Synthesis and Structure of $[Ph_4P]_2[Hg_3(SCH_2C_6H_4CH_2S)_4] \cdot 6MeOH$, a Novel Trinuclear Mercury Thiolate Complex with a Triply Bridging Sulphur Atom

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The toxicity of mercury for many organisms probably depends on its high affinity for biologically important ligands such as thiolates. The occurrence of metal thiolate bonds has been established for metallothioneins, a group of small cysteine-rich proteins which have been proposed to be involved in heavy metal detoxification [1]. In mammalian metallothioneins divalent metals such as Zn(II), Cd(II) and Hg(II) are bound in two domains in the form of $[M_4(S\text{-cys})_{11}]$ and $[M_3(S\text{-cys})_9]$ complexes [2].

We have previously reported the occurrence of $[Hg_2S_6]$, $[Hg_3S_8]$ and $[Hg_5S_{12}]$ sites in $\{[Hg_2(SCH_2CH_2S)_3]^{2-}\}_n$, $[Hg_3(SCH_2CH_2S)_4]^{2-}$ [3] and $[Hg_5(SCH_2CH_2S)_4(SC_2H_5)_4]^{2-}$ [4], respectively. In this paper we communicate the formation of the novel mercury complex $[Hg_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ (**1**), a homoleptic trinuclear thiolate containing a $[Hg_3S_8]$ core different from that observed in $[Hg_3(SCH_2CH_2S)_4]^{2-}$ (**2**). The anion **1** can be obtained if a methanolic solution containing an excess of $Na_2S_2\text{-}o\text{-xyl}$ is added to a solution of $HgCl_2$ in methanol under nitrogen atmosphere. It precipitates as $[Ph_4P]_2[Hg_3(S_2\text{-}o\text{-xyl})_4] \cdot 6MeOH$ (**3**) on addition of Ph_4PBr in the form of colourless crystals. The structure of **3** was determined by X-ray crystallography.

Crystal data. Syntex $P2_1$ four-circle diffractometer, Mo Kα radiation, graphite monochromator, scintillation counter, ω-scan, $T = 150$ K, empirical absorption corrections. $C_{86}H_{96}Hg_3O_6P_2S_8$, $M = 2154.51$, triclinic, space group $P\bar{1}$, $a = 11.964(9)$, $b = 13.894(11)$, $c = 26.953(20)$ Å, $\alpha = 79.10(7)$, $\beta = 80.22(7)$, $\gamma = 68.19(7)°$, $Z = 2$, $D_c = 1.749$ g cm^{-3}, μ(Mo Kα) = 78.74 cm^{-1}, $2\theta_{max} = 48°$, crystal dimensions $0.15 \times 0.14 \times 0.12$ mm, 12754 unique reflexions, $R(R_w) = 0.040$ (0.036) for 9675 reflexions with $F > 3.96\sigma(F)$ (901 variables, H atoms of the anion and the cations 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 of the cations and the anion refined with anisotropic temperature factors, C and O atoms of the methanol molecules refined with isotropic temperature factors neglecting their H atom contributions.

The three mercury atoms in **1** define a nearly rectangular (Hg(1)...Hg(2)...Hg(3) 89.0(1)°) and nearly isosceles (Hg(1)...Hg(2) 3.708(1), Hg(2)...Hg(3) 3.792(1) Å) triangle, in contrast to **2** where an approximately linear metal arrangement is found. These differences are caused by the two fundamental possibilities of linking three HgS_4 tetrahedra via common edges. They may be linked via adjacent (as realized in **1**) or opposite edges (as realized in **2**) with respect to the central HgS_4 unit.

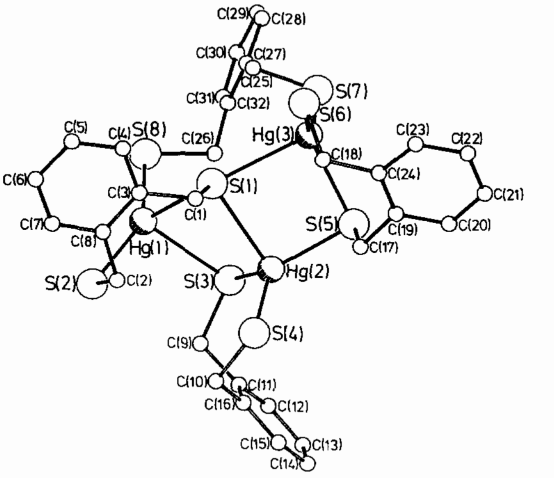

Fig. 1. Structure of the trinuclear $[Hg_3(SCH_2C_6H_4CH_2S)_4]^{2-}$ anion **1** without H atoms. Metal coordination: mean distances, Hg...Hg, 3.750; Hg–S_{term}, 2.423; Hg–(μ_2-S), 2.642; Hg–(μ_3-S), 2.775 Å; mean angles, S–Hg–S, 107.5°; Hg–(μ_2-S)–Hg, 90.3°; Hg–(μ_3-S)–Hg, 84.8° and 144.7°.

