

**Synthesis and X-Ray Crystal Structure of a 1,1-Dithiolate Cluster
Compound containing a Cube of eight Ag^I Atoms,
[Ag₈^I{S₂C=C(CN)₂}₆]⁴⁻**

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Summary The novel [Ag₈^I{S₂C=C(CN)₂}₆]⁴⁻ cluster compound contains a cube of Ag^I atoms (average Ag^I-Ag^I distance 3.02 Å) which is inscribed into an icosahedron of twelve S atoms so that each Ag^I atom is planar coordinated by a triangular arrangement of three S atoms.

THE reaction of AgNO₃ (2.26 g) in 3 ml of H₂O with a solution of 2.18 g of dipotassium 2,2-dicyanoethylene-1,1-dithiolate¹ [K₂S₂C=C(CN)₂] in the presence of 2.18 g of Buⁿ₄NBr yielded a yellow precipitate which was filtered off and dissolved in acetone. Pure (Buⁿ₄N)₄[Ag₈{S₂C=C-

(CN)₂}]₆] was precipitated by adding water. Single crystals were obtained by slow addition of diethyl ether to a solution of the compound in acetone. The structure was solved with direct methods and refined using least-squares techniques.†

The [Ag₈^I{S₂C=C(CN)₂}]₆⁴⁻ ion contains a slightly distorted cube of Ag^I atoms which is inscribed into an icosahedron of S atoms so that each Ag^I atom lies at the centre of a triangular arrangement of S atoms. The S–Ag–S angles are close to 120° [range 115.5(1) to 123.1(1)°; average 118.6°]. The six S–S edges of the S₁₂-icosahedron which are bridged by C atoms of the dithiolate ligands are shorter than the non-bridged S–S edges (see the Table).

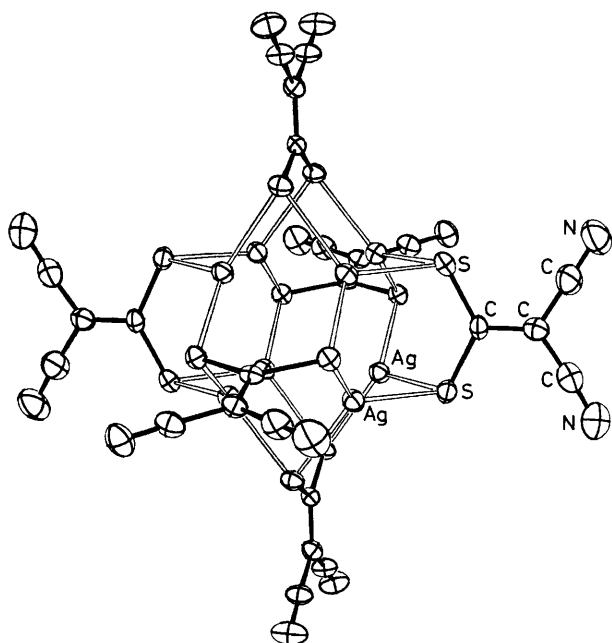


FIGURE. The structure of the [Ag₈^I{S₂C=C(CN)₂}]₆⁴⁻ ion. The anisotropic vibration ellipsoids correspond to a probability of 50%. The three bonds from each Ag^I atom to the sulphur atoms are drawn as 'open' bonds.

The complex anion has crystallographic inversion symmetry. Moreover, it contains three mutually perpendicular pseudo-twofold axes passing through C=C bonds in opposite ligands and four pseudo-threefold axes along body-diagonals of the Ag₈^I-cube. The structure of the complex ion is shown in the Figure.

A number of polynuclear Ag^I thiolate compounds have been described^{2,3} but no cubic arrangement of Ag^I atoms without a central halide ion has so far been reported. In Ag₈^I(SPh)₇²⁻ the symmetry of the Ag₈S₇ core is C_{2v} containing four 3-co-ordinated and one 2-co-ordinated Ag^I atom.^{2a} The Ag^I atoms in (AgS₂CNR₂)₆ form a distorted octahedron, bridged by dithiocarbamate S atoms.³ In [Ag₈^INi^{II}(Pen)₁₂Cl]⁵⁻, where Pen is the D-penicillaminato dianion [SC(CH₂)₂CH(NH₂)COO]²⁻, eight Ag^I atoms occupy the corners of a cube which is, however, centred by a chloride ion.⁴ In that case the Ag^I–Ag^I edges of the Ag₈^I-cube are significantly longer than those in the present compound (see the Table).

