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Synthesis, crystal structures, and third-order nonlinear optical properties of two novel complexes of H_4edbbp with Zn(II), Cd(II)

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Abstract

We synthesized a new organo-diphosphonic acid ligand $H_2O_3PCH(Ph)NH(CH_2)_2NH(Ph)CHPO_3H_2$ [ethane-1,2-diamino-*N*,*N′*-bis(benzyl phosphonic)acid, H_4edbbp] and its two complexes $[NH_3CH(CH_3)CH_2NH_3]_2M_2(edbbp)_2\cdot H_2O$ [M = Zn(II) (**1**), Cd(II) (**2**)] in this paper. The complexes **1**–**2** were structurally characterized by means of X-ray single crystal diffraction. The central ion (M = Zn or Cd) has a distorted square-pyramidal coordination environment by three oxygen atoms from phosphonate units and two nitrogen atoms of H_4edbbp. The fundamental structural units $[M_2(edbbp)_2]^{4-}$ are linked by extensive intermolecular hydrogen bonds between 1,2-propyldiamine cations and phosphonate oxygen atoms, forming a one-dimensional chain structure. The third-order nonlinear optical (NLO) properties of **2** were determined by Z-scan techniques. NLO refractive index n_2, $\chi^{(3)}$ of **2**'s, and hyperpolarizability γ values were calculated to be 1.31×10^{-17} m^2 W^{-1}, 3.19×10^{-11} and 8.57×10^{-30} esu, respectively. The results indicate that complex **2** exhibits very strong NLO absorption and self-focusing effects.

Keywords: Metal–organodiphosphonate complex; Synthesis; Crystal structures; Third-order NLO properties

1. Introduction

Recently, the considerable attention of research activity in the metal–organophosphonate chemistry has been focused on the design and assembly of multifunctional coordination compounds, because of their interesting structures and potential applications in the fields of ion exchange, catalyst, sensors, and nonlinear optics materials [1]. The generation of these molecular architecture rests on several factors: the performance of organic ligand, a species of the metal ion, and the reaction conditions [2]. By careful control of the synthesis conditions and the species of organic ligand employed, a few diphosphonate compounds with layered- or pillared-structure types have been reported [3]. For example, Clearfield and co-workers have reported the structure of layered compound $[Cd_2LCl(H_2O)]$ (H_3L = *N*-(phosphonomethyl)proline) [3a]. Haushalter and co-workers have described a pillared-type complex $[(VO)(H_2O)\{O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3\}]$ of ligand *N*,*N′*-piperazinebis-(methylenephosphonic acid) [3b]. Till now, people's research interest focuses on the design and synthesis of novel metal diphosphonate complexes with optimal magnetic properties, and do not give many efforts toward the study of their nonlinear optical (NLO) properties, especially the third-order NLO refractive properties. The design and synthesis of novel compounds with more perfect optical nonlinearities represent an active research field in modern chemistry and material science. This may be due to that the third-order NLO materials can be used for a number of photonic applications, such as optical signal processing, optical communication, optical computing, optical limiting effect, etc. [4].

Here our research interest focuses on new potential third-order NLO materials. Considering organo-diphosphonic acid ligand and metal ion may make an important contribution to optical nonlinearity of metal–organophosphonate complexes, we synthesized a new organo-diphosphonic acid ligand, $H_2O_3PCH(Ph)NH(CH_2)_2$-$NH(Ph)CHPO_3H_2$ (ethane-1,2-diamino-*N*,*N′*-bis(benzyl

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phosphonic)acid) (H_4edbbp), and its corresponding two complexes $[NH_3CH(CH_3)CH_2NH_3]_2M_2(edbbp)_2 \cdot H_2O$ (M = Zn(II) (**1**) and Cd(II) (**2**)). The crystal structures of the two complexes were characterized by X-ray diffraction. Moreover, the third-order NLO refractive property of complex **2** was also measured by Z-scan techniques in DMF solution. The calculated hyperpolarizability γ value is 8.57×10^{-30} esu. The results indicate that complex **2** exhibits strong third-order NLO refractive properties.

2. Experimental

2.1. Materials and physical techniques

All chemicals were of reagent quality obtained from commercial sources and used without further purification.

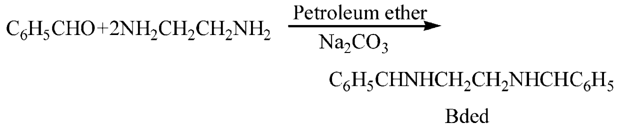
IR spectra were performed on a PE spectrophotometer with KBr pellets in the region of 400–4000 cm^{-1}. Carbon, hydrogen and nitrogen analyses were carried out on a Carlo-Erba 1106 elemental analyzer. ^1H NMR spectra were recorded at room temperature (RT) on a Bruker DPX-400 spectrometer.

