Crystal structure of 1,2-ethylenediamine-dizinc diphosphate(III), $Zn_2(C_2H_8N_2)(HPO_3)_2$

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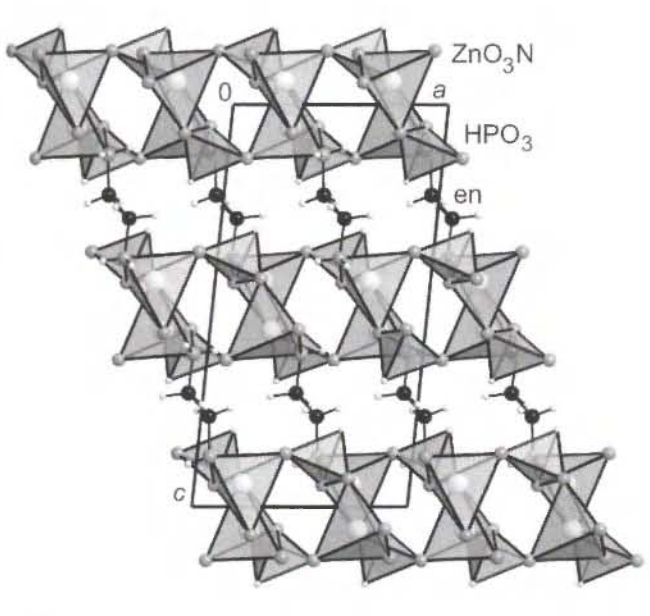

Abstract

$C_2H_{10}N_2O_6P_2Zn_2$, monoclinic, $P12_1/a1$ (no. 14), $a = 7.8357(8)$ Å, $b = 8.2543(8)$ Å, $c = 14.791(2)$ Å, $\beta = 95.76(1)°$, $V = 951.8$ Å^3, $Z = 4$, $R_{gt(F)} = 0.039$, $wR_{ref(F^2)} = 0.106$, $T = 293$ K.

Source of material

Single crystals of $Zn_2(en)(HPO_3)_2$ (en = $C_2H_4(NH_2)_2$) were grown hydrothermally in a Teflon autoclave (20 ml volume, filling degree 45 %) at 140 °C. The initial reaction mixture consisted of 0.32 g ZnO, 0.246 g H_3PO_3, 2 ml water, 0.143 g $Co(en)_3Cl_3$, and 0.156 g 2,2′-bipyridine.

Experimental details

All H atoms were found from Fourier difference maps. The positions of the H atoms attached to N and P were refined. While the displacement parameters of the H atoms bonded to N were refined, those bonded to P were restrained with $U_{iso} = 1.5\,U_{eq}(P)$. The H atoms attached to C were included in the riding model approximation ($U_{iso} = 1.2\,U_{eq}(C)$).

Discussion

Microporous metal phosphates have attracted considerable interest owing to their potential applications as catalysts, adsorbents and ion exchange materials. A growing number of zinc phosphates with different organic ligands has already been reported [1]. In comparison to the phosphate(V) ion, the phosphate(III) ion $[HPO_3]^{2-}$ possesses only three oxo-ligands capable of zinc coordination, with a considerable effect on the possible interconnection motifs in the zinc phosphate framework.

In the crystal structure of $Zn_2(en)(HPO_3)_2$ zinc is coordinated tetrahedrally by one amine-ligand of an en molecule and three oxo-ligands of different phosphate(III) ions. The tetrahedral coordination polyhedra of Zn and P are linked via three vertices each to form an open two-dimensional network. The layers consist of rings of four and eight tetrahedra of alternating ($HPO_{3/2}$) and ($ZnNO_{3/2}$) units, i. e., the P and Zn centers form the motif of a strongly puckered 4.8^2 net. The structure of the title compound is characterized by body-centered ordering of ZnO_3N and HPO_3 groups. Only the arrangement of the en molecules is responsible for a symmetry reduction, which is reflected in weak additional reflections. A topologically identical but less corrugated layer was previously encountered for $Zn_2(4,4'\text{-bipy})(PO_3F)_2$ [2]. The fluoro ligand in the latter compound and the hydrogen ligand in the title compound are both terminal. In both structures the zinc phosphate(III) and fluorophosphate layers, respectively, are linked by the organic constituents via nitrogen in a pillar-like manner.

