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Xanthate and Dithiocarbamate Complexes of Group II*b* Elements, and an Interesting Relationship Between Two Mercury(II) Ethylxanthate* Phases

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Abstract

Crystals of mercury(II) ethylxanthate, [Hg(C$_2$H$_5$OS$_2$)$_2$], obtained from acetone are monoclinic with $a = 9.300$ (2), $b = 6.693$ (2), $c = 19.585$ (9) Å, $\beta = 100.94$ (3)°, space group $P2_1/c$, $Z = 4$. The structure was determined by the heavy-atom method from 2111 diffractometer-measured reflections. The crystal consists of mica-like two-dimensional sheets formed by mutual bridging of Hg^{II} and ethylxanthate ions. The Hg^{II} ion is bonded to four S atoms with Hg–S distances of 2.417 (4), 2.421 (4), 2.789 (4) and 2.854 (4) Å. The coordination geometry is a very distorted tetrahedron with a large and a small S–Hg–S angle of 147.7 (1) and 84.3 (1)°, respectively. The sheets are stacked parallel to the (001) plane; alternate layers are related by a center of symmetry. In contrast, the same compound crystallized from CCl$_4$ belongs to $P2_1$. The structures within the layers are the same but the packing arrangements of the sheets are different in the two crystals.

Introduction

Both dithiocarbamates and xanthates are useful industrial chemicals with a common functional group

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* IUPAC name: mercury bis(*O*-ethyl dithiocarbonate).

–C(=S)S$^-$ (Rao, 1971). In 1978, Japan granted a patent for using an aqueous solution containing 0.01–0.25% xanthate and sodium tellurate to remove mercury from industrial waste gas at 313 K. These S-containing materials offer great potential for the industrial-waste treatment required in environmental protection.

We have reported several crystal structures of Hg^{II} complexes of diethyldithiocarbamate (dtc) in our studies of interactions between *N*,*N*,*N'*,*N'*-tetraethylthiuram disulfide (TETD) and mercurials (Chieh, 1978; Chieh & Leung, 1976). In these structures, the –C(=S)S$^-$ group was found to be a unidentate, bridging or chelating ligand. As part of this continuing study, mercury(II) ethylxanthate was synthesized and its crystal structure studied.

A structure of mercury(II) ethylxanthate has been reported previously (Watanabe & Hagihara, 1972; Watanabe, 1977). Their cell constants and space group differ from ours, yet the two sets of data are related (see below) in an interesting way. Our study has confirmed that the two phases from acetone and CCl$_4$ belong to $P2_1/c$ and $P2_1$ respectively.

In this paper, we are directing our attention to the close structural relationships among M(xanthate)$_2$ compounds, where M = Zn, Cd, and Hg. Factors leading to the differences between the structures of the xanthates and dithiocarbamates of these metals are explored.

Experimental

When 0·5 g of $HgCl_2$ crystals was added to an aqueous solution containing 0·575 g of potassium ethylxanthate (Hg^{2+}:ethylxanthate = 1:2), a grey precipitate was obtained. The product was dissolved in acetone and filtered to remove the black suspended material, leading to a clear solution that gave colorless prismatic crystals when the solvent had evaporated at 298 K. Upon examination with a microscope while trying to cut the crystal, we observed that it is composed of mica-like sheets with a (001) cleavage plane.

Photographic methods were used to determine the space group; cell constants, along with the orientation matrix, were refined by the least-squares method based on 15 reflections that were automatically centered on a Syntex $P2_1$ diffractometer.

Crystal data

$C_6H_{10}HgO_2S_4$, $M_r = 443\cdot0$, monoclinic, $a = 9\cdot300$ (2), $b = 6\cdot693$ (2), $c = 19\cdot585$ (9) Å, $\beta = 100\cdot94$ (3)°, $V = 1196\cdot9$ Å^3, $D_o = 2\cdot44$ (1) (by flotation), $Z = 4$, $D_c = 2\cdot456$ Mg m^{-3}, $F(000) = 824$. Systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$. Space group $P2_1/c$. λ(Mo $K\alpha$) $= 0\cdot71069$ Å, μ(Mo $K\alpha$) $= 13\cdot76$ mm^{-1}.

