Inorganica Chimica Acta, 77 (1983) L225–L227

Crystal and Molecular Structure of Orthorhombic Dichloro-Bis(o-ethylxanthato)tin(IV)

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Received July 23, 1983

During a previous study of tin(IV)dihalobisxanthates [1], the diiodide was obtained in two crystalline forms but only one form for the dichloride and dibromide, which were isomorphous. Recently we have isolated a second crystalline form for the dichloride.

Diagnostically the two forms can be distinguished by their infrared spectra, particularly in the 'C–O' and 'C–S' regions (Table I). Both forms, which cocrystallised from petroleum ether, also differ in appearance, form A being lighter in colour, allowing manual separation.

Intensity data were collected on an Enraf Nonius CAD-4F, four circle, single crystal, automatic diffractometer. Accurate cell dimensions were obtained from the setting angles of 25 reflections, using MOK$\bar{\alpha}$ radiation (0.71069 Å). A preliminary scan indicated systematic absences in agreement with the space group Pnma or $Pn2_1a$ [2]. Intensity data collection, which included Friedel pairs, resulted in the measurement of 3632 reflections in the range $2° \leqslant 2\theta \leqslant 50°$. The data were corrected for Lorentz, polarization and absorption effects, but no definite choice could be made between the two possible space groups, either from Friedel pairs or E-statistics. During the course of the structure determination the crystal structure proved to be noncentrosymmetric, and the analysis was continued in the space group $Pn2_1a$. Equivalent positions for $Pn2_1a$: x, y, z; $\bar{x}, \frac{1}{2} + y, \bar{z}$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; $\frac{1}{2} + x, y, \frac{1}{2} - z$. Transformation to standard setting: $a_{\text{stand}} = a$; $b_{\text{stand}} = c$; $c_{\text{stand}} = -b$. Of the measured reflections 2453 were unique and 2126 were considered observed, $1 \geqslant 2\sigma(I)$. Crystal data: $C_6H_{10}Cl_2O_2S_4Sn$, M = 432.0, orthorhombic, a = 6.912(1), b = 14.4605(7), c = 15.056(1) Å, V = 1504.9, Dm = 1.89 Mg m^{-3}, Z = 4, Dc = 1.907 Mg m^{-3}, F(000) = 840, space group $Pn2_1a$ (No. 33), MoK$\bar{\alpha}$ (graphite monochromatic) radiation 0.71069 Å, μ = 2.577 mm^{-1}.

The coordinates of all non-hydrogen atoms were obtained by Patterson and Fourier methods and

TABLE II. Atomic Coordinates of $Sn(S_2COEt)_2Cl_2$ (A), Standard Deviations in Parentheses.

Atom	X/a	Y/b	Z/c
Sn	0.00737(5)	0.00000(–)	0.44374(2)
ligand a			
Cl	−0.0026(3)	0.0544(2)	0.5926(1)
S(1)	−0.0932(2)	0.1441(1)	0.3645(1)
S(2)	0.3117(2)	0.1047(1)	0.4169(1)
C(1)	0.1472(9)	0.1754(4)	0.3708(4)
O	0.1867(6)	0.2571(3)	0.3390(3)
C(2)	0.3869(9)	0.2928(4)	0.3463(5)
C(3)	0.3930(12)	0.3841(4)	0.3030(6)
ligand b			
Cl	−0.3103(2)	−0.0621(1)	0.4491(1)
S(1)	0.1992(2)	−0.1415(1)	0.4855(1)
S(2)	0.0989(3)	−0.0871(1)	0.3023(1)
C(1)	0.2115(10)	−0.1567(5)	0.3729(5)
O	0.3097(7)	−0.2268(3)	0.3359(3)
C(2)	0.4203(11)	−0.2873(5)	0.3912(6)
C(3)	0.5094(11)	−0.3586(7)	0.3327(6)

TABLE I. Infrared Spectra of the Two Forms of the Tin(IV)dihalobisxanthate Complexes in the 'C–O' and 'C–S' Regions (cm^{-1}).

