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Preliminary Communication

Calixarene complexes of the molybdenum–molybdenum quadruple bond [☆]

Jacqueline A. Acho, Stephen J. Lippard *

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

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Abstract

We report here the first examples of metal–metal quadruple bonds supported by calixarene ligands in the complexes $[Mo_2(OAc)_2(H_2\text{-calix[4]arene})]$ (**1**) and $[Mo_2(OAc)_2(H_2\text{-}p\text{-tert-butylcalix[4]arene})]$ (**2**). Complexes **1** and **2** were prepared by first deprotonating calix[4]arene and *p*-tert-butyl-calix[4]arene, respectively, with two equivalents of KH, followed by the addition of $[Mo_2(OAc)_2(NCMe)_6][BF_4]_2$. X-ray crystallographic analysis revealed the solid state structure of $\mathbf{2}(THF)\cdot C_6H_6$. A molybdenum–molybdenum quadruple bond (2.1263(6) Å) is spanned by two bridging acetate ligands and a tetradentate, doubly-deprotonated calixarene macrocycle. Each Mo–Mo unit is weakly coordinated by an axial THF solvent molecule which is included in the calixarene basket of the neighboring complex.

Keywords: Molybdenum complexes; Calixarene complexes; Quadruple bond complexes; Dinuclear complexes

Calixarenes [1], named for their chalice-like cone conformation (Fig. 1), have attracted considerable attention because of their ease of preparation [2], ability to form inclusion complexes (see, for example, Ref. [3]), and multiple binding sites for transition metals (examples given in Ref. [4]). Although multiply metal–metal bonded alkoxide and aryloxide complexes are well known [5], no examples are available with the geometrically-hindered, methylene-tethered phenols of the calix[4]arene class. In the present study we synthesized quadruply-bonded dimolybdenum calixarene complexes by allowing the readily prepared, labile starting material $[Mo_2(OAc)_2(NCMe)_6][BF_4]_2$ [6,7] to react with calix[4]arene macrocycles.

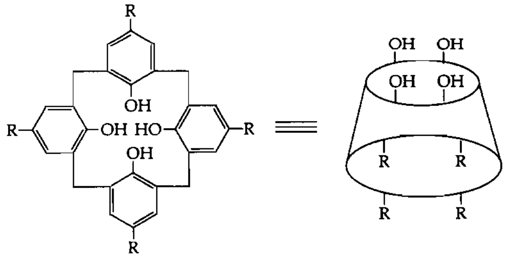

Fig. 1. Two representations of calix[4]arenes (calix[4]arene for R = H; *p*-tert-butyl-calix[4]arene for R = tert-butyl).

To a stirred solution of calix[4]arene (100 mg, 0.236 mmol) in 20 ml of THF were added 2 equiv. of KH (19 mg, 0.474 mmol). The effervescent reaction solution clarified after 1 h, and 1 equiv. of insoluble pink $[Mo_2(OAc)_2(NCCH_3)_6][BF_4]_2$ (172 mg, 0.236 mmol) was added. Over the next hour, the pink solid disappeared, producing a wine-red solution. The solvent was removed in vacuo and the product was extracted into toluene. Filtration through celite removed any residual starting material. Evaporation of the solvent from the filtrate afforded the red–orange, air-sensitive product $[Mo_2(OAc)_2(H_2\text{-calix[4]arene})]$ (**1**) (120 mg, 0.164 mmol) in 69% yield. The product could be recrystallized by slow diffusion of pentane into a toluene solution of **1** containing a few drops of THF. The compound $[Mo_2(OAc)_2(H_2\text{-}p\text{-tert-butyl-calix[4]arene})]$ (**2**) was similarly prepared by addition of $[Mo_2(OAc)_2(NCCH_3)_6][BF_4]_2$ (112 mg, 0.153 mmol) to a THF solution of *p*-tert-butyl-calix[4]arene (114 mg, 0.154 mmol) doubly-deprotonated by KH (12 mg, 0.299 mol). As the insoluble pink starting material reacted, a red–orange solution developed. The solvent was evaporated, the product extracted with pentane, and the

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[☆] This paper is dedicated to Professor F. Albert Cotton, teacher and friend, on the occasion of his 65th birthday.

* Corresponding author.

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pentane extract filtered through celite. Concentration of the pentane solution to dryness resulted in microcrystalline, air-sensitive orange–pink **2** (107 mg, 0.112 mmol) in 73% yield. Further purification by recrystallization from pentane at −40 °C afforded a mass of fluffy orange–pink needles. The formulations of **1** and **2** are supported by analytical data, by UV–Vis and IR spectroscopic features characteristic of quadruply-bonded dimolybdenum centers, and by ^{1}H NMR data showing four methylene doublets arising from a geometrically fixed calixarene ligand with approximately twofold symmetry[1].

