

# Thiacalixarenes as cluster keepers: synthesis and structural analysis of a magnetically coupled tetracopper(II) square

Gilles Mislin,<sup>a</sup> Ernest Graf,<sup>a</sup> Mir Wais Hosseini,<sup>\*a</sup> Alexander Bilyk,<sup>\*b</sup> Annegret K. Hall,<sup>\*b</sup> Jack M. Harrowfield,<sup>\*b</sup> Brian W. Skelton<sup>\*c</sup> and Allan H. White<sup>\*c</sup>

<sup>a</sup> Laboratoire de Chimie de Coordination Organique (URA 422 CNRS), Université Louis Pasteur, F-67000 Strasbourg, France. E-mail: hosseini@chimie.u-strasbg.fr

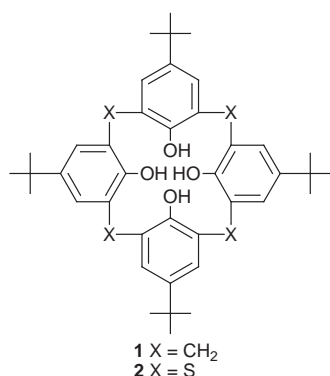
<sup>b</sup> Special Research Centre for Advanced Minerals and Materials Processing, University of Western Australia, Nedlands, WA 6907, Australia

<sup>c</sup> Crystallography Centre and Department of Chemistry, University of Western Australia, Nedlands, WA 6907, Australia

Received (in Basel, Switzerland) 25th November 1998, Accepted 17th December 1998

An X-ray structure determination of an antiferromagnetic copper complex of *p*-*tert*-butyltetra-thiacalix[4]arene has shown it to contain a square, phenoxo- and sulfur-bridged cluster of four Cu(II) ions sandwiched between two fully deprotonated calixarenes, thus forming a ditopic, divergent receptor; as prepared, the complex has each cavity occupied by a molecule of dichloromethane.

Inclusion based molecular network koilates may be obtained using cavity-containing molecules, koilands 'hollow molecular units', and connector molecules.<sup>1</sup> So far, study of such materials has been mainly oriented towards the understanding of structural characteristics. A development which remains to be achieved is the design and preparation of functional inclusion molecular networks. Calix[4]arene<sup>2</sup> derivatives, *e.g.* **1**, offer particular promise in this regard, as the fusion of calixarene units by bridging through entities such as Si(IV)<sup>3</sup> readily enables the divergent orientation of cavities of a size and nature sufficient to accommodate a variety of guests. The fact that a number of different metals (including Ti, Nb, Al, Zn, Mg and Eu)<sup>4</sup> may be used similarly as bridges adds a further dimension to the possible utility of these materials.



As a means of enhancing selectivity in metal ion binding, the functionalisation of calixarenes with sulfur-containing groups has been quite widely investigated.<sup>2,5,6</sup> In general, this has involved quite difficult synthetic chemistry but the recent discovery<sup>7</sup> of a facile, high-yielding pathway to the tetra-thiacalix[4]arene **2**, in which thiaether sulfur has replaced the methylene groups of calix[4]arene itself, has offered considerable prospects for expansion of the applications of such molecules.<sup>8</sup> Oxidation of the thiaether bridges to sulfoxide<sup>9</sup> and sulfone<sup>10,11</sup> groups offers a unique way of converting **2** to a number of interesting derivatives. Here, as part of a programme to systematically evaluate the metal ion coordinating ability of these new calixarenes (Fig. 1), we report the structure of a copper derivative, Cu<sub>4</sub>(**2**)<sub>2</sub>, of **2** in which a hollow molecular

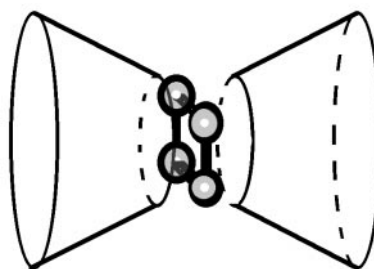


Fig. 1 Schematic representation of a hollow molecular unit obtained by fusion of two tetra-thiacalix[4]arenes by four metal centres.

