

57. Stereochemistry of Polynuclear Cadmium(II) Thioglycolates: Crystal Structure of Cadmium(II) Bisthioglycolate

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Summary. Crystals of cadmiumbisthioglycolate are monoclinic, $a = 10.06$, $b = 19.81$, $c = 8.74$ Å, $\beta = 107.36^\circ$, space group $P 2_1/c$, $Z = 4$. A detailed three-dimensional analysis shows that cadmium ions and mercaptide sulfur atoms form a two dimensional array of six-membered and four-membered rings (Fig. 1). All sulfur atoms bridge two cadmium ions. Of the two kinds of cadmium ions, one shows distorted tetrahedral coordination to four sulfurs, the other one distorted trigonal bipyramidal coordination (Fig. 4) to four sulfurs and to an axial alcohol oxygen atom.

Metal complexes of the isoelectronic d^{10} -cations, Ag(I), Cd(II) and In(III), with thioglycol have been investigated systematically in solution [1–3]. The cations Ag(I) and Cd(II) form polynuclear complexes because of the pronounced tendency of mercaptide sulfur atoms to form bridges between the metal cations. The decanuclear cation $Cd_{10}L_{16}^{4+}$ ($L = HOCH_2CH_2S^-$) is formed on alkalization to pH 4–6 of solutions containing a cadmium salt and an excess of thioglycol. The structure determination by X-ray crystallography [4] of the crystalline sulfate [2] showed Cd(II)-ions in distorted tetrahedral, trigonal bipyramidal and octahedral coordination (fig. 2). The mercaptide sulfur atoms act as bridges between two or three Cd(II)-ions. An attempt to crystallize the same cation as an iodide salt led to a new polynuclear species $(Cd_2L_3I)_4$ whose structure will be described in a later paper [5].

In subsequent preparative work uncharged 1:2 complexes of Cd(II)-ions and thioglycolate were studied [2]. Rapid addition of base to an acid solution of Cd(II)-ions and thioglycol results in a highly viscous or plastic precipitate which transforms to a white powder on aging. This powder is soluble in polar organic solvents, such as glacial acetic, dimethylsulfoxide and dimethylformamide, as well as in aqueous concentrated cadmium acetate, sodium hydroxide or ammonia. The compound can be obtained crystalline, when the solution containing Cd and thioglycol is stored in a desiccator under an ammonia-containing atmosphere. The absorption of NH_3 causes a slow rise of pH and when its value reaches about 8, colorless transparent crystals are produced. Analytical results indicate the composition CdL_2 for both, the white powder and the colorless crystals. The structure of the crystalline material was determined by X-ray methods and is shown schematically in fig. 1. The cadmium(II)-ions and sulfurs of the thioglycolate ions form infinite layers; successive layers are held together by hydrogen bridges between the hydroxyl groups of the thioglycolates. Within a layer of Cd and mercaptidesulfur chains of six-membered

rings are recognized, each ring containing three Cd and three S. Two of the three Cd are shared by neighbouring six-membered rings in an arrangement called 'spiro'-linkage in organic chemistry. Chains of six-membered rings are tied to each other by means of the third Cd. Each of these Cd-atoms is connected to an equivalent Cd-atom of a neighbouring chain *via* two bridging mercaptide sulfurs thus forming four-membered rings with the Cd again in a 'spiro'-position (Fig. 1 and 3). Whereas the first type of Cd is coordinated to four sulfurs only, the second kind shows trigonal bipyramidal coordination (Fig. 4) with a thioglycolate oxygen in an axial and sulfurs in the remaining positions. This is a consequence of the constraints involved in the formation of a four-membered ring producing an angle S–Cd–S of only 92° and thereby making enough space available to accommodate a fifth ligand in the coordination sphere.

