

THE MOLECULAR STRUCTURE OF (ACETYLACETONATO)DICHLORO-DIPHENYLANTIMONY IN THE CRYSTALLINE STATE

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SUMMARY

Crystals of (acetylacetonato)dichlorodiphenylantimony are monoclinic ($P2_1/c$) with cell dimensions $a=13.24$, $b=9.22$, $c=15.49$ Å and $\beta=109.24^\circ$ ($Z=4$). The structure determined by a three-dimensional X-Ray analysis was refined with 2633 independent diffractometer data to a final R value of 0.075. The antimony atom is hexacoordinated, with the phenyl groups in *trans*-positions.

INTRODUCTION

In recent years the synthesis and structural investigation of two series of organoantimony complexes $R_nSbCl_{(4-n)}X$ in which R represents a methyl or phenyl group, $n=1-4$ and X stands for an acetylacetonate or 8-oxyquinolate ligand have been the subject of several studies (*cf.* refs. 1-4 and references cited therein). PMR, UV, IR and Raman spectroscopy have been applied to elucidate the structures of these complexes²⁻⁴. In the series of organoantimony(V) acetylacetonates, $R_nSbCl_{(4-n)}Acac$, the diphenyl derivative has been found to show exceptional behaviour in that two isomers are present in solution^{1,5}. A comprehensive spectroscopic and dipole moment study of the complete series of compounds led to the conclusion that in the stereoisomer which shows the *Acac* proton PMR signals at highest field, the two phenyl groups occupy *trans*-positions in an octahedral structure, whereas in the "low-field" isomer the phenyl groups occupy *cis*- and the chlorine atoms *trans*-positions (*cf.* preceding paper²). Moreover the PMR data allowed the conclusion that in the *trans*-diphenyl isomer the phenyl groups have a preferred conformation perpendicular to the *Acac* ligand C-H axis².

Although the solid-state structure of several organoantimony(V) compounds has been determined in recent years using X-Ray diffraction techniques, [Ph_3SbCl_2]⁶, $Ph_3Sb(OMe)_2$ ⁷, Ph_4SbOH ⁸, Ph_4SbOMe ⁷, Ph_5Sb ^{9,10}], so far the structure of only one hexacoordinate organoantimony(V) compound has been elucidated, namely that of $Ph_2SbCl_3 \cdot H_2O$ ¹¹. This compound was found to possess a distorted octahedral structure in which the two phenyl groups occupy *trans*-positions.

In order to shed light on the solid-state structure of Ph_2SbCl_2Acac a single-crystal X-Ray diffraction study of this compound has been undertaken.

EXPERIMENTAL

Single crystals of $\text{Ph}_2\text{SbCl}_2\text{Acac}$, grown from carbon tetrachloride, were supplied by Dr. H. A. Meinema. Intensity measurements were made on an automatic Nonius three-circle diffractometer equipped with a scintillation counter and a discriminator. The ω -scan technique was applied; the radiation used was $\text{Cu-K}\alpha$. The cell dimensions measured on the same equipment were: $a = 13.24$, $b = 9.22$, $c = 15.49$ Å and $\beta = 109.24^\circ$. From systematic absences the space group was determined as $P2_1/c$. With four molecules in the unit cell the calculated density was 1.66 g/cm^3 . The intensity data were reduced to a set of observed amplitudes on an arbitrary scale. Absorption was neglected, since a high accuracy was not required for the purposes of this investigation. The maximum and minimum dimensions of the irregularly shaped crystals are 0.5 and 0.3 mm respectively; the linear absorption coefficient $\mu = 161 \text{ cm}^{-1}$.

Patterson analysis and subsequent Fourier synthesis with the heavy-atom technique lead to a structure which was refined by the block-diagonal least-squares method to a final R value of 0.075. Three reflexions were removed, because they were thought to be suffering from extinction. Their indices and values of the observed and calculated structure-factor moduli are: 200, 268, 317; $10\bar{2}$, 186, 238 and 022, 235, 274 respectively. Atomic form factors were used according to the analytical expression of Cromer and Mann¹². The anomalous part of the scattering power of Sb was taken from values given by Rietveld¹³.

The final parameters are given in Table 1. Numbering of the atoms in the mole-

TABLE 1

FINAL FRACTIONAL ATOMIC COORDINATES, THEIR ESTIMATED STANDARD DEVIATIONS AND THERMAL PARAMETERS

The β_{ij} coefficients are given by the expression for the temperature factor: $\sum_{i=1}^3 \sum_{j=1}^3 \exp(-h_i \cdot h_j \cdot \beta_{ij} \cdot 10^{-5})$.
Estimated standard deviations: $\sigma_{\text{Sb}} = 0.001$, $\sigma_{\text{Cl}} = 0.003$, $\sigma_{\text{O}} = 0.010$ and $\sigma_{\text{C}} = 0.015$ Å.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{23}$	$2\beta_{31}$
Sb	0.24770	0.08445	0.16169	448	483	187	-22	164	166
Cl(2)	0.3870	-0.0099	0.2938	800	906	340	247	324	1
Cl(3)	0.1006	0.0103	0.2112	773	1042	485	-588	-213	693

