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Synthesis and structure of an organic-soluble cage aluminophosphonate

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An X-ray study of the aluminophosphonate $[\mathrm{Bu^tPO_3AlBu^i}]_4$ showed it to possess a cubic inorganic $Al_4O_{12}P_4$ core structure surrounded by a sheath of organic groups leading to enhanced solubility properties in organic solvents.

Since 1982 when aluminophosphates were first recognised as structural analogues of aluminosilicates they have received increased attention, primarily as a result of their potential applications as microporous materials.[1] In the intervening time more than two dozen different structural types of aluminophosphates, exhibiting host–guest interactions, have been characterized.[2] However, synthetic routes to this type of compound have been limited mainly to preparations in aqueous or ethanolic solutions or *via* hydrothermal reactions. In most cases, in the absence of templates dense phases of $AlPO_4$ have been obtained. As an extension of our investigations in the area of zeolite chemistry,[3] we were interested in synthesizing an organic-soluble precursor of $AlPO_4$. Herein, we report the synthesis, structure and characterization of a highly soluble aluminophosphonate with organic substituents on both aluminium and phosphorus atoms.

The cage $[\mathrm{Bu^tPO_3AlBu^i}]_4$ was prepared by addition of an equimolar tetrahydrofuran solution of *tert*-butylphosphonic acid to triisobutylaluminium in *n*-hexane at 0 °C followed by stirring at room temperature for 6 h. Recrystallization of $[\mathrm{Bu^tPO_3AlBu^i}]_4$ from *n*-hexane afforded octahedron-shaped colourless crystals.

The compound crystallizes in the tetragonal space group $I4_1/a$, with four discrete molecules in the unit cell.† The molecular structure of $[\mathrm{Bu^tPO_3AlBu^i}]_4$, shown in Fig. 1, is best described as a cube possessing the symmetry element $\bar{4}$. The aluminium and phosphorus atoms are positioned on alternating corners and connected by μ-oxygen atoms forming puckered eight-membered $Al_2O_4P_2$ rings, with torsion angles in the range 54.7 to 69.6° (average 60.4°). Two Al and two P atoms in each ring are coplanar within mean deviation (0.021 Å), while the other four oxygen atoms in the ring deviate from the Al_2P_2 plane by 0.24 to 0.36 Å. These four oxygen atoms form a plane (deviation of 0.017 Å) parallel to the Al_2P_2 plane with a dihedral angle less than 1 Å.

Both the Al and P atoms are co-ordinated to three μ-O atoms and an alkyl group in a slightly distorted tetrahedral configuration [O–Al–O(C) 105.2(1)–114.2(2), O–P–O(C) 108.3(2)–111.0(2)]. The Al–O bond lengths [1.757(3)–1.764(3) Å, average 1.762 Å] are slightly longer than those found in tetrahedrally linked aluminium phosphates [1.721(4)–1.749(3) Å].[7] However, the P–O bond lengths of 1.521(3) Å are consistent with those found in the literature [1.506(4)–1.543(4) Å],[7] demonstrating the different effect of the alkyl group on Al and P atoms. Maeda *et al.* have reported the first organic–inorganic composite, aluminium methylphosphonate.[8] An adduct of cubic aluminium phosphate $[AlPO_4(HCl)(EtOH)_4]_4$ has previously been investigated by X-ray structural analysis.[9]

In C_6D_6, the ^{31}P NMR spectrum of $[\mathrm{Bu^tPO_3AlBu^i}]_4$ displays a singlet (δ 16.9, 85% H_3PO_4 as standard) consistent with the structure observed in the solid state. Its gas-phase composition, as observed in the mass spectrum at *m*/*z* 823 (*M* − Bu), exhibits the molecular ion minus one butyl group as the base peak.

In summary, the alkylaluminophosphonate has the same cubic structure as the previously reported soluble alkylaluminosiloxanes.[3] Varying the organic substituents on $[\mathrm{Bu^tPO_3AlBu^i}]_4$ leads to different sizes of the inorganic core. For example, when trimethylaluminium is used as a starting material, a hexamer is obtained on the basis of mass spectroscopy. Moreover, we are also studying cleavage of the Al–C bonds in compounds of the type $[\mathrm{Bu^tPO_3AlBu^i}]_4$ by hydrolysis with water at room temperature.

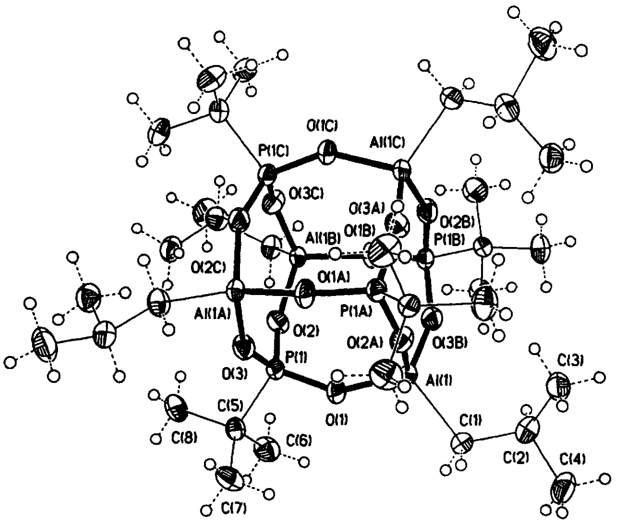

Fig. 1 Crystal structure of $[\mathrm{Bu^tPO_3AlBu^i}]_4$. Selected bond distances (Å): P–O 1.521(3), Al(1)–O(1) 1.764(3), Al(1)–O(2A) 1.757(3), Al(1)–O(3B) 1.764(3)

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† Crystal structure data: $C_{32}H_{72}Al_4O_{12}P_4$, $M = 880.70$, tetragonal, space group $I4_1/a$, $a = b = 19.376(2)$, $c = 12.765(2)$ Å, $U = 4792.4(10)$ Å^3, $Z = 4$, $D_c = 1.221$ g cm^{-3}, $F(000) = 1888$, $\lambda = 0.710\,73$ Å, $T = 153(2)$ K, μ(Mo-Kα) = 0.280 mm^{-1}. Intensity data were collected on a Siemens-Stoe AED2 four-circle diffractometer with a 0.4 × 0.4 × 0.3 mm crystal mounted on a glass fibre in a rapidly cooled perfluoropolyether[4] using an ω–2θ scan mode in the range $7.0 \leqslant 2\theta \leqslant 40.0°$, $-18 \leqslant h \leqslant 18$, $-18 \leqslant k \leqslant 18$, $-12 \leqslant l \leqslant 12$. From the total 4514 reflections, 1129 were independent. The structure was solved by direct methods.[5] All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 with 1127 reflections.[6] The positions of the hydrogen atoms were calculated and the torsion angles of methyl groups were refined.[6] Final $R_1 = 0.0632$, $R_w = 0.0982$, $w^{-1} = [\sigma^2(F_o^2) + (0.451P)^2 + 3.500P]$ where $P = (F_o^2 + 2F_c^2)/3$. Maximum and minimum heights in final Fourier-difference map 0.186 and −0.167 Å^3, respectively. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/212.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Bundesministerium für Bildung und Forschung and the Hoechst AG.

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Received 14*th June* 1996; *Communication* 6/04199J