Synthesis and X-Ray Crystal Structure Characterization of $Zn_2(HPO_4)_3{\cdot}H_3NCH_2CH_2NH_3$

Tianyou Song,*[a] Jianing Xu,[a] Yu-e Zhao,[a] Yong Yue,[b] Yihua Xu,[a] Ruren Xu,[a] Ninghai Hu,[c] Gecheng Wei[c] and Hengqing Jia[c]

[a] *Department of Chemistry, Jilin University, Changchun, China*
[b] *Wuhan Institute of Physics, the Chinese Academy of Science, Wuhan, China*
[c] *Changchun Institute of Applied Chemistry, the Chinese Academy of Science, Changchun, China*

A novel framework material, $Zn_2(HPO_4)_3{\cdot}H_3NCH_2CH_2NH_3$, has been synthesised and its crystal structure determined by single crystal X-ray diffraction.

The synthesis of open framework aluminophosphates from nonaqueous systems has been widely studied,[1,2] and recently, the syntheses of zincophosphates, ZnPO/dab-N, containing an organic template, from aqueous solution has been reported;[3,4] (dab = dabco, N = A, B, C, D). Here we report the synthesis and crystal structure of $Zn_2(HPO_4)_3{\cdot}H_3NCH_2CH_2NH_3$ (ZnPO/EDA-1).

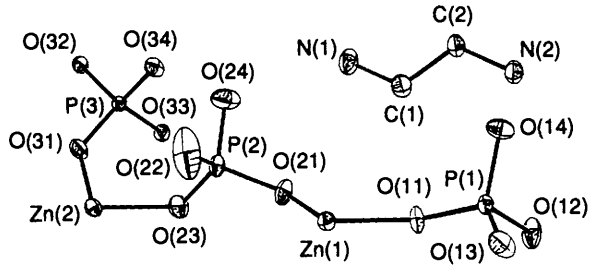

Fig. 1 The asymmetric unit of ZnPO/EDA-1

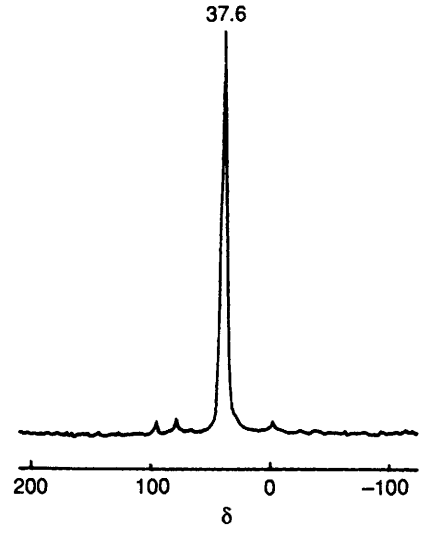

Fig. 2 ^{13}C NMR spectrum for single crystals of ZnPO/EDA-1 (relative to Me_4Si)

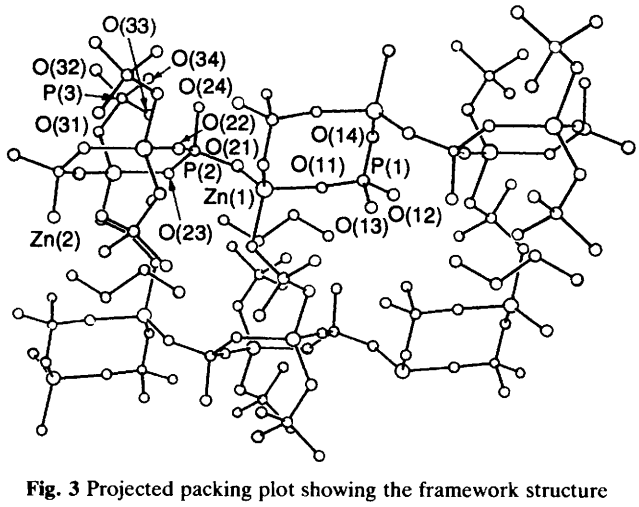

Fig. 3 Projected packing plot showing the framework structure

ZnPO/EDA-1 was synthesized from $Zn(MeCO_2)_2{\cdot}2H_2O$, H_3PO_4, $HOCH_2CH_2OH$ (EG) as the solvent and $H_2NCH_2CH_2NH_2$ (EDA) as the templating agent. The reaction mixture ($ZnO:P_2O_5:EDA:EG$ = 1 : 1.15 : 1.04 : 22.93) was heated at 140 °C for about 20 d in a Teflon-lined stainless steel autoclave under autogenous pressure. Comparison with X-ray powder diffraction patterns of known phosphate frameworks indicated that $Zn_2(HPO_4)_3{\cdot}H_3NCH_2CH_2NH_3$ had a unique, novel structure.

