Seeking tetrameric transition metal phosphonate with a D4R core and organising it into a 3-D supramolecular assembly†

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Received (in Cambridge, UK) 10th November 2006, Accepted 14th December 2006
First published as an Advance Article on the web 12th January 2007
DOI: 10.1039/b616439k

The first cubic zinc phosphonate [*t*BuPO$_3$Zn(2-apy)]$_4$ (1) whose core resembles the D4R SBU of zeolites, has been synthesised from a reaction between zinc acetate, *tert*-butylphosphonic acid and 2-aminopyridine at room temperature; the X-ray structure determination reveals that the molecules of 1, which crystallise in the tetragonal *I*4$_1$/*a* space group with crystallographically imposed $\bar{4}$ symmetry, form a 3-D supramolecular assembly aided by N–H···O hydrogen bonding.

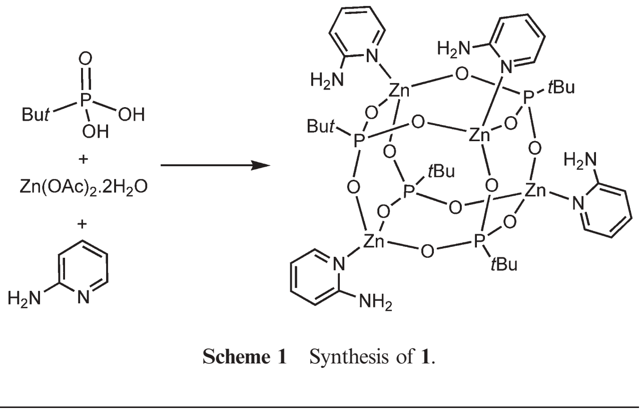
It has been known for nearly two decades that the reaction between a phosphonic acid and a divalent metal ion proceeds smoothly in water at near neutral pH to exclusively form metal phosphonates [RPO$_3$M(OH$_2$)]$_n$ that contain a layered polymeric structure which are used for a variety of applications.[1] Roesky *et al.* and others have, however, shown during the 1990s that discrete metal phosphonate and phosphate clusters could be obtained if the phosphorus source used bear a bulky R group and the reaction is carried out in an organic solvent such as hexane, toluene, or tetrahydrofuran, by excluding trace amounts of water.[2,3] Notable among these reactions is the 1 : 1 stoichiometric reaction between *tert*-butylphosphonic acid and group 13 metal alkyls yielding metal phosphonates [*t*BuPO$_3$MR]$_4$ (M = B, Al, Ga, and In) that are made up of a central M$_4$O$_{12}$P$_4$ core resembling the D4R SBU of zeolites.[4,5] Surprisingly, it has not been possible to isolate a D4R (or D6R) cluster containing a transition metal. For example, the reaction between a Zn(II) precursor and a phosphonic acid has been extensively probed by various research groups in recent years and molecular zinc phosphonate clusters with three,[6] four,[7–9] six,[6,7] seven,[10] or twelve[11] zinc atoms (existing in various sizes and shapes) have been isolated and structurally characterized (see ESI†). As mentioned above, none of these clusters contain a core that resembles the D4R SBU although the hexameric compound reported by Roesky *et al.*[7] can be considered as an extended D4R structure.

Our longstanding interest in synthesizing soluble molecular phosphates[12] combined with the fact that there are no known examples of transition metal phosphonates with a D4R core prompted us to investigate the possibility of preparing cubic zinc phosphonates by introducing certain modifications. Thus in the present study, we chose to use pyridine with an additional amino group in place of previously used THF or pyrazole auxiliary ligands. Secondly, we carried out the reaction in methanol at room temperature and also used zinc acetate as the source of zinc ions. Overall, the reaction depicted in Scheme 1 proceeds smoothly at 25 °C to yield [*t*BuPO$_3$Zn(2-apy)]$_4$ (**1**) in 39% yield. It is interesting to note that in all the earlier reported studies the reaction between *t*BuPO$_3$H$_2$ and a zinc source yielded either layered phosphonate [*t*BuPO$_3$Zn($\frac{2}{3}$H$_2$O)]$_n$[13] or other clusters.‡[6–11]

The pale yellow crystals of **1** obtained directly from the reaction mixture were found to be analytically pure. However spectroscopic measurements could not be carried out in solution due to its poor solubility in organic solvents, presumably due to the formation of a large number of hydrogen bonds (*vide infra*).

