Inorganica Chimica Acta, 85 (1984) 215–218

The Preparation, Spectral Studies, and the Crystal Structure of Dimethylbis(O-ethylxanthato)Tin(IV)

DAINIS DAKTERNIEKS, BERNARD F. HOSKINS, EDWARD R. T. TIEKINK and GEORGE WINTER

Department of Inorganic Chemistry, University of Melbourne, Parkville, Vic., Australia, 3052

Received September 5, 1983

Tin-119 NMR data indicate that the tin atom in $(CH_3)_2Sn(S_2COC_2H_5)_2$ *is four co-ordinated in dichloromethane solution. However, single crystal X-ray analysis shows the tin atom to be six co-ordinated in the solid state in which the bidentate xanthate ligands display gross asymmetry in their mode of co-ordination to the tin. The crystals are molecular and there is no association between neighbouring molecules. The unit cell of* $Me_2Sn(exa)_2$ *is orthorhombic, Pnma,* a = *14.165(1),* b = *7.6759(9),* c = *13.977(2)* Å *with Z = 4. The structure was refined by conventional least squares methods with final R 0.041 and* R_w *0.043 for 1229 unique reflections with* $I \geqslant 2\sigma(I)$.

Introduction

The crystal structure of tin(IV) ethylxanthate, $Sn(exa)_4$, shows the presence of two bidentate and two *cis* monodentate xanthate ligands [1]. The replacement of two xanthate ligands by the potentially bidentate 8-hydroxyquinolate anion (oxine) gives the compound $Sn(exa)_2(oxine)_2$ in which the tin atom retains its six co-ordination and the two xanthate ligands co-ordinate in a monodentate mode occupying *cis* positions in the co-ordination sphere [2]. However, in the essentially octahedral structures of $Sn(exa)_2X_2$ (X = Cl, Br, I) the two xanthate ligands remain bidentate with the halogen atoms occupying *cis* positions [3].

Recently tin-119 NMR spectroscopy has shown that in dichloromethane solution the compounds $Sn(exa)_4$ and $Sn(exa)_2X_2$ (X = Cl, Br, I) are also six co-ordinate at room temperature [4]. At low temperature the xanthate exchange is sufficiently slow to allow the simultaneous observation of both *cis* and *trans* isomers for the $Sn(exa)_2X_2$ series as well as an additional weak tin-119 resonance which has been assigned to the presence of an associated species containing bridging xanthate groups. We have now extended these studies to the complex, $Me_2Sn(exa)_2$.

Results and Discussion

$Me_2Sn(exa)_2$ was prepared from the reaction of dimethyltin dichloride and potassium ethylxanthate in ethanol. In the C–O, C–S and M–S regions of the infrared spectrum characteristic absorptions are observed: C–O: 1238, 1205; C–S: 1058, 1038, 1005; and M–S: 440, 405 and 330 cm^{-1}; the infrared spectrum does not alter significantly in CS_2 solution. In cyclohexane, the ultraviolet spectrum arising from internal transitions within the xanthate ligand shows absorptions at λ: 287, ϵ: 33700; 228, 29000; and 215 nm, 21000 mol^{-1} dm^3 cm^{-1}. Although sparingly soluble in absolute ethanol, the absorption at 287 nm remains unaffected but in aqueous ethanol this band shifts to 305 nm where the free xanthate anion absorbs.

The hydrogen-1 NMR spectrum in $CDCl_3$ shows the expected triplet and quartet due to the xanthate ligand protons (δ 1.43, δ 4.51 $^3J(H–H)$ 7.1 Hz) and a singlet with tin-119 and tin-117 satellites due to the methyl groups bonded to the tin atom (δ 1.46, $^2J(^{119}Sn–H)$ 79.1 Hz, $^2J(^{117}Sn–H)$ 75.7 Hz). The observation of proton-tin coupling indicates that the methyl groups do not exchange appreciably about the tin atom on the NMR time scale.

