

$(C_5H_{16}N_2) \cdot [Zn_3(HPO_3)_4] \cdot H_2O$: A new three-dimensional zincophosphite with 12-membered ring channels and infinite edge shared 4-membered ring ladders

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Abstract

Employing 3-dimethylamino-1-propylamine as a template, a new three-dimensional (3-D) zincophosphite $(C_5H_{16}N_2) \cdot [Zn_3(HPO_3)_4] \cdot H_2O$ has been prepared under hydrothermal conditions and characterized by single-crystal X-ray diffraction (XRD), FTIR, elemental analysis, powder XRD, and thermogravimetric analysis (TGA). The compound crystallizes in the triclinic space group $P\bar{1}$, with cell parameters, $a = 8.9884(2) \text{ \AA}$, $b = 10.326(2) \text{ \AA}$, $c = 11.917(2) \text{ \AA}$, $\alpha = 66.98(3)^\circ$, $\beta = 89.01(3)^\circ$, and $\gamma = 78.98(3)^\circ$, $V = 997.2(3) \text{ \AA}^3$ and $Z = 2$. The connectivity of the ZnO_4 tetrahedra and HPO_3 pseudo pyramids results in infinite edge-sharing, ladderlike chains of 4-membered rings, which are further linked by Zn–O–P bonds to form a 3-D structure that with interesting 12-membered ring channels along the [100] and [001] directions. The diprotonated amine molecules sit in the middle of the channels along the [100] direction and interact with the framework via hydrogen bonds. There also exist channels with 8-membered ring window along the [100] and [010] directions.

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1. Introduction

Considerable effort has been devoted to the study of open-framework metal phosphates following the discovery of microporous aluminophosphates $AlPO_4-n$ in 1982 [1], owing to their interesting structural chemistry and potential applications in catalysis, absorbent, ion exchangers, and gas separation [2–5]. Generally, these materials are prepared under hydrothermal or solvothermal conditions in the presence of organic amines, which may act as structure-directing agent or template to avoid the formation of dense phases. The employment of organic amines has promoted the formation of various metal phosphates with zero- (clusters), one- (chains or ladders), two- (layers), and three-dimensional (3-D) (continuous) structures. Among these compounds possessing helical channels

[6–7], chiral frameworks [8–10], and extra-large 20- and 24-membered ring pores [11–14] are more interesting.

Recently, some of the organically templated and inorganic–organic hybrid phosphites have been reported [15–18]. Compared to the tetrahedral phosphate group $[PO_4^{3-}]$, the phosphite $[HPO_3^{2-}]$ unit has a pseudo pyramidal geometry and can only make three P–O–M bonds. The known synthesized compounds such as $(C_2H_{10}N_2) \cdot [Cr_3(HPO_3)_3F_3]$ [19], $(H_3N(CH_2)_3NH_3) \cdot Be_3(HPO_3)_4$ [20], $(CN_3H_6)_2 \cdot Zn(HPO_3)_2$ [21], $(C_2H_{10}N_2)_{0.5} \cdot [V(HPO_3)_2]$ and $(C_2H_{10}N_2)_{0.5} \cdot [Fe(HPO_3)_2]$ [22], showed novel structures. Based on our previous work on the syntheses of inorganic–organic hybrid phosphates and organically templated phosphites [23–26], we extended our research into the investigation of the role of templates in hydrothermal system. In previous work, a series of open-framework zincophosphites with 8-, 12- and 16-membered rings have been synthesized and characterized [27–32]. We found that edge-sharing, ladderlike chains of 4-membered rings can act as second building units in some compounds

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[33–34]. Harrison et al. reported a one-dimensional (1-D) zincophosphate: $C_4N_2O_3H_8 \cdot ZnHPO_3$ synthesized under the presence of an amino acid (L-asparagine), which contains chiral edge shared 4-ring chains [33]. The L-asparagine plays a dual role of a metal ligand as well as of a structure-directing agent in the formation of the final compound.

