^{27}Al MAS NMR and XAS cross-study of the aluminophosphonate $Al(OH)(O_3PC_6H_5)$†

Letter

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An aluminium phenylphosphonate, $Al(OH)(O_3PC_6H_5)$, has been studied. Its poor long-range crystallographic organisation required the use of local probe techniques such as ^{31}P and ^{27}Al MAS NMR and XAS. An unexpectedly narrow and symmetric ^{27}Al MAS NMR signal was obtained, with an isotropic chemical shift that has not been observed earlier in aluminium phosphonates. XANES and EXAFS studies showed unambiguously that this signal had to be attributed to a five-fold coordination site, the first observed for a phosphonato-aluminium atom.

Much interest is being devoted to organic–inorganic materials because of the high potentiality that they present for the design of materials with specific chemical or physical properties. The good stability of the phosphorus–oxygen–metal bonds makes phosphonates especially interesting for heterogeneous catalysis. Metallic phosphonates have been studied with divalent, trivalent and tetravalent phosphonates.[1] Several trivalent metal phosphonates have been reported (see ref. 2 and references therein), among which aluminium phosphonates figure. In the past few years, many studies have focused on the latter compounds.[2–18] The aluminophosphonates reported up to now exhibit four-fold and six-fold coordination sites for the aluminium atom.

In the course of our work we have obtained the aluminophosphonate $Al(OH)(O_3PC_6H_5)$, which stands out in the aluminium phosphonate family by its relatively narrow and symmetric ^{27}Al MAS NMR signal, unexpected due to the strong quadrupolar effect. Moreover, the chemical shift of this signal seemed to fit with a five-fold coordination metal site, which would make from this compound the first aluminophosphonate with such a metal site. Synthesis of well-crystallised samples was unsuccessful, so that a crystal structure determination was not possible, even from powder diffraction data. However, X-ray absorption spectroscopy, associated with solid state NMR, proved to be a good tool in order to demonstrate the presence of the five-fold coordinated metal atom.

The synthesis of $Al(OH)(O_3PC_6H_5)$ starting from aluminium nitrate and phenylphosphonic acid led to a white powder. When heated, this compound showed a 4.5% weight loss at 268 °C; this weight loss, as well as the temperature at which it occurs, corresponds to the condensation of two $Al(OH)(O_3PC_6H_5)$ entities to release one water molecule. Cell parameters of the title compound were obtained from an X-ray powder diffraction pattern [$a = 16.386(3)$, $b = 5.527(1)$, $c = 8.262(2)$ Å, $\beta = 90.61(2)°$, $Z = 4$, figure of merit[19] $M(19) = 24$]. The ^{31}P MAS NMR spectrum exhibited a single site signal with an isotropic chemical shift δ_{iso} at -10.2. Low speed rotation (2440 Hz) allowed us to obtain the skew (κ) and the span (Ω), which are related to shielding tensor asymmetry and anisotropy:[20,21] -0.29 and 85.2 ppm were respectively obtained for these parameters. The skew (κ) was shown to be related to the connectivity of the phosphonato group, that is the number of metal atoms bonded to each phosphonato oxygen atom.[22–24] As the (κ) values obtained for $Al(\mu\text{-}OH)(O_3PCH_2C_6H_4Br)\cdot H_2O$, $Al(\mu\text{-}OH)(O_3PCH_2C_6H_5)\cdot H_2O$ and $\zeta\text{-}Al(OH)(O_3PCH_3)\cdot H_2O$[10,14] are -0.20, -0.20 and -0.38, respectively,[25] and as each of these compounds displays a (111) connectivity, we could also infer a (111) connectivity for the phosphonato group in $Al(OH)(O_3PC_6H_5)$.

The ^{27}Al MAS NMR spectra exhibited a single, narrow (FWHM = 450 Hz at 9.4 T) and symmetric signal with an isotropic chemical shift obtained at 20.2 ppm (Fig. 1, trace *a*). The quadrupolar coupling constant C_Q and the asymmetry factor η_Q were respectively obtained as 1905 KHz and 0.87, with an accuracy that has to be weighted (lowered) by the especially high symmetry of the signal. This η_Q value is close to the values of η_Q obtained for $Al(\mu\text{-}OH)(O_3PCH_2C_6H_4Br)\cdot H_2O$, $Al(\mu\text{-}OH)(O_3PCH_2C_6H_5)\cdot H_2O$ and $\zeta\text{-}Al(OH)(O_3PCH_3)\cdot H_2O$ (0.74, 0.74, 0.88, respectively) but the

