Reaction of Mercuric Iodide with Cryptand 222. Crystallographic Evidence for the Formation of Finite Octaiodotrimercurate(II) Ions $[Hg_3I_8]^{2-}$

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By the reaction of solutions of HgI_2 and cryptand 222, crystals of a compound consisting of $[Hg(cryptand\ 222)]^{2+}$ cations and previously unreported discrete $[Hg_3I_8]^{2-}$ anions are obtained, and are characterized by single crystal X-ray diffraction.

Cryptands, macrobicyclic ligands with two nitrogen and several oxygen atoms, show a strong tendency to form very stable complexes, cryptates, with various metal cations. Complexes of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, cryptand 222, have been prepared with alkali and alkaline earth metal, lanthanide and nickel(II) cations, the structures of some of which have been established by X-ray crystallography.[1] Recently we have investigated the reactions of some dihalides of Group 12 elements with cryptand 222. For $HgCl_2$ we found that, besides generation of the complex cation $[Hg(cryptand\ 222)]^{2+}$, the dimeric anion $[Hg_2Cl_6]$ was formed.[2]

Here, we report on an unexpected compound formed by the reaction of cryptand 222 with HgI_2. Yellow crystals were obtained by diffusion of an aqueous solution of the cryptand into a solution of HgI_2 in methanol (both 0.02 mol dm^{-3}). An X-ray structural analysis revealed that the crystals consist of $[Hg(cryptand\ 222)]^{2+}$ cations and finite octaiodotrimercurate(II) anions $[Hg_3I_8]^{2-}$ in equal amounts.†

Mercuric halides have been shown to form a variety of complex anions in the presence of an excess of halide ions. A series of mononuclear species $[HgX_n]^{2-n}$ with n = 3–6 is known for X = Cl, Br.[3] For X = I, only anions with n = 3 and 4 are known, although in many cases additional long bonds to neighbouring groups exist,[4,5] thus increasing the coordination number to 5 or 6. Discrete $[HgI_3]^-$ ions are rare, they are found in *e.g.* $[NBu^n_4][HgI_3]$.[6] Isolated $[HgI_4]^{2-}$ anions exist in $[Me_3S]_2[HgI_4]$.[7]

Polynuclear halogenomercurate anions may be formed from $[HgX_4]$ tetrahedra sharing common corners or edges. In $K[HgI_3]\cdot H_3O$, the $[HgI_3]$ moieties are linked through common corners to infinite chains.[8] Dinuclear anions $[Hg_2X_6]$ are known for X = Cl, Br and I, *e.g.* in $[NPr^n_4][Hg_2I_6]$.[9] Here two $[HgX_4]$ tetrahedra share common edges. In a paper on the structure of $Cs_2Hg_3I_8$, the existence of $[Hg_3I_8]^{2-}$ ions is stated; however, this compound does not contain discrete octaiodotrimercurate ions but the structure of the anion is best described by a two-dimensional network of $[HgI_4]$ tetrahedra joined at the apices.[10]

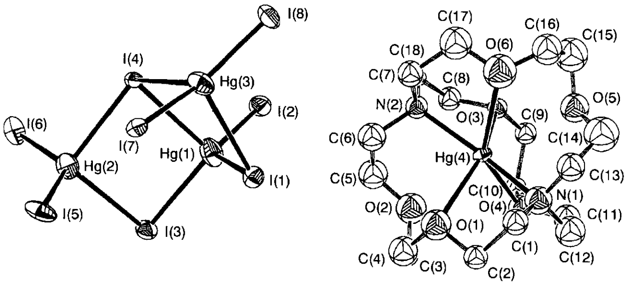

Fig. 1 X-Ray crystal structure of an ion pair of $[Hg(cryptand\ 222)][Hg_3I_8]$ with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Hg(1)–I(1) 2.736(7), Hg(1)–I(2) 2.654(5), Hg(1)–I(3) 2.815(6), Hg(1)–I(4) 3.085(6), Hg(2)–I(3) 2.985(6), Hg(2)–I(4) 3.035(6), Hg(2)–I(5) 2.669(6), Hg(2)–I(6) 2.651(8), Hg(3)–I(1) 3.198(7), Hg(3)–I(4) 3.213(7), Hg(3)–I(7) 2.613(5), Hg(3)–I(8) 2.599(6), Hg(4)–O(1) 2.76(6), Hg(4)–O(2) 2.82(6), Hg(4)–O(3) 2.55(4), Hg(4)–O(4) 2.55(5), Hg(4)–O(5) 2.83(6), Hg(4)–O(6) 2.64(7), Hg(4)–N(1) 2.23(7), Hg(4)–N(2) 2.24(5), I(1)–Hg(1)–I(2) 122.7(2), I(1)–Hg(1)–I(3) 106.5(2), I(1)–Hg(1)–I(4) 98.6(2), I(2)–Hg(1)–I(3) 120.1(2), I(2)–Hg(1)–I(4) 106.5(2), I(3)–Hg(1)–I(4) 96.9(2), I(3)–Hg(2)–I(4) 94.4(2), I(3)–Hg(2)–I(5) 103.2(2), I(3)–Hg(2)–I(6) 110.2(2), I(4)–Hg(2)–I(5) 109.8(2), I(4)–Hg(2)–I(6) 102.4(2), I(5)–Hg(2)–I(6) 131.0(2), I(1)–Hg(3)–I(4) 87.2(2), I(1)–Hg(3)–I(7) 100.2(2), I(1)–Hg(3)–I(8) 99.6(2), I(4)–Hg(3)–I(7) 96.8(2), I(4)–Hg(3)–I(8) 105.8(2), I(7)–Hg(3)–I(8) 150.5(2), Hg(1)–I(1)–Hg(3) 88.2(2), Hg(1)–I(3)–Hg(2) 87.1(2), Hg(1)–I(4)–Hg(2) 81.6(2), Hg(1)–I(4)–Hg(3) 82.2(2), Hg(2)–I(4)–Hg(3) 119.8(2).

