$[Hg_3(SCH_2CH_2S)_4]^{2-}$ and $\{[Hg_2(SCH_2CH_2S)_3]^{2-}\}_n$: Examples of Trinuclear and Quasi-isolated Binuclear Polymeric Mercury Thiolate Anions

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On varying the reaction conditions, treatment of $HgCl_2$ with ethane-1,2-dithiolate and Ph_4PBr in methanol yields either $[Ph_4P]_2[Hg_3(SCH_2CH_2S)_4]$ containing isolated trinuclear anions or $[Ph_4P]_2[Hg_2(SCH_2CH_2S)_3]$ with polymeric anions composed of quasi-isolated binuclear subunits; both mercury thiolates may reflect characteristic structural features of biologically active species.

Heavy metals are known to be environmental pollutants and probably their toxicity is based on their affinity for biologically important ligands such as thiolates. Metallothioneins, a group of small cysteine-rich proteins, which are able to bind Cu, Zn, Cd, and Hg have been proposed to be involved in heavy metal detoxification.[1] In this context mercury complexes with thiolato ligands have attracted a lot of research work over the last few years and anions such as $[Hg(SPh)_3]^-$,[2] $[Hg(SC_6H_4Cl)_4]^{2-}$,[3] and $[Hg_2(SMe)_6]^{2-}$,[4] as well as neutral polymeric $[Hg(SR)_2]_n$ thiolates[5] have been synthesized and crystallographically characterized. However, mercury complexes containing simple saturated bifunctional 1,2-dithiolates have not been structurally characterized, although related ligands such as BAL (British Anti Lewisite: 2,3-dimercaptopropanol) and some of its derivatives are used in the treatment of inorganic mercury poisoning.[6]

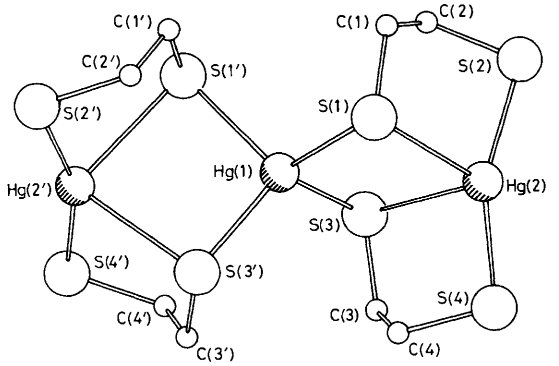

Figure 1. Structure of the trinuclear $[Hg_3(SCH_2CH_2S)_4]^{2-}$ anion (**2**) without H atoms; the primed atoms are related to the unprimed ones by a twofold axis. Metal co-ordination: distances, Hg(1) · · · Hg(2) 3.652(1), Hg(1)–S(1) 2.563(2), Hg(1)–S(3) 2.545(2), Hg(2)–S(1) 2.864(2), Hg(2)–S(2) 2.363(2), Hg(2)–S(3) 2.852(2), Hg(2)–S(4) 2.371(2) Å; angles, S(1)–Hg(1)–S(3) 101.1(3), S(1)–Hg(1)–S(1′) 115.0(1), S(1)–Hg(1)–S(3′) 116.0(1), S(3)–Hg(1)–S(3′) 107.6(1), S(1)–Hg(2)–S(2) 85.6(1), S(1)–Hg(2)–S(3) 87.5(1), S(1)–Hg(2)–S(4) 107.6(1), S(2)–Hg(2)–S(3) 113.6(1), S(2)–Hg(2)–S(4) 159.0(1), S(3)–Hg(2)–S(4) 83.8(1)°.

We report here the synthesis and structure of the first two complexes containing ethane-1,2-dithiolato ligands. When an excess of ethane-1,2-dithiolate is added to a solution of $HgCl_2$ in methanol, crystals of $[Ph_4P]_2[Hg_3(SCH_2CH_2S)_4]$ (**1**) containing the novel trinuclear isolated anion $[Hg_3(SCH_2CH_2S)_4]^{2-}$ (**2**) are precipitated on addition of Ph_4PBr. In the presence of Na_2S_2, however, $[Ph_4P]_2[Hg_2$-

$$[Ph_4P]_2[Hg_3(SCH_2CH_2S)_4]$$
(**1**)

$$[Hg_3(SCH_2CH_2S)_4]^{2-}$$
(**2**)

$$[Ph_4P]_2[Hg_2(SCH_2CH_2S)_3]$$
(**3**)

$$\{[Hg_2(SCH_2CH_2S)_3]^{2-}\}_n$$
(**4**)