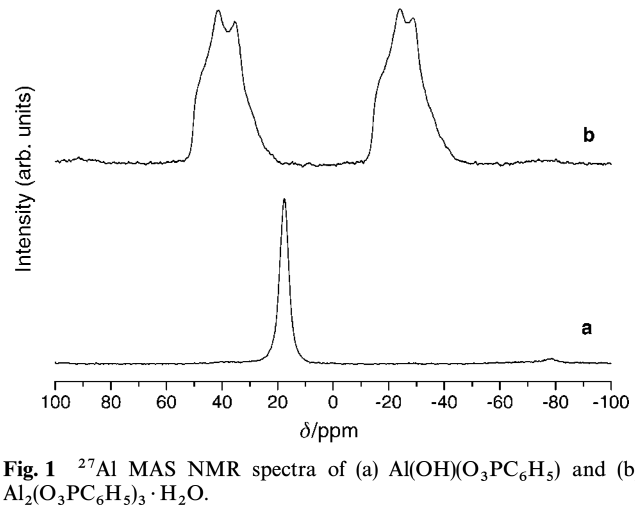

Fig. 1 ^{27}Al MAS NMR spectra of (a) $Al(OH)(O_3PC_6H_5)$ and (b) $Al_2(O_3PC_6H_5)_3\cdot H_2O$.

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† Electronic supplementary information (ESI) available: X-ray powder diffraction pattern of $Al(OH)(O_3PC_6H_5)$. See http://www.rsc.org/suppdata/nj/b1/b106545a/

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C_Q values for the same compounds are much higher: 6520, 6420 and 6193 KHz, respectively.[2] Thus, we might conclude that the lack of visible anisotropy in the ^{27}Al NMR signal of Al(OH)($O_3PC_6H_5$) is due to the relatively small coupling constant, that is to a small interaction between nuclear spin and electric field gradient rather than to some symmetry in the electric field gradient.[26] For comparison, the ^{27}Al NMR spectrum obtained for $Al_2(O_3PC_6H_5)_3 \cdot H_2O$[2] (Fig. 1, trace b) shows an intermediate case with FWHM, C_Q and η_Q at 1800 Hz at 9.4 T, 4450/4530 kHz and 0.48/0.57, respectively, where the two values of C_Q and η_Q refer to four-fold/six-fold coordinated metal atom signals. The second noteworthy feature of Al(OH)($O_3PC_6H_5$) is the value of the isotropic chemical shift at 20.2 ppm to be compared with the most common isotropic shifts for four-fold and six-fold coordination environments of the aluminium atom in phosphonates, which range from 50 to 40 and from 0 to -25 ppm, respectively. Therefore, the chemical shift for Al(OH)($O_3PC_6H_5$) would suggest a five-fold coordinated metal atom, which has not been seen previously for an aluminium phosphonate. Nevertheless, such a coordination was observed for an aluminophosphate ($Al_2P_3O_{12}{}^{3-}$ anion) with a ^{27}Al NMR isotropic chemical shift at 12.7 ppm; its crystallographic structure showed a five-fold coordinated aluminium atom (a distorted trigonal bipyramide) with two axial oxygen atoms at 1.908 and 1.872 Å and three shorter Al–O distances of 1.800, 1.789 and 1.777 Å.[27]

In order to probe the local environment around aluminium atoms, X-ray absorption near edge structure spectroscopy (XANES) was used at the Al K-edge. It has been established that the various energy resonances in the edge are a signature of the presence of six-fold or four-fold coordination environments for aluminium atoms.[28] This is perfectly illustrated in Fig. 2, which reports the Al absorption K-edge of Al(OH)($O_3PC_6H_5$) compared with several references that exhibit different coordination sites for the aluminium atoms: a four-fold coordination site for $AlPO_4$, a six-fold coordination site for $Al(HO_3PC_6H_5)(O_3PC_6H_5) \cdot H_2O$ and four-fold and six-fold coordination sites for $Al_2(O_3PC_6H_5)_3 \cdot H_2O$.[2] The XANES spectra of Al(OH)($O_3PC_6H_5$) cannot be superposed with any of the purely six-fold or four-fold coordinated aluminium atom reference spectra, nor with that corresponding to the presence of both environments. Moreover, the energy of its edge from the inflexion point (1565.9 eV) is located between those of $AlPO_4$ (1565.6 eV) and $Al(HO_3PC_6H_5)(O_3PC_6H_5) \cdot H_2O$ (1567.0 eV). This gives clear evidence of the presence of an intermediate five-fold coordinated aluminium atom. Because of the strong correlation between the coordination number and the Debye–Waller disorder parameter, it is difficult to extract quantitative information (*i.e.*, accurate coordination number) from the EXAFS study of the oxygen atoms' first neighbours shell of Al(OH)($O_3PC_6H_5$). Nevertheless, as shown in Fig. 3, the EXAFS signal for Al(OH)($O_3PC_6H_5$) presents an intermediate frequency between the ones of $AlPO_4$ (four-fold coordination site) and $Al(HO_3PC_6H_5)(O_3PC_6H_5)$ (six-fold coordination site), evidencing an intermediate Al–O distance for the title compound compared to the two references. This is confirmed by the fit of the oxygen atom contribution performed on these three compounds, using theoretical amplitude and phase shift files calculated with the FeFF7 code.[29] The Al–O distances found for $AlPO_4$ (four-fold coordination site) and $Al(HO_3PC_6H_5)(O_3PC_6H_5) \cdot H_2O$ (six-fold coordination site) are 1.72 and 1.98 Å, respectively. These distances are in agreement with those measured from crystallographic data on $AlPO_4$[30] and on aluminium phenylphosphonates,[2,9] which gives a higher reliability to the 1.83 Å average Al–O distance found for the five-fold coordinated aluminium atom in Al(OH)($O_3PC_6H_5$). Moreover, this distance is close to those observed in the $Al_2P_3O_{12}{}^{3-}$ anion (1.777–1.908 Å), which has an aluminium atom in a five-fold coordination environment.[27]

