

# Supramolecular metallocalixarene chemistry: linking metallocalixarenes through imido bridges

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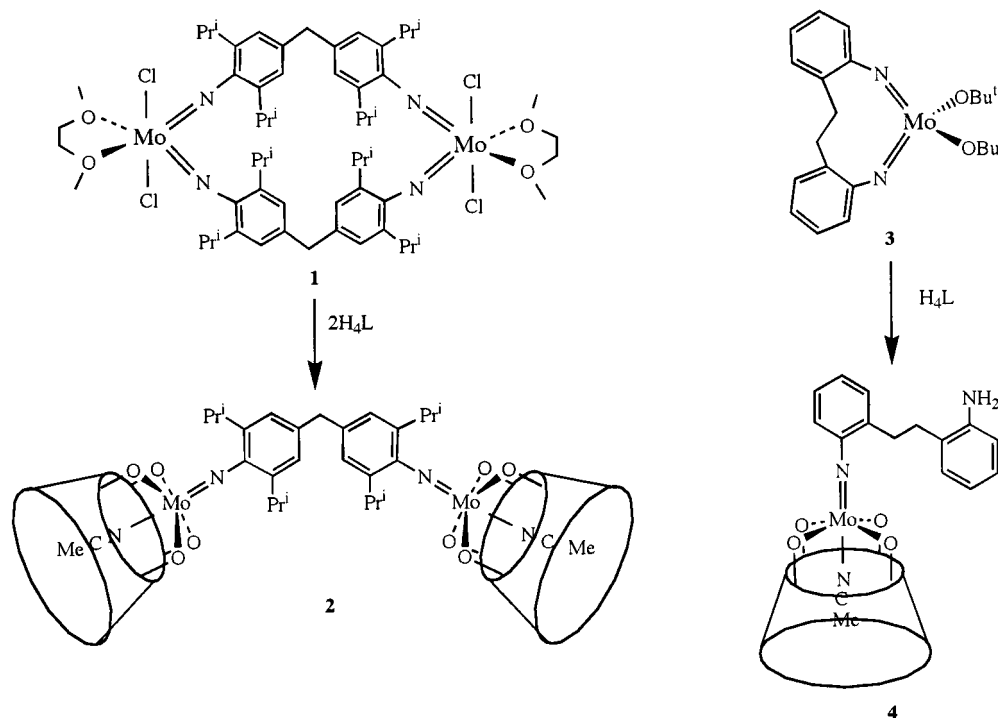
The synthesis and structures of two novel extended-array metallocalixarenes, derived from the ring-opening of imido-molybdenum precursors, are described.

The ability of calixarenes to act as receptors for a variety of guest molecules is a feature of central importance to their chemistry.<sup>1</sup> The development of supramolecular structures incorporating calixarenes offers an opportunity to extend calixarene host–guest interactions to two- and possibly three-dimensional lattices. Although supramolecular structures have been seen as a result of guest–host interactions,<sup>2</sup> and metal–oxo bridges,<sup>3</sup> clear methodologies for covalently linking metallocalixarenes have not, to our knowledge, been described. Here, we report the synthesis and solid state structures of two novel metallocalixarenes derived from the ring-opening of imido-molybdenum precursors. In one case the metallocalixarenes are linked by hydrogen bonding between pendant amino groups and in the other by a covalent linkage between imido ligands that gives rise to a two-dimensional array of ‘cup-to-cup’ metallocalixarene units.

