

Unusual Coordination of HgCl₂ by a Mixed Oxathioether Crown

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The oxathioether crown 1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-en-14,15-dicarbonitrile reacts with HgCl₂ to give an endocyclic complex in which macrocyclic coordination to Hg^{II} in the solid state is through only the O donor atoms.

Crown ethers having a mixed donor set of sulfur and oxygen heteroatoms differ in their metal binding properties^{1–3} from their purely sulfur⁴ or oxygen⁵ counterparts. We are specifically interested in oxa-crowned derivatives of dithiomaleonitrile, both as ligands themselves and as potentially key precursors to crowned octakis(alkylthio)tetraazaporphyrins.⁶ To date, such crowns have been synthesized only in modest yields.⁷ In addition, just two of their metal complexes have been structurally characterized and both involve an exocyclic, square-planar palladium(II) species that is coordinated by the macrocycle through the two S atoms of the dithiolene moiety.^{7b} With this in mind, we have developed an improved general synthesis of the macrocycles and report here on the preparation of 1,4,7,10-tetraoxa-13,16-dithiacyclooctadec-14-en-14,15-dicarbonitrile, **1**.

We have further prepared the HgCl₂ complex of **1**, thereby demonstrating the potential importance of O-chelation in heavy-metal complexes of oxathioether crowns. Schröder and coworkers^{2a} and others^{3a} have reported a variety of transition metal complexes of oxathioether crowns in which only the sulfur heteroatoms serve as ligands. There are, however, no structurally characterized complexes in which only the oxygen atoms of a mixed oxathioether crown are coordinated to the metal atom. In fact, to our knowledge, the only structurally characterized example in which the O atoms take part in the coordination of a metal ion is the recently reported silver(I) complex of 1,4,7-trioxa-10,13-dithiacyclopentadecane in which all five heteroatoms of the crown are ligated.^{2b} In contrast, we find that **1** captures a HgCl₂ molecule through a unique endocyclic coordination involving only O donor atoms.

Ligand **1** was originally prepared by Holdt and Teller^{7a} in 12% yield from disodium dithiomaleonitrile (Na₂mnt) and 1,16-dichloropentaethylene glycol using solutions of approx. 70 mmol dm⁻³ in protic media (ethanol–water). A more recent report shows an increase in yield to 15–18% by the same procedure.^{7b} We have found that the yields are doubled (30%) by modifying the existing procedures. First, pentaethylene glycol-ditoluene-*p*-sulfonate was used in crown-forming reactions with Na₂mnt because terminal ditosylates give better yields in comparison to analogous dichloro compounds for the synthesis of saturated polyazamacrocycles.⁸ In addition, lower concentrations of reactants were maintained by simultaneously adding both the nucleophile and electrophile dropwise to a polar, aprotic medium, DMF. This reduced the formation of polymeric byproducts.

The reaction of **1** with an equimolar amount of HgCl₂ in methanol caused the immediate formation of 1·HgCl₂, com-

plex **2**, as a white precipitate in high yield. The 1:1 stoichiometry was confirmed by analytical data. Diffusion of ethyl ether into a chloroform solution of **2** produced colourless, X-ray quality crystals of **2**.†

As shown in Fig. 1, complex **2** consists of an essentially linear HgCl₂ unit [Cl–Hg–Cl 174.85(6)°] incorporated into the macrocycle and oriented nearly perpendicular to the mean plane of the six heteroatoms. The Hg^{II} ion lies 0.0730 Å out of this plane. It is bonded strongly to two O atoms [Hg–O(2) 2.681(5), Hg–O(3) 2.657(4) Å] and weakly to the two remaining O atoms [Hg–O(1) 2.980(4), Hg–O(4) 2.932(4) Å] in an *endo* manner by the crown. The three O–Hg–O bond angles [O(1)–Hg–O(2), O(2)–Hg–O(3), O(3)–Hg–O(4)] are all between 61 and 64°. The S atoms, however, are >3.3 Å from the Hg^{II} ion [Hg···S(1) 3.396(2), Hg···S(2) 3.336(2) Å], well beyond typical Hg–S bonding distances (2.50–2.75 Å).^{3b,3c,9,10} As a result, counting the two Cl ligands, the Hg^{II} ion can be considered either four or six-coordinate. In contrast, Hg^{II} is 8-coordinate in the hexagonal-bipyramidal HgCl₂ complexes of the purely O-containing ligands 18-crown-6¹¹ and dibenzo-18-crown-6¹² and the HgI₂ complex of the mixed donor ligand diaza-18-crown-6.¹³

The asymmetric coordination of the macrocycle in **2** introduces only small changes in the bonding of the captured HgCl₂ molecule. The Cl–Hg–Cl bond angle in **2** is 174.85(6)° versus 178.9(5)° for free HgCl₂¹⁴ and the Hg–Cl bond lengths [Hg–Cl(1) 2.306(2), Hg–Cl(2) 2.316(2) Å] are only slightly longer than those found in the structure of HgCl₂ [av. 2.291(9) Å]. Similar bonding is seen in the HgCl₂ complexes of 18-crown-6¹¹ and dibenzo-18-crown-6¹² where the linear HgCl₂ molecule is coordinated *symmetrically* by the six O donor atoms of the macrocycle.