From the structural features obtained above, and by comparison with the known aluminium benzylphosphonate Al(μ-OH)($O_3PCH_2C_6H_4Br$)$\cdot H_2O$,[2] we can propose the following hypothesis for the structure. Al(μ-OH)($O_3PCH_2C_6H_4Br$)$\cdot H_2O$ shows a layered structure with a six-fold coordinated aluminium atom, a (111) connectivity for the phosphonato group and cell parameters of 16.4972(2), 7.0673(1), 9.4950(2) Å and 113.477(1)°, respectively for *a*, *b*, *c* and *β*. The *a* parameter for Al(OH)($O_3PC_6H_5$) is similar [16.386(3) Å] whereas *b* and *c* are *ca.* 1.5 and 1.2 Å smaller, *β* also being smaller. The hypothetical structure of an inorganic layer (the *bc* plane) for Al(OH)($O_3PC_6H_5$) is shown in Fig. 4. This figure has been obtained starting from the inorganic layer of Al(μ-OH)($O_3PCH_2C_6H_4Br$)$\cdot H_2O$[2]: the phenyl groups, linked to the phosphorus atoms, have not been shown for clarity and the oxygen atom of the water molecule coordinated to the aluminium atom in the benzyl derivative has been removed. Thus, we obtain a five-fold coordination site for the aluminium atom; we keep the (111) connectivity for the phosphonato group and the smaller cell parameters are consistent with the absence of the water molecule, which permits a higher packing of the structure. Of course bond lengths and angles would be different from those schematically shown in Fig. 4.

We have evidenced here several structural features of Al(OH)($O_3PC_6H_5$) in the absence of its crystallographic structure: (i) the aluminium atom is unambiguously shown to be in a five-fold coordination site based on its ^{27}Al MAS NMR signal and on the XANES study; such a site has not been reported in an aluminium phosphonate until now; (ii) the Al–O distance was determined and compared to references

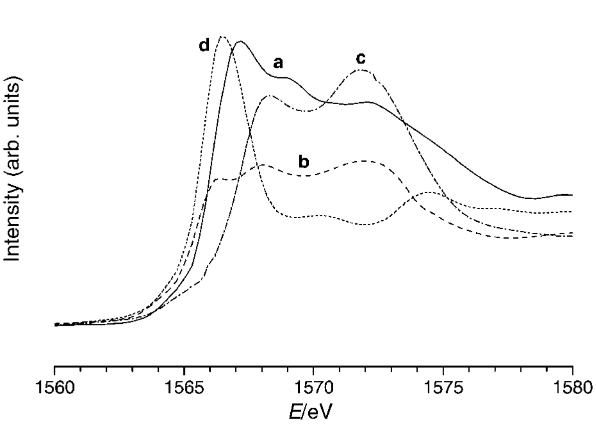

Fig. 2 XANES spectra of (a) Al(OH)($O_3PC_6H_5$), (b) four- and six-fold coordinated $Al_2(O_3PC_6H_5)_3 \cdot H_2O$, (c) six-fold coordinated $Al(HO_3PC_6H_5)(O_3PC_6H_5) \cdot H_2O$ and (d) four-fold coordinated $AlPO_4$.

