The First Calcium–Mercury Cocomplex: Synthesis and Crystal Structure

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A solution of $(OxS)_2Ca{\cdot}2HMPA$ [OxS^- = 2-mercaptobenzoxazolyl, $C_6H_4O{\cdot}(C{\cdots}S){\cdots}N^-$; HMPA = O:P $(NMe_2)_3$] dissolves solid $HgCl_2$ to give $[(OxS)CaCl{\cdot}2HMPA]_2{\cdot}(OxS)_2Ca{\cdot}(HgCl_2)_2$, **1**; in the solid state, the Cl atoms of intact $HgCl_2$ molecules coordinate to Ca^{2+} ions (which retain links to the N atoms of OxS^- ligands) and the S centres are thereby displaced from Ca^{2+} and capture the Hg.

We described recently the syntheses and structures of several alkaline earth metal (M = Ca, Sr, Ba) complexes of type $(Y{-}R{-}X)_2M{\cdot}xL$ and $(Y{-}R{-}X)_2M{\cdot}xL{\cdot}yH_2O$.[1] In these, the anionic ligand contains two electronegative centres (X, Y = combinations of N, O, S), for example and most notably 2-mercaptobenzoxazolyl [$C_6H_4O{\cdot}C(=S)N^-$, OxS^-]; L is a neutral Lewis base, *e.g.* HMPA [$O{=}P(NMe_2)_3$]. The key structural features are that, in the anhydrous complexes, X and Y chelate the M^{2+} ion, whilst in the aqua complexes [made by reacting Y–R–XH with solid $M(OH)_2$] one of these centres (say, Y) is displaced from M^{2+} by H_2O coordination to M^{2+}, but then stabilises the H_2O by hydrogen bonding to it. Such features suggested that solutions of the anhydrous

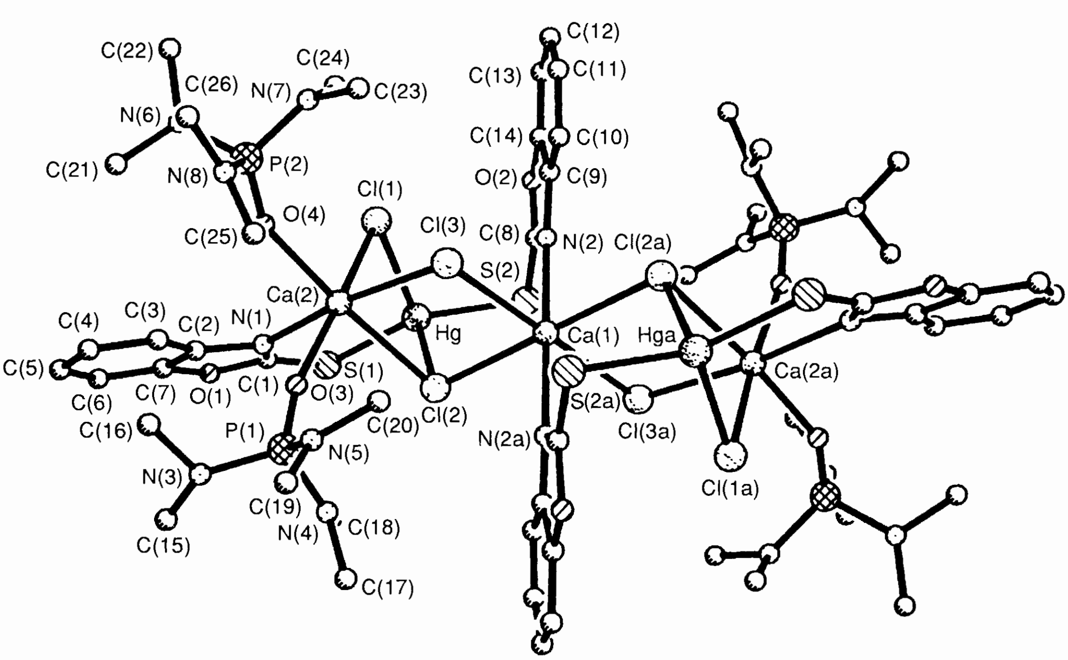
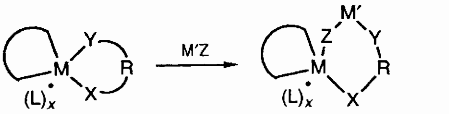


Fig. 1 The molecular structure of **1** showing the atom numbering scheme. H-atoms have been omitted for clarity.

complexes might dissolve metal salts, M′Z, M′Z$_2$, *etc.* Thus, Z could coordinate to M, displacing Y which would then bind to M′ [eqn. (1)].