2.2. Synthesis of ethane-1,2-diamino-N,N′-bis (benzyl phosphonic)acid (H_4edbbp)

The target compound H_4edbbp was synthesized by two step reaction in this paper. First of all, the benzaldehyde ethylenediamino schiff base (Bded) was prepared as follows (Scheme 1):

A mixture of benzaldehyde (0.24 mol) and ethylenediamino (0.1 mol) in petroleum ether (30 ml) was refluxed for 3 h. The resulting solution was allowed to stand at RT in a primrose solid powder. The compound was recrystallized from petroleum ether to yield 90% primrose crystalline powder, m.p. 60 °C. IR (KBr)/cm^{-1}: 1550 (C=N), 1024(C–C), 710(C_6H_5–). Anal. Calcd. for $C_{16}H_{16}N_2$ (%): C, 81.36; H, 6.78; N, 11.86. Found (%): C, 80.95; H, 6.56; N, 11.67.

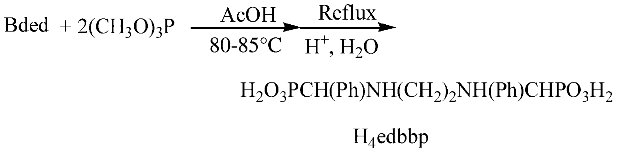
Thereafter, H_4edbbp was synthesized according to the synthetic route described below : a trimethyl phosphate (0.1 mol) was added dropwise to a solution of Bded (0.05 mol) in glacial acetic acid (100 ml), then the reaction mixture was stirred at 80–85 °C for 3 h, and the solvent was removed under reduced pressure to give an a viscous orange-yellow oil matter, adding concentrated HCl (80 ml) to above oil matter, and the mixture was stirred and refluxed for about 3 h. Excess HCl are removed under reduced pressure to give an acidified oil matter, distilled water (60 ml) was then added, and the resultant solution was stirred and refluxed for 1 h to give a white solid. The compound may be purified from NaOH and HCl solution to yield 24.1% white powder solid, m.p. 241–242 °C. IR (KBr)/cm^{-1}: 3423(–OH), 1626(NH), 1156(P=O), 1076 (–PO_3), 785, 572(C_6H_5–); Anal. Calcd. for $C_{16}H_{22}O_6N_2P_2$ (%): C, 48.0; H, 5.5; N, 7.0. Found (%): C, 47.5; H, 5.65; N, 6.95; ^1H NMR (NaOD + D_2O): δ 7.39(d, 10H), 3.71(t, 2H), 2.62(s, 4H).



$$C_6H_5CHO + 2NH_2CH_2CH_2NH_2 \xrightarrow[Na_2CO_3]{\text{Petroleum ether}} C_6H_5CHNHCH_2CH_2NHCHC_6H_5$$

Bded

Scheme 1.



$$\text{Bded} + 2(CH_3O)_3P \xrightarrow[80\text{-}85^\circ C]{AcOH} \xrightarrow[H^+, H_2O]{\text{Reflux}} H_2O_3PCH(Ph)NH(CH_2)_2NH(Ph)CHPO_3H_2$$

H_4edbbp

Scheme 2.

The synthetic route of H_4edbbp was shown in Scheme 2.

2.3. Preparation of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2(edbbp)_2 \cdot 20H_2O$ (1)

A solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0130 g, 0.044 mmol) in deionized water (4 ml) was added dropwise to a solution of H_4edbbp (0.0202 g, 0.051 mmol) in deionized water (2 ml), and adjusted pH = 7 by 1,2-propyldiamine aqueous solution. The mixed solution was then stirred for 30 min and filtered. The resulting solution was allowed to stand at RT, colorless crystals suitable for X-ray single crystal analysis were obtained over 24 h in 55% yield. IR (KBr)/cm^{-1}: 3411(OH), 1636(NH), 1051(–PO_3), 703, 603(–C_6H_5).

2.4. Preparation of $[NH_3CH(CH_3)CH_2NH_3]_2Cd_2(edbbp)_2 \cdot 25H_2O$ (2)

Complex **2** was prepared in a similar manner as that of complex **1**. Reaction of $Cd(NO_3)_2 \cdot 4H_2O$ (0.0141 g, 0.046 mmol) with H_4edbbp (0.0201 g, 0.051 mmol) in aqueous solution gave complex **2**. Colorless single crystals suitable for X-ray single crystals analysis were obtained over 24 h in 65% yield. IR (KBr)/cm^{-1}: 3400(OH), 1636(NH), 1050(–PO_3), 702, 591(–C_6H_5).