In this work, employing 3-dimethylamino-1-propylamine as a template, a new 3-D zincophosphate ($C_5H_{16}N_2$)· $[Zn_3(HPO_3)_4] \cdot H_2O$ with 12-membered ring channels has been hydrothermally synthesized, which contains infinite edge shared 4-membered ring ladders as second building units. The diprotonated amine molecules sit in the middle of the channels and interact with the inorganic host via H-bonds.

2. Experimental

2.1. Synthesis and characterization

The title compound was hydrothermally prepared from a mixture of ZnO, H_3PO_3 , 3-dimethylamino-1-propylamine, and distilled water with a molar composition of 15:30:8:1110. Typically, 1.231 g H_3PO_3 was first dissolved in 10 mL H_2O , then 0.601 g of ZnO was added with stirring. Finally, 0.50 mL of 3-dimethylamino-1-propylamine (98% Fluka) was added dropwise to the above reaction mixture. The mixture was sealed in a 23 mL capacity of Teflon-lined stainless steel autoclave under autogenous pressure, and heated at 160 °C for 120 h. After cooling colourless crystals for single crystal X-ray diffraction (XRD) were obtained. The yield was 85%, based on Zn.

2.2. General methods

The powder XRD patterns were recorded (Bragg–Brentano) on a Siemens D5005 diffractometer by using $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with a graphite monochromator. The step size was 0.02° and the count time was 4 s. The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer. The inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300DV ICP instrument. The infrared (IR) spectrum was recorded within the $400\text{--}4000 \text{ cm}^{-1}$ region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer in air with a heating rate of $10^\circ \text{C min}^{-1}$. The ^{31}P MAS-NMR spectra of the compounds were collected on a Varian Unity-400 NMR spectrometer.

2.3. Structure determination

A suitable colorless single crystal with dimensions $0.30 \times 0.27 \times 0.24 \text{ mm}^3$ was selected for single-crystal XRD analyses. The intensity data were collected on a

Table 1
Crystal data and structure refinement parameters for $(C_5H_{16}N_2) \cdot [Zn_3(HPO_3)_4] \cdot H_2O$

Empirical formula	$C_5H_{22}N_2O_{13}P_4Zn_3$
Formula weight	638.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	8.9884(2)
<i>b</i> (Å)	10.326(2)
<i>c</i> (Å)	11.917(2)
α (deg)	66.98(3)
β (deg)	89.01(3)
γ (deg)	78.98(3)
Volume (Å ³)	997.2(3)
<i>Z</i>	2
Calculated density (mg/m ³)	2.126
Absorption coefficient (mm ⁻¹)	3.962
<i>F</i> (000)	1072
Crystal size (mm)	0.30 × 0.27 × 0.24
θ range (deg)	3.06–27.43
Limiting indices	$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$
Reflections collected/unique	9837/4482 [<i>R</i> (int) = 0.0244]
Completeness to $\theta = 30.02$	98.4%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4482/0/269
Goodness-of-fit on <i>F</i> ²	1.143
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0305, <i>wR</i> ₂ = 0.0883
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0365, <i>wR</i> ₂ = 0.0913
Largest diff. peak and hole (e/Å ³)	0.844 and -0.692

Rigaku R-AXIS RAPID IP diffractometer by oscillation scans using graphite-monochromatic $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell refinement and data reduction were accomplished with the RAPID AUTO program. The total numbers of measured reflections and observed unique reflections were 9837 and 4482, respectively. The structure was solved in the space group $P\bar{1}$ by direct methods and refined on *F*² by full-matrix least-squares using SHELXTL97 [35]. The zinc and phosphorus atoms were first located, whereas the carbon, nitrogen, and oxygen atoms were found in the difference Fourier maps. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms residing on the amine molecules were placed geometrically. The hydrogen atoms residing on the phosphorus were located by Fourier maps. The crystallographic data and details on the refinements for the compound are summarized in Table 1.

