ACTA CHEMICA SCANDINAVICA 15 (1961) 167–174

The Crystal Structure of $SbCl_5 \cdot PO(CH_3)_3$

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The crystal structure of $SbCl_5 \cdot PO(CH_3)_3$ has been determined and refined from three-dimensional X-ray data. The compound is isomorphous with $SbCl_5 \cdot POCl_3$. The Sb—O and P—O bond lengths are 1.99 ± 0.02 Å and 1.61 ± 0.02 Å, respectively. The Sb—O—P bond angle is 139.0° ± 2.4°.

Comparisons are made with the structures of $PO(CH_3)_3$ and $SbCl_5 \cdot POCl_3$. The predictions of the bond length variations in these compounds based on the theory for inductive effects on polar bonds has been confirmed. The nature of the P—O bond is briefly discussed.

The compounds $PO(CH_3)_3$ and $POCl_3$ both form adducts with a great number of Lewis acids. Sheldon and Tyree [1] have concluded from the shifts in the phosphoryl-bond stretching frequency that the oxygen atom functions as the donor atom in both these molecules; this was also found in the structure determination of $SbCl_5 \cdot POCl_3$[2]. We have found it interesting to compare the structures of the two similar addition compounds $SbCl_5 \cdot POCl_3$ and $SbCl_5 \cdot PO(CH_3)_3$.

CRYSTAL DATA

Single crystals of the compound $SbCl_5 \cdot PO(CH_3)_3$ were prepared by Olovsson in a way described earlier [3]. The crystals were stable in air during the time of exposure.

The unit cell dimensions of these orthorhombic crystals are very similar to those of $SbCl_5 \cdot POCl_3$, and the two compounds belong to the same space-group *Pnma* (extinctions $0kl$ for $k + l$ odd and $hk0$ for h odd).

The cell-dimensions of $SbCl_5 \cdot PO(CH_3)_3$ were determined from powder photographs taken in a camera of the Guinier type using $CrK\alpha_1$-radiation and with silicon ($a = 5.4306$ Å) as internal standard. They are listed below together with those of $SbCl_5 \cdot POCl_3$.

$SbCl_5 \cdot PO(CH_3)_3$	$SbCl_5 \cdot POCl_3$
$a = 16.66 \pm 0.02$ Å	$a = 16.42 \pm 0.01$ Å
$b = 8.205 \pm 0.01$ Å	$b = 8.06 \pm 0.01$ Å
$c = 8.865 \pm 0.01$ Å	$c = 8.93 \pm 0.02$ Å

The crystals are needle-shaped with the a-axis as needle-axis. A needle was cut in an approximately cubic form (0.005 × 0.005 × 0.006 mm) and mounted with the c-axis as rotation axis. Weissenberg photographs were taken. 8 zones (0—7) were recorded with CuK-radiation using the multiple-film technique. In order to get a connection between the zones a needle was mounted along the a-axis (dimensions 0.01 × 0.02 × 0.25 mm) and 2 zones (0—1) were recorded in a similar way. (We are indebted to Mr. A. Czartoryski for help with the X-ray work.)

The 420 independent intensities were estimated visually. The relative $|F|^2$-values were obtained after correction using a modified Lu-procedure [4].

The number of molecules in the unit cell is 4. No correction was made for absorption errors, the linear absorption coefficient is 303.1 cm^{-1} for Cu$K\alpha$.

DETERMINATION OF THE ATOMIC POSITIONS

As this compound has very similar cell-dimensions and belongs to the same space-group as $SbCl_5 \cdot POCl_3$, it was assumed that the two structures were isomorphous. The intensities of the two compounds showed rather close agreement.

From the final parameters of the Sb, 5Cl and P positions of $SbCl_5 \cdot POCl_3$, the signs were determined for 300 of 420 observed $F(h,k,l)$. This, and the following calculations were made on the electronic computer BESK in Stockholm, using the programs made by Åsbrink *et al.*[5] and Westman *et al.*[6] For the structure-factor program the constants given by Vand *et al.*[7] were used. The signs thus obtained were used for a three-dimensional electron density calculation. New parameters for the assumed positions were then obtained and the O-atom was located.

New signs were determined and from a difference synthesis with (F_{obs} — F_{Sb}) as Fourier coefficients approximate coordinates could be assigned to the C-atoms.

