275. Stereochemistry of Polynuclear Cadmium(II)thioglycolates: Crystal Structure of $[ICd_8(SCH_2CH_2OH)_{12}]^{3+} \cdot 3\,I^- \cdot H_2O$

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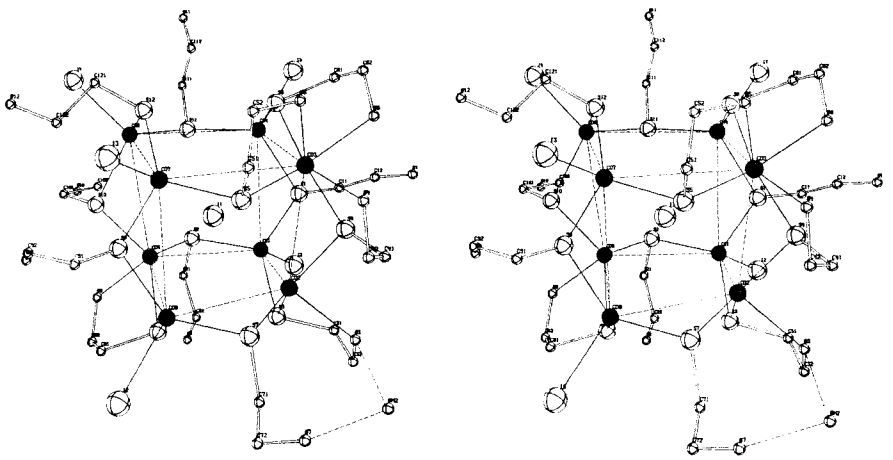
Summary. Crystals of the title compound are triclinic, $a = 27.87$ Å, $b = 10.77$ Å, $c = 12.94$ Å, $\alpha = 73.1°$, $\beta = 116.1°$, $\gamma = 120.0°$, space group $P\bar{1}$. The structure consists of octanuclear ions: Eight Cd(II) ions are found at the corners of a distorted cube, the center of the cube is occupied by an iodide, the twelve thioglycolate sulfur atoms bridge the twelve edges of the cube thereby forming a distorted icosahedron. Cadmium ions are either five or seven coordinate. The phase problem for this structure was solved using a combination of very high and very low E-values.

Polynuclear cadmium thioglycolate compounds have been investigated both in solution [1] and in the solid state [2] [3]. A decanuclear ion of composition $Cd_{10}L_{16}^{4+}$ ($L = HOCH_2CH_2S^-$) was identified by equilibrium studies [1] and its structure determined by crystallographic methods [3]. The arrangement of Cd- and S-atoms may be related to the sphalerite lattice.

An attempt to crystallize $Cd_{10}L_{16}^{4+}$ as an iodide salt led to a compound of composition Cd_2L_3I. The structure was determined from single crystal X-ray data and shows the polynuclear species $[ICd_8L_{12}]^{3+}$. $3\,I^-$ (Fig. 1). The cadmium ions form a somewhat distorted cube (average Cd ... Cd separation 4.10 Å), the thioglycolate sulfur atoms sit approximately above the centers of the twelve edges of the cube. Each sulfur



(CD2 L3 I) 4 (CD2 L3 I) 4

Fig. 1. *Stereoscopic drawing of the polynuclear species* $(ICd_8L_{12})^{3+} \cdot 5\,I^- \cdot H_2O$