3. Results and discussion

The experimental powder XRD pattern of the bulk product is in good agreement with the simulated one on the basis of the single-crystal structure, suggesting the phase purity of the as-synthesized samples. The differences in reflection intensity are probably due to a preferred

orientation in the powder sample. ICP analysis for the product gave the contents of Zn 30.45 wt% (calcd 30.74%) and P 19.23 wt% (calcd 19.41%), indicating a Zn: P ratio of 3:4. Elemental analyses were consistent with the theoretical values, calcd for the product: C, 9.41; H, 3.44; N, 4.39%. Found: C, 9.25; H, 3.27; N, 4.12%.

IR spectra of the compounds showed the characteristic bands of the organic amine cations at 1652, 1547, 1474, and 1377 cm^{-1} . The intense bands in the range 1150–1021 cm^{-1} were attributed to the asymmetric and symmetric stretching vibrations of the PO_3 groups. The symmetric and asymmetric PO_3 deformation can also be observed at approximately 600, 568, 527, and 478 cm^{-1} . A weak band at around 2397 cm^{-1} , indicated the presence of the H–P bond of the phosphite group.

The compound crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.9884(2)$ Å, $b = 10.326(2)$ Å, $c = 11.917(2)$ Å, $\alpha = 66.98(3)^\circ$, $\beta = 89.01(3)^\circ$, and $\gamma = 78.98(3)^\circ$. Selected bond lengths and angles are listed in Table 2. As shown in Fig. 1, the asymmetric unit of it contains 27 unique non-hydrogen atoms, 19 of which belong to the inorganic framework and 8 to the guest. The N1 atom of the amine molecules is disordered. There are three crystallographically distinct Zn atoms and four crystallographically distinct P atoms in the asymmetric unit. All Zn atoms adopt tetrahedral coordinations with typical geometrical parameters [$d_{\text{av}}(\text{Zn1-O}) = 1.936(2)$ Å, $d_{\text{av}}(\text{Zn2-O}) = 1.938(2)$ Å, $d_{\text{av}}(\text{Zn3-O}) = 1.942(3)$ Å]. Each Zn atom links four adjacent P atoms via bridging oxygen. Thus, there are no terminal Zn–O and Zn–O–Zn bonds. As expected, all P atoms form the centers of pseudo pyramid with hydrogen phosphite groups $d_{\text{av}}(\text{P1-O}) = 1.510(3)$ Å, $d_{\text{av}}(\text{P2-O}) =$

$1.520(3)$ Å, $d_{\text{av}}(\text{P3-O}) = 1.515(3)$ Å, and $d_{\text{av}}(\text{P4-O}) = 1.514(3)$ Å. The Zn–O–P bond angles are in the range $120.8(2)^\circ$ – $141.6(2)^\circ$. Each of the four distinct P atoms

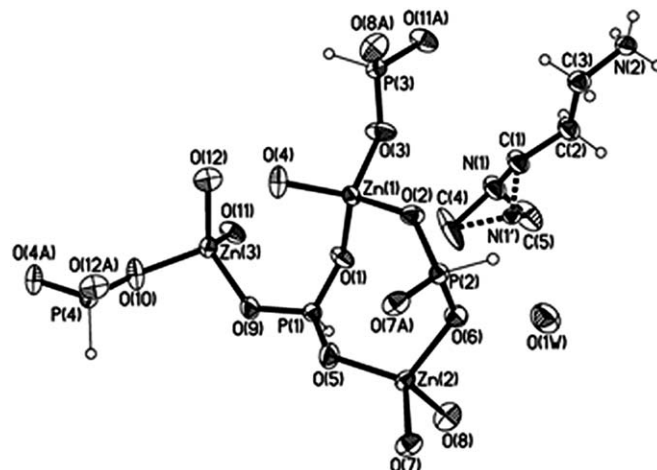


Fig. 1. ORTEP drawing of the asymmetric unit of $(\text{C}_5\text{H}_{16}\text{N}_2) \cdot [\text{Zn}_3(\text{HPO}_3)_4] \cdot \text{H}_2\text{O}$ (50% thermal ellipsoids).