REFINEMENT AND ASSESSMENT OF ACCURACY

In order to avoid termination errors in the localization of the maxima, the refinement of the coordinates was carried out in the following way. (Unfortunately a least-squares program is not yet available for the computer BESK, so that this method could not be used.)

One F_{obs} and one F_{calc} synthesis were calculated and backshift corrections were applied to the Sb-parameters.

One difference synthesis with ($F_{obs} - F_{Sb}$) and one synthesis with ($F_{Cl} + F_P + F_O + F_C$) as Fourier coefficients were then computed. Back-shift cor-

rections were applied to the Cl-, P-, O- and C_2-parameters. C_2 is the carbon atom in the eight-fold position 8(d) of *Pnma*. A back-shift correction applied to the parameters of atom C_1 would, however, bring that atom too close to the P atom, the bond length would only be of the order of 1.4 Å. The reason for this is probably that the $F_{obs} - F_{Sb}$ synthesis is affected by errors of different kind, such as termination effects, errors due to anisotropic thermal vibration of the Sb atom and errors in the observed F-values. From the shape of the $(CH_3)_3PO$-part of the molecule, it may be safely assumed, however, that the position of C_1 is not entirely wrong. In all similar structures it has been found that there are only small changes in the structure of the donor molecule by adduct formation $|SbCl_5 \cdot POCl_3$[2], $(TiCl_4 \cdot POCl_3)_2$[8] and $SnCl_4 \cdot 2POCl_3$[9]$|$.

In order to try to locate this atom more accurately, without making corrections for these errors, a difference-synthesis was calculated where the contributions from all atoms except the C_1-atom were subtracted from the observed F-values. The C_1-position derived from this function gave a more reasonable P—C distance, but the peak was rather broad, and the maximum position could not be located with good accuracy.

At this stage ln F_{obs}/F_{calc} was plotted against the calculated intensity giving a straight line. The linear variation of ln F_{obs}/F_{calc} was assumed to depend mainly on secondary extinction [10] and the correction was applied to the observed F-values.

Two successive back-shift corrections were then carried out, in the same way as before, for the Cl, P, O and C_2 atoms. No correction was applied to C_1 and no attempt made to locate the hydrogen atoms.

Cruickshank's method [11] was used to obtain an estimate of the standard deviations in the atomic coordinates. The last backshift corrections gave smaller shifts than the standard deviations.

In order to get better accuracy in the coordinates of atom C_1 a new difference synthesis was calculated in the same way as before. The maximum was, however, still rather broad. No attempt was made to estimate the standard deviations of the parameters of this atom.

The standard deviations obtained are given in Table 1 together with the final parameters. Using a temperature-factor of 4.07 Å^2 the reliability index $R = \Sigma||F_{obs}| - |F_{calc}||/\Sigma|F_{obs}|$ for all observed reflections is 0.13.

Table 1. Final atomic parameters and their standard deviations.

Atom	x	y	z	$\sigma(x)$ Å	$\sigma(y)$ Å	$\sigma(z)$Å
Sb	0.1454	0.2500	0.0710	0.002	—	0.002
Cl_1	0.2615	0.2500	0.9269	0.010	—	0.011
Cl_2	0.0258	0.2500	0.2150	0.011	—	0.013
Cl_3	0.2240	0.2500	0.2871	0.016	—	0.016
Cl_6	0.1424	0.9641	0.0541	0.011	0.012	0.011
P	0.0794	0.2500	0.7074	0.009	—	0.010
O	0.0749	0.2500	0.8890	0.019	—	0.021
C_1	0.4800	0.2500	0.8800			
C_2	0.1397	0.0707	0.6375	0.04	—	0.06

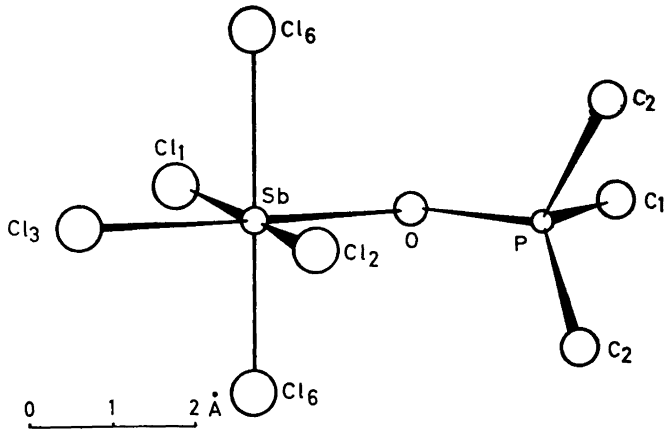

Fig. 1. The molecule of the addition compound $SbCl_5 \cdot PO(CH_3)_3$.

