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Organic-Soluble Cyclic and Cage Alkylaluminophosphates: X-ray Crystal Structure of $[(^t\mathrm{Bu})_2\mathrm{Al}(\mu_2\text{-O})_2\mathrm{P}(\mathrm{OSiMe}_3)_2]_2$

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Aluminophosphate (AlPO_4) materials and their silicon-substituted (SAPO) and metal-substituted (MAPO) derivatives are presently under investigation for use as catalysts, catalyst supports, ion-exchange reagents, and molecular sieves.[1−5] The porosity and utility of these materials arise from an interpenetrating network of channels and cages (e.g., α-cage, rpa-cage, sodalite units) large enough to act as inorganic hosts for organic molecules. Formation of these porous materials is achieved under hydrothermal conditions in the presence of fluoride or an organic amine. These added reagents appear to act as space fillers, as structure-directing agents, or as templates for constructing the cage network of the resulting porous material. However, factors which influence ring and cage formation under synthesis conditions are not fully understood. Furthermore, in most cases direct structural correlation between the template and the AlPO_4 product has not been established. The rational synthesis of new AlPO_4 materials with specific properties and pore sizes will be dependent on the elucidation of factors which control the formation of the cagelike structural units in these materials.[2]

We have taken a unique approach to this problem by initiating the synthesis of organic-soluble cyclic and cage aluminophosphates and aluminophosphonates with which to model template interactions in the synthesis of AlPO_4 molecular sieves and for use as convenient precursors for the designed synthesis of new phosphate materials. Our initial synthetic targets possess a cubic $\mathrm{Al}_4\mathrm{P}_4\mathrm{O}_{12}$ core analogous to the double-four-tetrahedral-atom-ring (D4R) secondary building units[6] in AlPO_4 materials. The targeted $\mathrm{Al}_4\mathrm{P}_4\mathrm{O}_{12}$ core also has an isoelectronic and structural relationship to the $\mathrm{Si}_8\mathrm{O}_{12}$ core of the well-studied octameric silsesquioxanes, $[\mathrm{RSiO}_{1.5}]_8$,[7,8] and a structural relationship to the $\mathrm{Al}_4\mathrm{Si}_4\mathrm{O}_{12}$ cores of the soluble aluminosiloxanes $[\mathrm{RN}(\mathrm{SiMe}_3)\mathrm{SiO}_3\text{-}\mathrm{Al}\cdot\mathrm{dioxane}]_4$ and the aluminosilicates $[\mathrm{Na}(\mathrm{THF})]_4[\mathrm{RN}(\mathrm{SiMe}_3)\text{-}\mathrm{SiO}_3\mathrm{AlEt}]_4$ recently prepared by Roesky.[9−11] A cubic $\mathrm{Al}_4\mathrm{P}_4\mathrm{O}_{12}$ core was previously crystallographically confirmed for the ethanol-soluble compound $[\mathrm{Al}(\mathrm{PO}_4)(\mathrm{HCl})(\mathrm{EtOH})_4]_4$.[12]

Two methods for the synthesis of cyclic and cage aluminophosphonates and aluminophosphates are being pursued. The first involves reaction of phosphonic acids with aluminum alkyls,[13] and the second utilizes $\mathrm{Me}_3\mathrm{SiCl}$ elimination from $(\mathrm{Me}_3\mathrm{SiO})_3\mathrm{P{=}O}$ and RAlCl_2. Our initial results on the second method are reported herein.

