

The Oxo-molybdenum(VI) Group over a Calixarene-oxo Surface: Calix[4]arene Complexing Inorganic and Organic Functionalities

Fabio Corazza,^a Carlo Floriani,^{*a} Angiola Chiesi-Villa,^b and Carlo Guastini^b

^a Section de Chimie, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

^b Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffraattometrica del CNR, Università di Parma, I-43100 Parma, Italy

Oxomolybdenum(VI) binds four oxygen atoms from the cone conformation of a calix[4]arene, and the resulting complex forms with a molecule of free calix[4]arene, a dimer trapping nitrobenzene, the crystal structure of which has been determined.

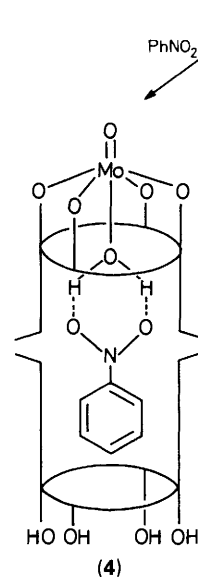
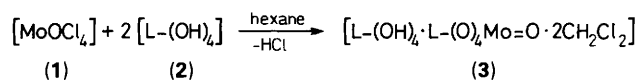
Calix[*n*]arenes¹ have not so far been considered as special oxo-matrices for binding inorganic or organometallic functionalities, in spite of the fact that they can have cone conformations with the oxygen atoms oriented almost as a surface. It is noteworthy that calixarenes functioning as ligands bring to the metal all the advantages of their peculiar properties.¹ From the few examples reported, the metal derivatization of calix[*n*]arenes is so far, however, more an accident than an established methodology.²

In an attempt to bind a single inorganic functionality to all the four oxygen atoms of calix[4]arene (2), we reacted it with [MoOCl₄]. [MoOCl₄] has the appropriate geometry and contains the interesting Mo^{VI}=O functionality.^{3,4}

The reaction between (1) and (2) was carried out many times in *n*-hexane but, independently of the different molar ratios used, they reacted in a 1 : 2 molar ratio.⁵ The blue solid formed, upon extraction with CH₂Cl₂, gave (3) as a blue crystalline solid (ca. 80%).

Complex (3)[†] is diamagnetic and poorly soluble in most organic solvents. It maintains the rather intriguing stoichiometry even when recrystallized from nitrobenzene. Such a recrystallization gave [L-(OH)₄·L-(O)₄Mo=O·PhNO₂·H₂O] (4)[‡] as green crystals and its crystal structure has been determined. An overall picture of (4) is given in Figure 1, with the most relevant structural parameters.

The structure should be interpreted on the basis of the isostructural calix[4]arene itself.⁶ In the unit cell there are



[†] Satisfactory analytical and ¹H NMR data have been obtained for (3) and (4).

[‡] Crystal data for (4): C₉₄H₁₁₅MoNO₁₂, *M* = 1546.9, tetragonal, space group *P4/mnc*, *a* = *b* = 12.890(2), *c* = 25.537(4) Å, *U* = 4243.0(1) Å³, *Z* = 2, *D_c* = 1.211 g cm⁻³, Mo-*K*_α radiation (*λ* = 0.71069 Å), *μ*(Mo-*K*_α) = 2.07 cm⁻¹, crystal dimensions 0.16 × 0.26 × 0.35 mm; 801 unique observed structure amplitudes [*I* > 2σ(*I*)] collected at room temperature on a CAD4 diffractometer in the range 6 < 2θ < 50°. The structure was solved starting from the co-ordinates of calix[4]arene. Some troubles were encountered in refining the structure because of the presence of a high degree of disorder involving molybdenum and nitrobenzene. It was solved considering the molybdenum atom and its *trans*-ligands statistically distributed over two positions related by a two-fold axis. Nitrobenzene was considered statistically distributed over four positions, two of them related by the same two-fold axis and the others related to each other by the four-fold axis. The atoms were assigned the site occupancy factors given in the table of atomic co-ordinates in the supplementary data. This model converged to *R* = 0.055 and then was considered satisfactory. All the non-hydrogen atoms except those of nitrobenzene were put in geometrically calculated positions and introduced in the final refinement as fixed contributors. During the refinement constraints were applied to the bond distances within nitrobenzene. All calculations were carried out using SHELX76. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

