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$\{Zn_3(Et_2O)_2[(EtO)PO_2(C_6H_5NH)]_6 \cdot 2THF\}$: A Trinuclear Zinc Amidophosphate with an Hourglass Structure

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The reaction of ZnMe$_2$ and the N-substituted phosphoramidic monoester $[Et_2NH_2][(EtO)PO_2(C_6H_5NH)]$ produces the trinuclear zinc cluster $Zn_3(Et_2O)_2[(EtO)PO_2(C_6H_5NH)]_6 \cdot 2THF$, demonstrating that the P–N bond can survive under mild solvothermal reaction conditions.

Metal phosphates (MPOs) have attracted immense interest during the last 2 decades in view of their practical applications as molecular sieves, absorbents, and catalysts. In addition, these inorganic frameworks often exhibit attractive structural features.[1] In the preparation of these materials, supramolecular design is a useful approach for molecular level control and rational syntheses of new compounds with tailored properties.[2] Oligonuclear MPOs may be regarded as building units (BUs) for the construction of porous MPOs as infinite networks.[3] For example, the single four-ring unit $[Zn(H_2PO_4)_2HPO_4]^{2-}$ undergoes an intriguing transformation to a porous layer structure under certain reaction conditions.[4]

The imido (RN^{2-}, R = H, alkyl, aryl) ligand is formally isoelectronic with an oxido (O^{2-}) ligand.[5] The partial replacement of oxido ligands in zinc phosphates by imido ligands might be expected to generate materials with more basic sites whose pore sizes are influenced by the nature of the R group. Two synthetic approaches have been investigated. The first involves heating of MPOs in a stream of ammonia gas at high temperatures (500−850 °C).[6] This procedure generates so-called "metal phosphate oxynitrides" (MPONs), which exhibit effective base-catalytic behavior.[6] MPONs have not been structurally characterized, but spectroscopic methods indicate that the basic sites involve NH and NH$_2$ groups.[6,7] An alternative procedure employs P−N reagents, such as $OP(NMe_2)_3$[8] or $OP(NH^tBu)_3$,[9] in hydrothermal or solvothermal reactions with metal salts. However, this method results in complete P−N bond cleavage to give novel zinc phosphate[8] or anionic copper halide[9] frameworks as a result of the templation effect of in situ generated secondary amines or $[^tBuNH_3]^+$, respectively. Thus, the experimental challenge in a chimie douce approach[10] to the synthesis of MPONs from amido−phosphorus reagents is the protection of the P−N bond. Esters of N-substituted phosphoramidic acids, EtOP(O)NRR′(OH), are potentially useful reagents for the synthesis of molecular MPONs, but they decompose readily via P−N bond cleavage to give unstable metaphosphates (Scheme 1a) and, hence, pyrophosphates.[11,12] With the idea that coordination to a metal center may inhibit the condensation of the N-substituted phosphoramidic ligand and, hence, prevent cleavage of the P−N bond, we have investigated the reaction of the N-substituted phosphoramidic monoester $[Et_2NH_2][(EtO)PO_2(C_6H_5NH)]$ with ZnMe$_2$. Here, we report the formation of the novel trinuclear zinc complex $Zn_3(Et_2O)_2[(EtO)PO_2(C_6H_5NH)]_6 \cdot 2THF$ (**1**), the first example of a structurally characterized metal amidoorthophosphate, which exhibits a fascinating hourglass framework.[13]

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(1) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.

(2) (a) Rao, C. N. R.; Natarajan, S.; Choudhury, A.; Neeraj, S.; Ayi, A. A. *Acc. Chem. Res.* **2001**, *34*, 80. (b) Lugmair, C. G.; Tilley, T. D.; Rheingold, A. L. *Chem. Mater.* **1997**, *9*, 339.

(3) Férey, G. *J. Solid State Chem.* **2000**, *152*, 37.

(4) Natarajan, S.; Wüllen, L. V.; Klein, W.; Jansen, M. *Inorg. Chem.* **2003**, *42*, 6265.

(5) The original definition of "isoelectronic" (isosteric) compounds restricts the term to species having the same number of atoms and the same number of electrons (Langmuir, I. *J. Am. Chem. Soc.* **1919**, *41*, 1542). Thus, according to this definition, N^{3-} is isoelectronic with O^{2-}. However, the composition of nitrides differs from that of the corresponding oxides as a result of the different charges on the anions.

