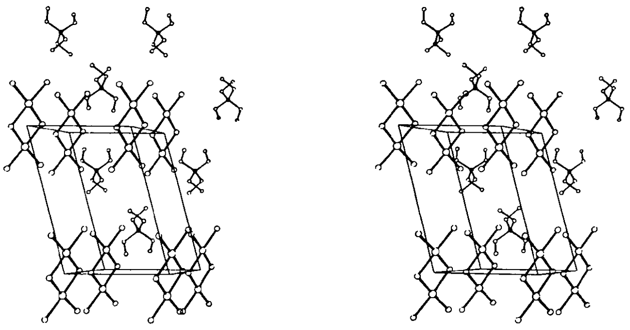

Fig. 2. Stereoscopic drawing of the unit-cell contents viewed approximately along **a**.

determinations are due largely to changes in positional parameters but are, in part, due to a small difference in cell parameters. It may be that the lack of an absorption correction has introduced a systematic error into the derived coordinates of the earlier refinement (see, for example, Mais, Owston & Wood, 1972). Our results confirm that there are slight deviations from planarity in the anion, with Br(1) and Br(2) 0·13 and −0·03 Å respectively from the plane defined by the Pt and bridging Br atoms. The angles at Pt and Br appear to be controlled primarily by the non-bonded contacts marked on Fig. 1. Thus the Br(1)···Br(2), Br(1)···Br(3) and Br(2)···Br(3′) contacts are approximately equal and the Pt···Pt′ and Br(3)···Br(3′) contacts are in proportion to their respective van der Waals diameters (Pauling, 1960). The revised geometry of the anion is now consistent with other halogen-bridged species. The conformation of the cation is controlled by eight C(α)···C(β) contacts with a mean value of 3·03 (1) Å. The remaining four C(α)···C(β) contacts have a mean value of 3·82 (1) Å. The lengths and angles in the cation are unexceptional and have been deposited with the structure factors. The packing is illustrated in Fig. 2. There are no interionic contacts shorter than 2·77 Å; a list of shorter contacts has been deposited with the structure factor table.

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Cadmium(II) Thiodiacetate Hydrate

BY S. H. WHITLOW

Inland Waters Directorate, Department of the Environment, Ottawa, Canada

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Abstract. $C_4H_6O_5SCd$, monoclinic, $P2_1$, $a=8{\cdot}009$ (1), $b=5{\cdot}352$ (1), $c=9{\cdot}143$ (2) Å, $\beta=116{\cdot}03$ (1), (20°C), $Z=2$, $D_x=1{\cdot}31$ g cm^{-3}. The complex is tridentate, cadmium being bonded to sulphur as well as to oxygen atoms at both ends of the thiodiacetate ligand. Additional bonds to a water molecule and to two adjacent ligands complete a distorted octahedral arrangement about cadmium. The Cd–S bond length is 2·663 (2) Å and Cd–O distances are in the range 2·258 (5) to 2·287 (6) Å.

Introduction. Cadmium thiodiacetate, prepared from a stoichiometric mixture of $Cd(NO_3)_2$ and thiodiacetic acid in aqueous solution, crystallizes as pale-yellow prisms with the (100) face prominent. After preliminary X-ray photographs, a crystal measuring 0·20 × 0·12 × 0·25 mm was selected for intensity measurements. It was mounted in a random orientation on an automated Picker diffractometer. Accurate unit-cell parameters were derived by a least-squares method from the positions of 38 high-angle reflexions (monochromatized Mo $K\alpha_1$ radiation, $\lambda=0{\cdot}70926$ Å) with a 1·5° take-off angle. $0k0$ reflexions with k odd were systematically absent and the non-centrosymmetric space group $P2_1$ was indicated by reflexion statistics. Intensity data were collected by θ–2θ scans for all hkl and $\bar{h}kl$ reflexions with $2\theta \leq 60°$. Scans of $(1{\cdot}9+0{\cdot}60 \tan\theta)°$ were measured at 2° min^{-1} with 60s backgrounds. Of 1139 observations, 1124 with $I > 1{\cdot}65\sigma$ (σ based on counting statistics) were used in the analysis. The intensities of three standard reflexions monitored during data collection varied < 5 % during the course of the measurements. Lorentz and polarization factors were applied to the data but no corrections for absorption were made. Absorption effects are estimated to introduce errors of <4% in the structure factors ($\mu = 32{\cdot}7$ cm^{-1}).