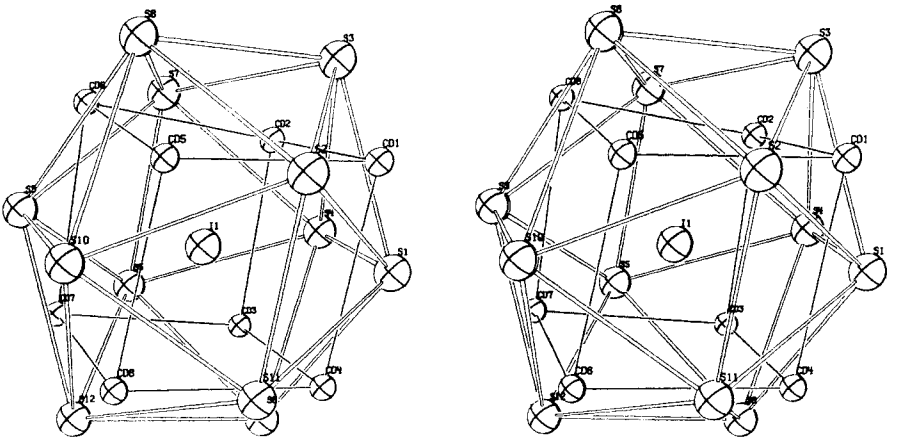
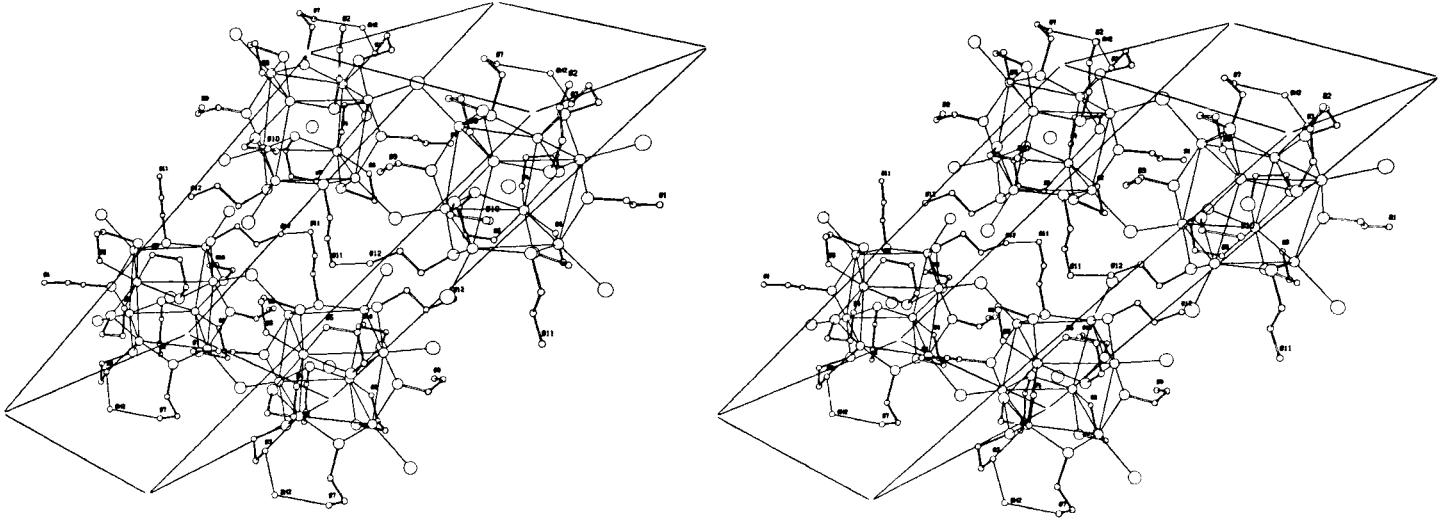


Fig. 2. *Stereoscopic drawing of the iodine centered Cd_8-cube inscribed into the S_{12}-icosahedron*

atom acts as a bridging ligand between two cadmium ions. The sulfur atoms form a distorted icosahedron (average S ... S separation 4.20 Å). The center of the cube is occupied with an iodide ion (Fig. 2). Two of the remaining three peripheral iodide ions form bridges between neighbouring polynuclear cations (Fig. 3). The central iodide may be considered to be eight coordinate with Cd–I distances ranging from 3.08 Å to 3.86 Å (average 3.53 Å). The atoms Cd (1), (4), (6), (7), (8) show distorted trigonal bipyramidal coordination with two axial iodides (d(Cd–I): 2.81 Å to 3.86 Å) and three equatorial sulfur ligands (average distance (Cd–S): 2.52 Å). The atoms Cd(2) and Cd(5) are also five coordinate with the central iodide and a thioglycolate oxygen atom as axial ligands and three sulfur atoms as equatorial ligands. The Cd(3) atom is seven coordinate, with three oxygen atoms, three sulfur atoms and the more distant central iodide (d(Cd–I): 3.863 Å) as ligands (Fig. 1). The same polynuclear arrangement of one halogen, eight metal and twelve sulfur atoms is found in the Cu(I) containing ions $[ClCu_8L'_{12}Cu_6]^n$ (n = −5, L' = $^-$S–C(CH_3)$_2$–CH(NH_2)–CO_2^- [4]; n = +7, L' = $^-$S–C(CH_3)$_2$–CH_2–NH_2 [5]). In both cases it was reported that the presence of halogenide is necessary for the formation of the polynuclear ion. This is in agreement with our observation that the polynuclear species formed in the absence of iodide are entirely different [2] [3]. However, polynuclear ions with an empty Cu(I)-cube have also been synthesized and characterized structurally [6]. It is interesting to note that in one case [4] the halogen centered polynuclear species is found in a cubic space group (F 432) with crystallographic threefold symmetry (3), in the other [5] the space group is *C2/c* with crystallographic twofold symmetry (2) of the polynuclear ion, whereas in the present case the space group is $P\bar{1}$ with no symmetry of the polynuclear ion.

