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Sodium Salt of a Cyclic Aluminophosphonate: Model Compound for the Six-Ring Secondary Building Units of Molecular Sieves[1]

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Our interest in the formation mechanism and catalytic activity of molecular sieves has lead us to synthesize model compounds for secondary building units (SBU)[2] found in zeolitic frameworks. Such molecules can be thought of as small fragments of three-dimensional structures surrounded by a shell of organic ligands and they can serve as archetypes of structural moieties found in porous solids. Their solubility in organic solvents allows the investigation of spectral and structural properties by convenient solution spectroscopic methods and the information gained from the study of these models can be utilized in the area of three-dimensional framework structures. An example of mimicking an active site in *heterogeneous* titanosilicate catalysts by a fully functional *molecular* titanosilsesquioxane model compound illustrates this point.[3] These reactive compounds can also be used as precursors for the syntheses of new materials by assembling the preformed building blocks into extended structures. This idea has been recently realized for silicate,[4] aluminosilicate,[5] and alumino- and galloaluminophosphate[6] mesoporous materials by using cubelike (D4R) $[Si_8O_{20}]^{8-}$, $[Al_4Si_4(OH)_8O_{12}]^{4-}$, and cluster $[(Al/Ga)O_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ precursors, respectively. The need for a wider variety of building blocks has led to the syntheses and structural characterization of a multitude of organic-soluble group 13 and 14 metallophosphonates and -siloxanes.[7] The simplest species possess square $M_2E_2O_4$ cores (M = Al, Ga; E = P, Si),[8,9] and they can be considered as models for the single four-ring (4R or 4) SBU. Furthermore, there is an extensive series of cubelike metallosiloxanes and metallophosphonates which feature a double four-ring motif (D4R or 4-4). More recent work carried out in our laboratory resulted in the synthesis of a larger drumlike molecule $[t\text{-BuPO}_3\text{AlMe}]_6$ (**1**)[10] which is analogous to a double six-ring (D6R or 6-6) SBU and aluminophosphonate cluster $[Cs_3(THF)_3F(i\text{-BuAl})_3(t\text{-BuPO}_3)_4]_2[(i\text{-BuAl})_2Al_2(\mu\text{-F})_2(t\text{-BuPO}_3)_4]$ (**2**)[11] which features both double four-ring and capped six-ring units (C6R or 6≡1). However, a number of other SBU analogues have not yet been obtained. Herein, we report the synthesis and spectroscopic and structural characterization of a new compound $[Na_3(THF)(t\text{-BuPO}_3\text{AlEt}_2)_3]_2$ (**3**). This is the first molecular model of an ubiquitous structural element in zeolites: the single six-ring (6R).

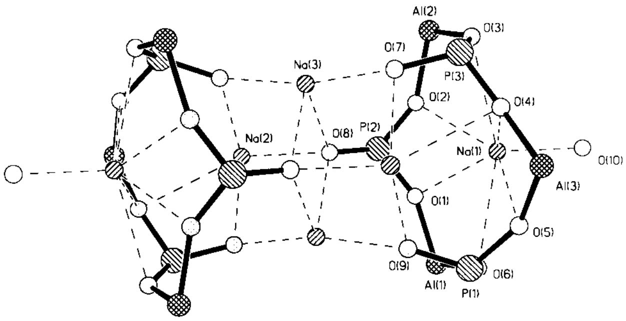

Figure 1. Molecular structure and the numbering scheme of **3**. All *t*-Bu and Et groups are omitted for clarity. Selected bond distances (Å): Al(1)−O(1), 1.776(6); Al(1)−O(6), 1.796(4); Al(2)−O(2), 1.808(6); Al(2)−O(3), 1.788(4); Al(3)−O(4), 1.784(4); Al(3)−O(5), 1.786(4); P(1)−O(5), 1.541(4); P(1)−O(6), 1.531(4); P(2)−O(1), 1.520(5); P(2)−O(2), 1.514(5); P(3)−O(3), 1.536(4); P(3)−O(4), 1.541(1).

