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COMMUNICATION

Metal complexes as host molecules: the X-ray crystal structure of $[Mo\{HB(3,5\text{-}Me_2pz)_3\}(NO)\{1,3\text{-}O_2\text{-}4\text{-}CH_2(C_6H_{13})C_6H_2\}]_4 \cdot 2CH_2Cl_2$

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Abstract—The reaction between $[Mo(HBpz_3)(NO)I_2]$ and tetrahexylcalix[4]resorcinarene affords container molecules in which two, three or four $\{Mo(HBpz_3)(NO)\}$ units are incorporated into the rim to produce a host site. A crystal structure of the tetrametallated derivative reveals that one nitrosyl ligand forms a hydrogen bond with a CH_2Cl_2 guest molecule included in the host site. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: molybdenum; nitrosyl; cyclophane; inclusion compound; hydrogen bond.

Macrocyclic molecules, and cyclophanes in particular, have played a central role in the development of "host–guest" and subsequently supramolecular chemistry [1]. The incorporation of transition-metal centres into cyclophane structures offers opportunities to introduce new properties such as magnetism or redox activity into the macrocyclic structure. In addition, there is the prospect that, when assembled into macrocyclic arrays, transition metal complexes themselves may act as recognition sites and interact with incorporated guest molecules. Such behaviour could provide new opportunities to study interactions in the second coordination sphere of metal complexes. Examples of such compounds based on anion binding to metallocene cations have recently been described by Atwood *et al.* [2]. In our laboratory we are investigating the use of octahedral metal centres with *cis*-substitution sites to construct metallocyclophanes. Thus, the redox-active $\{M(tp^*)(X)\}^{2+}$ [tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate; X = NO, M = Mo or W; X = O, M = Mo] moieties have been incorporated in metallocyclophanes containing from two up to five metal centres [3]. An alternative approach to metallocyclophane construction involves the addition of metal centres to a preformed macrocyclic ligand, which carries multiple metal binding sites on its outer rim, rather than a single metal binding site at its centre. Puddephatt *et al.* have introduced phosphinate groups into the rim of a calix[4]resorcinarene and then used these to bind metal ions [4]. More recently Floriani and co-workers have reported the direct metallation of the hydroxyl functionalized face of a calix[4]resorcinarene with $\{Zr(\eta^5\text{-}C_5H_5)_2\}$ units [5]. In this communication we describe the construction of metallomacrocyclic host molecules by direct metallation of a calix[4]resorcinarene with two, three and four molybdenum mononitrosyl units.

The reaction of $[Mo(tp^*)(NO)(I)]_2$ with tetrahexylcalix[4]resorcinarene ($resH_8$) affords bi-, tri- and tetrametallated resorcinarene derivatives $[\{Mo(tp^*)(NO)\}_n\{resH_{(8-2n)}\}]$ ($n = 2, 3, 4$), which may be identified by fast atom bombardment mass spectrometry (FABMS). However, in this case the steric demands

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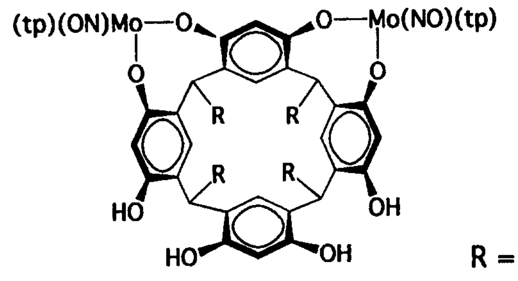
of the tp* ligand are not helpful and the products obtained are easily decomposed and difficult to isolate in pure form. More robust, air-stable products may be obtained using the less sterically demanding tp$^-$ (tp$^-$ = hydrotrispyrazol-1-ylborate) ligand. Hence, the bi-, tri- and tetrametallated derivatives (**1**, **2** and **3**, Fig. 1) can be isolated from the products of the reaction between $[Mo(tp)(NO)(I)]_2$ and tetrahexylcalix[4]resorcinarene after repeated column chromatography. Samples of **1**, **2** and **3** have been characterized by FABMS, IR and ^1H NMR spectroscopy and by elemental analyses [6]. These compounds constitute potential host molecules in which up to four {Mo(tp)(NO)} moieties form the walls of "container molecules". In $(CD_3)_2C{=}O$ the ^1H NMR spectra of **1** and **2** contain the signals expected for the structures shown. However, in CD_2Cl_2 or $CDCl_3$ solutions substantial changes are apparent in the chemical shifts of signals attributable to the tp and resorcinarene ligands suggesting that specific solvation interactions are occurring with these hydrogen-bond donor solvents. Solvatochromism studies of $[\{Mo(tp)(NO)X\}_x(NC_5H_4(CH{=}CH)_4H_4C_5N\text{-}4,4')]$ ($n = 1, 2$; X = Cl, I) have indicated [7] that hydrogen-bond donor solvents interact with coordinated nitric oxide in complexes of this type and similar interactions in **1** and **2** could account for the ^1H NMR results. The solid state (KBr discs) IR spectra of dried samples of **1** and **2** each contain two nitrosyl stretching frequencies at 1691 and 1678 cm^{-1} (**1**) and 1699 and 1683 cm^{-1} (**2**). However, these bands are absent in the solution IR spectra of **1** and **2** recorded in CH_2Cl_2 solution and instead new absorptions are observed in the region 1600–1640 cm^{-1}. In the case of **3** it has been possible to crystallize a dichloromethane solvate and determine its structure by a single-crystal X-ray diffraction study.