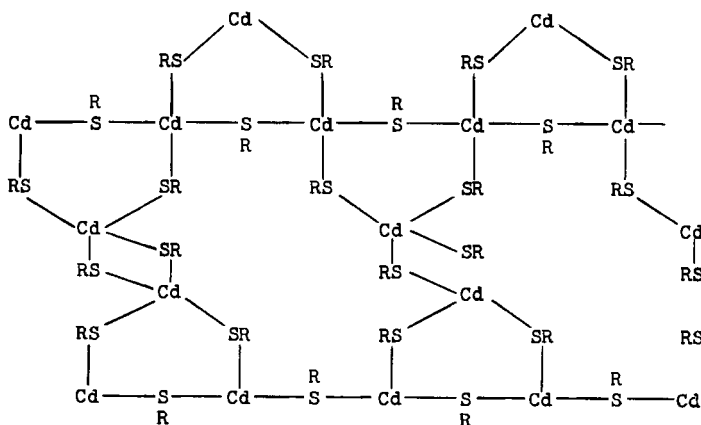


Fig. 1. Schematic representation of the layer structure of $\text{Cd}(\text{SCH}_2\text{CH}_2\text{OH})_2$

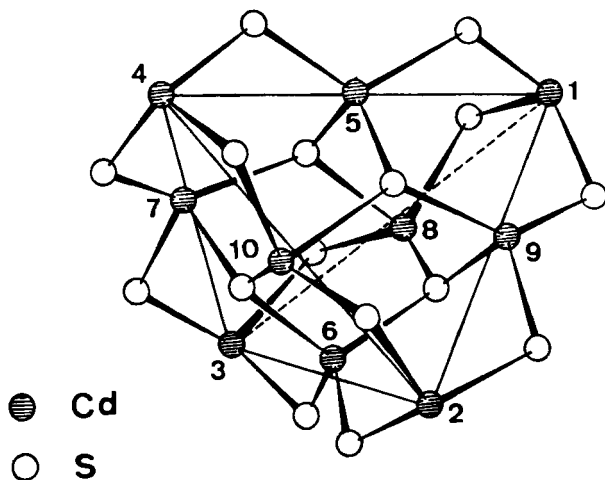


Fig. 2. Structure of the decanuclear cation $\text{Cd}_{10}(\text{SCH}_2\text{CH}_2\text{OH})_{16}^{4+}$

A comparison shows that the structural elements found in the decanuclear cation $\text{Cd}_{10}\text{L}_{14}^{4+}$ are also found in this structure. Such a structural element consists of two six-membered rings (formally $\text{Cd}_5\text{L}_8^{2+}$). Two of these elements are combined in the decanuclear $\text{Cd}_{10}\text{L}_{16}^{4+}$, one of them formed by the cadmium ions 1, 9, 5, 7 and 4, the other one by Cd 3, 8, 6, 10 and 2 (Fig. 2).