The structure of **1** in crystals of **3** is depicted in Fig. 1. The condensation mode observed here results in a thiolate-S atom which belongs to all three HgS_4 tetrahedra simultaneously. The asymmetric μ_3-S bridge with Hg–S(1)–Hg angles of 84.7(1), 84.8(1) and 144.7(1)° is similar to those observed in $[M_9(SCH_2CH_2S)_6]^{3-}$ (M = Cu, Ag) and $[Cu_7(SCH_2CH_2S)_4SC_2H_5]^{2-}$ [5].

The two shorter edges of the Hg_3-triangle are additionally bridged by μ_2-S atoms of two other ligands. The second S atoms of these three ligands are terminally coordinated to the three Hg atoms so that three chelate rings result. The fourth ligand is the only non-chelating one. It spans the longer edge of the Hg_3-triangle [Hg(1)...Hg(3) 5.256(1) Å] and its two S atoms are terminally bonded to Hg(1) and Hg(3), respectively.

The Hg–S bond lengths depend on the number of bonds formed by the S atoms. The mean values are

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2.775 Å for Hg–(μ_3-S), 2.642 Å for Hg–(μ_2-S) and 2.423 Å for Hg–S_{term}. The tetrahedral sulphur coordination of the Hg atoms is rather distorted. While the four (μ_2-S)–Hg–(μ_3-S) angles are extremely small (mean value: 90.0°), two very large S_{term}–Hg–S_{term} angles (mean value: 138.9°) are observed.

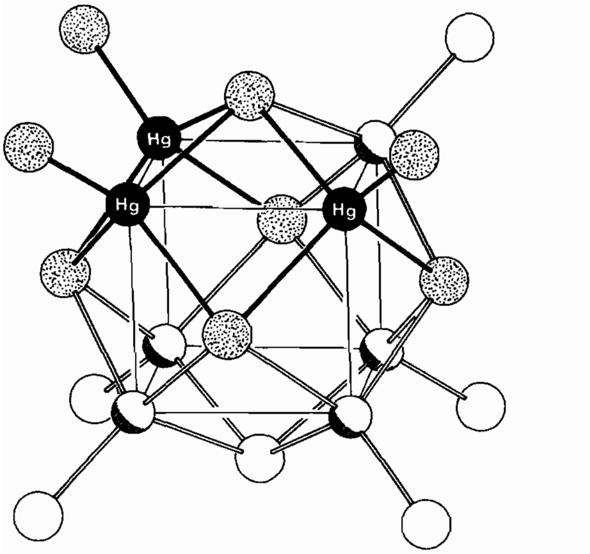

Fig. 2. The idealized [Hg_3S_8] core of **1** as a section of the [$M_8(\mu_4\text{-}S)_6S_8$] cubane system.

As depicted in Fig. 2, the [Hg_3S_8] fragment in **1** may be considered as a section of the [$M_8(\mu_4\text{-}S)_6S_8$] cluster, a paradigmatic unit which contains the [M_8S_6] cluster core present, for example, in the complex [$Co_8(\mu_4\text{-}S)_6(SPh)_8$]$^{4-/5-}$ [6], as well as in the mineralogically important pentlandites. A related heteronuclear cubane-type cluster consisting of an [Fe_7MoS_6] core has been discussed as a model for the metal–sulfur portion of the iron–molybdenum cofactor ('FeMo-co') present in the Mo–Fe protein of nitrogenase [7]. The bridging sulphur atoms of **1** derive from the μ_4-S atoms of the [$M_8(\mu_4\text{-}S)_6S_8$] frame by opening one or two adjacent M–S bonds leading to μ_3-S (S(1)) and μ_2-S (S(3), S(5)) atoms, respectively.

The [Hg_3S_8] core of **1** is structurally related to the [M_3(S-cys)$_9$] complex in the β-domain of mammalian metallothionein because of the presence of six-membered Hg_3S_3 heterocycles in both systems. The [M_3S_9] core observed in this protein [2] can be derived from the [M_3S_8] core present in **1** by opening the bond Hg(2)–S(1) and adding an S atom terminally to Hg(2). The realization of μ_3-thiolate ligands in simple coordination compounds with complete sulphur ligand spheres indicate that the coordinating properties of cysteinyl residues in biomolecules might be of similar versatility.

Supplementary Material

Further details of the crystal structure investigation (atomic coordinates, coefficients of the temperature factors, a complete list of bond distances and angles and tables of observed and calculated structure factors) are available from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, F.R.G. on quoting the depository number CSD-52477, the names of the authors, and the full citation of the journal.

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