The structure was solved by the X-RAY system of computer programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Coordinates for Cd and S were determined from a sharpened Patterson synthesis and the remaining atoms were differentiated from peaks of false symmetry by repeated Fourier summations. For least-squares refinement, the function $\sum w(\Delta F^2)$ was minimized with the weights taken as the inverse variances. After full-matrix refinement using isotropic thermal parameters R was 0·045. Hydrogen atoms attached to carbon were located on an electron-density difference synthesis but positions for those of the H_2O molecule were not determined. The four hydrogen atoms were included with constant contributions at optimized distances (C–H 1·0 Å) and $B = 4{\cdot}0$ Å^2. Further refinement including anisotropic thermal parameters and an empirical extinction parameter ($g = 1{\cdot}82 \times 10^{-3}$) (Larson, 1967) gave $R = 0{\cdot}032$, $R_w = 0{\cdot}034$. At convergence the average shift to error ratio was 0·15. The final Fourier difference synthesis showed slight residual electron density near the Cd site (± 2 e Å^{-3}), other fluctuations being $<0{\cdot}5$ e Å^{-3}. Final positional and thermal parameters are given in Table 1.*

Discussion. Cadmium poisoning from polluted water raises the question of cadmium transport both in water (Fleischer, Sarofim, Fassett, Hammond, Shacklette, Nisbet & Epstein, 1974) and within the human body (Friberg, Piscator, Nordberg & Kjellftrom, 1974). Chemical interaction between cadmium and biological molecules will be *via* O, N or S atoms, and Cd may well be tightly bound by chelating groups. Complexes of cadmium with model carboxylic acids have demonstrated different types of chelation; cadmium maleate (Post & Trotter, 1974) through two oxygen atoms of a carboxyl group, bis(thiocarbohydrazide-*N*,*S*)-cadmium dichloride (Bigoli, Braibanti, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1971) through nitrogen and sulphur, and cadmium oxydiacetate (Bo-

Table 2. *Bond distances* (Å) *and angles* (°)

Superscripts refer to atoms at

(i) $1-x, \frac{1}{2}+y, -z$; (ii) $1-x, \frac{1}{2}+y, 1-z$.

Cd—S	2·663 (2)	O(W)–Cd—O(1)	91·9 (2)
–O(1)	2·276 (6)	–O($2^{\rm i}$)	89·4 (2)
–O(3)	2·277 (5)	–O(3)	89·8 (2)
–O($2^{\rm i}$)	2·279 (5)	–O($4^{\rm ii}$)	94·8 (2)
–O($4^{\rm ii}$)	2·287 (6)	O(1)—Cd—O($2^{\rm i}$)	93·5 (2)
–O(W)	2·258 (5)	–O(3)	88·2 (2)
S——C(1)	1·776 (9)	–O($4^{\rm ii}$)	172·7 (2)
–C(3)	1·776 (7)	O($2^{\rm i}$) –Cd—O(3)	178·1 (2)
C(1)–C(2)	1·532 (10)	–O($4^{\rm ii}$)	83·8 (2)
C(2)–O(1)	1·248 (9)	O(3)—Cd—O($4^{\rm ii}$)	94·6 (2)
–O(2)	1·257 (10)	C(1)—S——C(3)	103·1 (4)
C(3)–C(4)	1·545 (11)	S———C(1)–C(2)	119·6 (6)
C(4)–O(3)	1·234 (7)	C(1)—C(2)–O(1)	121·8 (7)
–O(4)	1·251 (8)	–O(2)	113·9 (6)
S–Cd—O(1)	77·5 (1)	O(1)—C(2)–O(2)	124·3 (6)
–O($2^{\rm i}$)	103·4 (1)	S———C(3)–C(4)	119·7 (4)
–O(3)	77·7 (1)	C(3)—C(4)–O(3)	121·5 (6)
–O($4^{\rm ii}$)	96·5 (1)	–O(4)	111·9 (5)
–O(W)	163·7 (1)	O(3)—C(4)–O(4)	126·6 (8)

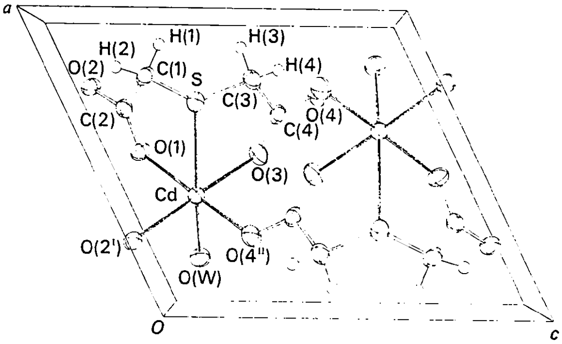

Fig. 1. A perspective view of the structure along *b* showing labelling.

Table 1. *Fractional atomic coordinates* (× 10^4) *and thermal parameters* (× 10^3)

