (33mg, 0.18mM) and ethanol (1ml). The mixture was heated in the pressure cooker for 30 minutes. The reaction mixture was allowed to cool undisturbed while the product crystallised out as dark green needles.

7.2.4. Synthesis of no carrier added $[^{99m}Tc(II)(NO)(bipy)Cl_3]$.

To 1 ml of generator eluant was added 1 ml of concentrated HCl. The mixture was heated in a pressure cooker for 30 minutes. The product of the reaction is sodium hexachlorotechnetate. The

resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine hydrochloride (1ml, 2.3M) and heated for a further 30 minutes. The resulting solution contains the species $[Tc(NO)Cl_4X]^-$ (X =Cl^-, H_2O). To this solution was added bipy (1.5ml, 0.1M in 50:50 ethanol:water) and the reaction allowed to proceed at room temperature for 2 hours.

7.2.5. Synthesis of carrier added $[^{99}Tc(II)(NO)(bipy)Cl_3]$.

To an aqueous solution of ammonium pertechnetate (1ml., 0.15mM) was added concentrated hydrochloric acid (1ml) and the mixture heated for 30 minutes. The product of the reaction is $[TcCl_6]^{2-}$ as the yellow ammonium salt. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine in water (1ml, 2.3M), and heated for a further 30 minutes. The resulting green solution contains the species $[Tc(NO)Cl_4X]^-$ (X=Cl, H_2O). To 2ml of this solution was added bipy (32mg, 0.2mM) and ethanol (1ml) and the mixture heated in the pressure cooker for 30 minutes. The reaction solution was allowed to cool undisturbed while the product crystallised out as green needles.

7.2.6. Preparation of carrier added $[^{99}Tc(II)(NO)(phen)Cl_3]$ for biodistribution studies.

3.6mg of the crystals as prepared above (7.2.3.) were dissolved in 50:50 ethanol:water to give a solution which was not purified further before injection.

7.2.7. Preparation of carrier added [^{99}Tc(II)(NO)(bipy)Cl$_3$] for biodistribution studies.

3.3mg of the crystals as prepared above (7.2.5) were dissolved in 50:50 ethanol:water to give a solution which was not purified further before injection.

7.3. Results.

7.3.1. Paper chromatography.

Complex	R_f in butan-2-one	R_f in saline
$[Tc(NO)(phen)_2Cl]^+$	0.85(2)	0.89(4)
$[Tc(NO)(phen)Cl_3]$	0.54(3)	0.73(5)
$[Tc(NO)(bipy)Cl_3]$	0.82(3)	0.85(4)

7.3.2. Electrophoresis.

The complex $[Tc(NO)(phen)_2Cl]^+$ moves a distance of 2.2cm per hour ($2.68 Vcm^{-2}$) towards the cathode.

No electrophoretic movement is observed for $[Tc(NO)(phen)Cl_3]$ or $[Tc(NO)(bipy)Cl_3]$

7.3.3. Infra-red spectra.

(As KBr disc)

$[Tc(NO)(phen)_2Cl]^+$ has $\nu(NO)$ at $1800cm^{-1}$ and $\nu(Tc-Cl)$ at $340cm^{-1}$

$[Tc(NO)(phen)Cl_3]$ has $\nu(NO)$ at $1770cm^{-1}$ and $\nu(Tc-Cl)$ at $330cm^{-1}$.

$[Tc(NO)(bipy)Cl_3]$ has $\nu(NO)$ at $1780cm^{-1}$ and $\nu(Tc-Cl)$ at $326cm^{-1}$

7.3.4. Analysis

$[Tc(NO)(phen)Cl_3]$

(calculated for $C_{12}H_8N_4OCl_3Tc.HCl$)

C 31.3(31.8), H 1.8(2.0), N 9.7(9.3)%

$[Tc(NO)(bipy)Cl_3]$

(calculated for $C_{10}H_8N_3OCl_3Tc$)

C 31.2(30.6), H 2.3(2.1), N 10.5(10.7)%

7.3.5. FAB mass spectra.

	Major ion m/z	Lower mass ions m/z
$[Tc(NO)(phen)_2Cl]^+$	524	
$[Tc(NO)(phen)Cl_3]$	414	379
		344
		309
$[Tc(NO)(bipy)Cl_3]$	434	399
		320
		290

The FAB mass spectra for $[Tc(NO)(phen)Cl_3]$ and $[Tc(NO)(bipy)Cl_3]$ are given in Figures 7.1. and 7.2. respectively.

7.3.6. Biodistribution studies.

The animal biodistribution data for $[Tc(NO)(phen)Cl_3]$ and $[Tc(NO)(bipy)Cl_3]$ are given in Tables 7.1. and 7.2. respectively.

Figure 7.1.

FAB mass spectrum of [Tc(NO)(phen)Cl$_2$].

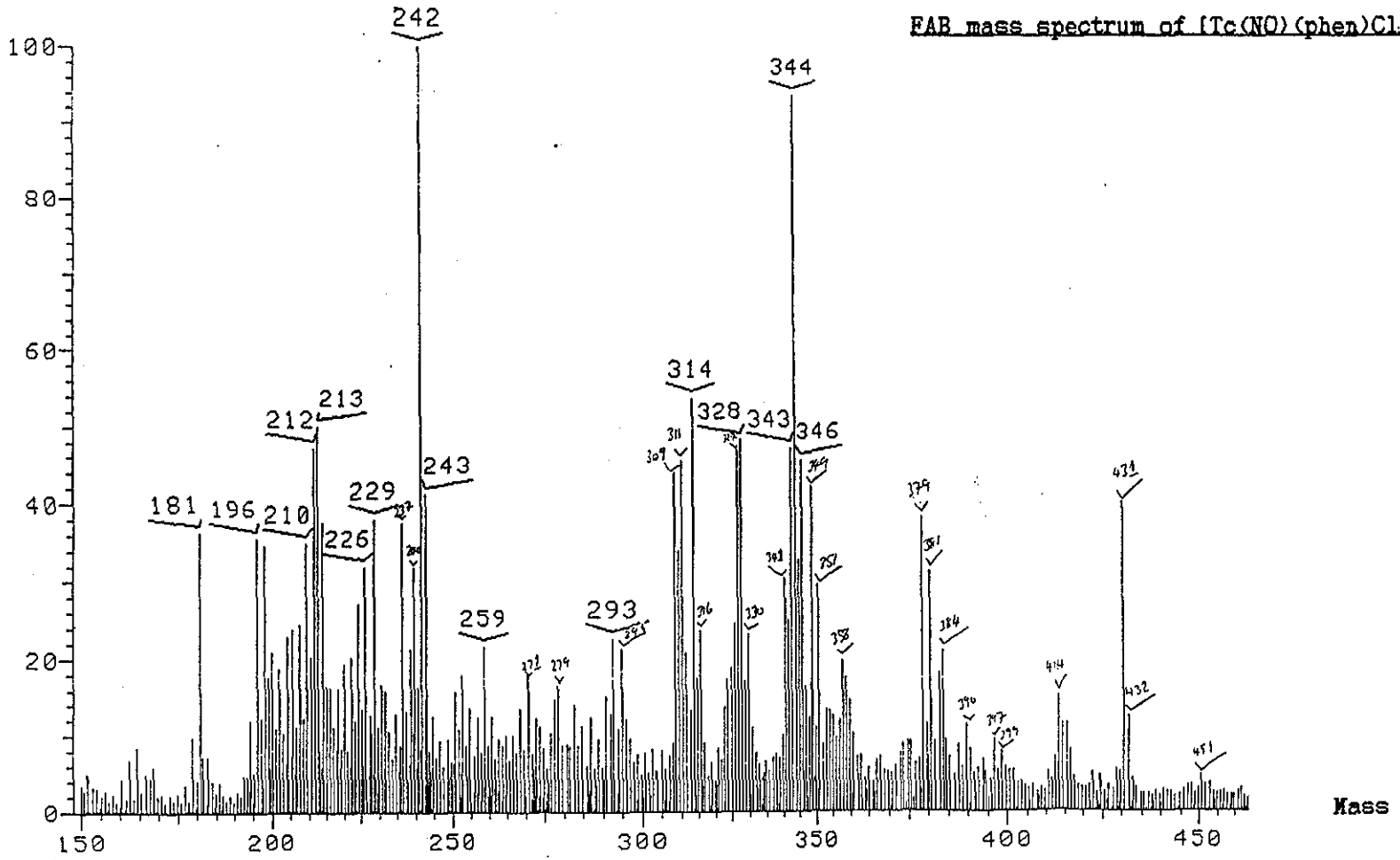


Figure 7.2.

FAB mass spectrum of [Tc(NO)(bipy)Cl$_3$].

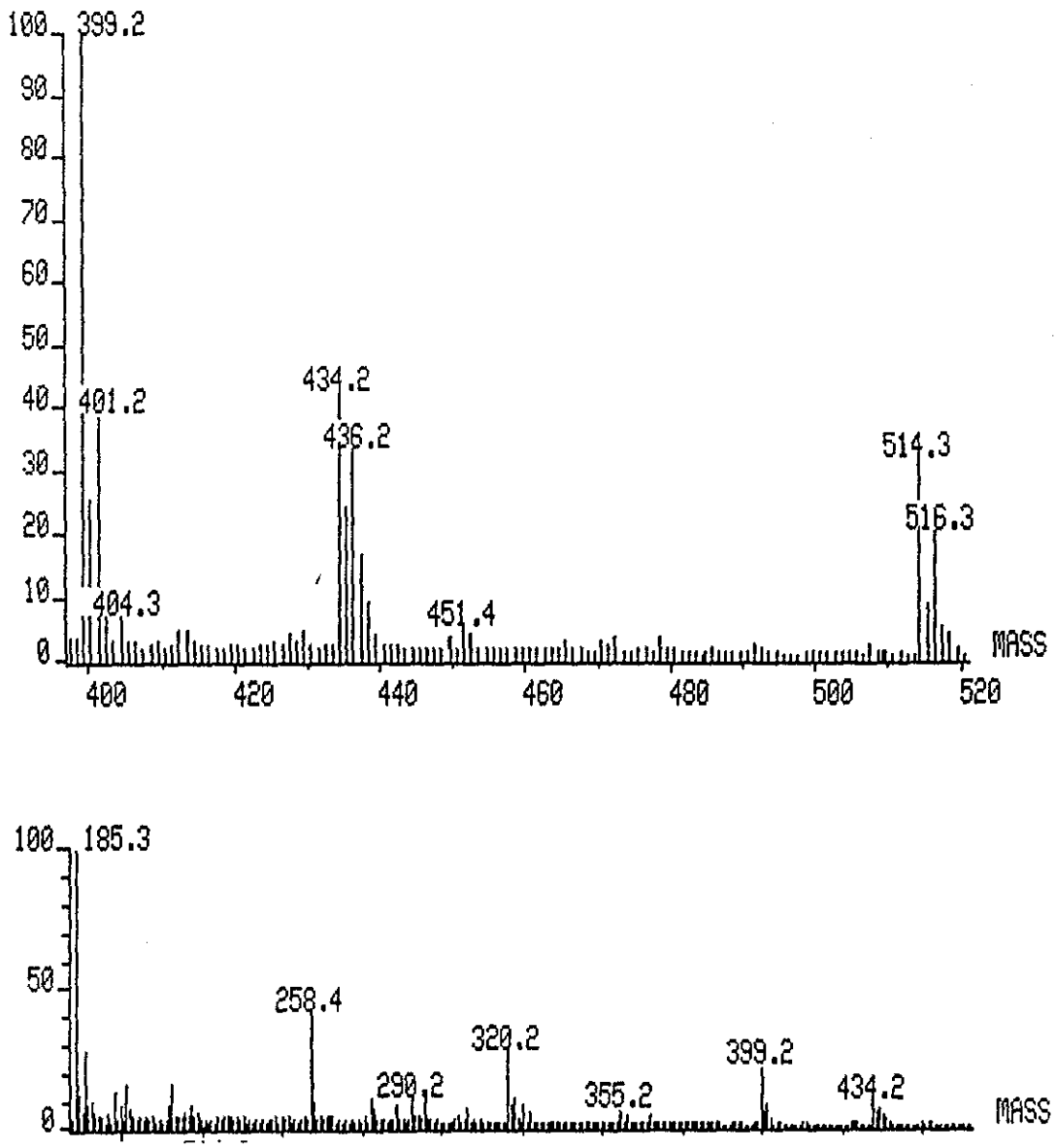


Table 7.1.

