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The Crystal and Molecular Structure of Dichlorobis(ethyl 3-oxobutanoato)tin(IV)

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The crystal structure of dichlorobis(ethyl 3-oxobutanoato)tin(IV), $Cl_2Sn(C_6H_9O_3)_2$, *has been determined from three-dimensional X-ray diffraction data. Unit-cell dimensions are* a = *11.818(5),* b = *10.408(4),* c = *14.155(6)* Å, *space group Pbcn,* Z = *4,* D_c = *1.71 g cm*$^{-3}$ *and* D_m = *1.74 g cm*$^{-3}$. *The structure was solved by the heavy-atom method from intensity data collected by diffractometric methods and refined by full-matrix least-squares methods to R = 0068 for 1299 observed reflections. The coordination about the Sn atom is a slightly distorted octahedron. The ethyl 3-oxobutanoate acts as a bidentate ligand bonding to the tin atom through the oxygen atoms. The chloro groups are in* cis *positions and the molecular symmetry is* C_2. *Sn–O(eq) bond length is 2.101(15)* Å. *The Sn–O(ax) and Sn–Cl distances are 2.066(15) and 2.347(7)* Å *respectively. The Cl–Sn–Cl angle is 98.1(1)°.*

Introduction

The reaction between tin(IV) halides and acetylacetone (acacH) has been the subject of a number of publications [1–4]. A recent X-ray diffraction study [5] established unambiguously the crystal structure of dichlorobis(acetylacetonato) ($Cl_2Sn(C_5H_7O_2)_2$) and confirmed the *cis* configuration for the chloro groups predicted by various authors.

Apparently no particular attention has been paid to the properties of $Cl_2Sn(etac)_2$ where etacH = acetoacetic ethyl ester (CH_3COCH_2COOEt). However β-diketones and β-ketoesters have two C=O groups in β-position and we may expect an analogy between them. Is the complex $Cl_2Sn(etac)_2$ *cis* or *trans*? Do ethoxy groups occupy 'axial' or 'equatorial' positions or both? In order to answer, we describe herein the solid state structure of $Cl_2Sn(etac)_2$ and draw some conclusions from comparison with the parent compound $Cl_2Sn(acac)_2$.

Experimental

Preparation

Into a 250 ml 3-neck flask fitted with a nitrogen inlet and mechanical stirrer was placed 30 ml of benzene and 5 g (0.02 mol) EtOTl. To this was added dropwise a solution of 2.6 g ethylacetoacetate (0.02 mol) in 30 ml benzene. After the addition of the ligand was completed, the reaction mixture was stirred for 15 minutes at room temperature. The solution of tin(IV) chloride (0.01 mol in 30 ml benzene) was added. TlCl was filtered out (Millipore 0.45μ filter). $Cl_2Sn(etac)_2$ crystallized by slow evaporation. Crystals were recrystallized from chloroform or benzene. M.p. 134–136 °C. Calcd for $C_{12}H_{18}O_6Cl_2Sn$: C, 32.1; H, 4.0; Cl, 15.8; Sn, 26.5. Found: C, 31.7; H, 4.1; Cl, 16.1; Sn, 26.7.

Crystal Data

Preliminary precession and Weissenberg photographs revealed Laue symmetry *mmm*. The observed systematic extinctions, 0kl for k ≠ 2n, h0l for l ≠ 2n and hk0 for h + k ≠ 2n are compatible with space group Pbcn. The crystal was a parallelepiped of approximate dimensions 0.16 × 0.18 × 0.20 mm. It was bounded by {001} faces perpendiculary to the great dimension and by all forms of {110}. Intensity data were collected on a Philips four-circle diffractometer using the crystal such that the *c* axis was parallel to ϕ. The setting angles of twenty reflections were used to determine least-squares values of the unit cell parameters. The results are: a = 11.818(5), b = 10.408(4), c = 14.155(6) Å at 20 ± 1 °C. The density calculated on the basis of four molecules of $Sn(C_6H_9O_3)_2Cl_2$ per unit cell is 1.71 g cm^{-3}, which is in good agreement with the observed value of 1.74 g cm^{-3} measured pycnometrically in cyclohexane. Intensity measurements utilized monochromatized MoKα radiation (λ = 0.7107 Å) and the θ–2θ scan technique (scan rate = 1°/min).

