Structure of Aluminium Methylphosphonate, AlMepO-β, with Unidimensional Channels formed from Ladder-like Organic–inorganic Polymer Chains

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The crystal structure of a microporous aluminium methylphosphonate AlMepO-β is described; the skeleton built up of fused four-ring chain forms unidimensional channels of approximately 5.8 Å cross-section fringed with methyl groups running parallel to the *c*-axis.

New microporous zeolitic materials have been extensively explored, especially in the field of aluminium phosphates.[1–3] We have already reported a synthesis of the first microporous inorganic–organic composite, aluminium methylphosphonate, designated AlMepO-β, under hydrothermal conditions.[4] Although the framework composition of $Al_2(CH_3PO_3)_3$ and the fundamental connectivity were revealed by elemental analyses, MAS NMR studies *etc.*, the small size of the crystals obtained prevented further single crystal structural analyses. Recently we also obtained another microporous phase, AlMepO-α, of a 3D layered microporous structure with the same framework composition as AlMepO-β.[5] This class of compounds is expected to have features of both microporous oxide and organic materials. We now report the unique framework structure of AlMepO-β.

To obtain large crystals suitable for a single crystal X-ray structural analysis, several additives were tried on the basis of the reported procedure.[4] The addition of dioxane (dioxane/ Al = 0.5) to the starting mixture of pseudo-boehmite and methylphosphonic acid was most effective for the formation of large single crystals. Needle-like crystals of maximum dimensions *ca.* 5 × 0.1 × 0.1 mm were obtained. Elemental analyses of the crystals which had been washed well with water and air-dried gave C: 13.3%, H: 3.6%, while the product with no additive gave C: 10.5%, H: 3.2% corresponding to the composition $Al_2(CH_3PO_3)_3 \cdot nH_2O$ ($n \approx 1.0$).[4] This suggests that water and dioxane molecules are included in the cavities of AlMepO-β, although it was impossible to determine the position of these molecules by single crystal X-ray structural analysis owing to disorder.

The asymmetric unit contains six crystallographically independent CH_3PO_3 tetrahedra that share oxygen atoms at their corners with three adjacent aluminium atoms (Fig. 1). Among the four independent aluminium atoms, one is 6-coordinated [Al_{Oh}] and the others are 4-coordinated [Al_{Th}], all of which are bound by phosphonates. This connectivity is consistent with the reported ^{27}Al and ^{31}P MAS NMR results.[4] As shown in Fig. 2, each Al_{Oh} is surrounded by eight nearest Al_{Oh} at distances between 8.43 and 9.33 Å. Both the two neighbours located almost along the *c*-axis are connected to the central Al_{Oh} by linearly fused triple four-rings. The two extreme rings are on the same side of the central four-ring (*cis*-linkage). Further two

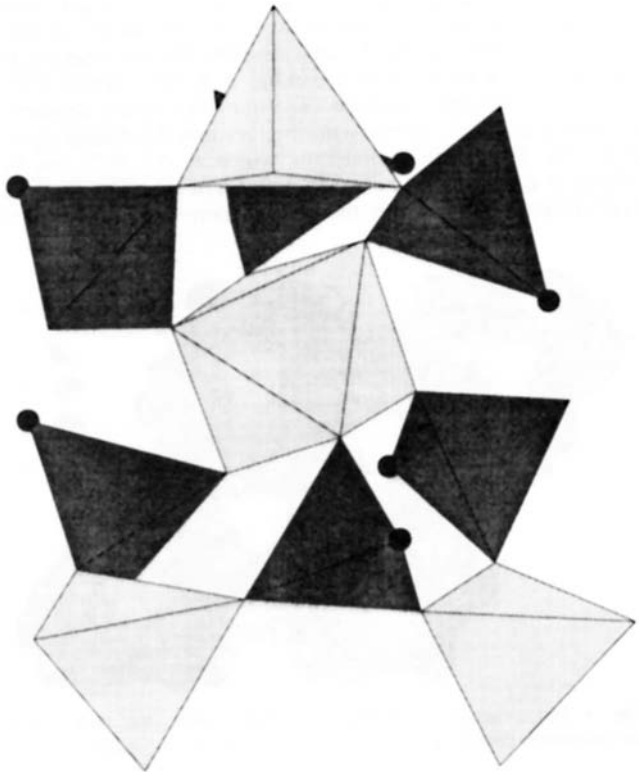

Fig. 1 The building blocks of AlMepO-β. The darker tetrahedra including a black ball (methyl group) denote [CH_3PO_3], the paler tetrahedra denote [AlO_4], and the central octahedron denotes [AlO_6].