The equimolar reaction of $NaAlEt_2H_2$ and *tert*-butylphosphonic acid in THF/toluene (1:1) provides compound **3** as a white crystalline solid in 14.5% yield.[12] Both ^1H and ^{13}C NMR spectra of **3** display pairs of signals for the ethyl groups at aluminum at room temperature (22 °C) suggesting the diastereotopicity. The ratio of intensities of *tert*-butyl and $AlEt_2$ proton signals (9:4:6) is consistent with the formula $[Na_3(THF)(t\text{-BuPO}_3\text{AlEt}_2)_3]_2$.

The molecular structure of **3** was elucidated by X-ray diffraction methods (Figure 1).[13] The molecule consists of two $Al_3P_3O_6$ six-rings (6R), related by an inversion center, which are interconnected by four sodium ions coordinated to the terminal phosphonate oxygens and one ring oxygen O(4). Furthermore,

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(1) Dedicated to Professor Karel Dostal.

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(12) A solution of *tert*-butylphosphonic acid (0.43 g, 3.1 mmol) in THF (20 mL) was added dropwise to a solution of $NaAlEt_2H_2$ (3.2 mmol, 1.6 mL of 2 M stock solution in toluene) in toluene (20 mL) at −78 °C. The reaction mixture was subsequently stirred for 16 h at room temperature, and then it was concentrated to 10 mL under vacuum. The resulting solution was filtered and stored at room temperature for a week. Hexagonal colorless crystals of **3** (0.096 g, 14.5%) were found to be suitable for X-ray diffraction studies. **3**: Mp: 249−252 °C (dec). IR (Nujol, cm^{-1}): ν 1481, 1262, 1208, 1188, 1093, 1021, 945, 839, 804, 688, 666, 506, 488. ^1H NMR (200.13 MHz, THF-d_8): δ −0.37, −0.24 (4 H, q, J_{HH} = 8.1 Hz, $AlCH_2$), 0.99, 1.00 (6 H, t, J_{HH} = 8.1 Hz, $AlCH_2CH_3$), 1.09 (9 H, d, J_{PH} = 14.9 Hz, CH_3). ^{13}C NMR (62.89 MHz, THF-d_8): δ 0.51, 1.05 (br s, $AlCH_2$), 10.24, 10.41 (s, $AlCH_2CH_3$), 26.55 (d, J_{PC} = 1.8 Hz, $PCCH_3$), 30.91 (d, J_{PC} = 151.0 Hz, $PCCH_3$). ^{31}P NMR (101.25 MHz, THF-d_8): δ 25.6. MS (EI, 70 eV): 1436 (M − Et, 25%), 947 ($[NaEt_2AlO_3Pt\text{-Bu}]_4$ − Et, 100%). Elem. Anal. (after drying under vacuum for 4 h). calcd for $C_{48}H_{114}Al_6Na_6O_{18}P_6$ (1465.09): C, 39.35; H, 7.84. Found: C, 39.28; H, 7.74.

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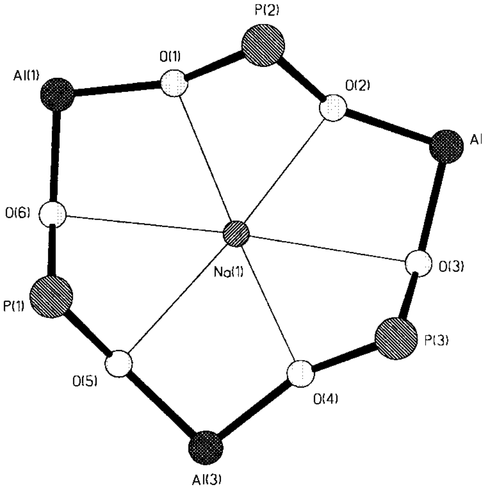