The [Ag₈^I{S₂C=C(CN)₂}]₆⁴⁻ ion is structurally more related to a number of Cu^I 1,1-dithiolate cluster compounds containing analogous Cu₈^IS₁₂ cores.⁵ The Cu₈^I cubes in these cluster compounds are considerably smaller than the Ag₈^I cube in the present compound (Table). The sizes of the S₁₂-icosahedra in [Ag₈^I{S₂C=C(CN)₂}]₆⁴⁻ and in [Ag₈^INi^{II}(D-Pen)₁₂Cl]⁵⁻ are quite comparable (see Table). The lengths of the S–S edges of the S₁₂-icosahedron which are bridged by ligand C atoms (in the present compound) or by Ni^{II} atoms (in the penicillamine cluster) are determined by the bridging atoms. They lie within a close range. The lengths of the other 'free' S–S edges are obviously determined by the lengths of the Ag^I–S bonds and the overall sizes of the Ag₈^IS₁₂ cores are therefore bigger than those in the Cu₈^IS₁₂-containing compounds (Table).

The edges of the Ag₈^I-cube in the penicillamine cluster are longer than those in the present cluster. This is the result of the presence of a central halide ion in the penicillamine compound (Table). Each Ag^I atom in the penicillamine compound lies close to the least-squares plane through the three S atoms to which it is bonded. The Ag^I atoms in the [Ag₈^I{S₂C=C(CN)₂}]₆⁴⁻ ion are displaced out of the plane through the S atoms to which they are bonded. All displacements are towards the centre of the cluster and

TABLE. Comparison of dimensions (range and average distances) of M₈^IS₁₂ cores in thiolato-compounds with cubic arrays of Ag^I or Cu^I atoms (all distances in Å). Estimated standard deviations in parentheses.

	[Ag ₈ ^I {S ₂ C=C(CN) ₂ }] ₆ ⁴⁻ ^a	[Cu ₈ ^I {S ₂ C=C(CN) ₂ }] ₆ ⁴⁻ ^b	[Ag ₈ ^I Ni ^{II} (Pen) ₁₂ Cl] ⁵⁻ ^c
M ^I –M ^I	2.957(2)—3.085(2) 3.017	2.782(3)—2.870(3) 2.829	3.412(3)—3.511(2) 3.477
M ^I –S	2.462(4)—2.517(4) 2.491	2.239(4)—2.261(4) 2.250	2.492(6)—2.524(6) 2.503
S–S (bridged)	3.086(6)—3.101(6) 3.095	3.077(7)—3.088(7) 3.080	3.174(8)—3.206(8) 3.190
S–S (other)	4.199(6)—4.389(6) 4.283	3.82(1)—3.94(1) 3.88	4.18(2)—4.409(7) 4.32
M ^I →S ₃ -plane	0.277(3)—0.336(3) ^d 0.295	0.22(1)—0.30(1) ^d 0.27	0.045(4)—0.162(4) 0.091

^a This work. ^b Ref. 5. ^c Ref. 4. ^d The M^I atoms are displaced from the least-squares plane through three S atoms towards the centre of the complex ion.

† Crystal data: space group P2₁/c, a = 15.756(2), b = 22.516(3), c = 18.078(3) Å, β = 107.50(1)°, D_m = 1.54, D_c = 1.46(3) g cm⁻³ (Z = 2). The intensities of 8481 independent reflections were measured (Mo-K_α radiation) and the present R value, for the 5211 reflections with I > 2σ(I), is 0.053. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

are comparable to those earlier found in the related Cu^I compound (Table). There is no other apparent reason for such displacements than an attractive interaction between the Ag₈^I atoms as earlier suggested for Cu^I cluster compounds.^{5b} Discussions with Professor J. Reedijk are gratefully acknowledged.

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