Thus, the anion found by us in the structure of the title compound seems to represent the first example of a real discrete $[Hg_3I_8]^{2-}$ anion. Fig. 1 shows the X-ray structure of an ion pair in the crystal, and Fig. 2 the packing of ions in the unit cell, proving the existence of discrete moieties. No contact distances Hg···I less than *ca.* 4.1 Å between adjacent anions are found.‡

The anion may be regarded as built up from three $[HgI_4]$ tetrahedra sharing two common edges [I(1)–I(4), I(3)–I(4)] as well as one corner [I(4)] common to all three tetrahedra. Thus we have two doubly bridging iodine ions [I(1), I(3)], one triply bridging iodine [I(4)], as well as five terminal iodine atoms. The complex ion may also be thought of as an $[Hg_2I_6]$ ion [consisting of Hg(1) and Hg(2), and I(1)–I(6)] onto which an HgI_2 molecule [I(7)–Hg(3)–I(8)] is added with relatively long bonds (*ca.* 3.21 Å) to I(1) and I(4). As a consequence the Hg–I bonds in the $[Hg_2I_6]$ subunit become unsymmetrical, being significantly longer for the triply bridging iodine atom I(4). The bond lengths between the mercury atom and the terminal ligands range from 2.60 to 2.66 Å. This corresponds well with *e.g.* the shortest distances found in the various forms of HgI_2.[11,12]

The geometry of the cation $[Hg(cryptand\ 222)]^{2+}$ corresponds to that found for $[Hg(cryptand\ 222)][Hg_2Cl_6]$.[2] The conformation of the cryptand is *endo-endo*, as in all the known cryptates of this ligand, and in the free cryptand molecule itself.[13] The Hg ion is octa-coordinated to the two nitrogen atoms and the six oxygen atoms of the ligand.

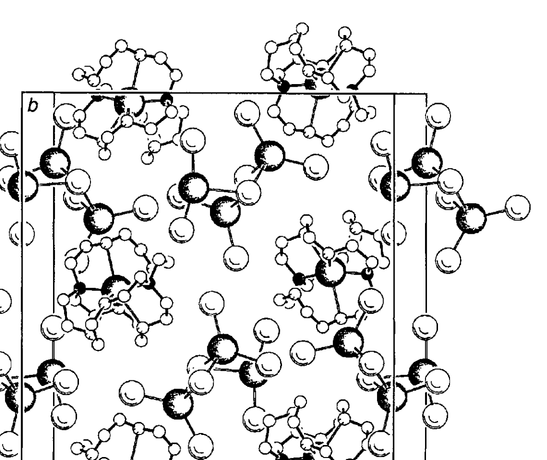

Fig. 2 PLUTON plot[16] of a unit cell of $[Hg(cryptand\ 222)][Hg_3I_8]$, showing the arrangement of discrete cations and anions

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Footnotes

† The compound was also characterized by IR spectroscopy and gave a satisfactory elemental analysis.

‡ *Crystal data*: $C_{18}H_{36}N_2O_6Hg_4I_8$, M = 2194.1, monoclinic, space group $P2_1/n$ (No. 14), a = 9.265(3), b = 20.695(5), c = 21.670(15) Å, β = 95.10(5)°, V = 4138(3) Å^3, Z = 4, D_c = 3.52 g cm^{-3}, D_m = 3.4(1) g cm^{-3}, μ(Mo-Kα) 207.3 cm^{-1}, F(000) = 3800. Data were measured on a Syntex $P2_1$ diffractometer using Mo-Kα radiation (graphite monochromator) and ω-scans. Numerical absorption correction. The structure was solved with the direct methods program SHELXS-86,[14] and refined (Hg, I anisotropic; C, O, N isotropic; H positions calculated) using SHELX-76,[15] to give R = 0.069, R_w = 0.070 for 1890 independent observed reflections [$I > 3\sigma(I)$, $2\theta < 55°$].

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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