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

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Abstract

Crystals of mercury(II) ethylxanthate, \([\text{Hg}(C_3H_5OS)\text{Z})_2]\), 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 \(\text{Hg}^{II}\) and ethylxanthate ions. The \(\text{Hg}^{II}\) ion is bonded to four \(\text{S}\) atoms with \(\text{Hg}-\text{S}\) 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 \(\text{S}-\text{Hg}-\text{S}\) 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 \(\text{CCI}_4\) 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 xanthsates are useful industrial chemicals with a common functional group \(-\text{C}(\equiv\text{S})\text{-S}^-\) (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 \(\text{S}\)-containing materials offer great potential for the industrial-waste treatment required in environmental protection.

We have reported several crystal structures of \(\text{Hg}^{II}\) complexes of diethyl dithiocarbamate (dtc) in our studies of interactions between \(N,N,N',N'\text{-tetraethylthiuram disulfide (TETD) and mercurials (Chieh, 1978; Chieh & Leung, 1976). In these structures, the } \text{-C}(\equiv\text{S})\text{-S}^- \text{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 \(\text{CCI}_4\) belong to \(P2_1/c\) and \(P2_1\), respectively.

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

When 0.5 g of HgCl₂ crystals was added to an aqueous solution containing 0.575 g of potassium ethylxanthate (Hg₂⁺: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 P2₁/diffractometer.

Crystal data

C₆H₁₀HgO₂S₄, Mᵣ = 443.0, monoclinic, a = 9.300 (2), b = 6.693 (2), c = 19.585 (9) Å, β = 100-94 (3)°, V = 1196.9 Å³, D_o = 2.44 (1) (by flotation), Z = 4, D_c = 2.456 Mg m⁻³, F(000) = 824. Systematic absences: h0l, l = 2n + 1; 0k0, k = 2n + 1. Space group P2₁/c.

A crystal, cut to the shape of a cube with edges of 0.10 mm, was mounted on a Syntex P2₁ automatic diffractometer with which the intensities of 2111 reflections (2θ < 45°) were collected by the 0-2θ scan method (1° below Mo Kα and 1° above Mo Kα) using graphite-monochromatized Mo Kα radiation. Among them, 249 had I < σ(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, μR = 1.1.

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 Hg²⁺ (Cromer, 1965) were used. The function minimized was \( \sum w(F_o^2 - |F_c|)^2 \) where \( w = (40 - F_o + 0.017F_o^2)^{-1/2} \) 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 \( R = \| \sum w(F_o - |F_c|)\|/\sum wF_o^2 \) and \( R_w \) (= \( \sum w(F_o^2 - |F_c|^2)/\sum wF_o^2)^{1/2} \) 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 Hg²⁺ ion is coordinated to...
Table 2. Bond lengths (Å) and angles (°)

(a) Around Hg

<table>
<thead>
<tr>
<th>Bond lengths (Å) and angles (°)</th>
<th>Hg—S(1) 2.854 (4)</th>
<th>Hg—S(2) 2.943 (10)*</th>
<th>Hg—S(2)' 2.417 (4)</th>
<th>Hg—S(I') 2.313 (8)*</th>
<th>S(1)HgS(2) 111.8 (1)</th>
<th>S(I')HgS(2) 112.6 (3)*</th>
<th>S(1)HgS(3) 91.1 (1)</th>
<th>S(2)HgS(3&quot;) 86.4 (3)*</th>
<th>S(1)HgS(4) 84.3 (1)</th>
<th>S(2)HgS(4) 81.8 (3)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg—S(1)S(2)'</td>
<td>111.8 (1)</td>
<td>S(2)'HgS(3&quot;) 148.8 (3)*</td>
<td>S(1)'HgS(3&quot;)</td>
<td>S(1)'HgS(3”) 99.1 (3)*</td>
<td>S(1)C(1)S(2) 123.6 (9)</td>
<td>S(1)C(1)O(1) 121.0 (1)</td>
<td>S(2)C(1)O(1) 115.0 (1)</td>
<td>C(1)O(1)C(2) 120.0 (1)</td>
<td>C(4)-S(3) 1.74 (2)</td>
<td>C(4)-S(4) 1.67 (2)</td>
</tr>
<tr>
<td>Hg—S(1)S(2)</td>
<td>2.854 (4)</td>
<td>S(2)HgS(4) 103.1 (4)</td>
<td>S(2)HgS(4) 98.4 (9)*</td>
<td>S(2)HgS(4) 101.7 (5)</td>
<td>S(3)C(4)S(4) 120.7 (9)</td>
<td>S(3)C(4)O(2) 115.1 (1)</td>
<td>S(4)C(4)O(2) 124.1 (1)</td>
<td>O(2)-C(5) 1.45 (2)</td>
<td>O(2)-C(5) 1.52 (5)</td>
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(b) Ethylxanthate

