

Molybdocalix[4]arene *N,O*-Schiff-base ligands

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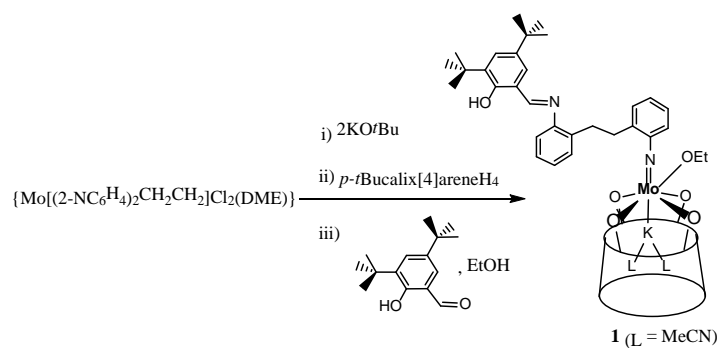
Dedicated to Jerry Atwood on the occasion of his 75th Birthday

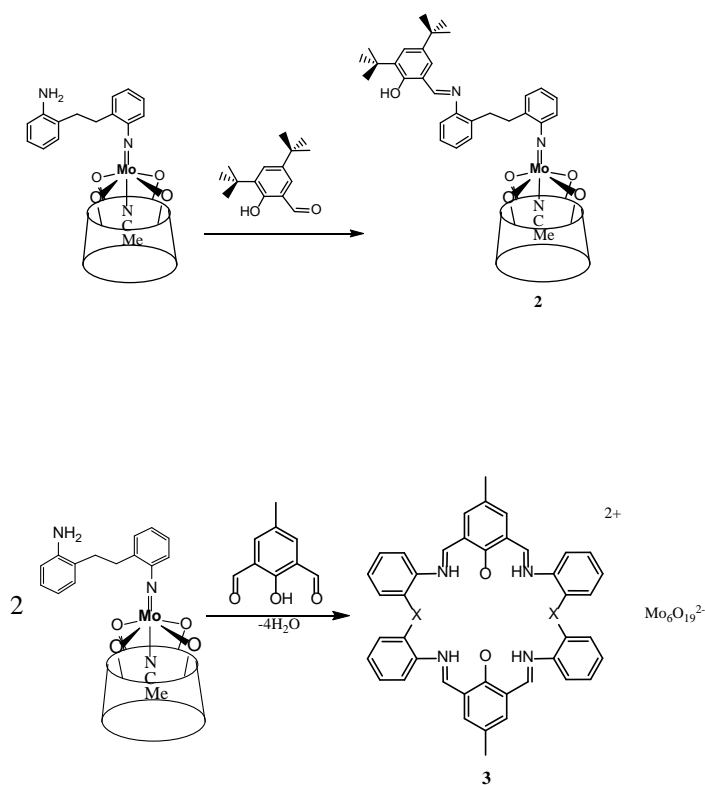
Abstract: The ‘one-pot’ reaction of 2-hydroxy-3,5-di-*tert*-butylsalicylaldehyde with *in-situ* generated ‘amino calixarene’ (from {Mo[(2-NC₆H₄)₂CH₂CH₂]Cl₂(DME)}, KO^{*t*}Bu and *t*butylcalix[4]areneH₄ L_{H4}) afforded, after work-up, the heterobimetallic salt K(NCMe)₂[Mo(NCMe)(OEt)(2-C₆H₄CH₂CH₂C₆H₄NH₂-2)L] (1·2MeCN). By contrast, use of the ‘amino calixarene’ [Mo(NCMe)(2-C₆H₄CH₂CH₂C₆H₄NH₂-2)L] afforded the potassium/ethoxide-free complex [Mo(NCMe)(2-C₆H₄CH₂CH₂C₆H₄N-2-CHC₆H₂-2′-(OH)-3′,5′-*t*Bu)L] (2·2MeCN). Reaction of **2** (two equivalents) with the dialdehyde [1,3-(CHO)₂-5-MeC₆H₃OH-2] led, following work-up, to the isolation of the cation-anion pair [C₄₆H₄₂N₄O₂]²⁺[Mo₆O₁₉]²⁻·C₂H₃N (**3**). The molecular structures of 1·2MeCN, 2·2MeCN and 3·MeCN are reported, for which it was necessary to use synchrotron radiation for data collection. Complex **1** contains an elliptical calixarene conformation as a result of π -interactions between the K⁺ and the arene groups and a distorted O₅N octahedral geometry at the molybdenum centre, whereas in ‘K⁺/ethoxide-free’ **2**, the calixarene retains the cone conformation and the metal possesses a distorted octahedral O₄N₂ coordination environment. In **3**, a protonated macrocyclic cation, formed via hydrolysis, has weak intermolecular interactions with the polyoxomolybdate anion.