Further details of the structure are reported in the experimental part. General aspects of Cd(II) coordination in this structure and in others have been discussed previously [7].



(DC2 L3 I) 4 (CD2 L3 I) 4

Fig. 3. *Stereoscopic drawing of the molecular packing.* The coordinates in Tables 1 and 2 correspond to the molecule in the upper left. The cell drawn is $-a/2 < x < a/2$ (up), $0 < y, < -b$ (front, left to right), $c/2 < z < -c/2$ (back, left to right). Bonds within the thioglycolate ligands are represented by double lines, other contacts by single lines.

Experimental Part

Preparation. Cadmium acetate (6.3 g, 22 mmol) was dissolved in 60 ml of water and thioglycol (2.6 g, 33 mmol) was added. Sodium iodide (6.0 g, 40 mmol) was dissolved in 10 ml of water. On mixing the solutions a precipitate is formed which is best recrystallized from sodium-iodide solution.

Analysis and density. Cadmium contents were determined by titration with EDTA, thioglycolate contents by titration with I_2-solution. The I_2- and EDTA-solution were calibrated relative to the same standard solution (0.1 M $CuSO_4$). The relative composition [SCH_2CH_2OH]/Cd^{II}] was found to be 1.487 ± 0.015. The percentage by weight of thioglycolate is 39.1 ± 0.3%, the one of cadmium is 38.3 ± 0.2%. Theoretical values are 39.4% and 38.3% for the monohydrate. The density determined from the difference method is 2.51 g/cm³, the calculated density for the monohydrate is 2.59 g/cm³.

Crystal data. $(Cd_2(SCH_2CH_2CH_2OH)_3I)_4 \cdot H_2O$, Mol.Wt. = 2368.5, colorless elongated prismatic crystals, triclinic, $a = 27.87$ Å, $b = 10.77$ Å, $c = 12.94$ Å, $\alpha = 73.1°$, $\beta = 116.1°$, $\gamma = 120.0°$ (determined from precession photographs), $P\bar{1}$ (C_i^2), $Z = 2$.

Intensity measurements. Linear diffractometer (Y190, Hilger and Watts), Mo$K\alpha$-radiation, measurements with β-filter only, 6633 symmetry independent reflections (sin $\theta/\lambda \leq 0.6$ Å^{-1}), linear absorption coefficient 51.31 cm^{-1}; no absorption correction. The standard reflection showed irregular fluctuations seemingly uncorrelated with time of exposure. This may account in part for the low accuracy of the analysis.

Structure analysis. The distribution of cadmium ions in the unit cell was determined by direct methods. Symbolic phases were found from Σ_2-relationships using the 150 strongest E-values. The starting set consisted of 3 origin defining reflections and six reflections with symbolic phases. Only two symbolic phases could be eliminated unequivocally. In order to eliminate more of the symbolic phases a simple procedure making use of the phasing information contained in very