Animal biodistribution data for [^{99}Tc(NO)(phen)Cl$_2$].

% injected dose/organ

	2 min sacrifice		60 min sacrifice	
	mean	S.D.*	mean	S.D.*
Muscle	22.83	5.35	17.02	0.99
Blood	3.98	1.37	3.49	0.67
Kidney	1.47	0.70	1.88	0.57
Bladder and urine	0.50	0.47	14.17	1.64
Lung	0.67	0.45	0.23	0.11
Liver	0.16	0.03	0.46	0.26
Spleen	0.21	0.07	0.23	0.03
Heart	0.40	0.13	0.29	0.03
Brain	0.08	0.03	0.04	0.00
Carcass and gut	67.70	4.72	62.20	0.96

Counts/gram ratio

Heart/blood	1.59	0.38	1.36	0.19
Heart/muscle	1.99	0.47	4.68	4.53
Heart/liver	35.14	17.06	10.63	5.60
Heart/lung	1.55	1.16	2.57	1.11

= standard deviation of three animals

Table 7.2.

Animal biodistribution data for [^{99m}Tc(NO)(bipy)Cl$_2$].

% injected dose/organ

	2 min sacrifice		60 min sacrifice	
	mean	S.D.*	mean	S.D.*
Muscle	24.17		18.95	3.76
Blood	7.17		2.02	0.36
Kidneys	2.64		1.08	0.24
Bladder and urine	8.66		21.88	6.88
Lung	0.45		0.10	0.03
Liver	3.43		3.35	0.53
Spleen	0.20		0.31	0.06
Heart	0.32		0.30	0.05
Brain	0.06		0.04	0.01
Carcass and gut	52.92		51.97	5.21
Count/gram ratio				
Heart/blood	0.99		2.12	0.92
Heart/muscle	1.69		2.02	0.36
Heart/liver	1.31		1.09	0.18
Heart/lungs	1.30		4.13	0.87

* = two animals only (poor injection in one of the three)

= standard devitation of three animals

7.4. Crystal structure - preliminary investigations

A suitable crystal was selected for X-ray analysis and it was established that the bipyridyltrichloronitrosyltechnetium(II) $[Tc(NO)(C_{10}H_8N_2)Cl_3]$ crystal is monoclinic, space group $P2_1/c$, with cell dimensions of a=8.18, b=6.90, c=13.124Å, β=112.16°.

The crystal structure was abandoned because of the poor quality of data from the crystal.

7.5. Discussion.

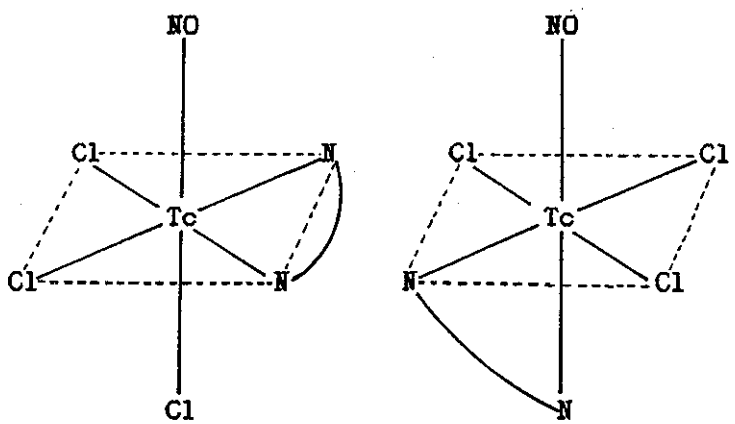
The reaction of $[Tc(NO)Cl_4]^-$ with phen or bipy proceeds to either $[Tc(NO)(phen)_2Cl]^+$, $[Tc(NO)(phen)Cl_3]$ or $[Tc(NO)(bipy)Cl_3]$ depending on the reaction conditions.

$[^{99m}Tc(NO)(phen)_2Cl]^+$ is prepared in the presence of chloride with an excess of ligand relative to the technetium concentration. For the reaction to proceed on a carrier added scale it was found necessary to remove excess chloride from the aqueous preparation or to start the reaction from solid $[Tc(NO)Cl_4][(C_4H_9)_4N]$.

In aqueous high chloride concentrations the neutral species $[^{99}Tc(NO)(phen)Cl_3]$ and $[^{99}Tc(NO)(bipy)Cl_3]$ are formed even with forcing conditions (heat and pressure).

The FAB+ mass spectrum of $[Tc(NO)(phen)_2Cl]^+$ has a major ion at $^M/_z$= 524 (calculated for $C_{24}H_{16}N_5OClTc$ $^M/_z$= 524) confirming the structure of the cation.

The $[Tc(NO)(phen)Cl_3]$ and $[Tc(NO)(bipy)Cl_3]$ complexes have two possible configurations, (a) with the one of the nitrogens of the ligand cis to the nitrosyl or (b) trans as in the nitrosyl acac complex described in chapter 5.



(a) (b)

Evidence that a cis complex is formed is provided by the FAB mass spectrum of $[Tc(NO)(bipy)Cl_3]$. This was obtained by dissolving the complex in pyridine and as a result the spectrum shows a major ion at $^M/_z$=434 (calculated for $[Tc(NO)(bipy)Cl_2py]^+$). Fragmentation occurs by loss of chlorine to $^M/_z$=399 (calculated as $[Tc(NO)(bipy)Cl_2py]$), loss of pyridine to $^M/_z$=320 (calculated

for [Tc(NO)(bipy)Cl] and loss of the nitrosyl ligand $^{M}/_{z}$=290 (calculated for [Tc(bipy)Cl].

The trans lablilising effect of the nitrosyl ligand has been observed in other complexes and, given the chelating effect of the bipyridine ligand, it would not be unexpected that ligand exchange of the chloride opposite the nitrosyl would take place in solution.

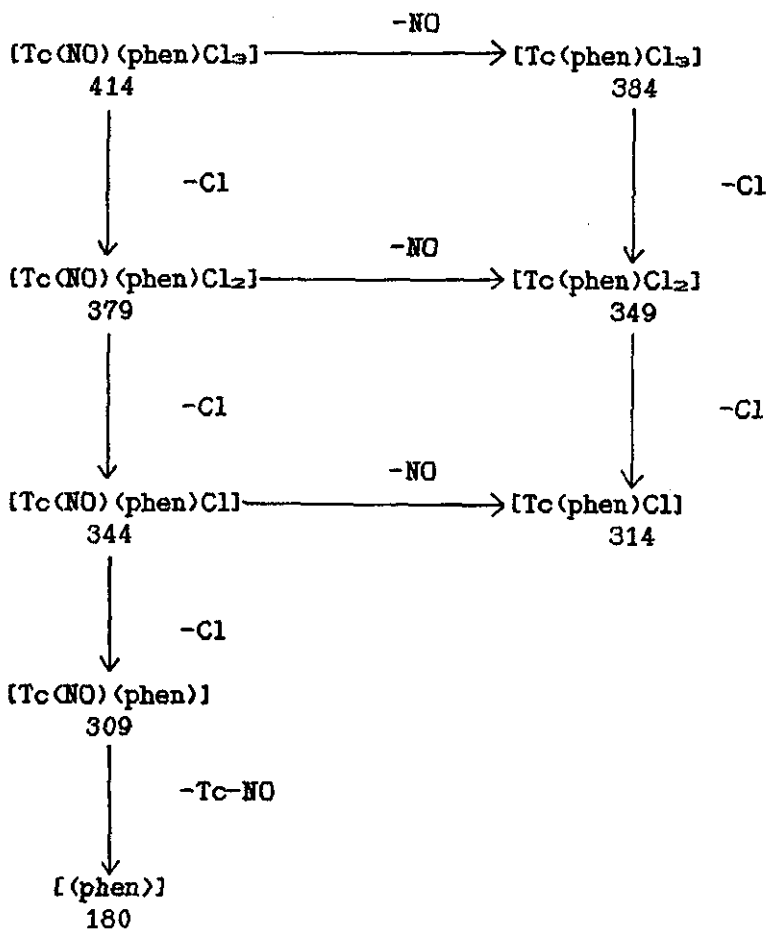
The spectrum also shows an ion at $^{M}/_{z}$=514 which may be attributable to a pyridinium salt of the complex.

The FAB mass spectrum of [Tc(NO)(phen)Cl_3] has a major ion at $^{M}/_{z}$=414 (calculated for $C_{12}H_8N_3OCl_3Tc$ $^{M}/_{z}$=414). Fragmentation occurs by the successive loss of each chlorine to $^{M}/_{z}$=379 [Tc(NO)(phen)Cl_2], $^{M}/_{z}$=344 [Tc(NO)(phen)Cl] and $^{M}/_{z}$=309 [Tc(NO)(phen)]. In addition there is for each of the above ions the corresponding ion through loss of the nitrosyl group. The fragmentation scheme is set out in Figure 7.3.

The FAB mass spectrum of [Tc(NO)(phen)Cl_3] suggests from the facile loss of the chlorine that this too may be trans to the nitrosyl with the phenanthroline ligand cis.

Figure 7.3.

FAB mass spectrum - fragmentation ions ($^{m}/_{z}$) of [Tc(NO)(phen)Cl_3]



The animal biodistribution data for the [Tc(NO)(phen)Cl_3] complex shows initial high muscle uptake which clears a little with time through the kidneys. There is almost no liver uptake and the level of activity in the blood does not clear. Heart uptake is modest.

The biodistribution data for the [Tc(NO)(bipy)Cl_3] is slightly different showing higher blood uptake and more liver. Muscle uptake is higher and the complex appears to clear more quickly. Again heart uptake of the complex is not significant.

Neither complex shows significant brain uptake which may be expected of a neutral complex, however, this could be an indication that they are not lipophilic enough, or that the nitrosyl is causing this change in the biological activity.

Without solutions of the crystal structures the configurations of the neutral complexes cannot be confirmed.