Keywords: Molybdenum; calixarene; Schiff base; molecular structures.

Introduction

In recent years, there has been considerable interest in the use of calix[*n*]arenes in a variety of catalytic/polymerization processes. [1] In our previous work, we have focussed on the direct metallation of the calixarene lower (phenolic)-rim to afford new pre-catalysts for either α -olefin polymerization [2, 3] or for the ring opening of ϵ -caprolactone. [4] In other work, we and others have had success using phenoxyimine ligands, primarily in ethylene polymerization catalysis, and ring opening polymerization of cyclic esters. [5 - 8] The discovery some time ago of the ‘amino calixarene’ [Mo(NCMe)(2-C₆H₄CH₂CH₂C₆H₄NH₂-2)L] (L= *p*-*tert*-butylcalix[4]arene) opened the door for the synthesis of new imine-containing molybdocalixarene ligand sets, [9] and the pyridylimine molybdocalix[4]arene complex [Mo(NC₆H₄CH₂CH₂C₆H₄N-2'-CHC₅H₅N)L] was subsequently reported. [10] Herein, we turn our attention to the reaction of the ‘amino calixarene’ with 2-hydroxy-3,5-di-*tert*-butylsalicylaldehyde, and find that a ‘one-pot’ procedure involving KO*t*Bu results in retention of K⁺ in the product and binding of ethoxide at the molybdenum centre. To obtain the K⁺/ethoxide-free Schiff-base, it proved necessary to first isolate the ‘amino calixarene’ – see scheme 1. Furthermore, in an attempt to target a hydroxyl-bis(imine) species, we isolated a salt containing a Schiff-base macrocycle as cation and a polyoxometallate as anion. Such macrocycles are of interest for their ability to coordinate multiple catalytically active metal centres. [11] The molecular structures of these three complexes herein have been determined using synchrotron radiation due to small crystal size and thin morphology. [12, 13]





Scheme 1. Preparative routes to **1** – **3**.

Results and Discussion

The reaction of 2-hydroxy-3,5-di-*tert*-butylsalicylaldehyde with *in-situ* generated ‘amino calixarene’ (from {Mo[(2-NC₆H₄)₂CH₂CH₂]Cl₂(DME)}, KO*t*Bu and *t*butylcalix[4]areneH₄ LH₄) in refluxing ethanol afforded an orange crystalline solid isolated in moderate yield (*ca.* 35 %). The IR spectrum contains a relatively strong band in the $\nu(\text{C}=\text{N})$ region at 1614 cm⁻¹. Small orange prisms suitable for an X-ray determination using synchrotron radiation were grown from a saturated solution of acetonitrile at ambient temperature. The diffraction study revealed that the complex to be the heterobimetallic salt K(NCMe)₂[Mo(NCMe)(OEt)(2-C₆H₄CH₂CH₂C₆H₄NH₂-2)L] (1·2MeCN), and the

molecular structure is shown in Figure 1 with selected bond lengths and angles given in Table 1.

Crystallographic data are presented in Table 2.