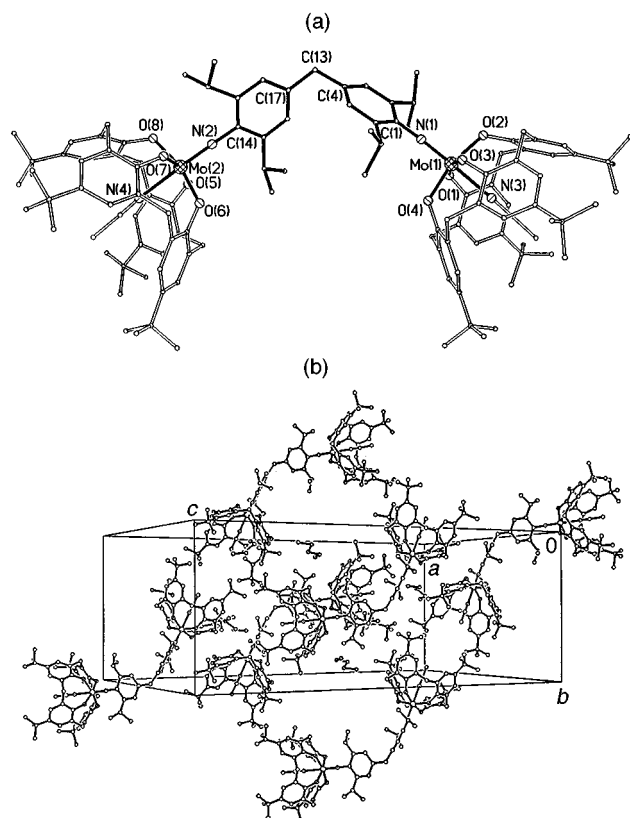
Treatment of the tetraimido dimolybdenum complex **1**<sup>4</sup> with two molar equivalents of H<sub>4</sub>L (H<sub>4</sub>L = calix[4]arene) in refluxing toluene affords, after work-up, the bridged complex {[Mo(NCMe)L]<sub>2</sub>[3,5-Pr<sub>2</sub>-4-NC<sub>6</sub>H<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>]} **2** according to Scheme 1.† Complex **2** is presumed to form *via* initial displacement of two chloride ligands (per molybdenum), followed by proton transfer to one of the imido ligands to

release the *para*-bridged dianiline. Crystals suitable for X-ray diffraction§ were grown from acetonitrile at room temperature. The molecular structure is shown in Fig. 1(a) and selected bond lengths and angles are given in the caption. Each molybdenum possesses a pseudo-octahedral geometry similar to that found in the monometallocalix[4]arene analogue of **1**.<sup>5</sup> The molybdenum atoms are displaced from the O<sub>4</sub> mean planes towards the imido nitrogens of the bridging ligand by 0.246 and 0.247 Å. The molecule has approximate C<sub>2</sub> symmetry, the rotation axis running through the C(13) atom. Significantly, the metallocalixarenes are organised in a ‘cup-to-cup’ arrangement which gives rise to a calixarene ‘socket’ [Fig. 1(b)], thus offering the potential for hosting guest molecules in the cooperatively aligned calixarene cavities.

In an extension of this work, we then targetted metallocalixarene species with pendant amino functionalities which we envisaged would allow the linking of metallocalixarene units *via*, for example, amide bonds. Treatment of the chelating bis(imido)molybdenum complex {Mo(OBu<sup>t</sup>)<sub>2</sub>[(2-NC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>]} **3** with H<sub>4</sub>L (one equivalent) in toluene affords, after work-up, the monoimido calixarene complex {[Mo(NCMe)L][2-NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-2’]} **4** in which the imido ligand contains a ‘free’ amino functionality (Scheme 1). Complex **4** is presumed to form *via* loss of two *tert*-butanol ligands followed by transfer of two protons to one of the imido ligands to release the pendant amino group.<sup>5</sup> The IR spectrum of **4** has a strong ν(N–H) stretch at 3165 cm<sup>–1</sup>, indicative of an



Scheme 1



**Fig. 1** Molecular structure of **2** without H atoms: (a) showing the atom labelling; (b) the crystal packing diagram showing the 'cup-to-cup' alignment of the metallocalixarene units. Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.735(5), Mo(1)–O(1) 1.936(5), Mo(1)–O(2) 1.941(4), Mo(1)–O(3) 1.936(5), Mo(1)–O(4) 1.949(5), Mo(1)–N(3) 2.304(6), Mo(2)–N(2) 1.716(5), Mo(2)–O(5) 1.948(5), Mo(2)–O(6) 1.942(4), Mo(2)–O(7) 1.920(4), Mo(2)–O(8) 1.953(5); Mo(1)–N(1)–C(1) 176.7(5), Mo(2)–N(2)–C(14) 178.8(5), C(4)–C(13)–C(17) 112.2(5) (a colour version is provided at: <http://www.rsc.org/suppdata/cc/1998/1969>).