Table 1. *Cadmium, sulfur and iodine coordinates and anisotropic temperature coefficients in the form:* $T = \exp[-(h^2b_{11} + \cdots + hkb_{12} + \cdots) \cdot 10^{-4}]$ (esd's in parentheses)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	0.2491 (1)	0.0127 (3)	0.0155 (4)	22 (1)	96 (5)	216 (6)	23 (3)	87 (4)	– 69 (8)
I(2)	0.4120 (2)	– 0.2998 (4)	0.0857 (5)	22 (1)	121 (5)	272 (8)	26 (4)	88 (5)	– 115 (10)
I(3)	0.0960 (2)	0.3413 (4)	– 0.0624 (4)	24 (1)	106 (5)	241 (7)	28 (4)	89 (5)	– 76 (9)
I(4)	0.1164 (2)	– 0.3022 (5)	0.3986 (5)	37 (2)	161 (6)	241 (8)	33 (5)	128 (6)	– 46 (11)
Cd(1)	0.3463 (2)	– 0.1481 (4)	0.0565 (5)	23 (1)	118 (6)	208 (8)	29 (5)	77 (5)	– 55 (10)
Cd(2)	0.3151 (2)	0.1532 (4)	– 0.1642 (4)	21 (1)	122 (6)	212 (8)	28 (4)	77 (5)	– 60 (10)
Cd(3)	0.1353 (2)	– 0.0249 (4)	– 0.2965 (5)	23 (1)	112 (6)	228 (8)	14 (4)	93 (5)	– 93 (10)
Cd(4)	0.1598 (2)	– 0.3520 (4)	– 0.0306 (5)	21 (1)	128 (6)	225 (8)	32 (4)	83 (5)	– 74 (10)
Cd(5)	0.3453 (2)	0.0620 (4)	0.2583 (4)	24 (1)	125 (6)	221 (8)	34 (4)	79 (5)	– 69 (10)
Cd(6)	0.3424 (2)	0.3983 (4)	0.0474 (5)	23 (1)	135 (6)	218 (8)	41 (4)	84 (5)	– 50 (10)
Cd(7)	0.1588 (2)	0.1717 (4)	– 0.0223 (5)	22 (1)	123 (6)	192 (7)	22 (4)	78 (5)	– 55 (10)
Cd(8)	0.1701 (2)	– 0.1619 (4)	0.2316 (5)	24 (1)	110 (6)	215 (8)	31 (4)	85 (5)	– 68 (10)
S(1)	0.2465 (6)	– 0.2640 (15)	– 0.0907 (15)	19 (3)	142 (19)	197 (24)	25 (12)	77 (14)	– 96 (33)
S(2)	0.3568 (6)	– 0.1600 (13)	0.2614 (15)	25 (4)	91 (16)	180 (23)	29 (12)	67 (14)	– 107 (30)
S(3)	0.4007 (6)	0.0969 (14)	– 0.0328 (16)	23 (3)	108 (18)	196 (24)	27 (12)	69 (15)	– 57 (32)
S(4)	0.2271 (6)	0.0026 (14)	– 0.3177 (16)	22 (3)	105 (18)	219 (25)	11 (12)	94 (15)	– 68 (32)
S(5)	0.1580 (6)	0.2001 (13)	– 0.2231 (16)	28 (4)	88 (16)	213 (25)	23 (12)	106 (16)	– 65 (30)
S(6)	0.0877 (6)	– 0.2577 (15)	– 0.1820 (16)	17 (3)	132 (21)	213 (26)	34 (13)	69 (15)	– 17 (35)
S(7)	0.3349 (6)	0.4092 (13)	– 0.1573 (15)	26 (4)	92 (17)	187 (23)	26 (12)	81 (15)	– 32 (30)
S(8)	0.4158 (6)	0.3024 (14)	0.1949 (16)	21 (4)	115 (19)	236 (26)	30 (12)	82 (15)	– 77 (34)
S(9)	0.2601 (6)	0.3073 (15)	0.1179 (16)	25 (4)	123 (20)	222 (25)	18 (13)	98 (16)	– 135 (35)
S(10)	0.2717 (6)	0.0221 (14)	0.3411 (16)	24 (4)	116 (17)	209 (24)	41 (12)	83 (15)	– 69 (31)
S(11)	0.1829 (6)	– 0.3533 (14)	0.1821 (15)	26 (4)	107 (17)	168 (23)	27 (12)	74 (15)	– 59 (30)
S(12)	0.0998 (6)	– 0.0631 (14)	0.0658 (16)	17 (3)	111 (18)	205 (24)	15 (11)	64 (14)	– 88 (32)

Table 2. *Coordinates of oxygen and carbon atoms and isotropic temperature coefficient* (csd's · 10^{-1} in parentheses)

