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The Crystal and Molecular Structure of Dichlorobis(2,4-pentanedionato)tin(IV)

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Dichlorobis(2,4-pentanedionato)tin(IV), $SnCl_2(C_5H_7O_2)_2$, crystallizes in the monoclinic space group C2/c with a = *13.937(4),* b = *7.864(2),* c = *13.746(4) Å, β = 107.75(1)°, Z = 4, D_c = 1.796(1) g/cc, and D_m = 1.78 g/cc. The crystal structure was solved by conventional Patterson and Fourier methods using 2053 independent reflection intensities measured by the θ–2θ scan method with a scintillation counter. Refinement by the full-matrix least squares method gave a final agreement factor R(F) of 0.036. The structure consists of discrete molecules with the tin atom in a distorted octahedral configuration. The chloro ligands are in* cis *positions and are related by a crystallographic two-fold axis. The important average bond distances are Sn–Cl (2.345(1)Å), Sn–O (2.058(7)Å), C–O (1.282(8)Å), C–C (conjugated) (1.386(12)Å), and C–C(sp^3) (1.488(5)Å). The Cl–Sn–Cl angle is 96.86(5)°.*

Introduction

The crystal structure of the related compound $(CH_3)_2Sn(C_5H_7O_2)_2$ revealed [1] a *trans* configuration for the methyl group as had been predicted by various authors [2] using other techniques. For the present compound, dichlorobis(2,4-pentanedionato) tin(IV), most previous studies favor a *cis* arrangement of the chloro groups. These studies include NMR [3], Ir–Raman [4, 5], and dipole moment measurement [6]. The latest IR study [5] concludes that the structure is *cis* both in solution and the solid state. Another NMR study [7] favors a planar arrangement of the 2,4-pentanedionato ligands and an alternation between two nonlinear "*trans*" arrangements of the chloro groups. Therefore, in order to unambiguously establish the solid state structure and to compare with the dimethyl analog, the present X-ray diffraction study was done.

Experimental

Preparation

Dichlorobis(2,4-pentanedionato)tin(IV), $Cl_2Sn(C_5H_7O_2)_2$, was prepared by the published method [8] which involves reaction of 2,4-pentanedione with tin tetrachloride in benzene. The compound was recrystallized from benzene-hexane to give well-formed colorless prismatic crystals. The melting point of 202–203 °C is in good agreement with the published value [9] of 202 °C.

X-Ray Data Collection and Reduction

From precession and Weissenberg photographs a monoclinic cell was found. The systematic absences were hkl(h + k = 2n + 1) and h0l (l = 2n + 1). The space group is then C2/c or Cc. The former was confirmed by the successful refinement in C2/c.

A crystal of approximate dimensions 0.25 × 0.50 × 0.50 mm was chosen for intensity measurements. The crystal was bounded by eight faces (100, $\bar{1}00$, 001, $00\bar{1}$, 110, $\bar{1}\bar{1}0$, $1\bar{1}0$, and $\bar{1}10$), consistent with the choice of space group C2/c. The crystal was mounted on a Picker Programmed Four-Angle Diffractometer with the *b* axis coincident with the φ axis for the intensity measurements. Twenty reflections were carefully centered manually and used to refine the cell dimensions and the orientation of the crystal. The cell dimensions resulting from that refinement were *a* = 13.937 [4], *b* = 7.864 [2], *c* = 13.746 [4] Å, and β = 107.75(2)°. These cell dimensions are in fair agreement with those reported earlier [10] of *a* = 14.00, *b* = 7.82, *c* = 13.84, and β = 107.5°. Intensity data were collected by the θ–2θ scan technique (scan rate = 1°/min) using niobium filtered MoKα radiation (λ = 0.7107 Å). The scan width (max 1.2° in 2θ) increased with 2θ to account for the α_1–α_2 splitting. Background was measured for 20 seconds at each end of the scans. Attenuators were used to maintain the maximum count rate at less than 8000 cps which is within the linear range of the scintillation detector. The intensities of 2740 reflections were measured in the 2θ range from 0 to 60°. Four standards were monitored after every fifty reflections and showed no significant change of intensity during the data collection. The raw intensities were reduced* to unscaled F_o^2 values by application

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*Please overleaf for footnote.