A single crystal X-ray diffraction study has been carried out to establish the structure of **1** in the solid state. The compound crystallises in the tetragonal *I*4$_1$/*a* space group and the molecule has crystallographically imposed $\bar{4}$ symmetry.§ The core structure of **1** is similar to the group 13 phosphonates[4] and the recently reported zinc phosphates.[12a] The molecule of **1** is built on a cubic framework containing four zinc and four phosphorus atoms at the alternate vertices (Fig. 1). Each of the Zn···P edges of the cube is bridged by an phosphonate oxygen in a μ_2 fashion, which results in the formation of six non-planar Zn$_2$O$_4$P$_2$ eight membered rings, which adopt distorted pseudo-C$_4$ crown conformation. The central Zn$_4$O$_{12}$P$_4$ cubic core is enclosed by the *tert*-butyl group on phosphorus and the Lewis base on zinc. As expected, the pyridine nitrogen of the 2-aminopyridine binds to Zn^{2+} ion whilst the exocyclic –NH$_2$ group shows no interaction with the metal.

The bond parameters observed for **1** are comparable to those found for the cubic zinc phosphates.[12a] There are no formal P–O and P=O bonds in **1**. The observed average P–O bond distances inside the cage is 1.518(2) Å, while the average Zn–O distance is 1.929(2) Å. The Zn–O–P angles vary over a wide range (127.7–151.6(1)°) and are considerably smaller than 180° that would be expected for a linear edge. The bond angles around both zinc and phosphorus atoms do not deviate appreciably from the ideal



Scheme 1 Synthesis of **1**.

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† Electronic supplementary information (ESI) available: Characterization data. See DOI: 10.1039/b616439k

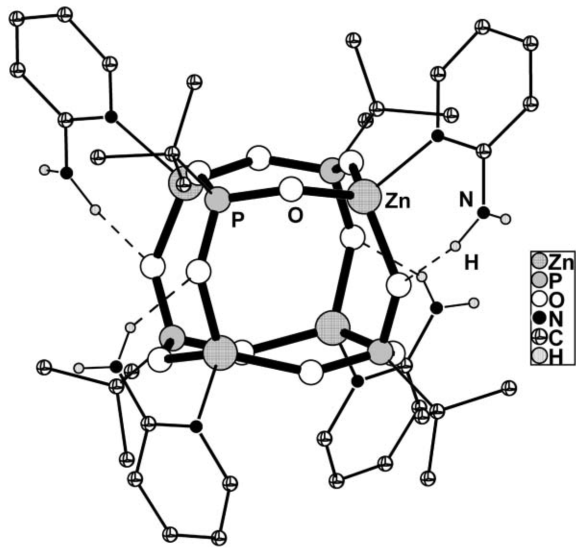

Fig. 1 Molecular structure of **1** showing the intramolecular hydrogen bonding between the peripheral amino group and framework oxygen atoms.

tetrahedral values. The dimensions of the cubic core can best be inferred from the distances of Zn···P edge (3.19 Å), P···P face diagonal (4.72 Å), Zn···Zn face diagonal (4.31 Å), and Zn···P body diagonals (5.54 Å).