Reaction of $(\mathrm{Me}_3\mathrm{SiO})_3\mathrm{P{=}O}$ with $^t\mathrm{Bu}_2\mathrm{AlCl}$ in THF yields $[(^t\mathrm{Bu})_2\mathrm{Al}(\mu_2\text{-O})_2\mathrm{P}(\mathrm{OSiMe}_3)_2]_2$ (**1**) as clear, colorless crystals which exhibit slight solubility in toluene and high solubility in THF.[14] NMR spectroscopic data (^{1}H, ^{13}C, ^{31}P) obtained on benzene-d_6 solutions are consistent with the formulation of **1** as a dimer containing an eight-membered $\mathrm{Al}_2\mathrm{P}_2\mathrm{O}_4$ ring.[15] The preference of aluminum for a coordination number of 4, the absence of coordinated solvent as indicated by NMR spectroscopy and elemental analysis, and the strain expected for a chelating phosphate ligand all argue strongly against **1** existing as a monomer. Furthermore, a cyclic dimer is consistent with the structures proposed for phosphinates of aluminum, gallium, and indium, $[\mathrm{R}_2\mathrm{MO}_2\mathrm{PR}'_2]_2$ (R = Me, Et; M = Al, Ga, In; R′ = Me, Ph, Cl, F), on the basis of infrared spectroscopic data,[16−19] and confirmed in the solid state by X-ray crystallography for $[\mathrm{Me}_2\mathrm{GaO}_2\mathrm{PPh}_2]_2$ and $[(^t\mathrm{Bu})_2\mathrm{GaO}_2\mathrm{PPh}_2]_2$.[20,21] The dimeric structure of **1** in the gas phase is indicated by mass spectrometry and confirmed for the solid state by X-ray crystallography.[22]

The molecular structure of **1** is shown in Figure 1. The eight-membered $\mathrm{Al}_2\mathrm{P}_2\mathrm{O}_4$ ring is composed of two μ_2-η^2-$\mathrm{O}_2\mathrm{P}(\mathrm{OSiMe}_3)_2$ bridges between distorted tetrahedral aluminum centers related by a crystallographically imposed inversion center. All angles at aluminum lie between 102.3(2) and 109.4(2)° except for the large C−Al−C angle of 121.3°, which is presumably due to the steric bulk of the two *tert*-butyl

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(1) Li, H.-X.; Davis, M. E. *Catal. Today* **1994**, *19*, 61.

(2) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756.

(3) Huo, Q.; Xu, R.; Li, S.; Ma, Z.; Thomas, J. M.; Jones, R. H.; Chippindale, A. M. *J. Chem. Soc., Chem. Commun.* **1992**, 875.

(4) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowder, C. *Nature* **1988**, *331*, 698.

(5) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannon, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.

(6) Dyer, A. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley and Sons: New York, 1994; Vol. 8, pp 4363−4391.

(7) Voronkov, M. G.; Lavrentyev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199.

(8) Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239.

(9) Montero, M. L.; Voigt, A.; Teichert, M.; Uson, I.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2504.

(10) Chandrasekhar, V.; Murugavel, R.; Voigt, A.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 918.

(11) Murugavel, R.; Chandrasekhar, V.; Roesky, H. W. *Acc. Chem. Res.* **1996**, *29*, 183.

(12) Cassidy, J. E.; Jarvis, J. A.; Rothon, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 1497.

(13) Mason, M. R.; Matthews, R. M.; Perkins, A. M.; Mashuta, M. S.; Richardson, J. F. Manuscript in preparation.

(14) A solution of $(\mathrm{Me}_3\mathrm{SiO})_3\mathrm{P{=}O}$ (3.66 g, 11.6 mmol; Aldrich) in 25 mL of THF was added dropwise to a stirred solution of $^t\mathrm{Bu}_2\mathrm{AlCl}$[28] (2.04 g, 11.6 mmol) in 30 mL of THF. The resulting clear and colorless solution was heated under reflux for 2 h. The volume of the solution was reduced *in vacuo*, and the concentrate was cooled at −20 °C overnight to produce clear colorless crystals. Yield of **1**: 2.47 g, 3.23 mmol, 56%.