(6) (a) Climent, M. J.; Corma, A.; Fornés, V.; Frau, A.; Guil-Lüpez, R.; Iborra, S.; Primo, J. *J. Catal.* **1996**, *163*, 392. (b) Fripiat, N.; Grange, P. *Chem. Commun.* **1996**, 1409. (c) Conanec, R.; Marchand, R.; Laurent, Y. *J. High Temp. Chem. Processes* **1991**, *1*, 157. (d) Conanec, R.; Marchand, R.; Laurent, Y.; Bastians, Ph.; Grange, P. *Mater. Sci. Forum* **1994**, *152*, 305. (e) Gandia, L. M.; Malm, R.; Marchand, R.; Laurent, Y.; Montes, M. *Appl. Catal. A* **1994**, *114*, L1. (f) Grange, P.; Bastians, Ph.; Conanec, R.; Marchand, R.; Laurent, Y. *Appl. Catal. A* **1994**, *114*, L191.

(7) Nitridooxophosphates, which exhibit sodalite-like structures, are obtained by the reaction of a metal halide, e.g., CuCl or LiCl, with $(NH_2)_2P(O)NP(NH_2)_3$ or $EP(NH_2)_3$ (E = O, S) at 350−700 °C *in the absence of a solvent*. Stock, N.; Irran, E.; Schnick, W. *Chem. Eur. J.* **1998**, *4*, 1822.

(8) Neeraj, S.; Cheetham, A. K. *Chem. Commun.* **2002**, 1738.

(9) Chivers, T.; Fu, Z.; Thompson, L. K. *Chem. Commun.* **2005**, 2339.

(10) Livage, J. *New J. Chem.* **2001**, *25*, 1 and references cited therein.

(11) (a) Clark, V. M.; Kirby, G. W.; Todd, A. *J. Chem. Soc.* **1957**, 1497. (b) Moffatt, J. G.; Khorana, H. G. *J. Chem. Soc.* **1961**, *83*, 649. (c) Chambers, R. W.; Khorana, H. G. *Chem. Ind. (London)* **1956**, 1022.

(12) Quin, L. D.; Jankowski, S. *J. Org. Chem.* **1994**, *59*, 4402.

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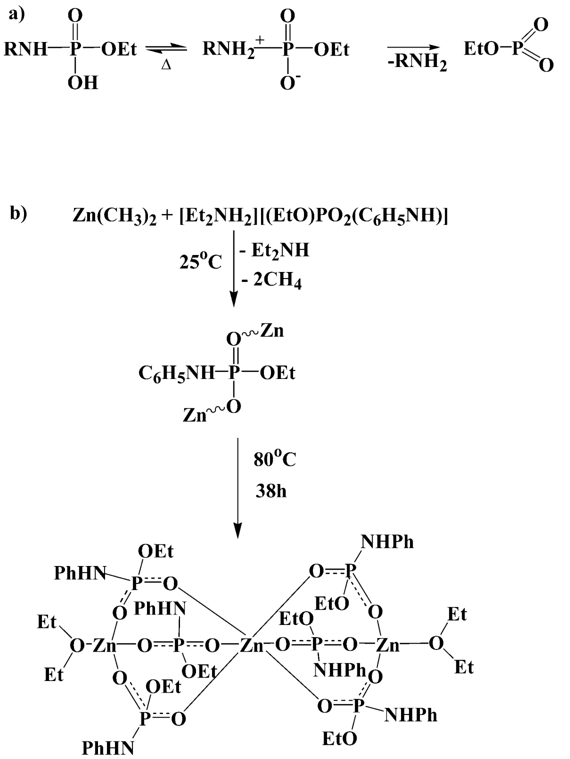
Scheme 1. (a) Decomposition of N-Substituted Phosphoramidic Monoesters[12] and (b) Synthesis of **1**



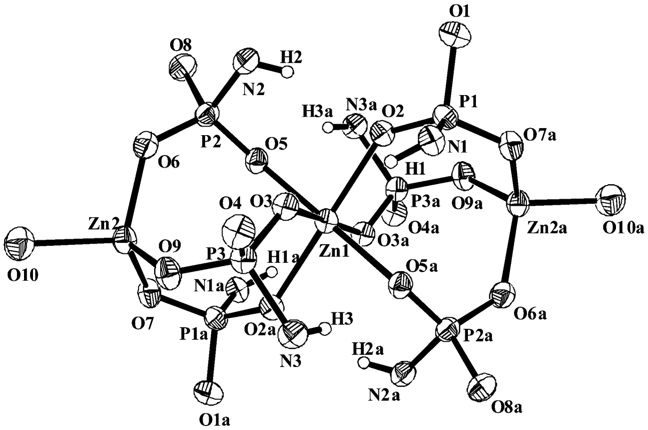


Figure 1. Molecular structure of **1** (20% thermal ellipsoids). The phenyl groups attached to nitrogen and the ethyl groups of OEt_2 ligands have been omitted for clarity.