The tin-119 spectrum of $Me_2Sn(exa)_2$ in dichloromethane shows a single sharp resonance δ –224 ppm at room temperature. Cooling this solution to –90 °C causes no change other than a small shift to lower frequency (δ –267 ppm). The carbon-13 spectrum of this solution at room temperature shows a single sharp resonance δ 221.9 ppm which is attributed to the OCS_2 carbon atom. No significant change in the position of this carbon-13 resonance occurs when the solution is cooled to –90 °C.

Tin-119 chemical shifts are dependent upon the co-ordination number of the tin atom [4, 5] with four co-ordinate species in general having shifts at higher frequency than six co-ordinate species (*e.g.* Me_2SnCl_2 δ –137 ppm $SnCl_4$ δ –150 ppm compared with $Sn(exa)_2Cl_2$ δ –762 ppm). The position of the tin-119 resonance for $Me_2Sn(exa)_2$ together with the

0020-1693/84/$3.00

fact that no additional resonances are found on cooling to −90 °C suggests that this compound is essentially four co-ordinate in solution with the xanthate anion acting as a monodentate ligand.

Crystallography

A crystal suitable for X-ray diffraction studies was grown by slow evaporation from a dichloromethane solution. Preliminary oscillation and equi-inclination Weissenberg photographs using $\mathrm{CuK}_{\bar{\alpha}}$ (nickel filtered) radiation indicated that the crystal was orthorhombic. The crystal was mounted on an Enraf-Nonius CAD-4F diffractometer. Accurate cell dimensions and their estimated standard deviations together with an accurate orientation matrix were obtained by a least squares refinement of the setting angles obtained for 25 reflections that were accurately centred by the SETANG procedure. The systematic absences were consistent with the non-centrosymmetric space group $Pn2_1a$ (C_{2v}^9, No. 33) or centrosymmetric Pnma (D_{2h}^{16}, No. 62), [6a].

The intensity data were collected at room temperature using $\mathrm{CuK}_{\bar{\alpha}}$ (nickel filtered) radiation. The $\omega : 2\theta$ scan technique was used to measure the intensities for 4608 reflections for which $1° \leqslant \theta \leqslant 75°$. Three reference reflections were measured after every 1800 seconds of X-ray exposure time, these showed there was no significant variation of intensity during the data collection. The intensities were corrected for Lorentz and polarization effects and for absorption (max. and min. transmission coefficients: 0.4711 and 0.2269) [6b]. After equivalent reflections were amalgamated there were 1681 (2939 for the non-centrosymmetric space group) unique reflections with an agreement index R_{amal} 0.032 (0.025) for the centrosymmetric space group, where $R_{amal} = [\Sigma(N\Sigma(W(F_{mean} - F)^2))/\Sigma(N - 1)\Sigma(WF^2)]^{1/2}$ the inner summations are over N equivalent reflections averaged to give F_{mean}, the outer summations are over all unique reflections and the weight, W, taken as $(\sigma(F))^{-2}$.

Crystal Data: $Me_2Sn(exa)_2$, $C_8H_{16}O_2S_4Sn$, M = 391.17, orthorhombic, a = 14.165(1), b = 7.6759(9), c = 13.977(2) Å, U = 1519.7 Å^3, D_m = 1.71, Z = 4, D_{calc} = 1.710 Mg m^{-3}, F(000) = 776, space group Pnma (D_{2h}^{16}, No. 62), $\mathrm{CuK}_{\bar{\alpha}}$ (nickel filtered 1.5418 Å, μ = 17.88 mm^{-1}, 1229 unique reflections with $I \geqslant 2\sigma(I)$, absorption corrections applied, oscillation and Weissenberg photographs, Enraf-Nonius CAD-4F four-circle diffractometer.