pairs of calix[4]arene molecules facing their cavities. They present a very high symmetry, each monomer having *C*₄ symmetry, and being related to the other by a two-fold axis perpendicular to the four-fold axis. Each pair could be considered the fundamental entity of the complex. A deprotonated calix molecule in a 'dimer' co-ordinates to molybdenum through the oxygen atoms [Mo-O(1), 1.901(5) Å] while the other is in its protonated form. Co-ordination around molybdenum is pseudo-octahedral with an oxo-group [Mo-O(2), 1.673(16) Å]⁷ and a weakly bonded water molecule [Mo-O(3), 2.408(16) Å] in the axial positions. All the other molybdenum-oxygen distances are quite normal⁷ as well as the bond distances and angles within the calix[4]arene itself.⁶ The molybdenum atom is displaced by 0.337(3) Å from the plane through the O(1) oxygen atoms. The O=Mo-O angles [100.2(3)°] are very close to those in [MoOCl₄] [102.8(3)°]. Each dimer provides a cavity in which the nitrobenzene can be accommodated, the oxygen atoms [O(1S)] pointing towards the water molecule [O(3)] having contact distances of 3.19(3) Å. These could be considered as weak hydrogen-bonding interactions. The disorder around either the four-fold axis or the two-fold axis perpendicular to it and running through C(1S) accounts for the relative long distance. A dimer where deprotonated and protonated calix[4]arene molecules are interchanged, as well as the dimer where nitrobenzene and water are rotated by 90° are equally probable and this justifies the statistical distribution observed. The same dimer having nitrobenzene pointing -NO₂ towards the free calix[4]arene is

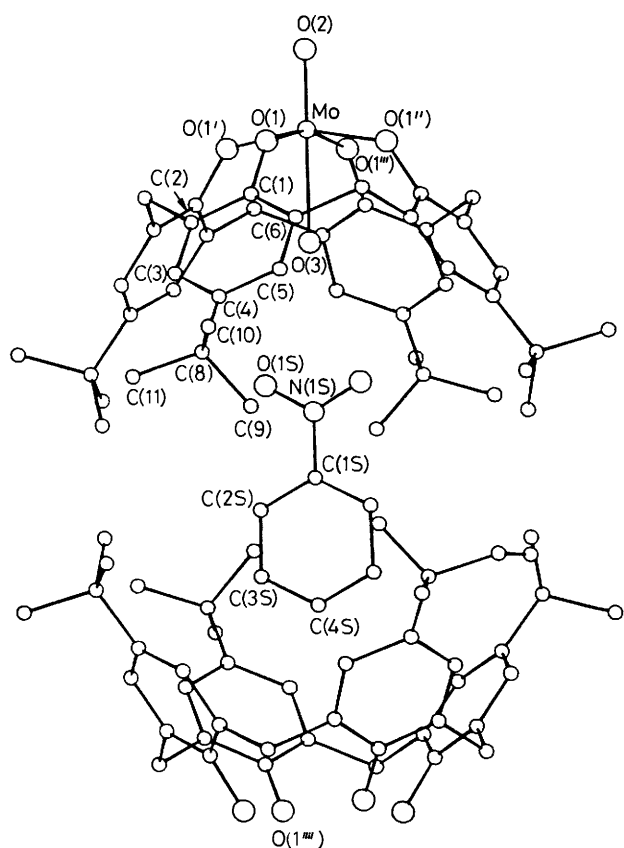


Figure 1. A view of the complex molecule. Bond distances (Å): Mo–O(1), 1.901(5); Mo–O(2), 1.673(16); Mo–O(3), 2.408(16); O(1)–C(1), 1.378(9); O(3)···O(1S), 3.19(3). Bond angles (°): O(2)–Mo–O(3), 180.0(4); O(1)–Mo–O(3), 79.8(3); O(1)–Mo–O(2), 100.2(4); O(1)–Mo–O(1'), 88.2(2); O(1)–Mo–O(1''), 159.6(2). Symmetry transformations: ' $\equiv y, \frac{1}{2} - x, z$;' " $\equiv \frac{1}{2} - y, x, z$;' "' $\equiv \frac{1}{2} - x, \frac{1}{2} - y, z$;' "" $\equiv x, \frac{1}{2} - y, \frac{1}{2} - z$.

not possible because of the inconsistent contact distances [*i.e.* O(3)–C(4S'''), 2.30 Å].

Some of the chemical peculiarities of the structure of (4) have to be emphasized. The water molecule is introduced during the crystallization from nitrobenzene. Neither water nor nitrobenzene, however, are responsible for the dimeric association which pre-exists in (3) obtained from hexane and dry CH₂Cl₂. The structure of (4) summarizes in a certain sense some of the peculiarities of the calixarene–transition metal entities. A functional group [Mo=O] is exposed over an oxo-surface matrix ready for reactivity. In the meantime, the cavity of the calixarene is acting as a guest for an organic substrate kept in its position by some weak interactions including hydrogen bonding.

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