Exoditopic Receptors I: Synthesis and Structural Studies on *p-tert*-Butyltetramercaptocalix[4]arene and its Mercury Complexes

Xavier Delaigue, Jack McB. Harrowfield, Mir Wais Hosseini,* André De Cian, Jean Fischer and Nathalie Kyritsakas

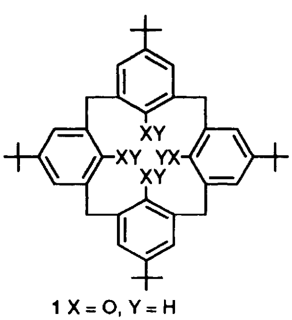
Université Louis Pasteur, Institut Le Bel, F-67000 Strasbourg, France

Reaction of mercury(II) acetate with the 1,3-alternate conformer of *p-tert*-butyltetramercaptocalix[4]arene, obtained by a highly efficient synthesis starting from *p-tert*-butylcalix[4]arene, leads to a binuclear complex in which both mercury ions are linearly coordinated to two arenethiolate groups.

The design and synthesis of binuclear complexes have been so far mainly based on ditopic receptors possessing convergent sets of binding sites (endoditopic receptors). In these complexes intrinsic molecular properties such as magnetic coupling, redox activity and optical features may be tuned with remarkable precision.[1] The extension of these molecular properties to materials may be envisaged through iterative assembly of exoditopic receptors, that is, binuclear species in which the two metal centres are located divergently. In principle, the design of the organic 'brick' and the choice of the interconnecting metal should allow the construction of materials with strictly controlled geometry and composition.

Molecular units possessing four coordination sites pointing outwards and occupying the apices of a pseudo-tetrahedron[2] may be of interest for construction of molecular wires. The design of such a ligand may be based on a preorganized backbone offering the possibility of anchoring four coordination sites in an alternating mode below and above the main plane of the backbone. In this regard, *p-tert*-butylcalix[4]arene **1**[3] may be the candidate of choice. Unfortunately, owing to strong intramolecular hydrogen bonding, the cone arrangement of **1** is the favoured conformation both in the solid state and in solution.[3] One may predict that the disruption of the internal hydrogen bond pattern and the induction of steric hindrance should favour the 1,3-alternate conformation in calix[4]arene derivatives. The hydrogen-bonding ability of thiol group in SH···H is roughly an order of magnitude less than the ability of alcohol to form OH···H hydrogen bond. Furthermore, the ionic radius of sulfur (1.85 Å) is substantially greater than that of oxygen (1.32 Å). Thus, replacement of all four OH groups in **1** by bulky SH moieties should lead to the tetramercapto *p-tert*-butylcalix[4]arene **4** in its 1,3-alternate conformation. The synthesis of **4** in exceedingly poor yield but demonstrating that a non-cone conformation was involved was first reported by Gutsche *et al.*[4]

Our strategy for the synthesis[†] of the tetramercapto derivative **4** of the *p-tert*-butylcalix[4]arene **1** was based on the Newman–Kwart rearrangement.[5] This reaction, the transformation of a *O*-phenyl-dimethythiocarbamate into an *S*-phenyldimethythiocarbamate, has been already applied successfully for the synthesis of 2,2′-dimercaptobiphenyl,[6] dimercaptocalixarenes[7] and tetramercapto metacyclophanes.[2] Subsequent to our success in finding an efficient synthesis of **4**, Gutsche *et al.* reported their improved synthesis as a communication.[8] In this, *p-tert*-butylcalix[4]arene **1**[9] was first transformed (43% yield) into its tetra-*O*-phenyl-dimethylthiocarbamate **2** by reaction with dimethylthiocarbamoyl chloride in the presence of NaH in diglyme ($MeOCH_2CH_2OCH_2CH_2OMe$). Attempts to increase the yield by running the reaction in THF (16%) and benzene (12%) failed. Since the thermal rearrangement of the tetra-*O*-phenyldimethylthiocarbamate **2** into the tetra-*S*-phenyl-dimethylthiocarbamate **3** was found to be rather capricious, we investigated the effect of the temperature by thermogravimetric analysis, which revealed that the starting compound **2** decomposed above 334 °C. Thus, performing the reaction under argon at 310–320 °C gave a reproducible yield of 88%. In contrast, the yield reported by Gutsche *et al.*[8] for the transformation of **2** to **3** in *p*-tolyl ether was 42%. Finally, the reduction of **3** by $LiAlH_4$ in dry THF afforded the desired compound **4** in 64% yield.