The most interesting aspect of the structure of **1** is the organisation of the D4R cubanes into a 3-D supramolecular assembly (Fig. 2). The presence of $-NH_2$ groups on the ortho position of 2-apy in **1** is the source of extensive intra- and intermolecular N–H···O hydrogen bonds, as it has been recently shown by us in the case of zinc mono aryl phosphate $[(RO)PO_3Zn(2\text{-apy})]_4$ (R = 2,6-diisopropylphenyl) (**2**).[12a] In the case of **1**, one hydrogen from each NH_2 group forms an intramolecular H-bond with the μ_2-O of the D4R framework whilst the other hydrogen is engaged in intermolecular H-bond with the μ_2-O of an adjacent cubane. Thus each cubane forms four intra- and four intermolecular hydrogen bonds. In contrast, only six of the available eight N–H hydrogen atoms are involved in H-bonding in **2** (of which four are intramolecular H-bonds and only two are inter-cubane H-bonds). Because of the doubling of the inter-cubane H-bonds, a supramolecular 3-D framework results in the title compound **1** while compound **2** forms only a 1-D chain. The increased number of intermolecular interactions in **1** appears to be the obvious result of size reduction of the organic substituent on phosphorus (2,6-diisopropylphenyl in **2** *versus tert*-butyl in **1**).

In view of the recent interest in luminescent properties of framework zinc phosphonates,[14] we have investigated the absorption and emission characteristics of **1** in the solid-state. The solid-state diffuse reflectance UV-vis spectrum shows three absorption maxima at 252, 326, and 402 nm. When excited at 325 nm, the compound shows a strong emission with three maxima at 364, 416, and 480 nm, suggesting the strong luminescent behaviour of the title compound.

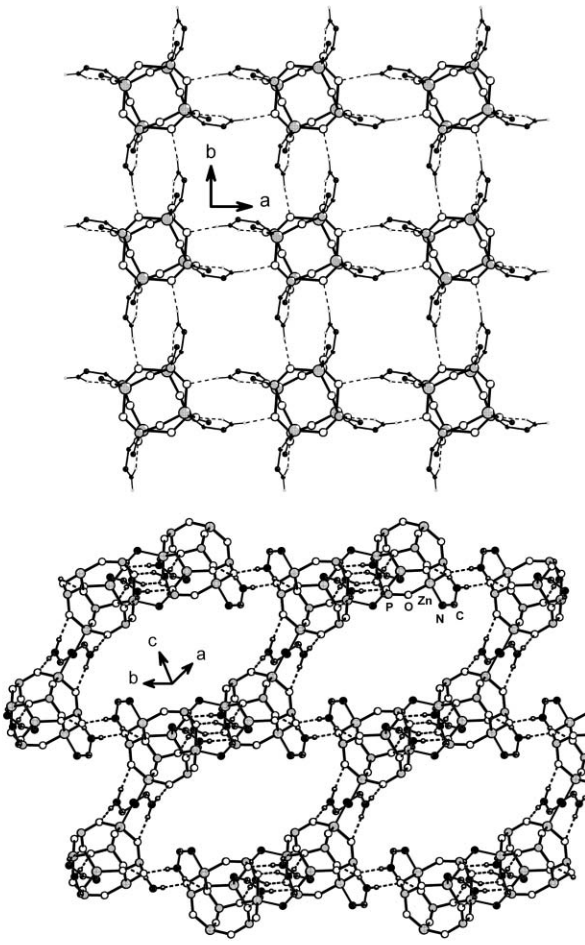

Fig. 2 Two different views of the 3-D supramolecular assembly formed by N–H···O hydrogen bonds in **1**. Methyl groups of the *tert*-butyl substituent and four C–H units of the 2-apy ligand are omitted for clarity.