A copy of the observed and calculated F-values can be obtained from this Institute by request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The main features of the structures of $SbCl_5 \cdot PO(CH_3)_3$ and $SbCl_5 \cdot POCl_3$ are the same. The structure of one adduct molecule is given in Fig. 1. The bond lengths and bond angles are given in Table 2 together with their standard deviations. The shortest packing distances are given in Table 3.

The bond lengths in this compound offer interesting comparisons with those in the corresponding adduct $SbCl_5 \cdot POCl_3$ and in the free donor molecule $PO(CH_3)_3$[12]. A number of points are discussed in the following.

Table 2. Bond distances and bond angles in $SbCl_5 \cdot PO(CH_3)_3$ and their standard deviations

	Distance (Å)	S.D. (Å)		Angle (°)	S.D.(°)
$Sb-Cl_1$	2.32	0.012	$O-Sb-Cl_1$	92.7	0.7
$Sb-Cl_2$	2.37	0.012	$Cl_1-Sb-Cl_3$	89.1	0.5
$Sb-Cl_3$	2.32	0.016	$Cl_3-Sb-Cl_2$	91.7	0.5
$Sb-Cl_6$	2.35	0.012	Cl_2-Sb-O	86.6	0.7
$Sb-O$	1.99	0.02	$Cl_6-Sb-Cl_6$	172.3	0.4
$P-O$	1.61	0.02	Cl_6-Sb-O	86.4	0.6
$P-C_1$	1.85		$Cl_6-Sb-Cl_1$	89.0	0.4
$P-C_2$	1.89	0.05	$Cl_6-Sb-Cl_3$	93.7	0.5
			$Cl_6-Sb-Cl_2$	90.9	0.4
			$Sb-O-P$	139.0	1.3
			$O-P-C_2$	110.7	1.9
			$O-P-C_1$	111.9	
			C_1-P-C_2	109.8	
			C_2-P-C_2	102.4	2.4

Table 3. Packing distances in $SbCl_5 \cdot PO(CH_3)_3$ (*cf.* Fig. 2 in the structure of $SbCl_5 \cdot POCl_3$ (Ref.[2]) where Cl_4 should be replaced by C_1 and Cl_5 by C_2.)

	Distance (Å)
$Cl_1 - C_1$	3.66
$Cl_{6A} - Cl_{1B}$	4.07
$Cl_{6A} - C_{1E}$	3.95
$Cl_{6A} - C_{2B}$	3.72
$Cl_{6A} - Cl_{3C}$	3.69
$C_{2A} - Cl_{3C}$	3.72
$C_{2A} - Cl_{1C}$	3.62
$C_{2A} - C_{1D}$	4.01
$C_{2A} - Cl_{2E}$	4.03

1. Firstly the predictions based on the theory for inductive effects on polar bonds proposed by Lindqvist [13] can be checked. If we compare $SbCl_5 \cdot PO(CH_3)_3$ with $SbCl_5 \cdot POCl_3$ we have to consider the inductive effect of the substitution of chlorine for the methyl group. This corresponds to an increased electron withdrawal from the phosphorus atom and complete predictions have been made for this case [13]. The P-O bond should be stronger, because the net charge on the oxygen atom is negative, and the Sb-O bond should be weaker because the net charge on the antimony atom is positive (see the reference paper for details.) The P-O bond length has actually decreased from 1.61 to 1.46 Å, and the Sb-O bond length increased from 1.99 to 2.18 Å. (The last values are those found in the $POCl_3$ adduct.) The predictions are thus fully confirmed and this example can be added to the examples presented in Table 4 of the earlier reference [13].

2. A comparison with the free donor molecule shows the effect of addition reactions, which also was discussed by Lindqvist [13]. The adduct formation would, according to that picture, cause an electron withdrawal from the donor atom. This would give rise to a loss of bond energy for the P-O bond, because the net charge on the phosphorus atom is positive. (The further assumption is then made that no important change of the valence state of the donor atom has taken place.) The P-O bond length has actually increased from 1.48 to 1.61 Å by the adduct formation, a very obvious effect.