2.5. Single-crystal X-ray diffraction

Crystal data and structure refinement for the two complexes are summarized in Table 1. All measurements were made on a Rigaku RAXIS-IV imaging plate with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Colorless single crystals of complexes **1** (0.3 × 0.2 × 0.2 mm), and **2** (0.3 × 0.3 × 0.2 mm) were selected and mounted on a glass fiber. All data were collected at a temperature of 195 K using the ω–2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

Table 1
Crystal data and structure refinement for complexes **1** and **2**

Compounds	**1**	**2**
Formula	$C_{38}H_{100}Zn_2N_8P_4O_{32}$	$C_{38}H_{110}Cd_2N_8P_4O_{37}$
Fw	1434.8	1556.8
Temperature (K)	195	195
Wavelength (Å)	0.71073	0.71073
Crystal sizes (mm)	0.30×0.20×0.20	0.30×0.30×0.20
Color	Colorless	Colorless
Crystal syst	Monoclinic	Triclinic
Space group	*P2₁/n*	*P-1*
a (Å)	14.745(2)	14.6705(15)
b (Å)	25.171(4)	15.5102(15)
c (Å)	17.675(3)	17.5653(17)
α (°)	90	68.3310(10)
β (°)	102.335(2)	71.3930(10)
γ (°)	90	79.2560(10)
V (Å^3)	6408.9(16)	3509.6(6)
Z	4	2
D_c (mg m^{-3})	1.394	1.481
Absorption coefficient (mm^{-1})	0.933	0. 788
F(000)	2744	1582
Reflections collected/unique	26,136/11,263	14,439/12,023
Data/restraints/parameters	11,263/0/831	12,023/0/875
Goodness-of-fit on F^2	1.036	1.129
$R1$, $wR2^a$	0.1688, 0.2098	0.0801, 0.1680
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å^{-3})	1.395, −0.863	1.586, −1.331

[a] $R1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2=\{\Sigma w(|F_o|-|F_o|)^2/\Sigma wF_o^2\}^{1/2}$.

The two structures were solved by direct methods and expanded using the Fourier technique. All the non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 11,263 observed reflections and 831 variable parameters for complex **1**, and 12,023 observed reflections and 875 variable parameters for complex **2**. All calculations were performed using the SHELX-97 crystallographic software package [5]. Selected bond lengths and bond angles of complexes **1–2** are listed in Table 2. Primary intermolecular hydrogen bonds are given in Table 3.

2.6. Nonlinear optical measurements

A DMF solution for complex **2** was placed in a 1-mm quartz cuvette for NLO measurements. The NLO properties were determined by procedures described in previous literature [6].

3. Results and discussion

3.1. Syntheses

Green and co-workers reported previously the synthesis of aromatic aminophosphonic acid $NH_2CH(Ph)PO_3H_2$ by the reaction of benzylidenediphenylamine with dimethyl phosphate at 130–140 °C without the presence of solvent [7]. However, the desired compound H_4edbbp was not obtained according to the literature [7]. Here we synthesized target ligand H_4edbbp by two step reaction under relatively mild conditions. Furthermore, H_4edbbp could also be prepared by one-pot reaction of trimethyl phosphate with benzaldehyde and ethylenediamine in glacial acetic acid at 80–85 °C directly. Its synthetic route is as follows (Scheme 3):

Trimethyl phosphate, which was used as a starting material, directly reacted with benzaldehyde and ethylenediamine in glacial acetic acid at 80–85 °C, to afford H_4edbbp. Compared with two step reaction, the synthetic route in one-pot reaction is simple and more effective for preparation of H_4edbbp. The ligand was insoluble in neutral water and common organic solvents, such as MeOH, EtOH, MeCN, THF, DMSO and DMF, but only soluble in aqueous alkali solution.

