Aluminophosphonate clusters: a new architecture

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The synthesis and characterisation (by single crystal X-ray diffraction and solid state ^{13}C, ^{27}Al, ^{31}P NMR) of a new Al–O–P cluster related to the 4≡1 Secondary Building Unit (SBU) of zeolites are presented.

Zeolites and porous derivatives are now commonly described as an assembly of SBUs (18 SBUs are reported).[1] The synthesis of clusters mimicking SBUs remains a chemical challenge as these clusters may be considered as suitable intermediates for the direct synthesis of microporous materials and also as spectroscopic references for solid state NMR studies.[2,3] Five types of Al–O–P clusters mimicking the following SBUs have been reported so far in the literature: the S4R (or 4) ring, the S6R (or 6) ring, the cubane-shaped D4R (or 4–4), the prismatic D6R (6–6) and the 6≡1 SBU.[4] Very recently, we have presented the first Al–O–P analogue of the 4≡1 SBU.[5] This SBU (Fig. 1d) is rarely encountered as only three zeolites can be considered as derivatives of 4≡1 units: natrolite, thomsonite and edingtonite.[1] The direct reaction of anhydrous AlCl$_3$ with phenylphosphonic acid C$_6$H$_5$PO(OH)$_2$ in cooled ethanol led to a cluster mimicking the 4≡1 unit (Fig. 1c) (with an additional oxo bond with respect to the 4≡1 unit), involving three sixfold coordinated Al atoms. Three or four ethanol ligands surrounding each Al atom were observed in the crystallographic structure.[5] The generalisation of this synthetic approach to various secondary alcohol molecules, instead of ethanol, led to the following conclusion: steric hindrance prevents the coordination of Al atoms by four alcohol molecules. A new geometry (*vide infra*) is then obtained.

The reaction of anhydrous AlCl$_3$ with phenylphosphonic acid C$_6$H$_5$PO(OH)$_2$ in *sec*-butanol led to single crystals, suitable for X-ray diffraction analysis at low temperature: [Al$_5$(μ_2-OH)$_2$-(μ_3-C$_6$H$_5$PO$_3$)$_4$(C$_4$H$_9$OH)$_{12}$]Cl$_5$·2C$_4$H$_9$OH (compound **1**).† The molecular structure of **1** is presented in Fig. 1, as well as selected bond lengths and angles.‡ To the best of our knowledge, such an inorganic Al–O–P core was never described in previous works. It exhibits five Al atoms linked by phenylphosphonate groups (P1, P10). Four Al atoms (Al2, Al3) are *sixfold coordinated*, involving three *sec*-butanol ligands (O20, O25, O30 and O35, O40, O45). A μ_2-(OH) (O50) hydroxo bridge links Al2 and Al3. This particular bonding makes a difference with the 4≡1 unit observed in the aluminosilicate solids. Indeed, no Al–OH–Al bond is observed for this particular compound's family. The Al1 atom is *fourfold coordinated*: it is linked to four P atoms *via* oxo bridges. Distances between O of ethanol ligands and Al are much longer than those related to Al and oxo bridges (Fig. 1). The mean bond length for the μ-OH bridge is about 1.87 Å. P atoms are fourfold coordinated: in addition to three O atoms, each P is bonded to one phenyl ring (C4→C9 and C14→C19). The average P–O bond length is 1.53 Å, whereas the mean P–C bond length is about 1.80 Å. These distances are comparable to those observed for parent derivatives.[3,5] A disorder model was applied for the Cl$^-$ counterions that are present in the structure. Because of charge neutrality of the compound, five chloride anions per structural unit are
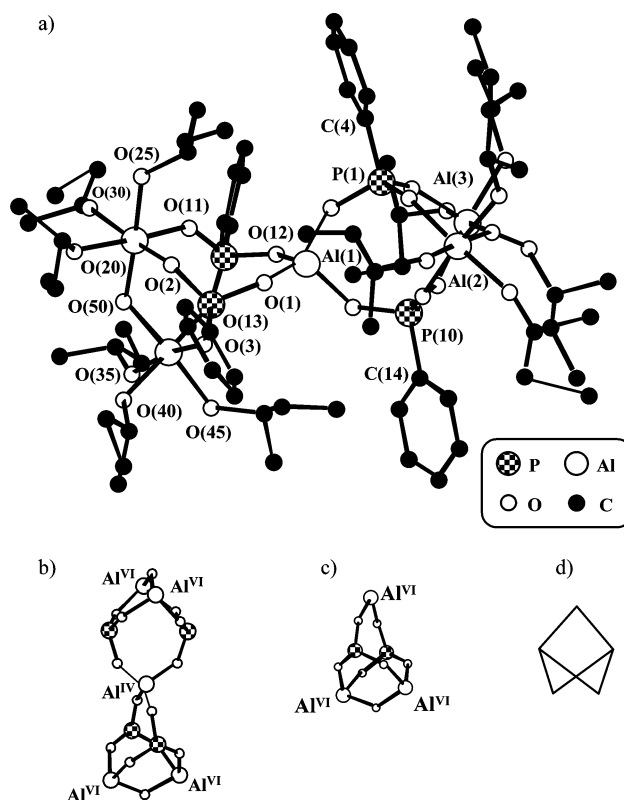