Table 2
Selected bond lengths (Å) and angles (deg) for $(\text{C}_5\text{H}_{16}\text{N}_2) \cdot [\text{Zn}_3(\text{HPO}_3)_4] \cdot \text{H}_2\text{O}$

Zn(1)–O(3)	1.908(3)	P(1)–O(5)	1.513(3)
Zn(1)–O(1)	1.916(3)	P(1)–H(1)	1.29(4)
Zn(1)–O(4)	1.945(2)	P(2)–O(7)#1	1.514(2)
Zn(1)–O(2)	1.974(2)	P(2)–O(6)	1.521(2)
Zn(2)–O(5)	1.906(3)	P(2)–O(2)	1.526(2)
Zn(2)–O(8)	1.925(2)	P(2)–H(2)	1.38(4)
Zn(2)–O(7)	1.954(2)	P(3)–O(3)	1.509(3)
Zn(2)–O(6)	1.965(3)	P(3)–O(8)#2	1.516(3)
Zn(3)–O(9)	1.936(3)	P(3)–O(11)#3	1.519(3)
Zn(3)–O(11)	1.941(3)	P(3)–H(3)	1.33(4)
Zn(3)–O(10)	1.944(3)	P(4)–O(10)	1.502(3)
Zn(3)–O(12)	1.949(3)	P(4)–O(12)#4	1.517(3)
P(1)–O(1)	1.508(2)	P(4)–O(4)#4	1.522(3)
P(1)–O(9)	1.509(3)	P(4)–H(4)	1.36(4)
P(1)–O(1)–Zn(1)	137.19(17)	P(2)#1–O(7)–Zn(2)	138.08(16)
P(2)–O(2)–Zn(1)	135.51(15)	P(3)#5–O(8)–Zn(2)	141.61(18)
P(3)–O(3)–Zn(1)	134.25(16)	P(1)–O(9)–Zn(3)	127.16(16)
P(4)#4–O(4)–Zn(1)	134.07(17)	P(4)–O(10)–Zn(3)	131.64(17)
P(1)–O(5)–Zn(2)	128.81(17)	P(3)#3–O(11)–Zn(3)	132.32(17)
P(2)–O(6)–Zn(2)	120.77(14)	P(4)#4–O(12)–Zn(3)	134.47(17)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y, -z+1$; #2: $x+1, y, z$; #3: $-x+2, -y, -z+2$; #4: $-x+2, -y-1, -z+2$; #5: $x-1, y, z$.