CHAPTER 8

SYNTHESIS, CHARACTERISATION AND BIOLOGICAL STUDIES OF THE CHLORONITROSYLTETRA(t-BUTYLISONITRILE) TECHNETIUM(I) CATION

8.1. Introduction.

The series of complexes of the general formula $[Tc(CNR)_6]^+$ have been well studied and characterised because of their potential as myocardial imaging agents. The parent compound where R = t-butyl is clinically the most advanced. Efforts to alter the disadvantages associated with these complexes, mostly high lung and liver uptake, have resulted in attempts to exchange one or more of the isonitrile ligands for a different isonitrile or entirely different ligand altogether.

Earlier efforts had resulted in the exchange of all six isonitriles for another isonitrile but more recently mixed complexes of the formula $[Tc(CNR^1)_k(CNR^2)_{6-k}]^+$ where R^1 and R^2 may be t-butyl-, cyclohexyl-, or (ethoxycarbonyl)methyl- and k = 0 - 6 have been prepared on a carrier added scale at least (129).

The mixed isonitrile/diphosphine complex $[Tc(CNR)_2(DEPE)_2]^+$ has been prepared on a no carrier added scale and has been tested in animals and humans for biological activity (83,84).

Mixed isonitrile/triphenylphosphine complexes have also been prepared and characterised and are described in more detail in chapter 1 (1.3.4).

Other studies of the reaction of $[^{99m}Tc(CNt\text{-butyl})_6]$ with NO gas at various temperatures found that a mixture of products is formed. Biological studies in rats of each component of the mixture showed different biological distributions but none with significant heart uptake. One of the complexes produced good images of the gall bladder in a human subject. The same reaction was attempted with the cyclohexyl- and benzyl- isonitrile analogues, the latter showing some myocardial uptake in the same human volunteer (162).

The nitrosyl/isonitrile complexes $[Tc(NO)(CNt\text{-butyl})_5]^{2+}$ and $[Tc(NO)(CNt\text{-butyl})_3Br_2]$ have been prepared. The latter complex was prepared from $[Tc(NO)Br_4]^-$ in an attempt to displace all four bromides by t-butyl isonitrile.

It has been found here that the reaction of $[Tc(NO)Cl_4]^-$ with t-butyl isonitrile does undergo complete ligand exchange to give $[TC(I)(NO)(CNt\text{-butyl})_4Cl]^+$. The complex has been characterised by

spectra. The biological distribution of the complex has also been examined.

8.2. Synthesis of the complex.

8.2.1. Synthesis of carrier added $[^{99}Tc(I)(NO)(CNt\text{-}butyl)_4Cl]^+$

To an aqueous solution of ammonium pertechnetate (1ml., 0.15mM) was added concentrated hydrochloric acid (1ml) and the mixture heated for 30 minutes. The product of the reaction is $[TcCl_6]^{2-}$ as the yellow ammonium salt. The resulting solution was cooled, diluted with water (1ml), mixed with a solution of hydroxylamine in water (1ml, 2.3M), and heated for a further 30 minutes. The resulting green solution contains the species $[Tc(NO)Cl_4X]^-$ (X = Cl^-, H_2O). Addition of tetrabutylammonium chloride solution (75% in water) allowed extraction of the $[Tc(NO)Cl_4X]^-$ into dichloromethane (5ml). The dichloromethane was evaporated off to leave a green solid which was redissolved in ethanol (20ml) and t-butylisonitrile (0.055ml, 0.9mM) added. The mixture was refluxed under nitrogen for 3 hours undergoing a colour change from bright green through dark green to pale yellow. The reaction mixture was cooled in ice and sodium hexafluorophosphate (100mg in 1ml) added. The white precipitate of tetrabutylammonium hexafluorophosphate was removed by filtration. The solvent was evaporated down to 10ml and the product crystallised as fine pale yellow needles on cooling.

8.2.2. Preparation of carrier added $[^{99}Tc(I)(NO)(NCt\text{-}butyl)_4Cl]^+$ for biological studies.

5.3 mg of the crystals prepared at 8.2.1 above were dissolved in 2 mls of 50:50 ethanol:water. No further purification was performed before injection of the complex.

8.3. Results.

8.3.1. Electrophoresis.

The complex moves 2.0cm ($8.75Vcm^{-1}$) in 1 hour toward the cathode.

8.3.2. Infra-red spectrum.

(KBr Disc) Absorptions at $1765cm^{-1}$ for $\nu(NO)$, $2195cm^{-1}$ for $\nu(CN)$.

8.3.3. ^1H NMR.

1.65 (singlet) ppm.

8.3.4. FAB+ mass spectrum.

The FAB mass spectrum (Figure 8.1.) has a major ion at $^m/_z$ = 496 and lower mass ion at $^m/_z$ = 413.

8.3.5 HPLC.

HPLC was performed under the following conditions:

Hamilton PRP-1 column (150 x 4.1 mm), flow rate = 1.0 ml/min, gradient from 0.1M sodium acetate to 100% acetone over 17 min.

Retention time: 8.1 min.

8.3.6 Biodistribution studies.

The data for the carrier added animal biodistribution data for $[^{99}Tc(I)(NO)(CNt\text{-butyl})_4Cl]^+$ are given in Table 8.1.

Figure 8.1.

FAB+ mass spectrum of $[Tc(NO)(CNt\text{-butyl})_4Cl]^+$

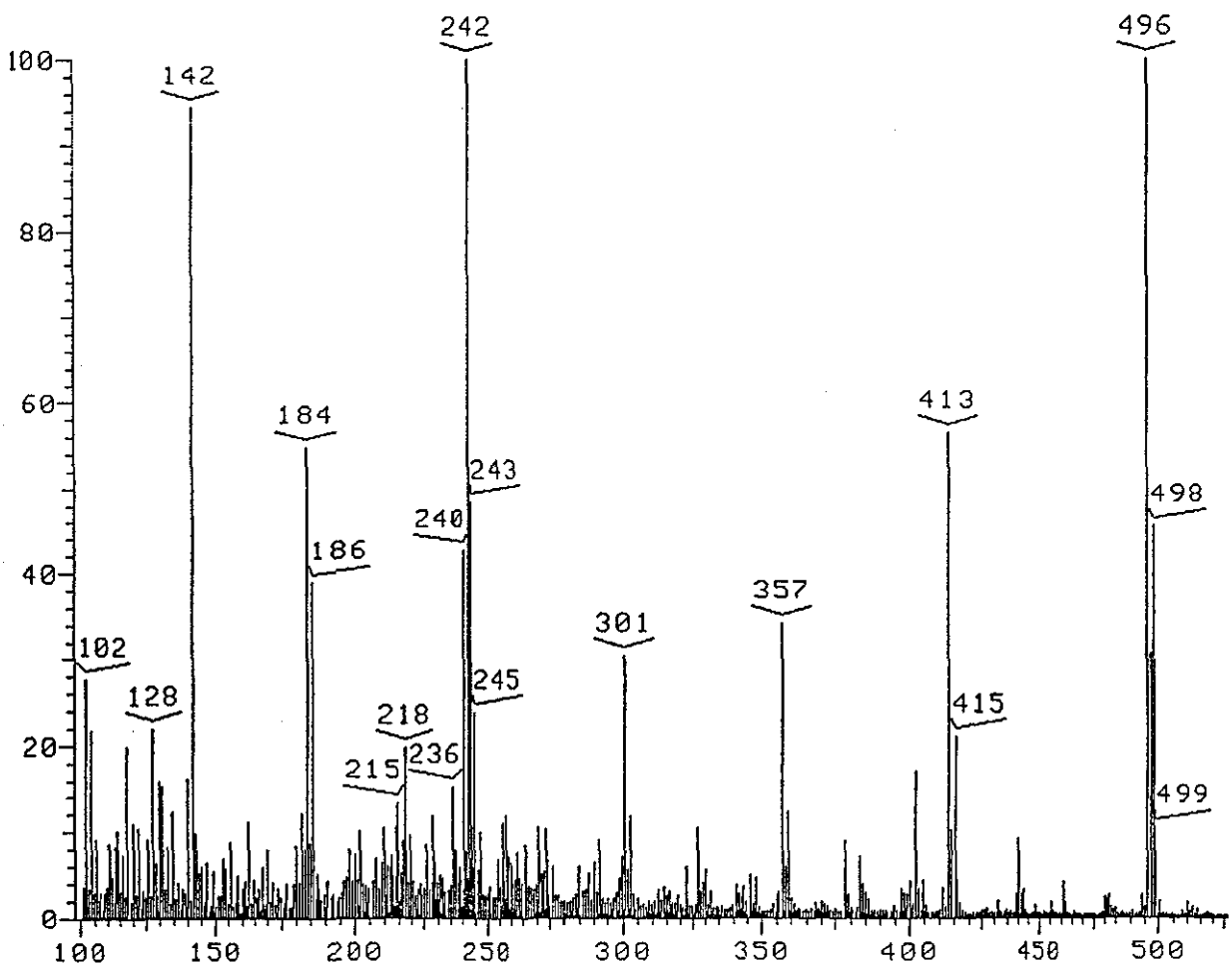


Table 8.1.

Animal biodistribution data for $[^{99}Tc(I)(NO)(CNt\text{-}butyl)_4Cl]^+$

% injected dose/organ

	2 min sacrifice		60 min sacrifice	
	mean	S.D.#	mean	S.D.#
Muscle	21.45	3.44	18.30	3.07
Blood	0.40	0.66		
Kidney	2.60	0.81	1.13	0.58
Bladder and urine	4.26	6.58	7.02	5.95
Lung	0.64	0.40	0.12	0.09
Liver	5.82	1.84	5.89	0.36
Spleen	0.56	0.23	0.26	0.09
Heart	1.09	0.28	1.37	0.28
Brain	0.04	0.01	0.04	0.02
Carcass and gut	63.14	4.02	65.76	2.66

Counts/gram ratio

Heart/muscle	6.19	1.73	8.98	2.95
Heart/liver	2.58	0.20	2.97	0.34
Heart/lung	3.34	2.35	26.02	20.69

= standard deviation of three animals

8.4. Discussion.

The reaction of $[Tc(NO)Cl_4]^-$ with t-butylisonitrile in refluxing ethanol produces $[Tc(NO)(CNt\text{-}butyl)_4Cl]^+$. There are two possible dispositions of the isonitrile ligands in the complex. Either all four ligands positioned meridionally with the chloride ligand trans to the nitrosyl or with an isonitrile ligand trans to the nitrosyl with the remaining three and a chloride in the equatorial plane.

^1H NMR spectrum of the complex shows a singlet at δ1.65 indicating that all of the isonitriles are equivalent. The chemical shift compares well with that of the complex $[Tc(NO)(CNt\text{-}butyl)_3Br_2]$ where two singlets are shown at δ1.43 and 1.47 in the ratio of 1:2, and is as expected for the two types of isonitrile in that complex (axial and equatorial) (68).

One strong C≡N stretch is seen in the infra red spectrum at 2195cm^{-1}. The high frequency of the absorption relative to the hexa-kis-t-butylisonitriletechnetium(I) complex (2090 and 2045 cm^{-1}) is indicative of a lack of backbonding to the technetium which is already being stabilised by backbonding to the nitrosyl. This, together with the fact that only one absorption is seen also implies the isonitrile ligands are positioned meridionally about the technetium. The infra red spectrum of $[Tc(NO)(CNt\text{-}butyl)_3Br_2]$ shows two C≡N absorptions at 2230 and 2160 cm^{-1}, both at high

frequency, as expected, with the higher frequency absorption being assigned to the isonitrile trans to the nitrosyl.