1 X = O, Y = H
2 X = O, Y = CSN(Me)$_2$
3 X = S, Y = CON(Me)$_2$
4 X = S, Y = H

Although both ^1H and ^{13}C NMR data indicated **4** to have the 1,3-alternate conformation, suitable mono-crystals were grown from CH_2Cl_2–hexane mixture and used for an X-ray structure determination.[‡] This confirmed the expected conformation (Fig. 1).

Compound **4** presents several interesting binding features: owing to its 1,3-alternate conformation each side of the ligand is composed of two SH groups as 'soft' and strong binding sites and two aromatic rings which may participate in the binding processes as 'soft' and probably weak interaction sites. In comparison, in calixarenes the OH groups may be regarded as 'hard', while the phenyl groups inherent in their structure must be regarded at least potentially as 'soft' binding sites and the binding of a wide range of metal ion species to these centres and to those in pendent groups has indeed been demonstrated.[10–15]

The known coordination chemistry of mercury(II) with calixarenes is limited to the formation of aryl-carbon bonded species intended for use as surfactants.[14,15] The thiophilicity of Hg^{II}[16] and the activity of thiols in the dealkylation of mercury[17] are expected to lead to the preferential binding of mercury at sulfur in mercaptocalixarenes. When mercuric acetate and *p-tert*-butyl-tetramercaptocalix[4]arene are mixed