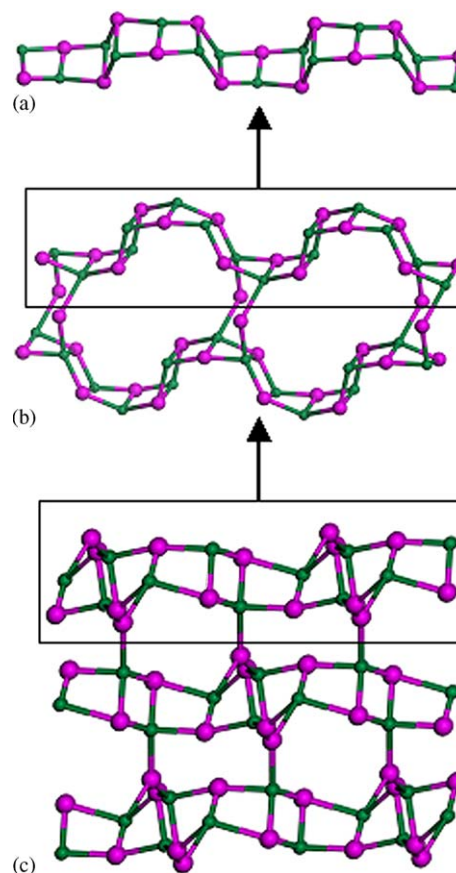


Fig. 2. (a) The infinite edge shared 4-membered ring ladders as second building units in the structure with Zn–O–P bonds represented by lines. The green spheres represent Zn atoms, the pink spheres represent P atoms. (b) The ladders are linked by P(3) through Zn(1)–O(3)–P(3)–O(11)–Zn(3) bonds to a two-dimensional layer along the a -axis. (c) Crystal structure of $(\text{C}_5\text{H}_{16}\text{N}_2) \cdot [\text{Zn}_3(\text{HPO}_3)_4] \cdot \text{H}_2\text{O}$ seen along the $[010]$ direction. For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.

makes three bonds to nearby Zn atoms via bridging oxygen. Thus, there are no terminal P–O bonds. Assuming the valence of Zn, P, O and H to be +2, +3, –2, and +1, respectively, the framework stoichiometry of $[\text{Zn}_3(\text{HPO}_3)_4]$ creates a framework charge of –2. The presence of one diprotonated 3-dimethylamino-1-propylamine molecule would account for +2.

Structure of the compound is built from strictly alternating ZnO_4 tetrahedra and HPO_3 pseudo pyramids that are linked through their vertices giving rise to the 3-D architecture (Fig. 2(c)). There are edge-sharing, ladderlike chains of 4-membered rings which can act as second building units in the structure (Fig. 2(a)). The 4-membered ring chain is made of Zn(1), Zn(2), Zn(3), P(1), P(2), and P(4) which are connected to each other by sharing edges as Zn–O–P. The oxygen neighbors of P(1), P(2), and P(4) are all connected within the four-membered ring chains, but Zn(1), Zn(2) and Zn(3) only have three of the four possible connections within the chains. The fourth connection of the Zn(1) and Zn(3) atoms is linked with the neighboring P(3) atom by Zn(1)–O(3)–P(3)–O(11)–Zn(3) bonds, leading to a two-dimensional (2-D) layer with 16-membered ring window along the *a*-axis (Fig. 2(b)), which are further linked by the third connection of P(3) through P(3)–O(8)–Zn(2) bonds to a 3-D structure. One intriguing feature of the compound is compared to the known 2-D compound $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4$ [35], which also contains edge shared 4-membered ring ladders. The main difference of the two structures is that, in the case of $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4$, the P(3) atom is three-connected to the 4-membered ring ladder, while in the title compound the P(3) atom is two-connected to the 4-membered ring ladder. Thus, $\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3 \cdot \text{Zn}_3(\text{HPO}_3)_4$ has a 2-D structure, while the title compound has a 3-D structure. Along the [100] direction, the connectivity between ZnO_4 tetrahedra and HPO_3 pseudo pyramids result in distorted 8- and 12-membered ring channels (Fig. 3(a)). The protonated amine molecules sit in the middle of the channels and interact with the framework

via hydrogen bonds (some typical H-bonds can be seen in support information), similar to those in other zincophosphites reported. The channel along [100] has dimensions $6.6 \times 5.3 \text{ \AA}$, $9.6 \times 7.3 \text{ \AA}$, respectively; along the [001] direction, there exist another 12-membered ring channel with dimension $10.6 \times 7.5 \text{ \AA}$ (Fig. 3(b)).

The TGA curve of the sample (Fig. 4) exhibits two continuous weight loss stages in the temperature ranges 80–220 and 250–520 °C, corresponding to the concomitant release of composed water (calcd: 2.82%; found: 2.17%) and the decomposition of organic amines (calcd: 16.29%; found: 15.08%), respectively. At 800 °C, the amorphous phase recrystallized mainly into a ZnP_2O_7 phase (JCPDS: 34-0623) with some other phase, which was confirmed by powder XRD analysis.

^{31}P MAS NMR spectra of the product showed four resonance peaks at 6.64, 4.25, 1.63, –0.71 ppm, relative to a standard of 85% H_3PO_4 . These values agreed well with the chemical shifts found in similar systems [6,21,29]. Four chemical shifts of P atoms correspond to four crystallographically equivalent phosphorus sites in the structure as indicated from X-ray structural analysis.