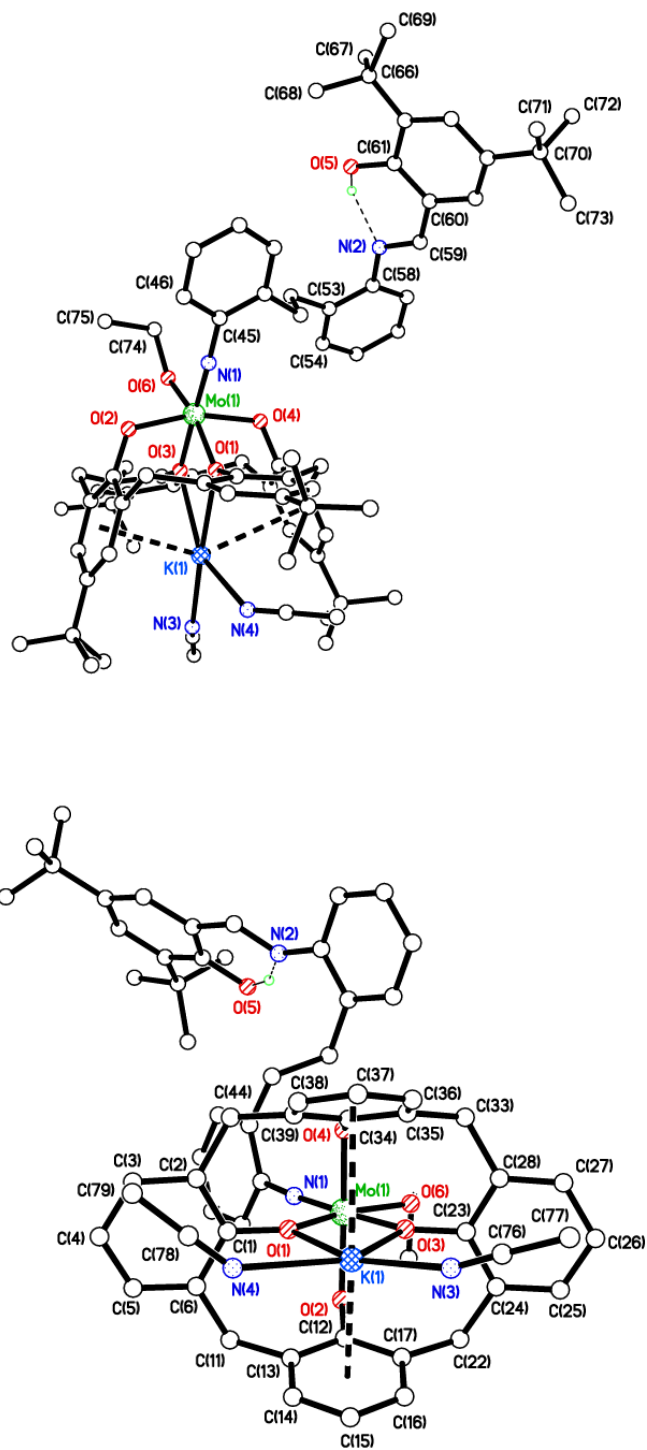


Figure 1. Two views of the molecular structure of $\text{K}(\text{NCMe})_2[\text{Mo}(\text{NCMe})(\text{OEt})(2\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2\text{-2})\text{L}]$ (**1**·2MeCN), showing the atom numbering scheme. Hydrogen atoms except those involved in H-bonds, and non-coordinated solvent molecules have been omitted for clarity. *t*Bu groups on the calixarene are also omitted for clarity in the lower figure.

In **1**, the molybdenum centre adopts a distorted octahedral environment comprising the calix[4]arene phenoxide oxygens, the nitrogen of the imido group and the coordination is completed by an ethoxide ligand. The imido group and ethoxide are positioned *trans* to calixarene phenoxide groups O(3) and O(1), respectively [$\text{N}(1)\text{--Mo}(1)\text{--O}(3) = 177.92(12)^\circ$, $\text{O}(1)\text{--Mo}(1)\text{--O}(6) = 163.64(9)^\circ$]. The calixarene is distorted such that two opposite phenoxide rings are drawn together by π -interaction involving $\text{K}(1)$ [K^+ to centroid of O(2) ring = $3.0652(17) \text{ \AA}$; K^+ to centroid of O(4) ring = $3.2054(16) \text{ \AA}$], which also binds to the oxygens O(1) and O(3) of the other two phenoxide groups as well as two molecules of acetonitrile. We have noted similar π interactions between potassium ions and calix[4]arenes in other systems, which also result in a distortion/‘pinching’ of the cone. [14, 15] The highly functionalized imido/salicylaldimine group in **1** is acting as a four electron donor [$\text{Mo}(1)\text{--N}(1) = 1.752(3) \text{ \AA}$; $\text{Mo}(1)\text{--N}(1)\text{--C}(45) = 174.0(3)^\circ$], and there is an intramolecular H-bond present involving N(2) and O(5); the O–H bond refined to $0.87(5) \text{ \AA}$, the $\text{N}\cdots\text{H}$ distance is $1.79(5) \text{ \AA}$ with a O–H \cdots N angle of $149(5)^\circ$.

Table 1. Selected structural data for complexes **1** and **2**.