uncoordinated  $\text{NH}_2$  group, together with a strong  $\nu(\text{C}=\text{N})$  stretch at  $1287\text{ cm}^{-1}$ . The structure was confirmed by an X-ray crystallographic study and is shown in Fig. 2(a). Each of the two aromatic rings of the imido ligand interact weakly with two aromatic carbons on an adjacent imido ligand [ $\text{C}(5)\cdots\text{C}(12\text{A})$  3.449,  $\text{C}(6)\cdots\text{C}(13\text{A})$  3.561 Å], and there is a hydrogen-bonding interaction between one of the amine hydrogens and a calixarene oxygen atom [ $\text{O}(4)\cdots\text{H}(2\text{AA})$  2.188 Å] [Fig. 2(b)].

The complexes described here represent the first steps towards the covalent linking of metallocalixarene units and the development of tailored supramolecular metallocalixarene arrays.

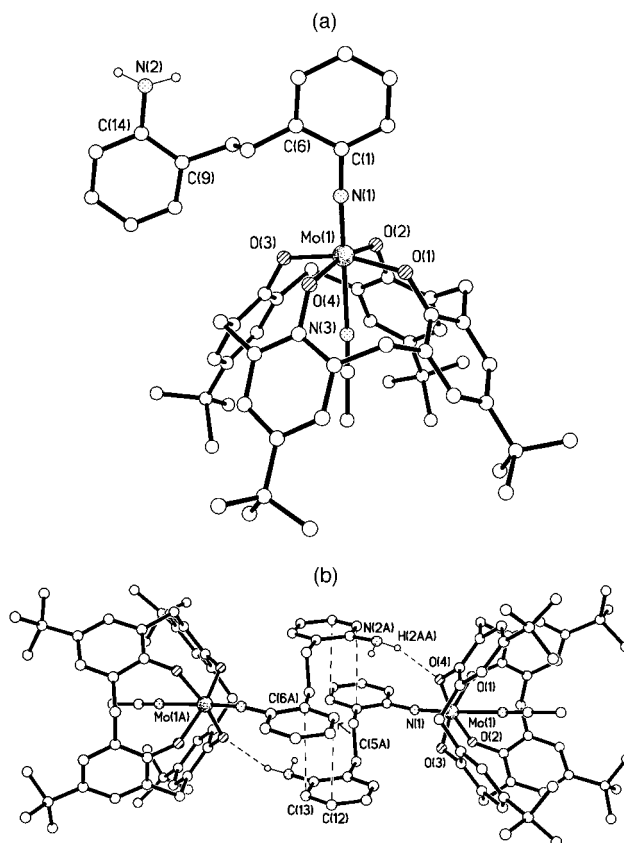
The Engineering and Physical Sciences Research Council is thanked for financial support.

## Notes and References

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‡ Satisfactory elemental analyses have been obtained on **2** and **4**. Selected spectroscopic data for **2**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 298 K)  $\delta$  7.12 (m, 20H, aromatic H), 4.68 [spt, 4H,  $^3J_{\text{HH}}$  6.8,  $\text{CH}(\text{CH}_3)_2$ ], 4.43 (d, 8H,  $^2J_{\text{HH}}$  12.2,  $\text{CH}_2$ ), 4.26 (s, 2H,  $\text{ArCH}_2\text{Ar}$ ), 3.23 (d, 8H,  $^2J_{\text{HH}}$  12.2,  $\text{CH}_2$ ), 1.53 [d, 24H,  $^3J_{\text{HH}}$  6.8 Hz,  $(\text{CH}_3)_2\text{CH}$ ], 1.21 [m, 72H,  $(\text{CH}_3)_3\text{C}$ ],  $-0.08$  (s, 6H, MeCN). For **4**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, 298 K)  $\delta$  8.05–6.50 (overlapping m, 16H, aromatic H), 4.42 (d, 4H,  $^2J_{\text{HH}}$  12.2,  $\text{CH}_2$ ), 3.95 (br s, 2H,  $\text{NH}_2$ ), 3.67 (t, 2H,  $^2J_{\text{HH}}$  7.4,  $\text{ArCH}_2$ ), 3.36 (t, 2H,  $^2J_{\text{HH}}$  7.4,  $\text{ArCH}_2$ ), 3.32 (d, 4H,  $^2J_{\text{HH}}$  12.2 Hz,  $\text{CH}_2$ ), 2.03 (s, 3H, MeCN), 1.21 [s, 36H,  $(\text{CH}_3)_2\text{CH}$ ],  $-0.08$  (s, 3H, MeCN).

