Chinese Journal of Chemistry, **2004**, *22*, 344—347 **Article**

Synthesis and Crystal Structure of a Novel Zincophosphite Containing Two-dimensional Inorganic-organic Network

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A novel 1,6-hexamethylenediamine-zincophosphite has been synthesized hydrothermally. Its single-crystal structure refinement has shown the zincophosphite with the composition $NH_3^+(CH_2)_6NH_3^+[Zn(HPO_3)_2]^{2-}$, M_r=343.55. It crystallizes in monoclinic, space group *C*2/*c* (No. 15), a=2.2391 nm, b=0.8695 nm, c=0.7919 nm, β=101.062(6)°, V=1.513 nm^3, D_c=1.508 kg/m^3, Z=4, F(000)=712, μ=1.849 mm^{-1}, R_1=0.0416, wR_2=0.1023. This phase exhibits infinite inorganic chains of vertex-linked ZnO_4 and HPO_3. Via the electrostatic attraction, 1,6-hexamethylenediamine cations and inorganic chains construct a novel interesting two-dimensional inorganic-organic network.

Keywords zincophosphite, hydrothermal synthesis, two-dimensional, network

Introduction

Low dimensional compounds generally include one-dimensional chain-like and two-dimensional layer-like structures. They have received considerable attention in recent years due to their structural diversity, interesting unusual properties different from those of three-dimensional compounds, possibility to transform to high dimensional phase, and application as special materials.[1-3] In the last two years several low dimensional organically-templated phosphites have been reported.[4-6] $[HPO_3]^{2-}$ can make three links to adjacent atoms via P-O-M (M=Zn, Al *etc*.) bonds. Thus in terms of network formation, it may be regarded as a pseudo pyramidal building unit. Similar to phosphates, using different organic template metal phosphites show a great structural diversity.[4-11] In this paper the synthesis and single crystal structure of $NH_3^+(CH_2)_6NH_3^+[Zn(HPO_3)_2]^{2-}$, a new 1,6-hexamethylenediamine-zincophosphite which contains an interesting two-dimensional inorganic-organic network, are described.

Experimental

Synthesis

$NH_3^+(CH_2)_6NH_3^+[Zn(HPO_3)_2]^{2-}$ was synthesized hydrothermally under autogenous pressure with 1,6-hexamethylenediamine (HMD) as a structure directing agent. The reaction mixture with the molar composition of 1.0 ZnO∶1.5 H_3PO_3∶1.0 HMD∶50 H_2O, was prepared by combining 1.62 g of ZnO, 2.64 g of H_3PO_3 (Tianjin Yaohua Chemicals Co.), 3.2 g of HMD (Tianjin Yaohua Chemicals Co.) and 18 mL of distilled water. The gel was stirred until it became homogeneous, transferred to a Teflon-lined stainless steel autoclave, and heated at 130 ℃ for 36 h. The product was recovered by filtration, washed with distilled water and dried in air at 80 ℃.

Crystal structure determination

A transparent crystal (*ca*. 0.25 mm×0.08 mm×0.06 mm) was selected and mounted on a Bruker SMART 1000 CCD area detector diffractometer [Mo Kα radiation, λ=0.071073 nm, T=(293±2) K]. After routine data collection and reduction,[12] the structural model was developed in space group *C*2/*c* (No. 15). The data were processed with the aid of the SHELXTL97 program system.[13] A total of 2364 reflections were collected (3.7°≤2θ≤50°), and these were merged to give 1293 unique reflections (R_{int}=0.0373). Data of the lattice parameters are as follows: a=2.2391 nm, b=0.8695 nm, c=0.7919 nm, β=101.062(6)°, V=1.513 nm^3, D_c=1.508 kg·m^{-3}, Z=4, F(000)=712, μ=1.849 mm^{-1}. Crystal data are summarized in Table 1.

Results and discussion

Selected bond distance and angle data are listed in Table 2. Hydrogen bond data are given in Table 3. Non-hydrogen atomic coordinates and equivalent isotropic displacement parameters are listed in Table 4. The $NH_3^+(CH_2)_6NH_3^+[Zn(HPO_3)_2]^{2-}$ structure is illustrated in Figures 1—3. The asymmetric unit contains 9 unique non-hydrogen atoms. The zinc atom is located on a diad axis and adopts tetrahedral coordination with

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Table 1 Crystallographic data for $NH_3^+(CH_2)_6NH_3^+$ $[Zn(HPO_3)_2]^{2-}$

