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Zinc(II) Complex with 1,2-Bis(2-pyridyl-1,2,4-triazol-3-yl)ethane and Dianions of 1-Hydroxyethane-1,1-diphosphonic Acid

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Abstract—The reaction of $ZnSO_4·7H_2O$ with 1,2-bis(2-pyridyl-1,2,4-triazol-3-yl)ethane (H_2L) and 1-hydroxyethane-1,1-diphosphonic acid (H_4EDP) in an aqueous medium affords complex $\{[Zn_2(H_2L)(H_2EDP)_2(H_2O)_2]·2H_2O\}_n$, which is studied by elemental analysis and IR spectroscopy. The structure of the complex is determined by X-ray diffraction analysis (CIF file CCDC no. 2043698). The complex has the 1D polymeric structure and represents a zigzag chain in which two zinc(II) cations are joined by two bis(phosphonate) anions into the centrosymmetric binuclear fragments linked by the bridging bis(triazolyl)ethane molecules. The zinc(II) cation additionally coordinates the water molecule and exists in the distorted octahedral coordination environment. The luminescence spectrum of the complex exhibits a broad emission band with a maximum at 408 nm and a quantum yield of 4%.

Keywords: 1-hydroxyethane-1,1-diphosphonic acid, spacered 1,2,4-triazole, zinc(II), X-ray diffraction analysis

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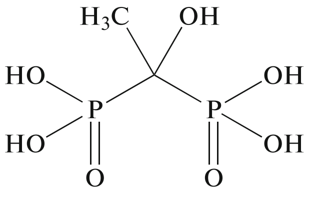
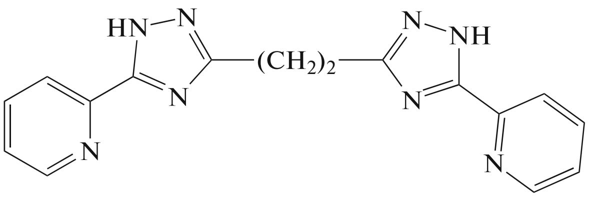
INTRODUCTION

2-Pyridyl-containing azole ligands are structural analogs of chelating 2,2'-dipyridyl and 1,10-phenanthroline and possess a high coordination ability. Therefore, ligands of this type evoke increased interest of researchers [1–3]. The binding of chelating groups by a hydrocarbon spacer and the use of additional extraligands make it possible to extend their coordination abilities and synthesize complexes with an original structure and properties mainly determined by the spacer length and nature [4–7]. The conditions for the synthesis and crystallization of the reaction products also significantly affect the structures of the synthesized complexes.

In this work, we describe the synthesis and structure of the polymeric zinc(II) complex based on dianions of 1-hydroxyethane-1,1-diphosphonic acid (H_4EDP) and 1,2-bis(2-pyridyl-1,2,4-triazol-3-yl)ethane (H_2L), which is a representative of the convenient type of proligands appropriate for self-assembling of coordination compounds of various nuclearity and topology [1, 4]. The zinc(II) complexes with the nitrogen-containing ligands and H_4EDP anions were described [8–10].



(H_4EDP)



(H_2L)

EXPERIMENTAL

1,2-Bis(2-pyridyl-1,2,4-triazol-3-yl)ethane was synthesized using a described procedure [4]. 1-Hydroxyethane-1,1-diphosphonic acid (etidronic acid, monohydrate, Aldrich) and $ZnSO_4·7H_2O$ (reagent grade) were used.

Synthesis of complex $\{[Zn_2(H_2L)(H_2EDP)_2(H_2O)_2]\cdot 2H_2O\}_n$ (I). A solution of H_4EDP (0.225 g, 1 mmol) in water (5 mL) was added to a suspension containing H_2L (0.5 mmol, 0.160 g) in water (10 mL), and the mixture was stirred at 70–80°C for 10 min to the complete dissolution of the reactants. A solution of $ZnSO_4\cdot 7H_2O$ (0.287 g, 1 mmol) in water (5 mL) was added to the resulting solution, and the mixture was cooled to room temperature with stirring, after which triethylamine (2 mmol) was slowly added to pH 6–7. The obtained solution was kept at room temperature for 2 days. The formed crystals were separated from the mother liquor by filtration, washed with water, and dried in air. The yield of colorless finely crystalline complex **I** was 0.140 g (15% based on H_2L).