The effect on the adjacent P-C bond is more difficult to predict. The net charge on the carbon atom in the phosphine $P(CH_3)_3$ is certainly negative, but in the oxide $PO(CH_3)_3$, the electron attraction of the oxygen atom probably has reduced this negative net charge appreciably as a secondary effect. It is then difficult to make safe predictions about the inductive effect, (the limitations are discussed in the above-mentioned paper [13]). The experimental values for the P-C bonds in the present compound are rather uncertain. The bond length has increased from 1.81 to 1.87 Å (averaged values) but the standard deviation might be as large as 0.1 Å. The P-C asymmetric stretching frequency shows, on the other hand, a positive shift, which might indicate a bond strengthening [14]. The problem is thus still open for discussion at this point.

3. It is a striking fact that, in the two $SbCl_5$ adducts compared, bond lengths between the same atoms show appreciable differences. The variations can be discussed in a very approximately resonance language. In the $POCl_3$ adduct the non-bonding structure $Cl_3P{=}O\ldots SbCl_5$ would dominate, while in the $PO(CH_3)_3$ adduct the semipolar form $(CH_3)_3P^+{-}O{-}\overline{SbCl_5}$ would be most important. In the free donor molecules the forms $Cl_3P{=}O$ and $(CH_3)_3P{=}O$ would dominate. Such an explanation can, however, only be used if multiple bonds are involved, although similar effects are obtained in all types of compounds [13]. It thus seems preferable to consider the inductive effect as the primary effect in all cases. The large magnitude of the effect of the substitution of Cl for CH_3 may, however, indicate that the polarizability is large for the P-O bond. This might be due to the existence of a double bond P=O, and to the possibility of a delocalization of electrons according to the resonance formulation.

This idea is supported by the results of an interesting theoretical discussion of the S—O bonds in sulfoxides and sulfones. Moffitt [15] has attributed all heteropolarity to the π electrons because these are more readily polarized than the σ electrons. It thus seems very probable that the P—O bonds in phosphine oxides and $POCl_3$ are double bonds in the same sense as the S—O bonds in sulfoxides and sulfones.

On the other hand there is a distinction between our approach and the suggestion: «If the bond were purely $P^+{-}O^-$ we should expect that an increase in electronegativity of the groups attached to phosphorus could only decrease the strength of the P—O bond» [16]. As has been shown in the discussion of inductive effects [13] an *increase* of the strength of a single bond can also be predicted, and is actually found in many cases. In a double bond, however, the inductive effect will mainly work on the π electrons and simple resonance formulations are possible in many cases.

4. Another approach has recently been suggested by Lindqvist [17], starting from a molecular model with an idealized electron density distribution. Predictions were then made about the deviations from this idealized structure obtaining in the real compound. These predictions were mainly based on a consideration of inductive effects, as changes in hybridization were supposed to be negligible. In this way it was predicted that in $SbCl_5 \cdot POCl_3$ the term $\{|Sb{-}Cl|-|Sb{-}O|-0.32\}$ Å should be equal in magnitude to the term $\{|P{-}Cl|-|P{-}O|-0.32\}$ Å, but different in sign. The actual values are -0.17 and $+0.18$ Å (all details are given in reference 17). It was also predicted that the corresponding terms in $SbCl_5 \cdot PO(CH_3)_3$ should be smaller in magnitude. The term $\{|Sb{-}Cl|-|Sb{-}O|-0.32\}$ Å is actually 0.03 Å in the present compound, thus vanishing within the limits of experimental error.

The other term $\{|P{-}C|-|P{-}O|-0.12\}$ Å has also decreased to 0.14 Å, but we have already pointed out that the limits of error for the P—C bond lengths are rather large, maybe of the order of 0.1 Å. Even if this uncertainty is considered, however, the difference does not seem to have changed as much as on the acceptor side. Lindqvist in his prediction [17] assumed that the negative net charge on the carbon atom would be large enough to permit predictions valid for clearly polar bonds. In point 2 of this discussion it was pointed out that the case is more doubtful. The result therefore does not inva-

lidate the reasoning based on an idealized electron distribution but caution should be exercised in the application to bonds of low polarity.