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Compound 1			
Zn(1)–O(7)	1.956(3)	Zn(2)–O(5)	1.952(3)
Zn(1)–O(1)	1.990(3)	Zn(2)–O(10)	1.980(3)
Zn(1)–O(4)	2.052(3)	Zn(2)–O(8)	2.060(3)
Zn(1)–N(2)	2.099(4)	Zn(2)–N(3)	2.136(4)
Zn(1)–N(1)	2.220(3)	Zn(2)–N(4)	2.224(3)
O(7)–Zn(1)–O(1)	109.14(12)	O(5)–Zn(2)–O(10)	104.99(14)
O(7)–Zn(1)–O(4)	103.32(12)	O(5)–Zn(2)–O(8)	105.33(12)
O(1)–Zn(1)–O(4)	95.73(12)	O(10)–Zn(2)–O(8)	95.55(12)
O(7)–Zn(1)–N(2)	118.16(13)	O(5)–Zn(2)–N(3)	110.59(14)
O(1)–Zn(1)–N(2)	131.13(14)	O(10)–Zn(2)–N(3)	143.09(15)
O(4)–Zn(1)–N(2)	85.25(13)	O(8)–Zn(2)–N(3)	84.47(12)
O(7)–Zn(1)–N(1)	94.92(12)	O(5)–Zn(2)–N4)	103.20(13)
O(1)–Zn(1)–N(1)	85.20(12)	O(10)–Zn(2)–N(4)	83.96(13)
O(4)–Zn(1)–N(1)	160.26(13)	O(8)–Zn(2)–N(4)	150.55(14)
N(2)–Zn(1)–N(1)	79.45(13)	N(3)–Zn(2)–N(4)	78.80(13)
Compound 2			
Cd(1)–O(3)#1	2.198(3)	Cd(2)–O(10)#2	2.189(4)
Cd(1)–O(4)	2.218(3)	Cd(2)–O(7)	2.200(3)
Cd(1)–O(1)	2.247(3)	Cd(2)–O(12)	2.272(3)
Cd(1)–N(1)	2.336(3)	Cd (2)–N(4)	2.339(4)
Cd(1)–N(2)	2.369(3)	Cd(2)–N(3)	2.365(3)
O(3)#1–Cd(1)–O(4)	102.55(11)	O(10)#2–Cd(2)–O(7)	113.36(14)
O(3)#1–Cd(1)–O(1)	96.62(11)	O(10)#2–Cd(2)–O(12)	96.81(11)
O(4)–Cd(1)–O(1)	102.93.(10)	O(7)–Cd(2)–O(12)	96.68(11)
O(3)#1–Cd(1)–N(1)	134.63(12)	O(10)#2–Cd(2)–N(4)	135.04(11)
O(4)–Cd(1)–N(1)	122.45(12)	O(7)–Cd(2)–N(4)	111.54(14)
O(1)–Cd(1)–N(1)	79.98 (10)	O(12)–Cd(2)–N(4)	80.02(11)
O(3)#1–Cd(1)–N(2)	107.33(11)	O(10)#2–Cd(2)–N(3)	108.05(13)
O(4)–Cd(1)–N(2)	80.57(11)	O(7)–Cd(2)–N(3)	81.12(11)
O(1)–Cd(1)–N(2)	154.54(11)	O(12)–Cd(2)–N(3)	153.83(14)
N(1)–Cd(1)–N(2)	77.10(11)	N(4)–Cd(2)–N(3)	76.68(12)

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

Table 3
Primary intermolecular hydrogen bonds for complexes **1** and **2**

D–H	*d*(D–H)	*d*(H···A)	∠DHA	*d*(D···A)	A
Complex 1					
N8–H8E	0.910	1.922	151.84	2.758	O2 $[-x+5/2, y-1/2, -z+3/2]$
N6–H6B	0.910	1.785	173.34	2.690	O3 $[-x+3/2, y-1/2, -z+3/2]$
N5–H5D	0.910	2.035	140.36	2.797	O5 $[-x+1/2, y-1/2, -z+3/2]$
N8–H8C	0.910	2.128	138.31	2.872	O7 $[-x+5/2, y-1/2, -z+3/2]$
N5–H5C	0.910	1.955	152.64	2.795	O11 $[-x+1/2, y-1/2, -z+3/2]$
N7–H7D	0.910	1.800	166.15	2.692	O12 $[-x+3/2, y-1/2, -z+3/2]$
Complex 2					
N5–H5B	0.910	1.884	166.75	2.777	O6
N5–H5C	0.910	1.923	153.24	2.766	O5 $[-x-1, -y+1, -z+1]$
N6–H6B	0.910	1.806	164.23	2.693	O6
N6–H6C	0.910	1.888	161.21	2.765	O3 $[-x, -y+1, -z+1]$
N8–H8D	0.910	1.730	176.16	2.639	O9
N7–H7D	0.910	1.938	148.03	2.752	O11 $[x+1, y, z]$

The complexes **1–2** were prepared by the reaction of transition metal ions (M = Zn(II), Cd(II)) with H_4edbbp in the presence of 1,2-propyldiamine in aqueous solution. Herein, 1,2-propyldiamine was employed as a template agent of the reaction. Although several inorganic or organic alkalies, such as sodium hydroxide, methylamine, ethylenediamine, and piperazine were also used as template agents of the reaction, the corresponding complexes were not obtained under the same experimental conditions. Our experimental results reveals that 1,2-propyldiamine can be used as an optimum directing structure agent in the preparation of the complexes $[NH_3CH(CH_3)CH_2NH_3]_2$-M_2(II)(edbbp)$_2 \cdot H_2O$ (M = Zn(II), Cd(II)).

Complexes **1**, **2** are unstable in the air. When they were removed from their mother liquors, they soon become amorphous under atmospheric condition. They are not soluble in water and common organic solvents, such as MeOH, EtOH, MeCN, THF and DMF. Single crystals suitable for X-ray crystallography for these compounds were collected by slow evaporation of their aqueous solution at RT.

$$2PhCHO + NH_2CH_2CH_2NH_2 + 2(CH_3O)_3P \xrightarrow[80\text{-}85°C]{AcOH} \xrightarrow[H^+,\, H_2O]{Reflux}$$

$$H_2O_3PCH(Ph)NH(CH_2)_2NH(Ph)CHPO_3H_2$$

H_4edbbp

Scheme 3.

