Isolation and comprehensive solid state characterization of $Cl_3Al–O–PCl_3$

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The crystal structure of $Cl_3Al–O–PCl_3$ contains covalent molecular units with an essentially linear Al–O–P axis, and a similar solution structure is indicated by NMR spectroscopy.

Binary mixtures of $AlCl_3$ and $OPCl_3$ have been under examination for nearly 150 years,[1] and the existence of various formulae has been envisaged. Conductivity measurements[2,3] and radiochlorine exchange studies[4] imply the formation of ionic systems of the type $[OPCl_2][AlCl_4]$[2,4] and $[Cl_2Al(OPCl_3)_2][AlCl_4]$.[3] The more complex salts $[Al(OPCl_3)_4][AlCl_4]_3$[5] and $[Al(OPCl_3)_6][AlCl_4]_3$[5,6] are postulated on the basis of Raman[5] and NMR[6] spectroscopic data. Most reports propose the covalent formulae, $Cl_3AlOPCl_3$,[7–16] $(Cl_3Al)_2OPCl_3$,[9,11] $Cl_3Al(OPCl_3)_2$,[9,13,17] or $(Cl_3Al)_2(OPCl_3)_3$,[7,15] on the basis of melting points,[17] thermal analysis,[16] vapour pressure measurements,[9,10] vibrational spectroscopy,[11,12,13] mass spectrometry,[14] NMR spectroscopy[5,7] or X-ray powder diffraction.[15] Nevertheless, definitive structural assignment for any of these is not yet available.

We now report the isolation and comprehensive solid state characterization of $Cl_3AlOPCl_3$, which can be crystallized from CH_2Cl_2 solution.† The melting point of the crystals (183–185 °C) corresponds to the well established dystectic for a 1 : 1 stoichiometry (186.5 °C,[17] 188 °C[8]). The crystal structure reveals $Cl_3AlOPCl_3$ as covalent molecular units without significant intermolecular interactions. As illustrated in Fig. 1, the plane defined by Cl(3), Al, O, P and Cl(1) lies on a crystallographic mirror plane so that the chlorine atoms adopt an eclipsed orientation. The Cl–Al and Cl–P bond lengths are typical of four-coordinate aluminium and phosphorus, respectively. Although the Al–O bond length is consistent with those in compounds containing C_3AlO units,[18] it is significantly longer than observed for $Cl_3AlOPPh_3$ [1.733(4) Å].[19]

The similarity of the solution and solid state ^{31}P and ^{27}Al NMR chemical shifts implies retention of the covalent structure in solution. Although the Raman spectroscopic features (band intensities, assignments and interpretations) described in the literature are somewhat varied, the five most intense bands for the crystalline material correspond with five of the six strong bands reported for the 1 : 1 binary mixture (591, 452, 350, 210, 168, 118 cm^{-1}),[5] which has therefore previously been incorrectly assigned the ionic formula $[Al(OPCl_3)_4][AlCl_4]_3$.

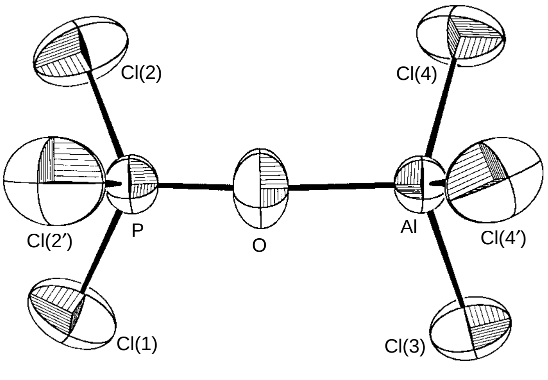

Fig. 1 ORTEP view of $Cl_3AlOPCl_3$. Selected bond lengths (Å) and angles (°): Al–O 1.780(4), Al–Cl(3) 2.093(2), Al–Cl(4) 2.103(2), P–Cl(1) 1.929(2), P–Cl(2) 1.929(1), O–P 1.436(3); Al–O–P 176.0(4), O–Al–Cl(3) 106.9(2), O–Al–Cl(4) 106.18(9), Cl(3)–Al–Cl(4) 112.78(5), Cl(4)–Al–Cl(4′) 111.47(5), Cl(1)–P–Cl(2) 108.07(7), Cl(2)–P–Cl(2′) 107.71(8), O–P–Cl(1) 110.9(2), O–P–Cl(2) 111.0(1).