Complex **1** was obtained in 39% yield according to the procedure illustrated in Scheme 1b.[14] An X-ray single-crystal analysis[15] revealed that **1** is comprised of a neutral trinuclear cluster with a $Zn_3P_6O_{12}$ core that incorporates two distinct zinc environments (Figure 1). The central Zn1 atom is located on an inversion center and adopts a regular octahedral coordination mode with six oxygen atoms of the PON ligand around it. The Zn1−O bond lengths range from 2.086(3) to 2.011(3) Å. The other zinc centers (Zn2) are tetrahedrally coordinated by three oxygen atoms of the PON ligand ($|d(\mathrm{Zn-O})| = 1.936(3)-1.938(4)$ Å) and one oxygen atom of the terminal Et_2O ligand (Zn−O1 = 2.027(4) Å). The O−Zn2−O bond angles range from 105.35(17) to 112.34(15)°. The structural parameters involving the Zn2 centers are typical for four-coordinate zinc in phosphate complexes.[4,19] Each bridging PON ligand engages in one Zn−O linkage with the central Zn1 atom and one Zn−O linkage to a terminal Zn2 atom in corner-sharing modes (P−O−Zn bond angle = 119.3(4)−131.5(2)°). The exocyclic P−O bond distances range from 1.587(4) to 1.591(4) Å, about 0.1 Å longer than the endocyclic P−O bond distances (1.490(3)−1.511(3) Å). These geometrical parameters are in good agreement with previous reports for related zinc phosphates and phosphonates.[4,19−21] The geometry at the nitrogen center of the amidophosphate ligand is almost planar (e.g., $\Sigma <$ N2 = 356.5°), indicating that the delocalization of the lone pair of electrons on nitrogen into the P−O antibonding (σ^*) orbital (the anomeric effect) does not contribute to the lengthening of the exocyclic P−O bonds.[22] The P−N bond distances of 1.635(5)−1.651(5) Å fall between typical single- and double-bond values.

There is an octahedral ZnO_6 core in the structure of **1**, which is believed to be an important component in highly cross-linked zinc phosphates on the basis of computer simulations[23] and experimental results.[24] The connection between the ZnO_6 octahedron and two ZnO_4 tetrahedra

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(13) A wide range of polymetaphosphimates, isoelectronic with *meta*phosphates, have been structurally characterized. They contain cyclic $(PO_2NH)_x^{x-}$ ($x = 3, 4$) ions. For a review, see: Marchand, R.; Schnick, W.; Stock, N. *Adv. Inorg. Chem.* **2000**, *50*, 193.

(14) A solution of $ZnMe_2$ (1.0 mL, 2.0 M, in toluene) was added dropwise to a solution of $[Et_2NH_2][(EtO)PO_2(C_6H_5NH)]$ (1.0 mmol, 0.27 g) in 10 mL of THF and stirred for 21 h at 25 °C. The solution was transferred to a 23-mL Teflon-lined steel autoclave and heated at 80 °C for 38 h. Colorless crystals of **1** were obtained by layering with Et_2O for 1 week (0.11 g, 39%). Anal. Found (calcd) for $C_{60}H_{94}N_6O_{21}P_6Zn_3$ (loss of one lattice THF molecule from **1**) (%): C, 44.14 (44.55); H, 5.98 (5.86); N, 4.84 (5.19). ^1H NMR (300 MHz, $CDCl_3$): δ 1.10 (12H, t, Et_2O), 1.13 (18H, t, CH_3CH_2O), 1.82 (8H, m, THF), 2.70 (8H, m, Et_2O), 3.73 (8H, m, THF), 3.83 (12H, m, CH_3CH_2O), 5.82 (6H, br s, N*H*), 6.75−7.04 (30H, m, C_6H_5). ^{31}P NMR (121.44 MHz, $CDCl_3$): δ 0.47 (s). IR (cm^{-1}, KBr pellet): ν 3277 m, 2968 m, 2885 m, 1606, s, 1483 vs, 1400 s, 1259 s, 1194s, 1049 vs, 946 s, 742 s. MS (ESI): m/z 1395, $([M - H - 2Et_2O - 2THF]^-$, negative mode).