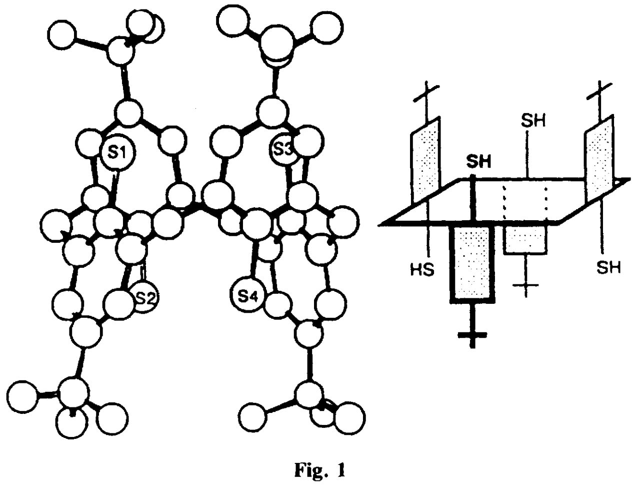


Fig. 1

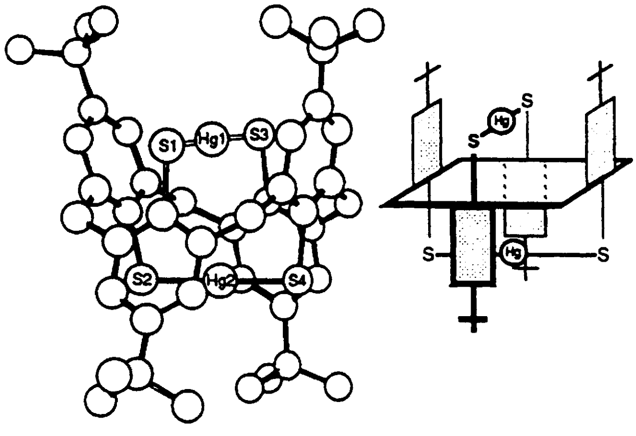


Fig. 2

in 1 : 1 and 2 : 1 metal : ligand ratios in THF, rapid formation of the 1 : 1 and 2 : 1 complexes of mercury(II) occurs and both may be isolated as pale-yellow crystalline solids. Interestingly, however, when a chloroform solution of the 1 : 1 complex is stored for several days, disproportionation to the free ligand **4** and 2 : 1 complex can be observed by NMR spectroscopy. The structures of the mono- and di-mercury complexes of **4** were investigated by X-ray studies. The surprising result obtained from the first attempt to solve the structure of a Hg/**4** complex, which was believed at the time to be the 1 : 1 species, was that the lattice appeared to contain a mixture of **4** containing zero, one and two metal ions, indicating thus that the metal ions were so well encapsulated by the ligand that externally there were negligible consequences of their presence. From the precise structure determination ultimately performed on the true 2 : 1 complex§ (Fig. 2), it was apparent that the mercury ions were indeed well-encapsulated, with strong, digonal binding to two thiolate sulfur atoms.

In the binuclear complex, both Hg ions are coordinated to two thiolate moieties with an average Hg–S distance of *ca.* 2.34 Å and an average S–Hg–S angle of *ca.* 178.5°. One essentially linear S–Hg–S unit projects upon the other at an angle of 89.3°, with the Hg–Hg distance being 3.66 Å. The average distance between two S atoms in the S–Hg–S units (4.59 Å) is shorter than that in the free ligand (4.97 Å), showing that the ligand must bow by 0.38 Å in order to accommodate the metal ion(s), though it may be noted that the free ligand and the dimercuric complex are isostructural. Linear two-coordination at Hg in $Hg(SR)_2$ compounds[16,18] has been established, and is commonly considered to be favoured because of relativistic effects on valence orbital splittings,[19,20] although weaker further interactions are not excluded and the coordination chemistry of Hg^{II} shows many aspects, which may be rationalised in terms of a '2 + 4' model.[18,21] In the binuclear complex the average distance between Hg ions and the centroids of the aromatic rings located on the same side is *ca.* 3.1 Å. Thus owing to the 1,3-alternate conformation of **4**, it appears possible that a mercury(II) species may have its secondary coordination requirements satisfied by polyhapto (π) interactions with two of the phenyl rings. Interactions of this type are known in several complex ion systems[22] with secondary coordination to π-aromatic ligands.

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Footnotes

† All compounds reported gave satisfactory microanalysis and were identified by ^1H, ^{13}C NMR and mass spectroscopy.

‡ *Crystal data* for **4**: $C_{44}H_{56}S_4$, $M = 713.2$, monoclinic, $a = 18.468(3)$, $b = 16.419(3)$, $c = 13.940(2)$ Å, $\beta = 101.82(2)°$, $U = 4137.3$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.145$ g cm^{-3}, μ(Cu-Kα) = 22.668 cm^{-1}. Crystal dimensions 0.24 × 0.20 × 0.20 mm. Data were measured at 173 K on a Philips PW1100/16 automatic diffractometer with graphite monochromated Cu-Kα radiation using ω scans. The structure was solved by direct methods and refined anisotropically using absorption corrected data to give $R = 0.051$, $R_w = 0.079$ for 3432 independent observed reflections $[|F_o| > 3\sigma(|F_o|), 2\theta \leq 102]$.

§ *Crystal data* for **4**-Hg_2 complex: $C_{44}H_{52}Hg_2S_4$, $M = 1110.3$, monoclinic, $a = 13.748(4)$, $b = 16.069(4)$, $c = 18.964(5)$ Å, $\beta = 100.58(2)°$, $U = 4118.2$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.791$ g cm^{-3}, μ(Mo-Kα) = 76.705 cm^{-1}. Crystal dimensions 0.40 × 0.28 × 0.26 mm. Data were measured at 173 K on a Enraf-Nonius CAD 4F automatic diffractometer with graphite monochromated Mo-Kα radiation using ω scans. The structure was solved by heavy atom method and refined anisotropically using absorption corrected data to give $R = 0.045$, $R_w = 0.053$ for 7219 independent observed reflections $[|F_o| > 3\sigma(|F_o|), 2\theta \leq 50]$. Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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