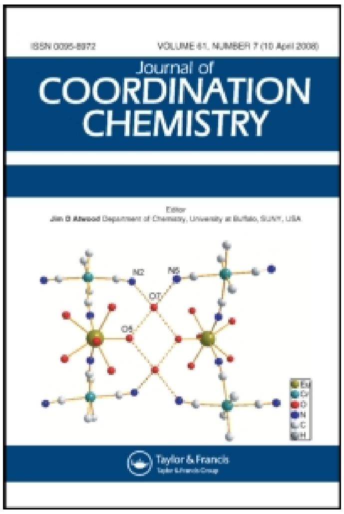

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Synthesis and crystal structure of a new zinc diphosphonate

Dongxu Xue[a]; Mingcai Yin[a]; Yaoting Fan[a]; Aixin Zhu[a]; Huijie Lu[a]; Hongwei Hou[a]
[a] Department of Chemistry, Zhengzhou University, Zhengzhou 450052, P.R. China

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Synthesis and crystal structure of a new zinc diphosphonate

DONGXU XUE, MINGCAI YIN, YAOTING FAN*, AIXIN ZHU,
HUIJIE LU and HONGWEI HOU

Department of Chemistry, Zhengzhou University,
Zhengzhou 450052, P.R. China

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A new zinc diphosphonate $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2(HNO_3)_2 \cdot 4H_2O$ [eddbp = $O_3PCH(Ph)NH(CH_2)_2NHCH(Ph)PO_3$] was hydrothermally synthesized with $Zn(NO_3)_2 \cdot 6H_2O$, ethane-1,2-diamino-*N*,*N′*-bis(benzylphosphonic acid) (H_4edbbp) and 1,2-propyldiamine. It consists of a centro-symmetric dimeric unit $[Zn_2(edbbp)_2]$, in which each zinc ion adopts a distorted square-pyramidal coordination geometry. Hydrogen bonds formed between phosphonate groups and protonated 1,2-propyldiamine molecules link the dimeric units into one-dimensional chains. The doubly protonated 1,2-propyldiamine molecules serve not only as charge compensating counter ions, but also as bridging groups. Hydrogen-bonding interactions among the phosphonate oxygen atoms, water molecules, nitric acid molecules and protonated 1,2-propyldiamine result in the formation of a three-dimensional supramolecular network.

Keywords: Zinc-organodiphosphonate; Synthesis; Crystal structure; Hydrogen bond

1. Introduction

Recently more and more attention has been paid to metal organophosphonates owing to their novel structures and potential applications in intercalation chemistry, ion exchange, sorption, catalysis, sensors, non-linear optic materials [1–4]. The structure of metal organophosphonates depends on a number of factors: the metal cation, the organic groups attached to the phosphonate anion, the reaction conditions such as the temperature and the pH value of the reaction system [5]. Generally, monophosphonic acids RPO_3H_2 can react with metal ions to yield layered compounds, in which the inorganic layers are separated by the organic portion of the phosphonate groups [6, 7]. However, diphosphonic acids as well as functionalized phosphonic acids have proved to be good candidates for the preparation of layered or pillared compounds [8–11]. In this paper, a new zinc diphosphonate $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2(HNO_3)_2 \cdot 4H_2O$ [eddbp = $O_3PCH(Ph)NH(CH_2)_2NHCH(Ph)PO_3$] was prepared by hydrothermal reaction of ethane-1,2-diamino-*N*,*N′*-bis(benzylphosphonic

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*Corresponding author. Email: yt.fan@zzu.edu.cn

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acid) (H_4edbbp) [12] with zinc nitrate under neutral-pH. The crystal structure was characterized by single-crystal X-ray diffraction; the differences between it and $[NH_3(CH)CH_3CH_2NH_3]_2Zn_2(edbbp)_2 \cdot 20H_2O$ [12] are discussed.

2. Experimental

2.1. *Materials and methods*

The ligand H_4edbbp was synthesized according to the literature method [12]. All other chemicals were of analytical reagent grade and used without further purification. IR spectra were performed on a PE spectrophotometer with KBr pellets in the region of 4000–400 cm^{-1}. Carbon, hydrogen and nitrogen analyses were carried out on a Carlo-Erba 1106 elemental analyzer.