(15) Spectroscopic and analytical data for **1** are as follows. ^{1}H NMR ($\mathrm{C}_6\mathrm{D}_6$, 500 MHz): δ 0.22 (18H, s, SiMe_3), 1.33 (18H, s, ^{t}Bu). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C}_6\mathrm{D}_6$, 125.5 MHz): δ 0.73 (SiMe_3), 30.6 ($\mathrm{C}(C\mathrm{H}_3)$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C}_6\mathrm{D}_6$, 121.5 MHz): δ −31.4 (s). MS (EI) *m/z* (assignment, relative intensity): 749 ($\mathrm{M}^+ - \mathrm{CH}_3$, 6), 707 ($\mathrm{M}^+ - {}^t\mathrm{Bu}$, 100), 651 (49), 493 (50). HRMS (EI) *m/z* for $\mathrm{C}_{27}\mathrm{H}_{69}\mathrm{Al}_2\mathrm{Si}_4\mathrm{P}_2\mathrm{O}_8$ ($\mathrm{M}^+ - \mathrm{CH}_3$): calcd, 749.3175; found, 749.3184. HRMS (EI) *m/z* for $\mathrm{C}_{24}\mathrm{H}_{63}\mathrm{Al}_2\mathrm{Si}_4\mathrm{P}_2\mathrm{O}_8$ ($\mathrm{M}^+ - {}^t\mathrm{Bu}$): calcd, 707.27062; found, 707.27067. Anal. Calcd for $\mathrm{C}_{28}\mathrm{H}_{72}\mathrm{Al}_2\mathrm{Si}_4\mathrm{P}_2\mathrm{O}_8$: C, 43.95; H, 9.49; Al, 7.05; P, 8.09. Found: C, 43.59; H, 9.88; Al, 6.99; P, 7.94.

(16) Coates, G. E.; Mukherjee, R. N. *J. Chem. Soc.* **1964**, 1295.

(17) Weidlein, J.; Schaible, B. *Z. Anorg. Allg. Chem.* **1971**, *386*, 176.

(18) Schaible, B.; Weidlein, J. *J. Organomet. Chem.* **1972**, *35*, C7.

(19) Olapinski, H.; Schaible, B.; Weidlein, J. *J. Organomet. Chem.* **1972**, *43*, 107.

(20) Hahn, F. E.; Schneider, B.; Reier, F.-W. *Z. Naturforsch. B* **1990**, *45*, 134.

(21) Landry, C. C.; Hynes, A.; Barron, A. R.; Haiduc, I.; Silvestru, C. *Polyhedron* **1996**, *15*, 391.

(22) Crystal data for **1**: $\mathrm{C}_{28}\mathrm{H}_{72}\mathrm{Al}_2\mathrm{P}_2\mathrm{Si}_4\mathrm{O}_8$, monoclinic, $C2/c$ (No. 15), a = 21.040(12) Å, b = 12.778(9) Å, c = 20.298(13) Å, β = 118.26(6)°, V = 4806(5) Å^3, Z = 4, D_{calc} = 1.057 g/cm^3, T = 296 K. Of 4564 data collected (maximum 2θ = 50°, Mo Kα, μ = 2.61 cm^{-1}), 4490 were unique. The final residuals for 199 parameters refined against 2007 unique data with $I > 3\sigma(I)$ were R = 5.4% and R_{w} = 5.5%.

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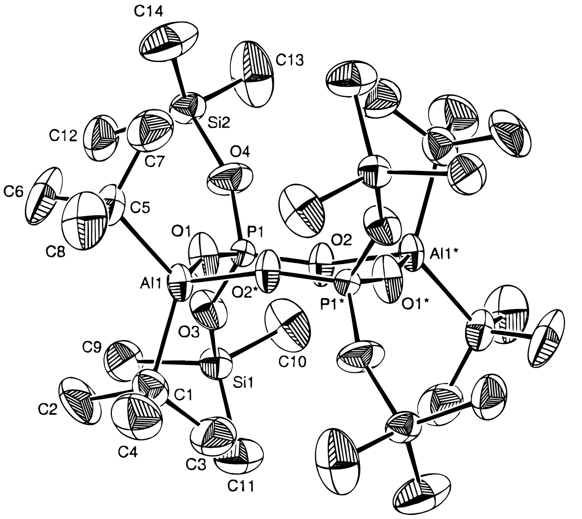