Atom	x/a	y/b	z/c	B_{iso}
O(1)	0.2147 (4)	−0.4630 (9)	−0.3404 (7)	19 (3)
O(2)	0.5362 (2)	0.0241 (6)	0.3763 (5)	9 (2)
O(3)	0.3720 (2)	0.2040 (6)	−0.2870 (4)	7 (2)
O(4)	0.1373 (2)	0.1369 (6)	−0.4777 (4)	7 (2)
O(5)	0.0309 (3)	−0.0038 (7)	−0.3878 (5)	10 (2)
O(6)	0.0693 (3)	−0.1864 (7)	−0.4503 (5)	10 (2)
O(7)	0.4097 (3)	0.6508 (7)	−0.3034 (5)	9 (2)
O(8)	0.4267 (2)	0.1659 (5)	0.4417 (4)	6 (2)
O(9)	0.3093 (3)	0.3527 (8)	0.3838 (6)	14 (3)
O(10)	0.3277 (3)	−0.2381 (8)	−0.6058 (6)	15 (3)
O(11)	0.0370 (3)	−0.7103 (7)	0.2083 (5)	10 (2)
O(12)	0.0903 (2)	0.1219 (6)	0.2842 (5)	8 (2)
OH_2	0.3947 (3)	0.4523 (7)	−0.4220 (6)	12 (3)
C(11)	0.2495 (4)	−0.3835 (11)	−0.1496 (9)	12 (4)
C(21)	0.4361 (4)	−0.1281 (9)	0.3541 (7)	7 (3)
C(31)	0.4147 (5)	0.0627 (12)	−0.1512 (9)	12 (4)
C(41)	0.2296 (5)	0.1180 (12)	−0.4417 (9)	12 (4)
C(51)	0.0946 (3)	0.2364 (8)	−0.3150 (6)	5 (3)
C(61)	0.0536 (4)	−0.3963 (11)	−0.3012 (9)	11 (–)
C(71)	0.4239 (4)	0.5092 (9)	−0.1349 (7)	8 (3)
C(81)	0.4500 (5)	0.4030 (13)	0.3295 (10)	14 (4)
C(91)	0.2619 (4)	0.4419 (10)	0.1524 (8)	9 (3)
C(101)	0.2922 (4)	−0.0743 (11)	0.5109 (9)	11 (4)
C(111)	0.1348 (3)	−0.5322 (9)	0.2303 (7)	7 (3)
C(121)	0.0637 (4)	−0.0405 (10)	0.1352 (7)	8 (3)
C(12)	0.2181 (4)	−0.3934 (10)	−0.2635 (8)	10 (3)
C(22)	0.4790 (3)	0.0111 (8)	0.2965 (6)	6 (3)
C(32)	0.4260 (3)	0.1880 (9)	−0.2312 (7)	6 (3)
C(42)	0.2023 (3)	0.2357 (9)	−0.4669 (7)	6 (3)
C(52)	0.0383 (4)	0.1020 (10)	−0.3230 (7)	8 (3)
C(62)	0.0260 (4)	−0.3391 (11)	−0.4112 (9)	11 (3)
C(72)	0.4380 (3)	0.6617 (8)	−0.1796 (6)	5 (3)
C(82)	0.4788 (4)	0.3039 (10)	0.4420 (8)	9 (3)
C(92)	0.2733 (5)	0.4095 (13)	0.2988 (10)	15 (4)
C(102)	0.3001 (4)	−0.2125 (10)	0.4973 (8)	10 (3)
C(112)	0.0674 (4)	−0.5610 (10)	0.1470 (8)	10 (3)
C(122)	0.1169 (3)	0.0812 (8)	0.2265 (6)	5 (3)

weak reflections was applied. About 150 small E-values were selected according to the criterion $E \leq 0.5 - 5^{*}\sigma(E)$. All Σ_2-relationships involving one weak and two strong E's were determined.

The contributors to a given weak reflexion were ordered according to their symbolic phase. In most cases there were only two groups of symbolic phases, a and b, say.

It was assumed that $a+b = \pi$ in order to make the sum on the right hand side of *Sayre*'s equation small:

$$E_{\mathbf{h}}\,(\text{small}) = K \sum_{\mathbf{k}} E_{\mathbf{k}}\,(\text{large}) \cdot E_{\mathbf{h}-\mathbf{k}}\,(\text{large})$$

$$= K\,(\mathrm{a} \sum_{\mathbf{k}'} |E_{\mathbf{k}} \cdot E_{\mathbf{h}-\mathbf{k}}| + \mathrm{b} \sum_{\mathbf{k}''} |E_{\mathbf{k}} \cdot E_{\mathbf{h}-\mathbf{k}}|)$$

The fact that $a+b = \pi$ is related to the so called negative quartet relation [8] which has been derived by *Hauptmann* [9] in a more general form. This procedure eliminated another three symbolic phases, leaving only one.