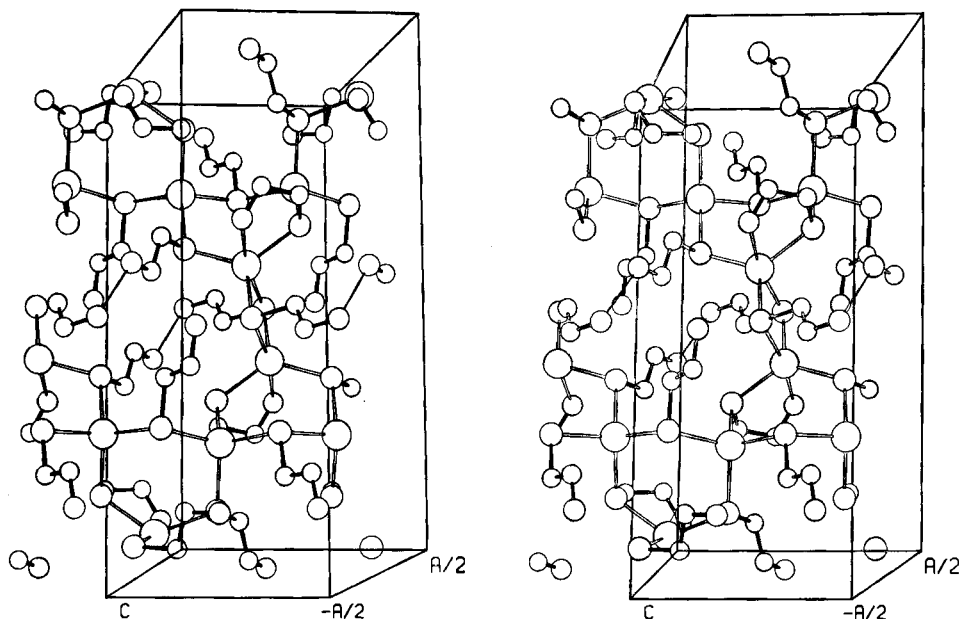


Fig. 3. Stereoscopic drawing of $\text{Cd}(\text{SCH}_2\text{CH}_2\text{OH})_2$. Solid bonds are used in the organic ligands, open bonds around cadmium. (Prepared with the program ORTEP, C. K. Johnson, Oak Ridge National Laboratory)

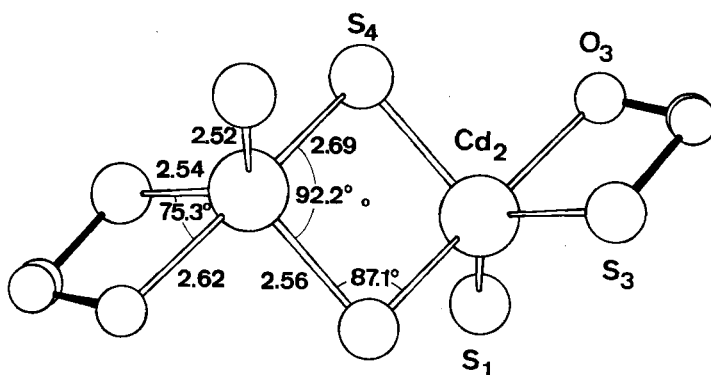


Fig. 4. Bond angles and bond lengths in the four-membered ring containing five coordinate Cd^{2+}

What conclusion can be drawn from the result of this structure analysis with regard to the structure of the white plastic precipitate? In order to answer this

question, powder diagrams were taken from both, the crystalline material and the white precipitate after it had aged for about a week and become solid. The two diagrams on visual inspection are identical. This result could possibly indicate that the plastic precipitate consists of the chains of six-membered rings mentioned earlier. The chains may be flexible as there are no conformational preferences in the six-membered Cd–S–ring of the solid with torsional angles ranging from 0–70° and bond angles ranging from 100–120°. In such a structure the cadmium ions that are not in a 'spiro' position, would have only three sulfur ligands. Their coordination sphere could be completed, however, by two or three thioglycol oxygen atoms, as has been found in $\text{Cd}_{10}\text{L}_{16}^{4+}$ for the cadmium ions 1, 2, 3 and 4 (Fig. 2). The process of aging could then consist in connecting chains of six-membered rings, *i.e.* replacing Cd–O-bonds by Cd–S-bonds to form the four-membered rings observed in the crystal structure. Quantitative details of the structure are given in a later section of this paper. A general discussion of cadmium coordination is given in another paper [8].

Experimental Part

Preparation. 2.6 g of cadmium acetate (11.3 mmol) were dissolved in 30 ml of water and mixed with 1.56 g of thioglycol (20 mmol) dissolved in another 30 ml of water. The mixture was stored in a desiccator together with a beaker of 1% aqueous ammonia solution. At pH \sim 8 transparent, colorless crystals, which are stable in air, started to crystallize (m.p.: 172°).

Analysis. Results from micro-analytical methods (C, H, S) and from atomic absorption spectroscopy (Cd) are:

Calc.	C 18.02	H 3.78	S 24.05	Cd 42.15%
Found	„ 18.01	„ 3.79	„ 23.83	„ 43.26 \pm 0.61%

In addition, Cd was determined by complexometric, thioglycolate by iodometric titration. The EDTA- and J_2 -solution were calibrated using the same standard solution (0.1M CuSO_4). The relative composition is $[\text{Cd}^{2+}]/[\text{—SCH}_2\text{CH}_2\text{OH}] = 0.5$. The density determined by floatation is 2.14 g/ml while the density calculated from the assumed composition and the cell constants is 2.11 g/ml.