A crystal, cut to the shape of a cube with edges of 0·10 mm, was mounted on a Syntex $P2_1$ automatic diffractometer with which the intensities of 2111 reflections ($2\theta < 45°$) were collected by the θ–2θ scan method (1° below Mo $K\alpha_1$ and 1° above Mo $K\alpha_2$) using graphite-monochromatized Mo $K\alpha$ radiation. Among them, 249 had $I < \sigma(I)$. During the data collection, 315 and 204 were repeatedly measured after every 48 reflections; their intensities fluctuated within 2%. The amplitudes were calculated with the application of Lorentz and polarization factors. All

reflections were included in the structural analysis. No absorption correction was made, $\mu R = 1\cdot1$.

The structure was solved by the heavy-atom method and refined by full-matrix least squares using a highly modified version of ORFLS (Busing, Martin & Levy, 1962). Atomic scattering curves from Cromer & Waber (1965) with an anomalous correction for Hg^{2+} (Cromer, 1965) were used. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = (40 - F_o + 0\cdot017F_o^2)^{-1/2}$ at the final stages of the refinement. This weighting function was based on the higher confidence in the medium-intensity reflections ($F_o = 30$) than in the weak or strong ones, as shown in the analysis based on ranges of F_o's. Its use also led to a small variation of $\sum w(\Delta F)^2/n$ vs ranges of F_o. The refinement was stopped when the parameter shifts were less than 0·1σ. The final R $[= \sum(|F_o| - |F_c|)/\sum F_o]$ and R_w $\{= [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}\}$ were 0·074 and 0·094 respectively; when the 249 reflections with $I < \sigma(I)$ were excluded, these factors became 0·069 and 0·089. The final difference Fourier map showed ripples (~1 e Å^{-3}) around the Hg location. Atomic coordinates are given in Table 1.*

Results and discussion

The crystal structure

The crystal structure consists of two-dimensional sheets formed by mutual bridging of mercury(II) and ethylxanthate ions. Every Hg^{2+} ion is coordinated to

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35037 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and U values* ($\times 10^3$ Å^2)

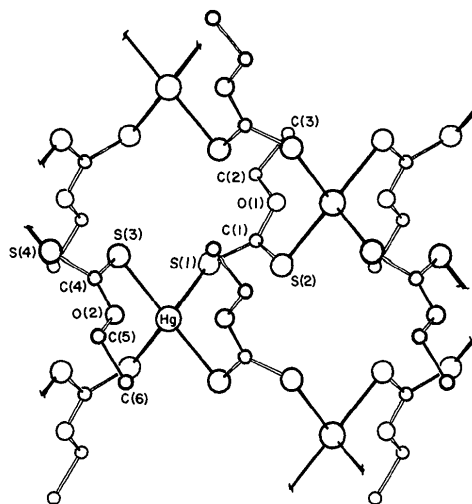|	x	y	z	U^*
Hg	2374·6 (6)	−251·5 (9)	2310·0 (3)	46·6 (5)
S(1)	2314 (4)	2139 (7)	1244 (2)	49 (2)
S(2)	5909 (4)	2064 (6)	2332 (2)	47 (2)
S(3)	951 (4)	2473 (6)	2652 (2)	47 (2)
S(4)	−715 (4)	2657 (7)	3798 (2)	51 (2)
O(1)	5357 (11)	4765 (13)	1398 (5)	40 (5)
O(2)	1235 (12)	−82 (14)	3647 (6)	45 (5)
C(1)	4823 (14)	3112 (21)	1637 (8)	56 (8)
C(2)	4497 (17)	5969 (26)	853 (9)	70 (9)
C(3)	5472 (23)	7748 (24)	772 (9)	79 (11)
C(4)	522 (15)	1523 (25)	3413 (8)	63 (9)
C(5)	970 (19)	−1001 (31)	4276 (9)	81 (12)
C(6)	1855 (23)	−2971 (26)	4337 (9)	85 (12)

* $U = (U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)/3$.

