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Koilands from thiophiles: mercury(II) clusters from thiacalixarenes

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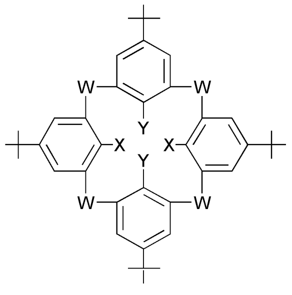
Tetra- and hexa-nuclear mercury(II) complexes have been obtained from tetrathiacalix[4]arene and tetramercaptotetrathiacalix[4]arene, respectively, and structurally characterised in the solid state; the complexes provide new digonal and trigonal receptors of the koiland type.

The coordination chemistry of the very numerous derivatives of calix[4]arene, **1**, reflects the versatility of these molecules as ligands in binding, not only through substituents and pendent groups, but even through the aromatic rings.[1,2] In the relatively new class of calix[4]arene derivatives gained by replacement of CH_2 junctions by S atoms,[3,4] the presence of sulfur donor atoms leads to an increase in the number of substituent coordination sites from four for compound **1** to eight for compound **2** (Scheme 1) and has already been shown to provide new types of polynuclear complexes.[5,6] Thiophilic metal ions such as Hg(II) would be expected to bind strongly to the thiaether bridges and even more strongly to thiolate (mercapto) substituents, and, assuming such coordination to involve binding of more than one ligand, Hg(II) coordination of tetrathiacalix[4]arenes such as **2** and its derivatives can be seen as a basis for the design of new koilands[7,8] or hollow molecular receptors based on the interconnection of at least two preorganised cavities. Subtle influences on cavity dimensions might also be expected to result both from the substituent donor atoms and their particular interaction with mercury(II).

Here, we report the synthesis and structural analysis of two new tetra- and hexa-nuclear mercury complexes using the tetrathiacalix[4]arene **2** and the tetramercaptotetrathiacalix[4]arene **3**.[9] Their structural chemistry provides an interesting contrast with that observed for the mono- and bi-nuclear mercury complexes of di- and tetra-mercaptocalix[4]arene derivatives **4** and **5**, respectively,[10–12] where thiolate–mercury interactions are associated with polyhapto-aromatic coordination of the metal and the mercury does not serve to link one calixarene to another.

The Hg(II) complex of **2** precipitated as a yellow powder on addition of a solution of $[Hg(dmso)_6](ClO_4)_2$ (260 mg) in dmf (2 mL) to a solution of **2** (100 mg) in dmf (4 mL) containing an excess of triethylamine (0.10 mL). Although the complex crystallised readily from various solvents, the crystals generally proved to be twinned, except in the case of mesitylene, from which a mesitylene/dmso solvate was obtained. The solid state structure of this material, $[Hg_4(\mathbf{2} - 4H)_2]\cdot 4(CH_3)_2SO\cdot 2C_6H_3Me_3$, (Fig. 1)† shows the complex unit to consist of a square of four Hg atoms sandwiched between two thiacalixarene units, with neither of the solvent molecules included within the calixarene cavity, perhaps because of its distortion away from the nearly fourfold symmetrical cone conformation of the free ligand[13] towards a form of essentially C_{2v} symmetry. The two fully deprotonated thiacalixarene units are interconnected by four Hg^{2+} cations, affording thus a neutral koiland possessing two cavities oriented divergently at 180° (Fig. 2). The edge length of the Hg_4 square is 3.734(5) Å, and each mercury cation is hexacoordinated to an O_4S_2 donor-set. Each Hg is bonded to two S atoms belonging to two different calix units and doubly-bridged to the neighbouring Hg by two O atoms. The coordination spheres around the metal centres are far from regular octahedral, with Hg–O bonds ranging from 2.318(7) to 2.620(3) and Hg–S distances of 2.603(3) and 2.620(3) Å. The $Hg_4(\mathbf{2} - 4H)_2$ complex resembles closely the tetra copper analogue previously obtained with the same ligand,[5] although the distortion of the ligand cone away from fourfold symmetry is more pronounced.