(15) Crystal data for **1**: $C_{64}H_{102}N_6O_{22}P_6Zn_3$, $M = 1689.45$, monoclinic, $P2_1/n$, $a = 16.020(3)$ Å, $b = 14.580(3)$ Å, $c = 17.620(4)$ Å, $\beta = 90.74(3)°$, $V = 4115.2(14)$ Å^3, $Z = 2$, μ(Mo Kα) = 1.053 mm^{-1}, $\theta_{max} = 25.03°$, 12391 reflections measured, 7157 unique ($R_{int} = 0.0318$) and used to refine 434 parameters. $R_1(2\sigma) = 0.0599$. The crystal was attached to a glass fiber. Data sets were collected at 298 K using a Nonius Kappa CCD diffractometer. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. After data reduction, the data were corrected for absorption based on equivalent reflections using SCALEPACK (Nonius, 1998).[16] The structure was solved by direct methods[17] and refined by full-matrix least-squares methods with SHELXL-97.[18] All non-hydrogen atoms were treated anisotropically with the exception of the disordered atoms. All hydrogen atoms were included at geometrically idealized positions except that the NH protons were located in the difference Fourier map.

(16) *SCALEPACK*; Nonius BV: Delft, The Netherlands, 1998.

(17) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

(18) Sheldrick, G. M. *SHELXL-97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(19) Rao, C. N. R.; Natarajan, S.; Neeraj, S. *J. Am. Chem. Soc.* **2000**, *122*, 2810.

(20) Chandrasekhar, V.; Kingsley, S.; Rhatigan, B.; Lam, M. K.; Rheingold, A. L. *Inorg. Chem.* **2002**, *41*, 1030.

(21) Yang, Y.; Pinkas, J.; Noltemeyer, M.; Schmidt, H.-G.; Roesky, H. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 664.

(22) Banavali, N. K.; Mackerell, A. D., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 6747.

(23) Mosey, N. J.; Müser, M. H.; Woo, T. K. *Science* **2005**, *307*, 1612.

through six phosphate tetrahedra generates a novel hourglass structure, which is different from the tooth-wheel BUs observed in three-dimensional networks.[24b] This is a new structural arrangement in zinc phosphates.

The spectroscopic data for **1** are consistent with retention of the solid-state structure in solution. The presence of the NH group in the anilido substituents is confirmed by a broad resonance centered at 5.82 ppm in the ^{1}H NMR spectrum, as well as an N−H stretch at 3277 cm^{-1} in the IR spectrum. The ^{1}H NMR spectrum displays resonances attributed to PhNH and EtO groups, Et_2O ligands, and lattice THF molecules, respectively, with the appropriate relative intensities. The ^{31}P NMR spectrum exhibits a singlet at 0.47 ppm, indicating that the crystallographically inequivalent phosphorus sites become chemically equivalent in solution. The ESI MS spectrum of a solution of **1** in chloroform at 298 K indicates that the $\{Zn_3[(EtO)PO_2(C_6H_5N)]\,[(EtO)PO_2(C_6H_5\text{-}NH)]_5\}^-$ anion is a stable fragment.

In summary, the first zinc amidophosphate was obtained as a trinuclear cluster with a novel hourglass structure under mild solvothermal conditions. The retention of the P−N bond in **1** demonstrates that coordination to a metal center can inhibit P−N bond cleavage of phosphoramidic esters under mild solvothermal conditions. The influence of the solvent on the nature of the polynuclear zinc clusters formed in this process and the application of this method to the synthesis of other metal amidophosphates are the subject of ongoing investigations.

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Supporting Information Available: Crystallographic data in CIF format and the ESI MS spectrum of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) (a) Kongshaug, K. O.; Fjellvåg, H.; Lillerud, K. P. *Microporous Mesoporous Mater.* **2000**, *39*, 341. (b) Ayi, A. A.; Choudhury, A.; Natarajan, S.; Neeraj, S.; Rao, C. N. R. *J. Mater. Chem.* **2001**, *11*, 1181.