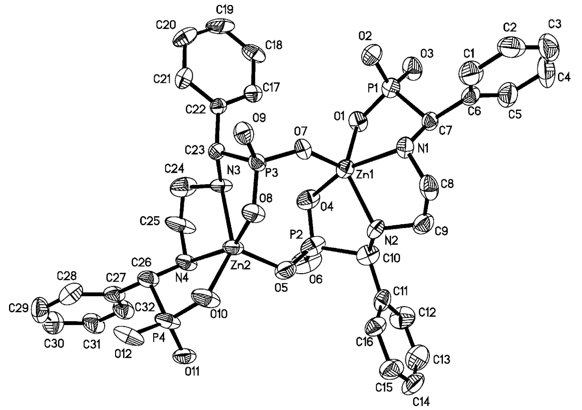


Fig. 1. The dimeric structural unit of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2$ (edbbp)$_2 \cdot 20H_2O$.

3.2. Crystal structure of $[NH_3(CH)CH_3CH_2NH_3]_2Zn_2$(II)(edbbp)$_2 \cdot 20H_2O$(1)

Complex **1** crystallizes in monoclinic with space group of *P2₁/n*. The asymmetric unit consists of two Zn atoms, two equivalent edbbp^{4-}, two protonated 1,2-propyldiamine cations, and 20 water molecules. Fig. 1 shows the structure unit of complex **1** with atomic numbering, the water molecules and protonated 1,2-propyldiamino cation are omitted for clarity. Each Zn ion is five-coordinate bonding to three oxygen atoms come from phosphonate units and two nitrogen atoms from the ligand. The Zn–O and Zn–N distances range from 1.952(3) to 2.060(3) Å and from 2.099(4) to 2.224(3) Å, respectively, which are close to that of the reported zinc diphosphonate compounds previously [9]. The equatorial plane of Zn(1) is defined by O(1), N(1), N(2), O(4) atoms with the largest deviation of Zn(1) at 0.4550 Å. The apical position is occupied by one phoshohonate oxygen atom O(7) from the neighbouring edbbp. The geometry around the Zn(1) atom can be best described as severely distorted square-pyramidal coordination sphere, with equatorial angles in the range 85.21(14)–160.76(14)°, and an axial angle O(7)–Zn(1)–O(1) of 109.14(12)°. The geometry around the Zn(2) is very similar to that of Zn(1), and the Zn(2) atom is pulled out of this plane defined by the four chelating atoms N(3), N(4), O(10), and O(8) at 0.4443 Å.

Both phosphonate groups of H_4edbbp are completely deprotonated, two NH_2– groups of 1,2-propyldiamine are 2H– protonated, thus each edbbp carries four negative charges and $[Zn_2(edbbp)_2]^{4-}$ unit are needed to balance the four positive charges of two protonated 1,2-propyldiamines. Each edbbp as tetradentate ligand chelates one Zn(II) ion and bridges another Zn(II) ion via O atom of a phosphonate group forming six five-membered rings and one eight-membered

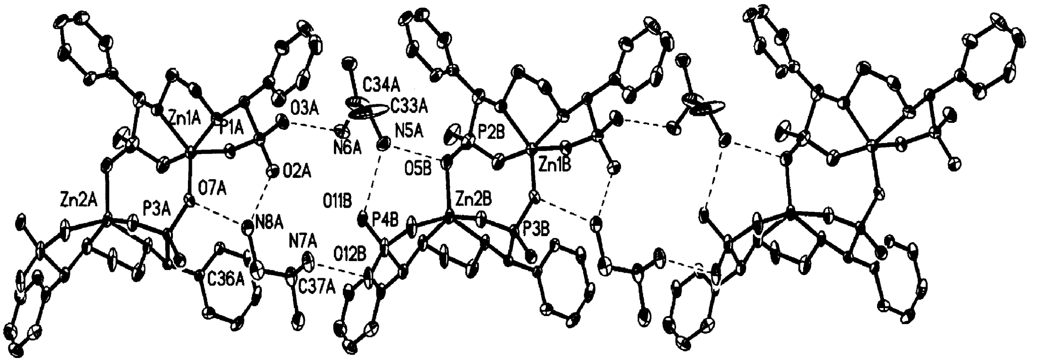


Fig. 2. One-dimensional chain structure of $[NH_3CH(CH_3)CH_2NH_3]_2Zn_2$ $(edbbp)_2 \cdot 20H_2O$.

ring. The arrangement of the eight-membered ring (Zn1–O4–P2–O5–Zn2–O8–P3–O7) is very similar to that in complex $Zn(O_3PCH_2CH_2NH_2)$ described by Bujoli et al. [10]. In edbbp, two $\{CPO_3\}$ moieties coordinate with zinc atoms by two different mode, one of them acts as a monodentate mode, the another adopts bidentate fashion bridging Zn(1) and Zn(2) atoms.