A total of 2158 reflections having $2\theta \leqslant 54°$ were collected from the octant hkl. The intensities of three standard reflections were monitored periodically at intervals of two hours. No significant fluctuations were observed during the data collection. The data were corrected* for background, Lp and absorption. Absorption correction trials with μ = 18.25 cm^{-1} showed transmission factors ranging from 0.732 to 0.791. Of the 2158 reflections examined, 859 were rejected when the ratio Signal/Noise $\leqslant 2$.

Structure Solution and Refinement

The positions of Sn, Cl and O atoms of the C=O groups were located from a three-dimensional Patterson synthesis and the remaining atoms from subsequent Fourier synthesis (hydrogen not included). Unit-weight full-matrix least-squares refinement employing anisotropic thermal parameters for all atoms resulted in a conventional unweighted residual $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 0.068.

No extinction corrections were made. The atomic form factors of neutral atoms were used [6] together with the tabulated values [7] of $\Delta f'$ and $\Delta f''$ for Sn and Cl. The effects of anomalous dispersion were included in F_c [8]. The shifts in parameters were all less than 0.1σ on the last cycle of refinement. Final atomic coordinates and thermal parameters are presented in Tables I, II. The final F_o and F_c values are available from the Editor.

TABLE I. Atomic coordinates for Dichlorobis(ethyl 3-oxobutanoato)tin(IV).

Atom	*x*	*y*	*z*
Sn	0.00	0.2097(2)	0.2500
Cl	−0.0653(5)[a]	0.3576(6)	0.3627(4)
O(1)	−0.0480(12)	0.0555(14)	0.3369(10)
O(2)	0.1603(12)	0.1891(15)	0.3062(10)
O(3)	−0.0187(13)	−0.1364(15)	0.4026(10)
C(1)	0.0235(20)	−0.0247(22)	0.3729(17)
C(2)	0.1407(20)	−0.0139(24)	0.3804(17)
C(3)	0.2005(20)	0.0867(23)	0.3503(17)
C(4)	0.3280(20)	0.0943(23)	0.3610(17)
C(5)	−0.1432(20)	−0.1625(23)	0.3930(17)
C(6)	−0.1625(20)	−0.3004(23)	0.4241(16)

[a] Standard deviations are given in parentheses here and elsewhere in the manuscript.

TABLE II. Anisotropic Thermal Parameters for Dichlorobis(ethyl 3-oxobutanoato)tin(IV).[a]

Atom	*U(1, 1)*	*U(2, 2)*	*U(3, 3)*
Sn	0.0241(1)	0.0253(1)	0.0442(1)
Cl	0.0406(2)	0.0392(2)	0.0565(2)
O(1)	0.0331(4)	0.0278(4)	0.0426(4)
O(2)	0.0233(4)	0.0304(4)	0.0547(5)
O(3)	0.0401(5)	0.0289(4)	0.0535(5)
C(1)	0.0404(6)	0.0419(6)	0.0256(5)
C(2)	0.0259(6)	0.0437(6)	0.0412(6)
C(3)	0.0224(6)	0.0285(6)	0.0373(6)
C(4)	0.0208(6)	0.0669(7)	0.0543(9)
C(5)	0.0333(6)	0.0327(6)	0.0330(6)
C(6)	0.0594(7)	0.0339(6)	0.0662(9)

Atom	*U(1, 2)*	*U(1, 3)*	*U(2, 3)*
Sn	0.0	−0.0063(1)	0.0
Cl	0.0010(2)	0.0037(1)	−0.0181(2)
O(1)	−0.0034(3)	−0.0030(3)	−0.0009(3)
O(2)	−0.0023(4)	−0.0078(4)	0.0023(4)
O(3)	0.0017(6)	−0.0045(5)	0.0049(4)
C(1)	−0.0020(6)	−0.0035(4)	0.0056(5)
C(2)	0.0075(5)	−0.0056(4)	0.0134(6)
C(3)	0.0117(5)	−0.0056(3)	−0.0120(5)
C(4)	0.0050(6)	−0.0196(5)	−0.0037(6)
C(5)	−0.0182(6)	−0.0031(5)	−0.0010(5)
C(6)	−0.0069(6)	−0.0143(8)	0.0231(7)

[a] Thermal parameters are of the form: $\exp(-2\pi^2\Sigma_i\Sigma_j U_{ij}a_i^* a_j^*)$.