2.2. *Preparation of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2(HNO_3)_2 \cdot 4H_2O$*

A mixture of zinc nitrate (1.0 mmol), H_4edbbp (1.0 mmol) and distilled water (8 mL) was adjusted by 1,2-propyldiamine aqueous solution to pH 7 and transferred into a 15 mL Teflon-lined stainless steel reactor. After heating to 160°C for 6 days, colorless single crystals were obtained in ca. 15% yield. Anal. Calcd for $C_{19}H_{35}N_5O_{10}P_2Zn$ (%): N, 11.28; C, 36.76; H, 5.68. Found: N, 11.08; C, 36.83; H, 5.96. IR (KBr, cm^{-1}): 3413 (OH); 1383 (NH); 1054 ($-PO_3$); 702, 603 ($-C_6H_5$).

2.3. *Crystallographic measurement and structure resolution*

A single crystal with dimensions $0.30 \times 0.20 \times 0.18\,mm^3$ was used for structure determination. The X-ray diffraction data were collected on a Rigaku-RAXIS-IV imaging plate with graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) at 293 K. The number of measured and observed reflections $[I > 2\sigma(I)]$ are 7798 and 4865 ($R_{int} = 0.0240$), respectively. The intensity data were corrected for Lorentz-polarization effects. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELX-97 crystallographic software package [13]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms, except for those of water molecules, were generated geometrically, assigned fixed isotropic thermal parameters and included in the structure factor calculations. The hydrogen atoms of water molecules were located from difference Fourier maps and refined isotropically. The main crystallographic data are summarized in table 1. Selected bond lengths and angles are listed in table 2. An X-ray crystallographic file in CIF format has been deposited at the Cambridge Crystallographic Data Centre (CCDC No. 242417).

3. Results and discussion

3.1. *Structure description*

$[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2(HNO_3)_2 \cdot 4H_2O$ is composed of centro-symmetric dimeric $[Zn_2(edbbp)_2]$ units, doubly protonated 1,2-propyldiamine cations, nitric acid and water. Figure 1 shows the dimeric $[Zn_2(edbbp)_2]$ unit with atom numbering. The water, nitric acid and 1,2-propyldiamine cations are omitted for clarity.

Table 1. Crystal data and structure refinement parameters.

Formula	$C_{19}H_{35}N_5O_{10}P_2Zn$
Formula weight	621.83
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal sizes (mm)	0.30 × 0.20 × 0.18
Color	Colorless
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	9.3151(9)
b (Å)	12.3984(12)
c (Å)	13.3412(13)
α (°)	108.69(0)
β (°)	105.95(0)
γ (°)	91.76(0)
V (Å^3)	1391.35(20)
Z	2
D_c (g cm^{-3})	1.484
Absorption coefficient (mm^{-1})	1.056
$F(000)$	649
Reflections collected/unique	7798/4865
Data/restraints/parameters	4865/30/358
Goodness-of-fit on F^2	1.094
R_1, wR_2	0.0496, 0.1306
$(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min}$ (e Å^{-3})	0.930, −0.496

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

Table 2. Selected bond lengths (Å) and angles (°).

Zn(1)–O(6)#1	1.971(3)
Zn(1)–O(1)	2.026(3)
Zn(1)–O(4)	2.030(3)
Zn(1)–N(1)	2.133(3)
Zn(1)–N(2)	2.168(3)
O(6)–Zn(1)–O(1)#1	100.79(11)
O(6)–Zn(1)–O(4)#1	108.93(11)
O(1)–Zn(1)–O(4)	92.24(11)
O(6)–Zn(1)–N(1)#1	113.01(12)
O(1)–Zn(1)–N(1)	86.53(11)
O(4)–Zn(1)–N(1)	137.51(13)
O(6)–Zn(1)–N(2)#1	99.60(13)
O(1)–Zn(1)–N(2)	159.14(13)
O(4)–Zn(1)–N(2)	85.24(11)
N(1)–Zn(1)–N(2)	81.52(13)

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

Each Zn(II) ion is five-coordinate with two oxygen atoms of phosphonate groups and two nitrogen atoms coming from one edbbp^{4-} ligand, the last position is completed by one oxygen atom from a neighboring ligand, forming a severely distorted square-pyramidal geometry with equatorial angles in the range 81.52(13)° to 92.24(11)° and an axial angle O6A–Zn(1)–N(1) of 113.01(12)°. The equatorial plane is defined by O(1), O(4), N(2) and N(1) atoms with the largest deviation of Zn(I) at 0.4388 Å. The apical position is occupied by one phosphonate oxygen atom O6A from the neighboring ligand. The Zn–O distances vary from 1.971(3) to 2.030(3) Å and the Zn–N distances range from 2.133(3) to 2.168(3) Å, comparable with those of reported zinc diphosphonates [12, 14, 15].