For $C_{20}H_{36}N_8O_{19}P_4Zn_2$

Anal. calcd., %	C, 28.36	H, 4.83	N, 11.83
Found, %	C, 28.66	H, 5.13	N, 11.62

IR (ν, cm^{-1}): 3218, 1620, 1610, 1569, 1481, 1455, 1402, 1349, 1288, 1238, 1127, 1031, 999, 906, 892, 754, 710, 645, 550, 449, 413.

Single crystals of complex **I** suitable for X-ray diffraction analysis (XRD) were grown by the recrystallization of the finely crystalline product from water under the hydrothermal synthesis conditions. For this purpose, compound **I** (20 mg) was placed in a sealed Teflon tube, 1–2 droplets of a 60% solution of etidronic acid were added, and the tube was heated to 80°C with a rate of 0.2°C/min. The temperature was maintained for 2 h, and the tube was slowly cooled with the same rate to room temperature. The formed crystals were separated by filtration.

XRD of the single crystals of complex **I** was carried out at 150 K on a Bruker Smart APEX II diffractometer equipped with a CCD detector and a monochromatic radiation source (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator) using a standard procedure [11]. An absorption correction was applied [12]. The structure was solved by a direct method and refined in the full-matrix anisotropic approximation for all nonhydrogen atoms. The calculations were performed using the SHELXL-2018/3 program [13]. Hydrogen atoms were generated geometrically and refined by the riding model. The hydrogen atoms at the O(3) and O(5) oxygen atoms of the phosphoryl groups were revealed from the difference Fourier synthesis and fixed using the AFIX functions with allowance for disordering over two positions with equivalent populations of 0.5.

The crystallographic parameters and structure refinement details for compound **I** are the following: $C_{20}H_{36}N_8O_{19}P_4Zn_2$, $FW = 947.19$, crystal size 0.1 × 0.1 × 0.08 mm, colorless crystals, $T = 150(2)$ K, triclinic crystal system, space group $P\bar{1}$, $a = 8.9186(5)$, $b = 10.2871(6)$, $c = 10.4426(6)$ Å, $\alpha = 110.053(2)°$, $\beta = 107.600(2)°$, $\gamma = 93.077(2)°$, $V = 844.51(8)$ Å^3, $Z = 1$, $\rho = 1.862$ g/cm^3, $\mu = 1.704$ mm^{-1}, $\theta = 2.14°–28.28°$, $-11 \le h \le 10$, $-13 \le k \le 13$, $-13 \le l \le 13$; total number of reflections 8794, 4142 independent reflections, 3688 reflections with $I \ge 2\sigma(I)$, $R_{\text{int}} = 0.0229$, $T_{\min}/T_{\max} = 0.6371/0.7461$, $S = 0.820$, $R_1 = 0.0382$, $wR_2 = 0.0888$ (for all data), $R_1 = 0.0333$, $wR_2 = 0.0849$ (for $I \ge 2\sigma(I)$), $\Delta\rho_{\min}/\Delta\rho_{\max} = -0.574/1.144$ e Å^{-3}.

The coordinates of atoms and other structural parameters of complex **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2043698); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Elemental analysis was carried out on a EURO Vector 3000A automated analyzer. IR spectra were recorded on a Spectrum Two FT-IR spectrometer equipped with a single reflection attenuated total reflectance (ATR) accessory (Perkin Elmer). The excitation and luminescence spectra of the polycrystalline samples were detected and studied on a FluoroMax-4 instrument (Horiba).

RESULTS AND DISCUSSION

Complex $\{[Zn_2(H_2L)(H_2EDP)_2(H_2O)_2]\cdot 2H_2O\}_n$ (**I**) is formed by the reaction of 1,2-bis(2-pyridyl-1,2,4-triazol-3-yl)ethane (H_2L), 1-hydroxyethane-1,1-diphosphonic acid (H_4EDP), and $ZnSO_4\cdot 7H_2O$ (in a ratio of 1 : 2 : 2) in water followed by neutralization with triethylamine. The structure of complex **I** was determined by XRD. The complex crystallizes as a zigzag 1D polymer and contains the binuclear fragments formed by the zinc cations and diphosphonate dianions (Fig. 1), which perform the chelate-bridging function coordinating the zinc(II) cations by the phosphoryl oxygen atoms. The distances between the zinc(II) cations in the dimer are 5.262 Å. The dimeric fragments are linked into a polymeric chain by spacered H_2L molecules. The shortest distance between the zinc(II) cations in the adjacent dimers is 8.045 Å. Selected bond lengths involving the zinc and phosphorus atoms are listed in Table 1.