Upon slow diffusion at r.t. of a CH_2Cl_2 solution (25 ml) of compound **3** (50 mg) into a MeOH solution (25 ml) of $Hg(OAc)_2$ (40.5 mg), the mercury complex of **3** was obtained overnight as a yellow powder. Yellow single crystals suitable for X-ray crystallography were obtained in a crystallisation tube upon slow diffusion (48 h) at r.t. of a $CHCl_3$ solution (2 ml) of compound **3** (6 mg) into a MeOH solution (2 ml) of $Hg(OAc)_2$ (4.8 mg). The complex unit within the crystal (Fig. 3)† consists of three fully deprotonated calixarene units, six Hg^{2+} cations, three H_2O and five $CHCl_3$ solvent molecules. Two inequivalent $Hg_6(\mathbf{3} - 4H)_3$ units are found within the unit cell but the differences between them are subtle and will be described elsewhere. Again, the solvent molecules are not included within the calixarene cavity, and the water molecules form a trigonal cluster (d_{O-O} = 2.83 Å). In marked contrast with free ligand **3**, which adopts the 1,3-*alternate* conformation in the crystalline phase,[9] the three calix units forming the hexanuclear complex adopt a deformed *cone* conformation with two of the opposite phenyl groups in almost parallel disposition and the other two flattened. All three ligands **3** are interconnected by the six Hg^{2+} cations affording again a neutral, trigonal koiland with three cavities oriented in a divergent fashion at *ca.* 120° (Fig. 1). The six Hg atoms are arranged in an almost perfect trigonal prismatic geometry with d_{Hg-Hg} between adjacent cations of *ca.* 3.90 Å. Each mercury cation is hexacoordinated to six S atoms



1 W = CH_2, X = Y = OH
2 W = S, X = Y = OH
3 W = S, X = Y = SH
4 W = CH_2, X = OH, Y = SH
5 W = CH_2, X = Y = SH

Scheme 1

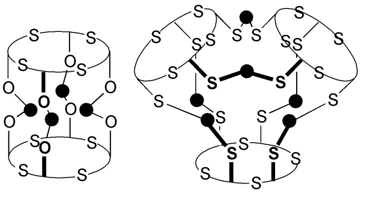


Fig. 1 Schematic representation of the digonal and trigonal koilands formed with the tetra- (left) and hexa- (right) nuclear Hg^{2+} (dark circles) complexes of the ligands **2** and **3**, respectively. For the sake of clarity, not all coordination bonds to the metal centres are represented.

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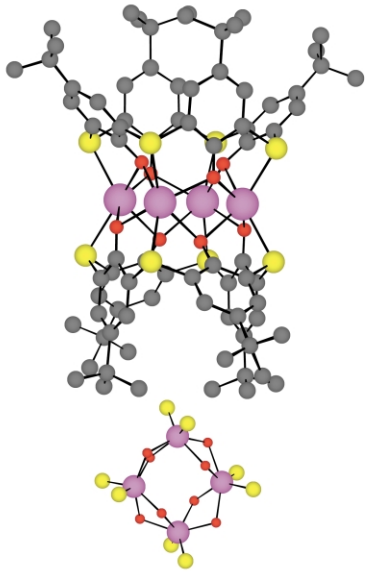

Fig. 2 Projection of [Hg_4(**2** − 4H)$_2$]·4(CH_3)$_2$SO·2$C_6H_3Me_3$. The substrate molecule is disposed about a site of crystallographic *222* symmetry (*2*-axes (i) through the calix cones, (ii) (iii) through the *trans*-pairs of Hg atoms in the obligate planar Hg_4 array). Hg(1)···Hg(2) is 3.7344(5), Hg(1)···O(11,21), S(2) 2.452(7), 2.318(7), 2.620(3) Å, Hg(2)···O(11), S(1), O(21) (1 − *x*, *y*, −*z*) 2.370(7), 2.603(3), 2.407(7) Å. O(11,21), S(1,2) lie 1.524(7), 1.042(7), 2.233(4), 2.331(4) Å out of the Hg_4 plane, phenyl planes 1,2 having dihedral angles of 43.5(3), 88.3(3) to it. For clarity, solvent molecules are omitted. The central $Hg_4O_8S_8$ cluster is depicted below.

but with two short Hg^{2+}–S^{-} distances of *ca*. 2.38 and 2.41 Å and four rather long Hg–S distances ranging from 2.95 to 3.06 Å. The short Hg–S bonds are *trans* to one another and involve thiolate centres belonging to two different units of deprotonated **3**. All six cations are unsymmetrically bridged by thiolate centres with one short (*ca*. 2.38–2.41 Å) and one rather long Hg–S distance (*ca*. 2.95–3.06 Å). The coordination geometry around the metal centres is again far from regular octahedral.