Fig. 1 (a) Molecular structure of **1** with labelling of Al, P and O atoms. Quaternary C atoms of phenyl groups are indicated. Other C atoms labels are omitted for clarity. Cl atoms and solvate molecules are omitted. (b) View of the inorganic core of **1**. (c) View of the inorganic core of the cluster mimicking the 4≡1 SBU. (d) SBU 4≡1. Al^{IV}: Al atom in 4-fold coordination. Al^{VI}: Al atom in 6-fold coordination. Selected bond lengths for **1**: Al1–O1 1.743(4) Å, Al1–O12 1.740(4) Å, Al2–O20 1.981(4) Å, Al2–O25 1.952(5) Å, Al2–O30 1.965(5) Å, Al3–O35 1.974(5) Å, Al3–O40 1.990(4) Å, Al3–O45 1.927(5) Å, P1–C4 1.798(5) Å, P10–C14 1.802(5) Å. Selected bond angles: O1–Al1–O12 110.51(17)°, O1–P1–C4 104.2(2)°, O2–P1–C4 107.6(2)°, O3–P1–C4 111.6(2)°, O11–P10–C14 108.5(2)°, O12–P10–C14 104.9(2)°, O13–P10–C14 110.2(3)°.

necessary. *Sec*-butanol molecules are present as ligands and solvate molecules with a disorder model (O95A, O95B). We note finally that similar cluster cores were obtained with iso-propanol (chloride and bromide derivatives).

Compound **1** was further characterised by multinuclear solid state NMR.§ Fig. 2 shows the ^{27}Al {^{1}H dec.} MAS spectrum of **1** obtained at v_{rot} = 13 kHz (B_0 = 7.0 T). Two main resonances are observed. The most deshielded resonance can be safely assigned to Al1 (fourfold coordinated Al) and is broadened by second-order quadrupolar effects. The simulation of the lineshape[6] led to the following (C_Q, η_Q, δ_{iso}) quadrupolar and isotropic shift parameters for Al1: (3.68 MHz, 0.25, 48.7 ppm). Resonances assigned to Al2 and Al3 are located at ≈ 0 ppm.
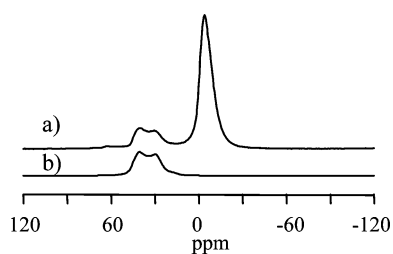
Fig. 2 (a) ^{27}Al {^{1}H dec.} MAS NMR spectrum of **1** (ν_{rot} = 13 kHz, B_0 = 7.0 T). (b) simulation of the fourfold coordinated ^{27}Al resonance,[6] using C_Q = 3.68 MHz, η_Q = 0.25 and δ_{iso} = 48.7 ppm.

However (at B_0 = 7.0 T), they are strongly overlapped, indicating a very similar chemical environment for Al2 and Al3. The (C_Q, η_Q, δ_{iso}) parameters for Al2, Al3 were determined at ν_{rot} = 3 kHz by extensive simulation of the SSBs (spinning side bands) patterns (satellite transitions): ($\approx$1.7 MHz, $\approx$0.5, $\approx$1.5 ppm). Quantitative ^{27}Al MAS experiments[7] led to the ratio 1 : 4 for Al1 : (Al2 + Al3), in agreement with the chemical formula of compound **1**. We note that very similar ^{27}Al MAS spectra were obtained for the (Cl, Br) *iso*-propanol derivatives cited above.

The ^{31}P CP MAS spectrum of **1** (not shown) exhibits two isotropic resonances in agreement with the crystallographic data. Isotropic shift (ppm), [line width (Hz)] and CSA parameters (δ_{11}, δ_{22}, δ_{33} (ppm); η_{CSA}) for each resonance are the following: 6.7, [143], (48.8, 11.3, −39.9; 0.80) and 7.7, [160], (48.5, 13.7, −40.0; 0.75). Such parameters were determined by slow CP MAS experiments and subsequent analysis of the SSBs patterns.

The ^{13}C CP MAS spectrum of **1** is shown in Fig. 3. Resonances centered at 132.1 ppm are assigned to the phenyl groups of the structure. The assignment of the resonances centered at 10.3, 26.1, 30.4 and 75.7 ppm is also straightforward (see Fig. 3).
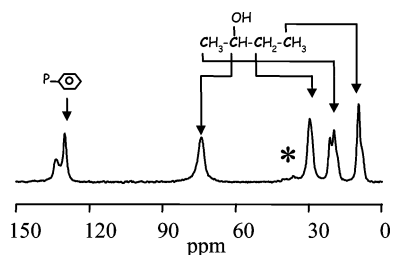

Fig. 3 ^{13}C CP MAS NMR spectrum of **1** (ν_{rot} = 7 kHz, B_0 = 7.0 T). *: spinning side bands of aromatic carbon resonances.

Finally, we note that compound **1** can be viewed as the combination of two 4=1 SBUs sharing a unique fourfold coordinated Al atom (Al1) (see Fig. 1b). Compound **1** is a good representation of bonding modes encountered in the EDI (edingtonite) zeolite type. Moreover, compound **1** may be viewed as a first step in the understanding of complex architectures and to the role of building units in the solid-state inorganic structures.[8,9]

Notes and references

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