Crystal Structure of Di(phosphoryl trichloride)hexachloroditin(IV) Di-μ-dichlorophosphate

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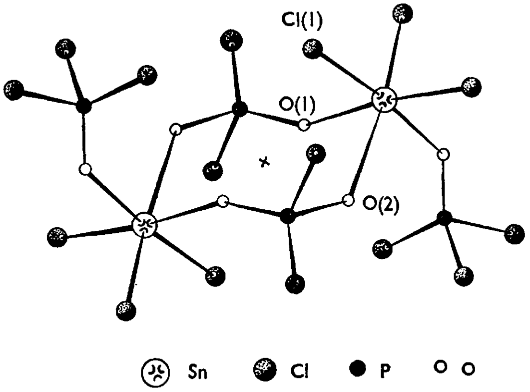
THE infrared spectrum of the compound formulated $SnOCl_2,2POCl_3$ shows a well-defined absorption band at 1065 cm.$^{-1}$, attributed to a tin–oxygen double bond stretching vibration.[1] In order to ascertain the presence of an Sn=O bond in the compound $SnOCl_2,2POCl_3$, we have studied its crystal structure.

The results showed that the double bond Sn=O is not present in $SnOCl_2,2POCl_3$. This compound is, in fact, a cyclic dimeric molecule (Figure) and must be formulated as $[(SnCl_3,POCl_3)^+(PO_2Cl_2)^-]_2$. The configuration about the tin atom is octahedral and the slight deformations are due to the steric effects of the three oxygen atoms on the three chlorine atoms [∠ O(1)–Sn–Cl(1) = 91° 28′ ± 1° 20′, ∠ O(2)–Sn–Cl(1) = 88° 10′ ± 1° 20′, ∠O(1)–Sn–O(2) = 79° 22′ ± 1° 35′, Sn–O(1) = 2·11 ± 0·023 Å, Sn–Cl = 2·33 ± 0·009 Å]. The two tin atoms are double-bridged by two dichlorophosphate groups. The ring thus formed with eight atoms, is centrosymmetric. The bond distances in the dichlorophosphate group: P–O= (1·50 ± 0·03 Å and P–Cl = 1·98 ± 0·025 A are not essentially different from those already found in $Mn(PO_2Cl_2)_2,(CH_3{\cdot}CO_2{\cdot}C_2H_5)_2$.[2]



FIGURE

Crystals of $[(SnCl_3,POCl_3)^+(PO_2Cl_2)^-]_2$ were obtained by bubbling a dry stream of Cl_2O through a solution of $SnCl_4$ in distilled $POCl_3$, as suggested by Dehnicke and Weidlein.[3] Crystal data are: M = 512·31, triclinic, a = 9·418, b = 10·681, c = 8·420 Å (each ± 0·012 Å), α = 107° 33′, β = 120° 41′, γ = 92° 27′ (each ± 20′), U = 674 Å^3, D_m = 2·50, Z = 1, D_c = 2·52; Space group $P\bar{1}$ (No. 2), λ = 0·71069 Å.

Intensities of 1033 independent non-zero reflexions were recorded on a PAILRED diffractometer using Mo-K_α radiation. The plate-shaped (0·8 × 0·3 × 0·09 mm.) crystal, very sensitive to moisture, was sealed in a Lindemann capillary tube. No absorption corrections were applied (μ = 36·5cm.$^{-1}$). The structure was derived from the three-dimentional Patterson function. The refinement to an R-value of 0·13 was carried out by isotropic, full matrix least-squares analysis.

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[2] J. Danielsen and S. E. Rasmussen, *Acta Chem. Scand.*, 1963, **17**, 1971.

[3] K. Dehnicke nnd J. Weidlein, private communication.