

[Hg₇(SC₆H₁₁)₁₂Br₂], a Novel Mercury Cage Molecule with Bridging and Terminal Thiolate Ligands and with Terminal and μ₆ Bromide

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Reaction of HgBr₂ with sodium cyclohexanethiolate in methanol, followed by recrystallisation from pyridine, gives the discrete molecular complex [Hg₇(SC₆H₁₁)₁₂Br₂], in which six Hg atoms form a distorted octahedron around a central Br, thiolate ligands are bridging or terminal, and a HgBr unit with terminal Br caps three thioliates on one side of the molecule.

Homoleptic thiolate complexes of mercury(II) adopt both discrete molecular and polymeric structures.¹ Mononuclear [Hg(SR)₂],² [Hg(SR)₃]⁻,³ and [Hg(SR)₄]²⁻ complexes^{3d,4} have been characterized, as well as the dinuclear [Hg₂(SMe)₆]²⁻,⁵ and the trinuclear [Hg₃(SCH₂CH₂S)₄]²⁻;⁶ polymeric chains or three-dimensional networks with thiolate bridges occur for some [Hg(SR)₂]⁷ and for [Hg₂(SCH₂CH₂S)₃]²⁻.⁶ [Hg(SCH₂CH₂CH₂NMe₃)₂]²⁺ is known to exist in both mononuclear and chain polymeric forms,⁸ and the structure of [Hg(SC₆H₁₁)₂] is intermediate, with rather bent monomer units linked by weaker Hg–S bonds into a chain.^{3a}

By contrast, for mercury(II) complexes containing both monodentate thiolate and halide ligands, only non-molecular structures have been reported. These involve either one-dimensional chains, as in [Hg(SR)Cl₂]_∞ with a zwitterionic thiolate containing a non-coordinating quaternary ammonium or protonated primary amine group⁹ and in [Hg(S-steroid)Br]_∞,¹⁰ or two-dimensional layers, as in [Hg(SMe)X]_∞ (X = Cl or Br)¹¹ and [Hg(SPrⁿ)Cl]_∞.¹² An adamantane-like cage structure has been proposed for [Hg₄L₄(SPrⁿ)₆]²⁻ on the basis of NMR spectroscopic data,¹³ but has not been confirmed crystallographically. Discrete molecular structures have been firmly established only for tetranuclear complexes which also involve coordination of Hg by amines, either as extra ligands^{11,14} or as additional functionality in chelating aminothioliates.¹⁵

We report here the synthesis and crystal structure of the novel heptanuclear complex [Hg₇(SC₆H₁₁)₁₂Br₂], which is the first example of a discrete molecular complex of mercury containing only halide and monofunctional thiolate ligands, and which displays a number of unusual features.

The complex was prepared by mixing methanolic solutions of Na[SC₆H₁₁] and HgBr₂, with thiolate : mercury molar ratios in the range 1–1.75 : 1 in several different experiments. It precipitated slowly, and was recrystallized from pyridine by slow evaporation, to give colourless crystals of approximately cubic shape, from which satisfactory analytical data were obtained.

The crystal structure[†] was determined from X-ray diffraction data measured at 200 K, initial attempts at higher

temperatures giving inadequate precision for the cyclohexyl groups. The molecule is shown in Fig. 1, and the central Hg₇S₁₂Br₂ core in Fig. 2. A central Br atom is surrounded by a distorted octahedral array of Hg atoms, with three Br–Hg distances of 3.036(1) Å and three of 3.174(2) Å; twelve Hg–Br–Hg *cis* angles lie in the range 80.2(1)–104.0(1)° together with three *trans* angles of 170.4(1)°. In marked contrast, the second Br atom is terminally bonded to the remaining Hg atom, with a much shorter Hg–Br distance of 2.616(3) Å. Six-coordination of a halogen atom in a molecular structure is rare, though it is common for halide ions in the sodium chloride extended array structure; the only previously reported example of which we are aware is [CINd₆(OPrⁱ)₁₇].²¹ Halogen-centred metal clusters have been found in some other thiolate complexes, with coordination numbers of 2, 4 and 8.²²