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of background, Lp, and absorption corrections (μ = 24.8 cm^{-1}). Sorting and averaging yielded 2103 independent reflections of which the 2053 with $F_o^2 > 2.0\ \sigma(F_o^2)$ were used to solve and refine the structure.

Solution and Refinement of the Structure

The Sn and Cl atoms were located from a three dimensional Patterson synthesis and the remaining atoms from subsequent Fourier and difference Fourier syntheses. Hydrogens were placed in keeping with the difference Fourier synthesis but at near "ideal" X-ray positions (C–H distance ≅ 0.95 Å [11]) and with temperature factors about 1 Å^2 larger than the carbon to which they are attached. Full-matrix least squares refinement minimizing $\Sigma w(F_o^2 - F_c^2)^2$ where $w = 1/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = \sigma^2(\text{counting}) + (0.050\ F_o^2)^2$ converged with $R(F^2) = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2 = 0.076$ and $wR(F^2) = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma w F_o^4]^{1/2} = 0.102$ using all 2053 reflections. The nonhydrogen atoms were refined anisotropically while the hydrogen atoms were held fixed. An isotropic extinction parameter [12] was included and refined to a value of $g = 7.98 \times 10^{-8}$. When twelve reflections (marked with * in the $F_o - F_c$ Table) which were obviously still effected by extinction were omitted from the refinement, $R(F^2) = 0.052$ and $wR(F^2) = 0.097$. The reported structure parameters are from this latter refinement. For C and O scattering factors were taken from Ibers [13a]; those of H from Stewart [13b]; and those of Sn and Cl from Cromer and Waber [13c]. Using the tabulated values [13d] of $\Delta f'$ and $\Delta f''$ for Sn and Cl, the effects of anomalous dispersion were included in F_c [13e]. The shifts in parameters were all less than 0.10 σ on the last cycle of refinement. The standard deviation of an observation of unit weight was 1.66. A

TABLE I. Positional Parameters[a] for Dichlorobis(2,4-pentanedionato)tin(IV).

Atom	X	Y	Z
Sn	0.0(1)	0.2653(1)	0.2500(1)
Cl	−0.0419(1)	0.0674(1)	0.1160(1)
O(1)	0.0364(2)	0.4603(3)	0.3554(1)
O(2)	−0.1447(2)	0.2826(3)	0.2568(2)
C(2)	0.1251(2)	0.4947(3)	0.4125(2)
C(3)	0.2138(2)	0.4334(4)	0.3979(2)
C(4)	0.2202(2)	0.3374(3)	0.3166(2)
C(5)	0.3201(3)	0.2925(6)	0.3066(4)
C(1)	0.1293(2)	0.6153(5)	0.4974(2)
H1(C5)	0.3263	0.1710	0.3052
H2(C5)	0.3699	0.3376	0.3630
H3(C5)	0.3246	0.3425	0.2450
H1(C1)	0.1948	0.6086	0.5461
H2(C1)	0.0808	0.5801	0.5295
H3(C1)	0.1166	0.7271	0.4721
H(C3)	0.2757	0.4618	0.4500

[a] Standard deviations from the least squares refinement are given in parentheses in these tables and elsewhere in the manuscript.

TABLE II. Anisotropic Thermal Parameters[a] for Dichlorobis(2,4-pentanedionato)tin(IV).