Formula	$C_6H_{20}N_2O_6P_2Zn$
Molecular weight	343.55
T/K	293(2)
Wavelength/nm	0.071073
Crystal system,	Monoclinic
Space group	*C*2/*c* (No. 15)
a/nm	2.2391
b/nm	0.8695
c/nm	0.7919
β/(°)	101.062(6)
V/nm^3	1.5131
Z	4
D_c/(kg • m^{-3})	1.508
M/mm^{-1}	1.849
F(000)	712
Crystal size/mm	0.25×0.08×0.06
θ range/(°)	1.85—25.00
Limiting indices	$-26\leqslant h\leqslant 21$, $-6\leqslant k\leqslant 10$, $-6\leqslant l\leqslant 9$
Reflections collected/unique	2364/1293 [*R*(int)=0.0373]
Completeness to theta=25.00	96.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1293/0/87
Goodness-of-fit of F^2	1.039
Final *R* indices [$I>2\sigma(I)$]	R_1=0.0416, wR_2=0.1023
R indices (all data)	R_1=0.0725, wR_2=0.1374
Largest diff. peak and hole/(e • nm$^{-3}\times 10^3$)	0.830 and −0.723

[a] $R_1=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$. [b] $wR_2=[\Sigma\,w(|F_o|-|F_c|)^2/\Sigma\,w|F_o|^2]^{1/2}$

geometrical parameters [d_{av}(Zn(1)—O)=0.1940 nm]. It makes four bonds to nearby P atoms via Zn−O−P bonds. The P atom has three O atom neighbours with average bond length [d_{av}(P(1)—O)=0.1517 nm], with a P—H bond occupying the fourth pseudo pyramidal vertex, and the length [*d*(P—H)=0.133 nm] is similar to that of the equivalent bond in solid H_3PO_3.[14] In $NH_3^+(CH_2)_6NH_3^+$ $[Zn(HPO_3)_2]^{2-}$, there are two bond angle with average value of Zn-O-P [θ_{av}=131.0(7)°] and a terminal P—O(2) bond as well as that often found in other zincophosphites.[15,16] The anionic $[Zn(HPO_3)_2]^{2-}$ component of the structure is charge balanced by organic cations. The cation $NH_3^+(CH_2)_6NH_3^+$ located at a center of symmetry. The strictly alternating HPO_3 and ZnO_4 tetrahedra form the zincophosphite chains.

The cationic $NH_3^+(CH_2)_6NH_3^+$ and anionic $[Zn(HPO_3)_2]^{2-}$ through electrostatic attraction construct a novel two-dimensional inorganic-organic network. The multidecker anthracene-silver with similar 2-D inorganic/organic network structure has been reported recently.[17] When the overall structure is viewed along *c*-axis (Figure 2) there are tie-shaped channels. The unit cell of the network (Figure 3) contains four $NH_3^+(CH_2)_6NH_3^+$ and four $[Zn(HPO_3)_2]^{2-}$. The distance between the up and the down anions is 0.4578 nm, and that between the left and right is 1.9563 nm. The distances between the up and the down cations are unequal, ranging from 0.4730 to 0.7279 nm. The well-ordered organic cations interact with the inorganic chains by not only electrostatic attraction but also the way of N—H···O hydrogen bonds.[16,18,19] It makes the structure more stable. Selected hydrogen bond distance and angle data are listed in Table 3.

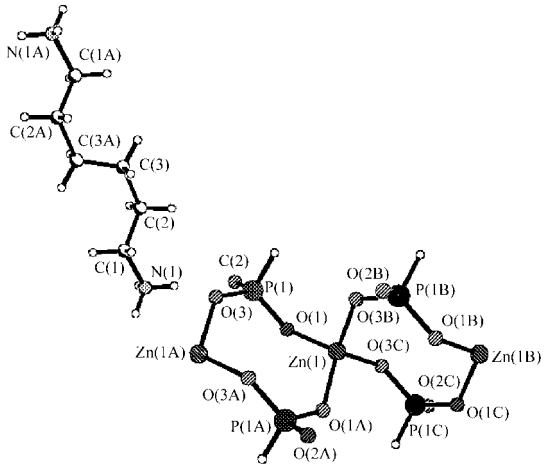

Figure 1 Asymmetric unit of $NH_3^+(CH_2)_6NH_3^+$ $[Zn(HPO_3)_2]^{2-}$, showing the atom labelling scheme (50% thermal ellipsoids).

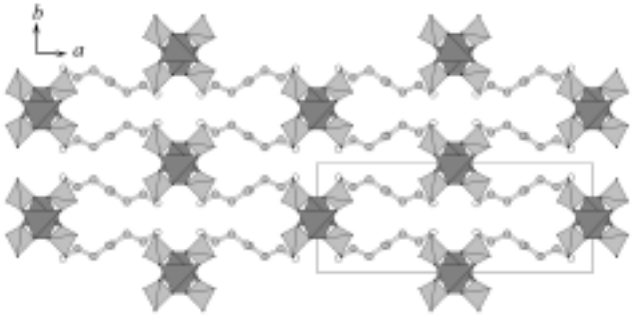

Figure 2 Polyhedral view along the *c* axis of $NH_3^+(CH_2)_6NH_3^+$ $[Zn(HPO_3)_2]^{2-}$ showing the 2-D network of dark (ZnO_4), light (HPO_3) tetrahedra and the organic cations.