Results and Discussion

The space group and the value of Z put the tin atom in a special position: two-fold axis or center of symmetry. The tin atom was found on the two fold axis which bisects the Cl–Sn–Cl angle and the molecular symmetry is C_2. The structure consists of discrete monomers $Cl_2Sn(C_6H_9O_3)_2$. The intermolecular distances involving non hydrogen atoms less than 4 Å are given in Table III. The shortest intermolecular distance of approach (3.52 Å) is between two C(1) related by the two-fold axis along *b*. We have noted in this table by a superscript* the atoms

TABLE III. Intermolecular Distances (Å).

Cl–C(6)	3.72(4)	O(3)–C(1)*	3.59(5)
O(1)–O(3)	3.86(4)	O(3)–C(2)*	3.74(5)
O(1)–C(6)	3.93(5)	O(3)–C(4)	3.64(5)
O(2)–C(6)*	3.98(5)	C(1)–C(1)*	3.68(6)
O(2)–C(5)	3.97(5)	C(1)–C(1)	3.52(5)
O(2)–C(6)	3.88(5)	C(2)–C(5)	3.69(6)
O(3)–O(1)*	3.86(4)	C(3)–C(5)	3.78(6)
O(3)–O(3)*	3.98(4)	C(3)–C(6)	3.91(6)

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*Calculations were performed on an IBM 370/168 computer of the CIRCE (CNRS) (Orsay) using the following programs: D. Cahen and J. A. Ibers (*J. Appl. Cryst. 5,* 298 (1972)) a modification of AGNOST; A. Rimsky local Fourier and Patterson synthesis program; ORXFLS 3, least-squares program, a modification of W. Busing and H. Levy's ORFLS progam; J. Rigoult local version of TLS program (D.P. Shoemaker and K. N. Trueblood).

of a molecular unit related by the center of symmetry in (000) to their homologues of another molecular unit. This relative proximity should explain the cleavage observed in a direction normal to [001].

The coordination about the tin atom is best described as a distorted octahedral coordination. The chloro groups are in *cis* positions. Of the remaining four octahedral positions two are occupied by the keto-oxygen atom of the ester group (equatorial position) and the other two are occupied by the keto-oxygen of the ligand (axial position). This is shown in Fig. 1.

Two least-squares planes have been calculated. As in the dimethyl [9] and dichloro [5] analogs, the ethyl 3-oxobutanoate ligand is nearly planar with the maximum deviation being 0.304 Å (O(1)) from the plane of equation $-2.34\,x + 4.92\,y + 12.15\,z - 4.18 = 0$. The tin atom is only −0.107 Å from this plane. The equation of the second plane through the two chloro groups, Sn atom and the two keto-oxygen atoms of the ester groups was $10.67\,x + 6.08\,z - 1.52 = 0$. The maximum deviation of any atom from this plane was 0.01 Å. The ligand containing plane makes an angle of 79° with this latter plane. A view of the unit cell is shown in Fig. 2. The intramolecular distances are presented in Fig. 1.