Each bis(phosphonate) H_2EDP^{2-} anion forms the six-membered chelate cycle Zn(1)O(1)P(1)C(9)-P(2)O(4) with the zinc(II) cation. The geometry of the chelate is close to the boat conformation. The bonds of the zinc(II) cation with the deprotonated oxygen atoms of the bis(phosphonate) anions (O(1) and O(4)) are nonequivalent (2.022(2) and 2.170(2) Å) and comparable with the length of the bond of the zinc(II) cations with the oxygen atom of the coordinated water molecule: Zn–O(7) 2.109(2) Å. The binding of the O(6) oxygen atom of the acid with the adjacent zinc(II) cation provides the joining of the monomeric fragments into the dimer, and the bridging Zn–O(6) bond length is 2.067(2) Å. The formed eight-membered cycle Zn(1)O(6)P(2)O(4)Zn(I)-

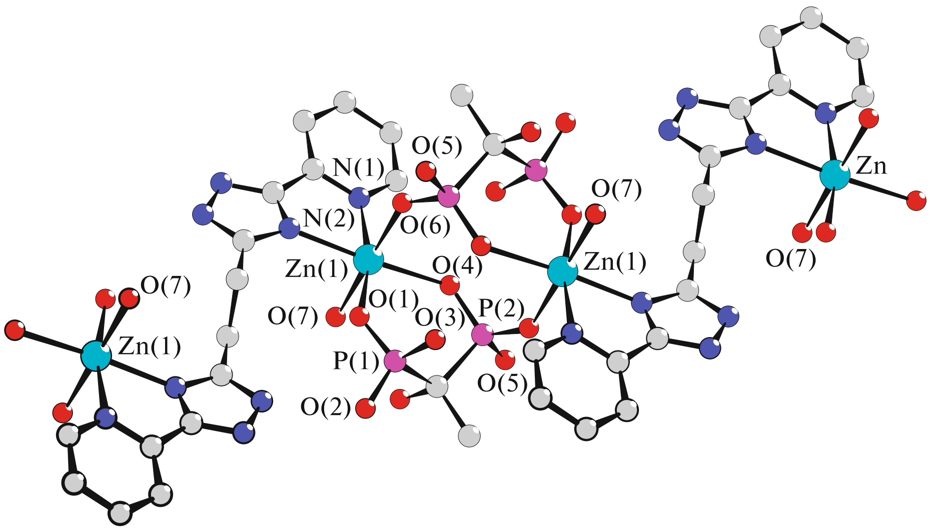


Fig. 1. Fragment of the crystal structure of complex **I**. Hydrogen atoms are omitted for clarity.

O(6)P(2)O(4) is bent, and its geometry is close to the boat conformation.

The spacered 2-pyridyl-1,2,4-triazole molecules bind the dimeric fragments into the polymeric chain due to the coordination of the N(1) and N(2) nitrogen atoms of the pyridyl and triazole fragments. The bonds of the Zn atoms with the nitrogen atoms of the triazole fragment (Zn(1)–N(2)) are 2.142(2) Å and shorter than the bonds with the nitrogen atoms of the pyridyl substituent: Zn(1)–N(1) 2.265(2) Å. The bond lengths and bond angles within the organic ligands are close to usual values [14]. The binding of the polymeric layers by the extraligands was observed earlier for the zinc(II) bis(phosphonate) complexes with 4,4'-bipyridyls and their spacered analogs [8, 9].

The hydrate water molecules occupy the cavities of the crystalline lattice and participate in the formation of the system of hydrogen bonds involving the heterocyclic nitrogen atoms and the oxygen atoms of the phosphoryl groups (Table 2). This hydrogen binding of the chains of the coordination polymer in the crystal results in the formation of the three-dimensional supramolecular structure.

The IR absorption spectrum of complex **I** exhibits broad intense bands with absorption maxima at 1237–550 cm^{-1} caused by stretching vibrations of the phosphorus–oxygen and phosphorus–carbon bonds along with the bands of spacered 2-pyridyl-1,2,4-triazole (1610–1288 cm^{-1}) [15]. A broad envelope is observed in the range about 3220 cm^{-1}, which includes stretching vibration bands of water molecules, whose bending vibrations are observed as a weak band with a maximum at 1620 cm^{-1}.