The structure was solved and refined in both the centrosymmetric and non-centrosymmetric space groups. The position of the tin atom was determined by a three-dimensional Patterson synthesis. Subsequent difference maps enabled the location of all non-hydrogen atoms. The structures were refined using a full-matrix least squares method in which the function $\Sigma w\Delta^2$ was minimized where w was the weight applied to each reflection and $\Delta = ||F_o| - |F_c||$. Both models were refined with anisotropic thermal parameters. Refinement was continued employing a weighting scheme for which w was modified according to the expression $w = [k/(\sigma^2(F) + 0.0001\ F^2)]$, where k is a constant. Refinement of both models converged with R 0.046, R_w 0.048, R_g 0.062, and k 3.34 for the centrosymmetric solution and R 0.052, R_w 0.054, R_g 0.066, and k 6.22 for the non-centrosymmetric space group, where $R = \Delta F/\Sigma|F_o|$, $R_w = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$, and $R_g = [\Sigma(w\Delta^2)/\Sigma(wF_o^2)]^{1/2}$. At this stage a R factor significance test was performed [6c] using R_g values as suggested by Sheldrick [7], which showed that the difference in the R_g values was significant at the level of 99.95% and on this basis Pnma was chosen to be the correct space group; an identical conclusion was obtained with the use of R_w values. However, it is noteworthy that the molecular geometries derived from both solutions showed no significant differences between chemically equivalent parameters.

Hydrogen atoms were included in the model in their calculated positions and were given isotropic temperature factors of 1.25(U_{iso} methylene carbon) for methylene hydrogens and 1.5(U_{iso} methyl carbon) for methyl hydrogens. The final refinement cycle yielded R 0.041 and R_w 0.043 and the residual electron density was 0.42 eA^{-3}. Analysis of the variance showed no significant features and indicated an appropriate weighting scheme was used.

The scattering factors used for all atoms were those collected by Sheldrick [7]. Structure determination and refinement were performed using the SHELX-76 [7] program system and the University of Melbourne's CYBER-175 computer system.

The fractional atomic co-ordinates and their estimated standard deviations are given in Table I and the numbering scheme used is shown in Fig. 1.

TABLE I. Fractional Atomic Co-ordinates (Standard Deviations in Parentheses).

Atom	x/a	y/b	z/c
Sn	0.33071(5)	0.25	0.57584(4)
S(1)	0.4834(2)	0.25	0.4881(2)
S(2)	0.5112(2)	0.25	0.6998(2)
S(3)	0.2615(2)	0.25	0.4112(2)
S(4)	0.1089(2)	0.25	0.5584(2)
C(1)	0.5526(7)	0.25	0.5913(7)
C(2)	0.7128(8)	0.25	0.6473(9)
O(1)	0.6446(5)	0.25	0.5671(5)
O(2)	0.0890(5)	0.25	0.3708(5)
C(3)	0.8096(9)	0.25	0.5961(11)
C(4)	0.1433(7)	0.25	0.4464(7)
C(5)	−0.0152(8)	0.25	0.3835(10)
C(6)	−0.0561(9)	0.25	0.2877(10)
C(7)	0.3106(6)	0.4993(10)	0.6362(6)

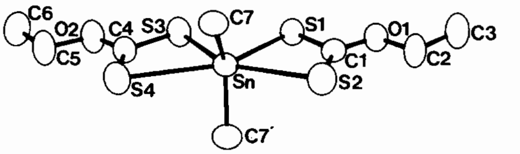

Fig. 1. Diagram showing the six co-ordinate nature of the tin atom in $Me_2Sn(exa)_2$; the numbering scheme used is also shown. The two xanthate moieties together with the tin atom lie on a crystallographic mirror plane; C7′ is related by the symmetry operation $\bar{x}$, ½ + y, $\bar{z}$.

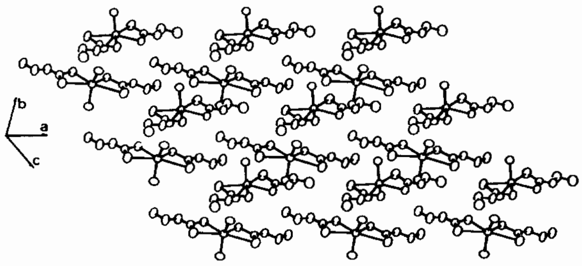

Fig. 2. Projection of half the unit cell contents of $Me_2Sn(exa)_2$ showing the molecular nature of the crystals and the absence of close intermolecular contacts.