§ Crystal data for **2**:  $\text{C}_{117}\text{H}_{144}\text{Mo}_2\text{N}_4\text{O}_8 \cdot 2\text{C}_5\text{H}_{12}$ ,  $M = 2070.5$ , monoclinic, space group  $I2/a$  (non-standard setting of  $C2/c$  avoiding large  $\beta$  angle),  $a = 34.891(2)$ ,  $b = 16.2235(11)$ ,  $c = 45.318(3)$  Å,  $\beta = 101.303(2)^\circ$ ,  $U = 25155(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.093\text{ g cm}^{-3}$ ,  $\mu = 0.251$



**Fig. 2** Molecular structure of **4** without hydrogen atoms: (a) showing the atom labelling; (b) showing the intermolecular interactions between adjacent metallocalixarene units. Selected bond lengths (Å) and angles (°): Mo(1)–N(1) 1.729(2), Mo(1)–O(1) 1.9419(18), Mo(1)–O(2) 1.9334(16), Mo(1)–O(3) 1.9323(18), Mo(1)–O(4) 1.9713(16), Mo(1)–N(3) 2.326(2); Mo(1)–N(1)–C(1) 171.60(19).

$\text{mm}^{-1}$  (Mo-K $\alpha$ ,  $\lambda = 0.71073$  Å),  $T = 160$  K. 51852 Reflections were measured on a Siemens SMART CCD area-detector diffractometer and corrected for absorption. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  values of all 16446 unique data ( $R_{\text{int}} = 0.1135$ ) with restraints on disordered substituents and solvent molecules;  $R' = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.2589$  for all data, conventional  $R = 0.0779$  on  $F$  values of 11304 reflections with  $F_o^2 > 2\sigma(F_o^2)$ ; goodness of fit = 1.086 on  $F^2$  for 1432 parameters and 423 restraints. Largest peak in final difference map  $1.224\text{ e Å}^{-3}$  ( $> 3.2$  Å from all atoms, possibly further unresolved disordered solvent). Programs: Siemens SMART (control), SAINT (integration), SHELXTL and local programs.

Crystal data for **4**:  $\text{C}_{60}\text{H}_{69}\text{MoN}_3\text{O}_4$ ,  $M = 992.12$ , triclinic, space group  $P\bar{1}$ ,  $a = 12.5913(8)$ ,  $b = 14.5121(9)$ ,  $c = 14.5797(8)$  Å,  $\alpha = 81.253(2)$ ,  $\beta = 84.564(2)$ ,  $\gamma = 84.657(2)^\circ$ ,  $U = 2612.9(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.261\text{ g cm}^{-3}$ ,  $\mu = 0.300\text{ mm}^{-1}$  (Mo-K $\alpha$ ,  $\lambda = 0.71073$  Å),  $T = 160$  K. 16442 Reflections were measured as for **2** yielding 11367 unique data ( $R_{\text{int}} = 0.0193$ ). The structure was solved by Patterson synthesis and refined as for **2** with restraints on one disordered *tert*-butyl group;  $R' = 0.1004$  for all data,  $R = 0.0412$  on  $F$  values of 9626 reflections with  $F_o^2 > 2\sigma(F_o^2)$ ; goodness of fit = 1.061 on  $F^2$  for 658 parameters and 139 restraints. Largest peak in final difference map  $0.686\text{ e Å}^{-3}$ . CCDC 182/971.

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Received in Basel, Switzerland, 5th March 1998; 8/01808A