Bond length (\AA)/Angle ($^\circ$)	1	2
Mo(1)–O(1)	1.984(2)	1.9465(13)
Mo(1)–O(2)	1.990(2)	1.9441(13)
Mo(1)–O(3)	2.014(2)	1.9324(12)
Mo(1)–O(4)	1.995(2)	1.9632(13)

Mo(1)–N(1)	1.752(3)	1.7268(15)
Mo(1)–N(3)	-	2.3173(15)
Mo(1)–O(1)–C(1)	137.06(19)	128.90(11)
Mo(1)–O(2)–C(12)	120.17(19)	126.58(11)
Mo(1)–O(3)–C(23)	136.4(2)	131.12(11)
Mo(1)–O(4)–C(34)	120.52(18)	128.60(11)
Mo(1)–N(1)–C(45)	174.0(3)	170.30(14)

In order to avoid K^+ incorporation in the product, the bis(*tert*-butoxide) compound $\{Mo[(2-NC_6H_4)_2CH_2CH_2](OtBu)_2\}$ was first isolated and then subsequently reacted p-*tert*-butylcalix[4]areneH₄ (LH₄) to afford the ‘amino calixarene’ $[Mo(NCMe)(2-C_6H_4CH_2CH_2C_6H_4NH_2-2)L]$, following which 2-hydroxy-3,5-di-*tert*-butylsalicylaldehyde was added to afford **2**. In the case of **2**, the room temperature ¹H NMR spectrum was consistent with a C_{4v}-symmetric cone conformation. The IR spectrum contained a strong band at 1614 cm⁻¹ assigned as the ν(C=N) stretch. As for **1**, it proved possible to grow small (yellow) crystals suitable for X-ray diffraction using synchrotron radiation. The molecular structure was indeed found to be the potassium/ethoxide-free complex $[Mo(NCMe)(2-C_6H_4CH_2CH_2C_6H_4N-2-CHC_6H_2-2'-(OH)-3',5'-tBu)L] (2 \cdot 2MeCN)$, and the structure is displayed in Figure 2. Selected bond lengths and angles are given in Table 1 for comparison with those of **1**. The molybdenum centre possesses a pseudo octahedral geometry with the molybdenum atom displaced from the mean plane (O₄) towards the imido/salicylalimine nitrogen N(1) by 0.2489(6) Å. As in **1**, the imido/salicylalimine group is acting as a four electron donor $[Mo(1)–N(1) = 1.7268(15)$ Å; $Mo(1)–N(1)–C(45) = 170.30(14)^\circ]$, but unlike **1**, this group is *trans* to an acetonitrile ligand residing in the calixarene cavity. Again, there is internal H-bonding involving N(2) and O(5). Pairs of molecules are

related by a centre of symmetry between the rings C(53)–C(58) and C(53')–C(58'), which $\pi\cdots\pi$ stack;
 closest $\pi\cdots\pi$ stacking distances are C(55)–C(57') = 3.511 Å and C(56)–C(58') = 3.573 Å.