Fig. 1. Two-dimensional sheet structure of mercury(II) ethylxanthate.

Table 2. Bond lengths (Å) and angles (°)

(a) Around Hg

Hg—S(1)	2·854 (4)	Hg—S(3)	2·421 (4)
Hg—S(2)	2·943 (10)*	Hg—S(3")	2·505 (9)*
Hg—S(2)¹	2·417 (4)	Hg—S(4)²	2·789 (4)
Hg—S(1')	2·313 (8)*	Hg—S(4)	2·749 (8)*
S(1)HgS(2)¹	111·8 (1)	S(2)¹HgS(3)	147·7 (1)
S(1')HgS(2)	112·6 (3)*	S(1')HgS(3")	148·8 (3)*
S(1)HgS(3)	91·1 (1)	S(2)¹HgS(4)²	95·2 (1)
S(2)HgS(3")	86·4 (3)*	S(1')HgS(4)	99·1 (3)*
S(1)HgS(4)²	84·3 (1)	S(3)HgS(4)²	110·0 (1)
S(2)HgS(4)	81·8 (3)*	S(3")HgS(4)	108·3 (3)*

(b) Ethylxanthate

C(1)—S(1)	1·68 (1)	C(4)—S(3)	1·74 (2)
C(1)—S(2)	1·69 (2)	C(4)—S(4)	1·67 (2)
C(1)—O(1)	1·33 (2)	C(4)—O(2)	1·30 (2)
O(1)—C(2)	1·45 (2)	O(2)—C(5)	1·44 (2)
C(2)—C(3)	1·52 (3)	C(5)—C(6)	1·55 (3)
HgS(1)C(1)	103·1 (4)	HgS(3)C(4)	100·9 (5)
HgS(2)C(1)	103·7 (11)*	HgS(3")C(2")	101·9 (10)*
Hg¹S(2)C(1)	100·7 (4)	Hg²S(4)C(4)	101·7 (5)
HgS(1')C(1')	102·1 (12)*	HgS(4)C(2)	98·4 (9)*
S(1)C(1)S(2)	123·6 (8)	S(3)C(4)S(4)	120·7 (9)
S(1)C(1)O(1)	121 (1)	S(3)C(4)O(2)	115 (1)
S(2)C(1)O(1)	115 (1)	S(4)C(4)O(2)	124 (1)
C(1)O(1)C(2)	122 (1)	C(4)O(2)C(5)	120 (1)
O(1)C(2)C(3)	105 (1)	O(2)C(5)C(6)	105 (1)

Symmetry code

(1)	1 − x, 0·5 + y, 0·5 − z	(')	−x, y − 0·5, −z
(2)	−x, −0·5 + y, 0·5 − z	(")	−x, y + 0·5, 1 − z

* Values in Watanabe's structure.

Table 3. Equations of least-squares planes in the form $(lX + mY + nZ) \times 10^{-4} = d$ referring to an orthogonal coordinate system X, Y and Z in Å

Plane		l	m	n	d	Maximum displacement*
1	S(1)S(2)C(1)O(1)	−5856	5433	6016	0·74	0·01 (1)
2	C(1)O(1)C(2)	−4808	5411	6900	1·43	—
3	HgS(1)C(1)	−5450	7835	2986	0·46	—
4	Hg¹S(2)C(1)	−7202	3591	5936	−0·17	—
5	S(3)S(4)C(4)O(2)	6323	5599	5355	3·59	0·01 (1)
6	C(4)O(2)C(5)	6298	5622	5360	3·60	—
7	HgS(3)C(4)	7481	4060	5250	3·27	—
8	Hg²S(4)C(4)	5810	7868	2084	1·71	—