<table>
<thead>
<tr>
<th>Bond lengths (Å) and angles (°)</th>
<th>C(1)-S(1) 1.68 (1)</th>
<th>C(1)-S(2) 1.69 (2)</th>
<th>C(1)-O(1) 1.33 (2)</th>
<th>O(1)-C(2) 1.45 (2)</th>
<th>C(2)-C(3) 1.52 (5)</th>
<th>C(3)-S(3) 1.57 (3)</th>
<th>C(4)-S(3) 1.74 (2)</th>
<th>C(4)-S(4) 1.67 (2)</th>
<th>C(4)-O(2) 1.30 (2)</th>
<th>O(2)-C(5) 1.44 (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg—C(1)</td>
<td>103.1 (4)</td>
<td>Hg—C(2)</td>
<td>103.7 (11)*</td>
<td>Hg—C(3)</td>
<td>101.7 (5)</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</table>

Symmetry code

(1) 1 - x, 0.5 + y, 0.5 - z
(2) -x, -0.5 + y, 0.5 - z

* Values in Watanabe's structure.

Table 3. Equations of least-squares planes in the form

\( (IX + mY + nZ) x 10^{-4} = d \) referring to an orthogonal coordinate system X, Y and Z in Å

<table>
<thead>
<tr>
<th>Plane</th>
<th>l</th>
<th>m</th>
<th>n</th>
<th>d</th>
<th>Maximum displacement*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S(1)S(2)C(1)O(1)</td>
<td>-5856</td>
<td>5433</td>
<td>6016</td>
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<td>2</td>
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<td>Hg—S(1)C(1)</td>
<td>-7202</td>
<td>3591</td>
<td>5936</td>
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<td>4</td>
<td>Hg—S(2)C(1)</td>
<td>-3702</td>
<td>3591</td>
<td>5936</td>
<td>1.07</td>
</tr>
<tr>
<td>5</td>
<td>S(3)C(4)S(4)</td>
<td>6323</td>
<td>5599</td>
<td>5555</td>
<td>3.59</td>
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<tr>
<td>6</td>
<td>C(4)O(2)C(5)</td>
<td>6298</td>
<td>5622</td>
<td>5360</td>
<td>1.60</td>
</tr>
<tr>
<td>7</td>
<td>Hg—S(3)C(4)</td>
<td>7481</td>
<td>4060</td>
<td>5250</td>
<td>3.27</td>
</tr>
<tr>
<td>8</td>
<td>Hg—S(4)C(4)</td>
<td>5810</td>
<td>7868</td>
<td>2084</td>
<td>1.71</td>
</tr>
</tbody>
</table>

Interplanar angles (°)

\[ 90 - (1) = 22.4 (4) \]
\[ 60 - (1) = 11.0 (4) \]
\[ 90 - (1) = 13.1 (4) \]

Displacements from plane 1: Hg, 1.05 (1); Hg, -0.53 (1) Å; Hg, 0.45 (1) Å.

