

Six-coordinate aluminium phosphinate

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Unique models of solid state aluminophosphate materials containing, for the first time, six-coordinate aluminium atoms, may be achieved in chelated phosphinate derivatives; the degree of aggregation of these species, specifically the remarkable transition from a dimeric molecule to a polymeric material, depends on just one methylene unit; thus, $[(\text{Bu}^t_4\text{salpen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_2$ **1** is dimeric while $[(\text{Bu}^t_4\text{salen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_\infty$ **2**, with one fewer methylene unit in the connection between the two nitrogens, is a polymeric material with the polymers aligned to form pores containing thf molecules.

Nanoporous or open-framework¹ group 13 phosphate materials have far-ranging applications in catalysis,² separations and many other areas.³ There are a limited number of naturally occurring aluminophosphates (turquoise is one example). However, synthetic chemistry has dramatically expanded this class of compounds and is providing new^{4,5} and unique⁶ materials with a wide range of new applications.⁷ In these materials the aluminium atom is often six-coordinate. Thus far, molecular models of these materials have contained four-coordinate aluminium,^{8–11} while none have six-coordinate atoms found in many materials.^{12,13} The present work demonstrates that six-coordinate aluminium may be achieved in chelated phosphinate derivatives, and that the degree of aggregation of these species, the transition from a dimeric molecule to a polymeric material, is dependent on just one methylene unit. Thus, $[(\text{Bu}^t_4\text{salpen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_2$ **1** is dimeric while $[(\text{Bu}^t_4\text{salen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_\infty$ **2** is a polymeric material.

The compounds are prepared by combining the chelated group 13 reagent with the phosphinic acid (Scheme 1).¹⁴ Use of $(\text{Bu}^t_4\text{salpen})\text{AlMe}$ in this reaction leads to the dimeric compound $[(\text{Bu}^t_4\text{salpen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_2$ **1**. The dimeric nature of **1** is supported by the spectroscopic data and verified by a crystal structure (Fig. 1).¹⁵ In the structure the aluminium atom is in an octahedral environment. The Al–O(ligand) distances, *ca.* 1.83 Å, are marginally shorter than the Al–O–P distances, *ca.* 1.93 Å. There are no known solid-state materials based on phosphinates $[\text{O}_2\text{P}(\text{H})\text{R}]$ but these bond distances are similar to that observed in an aluminium phenylphosphonate $(\text{O}_3\text{PR})^4$ with Al–O distances in the range 1.786(6)–1.951(6) Å. By comparison, these distances are just slightly shorter in derivatives containing four-coordinate aluminium such as $[\text{Me}_2\text{AlO}_2\text{P}(\text{OBu}^t)_2]$ (Al–O \approx 1.77 Å).¹² Aggregation of **1** is expected based upon previously reported compounds, including $[\text{Me}_2\text{Al}(\text{O}_2\text{PPh}_2)]_2$, first reported by Coates in 1964,¹⁶ which are most commonly dimeric with four-coordinate aluminium atoms. Although the bonding within compound **1** is not unusual the compound still

serves to demonstrate that molecular phosphinates of six-coordinate aluminium can be obtained.

Compound **2** differs from **1** in having one less methylene (CH_2) unit in the ligand ‘backbone’. Surprisingly, this leads to a dramatic change in the structure of the resulting compound. Thus, $[(\text{Bu}^t_4\text{salen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_\infty$ **2**, is found to consist of polymeric chains of $-(\text{Bu}^t_4\text{salen})\text{Al}(\text{OP}\{\text{H}\}\text{Ph})\text{O}-$ units (Fig. 2). The $-\text{O}-\text{Al}-\text{O}-\text{P}-$ backbone is not linear but curved at the O–P–O junctions with an angle of $119.1(3)^\circ$. The same angle in **1** is $116.81(8)^\circ$. The Al–O distances are also similar. Adjacent ligand Bu^t groups are arranged in a staggered configuration to reduce steric contacts. The effect of this arrangement is to make the polymers appear as columns in the packing diagram (Fig. 3). These columns are arranged so that the Bu^t groups point inwards towards channels containing thf molecules. In this manner the structure of **2** is similar to the structure of other inorganic phosphate solid state materials.¹⁷ It is likely that many other materials like this should be accessible when using ligands that coordinate in a linear manner.