unit is apparent. In the case of this transition metal, coordination to the calixarene appears to involve only oxygen and sulfur donor sites, though it is anticipated that, as with the simple calixarenes, other metals may be bound through interactions with, for example, the phenyl-ring  $\pi$ -electrons.<sup>12</sup>

Upon heating a dimethylformamide (DMF) solution of compound **2**, hydrated copper acetate and Et<sub>3</sub>N, a dark blue-black, crystalline complex was obtained.<sup>†</sup> The <sup>1</sup>H NMR spectrum of a solution of the complex in CDCl<sub>3</sub> at 298 K showed only a single, broad resonance, indicating that the complex was paramagnetic. Under the same conditions, an electron spin resonance could not be detected [a phenomenon known for many multinuclear Cu(II) systems,<sup>13</sup> but SQUID measurements of magnetic susceptibility (4–298 K; Fig. 2) could be interpreted, in the light of the structural information described below, in terms of antiferromagnetic coupling ( $J = 103 \pm 1 \text{ cm}^{-1}$ ) of four equivalent Cu(II) ions arranged in a

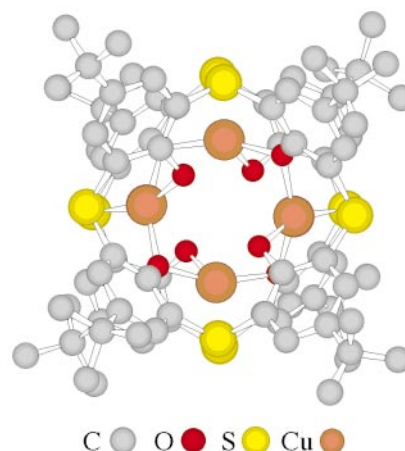
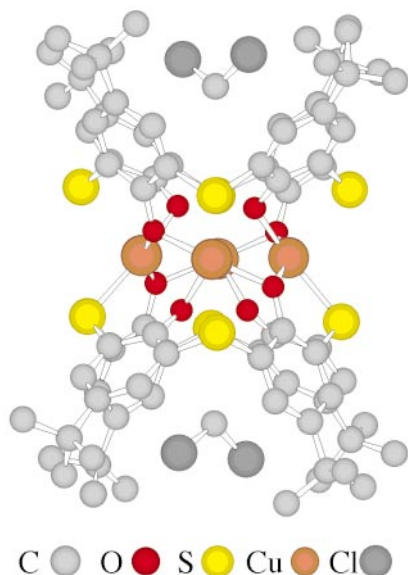


Fig. 2 A lateral view of the solid state structure of the tetranuclear copper complex possessing two cavities occupied each by one CH<sub>2</sub>Cl<sub>2</sub> molecule. For clarity, H atoms are omitted.



**Fig. 3** Top view of the crystal structure of the tetranuclear copper complex showing the square arrangement of the metal centres and their bridging by phenoxide groups.

square. The coupling is appreciably stronger than in a previously characterised  $\text{Cu}_4$  square array,<sup>14</sup> presumably as a consequence of a smaller separation between the metal atoms.