The most striking feature in the solid state structure of $Cl_3AlOPCl_3$ is the large Al–O–P angle [176.0(4)°], which is consistent with the near C_{3v} symmetry assigned for a species in the melt on the basis of Raman spectra,[5] and with the structure assigned to $Br_3AlOPBr_3$ on the basis of single crystal NQR and NMR spectroscopy,[20] but is surprising when compared with the bent structure of $F_5AsOPCl_3$ [As–O–P 136.6(4)°].[21] While there are numerous examples of compounds containing a linear oxygen centre, most involve a transition metal.[22] Those between p block elements {$(C_{10}H_8NO)_2Al–O–Al(NOC_{10}H_8)_2$,[23] $Ph_3Si–O–SiPh_3$,[24] $[(Me_2N)_3P–O–P(NMe_2)_3]^{2+}$,[25] $Ph(OMe)C–O–AlMe(BHT)_2$[26] and $X_3E–O–PPh_3$ (X_3E = Cl_3Al, Br_3Al, Cl_3Ga)[19]} maybe imposed by substituent steric strain, but such interactions are insignificant in the title compound, as the intramolecular Cl(Al)···Cl(P) distances [Cl(1)···Cl(3) 4.645(2), Cl(2)···Cl(4) 4.428(2) Å] are substantially greater than the sum of the van der Waals' radii for chlorine (3.6 Å).[27] Moreover, the Al–P separation [3.213(2) Å] is greater than that between the silicon centres in the non-linear (Si–O–Si, 146°) isoelectronic molecule $Cl_3Si–O–SiCl_3$ (3.13 Å,[28] also the close contact limit for silicon centres).[29] $Cl_3AlOPCl_3$ is a useful and simple example of a non-VSEPR structure, although novelties or exceptions to the VSEPR model[30] were recognized at the outset (*e.g.* $H_3SiOSiH_3$[31] and $Cl_5RuORuCl_5$),[32] and internuclear repulsions may play a role in the determination of molecular geometry.[29]

$Cl_3AlOPCl_3$ is best viewed as one of an extensive series of phosphoryl coordination complexes which exhibit a range of angles (134–180°) at the dicoordinate oxygen centre,[22,33] although the widest angle previously reported for complexes of $OPCl_3$ is 164.1(4)°.[34] The O–P bond in $Cl_3AlOPCl_3$ is typical, in that it is essentially unchanged from that reported for the gas phase structure of the free ligand $OPCl_3$ [1.449(5) Å].[35] Therefore, we envisage the coordinative interaction to involve a purely non-bonding electron pair on oxygen, and invoke a similar model to that proposed for coordination complexes containing organo-carbonyl ligands, the M–O–C bond angle of which has a shallow energy minimum and is readily distorted by a number of factors.[36]

The observations and conclusions presented here have important structural implications for other $OPCl_3$ complexes, including the recently reported $Cl_3FeOPCl_3$.[37]

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Footnotes and References

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† Combination of $OPCl_3$ (1.95 g) and $AlCl_3$ (1.70 g) each in CH_2Cl_2 (25 ml) affects rapid solvation of $AlCl_3$. Slow evaporation of the solvent (20 min)

gives a white crystalline material which was washed with CH_2Cl_2, yield 83%; recrystallised from CH_2Cl_2, yield 25%; mp 183–185 °C; Anal. Calc. Cl, 74.20; P, 10.80. Found: Cl, 74.20; P, 10.70%. IR (ν/cm^{-1}): 1233, 973, 642, 593, 521, 441, 347, 246. Raman (25 °C, cm^{-1}): 1225, 658, 636, 590, 559, 490, 435, 348, 310, 235, 209, 168, 136, 116, 84. NMR, solution (CH_2Cl_2): ^{31}P, δ 35; ^{27}Al, δ 93 ($\Delta\nu_{\frac{1}{2}}$, 270 Hz). CP MAS: ^{31}P, δ 33; ^{27}Al, δ 89.

Crystal data: $AlCl_6OP$, M = 286.7, monoclinic, space group $P2_1/m$, a = 6.341(2), b = 10.087(3), c = 8.122(2) Å, β = 111.07(2)°, U = 484.7 Å^3, Z = 2, D_c = 1.96 g cm^{-3}, μ = 19.7 cm^{-1}, T = 22(1) °C, 806 observed reflections [$I > 3\sigma(I)$], R = 0.038; R_w = 0.037, GOF = 1.01. CCDC 182/658.

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