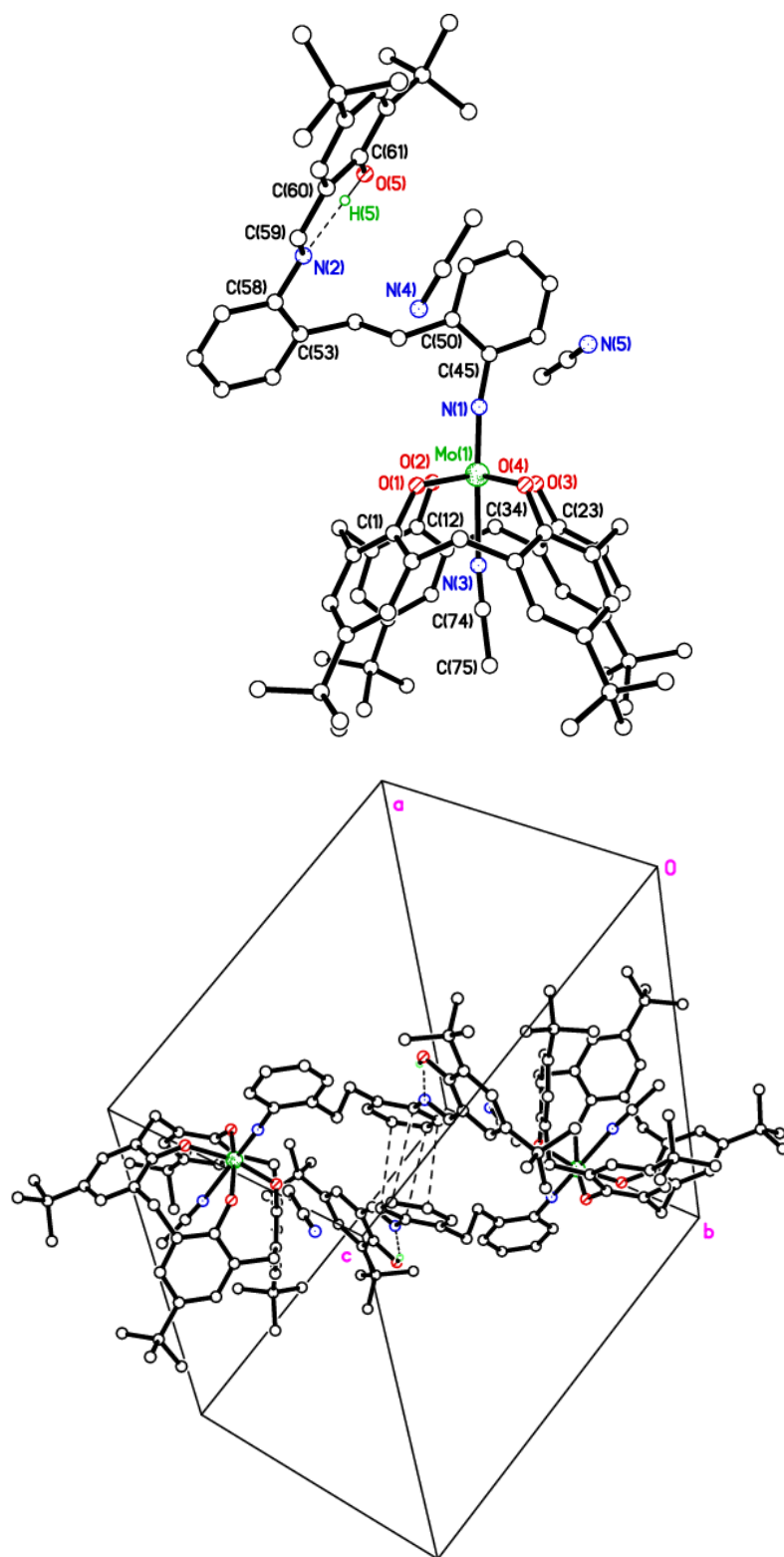


Figure 2. Top: Molecular structure of $[\text{Mo}(\text{NCMe})(2\text{-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{N-2-CHC}_6\text{H}_2\text{-2'-(OH)-3',5'-t\text{Bu})\text{L}](2\cdot 2\text{MeCN})$, showing the atom numbering scheme. Hydrogen atoms except those involved in H-bonds, have been omitted for clarity. Bottom: diagram showing the pairing up via $\pi\cdots\pi$ stacking. Symmetry operator in lower figure: $-x+1, -y+1, -z+1$.

Reaction of the isolated ‘amino metallocalix[4]arene’ $[\text{p-tert-butylcalix[4]areneMo}(\text{N-2-C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2\text{-2'})\text{(NCMe)}]$ [9] with 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde, $[\text{1,3-(CHO)}_2\text{-5-MeC}_6\text{H}_3\text{OH-2}]$ in refluxing ethanol afforded, following work-up, the orange-red crystalline salt $[\text{Mo}_6\text{O}_{19}][2,2'\text{-(CH}_2\text{CH}_2)(\text{C}_6\text{H}_4\text{NH})_2\text{-2,6-(4-MeC}_6\text{H}_3\text{O)}]_2(3\cdot\text{MeCN})$ in *ca.* 35 % yield. Small crystals suitable for X-ray diffraction using synchrotron radiation were obtained from a saturated acetonitrile solution on prolonged standing at ambient temperature. There is one acetonitrile of crystallization in the asymmetric unit. The geometrical parameters associated with the $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion are similar to those reported previously. [16] The macrocyclic cation adopts a twisted conformation (see Figure 3), and exhibits intramolecular H-bonding between each of the phenoxide oxygens and the two adjacent NH groups. The C=N bond lengths $[1.284(7) - 1.290(7) \text{ \AA}]$ are in the range of bond lengths previously reported for bis(imino)phenol-based macrocyclic Schiff bases exhibiting intramolecular H-bonding. [17 - 21] The cavity size for the cationic macrocycle is $5.6 \times 3.9 \text{ \AA}$, which compares favourably with that found in the neutral macrocycle $[6.5 \times 4.3 \text{ \AA}]$, but is far smaller than those reported $[16.0 \times 5.8 \text{ \AA}]$ for the bis(imino)phenol-based nickel complex reported by Na *et al*; it should be noted that for the latter nickel complex however the macrocycle is near planar ($5(1)^\circ$ between the phenolic benzene plane and C_6H_4 -benzene plane). [22]

Complex **1** packs such that pairs of anions lie close together with weak intermolecular, centrosymmetric pairs of Mo \cdots O interactions. There are also several weak C–H \cdots O cation \cdots anion interactions and C–H \cdots N cation \cdots acetonitrile contacts.