Single crystals (black tablets) of  $\text{Cu}_4(\mathbf{2})_2$  suitable for X-ray crystallography were readily obtained on addition of ethanol to a solution of the complex in dichloromethane.<sup>‡</sup> Two inequivalent  $\text{Cu}_4(\mathbf{2})_2$  units are found within the unit cell but the differences between them are subtle and will be described elsewhere. In both, the  $\text{Cu}_4$  array, sandwiched between two thiacalix entities in a 'cone' conformation similar to that of the free ligand,<sup>8</sup> is close to exactly square, with each copper in a six-coordinate  $\text{O}_4\text{S}_2$  donor-atom environment. The coordination sphere is far from regular, with one Cu–O bond *ca.* 0.5 Å longer than the other three and one Cu–S bond *ca.* 0.3 Å longer than the other. Fourfold symmetry for the  $\text{Cu}_4(\mathbf{2})_2$  unit is broken by the inclusion of one molecule of  $\text{CH}_2\text{Cl}_2$  within each of the divergent cavities of this hollow molecular building block (Fig. 2 and 3). Comparison with an analogous copper complex of *p*-*tert*-butylcalix[4]arene is not possible since no such structure has been determined but it has been suggested<sup>7</sup> that the far better extractant activity of **2** relative to **1** may be associated with the presence of the additional sulfur-donor centres and thus it is significant that the present structure demonstrates their involvement in the coordination of Cu(II). Other structures we are in the process of refining show that this mode of binding is certainly not restricted to Cu(II).

In summary, we note that this structure is both the first known of a Cu(II) complex of any calixarene and the first known of any complex of the tetrathiacalix[4]arene **2**. It is also that of the first intentionally synthesised paramagnetic koiland (hollow molecular building block), though others have been identified.<sup>4</sup> The use of this hollow molecular unit in the formation of magnetic inclusion networks in the crystalline phase is under current investigation.

## Notes and references

† The *p*-*tert*-butylthiacalix[4]arene **2** (270 mg, 0.37 mmol) was dissolved in DMF (8 mL) containing  $\text{Et}_3\text{N}$  (10 drops) and the resulting solution was added to a solution of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (150 mg, 0.75 mmol) in DMF (5 mL).  $\text{EtOH}$  (20 mL) was added to the dark brown solution and this was heated at reflux for 4 h. The reaction mixture was cooled to room temperature and filtered. The crude black solid was recrystallised twice from  $\text{CH}_2\text{Cl}_2$ – $\text{EtOH}$  to give the product as black prisms (190 mg, 57%). MS (FAB)  $m/z$  1685 ( $\text{M}^+$  1685, calc. 1689). Anal. Calc. for  $\text{C}_{80}\text{H}_{88}\text{O}_8\text{S}_8\text{Cu}_4 \cdot \text{CH}_2\text{Cl}_2$ : C, 54.87; H, 5.12; S, 14.47. Found: C, 54.80; H, 5.06, S, 14.27%. UV–VIS:  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ): 310 ( $4.29 \times 10^5$ ), 356 ( $6.41 \times 10^3$ ), 418 ( $4.57 \times 10^3$ ), 572 ( $2.77 \times 10^3$ ).

‡ Crystal/refinement data:  $[\text{Cu}_4(\text{C}_{40}\text{H}_{44}\text{O}_4\text{S}_4)_2 \cdot 2\text{CH}_2\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2$ ,  $M = 1943.1$ , monoclinic, space group  $P2_1/c$ ,  $a = 16.877(1)$ ,  $b = 28.872(2)$ ,  $c = 39.128(3)$  Å,  $\beta = 95.770(1)^\circ$ ,  $V = 18969$  Å<sup>3</sup>.  $D_c$  ( $Z = 8$  dimers) =  $1.361 \text{ g cm}^{-3}$ , 160847 (*i.e.*  $2\theta_{\text{max}} = 58^\circ$  sphere) 'SAINT'/'SADABS' processed CCD reflections ( $T_{\text{min,max}} = 0.33, 0.89$ ) merged to 33502 unique ( $R_{\text{int}} = 0.048$ ), 13828 with  $|F| > 4\sigma|F|$ , refining to conventional  $R$ ,  $R_w$  on  $|F|$  0.059, 0.058 {anisotropic thermal parameters (non-hydrogen atoms), ( $x, y, z, U_{\text{iso}}$ ) H included constrained at estimates}. Solvent occupancies were set at unity after trial refinement. CCDC 182/1133. See <http://www.rsc.org/suppdata/cc/1999/373/> for crystallographic files in .cif format.

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Communication 8/09184F