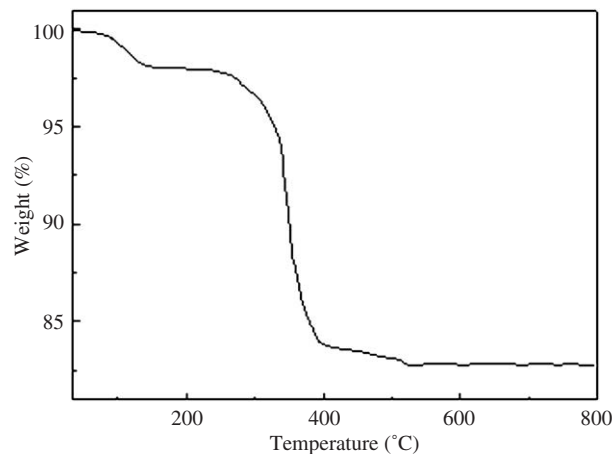


Fig. 4. The TGA curve of $(\text{C}_5\text{H}_{16}\text{N}_2) \cdot [\text{Zn}_3(\text{HPO}_3)_4] \cdot \text{H}_2\text{O}$.

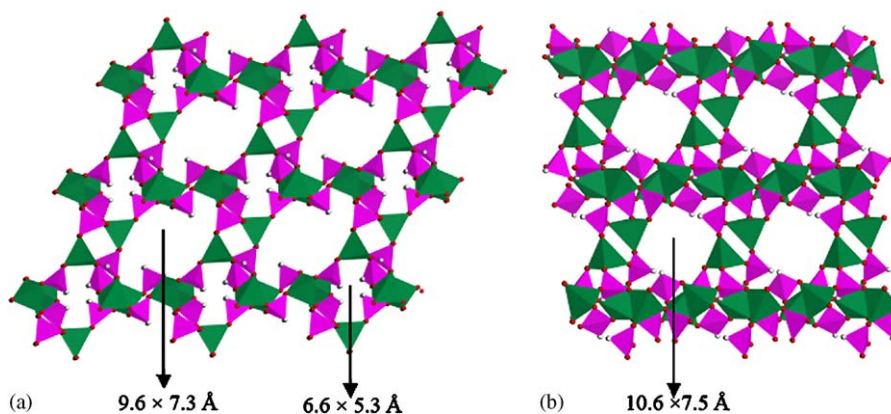


Fig. 3. (a) Polyhedral view of the structure $(\text{C}_5\text{H}_{16}\text{N}_2) \cdot [\text{Zn}_3(\text{HPO}_3)_4] \cdot \text{H}_2\text{O}$ in [100] direction, showing the 4-, 8- and 12-network. (b) View of the 3-D structure along the [001] direction showing the 12-membered ring channels. (ZnO tetrahedra, green; HPO_3 tetrahedra, pink; H white; O atoms, red spheres). For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.

4. Conclusions

In the presence of 3-dimethylamino-1-propylamine as a template, a new open-framework zincophosphate ($C_5H_{16}N_2$)·[Zn₃(HPO₃)₄]·H₂O has been prepared under hydrothermal conditions. The connectivity of the ZnO₄ tetrahedra and HPO₃ pseudo pyramids results in infinite edge-sharing, ladderlike chains of 4-membered rings, which are further linked by Zn–O–P bonds to form a 3-D structure. Along the [100] and [001] directions, there exist 12-membered ring channels. The diprotonated 3-dimethylamino-1-propylamine molecules sit in the middle of the channels and interact with the framework via hydrogen bonds.

5. Supplementary material

The supplementary material in the form of CIF file has been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary material no. CCDC-288425 and can be obtained by contacting the CCDC (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) quoting the article details and the corresponding SUP number.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2006.04.008](https://doi.org/10.1016/j.jssc.2006.04.008)

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