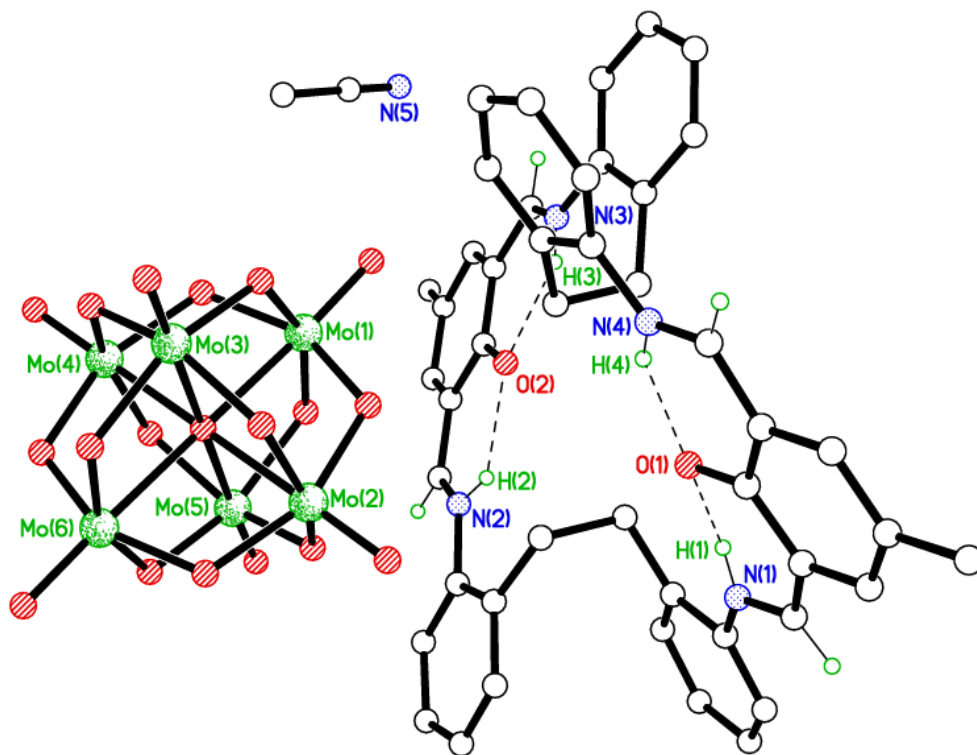


Figure 3. Molecular structure of $[\text{C}_{46}\text{H}_{42}\text{N}_4\text{O}_2]^{2+}[\text{Mo}_6\text{O}_{19}]^{2-} \cdot \text{MeCN}$ (**3**·MeCN), showing the atom numbering scheme. Hydrogen atoms except those involved in H-bonds have been omitted for clarity.

Conclusion

In conclusion, to synthesize alkali-metal-free Schiff-base complexes incorporating molybdocalix[4]arenes, the procedure is best carried out in a two-step synthesis which involves the initial isolation of the bis(*tert*-butoxide) complex prior to addition of calixarene. As seen in other systems, the presence of alkali metals leads to an elliptical calixarene conformation as a result of π -interactions. The presence of water in such systems can lead to hydrolysis of the imido-molybdenum

bond and, as evidenced in the reaction with 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde, can lead to the formation of polyoxomolybdates. The potential of these molybdocalix[4]arene Schiff-bases as ligands for catalytically active metals is currently under investigation in our laboratory.