The FAB+ mass spectrum has a major ion at $^{M}/_{z}$ = 496 (calculated for ($C_{20}H_{36}N_5ClOTc$ $^{M}/_{z}$ = 496). Fragmentation occurs via loss of a t-butylisonitrile group to $[Tc(NO)(CNt\text{-}butyl)_3Cl]^+$ $^{M}/_{z}$ = 413. This would not be expected given the evidence provided by the IR and NMR spectra as facile loss of the ligand trans to the nitrosyl is normally expected. However, the mass spectrum does confirm the presence of four isonitrile ligands.

The animal biodistribution data show good heart uptake and retention. In addition none of the initial lung uptake associated with the hexa-kis-t-butylisonitriletechnetium(I) cation is seen and liver uptake is only moderate.

CHAPTER 9

CONCLUSION

A simple method for the preparation of $[Tc(NO)Cl_4]^-$ as an alternative starting material for the synthesis of technetium complexes has been devised. The preparation works quantitatively for both carrier added [^{99}Tc] and no carrier added [^{99m}Tc] technetium concentrations starting from the readily available pertechnetate ion. The preparation is a two stage one proceeding first to the hexachlorotechnetate anion which, following reaction with hydroxylamine, produces the nitrosyltetrachloride technetium(II) anion.

The π acid character of the nitrosyl ligand stabilises the low oxidation state of the technetium by metal-ligand backbonding. A crystal structure determination has shown the anion to be six coordinate with the four chlorines positioned equatorially to the nitrosyl. The occupancy of the position trans to the nitrosyl depends on the environment of the anion as the trans labilising effect associated with such compounds has been demonstrated.

The $[Tc(NO)Cl_4]^-$ anion readily undergoes ligand exchange with a variety of ligands. The final oxidation state of the complex depends upon the nature and character of the replacement ligands.

Both technetium (I) cations and technetium(II) neutral complexes have been prepared by the reactions described in this work.

This potential for complex variation gives rise to an great number of possible new radiopharmaceuticals containing the Tc-NO moiety where choice of size, shape and charge is important in the design of these agents.

Biological studies in rats of the complexes prepared show that the presence of the nitrosyl significantly changes the biodistribution of the complexes where the coordinated ligand are diphosphines, diarsines or isonitrile. However, as most commercial radiopharmaceuticals come in the form of a freeze dried kit which is reconstituted on the addition of generator eluant, in its present formulation the two stage reaction is a disadvantage.

Regardless of this disadvantage, which could be overcome, this preparation of $[Tc(NO)Cl_4]^-$ provides a low valent alternative to the oxo- and dioxo- cores common in the higher oxidation state complexes of technetium which is readily amenable to ligand exchange both at carrier added and no carrier added concentrations.

CHAPTER 10

FURTHER WORK

This project can now be developed in two directions. There is obviously a great potential to fully explore the chemistry of technetium nitrosyls and to prepare and characterise a vast range of complexes from $[Tc(NO)Cl_4]^-$. ^{99}Tc NMR is not widely used and the technetium(I) complexes provide another opportunity for this line of research.

However, many of the groups currently studying the inorganic chemistry of technetium do so with one eye on the radiopharmaceutical chemistry and the potential application of their complexes for this purpose.

As already mentioned the two stage preparation of $[Tc(NO)Cl_4]^-$ is not ideal from a radiopharmaceutical point of view. Ideally, the reaction should be one step from pertechnetate. This project has already been developed in this direction by Amersham and their findings have been published (163, 164). However, forcing conditions and high concentrations of hydroxylamine are still to be overcome before a suitable commercial kit version of the reaction can be prepared.

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APPENDIX I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR

$[(C_4H_9)_4N][Tc(NO)Cl_4(CH_3OH)]$

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TCNOCL4

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	2	0	22	23	4	10	0	24	23	-3	5	1	33	-34	-5	9	1	15	14	-3	3	2	75	74
1	2	0	43	-36	5	10	0	28	-26	-2	5	1	19	-9	-4	9	1	18	-18	-2	3	2	18	20
2	2	0	8	18	6	10	0	24	24	-1	5	1	26	22	-2	9	1	20	21	-1	3	2	188	-179
4	2	0	115	108	7	10	0	14	-14	0	5	1	51	-55	-1	9	1	12	14	0	3	2	53	-44
1	3	0	49	-44	2	11	0	15	-13	1	5	1	40	-41	0	9	1	22	22	1	3	2	52	48
2	3	0	66	-64	4	11	0	12	-12	2	5	1	121	-120	2	9	1	12	13	2	3	2	72	67
3	3	0	47	-45	0	12	0	37	-39	3	5	1	33	-33	4	9	1	65	67	3	3	2	49	-46
4	3	0	93	-92	1	12	0	14	-14	4	5	1	60	-61	5	9	1	14	11	4	3	2	141	139
5	3	0	32	-34	1	13	0	18	-19	7	5	1	35	37	6	9	1	68	70	5	3	2	56	-58
6	3	0	107	-105	-4	2	1	177	175	8	5	1	61	-58	-4	10	1	18	18	6	3	2	35	38
7	3	0	38	-37	-2	2	1	96	100	-8	6	1	37	-36	-3	10	1	17	-18	7	3	2	41	-42
0	4	0	19	-26	-1	2	1	85	66	-7	6	1	12	7	-2	10	1	15	12	8	3	2	15	19
1	4	0	77	-73	0	2	1	214	222	-4	6	1	28	-27	0	10	1	40	43	-8	4	2	50	50
2	4	0	131	-124	1	2	1	29	33	-2	6	1	90	-87	1	10	1	30	32	-6	4	2	39	40
3	4	0	74	-73	2	2	1	112	113	-1	6	1	44	-45	2	10	1	21	23	-5	4	2	41	39
4	4	0	76	-74	4	2	1	11	11	0	6	1	60	-60	3	10	1	22	20	-4	4	2	109	105
5	4	0	9	-7	5	2	1	54	54	1	6	1	53	-55	4	10	1	18	17	-3	4	2	22	-22
7	4	0	25	-25	-8	3	1	9	6	2	6	1	60	-61	5	10	1	28	30	-2	4	2	62	64
1	5	0	102	-99	-7	3	1	38	38	3	6	1	59	-61	6	10	1	17	-14	-1	4	2	35	-34
2	5	0	42	-42	-6	3	1	13	12	7	6	1	20	-24	7	10	1	21	22	0	4	2	34	-31
3	5	0	89	-85	-5	3	1	138	135	8	6	1	27	26	-5	11	1	23	25	1	4	2	27	25
5	5	0	11	-12	-4	3	1	82	82	-7	7	1	19	-17	-2	11	1	18	-19	3	4	2	41	35
7	5	0	19	-17	-3	3	1	182	181	-6	7	1	14	14	-1	11	1	34	35	4	4	2	69	-69
8	5	0	29	31	-2	3	1	87	-86	-5	7	1	24	-24	1	11	1	28	28	5	4	2	25	27
0	6	0	37	-39	-1	3	1	71	73	-4	7	1	12	11	2	11	1	15	15	6	4	2	51	-50
1	6	0	16	13	0	3	1	54	-51	-3	7	1	73	-73	-2	12	1	26	26	7	4	2	12	13
2	6	0	59	-55	1	3	1	40	31	-2	7	1	80	-81	0	12	1	37	39	8	4	2	58	-56
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR TCNOCL4

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0	3	19	17	-21	0	0	20	14	18	3	5	20	20	-17	-1	7	21	15	-16	2	5	23	13	12
1	3	19	23	-24	2	0	20	20	19	5	5	20	17	-10	-2	8	21	12	-10	1	2	24	13	-9
3	3	19	15	-13	4	0	20	31	30	-5	6	20	17	-15	-2	0	22	17	-17	-1	2	25	12	4
-5	4	19	15	-15	6	0	20	14	13	-3	6	20	15	-12	0	0	22	14	-16	1	3	25	13	-12
-3	4	19	17	-15	-6	1	20	12	13															

APPENDIX II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR

$[Tc(NO)(NH_3)_4(H_2O)]Cl_2$

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR COMPOUND 1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	19	17	3	7	0	35	-35	3	0	1	4	-1	-4	4	1	35	-35	2	7	1	4	-3
3	0	0	30	-30	4	7	0	17	-16	4	0	1	50	49	-3	4	1	23	-23	3	7	1	32	-32
4	0	0	71	71	5	7	0	30	30	5	0	1	23	24	-2	4	1	21	20	4	7	1	6	-5
5	0	0	23	23	6	7	0	16	16	6	0	1	40	-40	-1	4	1	46	44	5	7	1	27	27
6	0	0	29	-29	0	8	0	66	66	7	0	1	13	-12	0	4	1	27	26	6	7	1	17	17
7	0	0	15	-16	1	8	0	8	8	-7	1	1	23	23	1	4	1	18	-19	7	7	1	23	-23
1	1	0	77	-80	2	8	0	30	-30	-6	1	1	28	28	2	4	1	50	-49	-6	8	1	19	19
2	1	0	15	-13	3	8	0	16	-16	-5	1	1	17	-16	4	4	1	41	41	-5	8	1	21	21
3	1	0	32	34	4	8	0	27	27	-4	1	1	63	-63	5	4	1	18	18	-4	8	1	18	-18
4	1	0	40	41	5	8	0	17	16	-2	1	1	47	47	6	4	1	33	-33	-3	8	1	18	-17
5	1	0	33	-33	6	8	0	9	-10	-1	1	1	23	22	7	4	1	11	-11	-1	8	1	28	28
6	1	0	38	-38	7	8	0	12	-12	1	1	1	36	-36	-7	5	1	16	16	0	8	1	16	16
0	2	0	61	-63	1	9	0	21	-21	2	1	1	63	62	-6	5	1	30	30	1	8	1	13	-13
1	2	0	26	-24	2	9	0	14	-15	3	1	1	56	54	-5	5	1	8	-9	2	8	1	26	-26
2	2	0	41	-39	3	9	0	8	8	4	1	1	26	-25	-4	5	1	61	-60	4	8	1	26	26
3	2	0	48	48	4	9	0	28	28	5	1	1	39	-39	-3	5	1	7	-7	5	8	1	9	9
5	2	0	43	-43	5	9	0	11	-10	6	1	1	8	-8	-2	5	1	64	64	6	8	1	21	-21
6	2	0	5	-4	6	9	0	28	-28	7	1	1	28	28	-1	5	1	26	25	7	8	1	6	-7
7	2	0	32	32	7	9	0	5	-4	-7	2	1	8	8	0	5	1	85	-85	-7	9	1	9	9
1	3	0	71	71	0	10	0	43	-43	-6	2	1	4	-4	1	5	1	35	-33	-6	9	1	22	21
2	3	0	5	5	1	10	0	8	-8	-5	2	1	48	-49	2	5	1	65	65	-4	9	1	40	-40
3	3	0	35	-37	2	10	0	20	20	-3	2	1	60	61	3	5	1	48	47	-3	9	1	7	-6
4	3	0	26	-27	3	10	0	19	20	-2	2	1	16	14	4	5	1	34	-33	-2	9	1	44	44
5	3	0	35	35	4	10	0	19	-19	-1	2	1	100	-101	5	5	1	32	-32	-1	9	1	17	17
6	3	0	26	26	5	10	0	22	-23	0	2	1	52	-50	7	5	1	24	24	0	9	1	53	-52
0	4	0	155	165	6	10	0	6	6	1	2	1	83	82	-7	6	1	9	8	1	9	1	23	-22
1	4	0	14	15	7	10	0	18	18	2	2	1	52	51	-6	6	1	9	-8	2	9	1	42	42
2	4	0	66	-67	1	11	0	41	42	3	2	1	52	-53	-5	6	1	40	-40	3	9	1	29	29
3	4	0	24	-24	2	11	0	5	5	4	2	1	27	-25	-4	6	1	6	5	4	9	1	24	-24
4	4	0	53	53	3	11	0	27	-28	5	2	1	14	14	-3	6	1	48	48	5	9	1	20	-21
5	4	0	20	20	4	11	0	11	-12	6	2	1	17	17	-2	6	1	8	9	6	9	1	5	4
6	4	0	22	-22	5	11	0	21	21	7	2	1	8	-8	-1	6	1	75	-74	7	9	1	15	15
7	4	0	14	-14	6	11	0	12	12	-7	3	1	27	-27	0	6	1	35	-34	-7	10	1	6	7
1	5	0	49	-49	0	12	0	28	28	-6	3	1	18	-18	1	6	1	58	58	-6	10	1	11	-11
2	5	0	19	-19	1	12	0	4	4	-5	3	1	24	24	2	6	1	39	38	-5	10	1	26	-26
3	5	0	21	22	2	12	0	12	-12	-4	3	1	39	38	3	6	1	37	-37	-4	10	1	8	7
4	5	0	40	40	3	12	0	11	-11	-3	3	1	12	-13	4	6	1	29	-29	-3	10	1	30	30
5	5	0	22	-22	4	12	0	12	12	-2	3	1	10	-11	5	6	1	10	10	-1	10	1	41	-41
6	5	0	38	-38	5	12	0	14	14	-1	3	1	5	-4	6	6	1	20	19	0	10	1	19	-19
0	6	0	56	-56	-7	0	1	5	-4	0	3	1	27	27	7	6	1	4	-4	1	10	1	31	31
1	6	0	17	-17	-6	0	1	38	38	1	3	1	18	18	-7	7	1	25	-24	2	10	1	26	25
2	6	0	7	8	-5	0	1	35	34	2	3	1	20	-19	-6	7	1	11	-11	3	10	1	21	-21
3	6	0	34	34	-4	0	1	44	-44	3	3	1	44	-44	-5	7	1	24	24	4	10	1	24	-23
4	6	0	14	-14	-3	0	1	32	-31	5	3	1	35	34	-4	7	1	21	21	6	10	1	17	18
5	6	0	35	-35	-2	0	1	33	32	6	3	1	17	17	-3	7	1	15	-15	-6	11	1	9	-9
7	6	0	26	27	-1	0	1	57	58	7	3	1	27	-27	-2	7	1	8	-8	-5	11	1	17	17
1	7	0	56	57	1	0	1	26	-27	-6	4	1	32	31	0	7	1	11	11	-4	11	1	16	16
2	7	0	4	5	2	0	1	73	-71	-5	4	1	29	29	1	7	1	13	13	-3	11	1	12	-12