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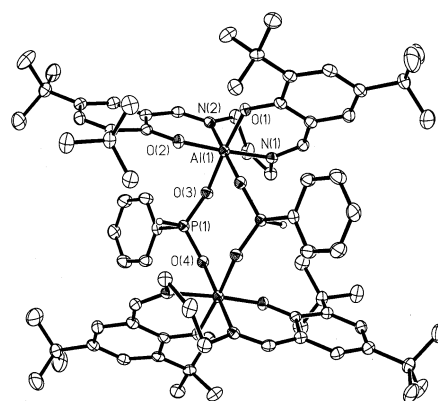
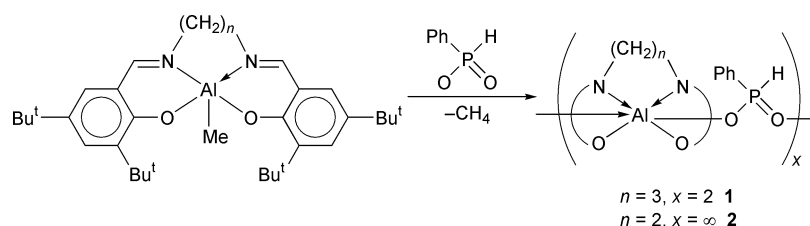


Fig. 1 ORTEP view of $[(\text{Bu}^t_4\text{salpen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_2$ **1**. Selected bond distances (Å) and angles ($^\circ$): Al(1)–O(1) 1.830(2), Al(1)–O(2), 1.830(2), Al(1)–O(3) 1.917(2), Al(1)–O(4') 1.900(2), Al(1)–N(1) 2.052(2), Al(1)–N(2) 2.034(2), P(1)–O(3) 1.507(2), P(1)–O(4) 1.507(2), P(1)–C(34) 1.801(2), P(1)–H(1) 1.30; O(1)–Al–O(3) $174.68(7)^\circ$, N(1)–Al(1)–O(2) $174.07(7)^\circ$, N(2)–Al(1)–O(4') $174.87(7)^\circ$, O(3)–Al(1)–O(4') $90.19(7)^\circ$, O(3)–P(1)–O(4) $116.81(8)^\circ$.



Scheme 1 Syntheses of $[(\text{Bu}^t_4\text{salpen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_2$ **1** and $[(\text{Bu}^t_4\text{salen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_\infty$ **2**.

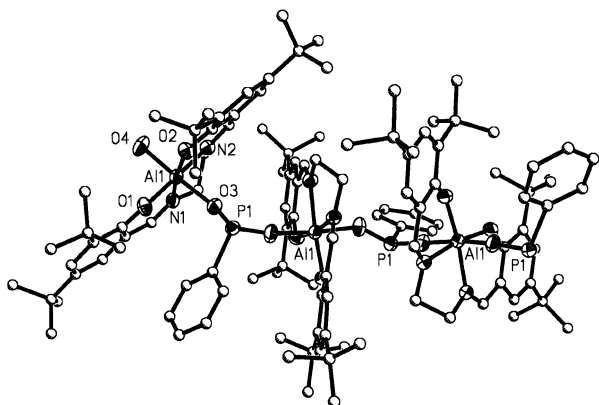


Fig. 2 ORTEP view (partial) of $[(\text{Bu}_4\text{salen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_\infty$ **2**. Selected bond distances (Å) and angles (°): Al(1)–O(1) 1.818(2), Al(1)–O(2) 1.817(2), Al(1)–O(3) 1.907(2), Al(1)–O(4) 1.890(2), Al(1)–N(1) 2.007(2), Al(1)–N(2) 2.008(2), P(1)–O(3) 1.435(2), P(1)–O(4) 1.476(2), P(1)–C(34) 1.788(2); O(3)–Al(1)–O(4) 174.80(7), N(1)–Al(1)–O(2) 169.72(7), N(2)–Al(1)–O(1) 170.51(7), O(3)–P(1)–O(4) 114.40(8). The P–H hydrogens were not found crystallographically owing to a disorder of the P atoms across two positions.

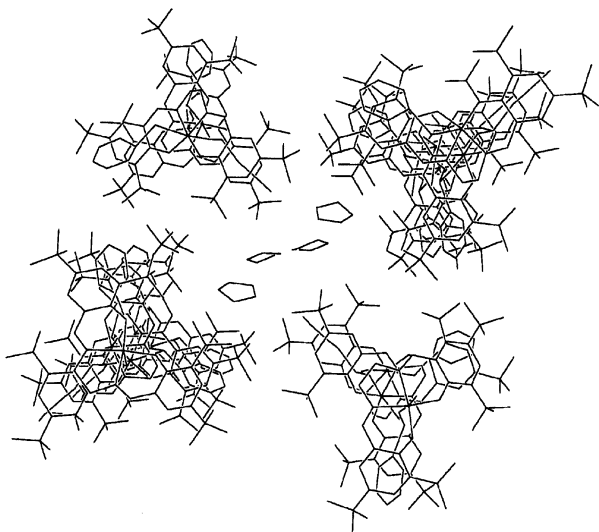


Fig. 3 Packing diagram of $[(\text{Bu}_4\text{salen})\text{Al}\{\text{O}_2\text{P}(\text{H})\text{Ph}\}]_\infty$ **2** showing the columnar arrangement of the polymers and the pores containing the molecules.