Six of the seven Hg atoms have a highly distorted fourfold coordination geometry, with two short and one long Hg–S and a long Hg–Br distance. They fall into two crystallographically independent sets of three equivalent atoms. Each can best be considered as having a primary approximately linear twofold HgS₂ coordination [2.365(4) Å, 2.420(4) Å, 150.4(1)°; 2.376(3) Å, 2.352(4) Å, 168.1(1)°] as in the chain polymeric [Hg(SC₆H₁₁)₂] structure [2.372(2) Å, 2.374(2) Å, 160.4(1)°],⁹ with additional weaker Hg–S [2.775(4) or 3.088(3) Å] and Hg–Br [3.036(1) or 3.174(2) Å] interactions approximately normal [79.5(1)–106.1(1)°] to the primary Hg–S bonds, responsible for holding the molecular cluster together. The seventh Hg atom has approximately regular tetrahedral

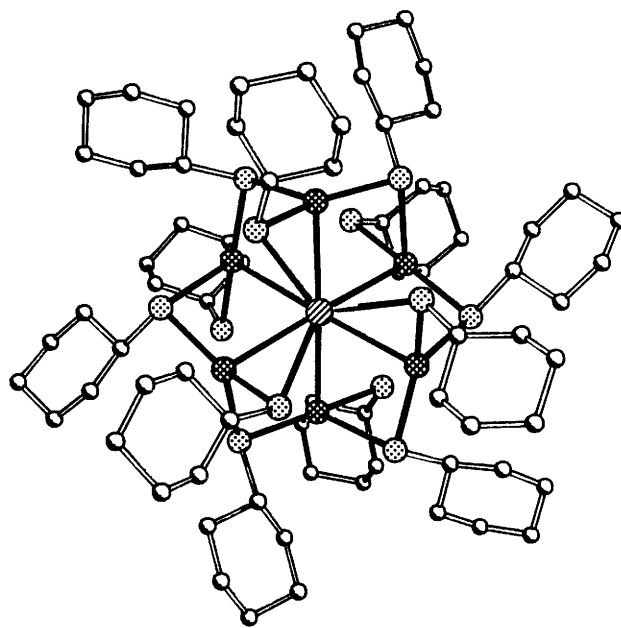


Fig. 1 The molecular structure of [Hg₇(SC₆H₁₁)₁₂Br₂], seen along the threefold rotation axis, which passes through one Hg and two Br atoms. H atoms are omitted for clarity.

[†] *Crystal data:* C₇₂H₁₃₂Br₂Hg₇S₁₂, *M* = 2946.5, rhombohedral, space group *R*3̄, with hexagonal axes *a* = *b* = 22.860(4), *c* = 14.823(2) Å at 200 K,¹⁶ *U* = 6708.0 Å³, *Z* = 3, imposing *C*₃ symmetry on the molecule. Intensities were measured to 2θ_{max} = 50° on a Stoe-Siemens diffractometer with Mo-Kα radiation (λ = 0.71073 Å)¹⁷ and corrected semiempirically for absorption (μ = 13.2 mm⁻¹, transmission 0.10–0.17). The structure was solved by heavy atom methods and refined¹⁸ to a minimum of Σ*w*Δ² [Δ = |*F*_o| – |*F*_c|, *w* = 1/σ²(*F*) with contributions to σ²(*F*) from counting statistics and an analysis of variance¹⁹] from 4703 unique observed reflections. Inclusion of a complete set of Friedel opposites allowed the refinement of η = +0.48(3) to indicate the correct absolute structure.²⁰ Isotropic H atoms were constrained, other atoms were refined anisotropically; *R* = 0.0406, *R*_w = (Σ*w*Δ²/Σ*w**F*_o²)^{1/2} = 0.0522, *S* = 1.10 for 279 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