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-2	11	1	10	-11	2	2	2	26	25	-7	6	2	17	-18	3	9	2	4	4	4	0	3	23	-23
0	11	1	11	11	3	2	2	42	-41	-6	6	2	22	-22	4	9	2	26	-26	5	0	3	38	-39
1	11	1	12	12	4	2	2	31	-31	-5	6	2	18	18	5	9	2	22	-22	6	0	3	20	20
3	11	1	22	-23	5	2	2	18	17	-4	6	2	26	26	6	9	2	16	16	7	0	3	33	33
5	11	1	21	21	6	2	2	31	31	-2	6	2	43	-42	7	9	2	17	17	-7	1	3	5	5
6	11	1	10	11	7	2	2	22	-22	-1	6	2	20	-21	-7	10	2	10	-10	-6	1	3	32	-33
-5	12	1	16	15	-7	3	2	21	-21	1	6	2	26	26	-6	10	2	20	-19	-5	1	3	12	-11
-4	12	1	8	-7	-5	3	2	32	32	2	6	2	4	4	-5	10	2	6	6	-4	1	3	24	24
-3	12	1	15	-15	-4	3	2	12	12	3	6	2	41	-40	-4	10	2	23	23	-3	1	3	36	37
-1	12	1	20	21	-3	3	2	44	-43	4	6	2	18	-17	-3	10	2	6	6	-2	1	3	42	-42
0	12	1	10	11	-2	3	2	45	-44	5	6	2	20	19	-2	10	2	33	-33	-1	1	3	56	-57
1	12	1	13	-14	-1	3	2	46	45	6	6	2	22	22	-1	10	2	19	-20	1	1	3	57	57
2	12	1	16	-16	0	3	2	20	19	7	6	2	21	-20	0	10	2	12	12	3	1	3	49	-49
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4	12	1	15	16	2	3	2	61	-63	-5	7	2	26	26	2	10	2	7	-7	5	1	3	25	25
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-5	0	2	13	14	4	3	2	40	40	-3	7	2	37	-37	4	10	2	6	-5	7	1	3	5	-5
-4	0	2	57	-57	5	3	2	15	16	-2	7	2	35	-34	5	10	2	17	17	-7	2	3	21	-22
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-1	0	2	100	101	7	3	2	11	-11	0	7	2	27	28	-5	11	2	20	20	-5	2	3	22	23
1	0	2	86	-86	-6	4	2	29	29	1	7	2	25	-24	-4	11	2	11	11	-4	2	3	28	28
2	0	2	64	62	-5	4	2	9	10	2	7	2	44	-44	-3	11	2	28	-28	-3	2	3	39	-40
3	0	2	79	79	-4	4	2	44	-44	3	7	2	23	23	-2	11	2	24	-24	-2	2	3	84	-84
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7	0	2	23	23	-1	4	2	69	69	6	7	2	13	-13	1	11	2	19	-19	1	2	3	6	-6
-7	1	2	25	25	0	4	2	45	-43	7	7	2	6	-6	2	11	2	31	-31	2	2	3	55	-55
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2	1	2	73	75	-6	5	2	16	-16	2	8	2	16	16	0	12	2	7	-7	-3	3	3	16	-16
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5	1	2	26	-26	-3	5	2	39	39	6	8	2	7	-6	3	12	2	20	20	0	3	3	3	3
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7	1	2	18	18	-1	5	2	34	-33	-7	9	2	15	16	-7	0	3	33	34	2	3	3	14	-14
-7	2	2	25	-25	0	5	2	17	-17	-6	9	2	14	-14	-6	0	3	9	-9	3	3	3	31	31
-6	2	2	21	-21	1	5	2	7	7	-5	9	2	20	-20	-5	0	3	32	-32	4	3	3	34	33
-5	2	2	30	30	2	5	2	54	53	-4	9	2	8	8	-4	0	3	12	11	5	3	3	16	-16
-4	2	2	21	22	3	5	2	4	-4	-3	9	2	22	22	-3	0	3	39	39	6	3	3	26	-26
-3	2	2	16	-17	4	5	2	42	-42	-2	9	2	7	7	-2	0	3	40	40	-7	4	3	29	29
-2	2	2	46	-45	5	5	2	28	-29	-1	9	2	15	-15	1	0	3	32	-30	-6	4	3	7	-7
-1	2	2	12	-13	6	5	2	23	23	0	9	2	10	-10	2	0	3	33	33	-5	4	3	26	-26
1	2	2	13	14	7	5	2	20	20	2	9	2	29	29	3	0	3	37	37	-4	4	3	8	7

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-3	4	3	33	32	1	7	3	16	-16	-4	11	3	12	-12	-3	2	4	13	-12	4	5	4	5	5
-2	4	3	32	31	2	7	3	17	-18	-3	11	3	5	-5	-1	2	4	5	5	5	5	4	31	31
-1	4	3	10	-11	3	7	3	19	19	-2	11	3	12	11	0	2	4	25	25	6	5	4	4	-4
0	4	3	22	-22	4	7	3	29	29	-1	11	3	10	10	1	2	4	16	-17	7	5	4	20	-21
1	4	3	25	-24	5	7	3	10	-10	1	11	3	13	-14	2	2	4	32	-32	-6	6	4	22	22
2	4	3	27	28	6	7	3	24	-24	2	11	3	11	-11	3	2	4	12	-12	-5	6	4	8	8
3	4	3	30	30	-7	8	3	20	20	3	11	3	14	14	4	2	4	35	35	-4	6	4	20	-20
4	4	3	18	-18	-5	8	3	17	-17	4	11	3	20	20	5	2	4	4	-5	-3	6	4	19	-19
5	4	3	32	-33	-3	8	3	21	20	5	11	3	9	-9	6	2	4	32	-32	-2	6	4	3	3
6	4	3	16	16	-2	8	3	23	22	6	11	3	17	-17	7	2	4	9	-8	-1	6	4	18	18
7	4	3	28	28	-1	8	3	7	-6	-5	12	3	11	-11	-7	3	4	16	16	0	6	4	14	14
-7	5	3	9	9	0	8	3	17	-17	-3	12	3	13	13	-6	3	4	19	19	1	6	4	24	-23
-6	5	3	30	-29	1	8	3	12	-11	-2	12	3	18	18	-5	3	4	14	-14	2	6	4	24	-24
-5	5	3	19	-18	2	8	3	20	20	-1	12	3	6	-6	-4	3	4	32	-32	4	6	4	27	28
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-2	5	3	42	-41	5	8	3	20	-20	3	12	3	8	8	0	3	4	54	-55	7	6	4	4	-5
-1	5	3	60	-59	6	8	3	11	10	4	12	3	9	-10	1	3	4	11	-11	-7	7	4	11	11
0	5	3	23	23	7	8	3	18	18	5	12	3	10	-10	2	3	4	35	34	-6	7	4	17	17
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2	5	3	8	-9	-6	9	3	20	-20	-6	0	4	17	-17	4	3	4	10	-10	-4	7	4	30	-29
3	5	3	51	-51	-5	9	3	16	-15	-5	0	4	39	-40	5	3	4	20	-20	-3	7	4	7	6
4	5	3	13	-13	-4	9	3	18	18	-4	0	4	21	20	6	3	4	6	5	-2	7	4	33	32
5	5	3	26	27	-3	9	3	33	33	-3	0	4	68	69	7	3	4	12	12	0	7	4	45	-45
6	5	3	13	13	-2	9	3	26	-26	-2	0	4	6	-7	-7	4	4	15	15	1	7	4	6	-6
7	5	3	7	-7	-1	9	3	42	-41	1	0	4	82	83	-6	4	4	15	-15	2	7	4	30	31
-7	6	3	21	-21	0	9	3	15	16	2	0	4	10	9	-5	4	4	31	-32	3	7	4	15	15
-6	6	3	12	-12	1	9	3	41	41	3	0	4	33	-33	-4	4	4	16	16	4	7	4	11	-11
-5	6	3	22	22	2	9	3	7	-7	4	0	4	14	-14	-3	4	4	54	54	5	7	4	13	-13
-4	6	3	23	22	3	9	3	34	-34	5	0	4	30	30	-2	4	4	3	-3	6	7	4	5	6
-3	6	3	34	-34	4	9	3	5	-6	6	0	4	15	15	-1	4	4	58	-57	7	7	4	8	8
-2	6	3	60	-58	5	9	3	19	19	7	0	4	4	-2	0	4	4	7	-6	-7	8	4	8	8
-1	6	3	24	24	6	9	3	7	7	-7	1	4	20	-21	1	4	4	63	62	-6	8	4	11	-11
0	6	3	51	51	7	9	3	5	-5	-6	1	4	15	-16	2	4	4	11	11	-5	8	4	18	-18
1	6	3	5	-5	-7	10	3	17	-17	-5	1	4	20	20	3	4	4	24	-24	-4	8	4	10	11
2	6	3	47	-47	-6	10	3	5	-5	-4	1	4	28	28	4	4	4	14	-14	-3	8	4	30	30
4	6	3	28	28	-5	10	3	18	17	-3	1	4	14	-14	5	4	4	23	24	-1	8	4	31	-30
5	6	3	7	8	-4	10	3	11	12	-2	1	4	27	-26	6	4	4	14	14	0	8	4	6	-6
6	6	3	18	-18	-3	10	3	22	-22	1	1	4	16	16	-7	5	4	21	-22	1	8	4	33	33
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7	2	6	18	18	0	6	6	17	-16	0	10	6	14	-14	-4	2	7	9	10	-5	6	7	13	-13
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7	5	6	9	8	4	9	6	10	9	1	1	7	9	-9	1	5	7	3	-2	-2	10	7	7	-7
-7	6	6	10	10	5	9	6	11	-11	2	1	7	17	18	2	5	7	18	19	-1	10	7	16	-17