Listings of anisotropic thermal parameters, all hydrogen atom parameters and the observed and calculated structure factors derived from the final set of parameters have been deposited with the Editors.

Description of Structure

All relevant bond lengths and angles are given in Tables II and III. The crystals consist of discrete molecular units of $Me_2Sn(exa)_2$ with the Sn atom and the xanthate moieties lying on a crystallographic mirror plane; a view of half the unit cell contents is shown in Fig. 2.

TABLE II. Interatomic Distances (Å) (Standard deviations in parentheses).

Atoms	Separation	Atoms	Separation
Sn–S(1)	2.486(3)	Sn–S(3)	2.501(3)
Sn–S(2)	3.088(3)	Sn–S(4)	3.151(3)
S(1)–C(1)	1.744(10)	S(3)–C(4)	1.745(10)
S(2)–C(1)	1.626(10)	S(4)–C(4)	1.640(10)
C(1)–O(1)	1.346(12)	C(4)–O(2)	1.307(12)
O(1)–C(2)	1.480(14)	O(2)–C(5)	1.487(13)
C(2)–C(3)	1.547(18)	C(5)–C(6)	1.459(19)
Sn–C(7)	2.111(8)		

In contrast to the bidentate ligands in $Sn(exa)_4$ and $Sn(exa)_2X_2$ there is a marked difference, approximately 0.1 Å, in the C–S distances within the xanthate ligands. This is also observed in the monodentate xanthate moieties of $Sn(exa)_4$ and $Sn(exa)_2(oxine)_2$; see Table IV. The short Sn–S distances (2.486 and 2.501 Å) in $Me_2Sn(exa)_2$ are again similar to the Sn–S distances of the monodentate xanthate ligands in $Sn(exa)_4$ (2.488 and 2.499 Å [1]) and of $Sn(exa)_2(oxine)_2$ (2.484 and 2.510 Å [2]). In the latter two compounds however, the second Sn–S distances (non-bonding) are approximately 5 Å whereas in $Me_2Sn(exa)_2$ these distances are 3.088 and 3.151 Å which are well within the sum of the van der Waals radii of 4.0 Å [8] for these atoms. Thus, the tin atom must be considered six co-ordinate within a distorted octahedral environment. The C7–Sn–C7′ angle of 130.1(3)° indicates the two methyl substituents lie intermediate between *cis* and *trans* geometry similar to that observed in $Me_2Sn(dtc)_2$ (dtc = diethyldithiocarbamate) [9] and $Me_2Sn(dtp)_2$ (dtp = dimethyldithiophosphate) [10].

Conclusions

The results of structure analyses of tin(IV) xanthates and mixed ligand tin(IV) xanthates which

TABLE III. Bond Angles (Deg.); Standard Deviations in Parentheses.

Atoms	Angle	Atoms	Angle
S(1)–Sn–S(2)	63.68(8)	S(3)–Sn–S(4)	62.49(8)
S(1)–Sn–S(3)	83.52(9)	S(2)–Sn–S(4)	150.31(8)
Sn–S(1)–C(1)	94.7(4)	Sn–S(3)–C(4)	96.7(3)
Sn–S(2)–C(1)	77.0(4)	Sn–S(4)–C(4)	77.2(4)
S(1)–C(1)–S(2)	124.7(6)	S(3)–C(4)–S(4)	123.7(6)
S(1)–C(1)–O(1)	109.5(7)	S(3)–C(4)–O(2)	109.7(7)
S(2)–C(1)–O(1)	125.7(8)	S(4)–C(4)–O(2)	126.7(8)
C(1)–O(1)–C(2)	116.2(8)	C(4)–O(2)–C(5)	119.2(9)
O(1)–C(2)–C(3)	103(1)	O(2)–C(5)–C(6)	107(1)
C(7)–Sn–S(1)	108.3(2)	C(7)–Sn–S(3)	108.4(2)
C(7)–Sn–S(2)	83.5(2)	C(7)–Sn–S(4)	84.1(2)
C(7)–Sn–C(7)*	130.1(3)		

*C(7)′ is related by the symmetry operation $\bar{X}$, ½ + Y, $\bar{Z}$.