The temperature factor is of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{13}hla^*c^* \cos\beta^* \ldots)]$.
Estimated standard deviations are in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	3824 (1)	0	2007 (1)	20·7 (2)	23·0 (2)	20·5 (2)	1·5 (3)	9·6 (1)	0·5 (3)
S	7167 (2)	2136 (3)	3309 (2)	28·1 (8)	19·9 (8)	23·8 (7)	−3·2 (6)	13·7 (6)	−2·5 (6)
C(1)	8107 (9)	431 (17)	2178 (8)	25 (3)	40 (6)	29 (3)	−9 (3)	18 (2)	−11 (3)
C(2)	6972 (9)	−1683 (13)	1049 (8)	25 (3)	24 (3)	20 (3)	3 (3)	10 (3)	−1 (3)
C(3)	8030 (9)	503 (15)	5189 (8)	29 (3)	39 (6)	20 (3)	−12 (3)	8 (2)	2 (3)
C(4)	6827 (9)	−1538 (14)	5456 (8)	26 (3)	28 (3)	24 (3)	3 (3)	16 (3)	5 (3)
O(1)	5391 (6)	−2247 (10)	893 (6)	24 (2)	28 (3)	34 (3)	−3 (2)	16 (2)	−8 (2)
O(2)	7774 (6)	−2740 (11)	305 (6)	23 (2)	49 (3)	30 (2)	−6 (2)	14 (2)	−17 (3)
O(3)	5346 (7)	−2232 (10)	4341 (6)	35 (2)	24 (3)	24 (2)	−6 (2)	10 (2)	5 (2)
O(4)	7537 (7)	−2315 (12)	6892 (6)	31 (2)	44 (3)	24 (2)	−4 (2)	9 (2)	11 (2)
O(W)	1480 (7)	−2803 (10)	1158 (6)	28 (2)	27 (3)	32 (3)	−1 (2)	14 (2)	2 (2)
H(1)	9300	−320	3000						
H(2)	8390	1680	1510						
H(3)	9220	−350	5310						
H(4)	8340	1780	6060						

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31158 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

man, 1974) tridentate chelation through two carboxyl groups and the ether oxygen atom. The present structure demonstrates tridentate chelation of cadmium involving for the first time bonds to oxygen and sulphur.

A view of the structure looking down the *b* axis is shown in Fig. 1; bond distances and angles are supplied in Table 2. The complex is tridentate with cadmium held by bonds to sulphur and oxygen atoms at either end of the thiodiacetate ligand. Additional contacts to two adjacent ligands and a water molecule complete a distorted octahedral coordination about cadmium. The Cd–O(carboxyl) bond lengths, 2·276 (6) to 2·287 (6) Å, are similar although the Cd–O(*W*) bond, 2·258 (5) Å, is significantly shorter. The relative freedom of the water molecule to move, and its position *trans* to the long Cd–S bond account for this shortening. None of the respective C–C or C–O bond lengths are significantly different from each other. This fact, together with the similar Cd–O bond lengths and the approximate mirror plane passing through sulphur stress the symmetrical nature of the complex.

Since each oxygen atom is bonded to only one Cd atom there are no Cd–O–Cd bridges as found in cadmium diacetate dihydrate (Harrison & Trotter, 1972). Continuity throughout the lattice is achieved as each thiodiacetate complex bonds to two adjacent Cd atoms related by twofold screw axes (Fig. 1). Limited hydrogen bonding provides further cohesion with an O(*W*)$\cdots$O(2) (at $x-1,y,z$) distance of 2·718 (7) Å and a contact of 2·898 (8) Å between O(*W*) and O(4) (at $1-x,y-\frac{1}{2},1-z$). The O(2)O(*W*)O(4) angle is 98·9 (2)°.

The conformation of the thiodiacetate ligand has changed considerably to facilitate chelation of the Cd atom. In thiodiacetic acid (Paul, 1967) the CCSCC backbone is nearly planar and the C–C bonds each form an angle of only 4·1° with the central CSC plane. In cadmium thiodiacetate the carboxyl groups still extend on the same side of the CSC plane, but now the C–C bonds make angles of 60·3 and 59·8° with the CSC plane. The present symmetrical conformation is very similar to that found for copper oxydiacetate (Whitlow & Davey, 1975). In simple chelates of this type the ligand is therefore able to assume a conformation which enhances chelation of the metal ion and may facilitate ion transport.

The biochemical behaviour of cadmium is conveniently considered in terms of the hard and soft acids and bases formalism (Ahrland, 1966). In this approach cadmium is generally considered a soft acid and as such will form strong covalent bonds with soft bases (*e.g.* RSH, RS$^-$, CN$^-$). The accumulation of Cd in the liver by the protein metallothionein, rich in cysteine, is a result of soft acid, soft base interactions (Friberg, Piscator, Nordberg & Kjellftrom, 1974). However, certain biological observations suggest that the behaviour of cadmium may be more complicated: the dietary uptake of Cd is inversely proportional to the concentration of calcium (a hard acid) and zinc (a borderline acid,) furthermore zinc opposed cadmium in the body, an excess of zinc reducing the toxicity of cadmium (Friberg, Piscator, Nordberg & Kjellftrom, 1974). These effects suggest that cadmium may well exhibit borderline behaviour as it competes *in vivo* with calcium and zinc for specific coordination sites. The present study of cadmium thiodiacetate demonstrates cadmium behaving as a borderline acid in a mixed-donor environment of S and O atoms (soft and hard bases, respectively). This ability of Cd to behave as a borderline acid may help to explain the antagonism between cadmium and zinc in biological systems.

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