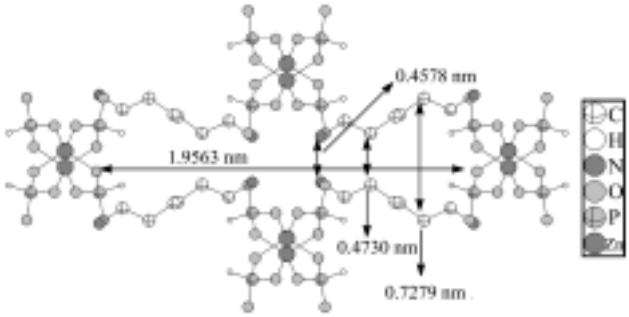

Figure 3 Unit cell of the 2-D inorganic-organic network.

Table 2 Selected bond distances (nm) and angles (°) for $NH_3^+(CH_2)_6NH_3^+[Zn(HPO_3)_2]^{2-}$

Zn(1)—O(3)#2	0.1931(4)	P(1)—O(1)	0.1534(4)
Zn(1)—O(3)#1	0.1931(4)	P(1)—H(1)	0.133(4)
Zn(1)—O(1)#3	0.1949(4)	O(3)—Zn(1)#2	0.1931(4)
Zn(1)—O(1)	0.1949(4)	N(1)—C(1)	0.1485(8)
P(1)—O(2)	0.1502(4)	C(1)—C(2)	0.1496(9)
P(1)—O(3)	0.1514(4)	C(3)—C(3)#4	0.1401(18)
O(3)#1-Zn(1)-O(3)#2	115.2(2)	O(2)-P(1)-O(1)	110.9(2)
O(3)#1-Zn(1)-O(1)#3	113.12(16)	O(3)-P(1)-O(1)	112.9(2)
O(3)#2-Zn(1)-O(1)#3	106.69(16)	P(1)-O(1)-Zn(1)	133.8(2)
O(3)#1-Zn(1)-O(1)	106.69(16)	P(1)-O(3)-Zn(1)#2	128.3(2)
O(3)#2-Zn(1)-O(1)	113.12(16)	N(1)-C(1)-C(2)	111.4(5)
O(1)#3-Zn(1)-O(1)	101.3(2)	C(1)-C(2)-C(3)	112.5(7)
O(2)-P(1)-O(3)	112.7(2)	C(3)#4-C(3)-C(2)	115.2(12)

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

Table 3 Hydrogen bond distances (nm) and angles (°)

	N—H/ nm	H···O/ nm	N-H···O/ (°)	N—H···O/ nm
N(1)—H(1C)···O(1)	0.0899	0.1968	167.90	0.2853
N(1)—H(1D)···O(2)	0.0898	0.1849	167.31	0.2732
N(1)—H(1E)···O(2)	0.0898	0.1872	177.85	0.2770

For the hydrogen bonds, the four values refer to the N—H and H···O bond distances (nm), the N—H···O bond angle (°) and the N—H···O bond distance (nm).

Table 4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($nm^3 \times 10^6$) for $NH_3(CH_2)_6NH_3Zn(HPO_3)_2$

	x	y	z	U(eq)
Zn(1)	0	4523(1)	7500	28(1)
P(1)	775(1)	3080(2)	4876(2)	28(1)
O(1)	248(2)	3102(4)	5860(5)	35(1)
O(2)	869(2)	1493(5)	4226(5)	46(1)
O(3)	711(2)	4287(4)	3474(5)	40(1)
N(1)	781(2)	1321(6)	694(6)	35(1)
C(1)	1306(3)	2170(8)	252(9)	48(2)
C(2)	1898(3)	1488(10)	1127(10)	67(2)
C(3)	2455(4)	2462(16)	851(11)	114(4)

We also studied the thermal stability of $NH_3^+(CH_2)_6NH_3^+[Zn(HPO_3)_2]^{2-}$. The structure of title compound did not change when it was heated in air at 325 ℃ for 2 h. The XRD patterns are shown in Figure 4. After being heated in air at 350 ℃ for 2 h, the structure collapsed. Usually chain-like phosphite has lower thermal stability,[5] but this phase is still stable at 325 ℃. It may be stabilized by the electrostatic attraction and N—H···O hydrogen bonds between the organic cations and inorganic anions.

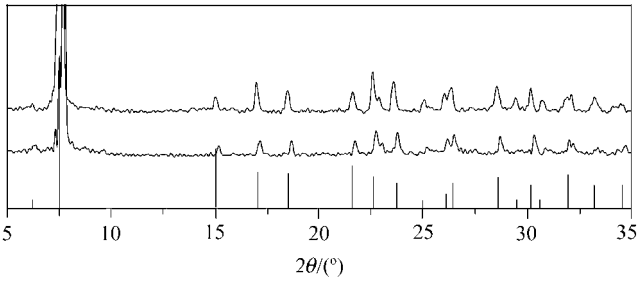

Figure 4 X-ray powder patterns of $NH_3^+(CH_2)_6NH_3^+[Zn(HPO_3)_2]^{2-}$ (top: as-synthesized; middle: heated in air at 325 ℃; bottom: simulated).

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