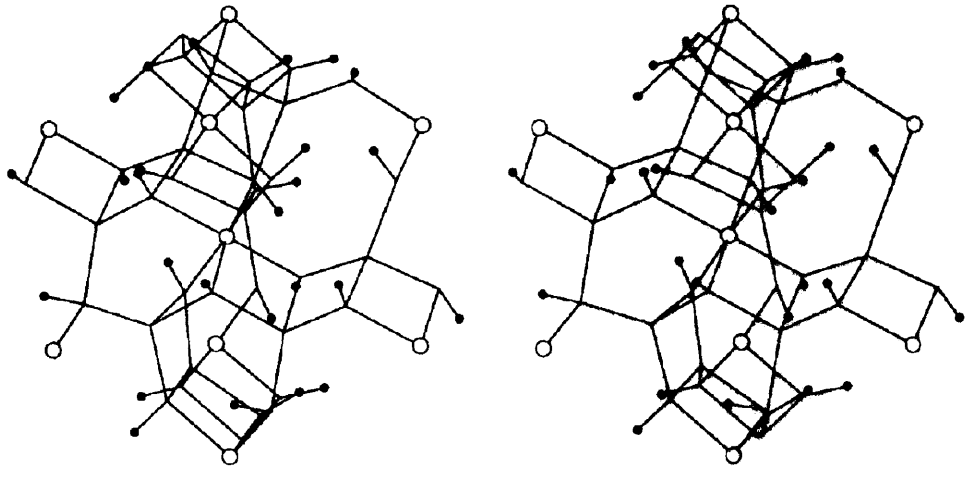

Fig. 2 Stereoplots of a part of the framework around Al_{Oh}. The black and white balls denote methyl groups and Al_{Oh}, respectively. The *c*-axis runs along the vertical direction.

neighbours of the remaining six are connected also with linearly fused triple four-rings, in which the two extreme rings are on opposite sides of the central ring (*trans*-linkage). The upper end ring of a *cis*-linkage is next to the upper end ring of a *trans*-linkage. The lower end of a *cis*-linkage shares a four-ring with the lower end of a *trans*-linkage. Therefore, Al_{Oh} is the terminus of two *cis*-linkages and two *trans*-linkages. All the aluminium atoms and five of the six independent phosphorus atoms are included in the chains of four-rings. The remaining phosphorus atoms which do not form that of the four-rings act as junctions of the chains as well as 6-connected Al_{Oh}. Thus, AlMepO-β can be regarded as textile made up of intertwined infinite ladder-like polymer chains.

The inorganic skeleton forms unidimensional 18-ring channels running parallel to the *c*-axis. The 18-ring contains $3Al_{OH}$, $6Al_{Th}$, and 9P atoms, similar to AlMepO-α.[5] Few microporous oxide-based materials containing 18-rings or larger pore openings have been reported so far.[6–9] All the methyl groups covalently bonded to the skeleton protrude into the channels to form channel walls as illustrated in Fig. 3. A cross section of the channel is rounded triangular. The diameter of the channels, estimated at 5.8 Å, agrees with the fact that 2,2-dimethylpropane, the molecular diameter of which is 6.2 Å,[10] can be adsorbed into the channel. Although there are also elliptical eight-rings in the skeleton, the shorter diameter is estimated at 1.4 Å which is too narrow for small molecules to pass through.

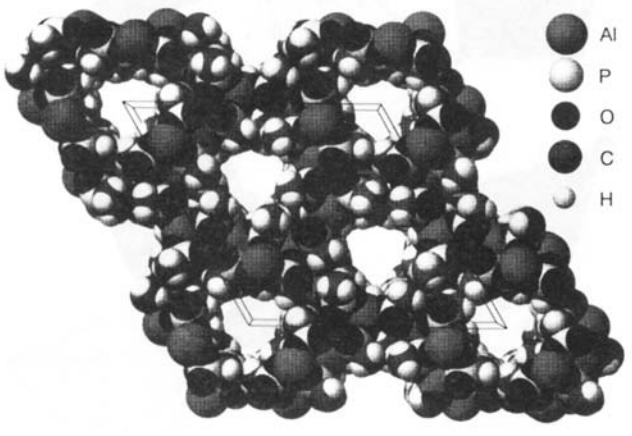

Fig. 3 The structure of AlMepO-β viewed along the *c*-axis. The rhombohedron denotes a unit cell ($a = b = 24.650$, $c = 25.299$ Å).

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Footnotes

† *Crystal data* for $C_6H_{18}Al_4O_{18}P_6$ (AlMepO-β): trigonal, space group $R3c$, $a = 24.650(2)$, $c = 25.299(5)$ Å, $V = 13312.4$ Å^3, $Z = 18$, $D_c = 1.509$ g cm^{-3}, crystal dimensions $0.8 \times 0.04 \times 0.04$ mm, μ(Mo-Kα) = 0.546 cm^{-1}, λ = 0.71069 Å, the refinement based on F^2 (312 parameters),[11] $wR2 = 0.2115$ (based on F^2 for all data), $R1 = 0.0555$ [based on F with $I > 2\sigma(I)$]. Data were collected on a Rigaku AFC-7 diffractometer using the ω–2θ technique for the range $4 < 2\theta < 50°$. The total number of reflections measured was 2571, of which 2514 were unique and 1580 had $I > 2\sigma(I)$. The structure was solved by direct methods.[12] Hydrogen atoms on the methyl groups were placed geometrically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ The diameters of the channels were calculated using the van der Waals radii[13] of corresponding atoms; O: 1.52, C: 1.70, H: 1.20 Å.

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