X-ray quality crystals of $\mathbf{2}(THF) \cdot C_6H_6$ could be grown by slow diffusion of pentane into a benzene solution of **2** containing a small amount of THF. The structure determination[2] confirmed that $\mathbf{2}(THF) \cdot C_6H_6$ contains a dimolybdenum core supported by two bidentate acetate ligands and a doubly-deprotonated calixarene macrocycle (Fig. 2). The Mo–Mo distance of 2.1263(6) Å and the eclipsed geometry of the Mo_2O_8 skeleton are consistent with a bond order of 4 [8,9] and compare favorably with other alkoxide [10,11] and phenoxide [12,13] complexes of the $[\mathrm{Mo}\overset{4}{-}\mathrm{Mo}]$ core (e.g. $[Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4]$, Mo(1)–Mo(2) = 2.110(3) Å; $[Mo_2(OC_6F_5)_4(NHMe_2)_4]$, Mo(1)–Mo(2) = 2.140(2) Å).

The bridging tetradentate coordination of the calixarene ligand in **2** is reminiscent of the bridging bis-bidentate coordination of the tetraazamacrocyclic H_2TMTAA (5,7,12,14-tetramethyldibenzo[*b,i*][1,4,8,11]-tetraazacyclotetradecine) ligand in $[Mo_2(O_2CR)_2(TMTAA)]$ [14]. In both cases, the $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ bond is spanned by the macrocycles. This mode of binding is different from the more common binding motif of the tetradentate macrocycles found in $[\{Mo(TMTAA)\}_2]$ [15,16], $[\{Mo(acacen)\}_2]$]17], $[\{Mo(TPP)_2\}]$ [18], $[\{Mo(OEP)\}_2]$ [19] and $[\{Mo(TOEP)\}_2]$ [20]. In these complexes, one macrocycle is coordinated to each molybdenum center, leaving the $[\mathrm{Mo}\overset{4}{-}\mathrm{Mo}]$ core unsupported.

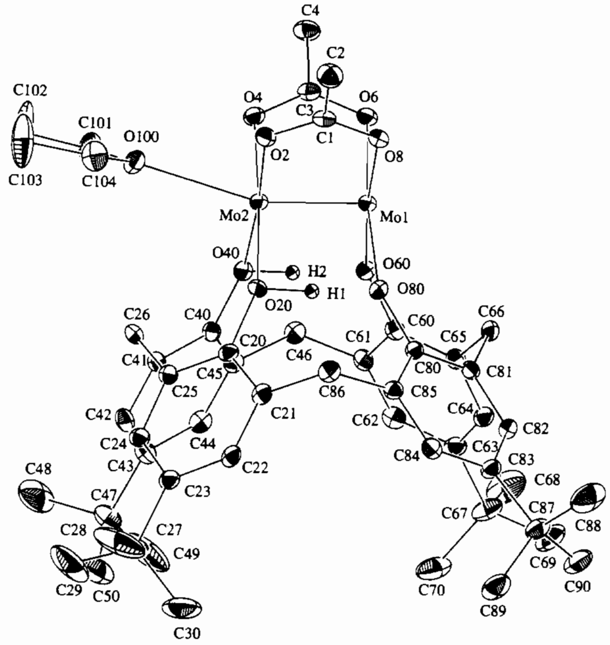

Fig. 2. An ORTEP drawing of $[Mo_2(OAc)_2(H_2\text{-}p\text{-tert-butylcalix[4]arene})(THF)]$ (**2**(THF)) showing the 30% thermal ellipsoids for all non-hydrogen atoms and the atom labeling scheme. The phenolic hydrogen atoms, H1 and H2, were located on a difference Fourier map and refined isotropically. Selected interatomic distances (Å) and angles (°) are as follows: Mo1–Mo2, 2.1263(6); Mo1–O60, 2.120(3); Mo1–O80, 2.107(3); Mo1–O6, 2.081(3); Mo1–O8, 2.083(3); Mo2–O20, 2.148(3); Mo2–O40, 2.144(3), Mo2–O2, 2.082(3); Mo2–O4, 2.095(3); Mo2–O20–C20, 145.8(3); Mo2–O40–C40, 145.4(3); Mo1–O60–C60, 143.7(3); Mo1–O80–C80, 146.4(3); Mo1–Mo2–O20, 93.08(9); Mo1–Mo2–O40, 94.07(9); Mo2–Mo1–O60, 93.35(8); Mo2–Mo1–O80, 93.73(9).