Interplanar angles (°)

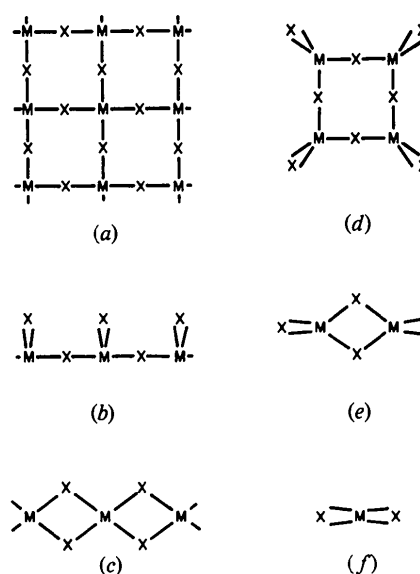|			
1–2	7·8 (4)	5–6	0·0 (4)
1–3	22·4 (4)	5–7	11·0 (4)
1–4	13·1 (4)	5–8	23·1 (4)

* Displacements from plane 1: Hg, 1·05 (1); Hg¹ (1 − x, 0·5 + y, 0·5 − z), 0·53 (1) Å, and from plane 5: Hg² (−x, 0·5 + y, 0·5 − z), −1·07 (1) Å; Hg, −0·45 (1) Å.

Fig. 2. Topological patterns: (a) for Zn, Cd or Hg ethylxanthates and Cd n-butylxanthate; (b) and (c) two possible chains; (d) tetramer of zinc(II) isopropylxanthate; (e) dimers of [M(dtc)₂]₂ (M = Zn, Cd, Hg); (f) monomer, [Hg(dtc)₂].

four S atoms, each from a separate xanthate, with Hg—S bond lengths of 2·417 (4), 2·421 (4), 2·789 (4) and 2·854 (4) Å, Table 2. This network is shown in Fig. 1 with the atomic labels given to the two independent ligands.

The coordination geometry around the Hg²⁺ ion is a very distorted tetrahedron. The S(2)¹HgS(3) angle, between two short Hg—S bonds, is the largest of the six, 147·7 (1)°, whereas the S(1)HgS(4)² angle formed by two long Hg—S bonds is the smallest, 84·3 (1)°. The same is true for other xanthate complexes of Group IIb ions (see below). Despite the difference in Hg—S distances, the C=S bond lengths are nearly the same with a mean of 1·70 (3) Å. The HgSC angles fall in the range 100·7–103·1°, Table 2.

The S₂C—O bond length, 1·32 (2) Å, and the planarity of these atoms, Table 3, indicate significant double-bond character for C—O, as was the case in the potassium salt (Mazzi & Tadini, 1963).

Xanthates of Group IIb

Crystals of many Group IIb xanthate complexes consist of two-dimensional sheets. Thus the Zn¹¹ (Ikeda &

Hagihara, 1966), Ca¹¹ (Iimura, Ito & Hagihara, 1972) and Hg¹¹ ethylxanthates and cadmium n-butylxanthate (Rietveld & Maslen, 1965) have the same topological patterns, Fig. 2(a).

The deviation of the MS₄ moiety from a tetrahedron increases in the order Zn < Cd < Hg with largest SMS angles of 115·2 (3), 121·29 (3) and 147·7 (1)°, respectively, for the ethylxanthates. The corresponding smallest angles are 102·6 (3), 94·47 (3) and 84·3 (1)°. The differences in the Zn—S distances are not significant, but the greatest differences in the Cd—S and Hg—S bond lengths are 11σ and 77σ respectively. In cadmium n-butylxanthate, the largest and smallest SCdS angles are 121·5 (3) and 95·3 (3)° respectively, consistent with the above trend (Rietveld & Maslen, 1965).