Figure 1. ORTEP drawing of $[(^tBu)_2Al(\mu_2\text{-}O)_2P(OSiMe_3)_2]_2$ (**1**). Thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Al(1)−O(1) = 1.790(4); Al(1)−O(2) = 1.805(4); P(1)−O(1) = 1.471(4); P(1)−O(2) = 1.469(4); O(1)−Al(1)−O(2) = 102.3(2); O(1)−P(1)−O(2) = 113.6(2); P(1)−O(1)−Al(1) = 160.9(3); P(1)−O(2)−Al(1) = 151.4(2).

substituents. Aluminum−oxygen distances of 1.790(4) and 1.805(4) Å are comparable to those found in the $Al_4P_4O_{12}$ core of $[Al(PO_4)(HCl)(EtOH)_4]_4$ (1.80−1.83(1) Å)[12] but slightly longer than the intra-ring Al−O distance of 1.718(4) Å found in the related cyclic aluminosiloxane $[(2,6\text{-}i\text{-}Pr_2C_6H_3)N(SiMe_3)\text{-}Si(OH)O(OAlBu\text{-}i\cdot THF)]_2$.[23] We note that **1** is an organic-substituted derivative of four-membered-ring secondary building units found in some $AlPO_4$ molecular sieves. All Al−O and P−O distances, as well as angles at aluminum, phosphorus, and oxygen, for **1** are within the range of values reported for $AlPO_4$ materials.[24]

Given the success of the Me_3SiCl elimination route for the preparation of **1**, the preparation of $[(^tBu)Al(\mu_2\text{-}O)_3P(OSiMe_3)]_4$ (**2**) was undertaken by reaction of $(Me_3SiO)_3P{=}O$ with $^tBuAlCl_2$ in refluxing THF.[25] After concentration and cooling, **2** crystallizes as a white solid in 56% yield. The ^1H NMR spectrum of **2** exhibits a single ^tBu resonance and an equally intense Me_3Si resonance, demonstrating that 2 equiv of Me_3SiCl is eliminated/equiv of aluminum. ^1H and ^{13}C NMR data also show no evidence for coordinated THF molecules. The ^{31}P NMR spectrum of **2** confirms the symmetry observed in the ^1H and ^{13}C NMR spectra, exhibiting only a single resonance at −28.4 ppm, just slightly downfield of that observed for **1** (−31.4 ppm). These chemical shifts are noteworthy since ^{31}P MAS NMR spectra for $AlPO_4$ materials generally exhibit resonances around −30 ppm.[1] Elemental analysis confirms **2** should be formulated as $[(^tBu)Al(\mu_2\text{-}O)_3P(OSiMe_3)]_n$, and mass spectral observation of a molecular ion peak at *m/z* 1008 and a strong

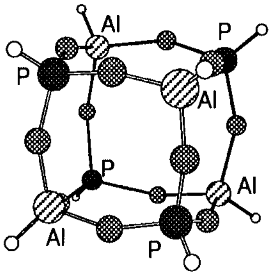

Figure 2. Chem 3D drawing of the proposed $Al_4P_4O_{12}$ core for $[(^tBu)Al(\mu_2\text{-}O)_3P(OSiMe_3)]_4$ (**2**). Aluminum and phosphorus atoms are shown with arbitrary substituents. Alkyl and siloxide substituents have been omitted for clarity.