The phenolic hydrogen atoms H1 and H2 form strong hydrogen bonds to the phenoxide oxygen atoms within the calixarene ligand parallel to the Mo–Mo vector (Fig. 2). In the solid state, these hydrogen bonds are short (O40···O60 = 2.403(4) Å, O20···O80 = 2.380(4) Å) and asymmetric (O20–H1 = 1.06(5), H1···O80 = 1.32(6) Å; O40–H2 = 0.99(5), H2···O60 = 1.43(5) Å). Similarly strong hydrogen bonding in $[Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4]$ (O···O = 2.46 Å) was proposed to contribute to the relatively short Mo–Mo bond in this complex [10]. The asymmetry of the hydrogen bonding in $\mathbf{2}(THF) \cdot C_6H_6$ is also reflected in the 0.02–0.04 Å shorter bond lengths for Mo–O(phenoxide) versus Mo–O(phenol).

In the bridging mode of calixarene binding found in $\mathbf{2}(THF) \cdot C_6H_6$, the average Mo–O(calix) distance is 2.13 Å and the average Mo–O–C(calix) angle is 145°, consistent with approximate sp^2 hybridization of the oxygen atoms. This geometric feature, and the relatively long Mo–Mo distance in $\mathbf{2}(THF) \cdot C_6H_6$ compared to that in $[Mo_2(OAc)_4]$ (Mo–Mo = 2.0934(8) Å) [21], suggest the presence of repulsive interactions between the filled pπ phenol and phenoxide oxygen atomic orbitals and the filled Mo–Mo δ orbitals. Similar interactions were

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[1] *Anal.* Calc. for $Mo_2O_8C_{32}H_{28}$ (**1**): C, 52.47; H, 3.85. Found: C, 52.47; H, 4.27%. IR (CsI, Nujol, cm^{-1}): ν(Mo–Mo), 376. ^{1}H NMR (THF-d$_8$, 300 MHz): δ 2.55 (d, J = 12 Hz, CH$_2$), 2.89 (s, O$_2$CCH$_3$), 3.04 (d, J = 12 Hz, CH$_2$), 3.72 (d, J = 12 Hz, CH$_2$), 4.54 (d, J = 12 Hz, CH$_2$), 6.55 (t, J = 6 Hz, Ph), 7.06 (d, J = 6 Hz, Ph), 16.94 (s, Mo–OHPh). UV–Vis (THF): λ_{max} (nm) (ϵ (Mo cm^{-1} M^{-1})): 380 (712), 512 (591).

Anal. Calc. for $Mo_2O_8C_{48}H_{60}$ (**2**): C, 60.25; H, 6.32. Found: C, 59.99; H, 6.15%. IR (CsI, Nujol, cm^{-1}): ν(Mo–Mo), 381. ^{1}H NMR (THF-d$_8$, 300 MHz): δ 1.21 (s, t-Bu), 2.87 (d, J = 12 Hz, CH$_2$), 2.52 (s, O$_2$CCH$_3$), 3.02 (d, J = 12 Hz, CH$_2$), 3.70 (d, J = 12 Hz, CH$_2$), 4.52 (d, J = 12 Hz, CH$_2$), 7.11 (s, Ph), 16.89 (s, Mo–OHPh). UV–Vis (THF): λ_{max} (nm) (ϵ (Mo cm^{-1} M^{-1})): 379 (1213), 514 (875).

[2] Crystal data for $[Mo_2(OAc)_2(H_2\text{-}p\text{-tert-butylcalix[4]arene})(THF)] \cdot C_6H_6$, ($\mathbf{2}(THF) \cdot C_6H_6$): $Mo_2O_9C_{58}H_{74}$, M_r = 1107.10, monoclinic, space group $P2_1/c$, a = 12.533(2), b = 23.515(3), c = 18.520(2) Å, β = 95.66(2)°, Z = 4, V = 5432(1) Å^3, ρ_{calc} = 1.35 g cm^{-3}. For 6251 unique observed reflections collected at −73.8 °C with $F^2 > 3\sigma(F^2)$, R = 0.040 and R_w = 0.042. Full details will be reported elsewhere.