Atom	x	y	z	$B (\text{\AA}^2)$	Atom	x	y	z	$B (\text{\AA}^2)$
O(4)	0.3652	0.1492	0.1043	2.9	C(14)	0.1806	0.5035	0.2650	4.7
O(5)	0.1348	0.1841	0.0471	2.6	C(15)	0.3685	0.4988	0.2891	5.2
C(6)	0.3490	0.2141	0.0295	2.3	C(16)	0.2785	0.5712	0.2962	5.5
C(7)	0.1521	0.2480	-0.0188	2.5	C(17)	0.2359	-0.1074	0.0827	2.5
C(8)	0.2504	0.2594	-0.0309	3.4	C(18)	0.3205	-0.2078	0.1053	4.7
C(9)	0.0547	0.3162	-0.0855	4.4	C(19)	0.1462	-0.1281	0.0070	4.3
C(10)	0.4511	0.2414	0.0062	4.4	C(20)	0.3141	-0.3267	0.0478	5.2
C(11)	0.2594	0.2933	0.2233	2.8	C(21)	0.1432	-0.2469	-0.0495	4.7
C(12)	0.1698	0.3638	0.2289	3.9	C(22)	0.2249	-0.3440	-0.0291	5.0
C(13)	0.3593	0.3589	0.2515	3.7					

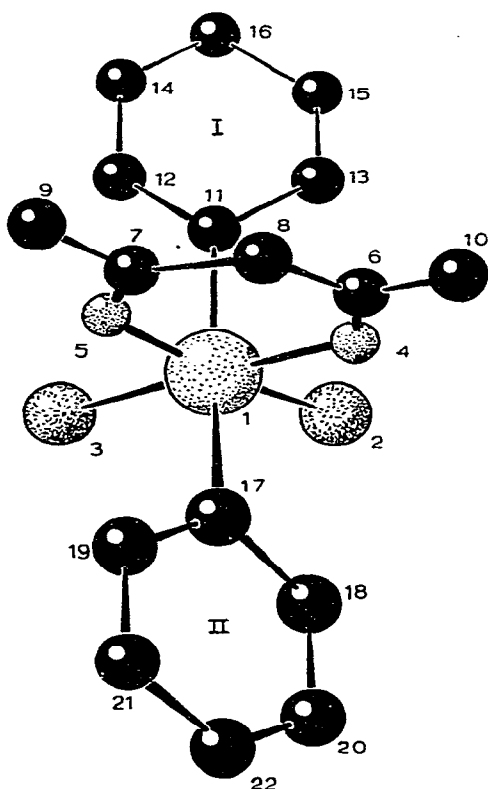


Fig. 1. Structure of the $\text{Ph}_2\text{SbCl}_2\text{Acac}$ molecule.

cule is as shown in Fig. 1. A list of the observed and calculated structure factors may be obtained on application to the authors.

DISCUSSION

Table 2 gives the bond lengths, bond angles and their estimated standard deviations for the $\text{Ph}_2\text{SbCl}_2\text{Acac}$ molecule. The complex has a distorted octahedral configuration in which the phenyl groups occupy trans positions. A *trans*-diphenyl structure has also been reported for the octahedral molecule of $\text{Ph}_2\text{SbCl}_3 \cdot \text{H}_2\text{O}$ ¹¹. For both compounds the deviation from linearity of the Ph-Sb-Ph configuration is significant. Within error we can say that the bend takes place in the pseudo mirror plane through Sb, C(11) and C(17), away from the chlorine atoms. The Sb-Cl distances (mean value: 2.42 Å) of $\text{Ph}_2\text{SbCl}_2\text{Acac}$ fall within the two non-equivalent Sb-Cl distances (2.34 and 2.48 Å) quoted for $\text{Ph}_2\text{SbCl}_3 \cdot \text{H}_2\text{O}$. The Sb-O distances for the acetylacetonato complex (Sb-O: 2.12 Å) and $\text{Ph}_2\text{SbCl}_3 \cdot \text{H}_2\text{O}$ (Sb-O: 2.20 Å) are appreciably different. The average distance of the atoms of the acetylacetonato group to the least-squares plane through this group is 0.03 Å, the maximum distance being 0.06 Å.

Distortion from C_{2v} symmetry is mainly due to the rotational positions of the phenyl groups. From PMR data² it was inferred that the normals of the phenyl groups were nearly parallel with the bisector of the Cl-Sb-Cl angle. We found deviations of

TABLE 2

BOND LENGTHS AND BOND ANGLES IN THE (ACETYLACETONATO)DICHLORODIPHENYLANTIMONY MOLECULE

Estimated standard deviations are given in parentheses.