Table 3. *Internuclear distances associated with cadmium atoms* (esd's in parentheses)

Cd(1)—I(1)	3.675 (2) Å	Cd(4)—I(1)	3.501 (6) Å	Cd(7)—I(1)	3.499 (3) Å
—I(2)	2.861 (3)	—I(3)	2.918 (6)	—I(3)	2.920 (3)
—S(1)	2.48 (2)	—S(1)	2.51 (1)	—S(5)	2.52 (2)
—S(2)	2.51 (2)	—S(6)	2.52 (2)	—S(9)	2.51 (2)
—S(3)	2.52 (2)	—S(11)	2.53 (2)	—S(12)	2.49 (2)
Cd(2)—I(1)	3.165 (5)	Cd(5)—I(1)	3.078 (7)	Cd(8)—I(1)	3.797 (5)
—O(3)	2.49 (3)	—O(8)	2.51 (5)	—I(4)	2.807 (6)
—S(3)	2.50 (2)	—S(2)	2.55 (2)	—S(10)	2.54 (2)
—S(4)	2.49 (2)	—S(8)	2.52 (2)	—S(11)	2.55 (2)
—S(7)	2.55 (2)	—S(10)	2.52 (1)	—S(12)	2.58 (2)
Cd(3)—I(1)	3.863 (7)	Cd(6)—I(1)	3.665 (6)		
—S(4)	2.551 (2)	—I(2)	2.893 (6)		
—S(5)	2.54 (2)	—S(7)	2.54 (2)		
—S(6)	2.55 (2)	—S(8)	2.54 (2)		
—O(4)	2.49 (5)	—S(9)	2.47 (1)		
—O(5)	2.72 (3)				
—O(6)	2.44 (7)				

Two *E-Fourier*-syntheses were now calculated, both of them showing the same pattern of peaks. In one of them the cube of Cd-atoms is centered around the crystallographic center of symmetry at (0,0,0), in the other around a pseudocenter of symmetry at (0,1/4,0). The latter solution led to the structure described here.

A Cd-phased *Fourier*-synthesis showed all iodine and sulfur position. After anisotropic, block diagonal least-squares refinement of the cadmium-, iodine- and sulfur atoms, carbon- and oxygen atoms of the thioglycolate molecules and of a water molecule could be located in chemically reasonable positions from a difference-*Fourier*-synthesis.

The C- and O-atoms were refined isotropically using 1766 F_o's $\geq 5\sigma(F_o)$ with $\sin\theta/\lambda \leq 0.35$ Å^{-1} [10] and applying unit weight. Since C(31) and C(32) were not resolved in the difference-*Fourier*-synthesis, their isotropic temperature factors were constrained to be equal. R ($\sin\theta/\lambda \leq 0.35$) = 0.094. For 143 out of the 148 light atom parameters the shifts in the last cycle of refinement were smaller than their estimated standard deviations (esd), for the remaining 5 parameters the shifts were between 1 and 2 esd's.

Positional and thermal parameters for I-, Cd- and S-atoms were further adjusted by two cycles of least-squares-refinement using 4468 F_o's $\geq 5\sigma(F_o)$ with $\sin\theta/\lambda \leq 0.6$ Å^{-1} and applying unit weight. R ($\sin\theta/\lambda \leq 0.6$) = 0.12. The final difference-*Fourier*-synthesis showed densities of 1.5 – 3 e/Å^3 in the neighbourhood of I-, Cd- and S-atoms and smaller densities elsewhere.

Results. – Positional and thermal parameters of the Cd, I and S atoms are given in Table 1, those of C and O in Table 2. Internuclear distances and angles associated with Cd, I and S atoms are given in Tables 3 and 4, those associated with the ligand in Table 5.

The average bond lengths and angles of the thioglycolate ligand as determined from the crystal structure of CdL_2 [3] are C(C–S) = 1.850 (5) Å, C(C–C) = 1.50 (1) Å, C(C–O) = 1.43 (1) Å and α(SCC) = 111.0 (4)°, α(CCO) = 111.0 (5)°. Since in the present determination the deviations from the above values are substantial, they were investigated by means of a normal probability plot (for the 36 distance observations). It was found that the distances in Table 5 are systematically too long by about a half a standard deviation and their esd's are underestimated by about a third of the value given [11]. The hydrogen bonds within and between polynuclear ions are given in Table 6 and shown in Fig. 3 as dotted lines.