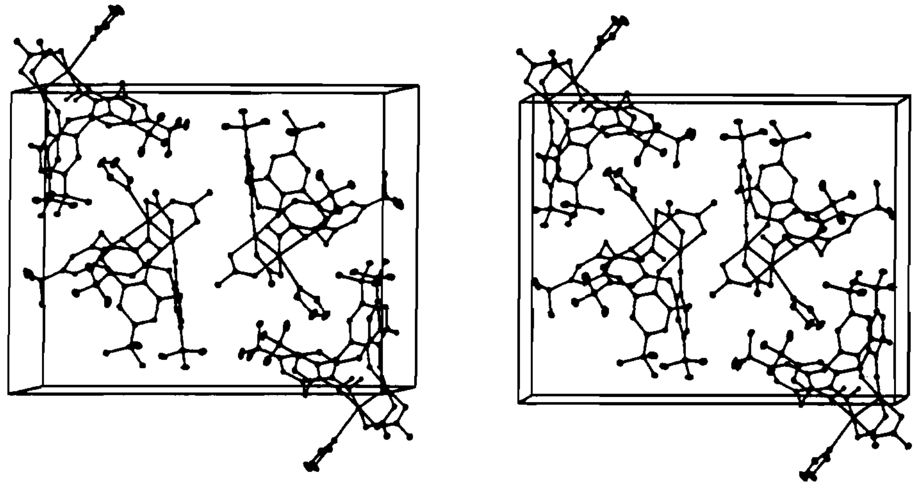

Fig. 3. A stereo ORTEP drawing of $[Mo_2(OAc)_2(H_2\text{-}p\text{-tert-butylcalix[4]arene})(THF)]\cdot C_6H_6$ (2(THF)·C_6H_6). Benzene molecules in the lattice were omitted for clarity.

proposed for $[Mo_2(O\text{-i-Pr})_4(py)_4]$ (Mo–Mo = 2.195 Å, Mo–O_{av} = 2.03 Å, Mo–O–C_{av} = 129°) and $[Mo_2(OCH_2\text{-t-Bu})_4(PMe_3)_4]$ (Mo–Mo = 2.133 Å, Mo–O_{av} = 2.04 Å, Mo–O–C_{av} = 129° [10]. In the case of **2**, this assignment is supported by a preliminary Fenske–Hall calculation, which revealed significant antibonding contributions from the lone pairs of both the phenol and phenoxide ligands to the Mo–Mo δ orbital[3]. Such an interaction is absent in $[Mo_2(OAc)_4]$ and hence the energy level of the δ orbital in **2** is higher than that of $[Mo_2(OAc)_4]$. This qualitative scheme is consistent with the observed red-shift of the $^1(\delta\text{–}\delta^*)$ transition of **2** (λ_{max}, 514 nm; ϵ, 875 M^{-1} cm^{-1}) compared to that of $[Mo_2(OAc)_4]$ (λ_{max}, 435 nm; ϵ, 150 M^{-1} cm^{-1}) [22]. Moreover, the relatively large intensities of the (δ–δ^*) bands in the observed UV–Vis spectra of **1** and **2** most likely result from 'intensity stealing' due to the mixing of calixarene ligand and metal–metal δ orbitals [23].

As indicated in Fig. 2, a molecule of THF is coordinated axially to one end of the dimolybdenum center. Although many quadruply metal–metal bonded complexes accept axial ligands, this phenomenon is less common among dimolybdenum than dichromium compounds, and typically there are two rather than one such axial ligand [5]. The Mo–O(THF) distance (O100–Mo2 = 2.552(3) Å) in **2**(THF)·C_6H_6 is among the shortest observed in the dimolybdenum complexes having axially-coordinated THF molecules (range 2.56–2.80 Å) [24]. A striking feature of the solid state structure of **2**(THF)·C_6H_6 is apparent in the unit cell packing diagram (Fig. 3). The coordinated THF molecule in **2**(THF)·C_6H_6 is nested in the calixarene basket of a neighboring molecule. Such inclusion of neutral molecules by calixarenes has previously been explained in part by invoking alkyl group–phenyl interactions [25]. In the present case, the closest *endo*-calix interaction of 3.50 Å occurs between C102 of the THF molecule and the plane of the phenyl ring C20–C25, a value comparable to that reported for other calixarene inclusion complexes [1,26].

In conclusion, compounds **1** and **2** are the first two members of a novel class of dimolybdenum quadruply-bonded species spanned by calixarene ligands. These preliminary studies suggest that binding of the calixarene across the $[Mo\overset{4}{-}Mo]$ bond induces an interaction between the filled oxygen pπ orbitals of the ligand and the Mo–Mo δ bond. The solid state structure of **2**(THF)·C_6H_6 reveals interactions among neighboring complexes by insertion of a coordinated THF molecule into the chalice of the adjacent calixarene ligand. This feature highlights the special capacity of the calixarene pocket to include neutral guests. Efforts to elucidate further the nature of bonding in this class of complexes by resonance Raman spectroscopy and theoretical calculations are in progress, as are chemical reactivity studies.

Supplementary material

Tables of anisotropic thermal parameters, interatomic bond distances and angles, final positional parameters, and observed and calculated structure factor amplitudes for $[Mo_2(OAc)_2(H_2\text{-}p\text{-tert-butylcalix[4]arene})]$ are available from author S.J.L.

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[3] T. Ren (Florida Inst. of Tech.), personal communication. Molecular orbital calculations by the SCF-Xα-SW method are in progress and will be included in a later report.

the Florida Institute of Technology for preliminary molecular orbital calculations on 2 and helpful discussions.

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