<i>Bond distances (Å)</i>			
Sb-Cl(2)	2.421 (3)	C(11)-C(12)	1.38(2)
Sb-Cl(3)	2.415 (3)	C(11)-C(13)	1.39(2)
Sb-O(4)	2.117(10)	C(12)-C(14)	1.39(2)
Sb-O(5)	2.116(10)	C(13)-C(15)	1.40(2)
Sb-C(11)	2.132(12)	C(14)-C(16)	1.38(2)
Sb-C(17)	2.127(12)	C(15)-C(16)	1.40(2)
O(4)-C(6)	1.26 (2)	C(17)-C(18)	1.40(2)
O(5)-C(7)	1.26 (2)	C(17)-C(19)	1.38(2)
C(6)-C(8)	1.40 (2)	C(18)-C(20)	1.40(2)
C(7)-C(8)	1.38 (2)	C(19)-C(21)	1.39(2)
C(6)-C(10)	1.53 (2)	C(20)-C(22)	1.38(2)
C(7)-C(9)	1.50 (2)	C(21)-C(22)	1.36(2)
<i>Bond angles (°)</i>			
Cl(2)-Sb-Cl(3)	95.7(1)	C(5)-C(7)-C(9)	114.1(1.5)
Cl(2)-Sb-O(4)	89.7(3)	C(6)-C(8)-C(7)	127.0(1.5)
Cl(2)-Sb-O(5)	175.2(3)	C(8)-C(6)-C(10)	119.7(1.5)
Cl(3)-Sb-O(4)	173.6(3)	C(8)-C(7)-C(9)	120.8(1.5)
Cl(3)-Sb-O(5)	88.2(3)	C(12)-C(11)-Sb	121.1(5)
O(4)-Sb-O(5)	86.5(4)	C(13)-C(11)-Sb	117.1(1.5)
C(11)-Sb-C(17)	171.6(5)	C(18)-C(17)-Sb	120.2(5)
Cl(2)-Sb-C(11)	91.3(4)	C(19)-C(17)-Sb	118.9(5)
Cl(2)-Sb-C(17)	94.5(4)	C(11)-C(12)-C(14)	118.9(1.5)
Cl(3)-Sb-C(11)	93.4(4)	C(12)-C(14)-C(16)	121.4(1.5)
Cl(3)-Sb-C(17)	91.9(4)	C(14)-C(16)-C(15)	118.9(1.5)
C(11)-Sb-O(4)	88.8(9)	C(16)-C(15)-C(13)	120.7(1.5)
C(11)-Sb-O(5)	84.9(9)	C(15)-C(13)-C(11)	118.4(1.5)
C(17)-Sb-O(4)	85.3(9)	C(13)-C(11)-C(12)	121.7(1.5)
C(17)-Sb-O(5)	88.9(9)	C(17)-C(18)-C(20)	118.9(1.5)
C(6)-O(4)-Sb	126.5(9)	C(18)-C(20)-C(22)	119.6(1.5)
C(7)-O(5)-Sb	127.9(9)	C(20)-C(22)-C(21)	120.9(1.5)
C(4)-C(6)-C(8)	126.7(1.5)	C(22)-C(21)-C(19)	121.0(1.5)
C(5)-C(7)-C(8)	125.2(1.5)	C(21)-C(19)-C(17)	118.7(1.5)
C(4)-C(6)-C(10)	113.5(1.5)	C(19)-C(17)-C(18)	120.8(1.5)

13 and 25° for the phenyl groups I and II respectively, their dihedral angle amounting to 38°.

With the hydrogen atoms left out of consideration, all intermolecular distances are greater than 3.5 Å.

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REFERENCES

- 1 H. A. Meinema and J. G. Noltes, *J. Organometal. Chem.*, 16 (1969) 257.
 - 2 H. A. Meinema, A. Mackor and J. G. Noltes, *J. Organometal. Chem.*, 37 (1972) 285.
 - 3 H. A. Meinema, E. Rivarola and J. G. Noltes, *J. Organometal. Chem.*, 17 (1969) 71.
 - 4 H. A. Meinema and J. G. Noltes, *Organoantimony Coordination Chemistry*, Institute for Organic Chemistry TNO, Utrecht, 1971.
 - 5 N. Nishii, Y. Matsumura and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 703.
 - 6 T. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 7 (1966) 742.
 - 7 K. W. Shen, W. E. McEwen, S. J. la Placa, W. C. Hamilton and A. P. Wolf, *J. Amer. Chem. Soc.*, 90 (1968) 1718.
 - 8 A. L. Beauchamp, M. J. Bennett and F. A. Cotton, *J. Amer. Chem. Soc.*, 91 (1969) 297.
 - 9 P. J. Wheatly, *J. Chem. Soc.*, (1964) 3718.
 - 10 A. L. Beauchamp, M. J. Bennett and F. A. Cotton, *J. Amer. Chem. Soc.*, 90 (1968) 6675.
 - 11 T. N. Polynova and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 8 (1967) 112.
 - 12 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, 24 (1968) 321.
 - 13 H. M. Rietveld, *Fysica Memo* 153, R. C. N., Petten, The Netherlands, 1966.
- J. Organometal. Chem.*, 37 (1972)