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Crystal structure of 4,4'-bipyridin-1,1'-dium poly[bis(μ_4 -benzene-1,3,5-triyltris(hydrogen phosphonato- $\kappa^4 O:O':O'':O''')$)zinc(II)], $C_{11}H_{11}NO_9P_3Zn$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.50 × 0.40 × 0.30 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.02 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 QUEST, φ and ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9136, 2951, 0.058
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2228
$N(\text{param})_{\text{refined}}$:	229
Programs:	Bruker [1], SHELX [2, 3]

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Abstract

$C_{11}H_{11}NO_9P_3Zn$, monoclinic, $P2_1/n$ (no. 14), $a = 12.619(2)$ Å, $b = 8.4948(12)$ Å, $c = 13.954(2)$ Å, $\beta = 90.588(3)^\circ$, $V = 1495.7(4)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0413$, $wR_{\text{ref}}(F^2) = 0.0965$, $T = 120(2)$ K.

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A part of the title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of 1,3,5-benzenetriphosphonic acid (0.2 mmol), 4,4'-bipyridine (0.2 mmol), $Zn(NO_3)_2 \cdot 6(H_2O)$ (0.2 mmol), H_2O (8 mL) was stirred for ten minutes. The mixture was transferred in a 25 mL stainless steel reactor with a Teflon

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8793(3)	0.6266(4)	0.5838(3)	0.0184(9)
H1	0.5353	0.6767	0.3839	0.045*
C2	0.8713(3)	0.6923(4)	0.4919(3)	0.0193(9)
H2A	0.8913	0.7988	0.4820	0.023*
C3	0.8342(3)	0.6031(4)	0.4154(3)	0.0184(9)
C4	0.8080(3)	0.4455(4)	0.4298(3)	0.0220(9)
H4	0.7819	0.3847	0.3775	0.026*
C5	0.8191(3)	0.3763(4)	0.5189(3)	0.0185(9)
C6	0.8523(3)	0.4689(4)	0.5952(3)	0.0210(9)
H6	0.8568	0.4233	0.6573	0.025*
C7	0.5234(4)	0.5763(5)	0.5151(3)	0.0241(10)
C8	0.5429(5)	0.6093(6)	0.6110(4)	0.0529(16)
H8	0.5271	0.5326	0.6583	0.063*
C9	0.5845(5)	0.7514(6)	0.6380(4)	0.0589(18)
H9A	0.5963	0.7735	0.7040	0.071*
C10	0.5485(4)	0.6932(5)	0.4503(3)	0.0375(12)
H10	0.6357	0.9487	0.5913	0.047*
C11	0.5921(4)	0.8323(6)	0.4804(4)	0.0425(13)
H11	0.6108	0.9104	0.4348	0.051*
N1	0.6084(3)	0.8582(4)	0.5728(3)	0.0389(10)
O1	0.7925(3)	0.0798(3)	0.4493(2)	0.0314(8)
O2	0.9045(3)	0.1362(4)	0.5960(3)	0.0581(12)
H2	0.9105	0.0389	0.6052	0.087*
O3	0.7065(3)	0.1413(4)	0.6030(2)	0.0409(9)
O4	0.9893(2)	0.8716(3)	0.65547(19)	0.0235(7)
O5	0.8261(2)	0.7936(3)	0.7396(2)	0.0283(7)
H5	0.8191	0.7476	0.7925	0.042*
O6	0.9827(2)	0.6163(3)	0.75222(19)	0.0251(7)
O7	0.8723(2)	0.8445(3)	0.29502(19)	0.0252(7)
O8	0.7032(2)	0.6910(3)	0.27114(19)	0.0255(7)
O9	0.8721(3)	0.5731(3)	0.2250(2)	0.0338(8)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H9	0.9214	0.5239	0.2526	0.051*
P1	0.92645(9)	0.72922(12)	0.68808(7)	0.0173(2)
P2	0.79970(9)	0.17005(12)	0.54090(7)	0.0197(3)
P3	0.81958(9)	0.68718(12)	0.29698(7)	0.0188(3)
Zn1	0.86114(4)	1.06319(5)	0.32777(3)	0.01940(15)

liner and heated from 298 to 453 K in 5 h and a constant temperature was maintained at 453 K for 72 h. After cooling to room temperature, yellow block crystals were collected in 57.2% yield based on Zn.

Experimental details

Coordinates of hydrogen atoms were added. Their *U*_{iso} values were set to 1.2*U*_{eq} of the parent atoms.

Comment

A large number of metal coordination compounds containing various metal cations and organic ligands have been obtained. Currently, linking metal cations and organic ligands to build coordination compounds has become a popular synthetic strategy [4, 5]. Especially metal organophosphonates have attracted wide attention for potential design of chain, layered, and open-framework materials with numerous combinations of metal sources and organophosphonate units. Use of rigid multifunctional phosphonates, has been recently explored to avoid formation of conventional dense layered structures with monophosphonic acids or diphosphonic acids and to favor formation of more open structures [6, 7]. The 1,3,5-benzenetriphosphonic acid (BTP) was found to form a variety of self-assembly networks in the presence of organic amines [8]. In spite of some reports, still a limited number of BTP-containing open-framework materials are known.

The asymmetric unit of the title structure contains one crystallographically independent zinc(II) ion, one 1,3,5-benzenetri(hydrogen phosphonato), and a half of 4,4'-bipyridine with a proton at the nitrogen. The zinc(II) is four-coordinated by O atoms from four 1,3,5-benzenetri(hydrogen phosphonato) ligands, forming a distorted tetrahedral geometry. The distances between Zn and the coordinated atoms are: d(Zn1...O1) = 1.917(3) Å, d(Zn1...O4) = 1.979(3) Å, d(Zn1...O7) = 1.919(3) Å, and d(Zn1...O8) = 1.929(3) Å, respectively. The Zn(II) coordination angles are in the normal range from 103.14(12)° to 113.95(12)°. The above mentioned bond distances and angles are all in their normal ranges [9]. The Zn(II) ions are linked

with phosphonate groups to form a two-dimensional framework parallel to the *ab* plane, with 4,4'-bipyridinium locating between adjacent layers. There are related structures. For example, zinc 1,3,5-benzenetriphosphonates (ZBP) was prepared in the presence of organic cations containing layers composed of inorganic 1D chains bridged with benzene rings, resembling layered metal phosphates rather than conventional layered phosphonates [10]. ZnBP-NH₄ synthesized from BTP assisted by urea reveals a 3D framework built from layers linked by ZnO₄ tetrahedra [11].

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