Compound	Form	'C–O'	'C–S'	Ref.
$Sn(S_2COEt)_2I_2$	A	1290, 1248, 1235	1027, 1013	1
$Sn(S_2COEt)_2I_2$	B	1269, 1255	1041, 1014	1
$Sn(S_2COEt)_2Cl_2$	A	1298, 1282, 1262	1025, 1013	This work
$Sn(S_2COEt)_2Cl_2$	B	1282, 1260	1041, 1014	1
$Sn(S_2COEt)_2Br_2$	B	1279, 1259	1041, 1014	1

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0020-1693/83/$3.00

refinement was achieved using a least squares refinement procedure, employing anisotropic thermal parameters. Hydrogen atoms were constrained at tetrahedral estimates (C–H = 1.08 Å) and a weighting scheme of $w = 1.5298/(\sigma^2(F) + 0.00025F^2)$ was employed; the refinement converging with R 0.027 and Rw 0.028, where $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$ and $Rw = [\Sigma w\|F_o| - |F_c\|^2/\Sigma w|F_o|^2]^{1/2}$. The final difference map showed peaks less than or equal to 1.5 e Å^{-3}, mainly close to the tin, sulphur and oxygen atoms.

Attempts to decide the absolute configuration were unsuccessful, since no significant difference could be detected between the two configurations.

Structure determination and refinement were performed using the SHELX-76 program system [3], the scattering factors for all atoms being those incorporated in the program; allowance was made for anomalous dispersion. Final atomic coordinates are listed in Table II; the labelling scheme is analogous to that used previously for $Sn(S_2COEt)_2Br_2$ (B) [1]. Listings of the anisotropic temperature factors, estimated hydrogen atom coordinates and the final observed and calculated structure factors were deposited with the editors.

Although crystal classifications for form A (orthorhombic, $Pn2_1a$) and form B (monoclinic, $C2/c$) are different, the molecular structures are similar (Fig. 1), there being only minor differences in the metal ligand geometries (Table III). The major difference lies in the conformation of the ethyl groups in the xanthate ligands. Whereas in form B the two xanthate ligands are equivalent (the tin atom lies on a two-fold axis), this is not so in form A, where the ethyl groups of the two xanthate moieties adopt different conformations (Fig. 1). There are also differences in the dimensions within the two xanthate ligands, which are given in Table IV.

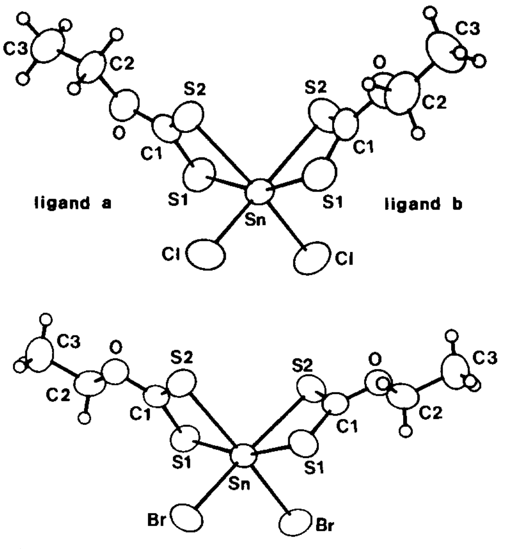

Fig. 1. The structures of $Sn(S_2COEt)_2Cl_2$ (A) and $Sn(S_2COEt)_2Br_2$ (B), showing the different conformation of the ethyl group on ligand a.

TABLE III. Comparison of Metal–Ligand Geometry for $Sn(S_2COEt)_2Cl_2$ (A) and $Sn(S_2COEt)_2Br_2$ (B) [1].