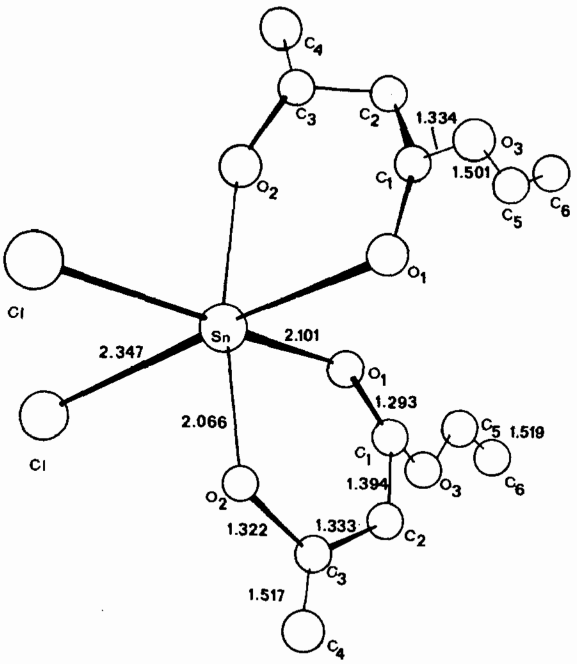


Fig. 1. Molecular geometry and bond distances (in Å) for $Cl_2Sn(C_6H_9O_3)_2$.

Selected bond distances and angles are given in Table IV. In contrast to the compound $Cl_2Sn(C_5H_7O_2)_2$, the Sn–O(2) distance (2.066 Å) is somewhat shorter than the Sn–O(1) distance (2.101 Å). This difference is significant from the standard deviations (Table IV). They agree with the sum of the covalent radii for tin and oxygen (2.11 Å) [10]. The ethyl 3-oxobutanoate bond distances are C(3)–O(2) (1.32 Å), C(2)–C(3) (1.33 Å), C(2)–C(1) (1.39 Å) and C(1)–O(1) (1.29 Å) compared with 1.29, 1.37, 1.40, 1.27, respectively, in the compound $Cl_2Sn(C_5H_7O_2)_2$. The conjugate C–C distances are slightly

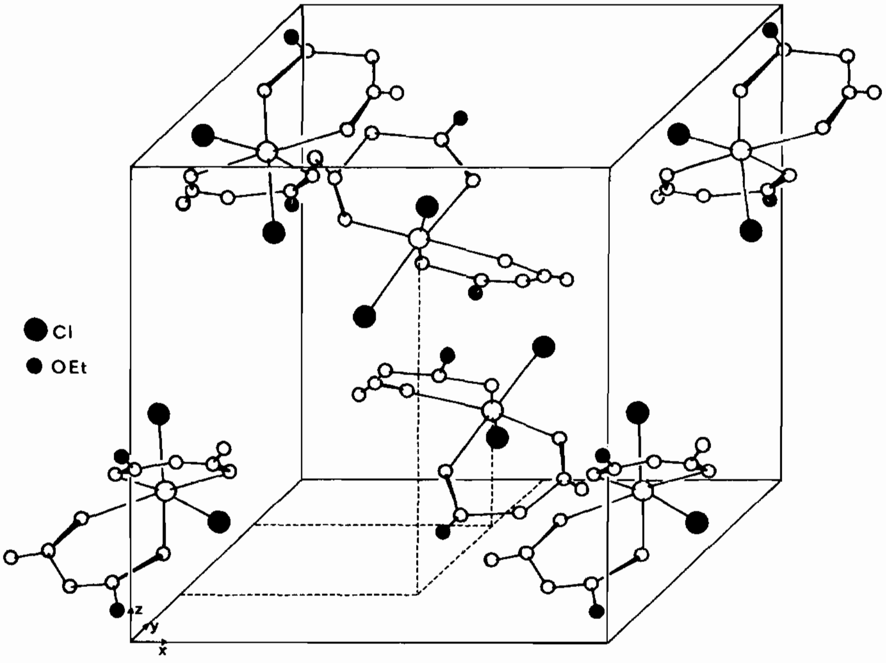
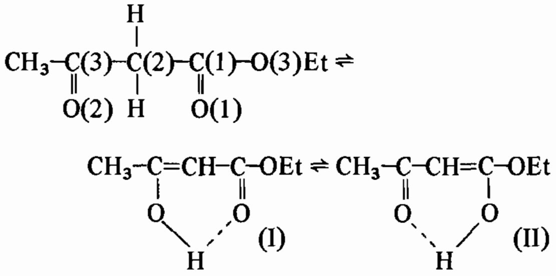


Fig. 2. View of the unit cell.

TABLE IV. Intramolecular Distances and Angles.