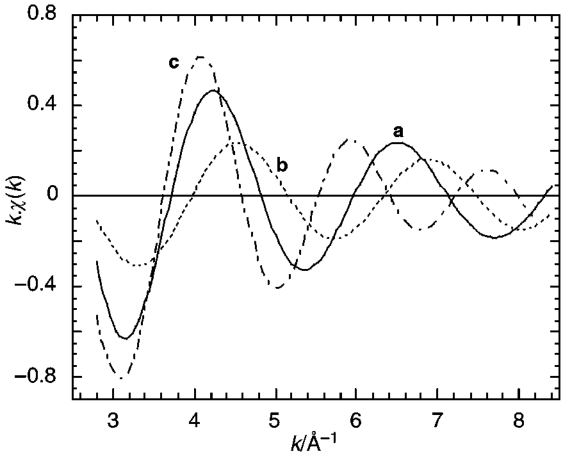

Fig. 3 EXAFS contribution of the oxygen shell for (a) five-fold coordinated Al(OH)($O_3PC_6H_5$), (b) four-fold coordinated $AlPO_4$ and (c) six-fold coordinated $Al(HO_3PC_6H_5)(O_3PC_6H_5) \cdot H_2O$.

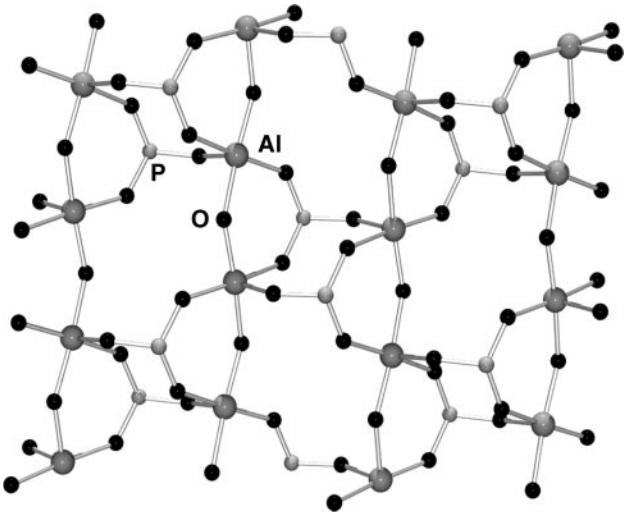

Fig. 4 Schematic hypothetical structure of the inorganic layer (*bc* plane) of $Al(OH)(O_3PC_6H_5)$; the phenyl groups have been omitted for clarity.

obtained with the same EXAFS conditions; (iii) from the ^{31}P MAS NMR spectrum, the connectivity of the phosphonato group appears to be (111). Crossing these local probe techniques has permit us to give some precise features of the structure for the title compound.

Experimental

$Al(OH)(O_3PC_6H_5)$ was prepared from aluminium nitrate and phenylphosphonic acid in water (mol. ratio Al : P : H_2O 1 : 1 : 1000) heated at 180 °C in a sealed tube for 2 weeks. Anal. found (calc.): Al 13.26 (13.49), P 15.27 (15.48), C 35.94 (36.02), H 3.12 (3.02)% Yield: 70%; $D_{exp} = 1.78$ g cm^{-3}). Thermogravimetric analysis was carried out on a NETZSCH 409 thermobalance, under flowing air, at 5 °C min^{-1}; the dehydration temperature was determined from the minimum of the derivative curve of the TGA graph. The X-ray powder diffraction pattern was recorded in the Debye–Scherrer geometry using an INEL diffractometer equipped with a CPS 120 detector, with Cu-Kα_1 radiation (40 kV, 30 mA). The powder was sieved (<63 nm) and placed in a 0.3 mm diameter capillary. Peak positions were determined using the WinPLOTR package;[31] these positions were then processed by the auto-indexing program DICVOL91.[32]

All solid state NMR spectra were recorded on a Bruker AMX 400 spectrometer (^{31}P: 162 MHz, spinning rate 10 KHz, 4 mm rotor, referenced to an 85% H_3PO_4 solution; ^{27}Al: 104.3 MHz, spinning rate 12 KHz, 4 mm rotor, referenced to 1.5 M aluminium chloride hexahydrate). Each NMR parameter was extracted using the Bruker WinFit software.

XAS data have been recorded on the SA32 beam line of the French storage ring Super-ACO using two YB_{66} crystals as monochromator; each experiment was recorded in the fluorescence mode using a monoelement Ge detector (Eurisys-Mesures) set at 90° of the incident photon direction. XANES experiments were recorded in the range 1550–1620 eV, 0.2 eV step, 1 s per step; EXAFS experiments were recorded in the range 1500–2000 eV, 1 eV step, 1 s per step. For each sample, the experiment was recorded between 6 and 10 times, and then averaged after careful examination of each data set. The energy scale was referenced to the Al K-edge inflexion point at 1559 eV, obtained from an aluminium foil standard.

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