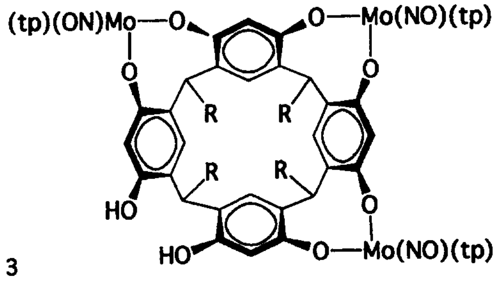
Structural studies [8]

The structure of the complex **3** is shown in Fig. 2 and contains two molecules of dichloromethane. Selected bond lengths and angles are given in Table 1. Although the four molybdenum atoms are not coplanar (deviations ±0.3 Å), to a first approximation they occupy the vertices of a nearly equilateral parallelogram with Mo(1)···Mo(3) [10.907 Å > Mo(2)···Mo(4) 8.636 Å]. The coordination geometry at molybdenum is essentially octahedral with mean deviations from ideal octahedral angles at the four molybdenum atoms, respectively, 6.9, 6.7, 7.2 and 6.6°. These values are similar to those found in monomeric complexes containing the {Mo(tp*)(NO)} moiety where the other two bonds completing the octahedron are relatively short; for example, in the bis-amido complex $[Mo(NO)tp^*(NHBu^n)_2]$ [12] the mean angular deviation from ideal octahedral is 7.1°. These deviations, however, show a consistent pattern. Comparing angles in the amido complex with the corresponding angles at the four molybdenum centres yields mean deviations of only 2.4, 1.7, 2.3 and 1.8°, respectively. It may, therefore be concluded that the geometry at molybdenum is not greatly affected by linking monomeric units into the four-centre cyclic structure. Further, the methyl substituents on the pyr-

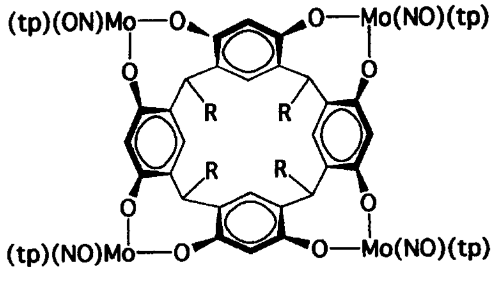


1

R = n-C_6H_{13}



2



3

Fig. 1. Formulae of **1**, **2** and **3**. ^1H NMR spectrum of **1** is consistent with the approximately C_s structure shown rather than the alternative approximately C_{2v} structure in which the Mo atoms occupy non-adjacent sites in the macrocycle rim.