The $[Zn_2(edbbp)_2]^{4-}$ units are linked by extensive intermolecular hydrogen bonds between 1,2-propyldiamine cations and phosphonate oxygen atoms, forming a one-dimensional chain structure with various voids (Fig. 2). These voids are created by six and 14-membered rings. The six-membered ring contains N8A, O2A, P1A, O1A, Zn1A, O7A atoms, whereas, the 14-membered ring is composed of atoms C36A, C37A, N7A, O12B, P4B, O11B, N5A, C33A, C34A, N6A, O3A, P1A, O2A, N8A. The short N–O distances indicate very strong mutual electrostatic interactions: $N(5)\cdots O(5) = 2.797$ Å, $N(5)\cdots O(11) = 2.795$ Å, $N(6)\cdots O(3) = 2.690$ Å, $N(7)\cdots O(12) = 2.692$ Å, $N(8)\cdots O(2) = 2.758$ Å, $N(8)\cdots O(7) = 2.872$ Å. In addition, the crystal lattice of complex **1** contains a lot of water molecules (about 20 water molecules per formula unit $[Zn_2(edbbp)_2]^{4-}$), which fill the spaces between the chains, forming extensive hydrogen bonds with phosphonate oxygen atoms or neighbouring water molecules. As shown in Fig. 3, the complex **1** shows an open-network supramolecular structure.

3.3. Crystal structure of $[NH_3(CH)CH_3CH_2NH_3]_2Cd_2(II)(edbbp)_2 \cdot 25H_2O$ (2)

The structure of complex **2** crystallizes in the triclinic space group *P-1*. The asymmetric structural unit consists of two Cd atoms, two equivalent edbbp, two protonated 1,2-propyl-diamine cations, and 25 water molecules. An ORTER view of the dimeric unit of complex **2** is shown in Fig. 4. The geometry of complex **2** is similar to that of complex **1**. Each Cd ion is at a five-coordinated geometry in which three oxygen atoms come from phosphonate units and two nitrogen atoms from the ligand, forming distorted square-pyramidal coordination geometry. The Cd–O distances are in the range of 2.189(3)–2.272(3) Å and Cd–N distances are in the range of 2.336(4)–2.369(3) Å, comparable to those of other cadmium diphosphonate complexes [11]. In complex **2**, 1,2-propyldiamine cations serve not only as charge compensating counter ions but as bridging functions for $[Cd_2(edbbp)_2]^{4-}$ units. As can be seen from Fig. 5, there exist two types of one-dimensional chain by means of extensive intermolecular

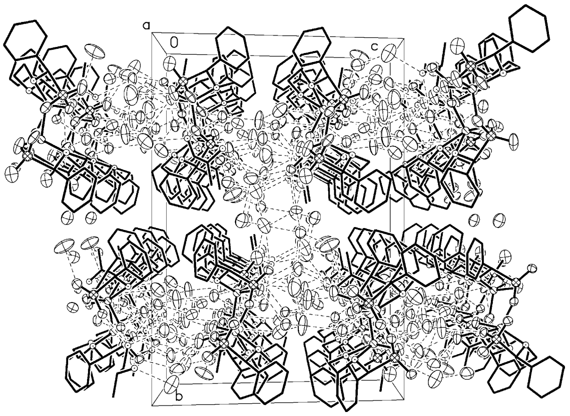


Fig. 3. The crystal packing viewing of $NH_3CH(CH_3)CH_2NH_3]_2Zn_2$ $(edbbp)_2 \cdot 20H_2O$ along the a axis.

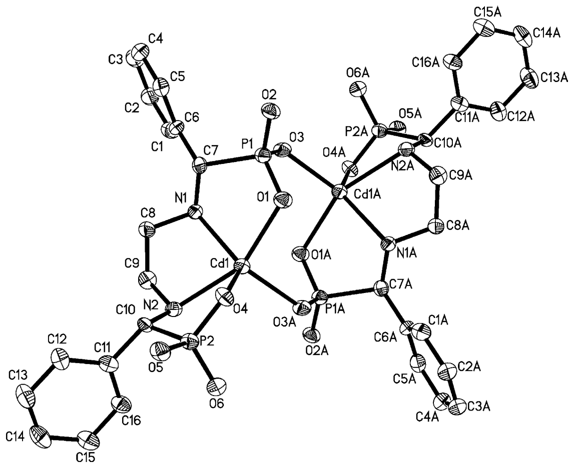


Fig. 4. The dimeric structural unit of complex **2** $[NH_3CH(CH_3)CH_2NH_3]_2$-Cd_2 $(edbbp)_2 \cdot 25H_2O$.