TABLE IV. Carbon to Sulphur Bond Distances in Tin(IV) Xanthates (Å).

	monodentate	bidentate
$Sn(exa)_4$ [1]	1.640(7), 1.627(8) 1.725(8), 1.737(8)	1.707(7), 1.687(7) 1.695(7), 1.689(7)
$Sn(exa)_2Br_2$ [3]	– –	1.708(8), 1.708(8) 1.690(9), 1.690(9)
$Sn(exa)_2I_2$ [3]	– –	1.709(6), 1.711(6) 1.674(6), 1.685(6)
$Sn(exa)_2(oxine)_2$ [2]	1.75(1), 1.74(1) 1.62(1), 1.64(1)	
$Sn(exa)_2Me_2$*		1.744(10), 1.745(10) 1.626(10), 1.640(10)

*This work.

are at present available show that in the solid state six co-ordination of the tin atom prevails. Interpretation of NMR spectra confirms that this co-ordination is retained in solutions of the tetrakis xanthates and dihalo xanthates [4]. The tin-119 NMR spectrum of $Me_2Sn(exa)_2$ however, clearly indicates a change in the co-ordination number of the tin atom from six, observed in the solid, to four in solution. The tendency towards four co-ordination in this complex is also manifested in the gross asymmetry of the bonding of the CS_2 moiety to the tin atom in the solid and a similar situation appears to exist in $Me_2Sn(dtc)_2$ [9] and in $Me_2Sn(dtp)_2$ [10]. For the latter a frozen intermediate between the two possible four coordinate (monodentate) structure has been proposed [10].

Experimental

Preparation

To dimethyltin dichloride (Fluka, A.G., 2 g) in 50 ml methanol was added a solution of potassium ethylxanthate (3.2 g, 50 ml ethanol), after stirring the solution for two hours the mixture was filtered and the filtrate was evaporated under reduced pressure to give an oil which was recrystallized from light petroleum (M.P. 105–106 °C).

Instrumentation

Infrared spectra were obtained from KBr discs and a NaCl solution cell on a Perkin-Elmer 457 and a Jasco-A-302 spectrophotometer. A Varian Techtron 635D spectrophotometer was used to record the U.V. spectra. NMR spectra were recorded on a JEOL FX100 spectrometer: hydrogen-1 at 100 MHz using internal deuterium lock, tin-119 and carbon-13 at 37.08 MHz and 25.0 MHz using external ^7Li lock. Tin-119 NMR spectra were referenced against external Me_4Sn. Carbon-13 and hydrogen-1 were referenced against internal TMS. High frequency positive convention is used. Temperatures were maintained using a JEOL NM5471 controller.

Acknowledgements

We are most grateful to the Commonwealth of Australia for a Postgraduate Research Award to one of us (E.R.T.T.).

References

1 C. L. Raston, P. R. Tennant, A. H. White and G. Winter, *Aust. J. Chem., 31,* 1493 (1978).

2 C. L. Raston, A. H. White and G. Winter, *Aust. J. Chem., 31,* 2641 (1978).

3 R. W. Gable, C. L. Raston, G. L. Rowbottom, A. H. White and G. Winter, *J. Chem. Soc. Dalton,* 1392 (1981).

4 D. Dakternieks, R. W. Gable and G. Winter, *Inorg. Chim. Acta, 75,* 185 (1983).

5 R. Colton and D. Dakternieks, *Inorg. Chim. Acta, 71,* 101 (1983).

6 'International Tables for X-ray Crystallography', a) Vol. 1; b) Vol. 4 p. 58; c) Vol. 4 p. 285.

7 G. M. Sheldrick, 'SHELX-76', Program for Crystal Structure Determination, University of Cambridge (1976).

8 A. Bondi, *J. Phys. Chem., 68,* 441 (1964).

9 J. S. Morris and E. O. Schlemper, *J. Cryst. Molec. Struct., 9,* 13 (1979).

10 K. C. Molloy, M. B. Hossain, D. van der Helm, J. J. Zuckerman and F. P. Mullins, *Inorg. Chem., 20,* 2172 (1981).