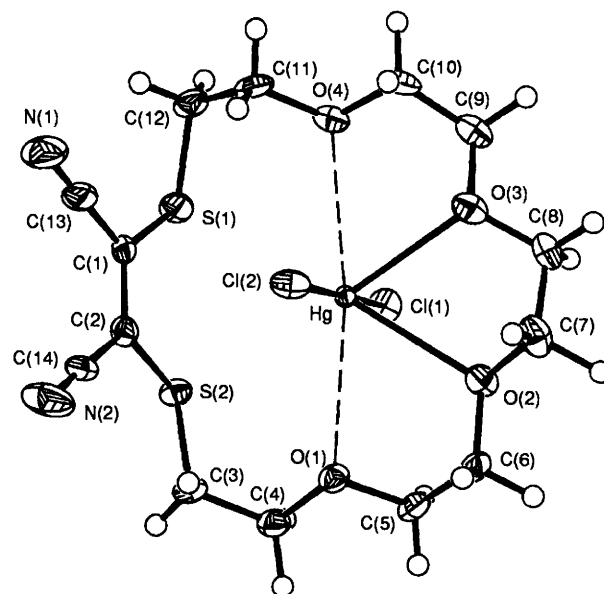
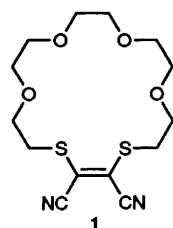


Fig. 1 View of **2** showing the atom labelling scheme. Thermal ellipsoids are scaled to the 50% probability level.

The endocyclic coordination of Hg^{II} by the O donor atoms in the presence of the S atoms of the dithiolene unit in **2** is unusual. Thioether¹⁰ and oxathioether^{3b,3c} crowns typically bind HgCl₂ through S donor atoms in an exocyclic fashion owing to the affinity of Hg^{II} for soft S donor atoms and the 'exodentate' conformation adopted by uncomplexed S-containing macrocycles.¹⁵ Indeed, in each of the HgCl₂ complexes with the related oxathioether crowns 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane^{3c} and 1,4,13,16-tetraoxa-7,10-dithia-[16](1,1')ruthenocenophane,^{3b} the Hg atom is tetrahedrally coordinated by two Cl atoms and two macrocyclic S atoms in an exocyclic fashion, without bonds to the O donor atoms of the crown. Presumably, electron withdrawal by the maleonitrile unit in **2** reduces the affinity of the S atoms for the Hg^{II} ion.

To examine the Hg coordination in solution, complex **2** dissolved in CHCl₃ was studied by ¹³C NMR spectroscopy. The average structure of **2** in solution retains C₂ symmetry as determined by the number of peaks present in the spectrum. All of the macrocyclic methylene carbon resonances are shifted in the spectrum of **2** relative to the free ligand. The ¹³C methylene resonances next to the O atoms shift upfield upon complexation (av. δ , CH₂O: **1**, 70.49; **2**, 69.32). Similar upfield shifts are observed for the complexation of alkali metals by crown ethers and are ascribed to a change in the conformation of the polyether moiety upon metal binding.¹⁶ The methylene resonance next to the S atom, however, shifts downfield, from δ 34.92 (for **1**) to δ 36.18 (for **2**), consistent with S-chelation of the Hg^{II} ion. Because ¹³C methylene resonances next to S atoms are thought to be relatively insensitive to conformational changes,¹⁷ shifts upon complexation are presumably a result of polarization of the C-S bond and, thus, are typically downfield.¹⁴ In solution, therefore, all of the heteroatoms (both S and O) interact with the metal ion in complex **2**.

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Footnote

† Crystal data for **2**: C₁₄H₂₀Cl₂HgN₂O₄S₂, *M* = 615.94, monoclinic, space group P2₁/n (no. 14), *a* = 7.709(2), *b* = 15.058(4), *c* = 17.746(3) Å, β = 98.75(2)°, *V* = 2036 Å³, *Z* = 4, *D*_c = 2.009 g cm⁻³, μ (Mo-K α) = 80.39 cm⁻¹. A colourless, columnar crystal (0.26 × 0.12 × 0.08 mm) was mounted on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-K α radiation. Data collection at -120 °C using the ω - θ technique to a maximum 2θ value of 50.0° gave 4024 reflections, 3730 unique (*R*_{int} = 0.070), of which 2590 with *I* > 3.00 σ (*I*) were used in all calculations. The structure was solved by direct methods (SHELXS-86) and refined by the full-matrix least-squares

technique (Texsan 5.0). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined with a group isotropic thermal parameter. At final convergence, *R* = 0.027, *R*_w = 0.028 for 288 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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