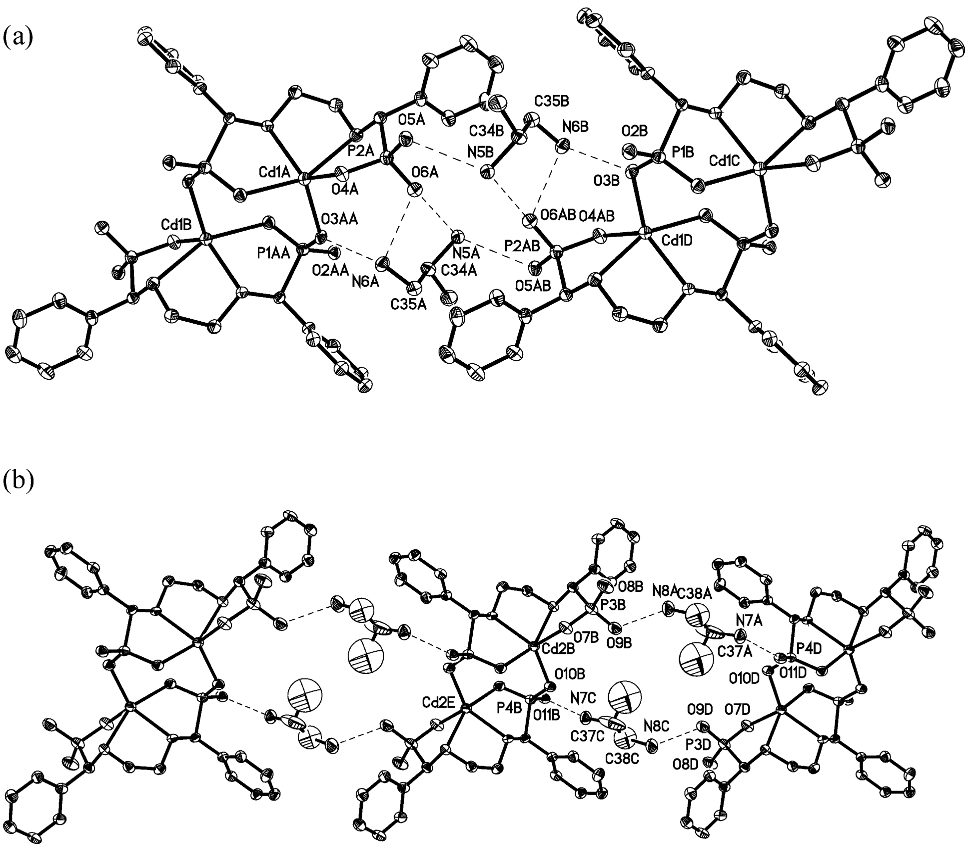


Fig. 5. Two one-dimensional chain structures of [NH$_3$CH(CH$_3$)CH$_2$NH$_3$]$_2$Cd$_2$(edbbp)$_2$·25H$_2$O: (a) formed by four strong intermolecular hydrogen bonds; (b) formed by two mutual hydrogen bonds.

hydrogen bonds between 1,2-propyldiamine cations and phosphonate oxygen atoms. One chain is constructed through four strong intermolecular hydrogen bonds (N5···-O6 = 2.777 Å, N5···O5 = 2.766 Å, N6···O3 = 2.765 Å and N6···O6 = 2.693 Å) (Fig. 5(a)). The other involves only two mutual hydrogen bonds (N8···O9 = 2.639 Å and N7···O11 = 2.752 Å) (Fig. 5(b)). The lattice water molecules are not coordinated to the Cd(II) ions, but form strong hydrogen bonds with phosphonate oxygen atoms or neighbouring water molecules. The large number of water molecules play an essential role in stabilizing the crystal lattice by filling space between chains through extensive hydrogen bonds.

It is generally accepted that the protonation of the phosphonate oxygens may block the assembly of the metal diphosphonate into higher dimensionalities [12]. In this study, although two phosphonate groups of H$_4$edbbp are fully deprotonated and there are six phosphonate oxygen atoms as potential chelating groups, only three of them are coordinated to the center ions. The remaining three phosphonate oxygen atoms are only involved in extensive hydrogen bonding network with 1,2-propyldiamine cations as well as with lattice water molecules. In the molecular structure of edbbp, the additional –Ph group attached to the methylene of edbbp provides not only a steric hindrance but also a possible hydrophobic environment. It is argued that the great steric hindrance of Ph group play an essential role in blocking the assembly of metal diphosphonates into extended structures. Another distinguished structural feature of metal–edbbp complexes is that there are a large number of lattice water molecules filling the space between chains, which is caused by the electrostatics between the organo-amine cations and the edbbp anions. The hydrogen bonds that hold the crystalline framework are relatively weak, and removal of the guest water molecules from the channels is accompanied by collapse of the structure.