The thermal behaviour of **1** has been studied by TGA and DSC. The first weight loss of 31.1% in the temperature range 170–200 °C is due to the loss of coordinated 2-apy ligand (theoretical 32%). The second weight loss (19.7%) corresponds to the loss of *tert*-butyl group in the range 200–300 °C, resulting in the formation of $Zn(PO_3)_2$. This phase remains stable in the region 325–475 °C and on further heating a third weight loss ($\sim$10.4%) is observed corresponding to the elimination of P_2O_5, to yield 0.5 equivalent of $Zn_2P_2O_7$ at above 550 °C.[3a] An independent thermolysis of bulk sample at above 400 °C yielded a mixture of zinc meta- and pyrophosphate materials as evidenced by PXRD. The sample heated at 600 °C for 10 h, however, yielded quantitative amounts of the zinc pyrophosphate as the only crystalline phase.[15]

To summarise, it is not only possible to impede the formation of a layered metal phosphonate in the reaction between a phosphonic acid and a transition metal cation but also redirect the reaction towards the formation of molecular clusters that resemble the D4R building block of zeolites. Further, it is possible to arrange these D4R cubanes (SBUs) into a 3-D supramolecular structure through simple non-covalent interactions. The structure of **1** further suggests that, in order to build super-structures, it is important to maximize the number of intermolecular hydrogen bonds emanating from each building block. Finally, the presence of $-NH_2$ groups on the surface of **1** offers new possibilities for further reactions with metal alkyls (*e.g.* AlR_3) in order to build dendritic heterometallic super structures.

This work was supported by DST, New Delhi, in the form of a *Swarnajayanti* Fellowship to R. M. We thank the National Single Crystal X-ray Diffractometer Facility and SAIF (IIT-Bombay) for the diffraction and spectroscopic data, respectively. S. S. thanks CSIR, New Delhi for a research fellowship.

Notes and references

‡ Synthesis of **1**. A solution of $Zn(OAc)_2.2H_2O$ (219 mg, 1 mmol) in methanol (20 mL) was added to a solution of 2-aminopyridine (95 mg, 1 mmol in methanol (20 mL). A solution of *tert*-butyl phosphonic acid (138 mg, 1 mmol) in methanol (20 mL) was added to the above mixture and stirred for 1 h. The resultant solution was filtered and left for crystallization to yield 102 mg of **1** (39%). Mp: >250 °C. Anal. Calcd for $C_{36}H_{60}P_4O_{12}N_4Zn_4$ (Mr = 1182.4): C, 36.57; H, 5.12; N, 9.77. Found: C, 36.05; H, 5.19; N, 10.68. IR (KBr, cm^{-1}): 3384(m), 3191(w), 2964(w), 2950(w), 2923(w), 2865(w), 1653(m), 1623(m), 1565(m), 1500(m), 1478(w), 1454(m), 1361(w), 1339(w), 1274(w), 1133(s), 1070(w), 1004(s), 852(w), 832(w), 772(w), 747(w), 661(w), 563(w), 522(w). DRUV-vis (nm): 252, 326, 402. Fluorescence (λ_{ex} = 326 nm): 364, 416, 480 nm. TGA: temp. range °C (weight loss): 170–200 (31.1%); 280–350 (19.7%); 500–570 (10.4%). DSC (°C): 305 (endo); 506 (endo); 461 (endo).

§ Crystal data for **1**: empirical formula $C_{36}H_{60}N_8O_{12}P_4Zn_4$, M_r = 1182.28, T = 293(2) K, λ = 0.71073 Å, tetragonal, $I4_1/a$, a = 20.1904(2), c = 12.8455(3) Å, V = 5236.5(1) $Å^3$, Z = 4, d_c = 1.50 Mg m^{-3}, μ = 1.992 mm^{-1}, $F(000)$ = 2432, size = 0.33 × 0.21 × 0.18 mm^3, θ range = 3.42 to 24.99°, reflections = 2303 (R_{int} = 0.0265), GOF = 1.135, $R1$ ($I > 2\sigma(I)$) = 0.0305, w$R2$ ($I > 2\sigma(I)$) = 0.0957. The diffraction data were obtained on an Oxford Diffraction XCalibur-S CCD system. The structure was solved by direct methods (SHELXS-96) and refined using SHELXL-97, as implemented in WinGX.[16] All non-hydrogen atoms were subjected to anisotropic refinement. CCDC 626721. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616439k

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