Experimental

General:

All manipulations were carried out under an atmosphere of dry nitrogen using conventional Schlenk and cannula techniques or in a conventional nitrogen-filled glove box. Diethyl ether and tetrahydrofuran were refluxed over sodium and benzophenone. Toluene was refluxed over sodium. Dichloromethane and acetonitrile were refluxed over calcium hydride. All solvents were distilled and degassed prior to use. IR spectra (nujol mulls, KBr windows) were recorded on a Nicolet Avatar 360 FT IR spectrometer. Elemental analyses were performed by the elemental analysis service at the London Metropolitan University and the University of Hull. The precursors 2,6-(CHO)₂-4-R-C₆H₂OH and (2-NH₂C₆H₄)₂O were prepared by the literature method. [23, 24] The complex {Mo[(2-NC₆H₄)₂CH₂CH₂]Cl₂(DME)} was prepared as reported previously. [25]

Synthesis of K(NCMe)₂[Mo(NCMe)(OEt)(2-C₆H₄CH₂CH₂C₆H₄NH₂-2)L] (1·2MeCN)

The complex {Mo[(2-NC₆H₄)₂CH₂CH₂]Cl₂(DME)} (1.00 g, 2.15 mmol) was treated with KO^{*t*}Bu (0.50 g, 4.5 mmol) in THF (30 ml) at 25 °C and stirred for 4 h. Following removal of the THF, p-*tert*-butylcalix[4]areneH₄ (1.39 g, 2.14 mmol) and toluene (30 ml) were added and the system was refluxed for 12 h. Removal of volatiles was followed by the addition of 2-hydroxy-3,5-di-*tert*-butylsalicylaldehyde (0.50 g, 2.1 mmol) in ethanol (30 ml) and the system was refluxed for 12 h. On cooling, volatiles were removed *in-vacuo*, and extraction of the residue into hot MeCN (30 ml) afforded small orange prisms of **1** on prolonged standing (1 - 2 days) at ambient temperature. Yield

1.14 g, 37 %. $C_{83}H_{103}N_6O_6KMo$ requires C 70.41, H 7.33, N 5.94 %. Found: C 69.98, H 7.24, N 5.77 %. IR (cm^{-1}): 3419(s), 3179(s), 3055(w), 2957(s), 2905(w), 2869(w), 1614(m), 1590(w), 1572(w), 1481(s), 1392(m), 1361(m), 1306(w), 1283(m), 1254(m), 1202(s), 1170(w), 1102(w), 1024(w), 971(w), 875(m), 841(w), 751(m), 677(w), 592(w), 558(w), 504(w), 430(w). Mass spec (Electrospray, positive): 1372 ($M^+ - OEt$).

Synthesis of $[Mo(NCMe)(2-C_6H_4CH_2CH_2C_6H_4N-2-CHC_6H_2-2'-(OH)-3',5'-tBu)L] \cdot (2 \cdot 2MeCN)$

The complex $\{Mo(OtBu)_2[(2-NC_6H_4)_2CH_2CH_2]\}$ (1.00 g, 2.22 mmol) and p-*tert*-butylcalix[4]areneH₄ (1.44 g, 2.22 mmol) were refluxed in toluene (30 ml) for 12 h. Following removal of the volatiles *in vacuo*, 2-hydroxy-3,5-di-*tert*-butylsalicylaldehyde (0.52 g, 2.2 mmol) and ethanol (30 ml) were added and the system was refluxed for 12 h. Volatiles were removed and the resulting yellow solid was extracted in hot MeCN (30 ml) and on prolonged standing (1 - 2 days), small yellow prisms of **2** formed. Yield 1.77 g, 62 %. $C_{75}H_{89}N_3O_5Mo$ (sample dried *in vacuo* for 12 h; – 2MeCN) requires C 74.54, H 7.42, N 3.48 %. Found: C 73.82, H 7.39, N 3.46 %. IR (cm^{-1}): 3176(s), 3054(w), 2956(s), 2905(w), 2868(w), 2715(w), 2251(w), 1955(w), 1918(w), 1754(w), 1614(s), 1590(w), 1572(w), 1483(s), 1392(m), 1361(m), 1305(w), 1285(w), 1250(m), 1203(s), 1171(w), 1103(w), 1024(w), 967(w), 947(w), 918(w), 873(m), 840(w), 801(s), 750(m), 706(w), 673(w), 590(w), 557(w), 504(w), 430(w). Mass spec (ASAP, solid): 1208 ($M^+ - 2MeCN$), 1167 ($M^+ - 3MeCN$).