3.4. NLO properties

Till date, several groups have studied the NLO properties of some metal–organophosphonate compounds [13], but these investigations were focused on second order NLO properties, third-order NLO properties of these compounds are lacking.

The NLO properties of complexes **1** and **2** were measured as described in the literature [4b] except that the concentration was 1.3×10^{-3} mol dm^{-3} for complex **1** or 6.2×10^{-3} mol dm^{-3} for complex **2** in a DMF solution. We found that complex **2** possesses strong NLO refractive effects, but complex **1** has no NLO refractive under the same condition. Fig. 6 depicts NLO refractive properties of complex **2**. The data are assessed by dividing

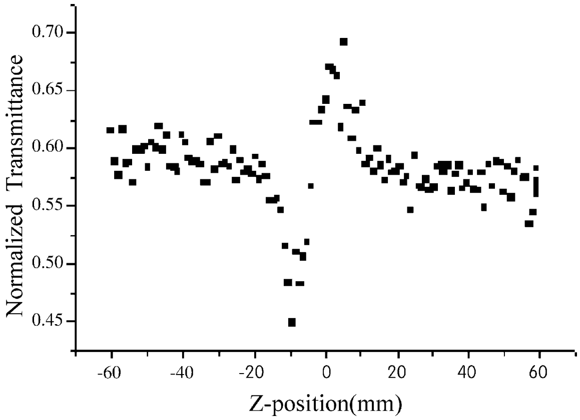


Fig. 6. The data were assessed by dividing the normalized Z-scan data obtained under the closed aperture configuration by the normalized Z-scan data obtained under the open aperture configuration. The self-focusing effects of complex **2** in 6.2×10^{-3} mol dm^{-3} DMF solution at 532 nm.

the normalized Z-scan data obtained under the open aperture configuration. The third-order NLO refractive index n_2 can be derived by Eq. (1)

$$n_2 = \frac{\lambda\alpha_0}{0.812\pi I(1-\mathrm{e}^{-\alpha_0 L})}\Delta T_{V-P} \qquad (1)$$

where ΔT_{V-P} is the difference between normalized transmittance values at valley and peak portion. I is the peak irradiation intensity at focus (4.2×10^{12} W/m^2), α_0 is the linear absorption coefficient, L is the sample thickness (1 mm in this study), and λ is the wavelength of the laser (532 nm). Fig. 6 shows the NLO refractive effects of complex **2**. The ΔT_{V-P} and α_0 values of the compound are 0.243 and 1.60 cm^{-1}, respectively. The data show that the compound has the positive sign for the refractive nonlinearity, which gives rise to self-focusing behavior. The calculated refractive index n_2 value is 1.31×10^{-17} m^2 W^{-1}.

In accordance with the n_2 value, the effective third-order NLO susceptibility $\chi^{(3)}$ value can be calculated by $\chi^{(3)}=cn_0^2n_2/80\pi$, where c is speed of light in a vacuum, n_0 is the linear refractive index of the sample ($\sim$1.43), and n_2 is the third-order nonlinear refractive index. Thus, the calculated $\chi^{(3)}$ value is 3.19×10^{-11} esu. The corresponding modulus of the hyperpolarizability value γ is obtained from $|\gamma|=\chi^{(3)}/NF^4$, where N is the number density of complex **2** in the sample (in cm^{-3}) ($N=10^{-3}\times CN_A$, C is the molar concentration of the compound in a DMF solution, N_A is the Avagadro constant); $F^4=3$ is the local field correction factor. The calculated γ value of complex **2** is 8.57×10^{-30} esu. The γ value is similar to that of the reported 3D supramolecule compound $[Zn(TIPT)Cl_2]\cdot 2CH_3OH$ [4a], several orders of magnitude larger than those of the reported ferrocenyl complexes, such as NiL^2_2, PdL^2_2 ($L^2=FcC(CH_3)=N_2HCS_2CH_2C_6H_5$), and $[Ag(L)_2](NO_3)\cdot(MeOH)\cdot(EtOH)$, $[HgI_2(L)]$ {L=1,2-bis [(ferrocen-1-ylmethylene)amino]ethane [4b], but smaller than that of several reported ferrocenyl organometallics complexes, such as $[Hg_2(OAc)_4(4\text{-BPFA})_2(CH_3OH)_2]$, $[Cd_2(OAc)_4(4\text{-BPFA})_2]$ [4c]. This result shows that complex **2** owns strong third-order optical nonlinearity. To the best of our knowledge, complex **2** is the first example with third-order NLO properties in the reported metal–organophosphonate compounds. We believe that our exploration may provide a useful guide to the design of metal organo-diphosphonic complexes with third-order NLO materials.

4. Supporting information available

Crystallographic data in CIF format. CCDC-225313(1) and -225314(2) contain the supplementary crystallographic data for this paper. This material is available free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk]

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2004.07.013

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