The luminescence of the zinc(II) bis(phosphonate) complexes with the pyridyl-containing ligands caused by π–π* transitions inside the nitrogen-containing heterocycle (λ_{em} = 420–450 nm, λ_{exc} = 330–365 nm) was described [8, 9]. The luminescence spectrum of complex **I** contains a similar broad emission band with a maximum at 408 nm (λ_{exc} = 350 nm) and a quantum yield of 4%. The coordinates on the chromaticity diagram are $x = 0.6$, $y = 0.16$ (Fig. 2). The luminescence band of free H_4EDP molecules is observed in the range about 360 nm (λ_{exc} = 320 nm) [10], which makes it possible to exclude the electronic transitions inside the diphosphonate ligand as the luminescence source of complex **I**.

Thus, it was found that the use of 1-hydroxyethane-1,1-diphosphonic acid dianion favoring

Table 1. Selected bond lengths involving the zinc and phosphorus atoms in the molecular structure of complex **I**

Bond	*d*, Å	Bond	*d*, Å
Zn(1)–O(1)	2.022(2)	P(1)–O(1)	1.502(2)
Zn(1)–O(4)	2.170(2)	P(1)–O(2)	1.511(2)
Zn(1)–O(6)	2.067(2)	P(1)–O(3)	1.571(2)
Zn(1)–O(7)	2.109(2)	P(2)–O(4)	1.516(2)
Zn(1)–N(1)	2.265(2)	P(2)–O(5)	1.580(2)
Zn(1)–N(2)	2.142(2)	P(2)–O(6)	1.503(2)

Table 2. Geometric parameters of hydrogen bonds in the structure of complex **I**

Contact D–H···A	Distance, Å			Angle DHA, deg	Symmetry of atom A
	D–H	H···A	D···A		
N(4)–H(4*B*)···O(2)	0.88	1.82	2.683(3)	168	$-x+1, -y, -z$
O(3)–H(3*B*)···O(4)	0.84	1.79	2.629(2)	174	$-x+1, -y+1, -z+1$
O(5)–H(5*A*)···O(2*w*)	0.84	1.95	2.774(3)	168	x, y, z
O(5)–H(5*A*)···O(1*wA*)	0.83	1.88	2.701(8)	168	x, y, z
O(7)–H(7*A*)···O(8)	0.89	1.87	2.711(3)	155	x, y, z
O(7)–H(7*B*)···N(3)	0.89	2.13	2.844(3)	137	$-x, -y, -z$
O(8)–H(8*C*)···O(2)	0.84	1.91	2.687(2)	152	$-x+1, -y+1, -z$
O(2*w*)-H(2*wB*)···O(2)	0.87	2.08	2.878(4)	153	$-x+1, -y, -z$

the formation of the polynuclear structures in the presence of ditopic 1,2-bis(2-pyridyl-1,2,4-triazol-3-yl)ethane in the reaction with zinc(II) ions afforded the binuclear fragments linked to each other by spacered triazole to form the polymeric chain. Remarkably, the spacered triazole ligand in the considered complex exhibited the bridging function, while in the earlier described complexes H_2L demonstrated only the terminal coordination mode [4]. Evidently, the additional complex formation with etidronic acid extends the coordination abilities of spacered triazoles, which can be promising for the target synthesis of polynuclear clusters.

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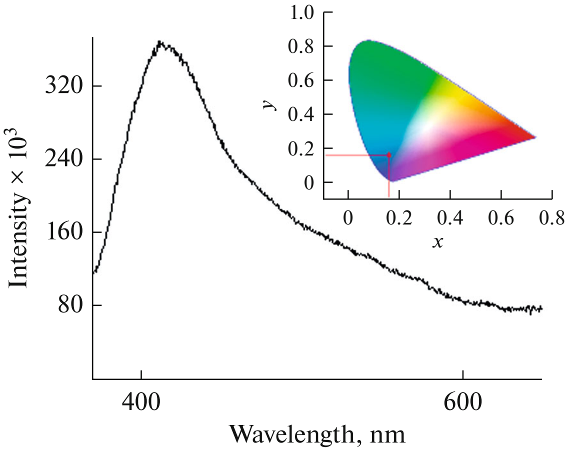

Fig. 2. Luminescence spectrum of complex **I** and (inset) chromaticity diagram.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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