	FORM (A)		FORM (B)
(a) distances (Å)	ligand a	ligand b	
Sn–X	2.376(2)	2.374(1)	2.537(2)
Sn–S(1)	2.500(2)	2.518(1)	2.520(3)
Sn–S(2)	2.623(1)	2.554(2)	2.588(3)
(b) angles (°)			
Xa–Sn–Xb		93.80(7)	95.34(6)
Xa–Sn–S(1a)		99.56(7)	97.55(7)
Xa–Sn–S(2a)		88.71(7)	90.19(7)
Xa–Sn–S(1b)		92.80(7)	94.23(7)
Xa–Sn–S(2b)		163.13(7)	164.60(6)
Xb–Sn–S(1a)		94.26(5)	94.23(7)
Xb–Sn–S(2a)		164.89(5)	164.60(6)
Xb–Sn–S(1b)		99.86(5)	97.55(7)
Xb–Sn–S(2b)		94.07(6)	90.19(7)
S(1a)–Sn–S(2a)		70.63(5)	70.76(8)
S(1a)–Sn–S(1b)		160.56(5)	162.48(8)
S(1a)–Sn–S(2b)		94.71(5)	96.36(8)
S(2a)–Sn–S(1b)		94.89(5)	96.36(8)
S(2a)–Sn–S(2b)		87.57(5)	88.17(9)
S(1b)–Sn–S(2b)		71.15(5)	70.76(8)

TABLE IV. Comparison of Xanthate Ligand Parameters for $Sn(S_2COEt)_2Cl_2$ (A) and $Sn(S_2COEt)_2Br_2$ (B) [1].

	FORM (A)		FORM (B)
(a) Distances	ligand (a)	ligand (b)	
C(1)–S(1)	1.725(6)	1.712(8)	1.708(8)
C(1)–S(2)	1.679(6)	1.658(8)	1.690(9)
C(1)–O	1.304(7)	1.341(9)	1.305(10)
O–C(2)	1.481(8)	1.429(9)	1.49(1)
C(2)–C(3)	1.473(9)	1.489(12)	1.52(1)
(b) Angles			
Sn–S(1)–C(1)	85.7(2)	83.3(2)	84.8(3)
Sn–S(2)–C(1)	82.7(2)	83.2(3)	83.0(3)
S(1)–C(1)–S(2)	121.0(4)	122.3(4)	121.0(5)
S(1)–C(1)–O	114.8(4)	122.3(5)	121.8(7)
S(2)–C(1)–O	124.2(5)	115.5(5)	117.1(6)
C(1)–O–C(2)	119.0(5)	119.4(6)	119.5(6)
O–C(2)–C(3)	107.8(5)	107.5(7)	105.2(7)

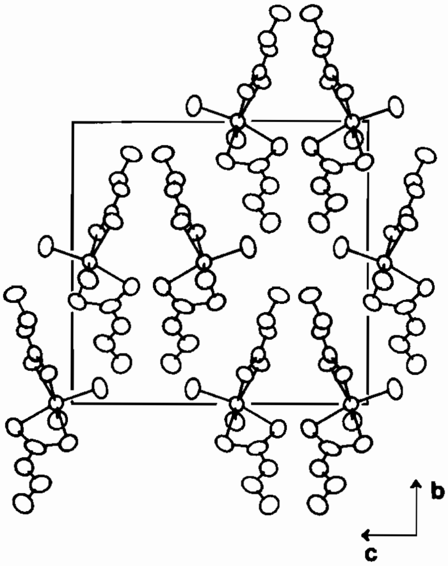

Fig. 2. The unit cell of $Sn(S_2COEt)_2Cl_2$ (A), viewed down the [100] direction.

The unit cell of $Sn(S_2COEt)_2Cl_2$ (A) is shown in Fig. 2. There are no significant intermolecular contacts.

Two crystalline forms are also known for nickel ethylxanthate [4, 5] and mercury ethylxanthate [6, 7]. In both cases, however, the differences are due only to variations in the packing of essentially identical molecular structures.

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