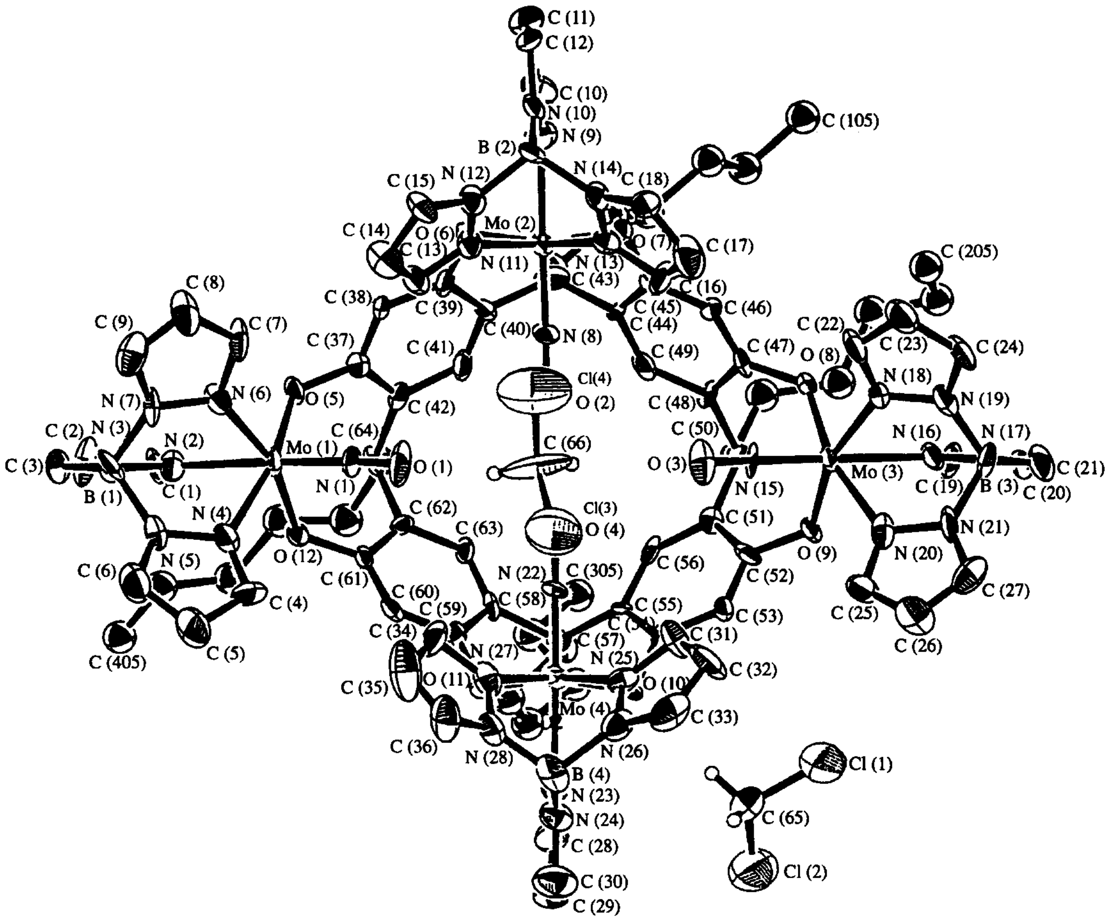


Fig. 2. ORTEP [11] view of complex **3** looking down the central cavity; thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. The atoms of the hexyl side chains have been assigned arbitrary isotropic thermal parameters ($U = 0.07$ Å^2); only the terminal methyl carbon atoms of these chains have been labelled.

Table 1. Selected bond lengths (Å) and angles (°) at the molybdenum atoms. N(n) denotes the nitrosyl nitrogen atoms, N(t) denotes the pyrazolyl nitrogen atom *trans* to N(n), N(c) denotes the pyrazolyl nitrogen atoms *cis* to N(n), O(n) denotes the nitrosyl oxygen atom

	Mo(1)	Mo(2)	Mo(3)	Mo(4)
Mo—N(n)	1.82(2)	1.79(2)	1.72(2)	1.74(2)
Mo—O	1.922(23)	1.958(11)	1.930(16)	1.934(13)^a
Mo—N(t)	2.23(2)	2.23(2)	2.20(2)	2.22(2)
Mo—N(c)	2.199(24)	2.212(4)	2.188(49)	2.165(9)^a
N(n)—O(n)	1.17(2)	1.14(2)	1.18(2)	1.17(2)
N(n)—Mo—N(t)	175.5(9)	175.3(8)	176.8(8)	175.6(8)
N(n)—Mo—N(c)	93.4(8)	92.5(3)	95.4(0)	92.5(1)^a
N(n)—Mo—O	97.6(3)	96.4(11)	96.4(3)	96.5(8)^a
N(t)—Mo—O	85.3(12)	86.4(4)	85.8(3)	86.2(0)^a
N(t)—Mo—N(c)	83.3(2)	84.1(8)	82.1(0)	84.2(6)^a
N(c)—Mo—O trans angle	165.3(28)	163.9(5)	164.2(13)	164.4(12)^a
N(c)—Mo—O cis angle	92.0(35)	90.6(2)	92.5(17)	90.7(10)^a
N(c)—Mo—N(c)	77.8(7)	75.6(6)	76.0(7)	76.1(7)
O—Mo—O	95.9(5)	101.8(5)	96.8(6)	100.9(5)
Mo—O—C	126.6(7)	121.1(3)	127.7(11)	119.2(14)^a
Mo—N(n)—O(n)	175(2)	178(2)	174(2)	177(2)

^{a}Mean of two measurements; estimated standard deviations calculated as $(|x1-x2|)/2$.

azolyl rings, present in the amido complex, but not in the title compound, appear to have little effect on the coordination geometry. Corresponding angles at the four molybdenum atoms agree closely, especially those between opposed molybdenums. Thus, the mean angular deviations between the coordination geometries at Mo(1) and Mo(3), and between Mo(2) and Mo(4) are 1.2 and 0.3°, respectively. Between adjacent centres, mean angular deviations are in the range 1.4–1.7°. The O—Mo—O angles show a small, but systematic, trend, 95.9(5) and 96.8(6)° at Mo(1) and Mo(3), 101.8(5) and 100.9(5)° at Mo(2) and Mo(4). The Mo—O—C angles also exhibit a trend, so that the oxygen atoms involved in large O—Mo—O angles have a relatively small Mo—O—C angle, 126.6(7) and 127.7(11)° at Mo(1) and Mo(3), 121.1(3) and 119.2(14)° at Mo(2) and Mo(4). Bond lengths are generally normal. The shortest Mo—N bonds are to the nitrosyl ligands with the Mo—N(pyrazolyl) bonds *trans* to this bond, tending to be slightly longer than the other Mo—N(pyrazolyl) bonds.