Many xanthates of Group IIb ions consist of two-dimensional nets, Fig. 2(a), rather than chains, Fig. 2(b,c), or three-dimensional nets, despite the numerous possible ways of building them (Wells, 1977). The crystal structure of zinc isopropylxanthate consists of tetramers, Fig. 2(d) (Ito, 1972).

Xanthates and dithiocarbamates of Group IIb

The common functional group, $-C(=S)S^-$, binds to each Group IIb ion in a similar way, yet, in contrast to the two-dimensional networks or tetramers of xanthates, the diethyldithiocarbamates (dtc) of Group IIb ions, $[Zn(dtc)_2]_2$ (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), $[Cd(dtc)_2]_2$ (Torelli, Vaciago & Zambonelli, 1968), and α-$[Hg(dtc)_2]_2$, are dimers, Fig. 2(e), in their crystals. However, β-$[Hg(dtc)_2]$ is a mononuclear complex, Fig. 2(f), with two short linear Hg–S bonds of 2·398 (4) Å (Iwasaki, 1973), a common feature for Hg^{2+} but not for Zn^{2+} or Cd^{2+} compounds. In addition, crystals of zinc(II) hexamethylene dithiocarbamate (Agre & Sugman, 1972), zinc(II) dimethyl dithiocarbamate (Klug, 1966) and zinc(II) diethyl diselenocarbamate (Bonamico & Dessy, 1971) also consist of dimers.

When a dithiocarbamate or xanthate ion is a bridging ligand, the two metal ions position themselves as shown in the following forms:
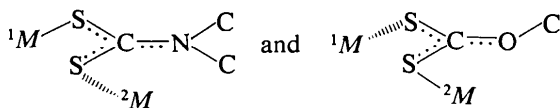
Values of these MSC angles are in the range 90–109° due to the repulsion of the lone electron pairs on the S atoms. Ideally, the HgSC groups are free to rotate around the S–C bonds. The deviations of ^1M and ^2M from the aforementioned planes are different in the two types of complexes. In dithiocarbamate complexes of Group IIb metals, the displacements of ^1M from their respective planes are between 0·18 and 0·27 Å. The second metal ions, ^2M, however, are displaced by 1·81–2·53 Å because of steric hindrance. In the xanthates, there is room to accommodate ^2M in the plane defined by S₂COC. The Hg atoms bonded to S(2) and S(3), Fig. 1, have small displacements: Hg¹, 0·53 and Hg, −0·45 Å (Table 3). Hg atoms deviate similarly from the S₂C–NC₂ planes in α-$[Hg(dtc)_2]_2$, by 2·16 and 2·53 Å. The ^1M atoms, Hg and Hg² (Table 3), deviate by 1·05 and −1·07 Å from their respective S₂C–O planes. These conformational differences are probably responsible for their preference for two-dimensional nets and tetramers vs dimers. Eight-membered rings are formed in the dimers of dtc complexes but 16-membered rings are found in both two-dimensional nets and tetramers of xanthates.
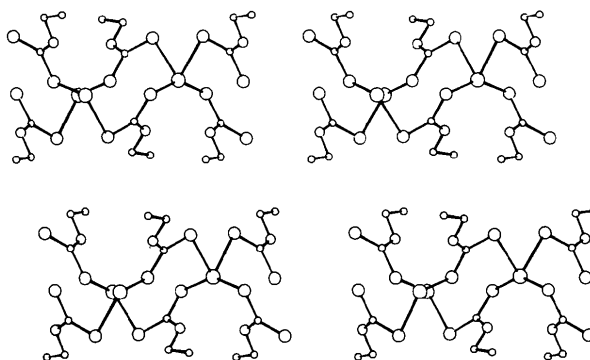

Fig. 3. Packing diagram viewed from −b.

Two related phases

The cell constants of the two phases are compared as follows:

	Present work		Watanabe (1977)
$a =$	9·300 Å	$c =$	9·104 Å
$b =$	6·693	$b =$	6·903
$c =$	19·585	$2a =$	19·808
$\beta =$	100·94°	$\beta =$	100·2°
Space group $P2_1/c$		$P2_1$.	