The coordination geometry around the Hg\(^{2+}\) ion is a very distorted tetrahedron. The S(2)IHgS(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 deviation of the MS\(_4\) 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), 95.3 (3) and 84.3 (1)°. 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).

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)\(_2\)].

Xanthates of Group IIB

Crystals of many Group IIB xanthate complexes consist of two-dimensional sheets. Thus the Zn\(^{1+}\) (Ikeda & Hagiwara, 1966), Ca\(^{1+}\) (Iimura, Ito & Hagiwara, 1972) and Hg\(^{2+}\) ethylxanthates and cadmium n-butylxanthate (Rietveld & Maslen, 1965) have the same topological patterns, Fig. 2(a).

The deviation of the MS\(_4\) 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), 94.4 (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, $\text{-C(=S)S-}$, binds to each Group IIb ion in a similar way, yet, in contrast to the two-dimensional networks or tetramers of xanthates, the diethylidithiocarbamates (dtc) of Group IIb ions, $[\text{Zn(dtc)}_2]_2$ (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), $[\text{Cd(dtc)}_2]_2$ (Torelli, Vaciago & Zambonelli, 1968), and $\alpha\{\text{Hg(dtc)}_2\}_2$, are dimers, Fig. 2(e), in their crystals. However, $\beta\{\text{Hg(dtc)}_2\}$ 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:

\[
\begin{align*}
1M & \quad \begin{array}{c}
\text{S} \quad \text{C} \quad \text{N} \quad \text{C} \\
\text{C} & \quad \text{O}
\end{array} \\
& \quad 2M
\end{align*}
\]

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 $\text{S}_2\text{CO}$. The Hg atoms bonded to S(2) and S(3), Fig. 1, have small displacements: Hg$^1$, 0.53 and Hg$^2$, $-0.45$ Å (Table 3). Hg atoms deviate similarly from the S$\text{C}_2\text{N}_2$ planes in $\alpha\{\text{Hg(dtc)}_2\}_2$, by 2.16 and 2.53 Å. The $1M$ atoms, Hg and Hg$^2$ (Table 3), deviate by 1.05 and $-1.07$ Å from their respective S$\text{C}_2\text{O}$ 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.

**Two related phases**

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

<table>
<thead>
<tr>
<th></th>
<th>Present work</th>
<th>Watanabe (1977)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>9.300 Å</td>
<td>9.104 Å</td>
</tr>
<tr>
<td>$b$</td>
<td>6.693 Å</td>
<td>6.903 Å</td>
</tr>
<tr>
<td>$c$</td>
<td>19.585 Å</td>
<td>19.808 Å</td>
</tr>
<tr>
<td>$\beta$</td>
<td>100.94°</td>
<td>100.2°</td>
</tr>
</tbody>
</table>

Space group $P2_1/c$

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 Syntax $P2_1$ 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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References


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$_{8}$N$_{2}$)$_{2}$(C$_{2}$H$_{3}$O$_{2}$)]$^{+}$ClO$_{4}$H$_{2}$O, C$_{2}$H$_{15}$CuN$_{4}$O$_{6}$$^{+}$ClO$_{4}$H$_{2}$O (I), and tetrafluoroborate (II) have been determined by X-ray analysis. (I) crystallizes in the triclinic space group $P1$ 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$_{3}$CO)$_{2}$]$^{+}$ 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$_{4}$O$^{+}$ chromophore is best considered as having a distorted square-pyramidal stereochemistry rather than the more usual trigonal-bipyramidal stereochemistry of the [Cu(bpy)$_{2}X$]$^{+}$ 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)$_{2}X$]Y complexes, bpy = 2,2'-bipyridyl, in forming a cis-distorted octahedral CuN$_{4}$O$^{+}$ chromophore in bis(2,2'-bipyridyl)nitriocopper(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$_{3}$CO)$_{2}$]Y complexes