In conclusion, upon complexation of Hg^{2+} cation by the tetrathiacalix[4]arene **2** and the tetramercaptotetrathiacalix-[4]arene **3**, two new tetra- and hexa-nuclear complexes have been obtained and structurally characterised in the solid state by X-ray crystallography. Unlike complexes of simpler mercaptocalixarenes,[10,11] Hg(II) binding does not appear to involve significant interactions with the aromatic ring electrons and, perhaps as a consequence, involves sulfur-bridged cluster formation and the association of more than one calixarene unit with these clusters. Both complexes are thus of the koiland type, presenting two and three preorganised cavities, respectively, with the cavities strongly distorted towards twofold symmetry. This suggests that quite different inclusion properties to those of complexes where the thiacalixarene cone has near fourfold symmetry[5,6] may result. The ability of both complexes to form inclusion networks is currently under investigation.

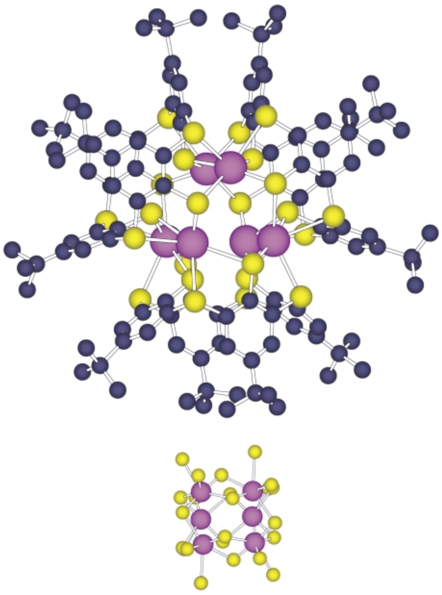

Fig. 3 The crystallographically determined structure of the hexanuclear mercury complex Hg_6(**3** −4H)$_3$·3H_2O·5$CHCl_3$ (top) and the metal cluster with its primary coordination sphere (bottom). H atoms and solvent molecules are omitted for clarity.

Notes and references

† *Crystal data* for: [Hg_4(**2** − 4H)$_2$]·4(CH_3)$_2$SO·2$C_6H_3Me_3$: $C_{106}H_{136}Hg_4O_{12}S_{12}$, M = 2789.4, orthorhombic, space group *Pban* (no. 50), $a = 17.764(1)$, $b = 21.016(2)$, $c = 14.929(1)$ Å, $Z = 2$, $V = 5573.4(7)$ Å^3, $D_c = 1.66$ g cm^{-3}$T \approx 153$ K. Full sphere of absorption corrected CCD diffractometer data ($2\theta_{max} = 58°$; Mo-Kα radiation, $\lambda = 0.7107_3$ Å), 88663 reflections merged to 7521 unique ($R_{int} = 0.11$), 3750 ($F > 4\sigma(F)$) refining to $R = 0.056$, R_w (statistical weights) = 0.067. The precision of the determination is limited by the difficulties of modelling disordered solvent, mesitylene and dmso seemingly occupying the same lattice sites in 1:2 ratio, in accord with NMR measurements; disorder is also evident in *tert*-butyl substituents.

For Hg_6(**3** − 4H)$_3$: (yellow, 173 K), 6($C_{20}H_{22}HgS_4$)·3H_2O·5$CHCl_3$, M = 5972.14 hexagonal, space group $P\bar{3}c1$, $a = b = 22.0184(2)$, $c = 51.6679(5)$ Å, $\gamma = 120°$, $U = 21693.2(3)$ Å^3, $Z = 4$, $D_c = 1.828$ g cm^{-3}, Mo-Kα radiation, $\mu = 6.923$ mm^{-1}, 6062 data with $I > 3\sigma(I)$, $R = 0.064$, R_w = 0.081.

CCDC reference numbers 179244 and 178503. See http://www.rsc.org/suppdata/cc/b2/b201379g/ for crystallographic data in CIF or other electronic format.

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