This relationship and Watanabe's short length of 2·313 (8) Å for the Hg–S bond led us to the following tests. Reflections with only $l = 2n$ were selected and transformed to Watanabe's unit cell and then a Patterson map was calculated. On this map were also peaks corresponding to atoms of a $P2_1/c$ structure compressed in a small cell. One cycle of least squares, varying only positional parameters from Watanabe's structure, gave an R of 0·65. A better R factor, 0·33, was obtained when both the + and − images of his structure were included in the structure factor calculation, i.e. $P2_1/m$ is assumed for a $P2_1$ structure. These tests confirm that such an error cannot be made. Furthermore, using rotation photographs and a Syntex $P2_1$ diffractometer, we obtained the cell constants $a = 9·915$ (5), $b = 6·926$ (2), $c = 9·110$ (6) Å, and $\beta = 100·13$ (5)° with a crystal from CCl_4, in agreement with Watanabe's results. Thus the two different phases do exist.

Within a layer, the structures of the two phases are the same. The major difference is in the packing of the layers. A packing diagram, viewed from the edges of the layers, is shown in Fig. 3. The alternate layers are related to each other by centers of symmetry; in contrast, adjacent layers of Watanabe's structure with space group $P2_1$ have the same orientation. The layers are held together by van der Waals forces and there is no reason to expect a large lattice-energy difference between the two phases. The idealized structure, with space group $P2_1/c$, is a perfect alternate-layer twin of

the $P2_1$ structure. That two related phases were obtained by using acetone or CCl_4 as a solvent is an interesting phenomenon.

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The Structures of Acetatobis(2,2'-bipyridyl)copper(II) Perchlorate Monohydrate and Tetrafluoroborate – Cation Distortion Isomers

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Abstract

The structures of acetatobis(2,2'-bipyridyl)copper(II) perchlorate monohydrate, $[Cu(C_{10}H_8N_2)_2(C_2H_3O_2)]ClO_4.H_2O$, $C_{22}H_{19}CuN_4O_2^+.ClO_4^-.H_2O$ (I), and tetrafluoroborate (II) have been determined by X-ray analysis. (I) crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.338$ (2), $b = 9.660$ (2), $c = 14.912$ (3) Å, $\alpha = 100.35$ (5), $\beta = 95.99$ (5), $\gamma = 84.90$ (5)°, $Z = 2$. (II) crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.333$ (2), $b = 28.078$ (4), $c = 11.601$ (3) Å, $\beta = 111.42$ (5)°, $Z = 4$. Both structures involve a $[Cu(bpy)_2(CH_3CO_2)]^+$ cation with a stereochemistry intermediate between five- and six-coordinate, with the second acetate O atom involved in semi-coordinate off-the-z-axis bonding to the Cu^{II} ion. The local CuN_4OO' chromophore is best considered as having a distorted square-pyramidal stereochemistry rather than the more usual trigonal-bipyramidal stereochemistry of the $[Cu(bpy)_2X]^+$ cation. The cations of (I) and (II) involve significantly different Cu–ligand bond lengths and angles and represent a pair of cation distortion isomers which may be distinguished by their electronic reflectance spectra.

Introduction

The nitrite ion is unique in the stereochemistry of the $[Cu(bpy)_2X]Y$ complexes, bpy = 2,2'-bipyridyl, in forming a *cis*-distorted octahedral CuN_4OO' chromophore in bis(2,2'-bipyridyl)nitritocopper(II) nitrate (Procter & Stephens, 1969; Procter, Hathaway, Billing, Dudley & Nicholls, 1969). As the nitrite and acetate anions have comparable bonding roles with the Cu^{II} ion, frequently bonding as bidentate chelate ligands but with non-equivalent Cu–O distances (Hathaway, 1973), a series of $[Cu(bpy)_2(CH_3CO)_2]Y$ complexes