Atom	U(1,1)	U(2,2)	U(3,3)	U(1,2)	U(1,3)	U(2,3)
Sn	0.0326(2)	0.0557(2)	0.0376(2)	0.0(1)	−0.0001(1)	0.0(1)
Cl	0.0543(4)	0.0767(5)	0.0636(4)	0.0103(3)	−0.0077(3)	−0.0238(3)
O(1)	0.0521(9)	0.0717(11)	0.0488(9)	−0.0062(8)	0.0112(7)	−0.0081(8)
O(2)	0.0371(10)	0.0840(13)	0.0513(12)	0.0008(8)	0.0075(9)	0.0046(9)
C(2)	0.0624(14)	0.0576(13)	0.0418(11)	−0.0154(11)	0.0101(10)	0.0013(9)
C(3)	0.0468(11)	0.0665(15)	0.0551(14)	−0.0136(11)	−0.0020(10)	−0.0035(11)
C(4)	0.0372(10)	0.0549(12)	0.0569(12)	−0.0050(9)	0.0045(9)	0.0052(10)
C(5)	0.0392(15)	0.0938(22)	0.0990(30)	−0.0074(16)	0.0113(17)	−0.0138(24)
C(1)	0.0836(18)	0.0805(21)	0.0663(16)	−0.0256(15)	0.0234(14)	−0.0239(15)
H1(C5)	0.0950					
H2(C5)	0.0950					
H3(C5)	0.0950					
H1(C1)	0.0950					
H2(C1)	0.0950					
H3(C1)	0.0950					
H(C3)	0.0950					

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

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*All calculations were performed on the IBM 370/168 computer system of the University of Missouri. The following programs from other scientists were used: W. C. Hamilton and J. A. Ibers, NUPIK, Picker input program; R. Doedens and J. A. Ibers, NUCLS, least-squares program, a modification of W. Busing and H. Levy's ORFLS program; A. Zalkin, FORDAP, Fourier synthesis program; W. Busing and H. Levy, ORFFE, function and error program; C. Johnson, ORTEP, thermal ellipsoid plot program; W. C. Hamilton, HORSE, general absorption program; W. C. Hamilton, SORTH, sorting program.

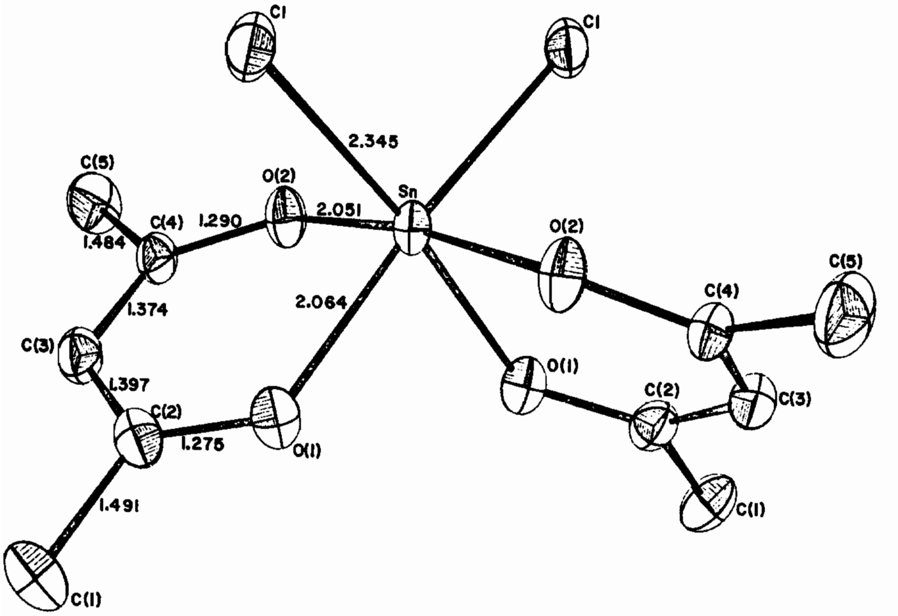

Figure 1. Molecular geometry, atom labelling and bond distances for dichlorobis(2,4-pentanedionato)tin(IV). The standards are Sn–Cl (±0.002); Sn–O (±0.002); C–O (±0.003); and C–C (±0.004).