Crystal data. $\text{Cd}_2\text{C}_8\text{H}_{20}\text{O}_4\text{S}_4$, M.W. = 533.29. Colorless, prismatic crystals. Monoclinic, $\mathbf{a} = 10.06 \text{ \AA}$, $\mathbf{b} = 19.81 \text{ \AA}$, $\mathbf{c} = 8.744 \text{ \AA}$, $\beta = 107.37^\circ$, space group $P 2_1/c$ (C_{2h}^8), $Z = 4$. (Cell constants determined on a four-circle diffractometer).

Intensity measurements. Four-circle diffractometer (Y 290, Hilger and Watts), Mo K_α radiation, graphite monochromator. About 5300 symmetry-independent reflections measured with $\theta \leq 32^\circ$, linear absorption coefficient 29.93 cm^{-1} , no absorption correction. Dimensions of crystal used for intensity measurements: 0.15 mm by 0.13 mm by 0.25 mm.

Structure analysis and refinement. From a Patterson synthesis the positional parameters of the two cadmiums in the asymmetric unit were determined. The subsequent Cd-phased Fourier synthesis, showed the positions of the sulfur atoms. The (2 Cd + 4 S)-phased synthesis showed all carbon and oxygen atoms. This trial structure was refined by full-matrix least-squares analysis. In the final cycles, the model contained anisotropic temperature factors for Cd and S, isotropic for C and O. The final refinement led to a R-factor of 4.1% using the 4265 reflexions with $F > 4 \sigma$ (F) and a weighting system of the form

$$w = \{1 + (F_0 - 15)^2/622\}^{-1}$$

The quantity $\langle w (\Delta F_0)^2 \rangle$ calculated for arbitrary ranges in F takes values between 0.92 and 1.96. Scattering by hydrogen atoms and anomalous scattering by the cadmium ions were not taken into account. A final $(F_0 - F_c)$ -synthesis showed residual densities of about 1.4 e/\AA^3 in the vicinity of the cadmium atoms, about -0.5 e/\AA^3 in the vicinity of sulfur atoms and of about 0.5 to 1.0 e/\AA^3 in places where hydrogen atoms may be expected from stereochemical considerations.

Scattering factors for C, O and S⁻ were taken from [6], those of Cd²⁺ (*Thomas-Fermi-Dirac* statistical model) from [7]. In view of the residual densities observed in the (F_o – F_c)-synthesis, it might have been a better approximation to use neutral-atom scattering factors instead of those for S⁻ and Cd²⁺.

Results. Coordinates and their estimated standard deviations are given in Table 1, thermal motion parameters in Table 2. The values of anisotropic thermal motion parameters for Cd²⁺ and S⁻ are probably affected by absorption errors. All standard deviations should be considered as lower limits.

Some of the bond lengths and bond angles are shown in tables 3 and 4. The average Cd-S bond length for tetrahedral coordination is 2.56 Å (2.50 Å and 2.53 Å in [4]), the average bond length

Table 1. *Atomic coordinates* (and their estimated standard deviations *10⁴)

ATOM		x	y	z
Cd	1	0.0679 (3)	0.2581 (3)	0.1904 (3)
Cd	2	-0.0701 (3)	0.4177 (3)	0.4248 (3)
S	1	-0.0163 (12)	0.3788 (11)	0.1756 (11)
S	2	0.2098 (11)	0.2468 (10)	0.4891 (10)
S	3	-0.0954 (12)	0.1577 (12)	0.1489 (11)
S	4	0.1813 (11)	0.0346 (10)	0.0941 (11)
O	1	-0.3494 (42)	0.0440 (43)	0.3413 (44)
O	2	0.4214 (41)	0.0821 (41)	0.4161 (42)
O	3	-0.3209 (40)	0.3664 (39)	0.3155 (40)
O	4	0.4431 (37)	0.4293 (38)	0.3284 (38)
C	12	-0.2191 (60)	0.0468 (59)	0.4663 (61)
C	11	-0.1852 (49)	0.1192 (48)	0.5187 (50)
C	22	0.3845 (57)	0.1522 (56)	0.4256 (57)
C	21	0.2635 (50)	0.1582 (49)	0.4905 (50)
C	32	-0.3263 (64)	0.3049 (65)	0.3961 (66)
C	31	-0.2745 (58)	0.1873 (56)	0.0765 (59)
C	42	0.3702 (53)	0.4199 (50)	0.4446 (54)
C	41	0.2741 (49)	0.4780 (49)	0.4431 (50)