Distances (Å)		*Angles* (deg.)	
Sn–Cl	2.347(7)	Cl–Sn–Cl	98.1(1)
Sn–O(1)	2.101(15)	Cl–Sn–O(1)	90.8(1)
Sn–O(2)	2.066(15)	Cl–Sn–O(2)	96.2(1)
O(1)–C(1)	1.293(17)	O(1)–Sn–O(1)	80.4(1)
O(2)–C(3)	1.322(18)	O(1)–Sn–O(2)	86.7(1)
C(1)–O(3)	1.334(17)	O(2)–Sn–O(2)	168.1(9)
C(1)–C(2)	1.394(21)	Sn–O(1)–C(1)	123.1(2)
C(2)–C(3)	1.333(21)	O(1)–C(1)–O(3)	116.2(2)
C(3)–C(4)	1.517(24)	Sn–O(2)–C(3)	126.5(3)
C(5)–O(3)	1.501(20)	C(1)–C(2)–C(3)	124.4(4)
C(5)–C(6)	1.519(24)	O(2)–C(3)–C(2)	126.4(3)
Cl–Cl	3.544(14)	O(2)–C(3)–C(4)	111.1(1)
		O(3)–C(5)–C(6)	107.0(1)
		C(1)–O(3)–C(5)	119.8(2)
		C(2)–C(3)–C(4)	122.4(3)
		O(1)–C(1)–C(2)	129.0(4)

different and may be explained by a larger contribution of structure (I) than of structure (II) in the equilibria:



and this results in a greater shortening of the bonds C(3)–C(2) and C(1)–O(1). In accordance with this explanation the C(2)–C(1) distance is, as observed, longer than the C(3)–C(2) distance. The C(1)–O(3) distance (1.33 Å) presents a double-bond character and the conjugation of bonds should explain the planarity of all the ligand. The Sn–Cl distance of 2.347 Å is comparable to that of 2.345 Å in $SnCl_2(C_5H_7O_2)_2$, somewhat shorter than the sum of the covalent radii (2.39 Å) [10] found in $SnCl_4 \cdot 2$ HMPA [11], where the four Cl atoms are coplanar (2.38–2.40 Å) and Sn on a pseudocenter of symmetry. The intrachelate ring angles at C(1), C(2), and C(3) (124°–129°) are, as in $SnCl_2(C_5H_7O_2)_2$, indicative of some opening of these angles on chelation. The structures of $SnCl_2(C_5H_7O_2)_2$ and $SnCl_2(C_6H_9O_3)_2$ are thus closely related. It should be pointed out that $SnCl_2(C_6H_9O_3)_2$ has been assigned the *cis* stereochemistry on the basis of previous dipole moment study in benzene (μ = 5.73 ± 0.03 D) [12], as compared with $SnCl_2(C_5H_7O_2)_2$ [4].

PMR and ^{13}C NMR studies on the compound were performed in $CDCl_3$ solution and showed a great complexity of the spectra [13]. This may be accounted for by configurational rearrangements of dichlorobis(ethylacetylacetato)tin complex, as described earlier for the dichlorobis(acetylacetonato)-tin complex [3]. The influence of changing the nature of the ligand on the spectra is under active investigation.

References

1 J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc. A*, 1749 (1966).
2 J. W. Faller and A. Davison, *Inorg. Chem.*, *6*, 182 (1967).
3 R. W. Jones and R. C. Fay, *Inorg. Chem.*, *12*, 2599 (1973).
4 W. H. Nelson, *Inorg. Chem.*, *6*, 1509 (1967).
5 G. A. Miller and E. O. Schlemper, *Inorg. Chim. Acta*, *30*, 131 (1978).
6 'International Tables for X-ray Crystallography', vol. 4, Kynoch Press, Birmingham, England, 1974, p. 73.
7 *Ibidem*, vol. 3, 1962, p. 213.
8 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, *17*, 781 (1964).
9 G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, *12*, 677 (1973).
10 L. Pauling, 'The Nature of the Chemical Bond', 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p. 224.
11 J. Angenault, J. C. Couturier, Y. V. Kondratiev and A. Rimsky, unpublished results.
12 D. Bertin, H. Lumbroso and J. Angenault, unpublished results.
13 G. Dana and J. Angenault, unpublished results.