(1)

This idea was first probed by using a solution of (OxS)$_2$Ca·2HMPA to 'capture' PtCl$_2$. However, the structural formula of the product proved to be [(HMPA)$_3$Ca·(μ_2-Cl)$_3$·Ca(HMPA)$_3$]$^+$·[Pt(OxS)$_4$·CaCl]$^-$, in which no Pt–Cl bonds remained.[2] Here we describe a much closer realisation of the above idea, whereby a solution of (OxS)$_2$Ca·2HMPA dissolves solid HgCl$_2$ to give [(OxS)CaCl·2HMPA]$_2$·(OxS)$_2$-Ca·(HgCl$_2$)$_2$, **1** [eqn. (2)]. In the solid-state structure of this, the first Ca–Hg cocomplex, the HgCl$_2$ is *intact*: the Cl atoms coordinate to Ca^{2+} ions, which retain links to N atoms of OxS$^-$ ligands, and the S centres displaced from Ca^{2+} bind to Hg.

$$3[(OxS)_2Ca{\cdot}2HMPA] + 3HgCl_2 \rightarrow \mathbf{1} + (OxS)_2Hg{\cdot}2HMPA \qquad (2)$$

Solid mercury(II) chloride dissolves in a hot toluene solution of (OxS)$_2$Ca·2HMPA to give a yellow solution. On cooling, a crop of crystals of **1** mixed with a semi-crystalline material [(OxS)$_2$Hg·2HMPA, eqn. (2)] forms. Filtration and refrigeration of the filtrate affords pure **1** in high yield.† An X-ray diffraction study‡ on **1** has revealed a pentametallanuclear (3Ca, 2Hg) species (Fig. 1). It is best considered as consisting of a central (OxS)$_2$Ca unit with, on either side, HgCl$_2$ and (OxS)CaCl·2HMPA molecules. Taking just one such side, the L-shaped HgCl$_2$ 'ligand' [Cl(1)HgCl(2), 90.1(1)°] uses both its Cl atoms to bridge to the Ca^{2+} of (OxS)CaCl·2HMPA [Cl(1)–Ca(2), 2.769(3); Cl(2)–Ca(2), 2.788(4) Å]. One of these Cl atoms [Cl(2)] also bridges to the Ca of the central (OxS)$_2$Ca unit [Cl(2)–Ca(1), 2.766(3) Å] which is further coordinated by the Cl[Cl(3)] of a (OxS)CaCl·2HMPA molecule [Cl(3)–Ca(1), 2.729(3) Å]. This results in a Ca(1)Cl(2)Cl(3)Ca(2) ring. Unsurprisingly, one Hg–Cl bond [Hg–Cl(2), 2.811(3) Å] is much longer than the other [Hg–Cl(1), 2.580(3) Å] since Cl(2) is attached to two Ca^{2+} ions. These various Cl–Ca coordinations have the effect of displacing the S atoms of OxS$^-$ anions from the Ca^{2+} in both the (OxS)$_2$Ca central and (OxS)CaCl·2HMPA terminal moieties, and these S atoms then attach to Hg [S(2)–Hg, 2.398(1); S(1)–Hg, 2.384(1) Å].