Table 2. *Thermal motion parameters and their estimated standard deviations* (in units of last significant digit)

ATOM		U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cd	2	0.0441 (2)	0.0304 (2)	0.0326 (2)	0.0032 (2)	0.0164 (2)	-0.0005 (2)
Cd	1	0.0416 (2)	0.0326 (2)	0.0298 (2)	0.0014 (2)	0.0139 (2)	0.0008 (2)
S	1	0.0418 (5)	0.0333 (5)	0.0299 (4)	0.0091 (8)	0.0143 (8)	-0.0022 (7)
S	2	0.0398 (5)	0.0298 (4)	0.0239 (4)	-0.0018 (7)	0.0130 (7)	0.0011 (7)
S	3	0.0437 (5)	0.0386 (5)	0.0310 (5)	-0.0077 (9)	0.0156 (8)	-0.0067 (8)
S	4	0.0324 (4)	0.0302 (4)	0.0302 (4)	-0.0050 (7)	0.0117 (7)	-0.0037 (7)

ATOM	B	ATOM	B	ATOM	B
O	1	C	12	C	32
	4.02 (7)		3.87 (9)		4.18 (10)
O	2	C	11	C	31
	4.05 (7)		3.04 (7)		3.75 (9)
O	3	C	22	C	42
	3.46 (6)		3.63 (8)		3.33 (8)
O	4	C	21	C	41
	3.35 (6)		3.11 (7)		3.06 (7)

Table 3. Bond length and bond angles associated with ligand molecules

	1	2	3	4 ^{a)}	av.
l (C—S)	1.84	1.84	1.82	1.85 ± 0.005 Å	1.84
l (C—C)	1.52	1.49	1.51	1.50 ± 0.01 Å	1.51
l (C—O)	1.44	1.45	1.42	1.43 ± 0.01 Å	1.44
α (SCC)	109	110	113	111 ± 0.4°	111
α (CCO)	110	111	112	111 ± 0.5°	111
α (CSCd)	104	100	104	104 ± 0.2°	
α (CSCd)	106	99	109	98 ± 0.2°	103
ω (SCCO)	179	176	59	180 ± 2°	—

^{a)} Standard deviations calculated from inverted matrix of normal equations. See text.

Table 4. Bond lengths and angles with estimated standard deviations associated with cadmium and sulfur atoms (esd in units of last significant digit)

Cd (1) — S (1)	2.526 (1) Å	O (3) — Cd (2) — S (1)	89.9 (1)°
Cd (1) — S (2)	2.584 (1)	O (3) — Cd (2) — S (3)	75.3 (1)
Cd (1) — S' (2)	2.578 (1)	O (3) — Cd (2) — S (4)	88.4 (1)
Cd (1) — S (3)	2.535 (1)	S (1) — Cd (2) — S (3)	125.8 (1)
Cd (2) — S (1) eq	2.517 (1)	S (1) — Cd (2) — S (4)	115.1 (1)
Cd (2) — S (3) eq	2.535 (1)	S (3) — Cd (2) — S (4)	116.2 (1)
Cd (2) — S (4) eq	2.556 (1)		
Cd (2) — S' (4) ax	2.692 (1)	Cd (2) — S (1) — Cd (1)	113.6 (1)°
Cd (2) — O (3) ax	2.621 (3)	Cd (1) — S (2) — Cd' (1)	116.2 (1)
		Cd' (1) — S (3) — Cd (2)	111.3 (1)
S (1) — Cd (1) — S (2)	102.1 (1)°	Cd' (2) — S (4) — Cd (2)	87.8 (1)
S (1) — Cd (1) — S' (2)	104.3 (1)		
S (1) — Cd (1) — S (3)	122.8 (1)		
S (2) — Cd (1) — S' (2)	115.8 (1)		
S (2) — Cd (1) — S (3)	102.5 (1)	Cd (1) — S (2) — Cd' (1) — S (3)	53.6 (2)°
S' (2) — Cd (1) — S (3)	109.9 (1)	S (2) — Cd' (1) — S (3) — Cd (1)	0.3 (2)
S' (4) — Cd (2) — S (1)	100.0 (1)	Cd' (1) — S (3) — Cd (2) — S (1)	—34.0 (2)
S' (4) — Cd (2) — S (3)	94.4 (1)	S (3) — Cd (2) — S (1) — Cd (1)	13.6 (2)
S' (4) — Cd (2) — S (4)	92.2 (1)	Cd (2) — S (1) — Cd (1) — S (2)	34.9 (2)
S' (4) — Cd (2) — O (3)	168.7 (1)	S (1) — Cd (1) — S (2) — Cd' (1)	—72.3 (2)