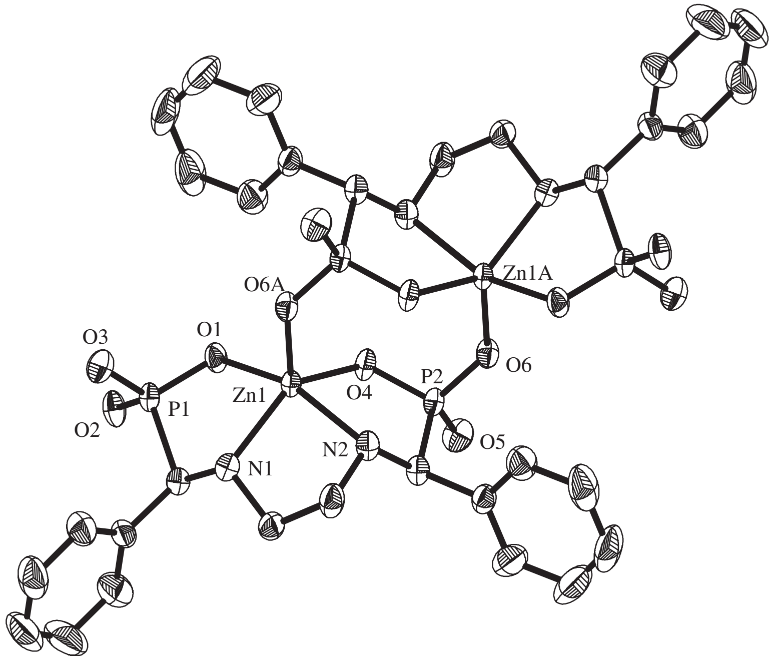
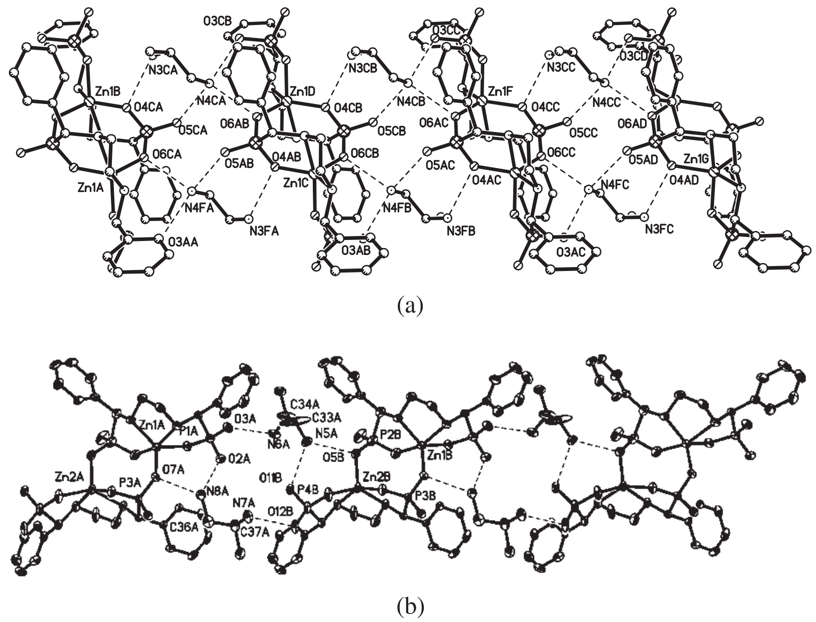


Figure 1. The dimeric structural unit of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2(HNO_3)_2 \cdot 4H_2O$ with 50% thermal ellipsoids.



(a)

(b)

Figure 2. The one-dimensional chain structures of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2(HNO_3)_2 \cdot 4H_2O$ (a) and $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2 \cdot 20H_2O$ (b).