peak at *m/z* 951 corresponding to loss of a *tert*-butyl substituent demonstrates **2** to be a tetramer, $n = 4$. Consistent with the above data,[26] we propose that **2** consists of a cubic $Al_4P_4O_{12}$ core with one *tert*-butyl substituent per aluminum and one trimethylsiloxide substituent per phosphorus atom (Figure 2). Although crystallographic characterization of **2** has thus far been thwarted by twinning of the crystals, we note crystallographic confirmation of a related $Ga_4P_4O_{12}$ core in $[(^tBu)Ga(\mu_2\text{-}O)_3PPh]_4$.[27]

Preliminary reactivity studies indicate that **1** and **2** are stable to dry oxygen in benzene-d_6 solutions over several days, but both rapidly hydrolyze in the presence of moisture. We are presently exploring reactions of the remaining trimethylsiloxide substituents on phosphorus with the aim of rationally linking cages together for the synthesis of new phosphate materials. Results of these studies will be reported elsewhere.

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Supporting Information Available: Text describing structure solution and refinement, tables of crystal data and refinement details, positional and thermal parameters, complete bond distances and angles, and torsion angles, and a fully labeled structure diagram for **1** (15 pages). Ordering information is given on any current masthead page.

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(23) Montero, M. L.; Uson, I.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2103.

(24) For examples, see: (a) Cheetham, G.; Harding, M. M. *Zeolites* **1996**, *16*, 245. (b) Bennett, J. M.; Kirchner, R. M. *Zeolites* **1992**, *12*, 338. (c) Wright, P. A.; Natarajan, S.; Thomas, J. M.; Bell, R. G.; Gai-Boyes, P. L.; Jones, R. H.; Chen, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1472. (d) Simmen, A.; McCusker, L. B.; Baerlocher, Ch.; Meier, W. M. *Zeolites* **1991**, *11*, 654. (e) Richardson, J. W., Jr.; Smith, J. V.; Pluth, J. J. *J. Phys. Chem.* **1989**, *93*, 8212. (f) Richardson, J. W., Jr.; Pluth, J. J.; Smith, J. V. *Acta Crystallogr.* **1988**, *B44*, 367.

(25) A solution of $(Me_3SiO)_3P{=}O$ (3.21 g, 10.2 mmol) in 25 mL of THF was added dropwise to a stirred solution of $^tBuAlCl_2$[28] (1.58 g, 10.2 mmol) in 25 mL of THF. The resulting clear and colorless solution was heated under reflux for 2 h. The volume of the solution was reduced *in vacuo*, and the concentrate was cooled at −20 °C overnight to produce clear and colorless crystals. Yield of **2**: 1.45 g, 1.44 mmol, 56%.

(26) Spectroscopic and analytical data for **2** are as follows. ^1H NMR (C_6D_6, 500 MHz): δ 0.21 (36H, s, $SiMe_3$), 1.27 (36H, s, ^tBu). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.5 MHz): δ 0.41 ($SiMe_3$), 29.3 ($C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ −28.4 (s). MS (EI), *m/z* (assignment, relative intensity): 1008 (M^+, 0.3), 993 ($M^+ - CH_3$, 21), 951 ($M^+ - {}^tBu$, 100). HRMS (EI) *m/z* for $C_{27}H_{68}Al_4Si_4P_4O_{16}$ ($M^+ - CH_3$): calcd, 993.1830; found, 993.1834. HRMS (EI) *m/z* for $C_{24}H_{63}Al_4Si_4P_4O_{16}$ ($M^+ - {}^tBu$): calcd, 951.1405; found, 951.1399. Anal. Calcd for $C_{28}H_{72}Al_4Si_4P_4O_{16}$: C, 33.32; H, 7.19; Al, 10.70; P, 12.28. Found: C, 32.92; H, 7.13; Al, 10.93; P, 12.15.

(27) Mason, M. R.; Mashuta, M. S.; Richardson, J. F. Manuscript submitted.

(28) Lehmkuhl, H.; Olbrysch, O.; Nehl, H. *Liebigs Ann. Chem.* **1973**, 708.