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	10	7	12	12	3	10	7	11	-12															

APPENDIX III

OBSERVED AND CALCULATED STRUCTURE FACTORS (X10) FOR

$[(C_6H_5)_4As][Tc(NO)Cl_2(acac)]$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
3	1	0	1220	-1206	2	5	0	459	469	-5	-9	1	199	230	-6	-4	1	349	-322	-5	2	1	234	-139
4	1	0	449	-439	3	5	0	230	244	-4	-9	1	175	222	-5	-4	1	127	-130	-4	2	1	205	220
5	1	0	407	375	4	5	0	282	289	-2	-9	1	280	289	-4	-4	1	310	-337	-3	2	1	289	-284
6	1	0	249	-194	6	5	0	306	297	1	-9	1	252	-242	-3	-4	1	298	-293	-1	2	1	176	174
7	1	0	124	155	8	5	0	157	-168	3	-9	1	267	-329	-1	-4	1	155	-150	0	2	1	425	403
-3	2	0	112	-122	-3	6	0	260	-247	8	-9	1	150	-36	0	-4	1	719	773	1	2	1	242	217
-2	2	0	943	-885	-2	6	0	411	431	-6	-8	1	182	186	1	-4	1	729	746	2	2	1	1525	1446
-1	2	0	1049	-950	-1	6	0	137	-114	-3	-8	1	415	-473	2	-4	1	1602	1603	3	2	1	1073	1017
0	2	0	1509	-1522	0	6	0	611	641	-2	-8	1	128	-147	4	-4	1	286	292	4	2	1	360	296
1	2	0	928	924	1	6	0	697	730	-1	-8	1	442	-421	5	-4	1	188	-167	5	2	1	387	395
2	2	0	880	-832	2	6	0	551	591	3	-8	1	236	269	6	-4	1	223	-285	6	2	1	381	-378
3	2	0	1533	1497	3	6	0	357	340	5	-8	1	155	187	-4	-3	1	1210	1164	8	2	1	161	-233
4	2	0	837	808	4	6	0	225	-229	-7	-7	1	187	-189	-3	-3	1	115	125	-7	3	1	131	-216
5	2	0	772	728	6	6	0	379	-378	-5	-7	1	354	-353	-2	-3	1	823	848	-5	3	1	336	-338
6	2	0	194	203	-5	7	0	154	-166	-4	-7	1	143	-147	-1	-3	1	163	-142	-4	3	1	327	334
-6	3	0	154	-176	-4	7	0	164	172	-3	-7	1	146	-122	0	-3	1	475	448	-3	3	1	133	149
-5	3	0	378	-411	2	7	0	639	-667	-2	-7	1	371	381	1	-3	1	1319	-1221	-2	3	1	557	584
-4	3	0	555	-491	3	7	0	268	-275	-1	-7	1	626	669	2	-3	1	1071	-1001	-1	3	1	147	-125
-3	3	0	100	52	4	7	0	486	-538	1	-7	1	465	436	3	-3	1	550	-563	0	3	1	573	-563
-2	3	0	704	-617	6	7	0	116	-16	2	-7	1	133	-118	4	-3	1	793	-766	1	3	1	319	255
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1	3	0	202	199	-1	8	0	147	151	6	-7	1	130	-161	-3	-2	1	301	-340	4	3	1	992	-981
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4	3	0	204	-246	4	8	0	168	165	-3	-6	1	516	554	0	-2	1	943	-991	7	3	1	140	147
5	3	0	431	-397	5	8	0	294	300	-2	-6	1	224	256	1	-2	1	275	313	-6	4	1	241	306
6	3	0	143	-138	6	8	0	379	368	-1	-6	1	568	588	2	-2	1	1241	-1198	-5	4	1	97	55
7	3	0	441	-490	-4	9	0	322	-334	0	-6	1	564	-558	3	-2	1	430	427	-4	4	1	345	290
-6	4	0	167	-171	-2	9	0	249	-244	1	-6	1	104	-126	4	-2	1	194	191	-3	4	1	368	374
-5	4	0	300	302	-1	9	0	189	182	2	-6	1	536	-522	5	-2	1	791	823	0	4	1	541	-525
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-3	-6	3	480	-494	6	-2	3	226	-248	-6	3	3	223	205	1	8	3	144	124	6	-7	4	162	179
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-7	-4	4	157	125	-1	0	4	1214	-1235	-3	4	4	357	337	-2	-10	5	264	-301	-4	-4	5	497	-517
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4	-5	8	121	139	6	0	8	383	365	-5	6	8	142	173	0	-4	9	544	-538	-3	2	9	468	482
5	-5	8	207	-225	7	0	8	130	-106	0	6	8	190	-198	1	-4	9	318	-287	1	2	9	328	-369
-6	-4	8	147	-147	-7	1	8	124	92	1	6	8	359	-355	3	-4	9	145	-106	2	2	9	272	-297
-5	-4	8	204	211	-6	1	8	183	-206	4	6	8	217	230	4	-4	9	284	278	3	2	9	444	-476
-3	-4	8	188	168	-4	1	8	317	-326	-1	7	8	184	-168	6	-4	9	237	244	6	2	9	267	248
-2	-4	8	215	214	-3	1	8	130	98	0	7	8	133	157	-7	-3	9	160	189	-3	3	9	260	-270
-1	-4	8	111	61	-2	1	8	120	-134	1	7	8	145	-156	-5	-3	9	152	126	-1	3	9	170	-164
0	-4	8	196	182	-1	1	8	144	122	2	7	8	298	320	-4	-3	9	432	-429	0	3	9	118	103
1	-4	8	832	-798	0	1	8	394	391	0	8	8	191	174	-1	-3	9	170	-175	1	3	9	142	-144
3	-4	8	692	-709	1	1	8	405	398	0	9	8	140	-117	0	-3	9	357	344	2	3	9	398	404
6	-4	8	117	129	2	1	8	815	849	0	-12	9	183	150	2	-3	9	633	636	3	3	9	134	161
-6	-3	8	177	183	5	1	8	156	-132	2	-11	9	173	-155	4	-3	9	538	517	4	3	9	325	337
-5	-3	8	139	134	6	1	8	185	-181	-2	-10	9	190	-201	5	-3	9	160	-171	5	3	9	169	113
-4	-3	8	186	226	8	1	8	161	-121	-1	-10	9	180	-125	-6	-2	9	283	-294	8	3	9	188	-155
-3	-3	8	240	-219	-4	2	8	174	187	0	-10	9	228	-199	-2	-2	9	401	416	-3	4	9	251	-268
-1	-3	8	478	-480	-2	2	8	503	529	-2	-9	9	152	-185	0	-2	9	364	386	-2	4	9	253	255
1	-3	8	250	-255	0	2	8	367	390	1	-9	9	194	186	1	-2	9	280	-295	-1	4	9	138	-165
3	-3	8	390	402	1	2	8	277	-269	2	-9	9	266	244	3	-2	9	387	-371	0	4	9	303	311
4	-3	8	246	229	2	2	8	197	-203	-6	-8	9	126	-140	4	-2	9	307	-318	4	4	9	177	-179
5	-3	8	409	424	3	2	8	306	-281	-3	-8	9	198	176	5	-2	9	297	-302	6	4	9	305	-272
-7	-2	8	127	-173	4	2	8	517	-530	-2	-8	9	185	216	6	-2	9	219	-219	-4	5	9	270	266
-5	-2	8	435	-421	7	2	8	244	232	3	-8	9	380	-378	-6	-1	9	219	198	-3	5	9	133	119
-3	-2	8	376	-391	-6	3	8	180	236	-5	-7	9	143	118	-4	-1	9	377	381	-1	5	9	177	151
0	-2	8	160	138	-4	3	8	378	341	-4	-7	9	264	259	-3	-1	9	143	-118	2	5	9	281	-281
1	-2	8	417	441	-3	3	8	148	-164	-2	-7	9	156	180	-2	-1	9	389	427	3	5	9	165	180
2	-2	8	196	-173	-1	3	8	292	-306	-1	-7	9	401	-396	-1	-1	9	420	-405	4	5	9	203	-204
3	-2	8	444	461	1	3	8	177	-214	0	-7	9	129	145	0	-1	9	252	-267	-2	6	9	266	-261
4	-2	8	390	-388	2	3	8	300	-323	1	-7	9	353	-333	3	-1	9	262	282	0	6	9	409	-383
6	-2	8	332	-344	3	3	8	207	193	5	-7	9	153	191	5	-1	9	451	445	1	6	9	191	171
-7	-1	8	139	-202	5	3	8	399	366	-5	-6	9	200	-218	7	-1	9	208	209	2	6	9	164	-189
-4	-1	8	240	241	6	3	8	174	166	-3	-6	9	440	-439	-6	0	9	194	235	3	6	9	176	191
-3	-1	8	260	282	7	3	8	192	176	0	-6	9	171	162	-5	0	9	266	-290	0	7	9	152	141
-2	-1	8	197	232	-5	4	8	144	-145	1	-6	9	269	256	-3	0	9	368	-374	1	7	9	194	165
-1	-1	8	405	447	-4	4	8	284	-286	3	-6	9	153	139	-2	0	9	538	-557	2	7	9	139	87
0	-1	8	300	-333	-3	4	8	221	-231	4	-6	9	139	-153	-1	0	9	153	-162	-1	9	9	158	-148
2	-1	8	502	-538	-2	4	8	325	-320	6	-6	9	145	-155	0	0	9	274	-305	1	-11	10	156	-130
3	-1	8	307	-283	0	4	8	141	-158	-7	-5	9	170	-160	1	0	9	209	217	2	-10	10	154	135