5. If is a very interesting fact that the difference |Sb—Cl| — |Sb—O| does not differ significantly from the predicted value 0.32 Å for the idealized electron distribution. This means that the attraction of the electrons on the bridging oxygen atom is almost equal on both sides. The Sb—O bond should therefore be of the same length as in compounds with symmetrical oxygen bridges. No accurate structure determinations have, however, been reported of such compounds.

If the anomaly on the donor side is mainly due to the P—C bond, we would expect, in the same way that the P—O bond would be similar in length to that in symmetric P—O—P bridges. A few examples of relatively accurate structure determinations have been reported for compounds of this type. The recommended average value given in *Tables of Interatomic Distances* [18] is 1.63 ± 0.01 Å, while our experimental value is 1.61 ± 0.02 Å. A detailed account has then not been taken of possible inductive effects, but the agreement seems promising.

6. The much larger effect on the $PO(CH_3)_3$ molecule by adduct formation is also reflected in the fact that it is a much better donor molecule than $POCl_3$. This has been shown by spectroscopic [19] and thermochemical studies [20]. In the discussion of the thermochemical balance for donor-acceptor reactions [13] it was pointed out that both the strength of the new donor-acceptor bond and the inductive effects on adjacent bonds must be considered. The comparison of the two adducts discussed here shows that the weakening of the P—O bond is an important part of the thermochemical balance, even if it is more than compensated by the larger gain of energy in the donor-acceptor bond Sb—O.

7. The Sb—Cl bond lengths are not significantly different from those in the $POCl_3$ adduct, the average value being 2.34 Å compared with 2.33 Å. These values are significantly shorter than the bond length 2.47 Å found in $SbCl_6^-$. This difference has been discussed by Lindqvist [13]. The Sb—O—P bond angle in this compound is slightly smaller than in $SbCl_5 \cdot POCl_3$; no reasonable explanation of this fact is suggested.

We wish to thank Professor Hägg for all facilities put at our disposal. This work has been sponsored by a grant from *Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force,* through its European Office under Contract No. AF 61(052)—43. This grant is gratefully acknowledged. Facilities for use of the electronic digital computer BESK were given by the *Swedish Board for Computing Machinery.*

REFERENCES

1. Sheldon, J. C. and Tyree, S. Y. *J. Am. Chem. Soc.* **80** (1958) 4775.
2. Lindqvist, I and Brändén, C.-I. *Acta Cryst.* **12** (1959) 642.
3. Lindqvist, I. and Olovsson, G. *Acta Chem. Scand.* **13** (1959) 1753.
4. Löfgren, T. *Acta Cryst.* **13** (1960) 156.
5. Åsbrink, S., Blomqvist, G. and Westman, S. *Arkiv Kemi* **14** (1959) 545.
6. Westman, S., Blomqvist, G. and Åsbrink, S. *Arkiv Kemi* **14** (1959) 535.
7. Vand, V., Eiland, P. F. and Pepinsky, R. *Acta Cryst.* **10** (1957) 303.
8. Brändén, C.-I. and Lindqvist, I. *Acta Chem. Scand.* **14** (1960) 726.

9. Brändén, C.-I. *To be published.*
10. Vand, V. *J. Applied Phys.* **26** (1955) 1191.
11. Cruickshank, D. W. J. *Acta Cryst.* **2** (1949) 65.
12. Wang, H. K. Forsvarets forskningsinstitutt (Norway) Intern rapport IR-K-225 (1960).
13. Lindqvist, I. *Nova Acta Regiae Soc. Sci. Upsaliensis* (IV) **17** (1960) No. 11.
14. Zackrisson, M. and Aldén, K.-I. *Acta Chem. Scand.* **14** (1960) 994.
15. Moffitt, W. *Proc. Roy. Soc. London A* **200** (1950) 409.
16. Cotton, F. A., Barnes, R. D. and Bannister, E. *J. Chem. Soc.* **1960** 2199.
17. Lindqvist, I. *Acta Chem. Scand.* **14** (1960). 1112
18. *Tables of Interatomic Distances.* Chemical Society, London, Special Publ. (1958) No. 12.
19. Kinell, P.-O., Lindqvist, I. and Zackrisson, M. *Acta Chem. Scand.* **13** (1959) 190.
20. Lindqvist, I. and Zackrisson, M. *Acta Chem. Scand.* **14** (1960) 453.

Received September 27, 1960.