Table 1. Data collection and handling.

Crystal:	pale yellow platelet, size 0.025 × 0.090 × 0.125 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	53.81 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7 & Mercury CCD, φ/ω
$2\theta_{max}$:	59.7°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7741, 2204
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1511
$N(param)_{refined}$:	149
Programs:	SHELXS-97 [3], SHELXL-97 [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.661(5)	0.153(5)	0.313(3)	0.027
H(2)	4e	0.344(5)	0.139(5)	0.192(3)	0.028
H(1A)	4e	0.602(7)	0.728(8)	0.404(4)	0.07(2)
H(1B)	4e	0.480(7)	0.622(8)	0.387(4)	0.06(2)
H(2A)	4e	0.5288	0.7904	0.2713	0.054
H(2B)	4e	0.6867	0.6748	0.2671	0.054
H(3A)	4e	0.3522	0.5635	0.2480	0.053
H(3B)	4e	0.5154	0.4633	0.2307	0.053
H(4A)	4e	0.523(6)	0.617(6)	0.108(3)	0.03(2)
H(4B)	4e	0.409(7)	0.731(7)	0.132(3)	0.06(2)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4*e*	0.71829(6)	0.46566(5)	0.43754(3)	0.0200(3)	0.0189(3)	0.0217(3)	–0.0007(2)	–0.0002(2)	0.0020(2)
Zn(2)	4*e*	0.27736(6)	0.45863(5)	0.05836(3)	0.0203(3)	0.0212(3)	0.0211(3)	0.0015(2)	–0.0002(2)	–0.0018(2)
P(1)	4*e*	0.5892(1)	0.1110(1)	0.38719(6)	0.0199(6)	0.0183(6)	0.0166(5)	–0.0015(4)	0.0021(4)	–0.0002(4)
O(11)	4*e*	0.4108(4)	0.0421(4)	0.3655(2)	0.019(2)	0.040(2)	0.027(1)	–0.007(1)	0.003(1)	–0.006(1)
O(12)	4*e*	0.7124(4)	–0.0146(4)	0.4322(2)	0.027(2)	0.031(2)	0.020(1)	0.008(1)	–0.001(1)	0.000(1)
O(13)	4*e*	0.5888(4)	0.2664(4)	0.4412(2)	0.037(2)	0.020(2)	0.039(2)	–0.008(1)	0.014(1)	–0.007(1)
P(2)	4*e*	0.4097(1)	0.1065(1)	0.11323(6)	0.0172(6)	0.0217(6)	0.0166(5)	0.0010(4)	0.0021(4)	–0.0015(4)
O(21)	4*e*	0.2874(4)	–0.0233(4)	0.0712(2)	0.027(2)	0.039(2)	0.022(1)	–0.009(1)	–0.000(1)	–0.002(1)
O(22)	4*e*	0.4057(4)	0.2580(4)	0.0558(2)	0.040(2)	0.026(2)	0.044(2)	0.009(2)	0.012(2)	0.006(1)
O(23)	4*e*	0.5904(4)	0.0405(4)	0.1341(2)	0.019(2)	0.045(2)	0.027(1)	0.007(1)	0.002(1)	0.008(1)
N(1)	4*e*	0.5667(6)	0.6426(6)	0.3807(2)	0.026(2)	0.033(2)	0.021(2)	0.006(2)	0.002(2)	0.005(2)
C(2)	4*e*	0.5695(6)	0.6806(6)	0.2827(3)	0.031(3)	0.046(3)	0.032(2)	0.000(2)	0.006(2)	0.005(2)
C(3)	4*e*	0.4641(6)	0.5703(6)	0.2255(3)	0.035(3)	0.035(3)	0.040(2)	–0.004(2)	0.016(2)	0.000(2)
N(4)	4*e*	0.4401(6)	0.6172(5)	0.1262(2)	0.023(2)	0.035(2)	0.022(2)	–0.004(2)	0.005(2)	–0.004(2)

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