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
3	-10	10	177	179	-5	-2	10	192	197	-1	5	10	342	-331	2	-2	11	374	-372	2	-7	12	149	-134
1	-9	10	194	173	-3	-2	10	403	456	1	5	10	227	-242	3	-2	11	291	270	0	-6	12	252	-246
2	-9	10	130	-125	-1	-2	10	118	145	-3	6	10	151	-147	5	-2	11	175	147	2	-6	12	199	-175
-3	-8	10	215	209	0	-2	10	239	-233	0	6	10	147	179	-4	-1	11	287	-257	-4	-5	12	221	-183
-2	-8	10	216	-212	3	-2	10	486	-486	-2	7	10	143	138	-2	-1	11	391	-378	-2	-5	12	338	-340
-1	-8	10	142	152	-7	-1	10	157	233	-1	7	10	254	254	3	-1	11	127	97	1	-5	12	192	204
0	-8	10	181	-163	-5	-1	10	189	206	0	8	10	201	-201	4	-1	11	151	146	-6	-4	12	200	-211
1	-8	10	121	-86	-2	-1	10	130	-152	0	-10	11	180	194	7	-1	11	152	-138	-4	-4	12	147	-178
2	-8	10	214	-182	-1	-1	10	509	-555	-2	-9	11	135	139	-6	0	11	155	-163	-3	-4	12	239	249
6	-8	10	139	147	1	-1	10	309	-342	-3	-8	11	137	-147	-3	0	11	245	241	-1	-4	12	234	230
-6	-7	10	257	-70	2	-1	10	331	325	2	-8	11	124	-93	-2	0	11	199	234	0	-4	12	319	295
-4	-7	10	226	-221	4	-1	10	332	280	3	-8	11	275	259	-1	0	11	198	207	1	-4	12	145	124
-2	-7	10	257	-257	6	-1	10	145	129	-4	-7	11	224	-214	0	0	11	230	246	2	-4	12	188	172
2	-7	10	240	216	-5	0	10	180	-153	-2	-7	11	145	-162	1	0	11	166	-187	3	-4	12	145	-133
4	-7	10	273	248	-3	0	10	337	-338	-1	-7	11	197	194	3	0	11	409	-393	5	-4	12	221	-211
-6	-6	10	140	-168	-2	0	10	251	251	1	-7	11	227	210	5	0	11	209	-205	-5	-3	12	177	194
-2	-6	10	251	251	0	0	10	303	301	5	-6	11	172	154	-5	1	11	136	131	-2	-3	12	129	142
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1	-6	10	124	-122	4	0	10	229	-225	-1	-6	11	340	372	-1	1	11	324	-351	1	-3	12	297	-337
3	-6	10	125	-144	6	0	10	182	-185	0	-6	11	155	-126	1	1	11	400	-393	3	-3	12	275	-276
6	-6	10	136	-135	-6	1	10	135	125	3	-6	11	210	-174	3	1	11	197	-194	-7	-2	12	149	145
8	-6	10	154	-53	-4	1	10	237	221	-7	-5	11	143	163	-5	2	11	148	-173	-3	-2	12	272	-273
-4	-5	10	384	377	-2	1	10	401	392	-5	-5	11	174	197	-3	2	11	331	-326	-1	-2	12	334	-343
-2	-5	10	329	349	-1	1	10	220	214	-1	-5	11	310	-305	0	2	11	147	153	0	-2	12	177	174
-1	-5	10	155	-144	2	1	10	334	-329	0	-5	11	182	-176	1	2	11	210	236	2	-2	12	160	173
1	-5	10	470	-420	4	1	10	225	-214	1	-5	11	303	-298	2	2	11	196	224	3	-2	12	219	204
4	-5	10	113	-97	5	1	10	160	134	2	-5	11	120	58	3	2	11	328	340	4	-2	12	149	130
5	-5	10	263	277	7	1	10	251	239	4	-5	11	171	131	5	2	11	149	169	5	-2	12	132	147
-6	-4	10	184	171	-4	2	10	123	126	-5	-4	11	154	-140	6	2	11	225	-190	-5	-1	12	183	-165
-5	-4	10	124	-104	-3	2	10	184	-220	-3	-4	11	296	-303	-5	3	11	183	-224	-3	-1	12	153	-120
-4	-4	10	121	100	-2	2	10	188	-204	-2	-4	11	178	172	-2	3	11	154	170	-2	-1	12	267	279
-3	-4	10	233	-260	0	2	10	370	-386	-1	-4	11	246	-238	-1	3	11	169	184	-1	-1	12	236	243
-1	-4	10	228	-212	2	2	10	226	-221	0	-4	11	386	396	1	3	11	232	205	1	-1	12	209	205
0	-4	10	257	-274	3	2	10	198	194	2	-4	11	362	360	2	3	11	177	-181	2	-1	12	135	-123
1	-4	10	392	374	5	2	10	135	141	3	-4	11	141	142	-3	4	11	171	177	4	-1	12	294	-252
3	-4	10	297	307	-5	3	10	135	-102	6	-4	11	181	-170	-2	4	11	168	-130	6	-1	12	149	-133
5	-4	10	172	141	-4	3	10	276	-274	-7	-3	11	133	-129	0	4	11	276	-296	-4	0	12	182	169
-6	-3	10	161	-183	-2	3	10	212	-215	-4	-3	11	247	263	2	4	11	194	-191	-3	0	12	269	271
-5	-3	10	244	-273	-1	3	10	148	180	-2	-3	11	238	250	-2	5	11	263	-260	-1	0	12	232	201
-4	-3	10	118	-135	0	3	10	120	105	-1	-3	11	218	221	2	5	11	218	220	0	0	12	286	-317
-3	-3	10	132	99	1	3	10	209	256	2	-3	11	166	-158	-2	6	11	142	113	2	0	12	336	-343
-2	-3	10	260	-263	2	3	10	208	226	4	-3	11	350	-329	0	6	11	326	281	6	0	12	169	166
-1	-3	10	535	537	4	3	10	226	217	-6	-2	11	231	250	1	-9	12	226	-195	-4	1	12	185	-174
1	-3	10	495	492	5	3	10	240	-235	-4	-2	11	120	86	-3	-8	12	165	-181	-3	1	12	122	-40
3	-3	10	223	199	7	3	10	169	-150	-3	-2	11	180	154	-1	-8	12	130	-135	-2	1	12	442	-415
4	-3	10	309	-279	-3	4	10	175	190	-2	-2	11	267	-298	0	-8	12	124	100	0	1	12	182	-157
5	-3	10	232	-221	1	4	10	240	-274	0	-2	11	329	-388	2	-8	12	261	230	2	1	12	140	156
7	-3	10	134	-145	3	4	10	296	-331	1	-2	11	145	153	-2	-7	12	312	307	4	1	12	265	278

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
-6	2	12	132	-142	-3	-7	13	139	139	1	-1	13	276	-292	0	-7	14	193	-177	1	-1	14	132	-133
-4	2	12	256	-247	1	-7	13	264	-252	2	-1	13	130	-121	2	-6	14	141	151	2	-1	14	134	-119
-2	2	12	145	110	3	-7	13	166	-158	3	-1	13	327	-306	-2	-5	14	183	168	3	-1	14	129	-117
0	2	12	333	345	-3	-6	13	199	-209	-3	0	13	126	-116	0	-5	14	223	223	-3	0	14	141	-142
1	2	12	217	185	-1	-6	13	260	-266	-1	0	13	235	-216	1	-5	14	128	-101	-1	0	14	192	-208
2	2	12	311	310	-3	-5	13	185	-180	0	0	13	121	-155	-1	-4	14	277	-243	0	0	14	112	124
3	2	12	165	-173	0	-5	13	236	220	1	0	13	166	-165	1	-4	14	147	-161	2	0	14	239	229
-2	3	12	168	149	1	-5	13	188	178	3	0	13	146	136	2	-4	14	159	-133	-2	1	14	220	193
1	3	12	293	-300	3	-5	13	139	108	-3	1	13	166	-160	-3	-3	14	206	-185	0	1	14	305	279
3	3	12	169	-173	-1	-4	13	155	147	-1	1	13	130	126	1	-3	14	220	215	0	2	14	151	-139
-3	4	12	185	-174	2	-4	13	219	-210	1	1	13	406	384	3	-3	14	390	341	0	3	14	151	-161
-1	4	12	205	-201	-2	-3	13	322	-341	3	1	13	290	282	-3	-2	14	188	147	1	-6	15	155	161
0	4	12	155	-155	0	-3	13	273	-269	-3	2	13	219	179	-1	-2	14	354	337	0	-3	15	175	184
3	4	12	252	277	-1	-2	13	137	101	-1	2	13	318	307	1	-2	14	155	145	0	-1	15	217	-216
-1	5	12	152	139	0	-2	13	235	223	0	3	13	142	-126	2	-2	14	154	-124	1	0	15	143	157
-1	6	12	204	225	2	-2	13	330	314	1	3	13	265	-258	-3	-1	14	215	237	0	1	15	136	141
0	-9	13	148	-163	-2	-1	13	373	382	-1	4	13	193	-170	0	-1	14	153	-130	-1	2	15	191	-179
0	-8	13	152	115	0	-1	13	196	182	0	4	13	160	163										

APPENDIX IV

THE CRYSTAL STRUCTURE OF CHLORONITROSYL-BIS-(O-PHENYLENE)-BIS-(DIMETHYLARSINE)TECHNETIUM(I) CHLORIDE, TETRABUTYLAMMONIUMCHLORIDE

Thomas A. Hamor and Hilary J. Banbery, Department of Chemistry, University of Birmingham.

Abstract

$[Tc(C_{10}H_{16}As_2)_2ClNO]Cl.[N(C_4H_9)_4]Cl$, M_r=1049.9, monoclinic, space group C 2/c, a=20.069(5), b=13.249(2), c=20.431(12)Å, β=116.03(5)°, V=4881.4Å^3, z=4, D_c=1.429gcm^{-3}, λ(MoKα)=0.71069Å, F(000)=361, R=0.084 for 2703 unique observed reflexions.

Experimental

A crystal of size 1.0 x 0.2 x 0.2 mm was selected from the material for X-ray analysis. Measurements were made on an Enraf-Nonius CAD-4 diffractometer with MoKα radiation. Lattice parameters were determined from the setting angles of 25 reflexions (θ 9-15). Intensity data were measured with ω-2θ scans in the range 2<θ<25°, index range h -21→23, k 0→15, l -24→3.

Three standard reflexions, measured every 2h, showed no significant variation over the period of data collection. 5363 reflexions were scanned, of which 4301 were unique, R_{int}=0.08, and 2703 were considered observed [F>5σ(F)] and were used in the analysis. No absorption correction was applied.

The structure was solved using Patterson and Fourier methods. The H atoms were placed in calculated positions, riding on their bonded C atoms. Coordinates for all non-H atoms were refined using full-matrix least squares on F values with weights $w=1/\sigma^2(F)$ from counting statistics. H atoms of methyl groups were placed in calculated positions and refined subject to rigid group restraints.

The non-H atoms of the complex cation and the tetrabutylammonium cation were assigned anisotropic thermal parameters. H atoms were assigned one overall isotropic temperature factor (0.07Å^2). The weighting scheme used was $w=1/[\sigma^2(F)+0.001F^2]$. The refinement was terminated when all shift/e.s.d. ratios were less than 0.02 and R=0.084, wR=0.116, for the 2703 observed reflexions. The residual electron density in a final difference map was within ±1.28 eÅ^{-3}, with all main peaks close to the technetium or arsenic atoms.