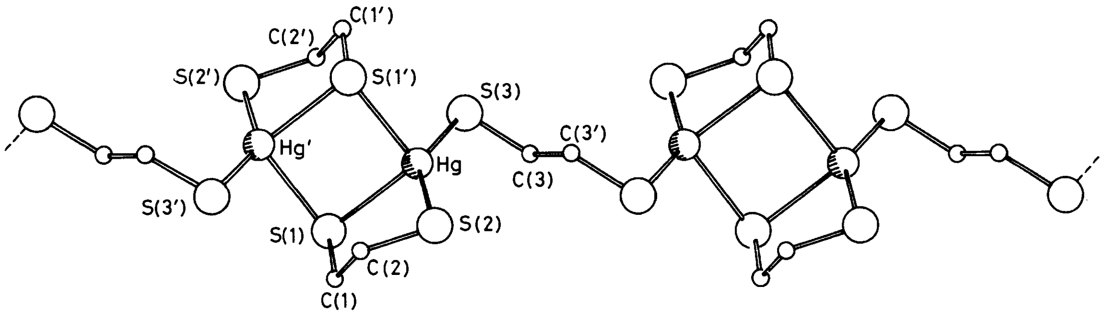

Figure 2. Section of the polymeric $\{[Hg_2(SCH_2CH_2S)_3]^{2}\}_n$ anion (**4**) showing two characteristic binuclear subunits without H atoms; the primed atoms are related to the unprimed ones by a centre of symmetry. Metal co-ordination: distances, Hg · · · Hg' 3.674(1), Hg–S(1) 2.674(1), Hg–S(1') 2.722(1) Hg–S(2) 2.442(1), Hg–S(3) 2.420(1) Å; angles, S(1)–Hg–S(1') 94.2(1), S(1)–Hg–S(2) 86.4(1), S(1)–Hg–S(3) 118.8(1), S(1')–Hg–S(2) 104.4(1), S(1')–Hg–S(3) 99.3(1), S(2)–Hg–S(3) 143.8(1)°.

$(SCH_2CH_2S)_3]$ (**3**), with infinite $\{[Hg_2(SCH_2CH_2S)_3]^{2-}\}_n$ (**4**) chains, crystallizes from the solution. The structures of (**1**) and (**3**) were determined by *X*-ray crystallography.†

In (**2**) the central Hg atom lies on a crystallographically imposed twofold axis and has four S neighbours which define a slightly distorted tetrahedron (mean Hg–S 2.554 Å) while the sulphur co-ordination of the terminal Hg atoms is extremely irregular as a consequence of the restricted S · · · S bite. Its structure is given in Figure 1. The four S atoms associated with each of these metal centres (mean $Hg–S_{bridge}$ 2.858, mean $Hg–S_{terminal}$ 2.367 Å) form S–Hg–S angles which range from 83.8 to 159.0°.

The one-dimensionally infinite chain (**4**) is formed in the crystallisation process from soluble species and consists of centrosymmetric quasi-isolated subunits with binuclear $[Hg_2S_6]$ frames linked *via* bridging $-CH_2-CH_2-$ groups. A section of the polymeric anion (**4**) showing two of these subunits is depicted in Figure 2. The metal–sulphur framework of each individual subunit can be described in terms of two HgS_4 tetrahedra which share a common edge. The Hg–S distances associated with the bridging S atoms (mean value 2.698 Å) are *ca.* 0.27 Å longer than the terminal Hg–S bonds (mean value 2.431 Å). As a consequence of the restricted intraligand S · · · S separation the S–Hg–S valence angles in (**4**) cover the range from 86.4 to 143.8°.

Our results indicate that thiolato-bridged polynuclear complexes have to be considered as intermediates in mercury detoxification by drugs containing 1,2-dithiolate-type agents.

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† *Crystal data.* Syntex P2_1 four circle diffractometer, Mo-K_α radiation, graphite monochromator, scintillation counter, 2θ–θ scan mode, T = 150 K, empirical absorption corrections. Compound (**1**): $C_{56}H_{56}P_2Hg_3S_8$, M = 1649.29, monoclinic, a = 22.713(7), b = 9.501(2), c = 29.323(7) Å, β = 119.42(2)°, space group $C2/c$, Z = 4, D_c = 1.988 g cm^{-3}, μ(Mo-K_α) = 88.9 cm^{-1}, $2\theta_{max.}$ = 52°, crystal dimensions 0.30 × 0.25 × 0.22 mm, 5862 total reflections, R (R_w) = 0.060 (0.039) for 4536 reflections with $F > 3.92\sigma(F)$ {312 variables, H atoms fixed at idealized positions with isotropic temperature factors tied to the equivalent isotropic temperature factors of the C atoms to which they are bonded [U(H) = 1.2 $U_{eq.}$(C)], all other atoms refined with anisotropic temperature factors together with an overall scale factor}. Compound (**3**): $C_{54}H_{52}P_2Hg_2S_6$, M = 1356.52, monoclinic, a = 10.393(2), b = 14.329(2), c = 17.103(4) Å, β = 96.91(2)°, space group $P2_1/n$, Z = 2, D_c = 1.782 g cm^{-3}, μ(Mo-K_α) = 65.3 cm^{-1}, $2\theta_{max.}$ = 54°, crystal dimensions 0.25 × 0.21 × 0.18 mm, 5548 total reflections, R (R_w) = 0.024 (0.026) for 4872 reflections with $F > 3.92\sigma(F)$ [393 variables, all atoms refined with anisotropic (Hg, S, P, C) or isotropic (H) temperature factors together with a common scale factor]. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.