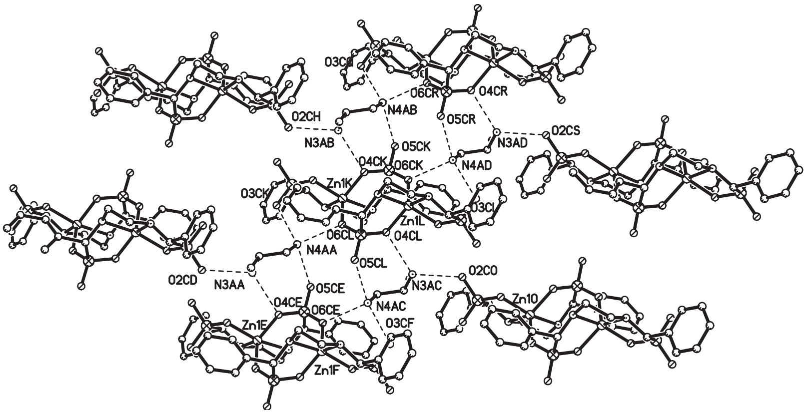


Figure 3. The two-dimensional layer in $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2(HNO_3)_2 \cdot 4H_2O$.

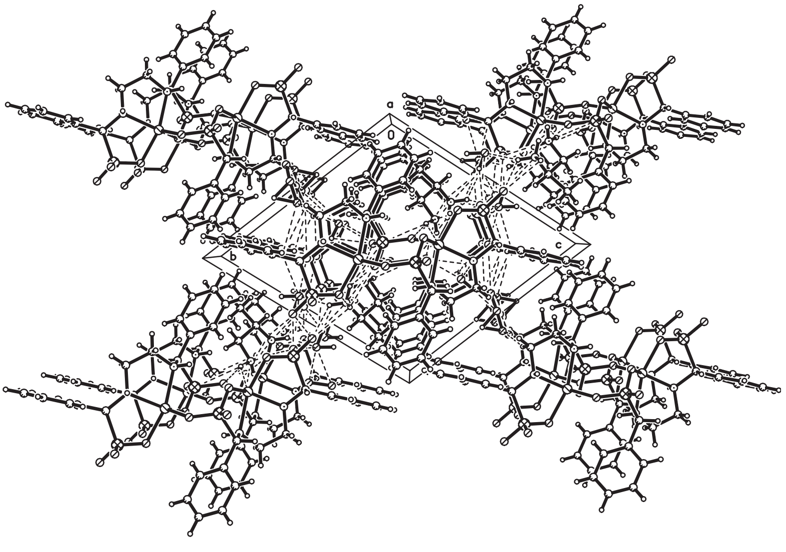


Figure 4. The crystal packing viewing of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2(HNO_3)_2 \cdot 4H_2O$ along the *a* axis.

In the title complex, each edbbp^{4-} ligand chelates one Zn(II) ion and bridges another Zn(II) ion via an O atom of a phosphonate group (figure 1), the same as $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2 \cdot 20H_2O$ [12]. The $[Zn_2(edbbp)_2]$ units are linked together by strong hydrogen-bonding interactions (N4···O3 = 2.818 Å, N4···O6 = 2.733 Å, N4···O5 = 2.708 Å, N3···O4 = 2.765 Å) formed between the phosphonate oxygen atoms and the protonated 1,2-propyldiamine nitrogen atoms, resulting in the formation of one-dimensional chain structures (figure 2a), which are further connected by hydrogen-bonding of N3···O2 = 2.797 Å and a two-dimensional layer is constructed (figure 3).

In addition, numerous hydrogen bonds are formed among the phosphonate oxygen atoms, water molecules, nitric acid molecules, making it a three-dimensional supramolecular network, as shown in figure 4.

Although the dimeric unit of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2\ (HNO_3)_2 \cdot 4H_2O$ is similar to that of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2 \cdot 20H_2O$ [12], the arrangements of their one-dimensional chain structures are different (figure 2). Furthermore, the single crystals of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2(HNO_3)_2 \cdot 4H_2O$ are very stable in air, while those of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2 \cdot 20H_2O$ are unstable probably due to the existence of much lattice water. The differences are derived from the synthetic methods. Compared with the conventional solution reaction method used for $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2 \cdot 20H_2O$, under hydrothermal reaction conditions, less solvent molecules appear in the title complex, indicating that by selection of suitable reaction methods, new metal organophosphonates with novel structures and good stability can be obtained.

Acknowledgements

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