Table 4. *Angles associated with cadmium, iodine and sulfur atoms* (esd's in parentheses)

S(1)	Cd(1)	S(2)	120 (1)°	O(8)	Cd(5)	S(10)	88 (1)°
S(1)	Cd(1)	S(3)	107 (1)	I(1)	Cd(5)	S(2)	91 (1)
S(2)	Cd(1)	S(3)	116 (1)	I(1)	Cd(5)	S(8)	94 (1)
I(2)	Cd(1)	S(1)	108 (1)	I(1)	Cd(5)	S(10)	91 (1)
I(2)	Cd(1)	S(2)	101 (1)	I(1)	Cd(5)	O(8)	166 (2)
I(2)	Cd(1)	S(3)	103 (1)				
I(1)	Cd(1)	S(1)	68 (1)	S(7)	Cd(6)	S(8)	112 (1)
I(1)	Cd(1)	S(2)	79 (1)	S(7)	Cd(6)	S(9)	128 (1)
I(1)	Cd(1)	S(3)	82 (1)	S(8)	Cd(6)	S(9)	107 (1)
I(1)	Cd(1)	I(2)	174 (1)	I(2′)	Cd(6)	S(7)	100 (1)
				I(2′)	Cd(6)	S(8)	99 (1)
S(3)	Cd(2)	S(4)	125 (1)	I(2′)	Cd(6)	S(9)	107 (1)
S(3)	Cd(2)	S(7)	113 (1)	I(1)	Cd(6)	S(7)	84 (1)
S(4)	Cd(2)	S(7)	121 (1)	I(1)	Cd(6)	S(8)	81 (1)
O(3)	Cd(2)	S(3)	75 (1)	I(1)	Cd(6)	S(9)	69 (1)
O(3)	Cd(2)	S(4)	86 (1)	I(1)	Cd(6)	I(2′)	175 (1)
O(3)	Cd(2)	S(7)	99 (1)				
I(1)	Cd(2)	S(3)	94 (1)	S(5)	Cd(7)	S(9)	113 (1)
I(1)	Cd(2)	S(4)	92 (1)	S(5)	Cd(7)	S(12)	122 (1)
I(1)	Cd(2)	S(7)	95 (1)	S(9)	Cd(7)	S(12)	113 (1)
I(1)	Cd(2)	O(3)	164 (2)	I(3)	Cd(7)	S(5)	99 (1)
				I(3)	Cd(7)	S(9)	104 (1)
S(4)	Cd(3)	S(5)	110 (1)	I(3)	Cd(7)	S(12)	102 (1)
S(4)	Cd(3)	S(6)	114 (1)	I(1)	Cd(7)	S(5)	77 (1)
S(5)	Cd(3)	S(6)	114 (1)	I(1)	Cd(7)	S(9)	72 (1)
O(4)	Cd(3)	S(4)	78 (1)	I(1)	Cd(7)	S(12)	85 (1)
O(4)	Cd(3)	S(5)	82 (1)	I(1)	Cd(7)	I(3)	172 (1)
O(4)	Cd(3)	S(6)	153 (1)				
O(5)	Cd(3)	S(4)	151 (1)	S(10)	Cd(8)	S(11)	109 (1)
O(5)	Cd(3)	S(5)	75 (1)	S(10)	Cd(8)	S(12)	117 (1)
O(5)	Cd(3)	S(6)	88 (1)	S(11)	Cd(8)	S(12)	116 (1)
O(6)	Cd(3)	S(4)	92 (2)	I(4)	Cd(8)	S(10)	104 (1)
O(6)	Cd(3)	S(5)	144 (2)	I(4)	Cd(8)	S(11)	105 (1)
O(6)	Cd(3)	S(6)	80 (2)	I(4)	Cd(8)	S(12)	106 (1)
O(4)	Cd(3)	O(5)	74 (2)	I(1)	Cd(8)	S(10)	75 (1)
O(4)	Cd(3)	O(6)	76 (2)	I(1)	Cd(8)	S(11)	72 (1)
O(5)	Cd(3)	O(6)	73 (2)	I(1)	Cd(8)	S(12)	78 (1)
I(1)	Cd(3)	S(4)	77 (1)	I(1)	Cd(9)	I(4)	176 (1)
I(1)	Cd(3)	S(5)	70 (1)				
I(1)	Cd(3)	S(6)	75 (1)	Cd(1)	I(2)	Cd(6′)	116 (1)
				Cd(4)	I(3′)	Cd(7′)	121 (1)
S(1)	Cd(4)	S(6)	109 (1)				
S(1)	Cd(4)	S(11)	116 (1)	Cd(1)	S(1)	Cd(4)	116 (1)
S(6)	Cd(4)	S(11)	120 (1)	Cd(1)	S(2)	Cd(5)	102 (1)
I(3′)	Cd(4)	S(1)	104 (1)	Cd(1)	S(3)	Cd(2)	100 (1)
I(3′)	Cd(4)	S(6)	102 (1)	Cd(2)	S(4)	Cd(3)	107 (1)
I(3′)	Cd(4)	S(11)	102 (1)	Cd(3)	S(5)	Cd(7)	116 (1)
I(1)	Cd(4)	S(1)	71 (1)	Cd(3)	S(6)	Cd(4)	114 (1)
I(1)	Cd(4)	S(6)	83 (1)	Cd(2)	S(7)	Cd(6)	101 (1)
I(1)	Cd(4)	S(11)	78 (1)	Cd(5)	S(8)	Cd(6)	100 (1)
I(1)	Cd(4)	I(3′)	174 (1)	Cd(6)	S(9)	Cd(7)	115 (1)
				Cd(5)	S(10)	Cd(8)	109 (1)
S(2)	Cd(5)	S(8)	118 (1)	Cd(4)	S(11)	Cd(8)	115 (1)
S(2)	Cd(5)	S(10)	116 (1)	Cd(7)	S(12)	Cd(8)	110 (1)
S(8)	Cd(5)	S(10)	126 (1)				
O(8)	Cd(5)	S(2)	102 (1)				
O(8)	Cd(5)	S(8)	75 (1)				