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- 14 $[(\text{Bu}_4\text{salpen})\text{AlO}_2\text{P}(\text{H})\text{Ph}]_2$ **1**: to a stirring solution of $(\text{Bu}_4\text{salpen})\text{AlMe}$ (0.500 g, 0.91 mmol) in THF (40 mL) was added a solution of phenylphosphonic acid (0.129 g, 0.91 mmol) in 20 mL of THF at -78°C . After 3 h of stirring, the THF was removed under vacuum yielding a yellow solid which was dissolved in CH_2Cl_2 (20 mL) and allowed to stand for several days at room temperature during which time yellow crystals formed. Yield: 0.340 g (55.3%); mp $>400^\circ\text{C}$. ^1H NMR (CDCl_3 , 200 MHz): δ 1.06 [s, 36H, $\text{C}(\text{CH}_3)_3$], 1.31 [s, 36H, $\text{C}(\text{CH}_3)_3$], 2.14(m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.25, 3.49 (m, 8H, NCH_2), 7.25 (d, $^1J_{\text{PH}}$ 556 Hz, 2H, PH), 6.61, 6.96, 7.20, 7.42 (m, 18H, PhH), 7.91 (s, 4H, PhCH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 80.9 MHz): δ 7.24 (s). IR(KBr; ν/cm^{-1}): 3053m, 2956s, 2902s, 2867s, 2402w, 2362w, 2157w, 1632s, 1548s, 1536s, 1475s, 1462s, 1440s, 1416s, 1386s, 1360s, 1341m, 1327s, 1277m, 1259s, 1234s, 1207s, 1172s, 1140s, 1087m, 1071s, 974s, 841m, 787m, 750m. MS(EI, positive): m/z 1346.5 (82.4%, Dimer⁺), 672.0 (91.2%, M⁺). $[(\text{Bu}_4\text{salen})\text{AlO}_2\text{P}(\text{H})\text{Ph}]_\infty$ **2**: to a stirring solution of $(\text{Bu}_4\text{salen})\text{AlMe}$ (0.540 g, 1.01 mmol) in THF (40 mL) was added a solution of phenylphosphonic acid (0.144 g, 1.01 mmol) in 20 mL of THF at -78°C . After 3 h of stirring, the solution was allowed to stand at ambient temperature overnight to yield clear yellow crystals. Yield: 0.380 g (56.4%); mp: the color of the crystal became darker at 340°C and the crystal melted at $361\text{--}362^\circ\text{C}$. ^1H NMR (CDCl_3 , 200 MHz): δ 1.19 [s, 18H, $\text{C}(\text{CH}_3)_3$], 1.28 [s, 18H, $\text{C}(\text{CH}_3)_3$], 3.05(br, 4H, NCH_2), 6.66 (d, $^1J_{\text{PH}}$ 552 Hz, 1H, PH), 6.51, 6.70, 6.92, 7.43 (m, 9H, PhH), 7.28 (s, 2H, PhCH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 80.9 MHz): δ 7.08 (s). IR(KBr; ν/cm^{-1}): 3054w, 2954s, 2905m, 2867m, 2385w, 1656s, 1548m, 1536m, 1477m, 1462m, 144(s, 1416m, 1390m, 1335m, 1197s, 1171s, 1141m, 1080m, 970m, 875m, 770m, 760m, 610m. MS(EI, positive): m/z 1317.7 (41%, Dimer⁺), 658.3 (100%, M⁺).
- 15 *Crystal data*: $1\cdot 4\text{CH}_2\text{Cl}_2$: $\text{C}_{82}\text{H}_{116}\text{Al}_2\text{Cl}_8\text{N}_4\text{O}_8\text{P}_2$, $M = 1685.29$, triclinic, space group $P\bar{1}$ $a = 9.337(1)$, $b = 16.245(2)$, $c = 16.297(2)$ Å, $\alpha = 66.95(1)$, $\beta = 73.91(1)$, $\gamma = 78.89(1)^\circ$, $V = 2175.6(4)$ Å³, $T = 173(1)$ K, $Z = 1$, (Mo-K α) $D_c = 1.286$ g cm⁻³, 15256 reflections measured, 7657 unique ($R_{\text{int}} = 0.0312$) which were used in all calculations, final R values were 0.0425 [$F > 4\sigma(F)$] and 0.0632 (all data). $2\cdot\text{thf}$: $\text{C}_{142}\text{H}_{209.5}\text{Al}_3\text{N}_6\text{O}_{19}\text{P}_3$, $M = 2478.51$, monoclinic, space group $P2_1/c$, $a = 16.650(1)$, $b = 27.518(2)$, $c = 31.149(2)$ Å, $\beta = 92.28(1)^\circ$, $V = 14260(2)$ Å³, $T = 173(1)$ K, $Z = 4$, (Mo-K α) $D_c = 1.154$ g cm⁻³, 18627 reflections measured, 36396 unique ($R_{\text{int}} = 0.0393$) which were used in all calculations, final R values were 0.0765 [$F > 4\sigma(F)$] and 0.1059 (all data). CCDC 182/1741. See <http://www.rsc.org/suppdata/cc/b0/b004342g/> for crystallographic files in .cif format.
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