Figure 2. $Al_3P_3O_6$ ring in **3** showing the coordination array around Na(1). Distances across the ring (Å): O(1)−O(4), 4.64; O(2)−O(5), 4.92; O(3)−O(6), 5.50. Al−O−P bond angles (deg): O(1), 159.1(4); O(2), 151.5(4); O(3), 134.6(3); O(4), 157.0(3); O(5), 147.4(3); O(6), 137.6(2). Na(1)−O_{ring} distances (Å): O(1), 2.621(6); O(2), 2.545(6); O(3), 2.843(5); O(4), 2.535(5); O(5), 2.740(4); O(6), 2.820(5).

the $Al_3P_3O_6$ units are capped by sodium ions coordinated to the six oxygen atoms of the ring in a crown-ether binding mode (Figure 2) with Na−O_{ring} distances in the range from 2.535(5) to 2.843(5) Å. One THF molecule (Na(1)−O(10) = 2.225(4) Å) completes the seven-coordinate environment of this sodium center. Such a coordination arrangement around Na(1) closely resembles the cation sites in zeolites sodalite[14] and Linde A,[15] where somewhat shorter Na−O distances (2.35 Å) were found. Both Na(2) and Na(3), sandwiched between the $Al_3P_3O_6$ rings, are four-coordinate. The aluminum atoms reside in a distorted tetrahedral coordination sphere. The O−Al−O and C−Al−C angles are in the range of 95.1(3)−97.1(2) and 123.6(4)−126.2(4)°, respectively. The *t*-$BuPO_3$ groups retain an ideal tetrahedral geometry around the phosphorus center. The two faces of the $Al_3P_3O_6$ rings are inequivalent, thus rendering the $AlEt_2$ groups diastereotopic.

As [*t*-$BuPO_3AlMe$]$_6$ (**1**) also consists of two $Al_3P_3O_6$ six-rings (in this case, however, interconnected via bridging μ_2-O atoms), it is worth to compare metric parameters within the $Al_3P_3O_6$ ring of **3** and **1**. This comparison reveals slightly shorter Al−O (av 1.752(3) Å) and P−O (av 1.515(3) Å) distances in **1** and also larger variations in bond distances and angles in **3** (Al−O, 1.776(6)−1.808(6) Å; P−O, 1.514(5)−1.541(4) Å). In **1**, the P−O−Al angles within the $Al_3P_3O_6$ ring are in a narrow interval 148.4(1)−151.9(1)°. On the other hand, the Al−O−P angles in the distinctly puckered $Al_3P_3O_6$ rings of **3** vary from 134.6(3) to 159.1(4)°. In the undistorted six-ring of **1**, the O−O distances across the ring are in the range of 5.28−5.31 Å while the corresponding distances in **3** (Figure 2) are considerably shortened (by more than 0.2 Å) as the interaction of Na(1) with oxygens deforms the ring. This distortion of the $Al_3P_3O_6$ ring in **3** is also reflected in its ^{31}P NMR spectrum (singlet, 25.6 ppm). A shift to lower field with respect to the *t*-BuP(OAl)$_2$(OCs) signal of C6R units in **2** (14.7 ppm) is consistent with closing of the average Al−O−P angle[16] from 158.3° in **2** to 147.9° in **3**.

We are currently studying conversion of **3** into other types of SBU, such as D6R and C6R.

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Supporting Information Available: Listing of tables of crystal data and structure refinement details, positional and thermal parameters, complete set of bond lengths and angles, and molecular structure diagram (10 pages). Ordering information is given on any current masthead page.

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[13] Crystal data for **3**·C_7H_8: $C_{63}H_{138}Al_6Na_6O_{20}P_6$, fw = 1701.4, triclinic, $P\bar{1}$, $a = 12.948(3)$ Å, $b = 13.233(3)$ Å, $c = 16.543(3)$ Å, $\alpha = 86.84(3)°$, $\beta = 69.85(3)°$, $\gamma = 62.19(3)°$, $V = 2334.4(8)$ Å^3, $Z = 1$, $D_{calcd} = 1.210$ g·cm^{-3}, $T = 153(2)$ K, $\mu = 2.57$ cm^{-1}, 6122 independent reflections, $R1 = 0.0683$ for $I > 2\sigma(I)$, $wR2 = 0.1789$ for all data. The data were collected on a Stoe-Siemens-AED2 four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å).

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