Synthesis of $[C_{46}H_{42}N_4O_2]^{2+}[Mo_6O_{19}]^{2-} \cdot MeCN$ (**3**·MeCN)

$\{Mo[(2-NC_6H_4)_2CH_2CH_2]Cl_2(DME)\}$ (1.00 g, 2.15 mmol) and [1,3-(CHO)₂-5-MeC₆H₃OH-2] (0.17 g, 1.0 mmol) were refluxed in ethanol (30 ml) for 12 h. On cooling, volatiles were removed *in vacuo*, and the residue was extracted into MeCN (20 ml). Prolonged standing (1 - 2 days) at ambient temperature afforded small orange prisms of **3**·MeCN. Yield 0.20 g, 35 % (based on Mo). $C_{46}H_{42}N_4O_2^{2+} \cdot Mo_6O_{19}^{2-}$

$\cdot\text{C}_2\text{H}_3\text{N}$ requires C 35.95, H 2.83, N 4.37 %. Found: C 35.59, H 2.77, N 4.17 %. IR (cm^{-1}): 3163w, 1658w, 1632w, 1568s, 1408s, 1305m, 1261s, 1207w, 1153m, 1096s, 973w, 802m, 722s. Mass spec (ASAP, solid): 1603 (M^+), 651 ($\text{M}^+ - \text{MeCN} - \text{Mo}_6\text{O}_{19}$).

Crystallography for 1·2MeCN, 2·2MeCN, and 3·MeCN.

Intensity measurements were made on a Bruker SMART 1K or APEX II CCD area detector diffractometer using synchrotron radiation ($\lambda = 0.6942 \text{ \AA}$) at Daresbury SRS Station 9.8 [12, 26], using silicon 111-monochromated radiation. Further details are given in Table 2. Data were corrected for Lp effects and for absorption based on repeated and symmetry equivalent measurements. The structures were solved by direct methods and refined on F^2 for all data, with anisotropic displacement parameters for all non-H atoms. [27, 28] H atoms attached to C were constrained, those in OH and NH groups had coordinates refined. In 1·2MeCN the *t*Bu methyl groups at C(18) and C(70) were modelled as two-fold disordered with major occupancy 51.0(10) and 62(5)% respectively. For 3·2MeCN the N–H distances were gently restrained to be similar.

CCDC 1574780-1574782 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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Supporting Information Available: X-ray crystallographic files CIF format for the structure determinations of compound **1**·2MeCN, **2**·2MeCN and **3**·MeCN.

Table 2. Crystallographic data for complexes **1**·2·MeCN, **2**·2MeCN and **3**·MeCN

Compound	1 ·2(MeCN)	2 ·2MeCN	3 ·MeCN
Formula	C ₈₃ H ₁₀₃ N ₆ O ₆ KMo	C ₇₉ H ₉₅ N ₅ O ₅ Mo	C ₄₈ H ₄₅ N ₅ O ₂₁ Mo ₆
Formula weight	1415.75	1290.53	1603.53
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions			
<i>a</i> (Å)	13.7893(5)	14.1648(5)	11.5285(9)
<i>b</i> (Å)	15.6324(6)	16.0563(6)	31.447(3)
<i>c</i> (Å)	20.0884(8)	16.3360(6)	14.7263(11)
<i>α</i> (°)	67.356(2)	68.9642(4)	
<i>β</i> (°)	81.686(2)	87.5746(5)	96.118(3)
<i>γ</i> (°)	77.285(2)	85.2534(5)	
<i>V</i> (Å ³)	3889.8(3)	3455.6(2)	5308.4(8)
<i>Z</i>	2	2	4
Temperature (K)	160(2)	150(2)	160(2)
Wavelength (Å)	0.6942	0.6942	0.6942
Calculated density (g.cm ⁻³)	1.21	1.24	2.01
Absorption coefficient (mm ⁻¹)	0.26	0.23	1.36
Transmission factors (min./max.)	0.969 and 0.995	0.949 and 0.991	0.782 and 0.987
Crystal size (mm ³)	0.12 × 0.04 × 0.02	0.23 × 0.06 × 0.04	0.19 × 0.03 × 0.01
<i>θ</i> (max) (°)	29.3	29.7	27.5
Reflections measured	28583	40051	28654
Unique reflections	18950	20566	12740

R_{int}	0.040	0.037	0.051
Reflections with $F^2 > 2\sigma(F^2)$	16812	16065	8599
Number of parameters	950	835	735
$R_1 [F^2 > 2\sigma(F^2)]$	0.075	0.048	0.060
wR_2 (all data)	0.156	0.124	0.143
GOOF, S	1.223	1.036	0.94
Largest difference peak and hole ($\text{e } \text{\AA}^{-3}$)	1.54 and -1.92	0.52 and -0.56	1.90 and -2.93

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