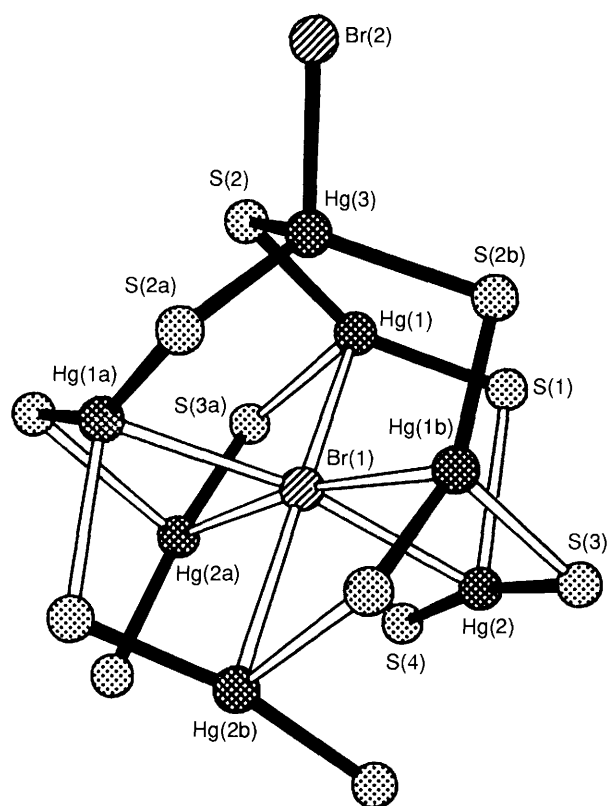


Fig. 2 The structure of the central $\text{Hg}_7\text{S}_{12}\text{Br}_2$ core, with the atom numbering scheme for all crystallographically unique atoms and some symmetry-equivalent atoms, in a general view direction. Primary bonds are shown filled, secondary bonds hollow. Key dimensions: $\text{Hg}(1)\text{--Br}(1)$ 3.036(1), $\text{Hg}(2)\text{--Br}(1)$ 3.174(2), $\text{Hg}(3)\text{--Br}(2)$ 2.616(3), $\text{Hg}(1)\text{--S}(1)$ 2.365(4), $\text{Hg}(1)\text{--S}(2)$ 2.420(4), $\text{Hg}(1)\text{--S}(3a)$ 2.775(4), $\text{Hg}(2)\text{--S}(1)$ 3.088(3), $\text{Hg}(2)\text{--S}(3)$ 2.376(3), $\text{Hg}(2)\text{--S}(4)$ 2.352(4), $\text{Hg}(3)\text{--S}(2)$ 2.568(3) Å; $\text{S}(1)\text{--Hg}(1)\text{--S}(2)$ 150.4(1), $\text{S}(3)\text{--Hg}(2)\text{--S}(4)$ 168.1(1), $\text{Br}(2)\text{--Hg}(3)\text{--S}(2)$ 105.0(1), $\text{S}(2)\text{--Hg}(3)\text{--S}(2a)$ 113.6(1) $^\circ$. Symmetry operations: (a) $-y, x - y, z$; (b) $-x + y, -x, z$.

HgBrS_3 geometry, with bond lengths 2.616(3) Å for $\text{Hg}\text{--Br}$, 2.568(3) Å for $\text{Hg}\text{--S}$, and with angles 105.0(1) $^\circ$ for $\text{Br}\text{--Hg}\text{--S}$, 113.6(1) $^\circ$ for $\text{S}\text{--Hg}\text{--S}$.

Of the twelve thiolate ligands, three are terminally bonded to only one Hg each, giving the shortest $\text{Hg}\text{--S}$ bonds [2.352(4) Å] in the molecule. The other nine (in three sets of three equivalents each) bridge pairs of Hg atoms with varying degrees of asymmetry [$\text{Hg}\text{--S}$ 2.420(4) and 2.568(3) Å; 2.376(3) and 2.774(4) Å; 2.365(4) and 3.088(3) Å]. There are no significant differences among $\text{S}\text{--C}$ bond lengths or the geometry of cyclohexyl groups, all of which adopt the expected chair conformation with sulfur in an equatorial position. The twelve S atoms form a relatively undistorted icosahedron surrounding the Hg_6 octahedron; six of the twenty S_3 triangles are capped internally and one is capped externally by Hg atoms.

The variety of Hg coordination geometries found within this molecule, from essentially regular tetrahedral through an intermediate two/three-coordination by thiolates to almost linear two-coordination, may be related to the metal sites in Hg-metallothioneins. In a study of the titration of a Cd_7 -metallothionein with Hg^{II} , spectroscopic evidence suggests that initial replacement of Cd by Hg involves tetrahedral coordination of Hg by S, but the incorporation of more than four Hg ions probably leads to a progressive change to essentially linear coordination.²³ Further studies of related complexes are underway.

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