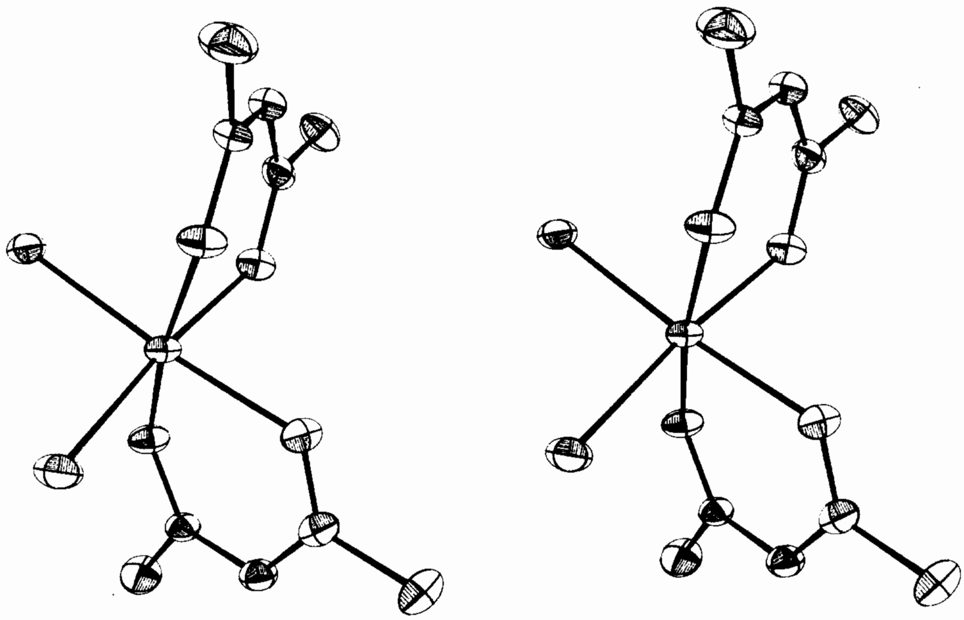

Figure 2. Stereoscopic view of the molecular structure of dichlorobis(2,4-pentanedionato)tin(IV).

final difference Fourier synthesis revealed maximum residuals in the near vicinity of the tin atom (>1.0 $e^-/Å^3$). The final positional parameters are in Table I and the thermal parameters in Table II. The final F_o and F_c values are available from the Editor.

Results and Discussion

The structure consists of discrete molecular units of $Cl_2Sn(C_5H_7O_2)_2$. The chloro groups are in *cis* positions in the distorted octahedral coordination of the tin(IV) atom. The other four positions are occupied by the oxygen atoms of the two bidentate 2,4-pentanedionate ligands as shown in Figure 1. The molecule is required by the space group and the value of Z to possess either a two fold axis or a 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 crystal contains an enantiomeric mixture of the dissymetric molecules.

TABLE III. Bond Angles in Dichlorobis(2,4-pentanedionato)-tin(IV).

O(2)–Sn–O(2)[a]	172.4(1)	O(1)–C(2)–C(1)	114.6(2)
O(1)–Sn–Cl	173.4(1)	O(1)–C(2)–C(3)	125.0(2)
O(1)–Sn–O(2)	87.3(1)	C(1)–C(2)–C(3)	120.4(3)
O(1)–Sn–O(1)[a]	84.0(1)	C(2)–C(3)–C(4)	125.9(3)
O(1)–Sn–O(2)[a]	87.0(1)	O(2)–C(4)–C(3)	125.4(2)
Cl–Sn–Cl[a]	96.86(5)	O(2)–C(4)–C(5)	114.4(3)
Sn–O(1)–C(2)	125.0(2)	C(3)–C(4)–C(5)	120.2(3)
Sn–O(2)–C(4)	124.5(2)		

[a] Related by the molecular two-fold axis.