Product **1** is the first Ca–Hg cocomplex containing organic ligands.[3] Other known group 2-Hg species having such ligands are [Mg$_4$(OCH$_2$CH$_2$OMe)$_6$·(MeOCH$_2$CH$_2$OMe)$_2$]$^{2+}$·[Hg-(SiMe$_2$Ph)$_3$]$_2$$^{2-}$,[4] SrHg(SeCN)$_4$·(pyridine)$_4$,[5] and BaHg-(CN)$_4$·(pyridine)$_4$.[6] All can be considered as comprising essentially group 2-containing cations and Hg-containing anions, with the two metals sometimes being linked by

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† **1**: Solid HgCl$_2$ (0.543 g, 2 mmol) was added to a solution of (OxS)$_2$Ca·2HMPA (1.396 g, 2 mmol) in toluene (20 ml) under a nitrogen atmosphere. On heating at 100 °C for 2 h, the solid dissolved to give a clear yellow solution. Cooling to room temperature produced an oil, from which grew a crop of crystalline **1** and powdered [believed to be (OxS)$_2$Hg·2HMPA] material. Filtration and refrigeration of the filtrate over 2 days afforded colourless crystals of **1**; these contain one toluene solvate molecule per structural formula unit. Yield, 68%; m.p. decomp. 105 °C; satisfactory elemental analysis obtained for **1**·toluene. ^{1}H NMR (250 MHz, [^{2}H$_6$]DMSO, 25 °C) δ 6.97–7.33 [m, 21H of 4(OxS$^-$) + C$_6$*H*$_5$·Me], 2.53 (d, 72H of 4HMPA), 2.30 (s, C$_6$H$_5$*Me*).

‡ *Crystal data* for **1**·toluene: {Ca[C$_6$H$_4$O.(C$\cdots$S)$\cdots$N]·2[O=P(NMe$_2$)$_3$]·HgCl$_2$}$_2$·{Ca[C$_6$H$_4$O·(C$\cdots$S)$\cdots$N]$_2$Cl$_2$}·2C$_7$H$_8$, M = 2235.9, monoclinic, space group $P2_1/n$ (alt. setting of $P2_1/c$, No. 14), a = 19.316(4), b = 12.063(2), c = 20.643(4) Å, β = 106.72(3)°, U = 4606.6(15) Å^3, T = 120 K, Z = 2 (dimer), D_c = 1.61 g cm^{-3}, $F(000)$ = 2244, μ(Mo-Kα) = 38.86 cm^{-1}. 9035 Intensity data ($2\theta_{max}$ = 50.0°) were recorded on a Stoe four-circle diffractometer using graphite monochromated Mo-Kα radiation. The data were corrected for absorption and averaged to give 5912 unique observed reflections with $F > 4\sigma(F)$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least-squares to R = 0.072 with all non-H atoms anisotropic; H-atoms were placed in idealised positions and allowed to ride on the relevant C-atom, C–H 0.96 Å. A disordered molecule of toluene was located in the crystal lattice and refined. The atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

inorganic anions such as $SeCN^-$ or CN^-. Multidonor organic anions such as that of oxazolidone $[O{=}\overline{C{\cdot}O(CH_2)_2N}^-]$ have also been used to generate polymeric Hg–M heterometallics having metal atoms as part of a macrocyclic system, *e.g.* as in $[Hg_2(C_3H_4NO_2)_4{\cdot}Gd(NO_3)_3]_n$.[7] The distinctiveness of **1** lies in its *molecular* nature and in the fact that the heavy metal precursor, $HgCl_2$, has been captured *intact*.

The synthetic idea outlined above [eqn. (1)], and realised for **1**, seems likely to have wide applications. Within the original metal chelated complex, $(\overline{Y{-}R{-}X)_nM}{\cdot}xL$, M can be altered (*e.g.* to M = a group 1 metal[8]), as can L and the $Y{-}R{-}X^-$ anion. In particular, Y and X can be 'tailored', using hard/soft concepts, such that one of them suits the original metal (M) but the other is more compatible with the metal of the M′Z *etc.* salt to be captured. In this way, we have used various such metal chelate complexes (M = Li; Ca, Sr, Ba; Al) to capture salts such as $PtCl_2$, $PdCl_2$, $NiCl_2$, $TiCl_3$ and TlCl. The M–Pt cocomplexes may have relevance to anticancer chemotherapy studies, since the natural 'bases' in DNA and RNA are themselves 'acids' of type Y–R–XH.[2] All such cocomplexes have obvious relevance to metal separation.

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