The Structure of a Novel Polynuclear Complex related to the Sphalerite Lattice

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Summary The structure is built from decanuclear cations, $[Cd_{10}(S–CH_2–CH_2–OH)_{16}]^{4+}$, in which the 10 Cd atoms and the 16 S atoms are arranged approximately as in a portion of the cubic ZnS (sphalerite) structure.

IN the course of an investigation of the complex formation between Cd^{2+} and thioglycol, crystalline salts of composition $Cd_5(S–CH_2–CH_2–OH)_8X_2$, X = NO_3^-, ClO_4^-, $\frac{1}{2}(SO_4^{2-})$ have been isolated.[1]

Crystals of the sulphate (as a dihydrate) are monoclinic, $a = 25{\cdot}21$, $b = 12{\cdot}27$, $c = 25{\cdot}52$ Å, $\beta = 96{\cdot}5°$, space group $I2/c$ (C_{2h}^6) with 40 Cd atoms in the unit cell. Three-dimensional X-ray intensity data were recorded on a Hilger and Watts Linear Diffractometer, using Mo-K_α radiation with balanced filters. A partial structure was derived by direct methods. Electron density and difference syntheses led gradually to the recognition of all atoms except hydrogen, and subsequent least-squares refinement reduced the R-factor to 0·09 for the 3500 most reliable F-values.

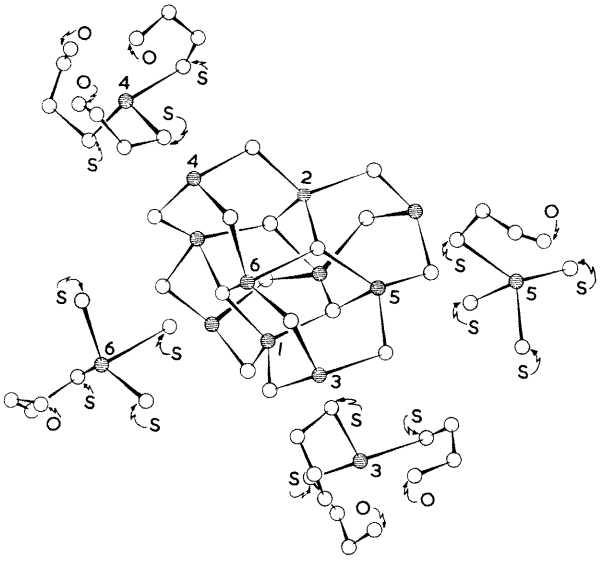

FIGURE. *The central part of the figure shows the arrangement of the* 10 Cd *and the* 16 S *atoms in the complex cation. At the periphery, detailed views are given for* Cd *atoms having additional O-neighbours from thioglycol ligands.*

The structure is built from decanuclear cations, $[Cd_{10}(S–CH_2–CH_2–OH)_{16}]^{4+}$, in which the 10 Cd atoms and the 16 S atoms are arranged approximately as in a portion of the cubic ZnS (sphalerite) structure. If the structure of the complex is examined in more detail, three types of Cd atoms may be distinguished. Atoms 1 and 2, situated on the crystallographic twofold axis, are surrounded only by four S-neighbours (Cd–S = 2·51 Å)† in tetrahedral co-ordination. Atoms 5 and 6 (and the symmetry equivalent atoms) have in addition one extra O-neighbour from a thioglycol ligand. The co-ordination is trigonal bipyramidal with the O in one of the axial positions [Cd–S (*eq*) = 2·52 Å, Cd–S (*ax*) = 2·86 Å, Cd–O = 2·41 Å]. Finally, atoms 3 and 4 (and symmetry related atoms) have only three S-neighbours but an approximately octahedral co-ordination is completed by three additional O-atoms from thioglycol ligands (Cd–S = 2·56 Å, Cd–O = 2·46 Å). A more detailed discussion of the oxygen positions would have to include consideration of the extended system of hydrogen bonds in the crystal.

This work was supported by the Swiss National Science Foundation. I thank Professor G. Schwarzenbach for suggesting this structure analysis.

(*Received, April* 25*th,* 1969; *Com.* 568.)

† Average values of all bond lengths of the same type are given.

G. Schwarzenbach, K. Gautschi and J. Peter, *Proceedings* 10*th I.C.C.C.*, Tokyo and Nikko, Japan, Sept. 1967.