Intermolecular contacts are not unusually short. The only intermolecular distances involving nonhydrogen atoms less than 3.7 Å are Cl–C(5) = 3.655(4) Å, O(1)–C(1) = 3.555(4) Å, and O(2)–C(1) = 3.417(4) Å. As in the dimethyl analog [1] the 2,4-pentanedionate ligand is nearly planar with the maximum deviation of any nonhydrogen atom being 0.205(2) Å for O(1) from the plane of equation $-1.07x - 5.76y + 9.18Z - 0.78 = 0$. The tin atom is only 0.01 Å from that plane.

The anisotropic thermal motion is best observed in the stereoscopic view (Figure 2). While most of the atoms are vibrating fairly isotropically, C(5) derivates the most with much larger vibration perpendicular to the C–C bond than along it. In general, the maximum vibrations of the atoms are nearly perpendicular to the interatomic directions and the minimums nearly along those axes, as is usually observed.

The intramolecular distances are presented in Figure 1 and the bond angles in Table III. The average Sn–O distance (2.058(7) Å) is much shorter than that (2.19(1) Å) observed for the *trans* dimethyl analog [1] and is significantly shorter than that (2.11(2) Å) observed [14] for $(C_5H_7O_2)_2SnCo_2(CO)_7$ where the 2,4-pentanedianato ligands are chelating in a similar manner to that observed here. In the tin–cobalt compound [14] the two Co atoms are in *cis* positions in the tin octahedron. To our knowledge, these are the shortest known Sn–O distances. The 2,4-pentanedionate bond distances in the Co–Sn compound are C–O (1.30(2) Å), C–C (conjug.) (1.36(4) Å), and C–C(sp^3) (1.55(2) Å) compared with 1.282(8), 1.386(12), and 1.488(5) Å, respectively, in the present compound. Except for the C–C(sp^3) distance, these values agree within experimental error with each other and with those observed in the *trans* dimethylbis(2,4-pentanedionato)tin(IV) complex [1] of 1.28(2), 1.40(4) and 1.52(2) Å, respectively. The conjugated C–C distances are unequal in the present compound (1.374(4) and 1.397(4) Å) as they are (1.36(2) and 1.44(2) Å) in the *trans* dimethyl compound [1]. This difference is apparently real as it has also been observed in other complexes with chelating 2,4-pentanedionate such as $Be(C_5H_7O_2)_2$ [15] where the two average C–C distances in the four independent 2,4-pentanedionate ligands are 1.37(1) and 1.40(2) Å. The Sn–Cl distance of 2.345(1) Å is comparable to that of 2.33(2) Å in $SnCl_4 \cdot 2POCl_3$ [16] and near the sum of the covalent radii (2.39 Å) [17]. The bond angles in the tin octahedron all deviate from ideal octahedral values, apparently largely due to the steric requirements of the chloro ligands (the Cl–Sn–Cl angle is 96.86(5)°). The intra-chelate ring angles at C(2), C(3), and C(4) are all significantly larger (125.0–125.9°) than the "ideal" 120° value, indicative of some opening of these angles on chelation. A similar effect has been observed in other bidentate 2,4-pentadionate complexes. For example, in azidobis(2,4-pentanedionato)manganese-(III) [17], these angles range from 124.2–124.5°. The "opening" in the Mn(III) complex is less pronounced because of the smaller size of Mn(III) (Mn–O = 1.910 Å) compared with Sn(IV) (Sn–O = 2.058 Å).

The observed *cis* configuration of the chloro groups is in keeping with the findings of other workers [2–7] in solution as well as the solid state. The possibility of preparation of a *trans* isomer analogous to the *trans*-dimethylbis(2,4-pentanedionato)tin(IV) [1], under certain conditions cannot be eliminated.

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