(Cd—S_{eq}) for trigonal bipyramidal coordination is 2.54 Å (2.52 Å and 2.53 Å in [4]). The bond length Cd—S_{ax} (2.69 Å) is considerably shorter than in [4] (2.84 Å), the bond Cd—O_{ax} (2.62 Å) is longer than in [4] (2.41 Å), but the sum of the two distances is almost the same in the two complexes (5.31 Å, 5.25 Å in [4]). The factors determining these variations seem to be extremely complex and may include the 'soft' nature of B-metal cations, constraints related to ring formation and non-bonded repulsions.

A similar situation is found for the distribution of S—Cd—S bond angles, ranging from 102° to 123° for tetrahedrally coordinated Cd (100°–118° in [4]). Only the angle O_i—Cd—S_i, where O_i and S_i are connected by an ethylenic fragment, is rather constant at about 75° (75°, 77° in [4]).

The thioglycolate fragments do not show any unusual structural features, nor do they make short nonbonded contacts to other parts of the structure (Table 3). The hydrogen bonds are normal at 2.68 Å to 2.73 Å. Some aspects of the coordination of cadmium(II) ions are discussed in subsequent papers together with the structure determination of Cd₂L₃I [5] [8].

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58. Stereochemistry from X-Ray Diffraction Studies of Three Palladium(II) Complexes with Terdentate Chelating Amines

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Summary. X-ray crystal structure analysis of three Pd(II) complexes with *cis*-3,5-diaminopiperidine (DAPI) shows that the metal ion has a square planar coordination. The DAPI groups are *trans* in the protonated and mixed complexes. Most surprisingly, the unprotonated complex has a basket-like structure with the DAPI groups *cis*.

The usual coordination geometry of divalent palladium or platinum is square planar. True octahedral complexes of Pd(II) and Pt(II) are rare [1] and, as far as the authors are aware, no octahedral complexes of Pd(II) with nitrogen donors have been reported in the literature. Attempts have recently been made by *Schwarzenbach et al.* [2] to force the Pd(II) ion into an octahedral coordination by employing the terdentate ligand *cis*-3,5-diaminopiperidine (DAPI), $C_5NH_9(NH_2)_2$, in the expectation that the three nitrogens of the ligand might coordinate to form one of the faces of the octahedron. With this object in view, complexes with the protonated (HDAPI⁺) as well as with the unprotonated ligand have been prepared. The crystal structure analysis of these compounds has been undertaken to obtain the actual geometry of the complexes.

Intensity data for all the complexes were collected on a *Picker* FACS-1 automated X-ray diffractometer. They were corrected for absorption. The structures were solved by *Patterson* and *Fourier* techniques and refined by least squares [3].

1. $[Pd(HDAPI)_2](ClO_4)_4 \cdot 2H_2O$: Orthorhombic, *Pbca*, $a = 14.575$ (14), $b = 10.815$ (8), $c = 16.176$ (15) Å, $Z = 4$; 2259 reflections measured; $R = 0.046$. The molecular structure is shown in Figure 1. Pd(II), which occupies a centre of symmetry, is coordinated by nitrogens of the four primary amino groups in a square planar arrangement at distances 2.072 (5) and 2.070 (6) Å. Two ring nitrogens at a larger distance of 3.358 (7) Å complete a highly distorted octahedron. The Pd-N(3) direction makes an angle of 40° with the normal to the square plane. The two DAPI groups