Atomic scattering factors were taken from International Tables for X-Ray Crystallography (1974); computations were carried out

using SHELX (Sheldrick, 1978) and PLUTO78 (Motherwell and Clegg, 1978).

Bond lengths and angles for the complex cation are given in Tables 1. and 2. respectively. Figure 1. shows the numbering scheme of the atoms in the complex cation and Figure 2. shows the relative positions of both the complex cation and tetrabutylammonium cation in the unit cell.

Discussion

The packing of the molecules shows disorder, the technetium atom lying on an inversion centre, with the nitrosyl and chloro- substituents becoming equivalent. Consequently the chlorine atom and nitrosyl group were indistinguishable on a Fourier difference map. A large peak at 2.4Å from technetium was taken to represent the chloro- substituent. The positions of the oxygen and nitrogen atoms in the nitrosyl group were then calculated using the coordinates of the chlorine atom, and the known covalent radii of the atoms, such that the Tc-N-O angle was close to 180°.

Thermal parameters for all carbon atoms are high, and this can be accounted for by the disordered structure. Thus bond lengths are not accurate enough to warrant detailed discussion.

There is also evidence for disorder in the positions of the atoms of the tetrabutylammonium cation with some unrealistically high thermal vibration parameters.

Table 1.

Bond distances for $[Tc(NO)(diars)_2Cl]Cl.[(C_2H_5)_4N]Cl$

	Å
Tc-As(1)	2.480(1)
Tc-As(2)	2.504(2)
Tc-Cl(1)	2.411(13)
Tc-N(1)	1.979
As(1)-C(12)	1.922(17)
As(1)-C(1)	1.935(21)
As(2)-C(21)	1.898(18)
As(2)-C(22)	1.896(18)
As(2)-C(6)	1.942(16)
Cl(1)-N(1)	0.434(13)
Cl(1)-O(1)	0.730(13)
N(1)-O(1)	1.158
C(1)-C(2)	1.411(20)
C(1)-C(6)	1.415(26)
C(2)-C(3)	1.299(43)
C(3)-C(4)	1.466(44)
C(4)-C(5)	1.386(26)
C(5)-C(6)	1.398(34)
N(1C)-C(1C)	1.512(36)
N(1C)-C(1D)	1.445(38)
C(1C)-C(2C)	1.188(39)
C(2C)-C(3C)	1.419(42)
C(3C)-C(4C)	1.299(51)
C(1D)-C(2D)	1.183(94)
C(2D)-C(3D)	1.594(94)
C(2D)-C(4D)	1.967(3)
C(3D)-C(4D)	1.103(82)

Table 2.

Bond angles for $[Tc(NO)(diars)_2Cl]Cl.[(C_4H_9)_4N]Cl$

As(1)-Tc-As(2)	83.1(1)
As(1)-Tc-Cl(1)	89.0(3)
As(2)-Tc-Cl(1)	89.3(4)
As(1)-Tc-N(1)	88.6
As(2)-Tc-N(1)	88.1
Cl(1)-Tc-N(1)	1.3(4)
Tc-As(1)-C(12)	119.3(4)
Tc-As(1)-C(1)	109.1(4)
C(12)-As(1)-C(1)	102.6(8)
Tc-As(2)-C(21)	119.6(8)
Tc-As(2)-C(22)	119.4(7)
C(21)-As(2)-C(22)	103.2(9)
C(22)-As(2)-C(6)	99.2(9)
Tc-Cl(1)-N(1)	5.7(16)
Tc-Cl(1)-O(1)	174.6(16)
N(1)-Cl(1)-O(1)	168.8(31)
Tc-N(1)-Cl(1)	173.0(19)
Cl(1)-N(1)-O(1)	7.0(19)
Cl(1)-O(1)-N(1)	4.2(12)
As(1)-C(1)-C(2)	120.6(15)
As(1)-C(1)-C(6)	120.1(11)
C(2)-C(1)-C(6)	119.3(19)
C(1)-C(2)-C(3)	120.6(20)
C(2)-C(3)-C(4)	121.4(20)
C(3)-C(4)-C(5)	119.4(26)
C(4)-C(5)-C(6)	118.2(22)
As(2)-C(6)-C(1)	118.2(15)
As(2)-C(6)-C(5)	120.6(13)
C(1)-C(6)-C(5)	121.0(15)

Figure 1.

Molecular structure and atom numbering for the chloronitrosyl-bis-(o-phenylene)-bis-(dimethylarsine)technetium(I) cation.

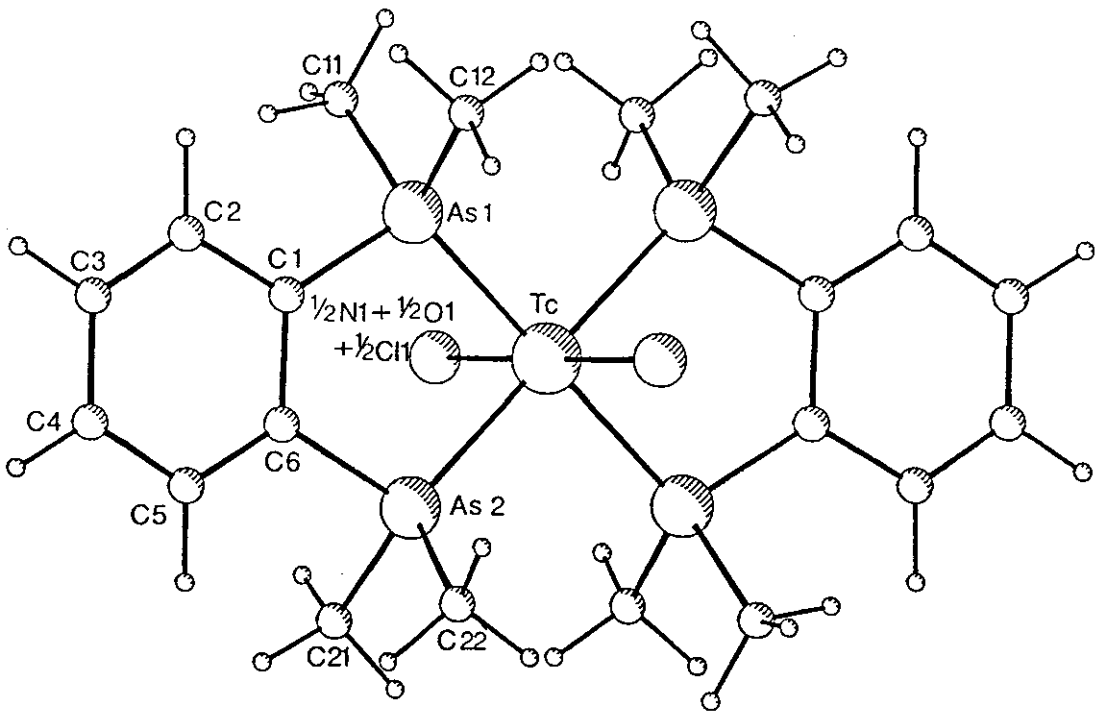
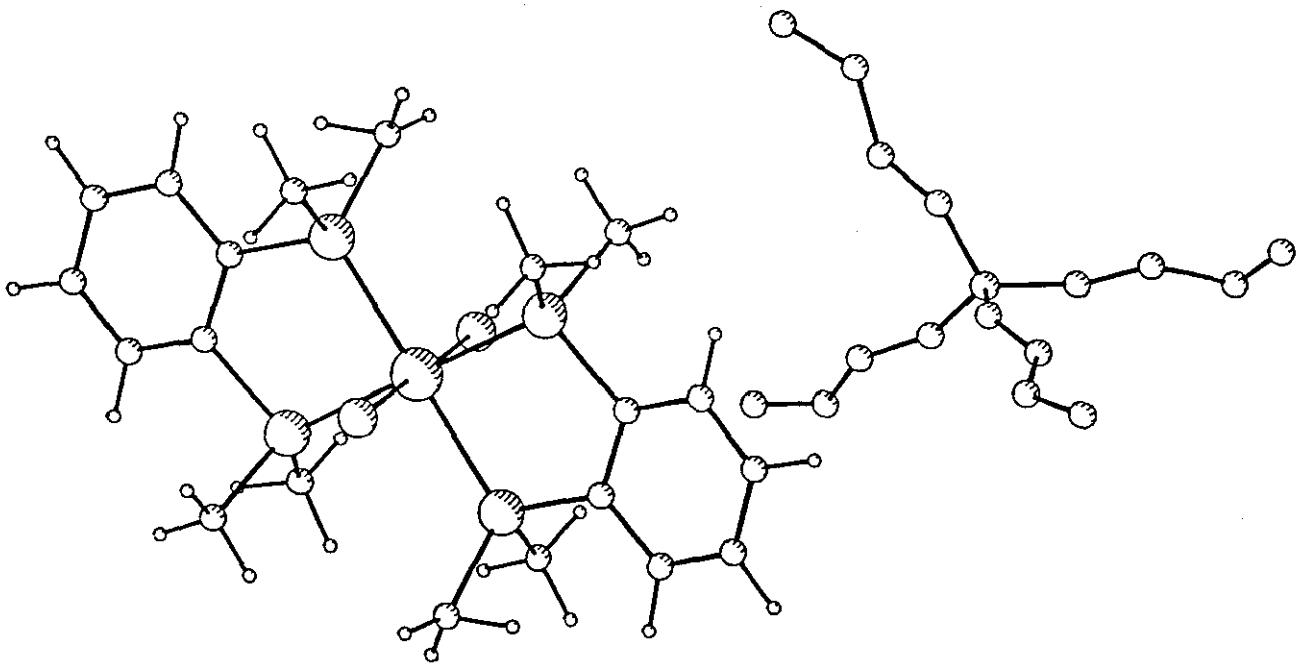


Figure 2.

View of the complex cation and tetrabutylammonium cation in their relative positions in the unit cell.



APPENDIX V

PUBLICATIONS

Synthesis and biological studies of the [^{99m}Tc]Tetrachloronitrosyltechnetium(II) anion - an alternative low valent technetium starting material.

C.T. Cheah, J.L. Newman, D.P. Nowotnik and J.R. Thornback,
J. Nucl. Med. Biol., 1987, 14, 573.

Structure of the tetra-n-butylammonium salt of the tetrachloro(methanol)nitrosyltechnetium(II) anion.

D.S. Brown, J.L. Newman, J.R. Thornback and A. Davison,
Acta. Cryst., 1987, C43, 1692.

The structure of the tetraphenylarsonium salt of the trichloro(pentane-2,4-dionato)nitrosyltechnetium(II) anion.

D.S. Brown, J.L. Newman and J.R. Thornback,
Acta. Cryst., 1988, C44, 973.

The synthesis and characterisation of the trichloronitrosyl(acetylacetonato)-technetium(II) anion, a novel technetium(II) complex.

D.S. Brown, J.L. Newman, J.R. Thornback, R.M. Pearlstein, A. Davison and A. Lawson, Inorg. Chim. Acta., 1988, 150, 193.

Preparation of ^{99m}Tc radiopharmaceuticals
European Patent Number 0 291 281 (1988)
I.A. Latham, J.L. Newman and J.R. Thornback.