Table 5. *Bond lengths and bond angles associated with ligand molecules.* The angle α_1(C—S—Cd) is to the cadmium atom with the smaller index, α_2(C—S—Cd) is the one to the cadmium atom with the larger index (esd's in parentheses)

	1	2	3	4	5	6
(C—S)	1.73 (9) Å	1.89 (5) Å	1.91 (8) Å	1.73 (11) Å	1.80 (5) Å	2.03 (10) Å
(C—C)	1.34 (13)	1.60 (11)	1.43 (14)	1.67 (10)	1.50 (11)	1.41 (13)
(C—O)	1.36 (11)	1.43 (6)	1.43 (4)	1.54 (6)	1.49 (10)	1.58 (12)
α(S—C—C)	115 (8)°	108 (6)°	109 (8)°	115 (7)°	111 (6)°	109 (8)°
α(C—C—O)	131 (10)	102 (6)	106 (7)	103 (7)	111 (7)	113 (9)
α_1(C—S—Cd)	106 (4)	107 (3)	106 (4)	103 (4)	103 (3)	98 (3)
α_2(C—S—Cd)	118 (4)	108 (3)	96 (4)	103 (4)	104 (3)	97 (3)
ω(S—C—C—O)	172	178	−66	−61	−69	58
	7	8	9	10	11	12
(C—S)	2.07 (5) Å	1.93 (12) Å	1.61 (9) Å	2.10 (10) Å	1.83 (8) Å	1.75 (4) Å
(C—C)	1.48 (12)	1.68 (14)	1.73 (14)	1.68 (12)	1.62 (8)	1.65 (12)
(C—O)	1.45 (9)	1.47 (10)	1.36 (11)	1.29 (11)	1.55 (12)	1.52 (5)
α(S—C—C)	106 (8)°	106 (7)°	106 (7)°	102 (6)°	106 (6)°	104 (6)°
α(C—C—O)	101 (7)	103 (8)	128 (10)	97 (8)	96 (7)	110 (6)
α_1(C—S—Cd)	98 (3)	100 (4)	108 (4)	110 (3)	108 (3)	111 (3)
α_2(C—S—Cd)	100 (3)	105 (4)	109 (4)	104 (3)	110 (3)	103 (3)
ω(S—C—C—O)	−73	−60	40	163	−177	174

Table 6. *Length of the hydrogen bonds* (The position of the first oxygen atom is at [x, y, z], the position of the second oxygen atom is given in the last column of the table)

O(2)	... O(8)	2.83	$[1-x, \bar{y}, 1-z]$
O(3)	... OH_2	2.68	[x, y, z]
O(4)	... O(12)	2.79	[x, y, z−1]
O(5)	... O(5)	2.65	$[\bar{x}, \bar{y}, -1-z]$
O(7)	... O(10)	2.76	[x, 1+y, z−1]
O(7)	... OH_2	2.75	[x, y, z]
O(9)	... OH_2	2.63	[x, y, 1+z]
O(11)	... O(12)	2.61	[x, y−1, z]

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