The structure† of ZnPO/EDA-1 was elucidated by direct methods and refined using block-matrix least squares. The asymmetric unit (Fig. 1) appeared to be $Zn_2(HPO_4)_3{\cdot}H_3NCH_2CH_2NH_3$. ^{13}C NMR showed the presence of $H_3NCH_2CH_2NH_3^{2+}$. The chemical shifts (Fig. 2) were the same as those of $H_2NCH_2CH_2NH_2{\cdot}2HBr$.‡ H^+ in HPO_4^{2-} and was added to balance the charges. Thus the framework can be considered to be built up from ZnO_4 and HPO_4 tetrahedra, forming a three-dimensional network. The framework contains two types of zinc atoms and three types of phosphorus atoms. All the zinc and phosphorus atoms are tetrahedrally coordinated to oxygen atoms. One of the phosphorus atoms, P(1), is bound to two zinc atoms *via* an oxygen bridge, forming two P–O–Zn links, while the other two phosphorus atoms, P(2) and P(3), form three P–O–Zn bonds respectively with three zinc atoms *via* oxygen bridges. Each zinc atom is bound to four phosphorus atoms *via* an oxygen atom. The linkage of Zn and P tetrahedra displays a strict alternation of zinc and phosphorus, and there are no Zn–O–Zn or P–O–P bonds present in the structure.

The crystal structure (Fig. 3) is built up with two different four-membered ring configurations: a Zn(1)–P(1)–Zn(1)–P(1) unit and a Zn(2)–P(2)–Zn(2)–P(2) unit (*via* an oxygen bridge). These four-membered rings are linked together *via* Zn(1)–O(21)–P(2) bonds to form infinite chains, Zn(2) in one chain is linked together *via* O(3)–P(3)–O(33) with Zn(1) in another chain to form distorted infinite sheets in a 2-D network. One sheet is linked together *via* P(3)–O(32) with Zn(2) in another sheet to form a 3-D network. There are distorted eight- and twelve-membered ring channels in the 3-D network. Cationic molecules of doubly protonated, $^+H_3NCH_2CH_2NH_3^+$, are located in these channels and balance the charge of the inorganic unit.

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Footnotes

† *Crystal data* for $Zn_2(HPO_4)_3{\cdot}H_3NCH_2CH_2NH_3$, M = 480.8; space group $P\bar{1}$, a = 8.215(3), b = 8.557(3), c = 9.760(3) Å, α = 93.81(3), β = 95.38(3), γ = 109.75(3)°, V = 639.39 Å^3, Z = 2, D_c = 2.50 g cm^{-3}; number of reflections for cell refinement 25; crystal size 0.46 × 0.32 × 0.50 mm, graphite monochromator, Nicolet R 3M/E X-ray four-circle

diffractometer, Mo-Kα, $\lambda = 0.71059$ Å, scan mode $3° < 2\theta < 60°$, 2989 unique reflections out of 4054 measured intensities, $\mu = 43.0$ cm^{-1}, $R = 0.03$. SHELXTL.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ ^{13}C NMR 1980 Sadtler Research Laboratories, Division of Bio-Rad Laboratories, Inc, 9796 C.

References

1 Q. Huo and R. Xu, *J. Chem. Soc., Chem. Commun.*, 1990, 783.
2 Q. Huo and R. Xu, *J. Chem. Soc., Chem. Commun.*, 1992, 168.
3 W. T. A. Harrison, T. E. Marfin, T. E. Gier and G. D. Stucky, *J. Mater. Chem.*, 1992, **2**(2), 175.
4 W. T. A. Harrison, T. M. Nenoff, M. M. Eddy, T. E. Nartin and G. D. Stucky, *J. Mater. Chem.*, 1992, **2**(11), 1127.