As illustrated in Fig. 2, the lower rim of the central cavity is defined by the 16 atom, planar to within ±0.53 Å, carbocyclic ring, C(40)—C(43)—C(44)—C(49)—C(48)—C(50)—C(51)—C(56)—C(55)—C(57)—C(58)—C(63)—C(62)—C(64)—C(42)—C(41). The critical distances, defining the effective size of the cavity, are C(41)—H···C(56)H and C(49)—H···C(63)—H, the C···C distances being 5.19 and 5.12 Å, respectively, and the corresponding H···H distances 3.93 and 3.88 Å. The four nitrosyl ligands are oriented *syn* with respect to the central cavity and the upper rim of the cavity is almost completely blocked by the nitrosyl ligands at Mo(2) and Mo(4), O(2)···O(4) 2.80 Å. The hexyl side chains do not encroach on the central cavity, apart from a minor encroachment by one terminal methyl group, C(305).

In the crystal, one molecule of dichloromethane is sited almost symmetrically above the four nitrosyl ligands, with the hydrogen atoms pointing towards O(1) and O(3) (Fig. 2), H(66A)···O(1) 2.47 Å, angle C(66)—H(66A)···O(1) 161°, H(66B)···O(3) 2.80 Å, angle C(66)—H(66B)···O(3) 159°. The chlorine atoms overlie the oxygen atoms of the other two nitrosyls, Cl(3)···O(4) 3.917 Å, Cl(4)···O(2) 3.728 Å. The second dichloromethane molecule lies close to O(10) of the complex, with H(65)···O(10) 2.57 Å, angle O(65)—H(65)···O(10) 168°. These H···O distances are greater than is normally considered to indicate C—H···O hydrogen bonding in organic compounds [13] but two are less than the van der Waals sum for H and O of 2.6 Å. In particular, the H(66A)···O(1) distance of 2.47 Å is significantly shorter than the distance of *ca* 2.6 Å typically found for C—H hydrogen bonding to the oxygen atoms of terminally coordinated carbonyl ligands [14].

The construction of host molecules in which *d*-block metal coordination entities constitute part of the "walls" of the container presents new opportunities for studying intermolecular interactions involving the second coordination spheres of metal complexes. In the examples presented here a specific interaction between a hydrogen bond donor solvent and coordinated nitric oxide has been structurally identified.

Supplementary material. Atomic coordinates, thermal parameters, full lists of bond lengths and angles, crystal data and refinement details.

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6. After drying *in vacuo* at 100°C **1, 2** and **3** gave satisfactory C, H and N analyses for the unsolvated compounds. The ^1H NMR spectra were in accord with the formulations shown and the pattern of signals for **1** is consistent with the molybdenum atoms occupying adjacent rather than non-adjacent sites in the rim of the calixresorcinarene.
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8. 8274 independent reflections (θ 1.8–22.0°), with $I > \sigma(I)$, measured on a Rigaku R-AXIS II area detector diffractometer, were used in the analysis. Crystal data: $C_{88}H_{104}B_4Mo_4N_{28}O_{12} \cdot 2CH_2Cl_2$, $M_r = 2342.8$, monoclinic, space group $P2_1/c$, $a = 20.107(5)$, $b = 14.802(4)$, $c = 38.241(7)$ Å, $\beta = 97.29(3)°$, $U = 11289$ Å^3, $Z = 4$, $D_c = 1.378$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 0.595$ mm^{-1}, $\lambda = 0.71069$ Å. The structure was determined [9] by direct methods and refined [10] by least-squares using anisotropic thermal parameters for all the non-hydrogen atoms, except for the outer five atoms of the four hexyl side chains. These atoms were located with some difficulty from Fourier difference syntheses and included in the refinement with fixed coordinates; only their isotropic temperature factors were refined. Hydrogen atoms were placed in calculated positions and assigned isotropic temperature factors. Final $R = 0.0842$ for 4749 observed reflections $[I > 2\sigma(I)]$ and 0.1245 for all 8274 data. Residual electron density in a final difference map is within the range -0.59 to 0.64 e Å^{-3}. We attribute the relatively high value of the discrepancy factors to the difficulty of modelling the hexyl chains, which may be affected by disorder.
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