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Oxovanadium(IV) Complex with 1-Hydroxyethane-1,1-Diphosphonic Acid and Bis(2-Pyridyl-1,2,4-Triazol-3-yl)methane

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Abstract—The synthesis of oxovanadium(IV) complex with 1-hydroxyethane-1,1-diphosphonic acid (H_4EDP) anion and bis(2-pyridyl-1,2,4-triazol-3-yl)methane (H_2L) is described. The reaction of $VOSO_4$ with H_4EDP and H_2L followed by neutralization of the reaction mixture with Et_3N gives the trinuclear complex $[(VO)_4(H_2L)_2(EDP)_2(H_2O)_2]\cdot 4H_2O$ (**I**), which was studied by IR and ESR spectroscopy. The molecular and crystal structures of complex **I** were determined by X-ray diffraction (CIF file CCDC no. 2022772).

Keywords: oxovanadium(IV), spacered 1,2,4-triazole, X-ray diffraction analysis

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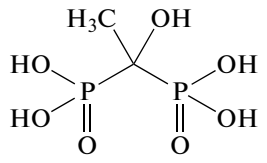
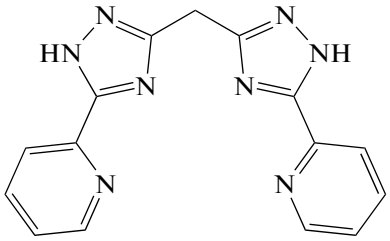
INTRODUCTION

Transition metal and lanthanide phosphonates and bis-phosphonates are of interest for researchers as bases for new hybrid materials [1–10]. As compared with traditional inorganic materials, metal bis-phosphonates can be obtained under milder conditions and possess higher thermal and chemical stability [1]. Ligands of this type are capable of different modes of binding to metal cations [2]; in combination with the diversity of coordination polyhedra, this leads to the formation of nontrivial molecular and supramolecular structures. The introduction of additional organic extra ligands such as aromatic or aliphatic amines brings about additional possibilities for the control over structure and properties of the resulting hybrid materials [7].

This study addresses the reaction of oxovanadium(IV) sulfate with 1-hydroxyethane-1,1-diphosphonic acid (H_4EDP) and bis(2-pyridyl-1,2,4-triazol-3-yl)methane (H_2L). Previously, it was shown that spacered triazole H_2L is a convenient matrix for the synthesis of complexes of different nuclearity and topology [11]. The coordination compounds and hybrid materials based on vanadium bis-phosphonates have been reported previously [8–10].



H_4EDP



H_2L

EXPERIMENTAL

Bis(2-pyridyl-1,2,4-triazol-3-yl)methane used in the study was prepared by a previously reported procedure [11], 1-hydroxyethane-1,1-diphosphonic acid (etidronic acid monohydrate) was a commercial chemical (Merck), and $VOSO_4\cdot 7H_2O$ was a reagent grade commercial chemical.

Synthesis of $[(VO)_4(H_2L)_2(EDP)_2(H_2O)_2]\cdot 4H_2O$ (I). A solution of H_4EDP (0.224 g, 1 mmol) was added to a suspension containing H_2L (0.152 g, 0.5 mmol) in

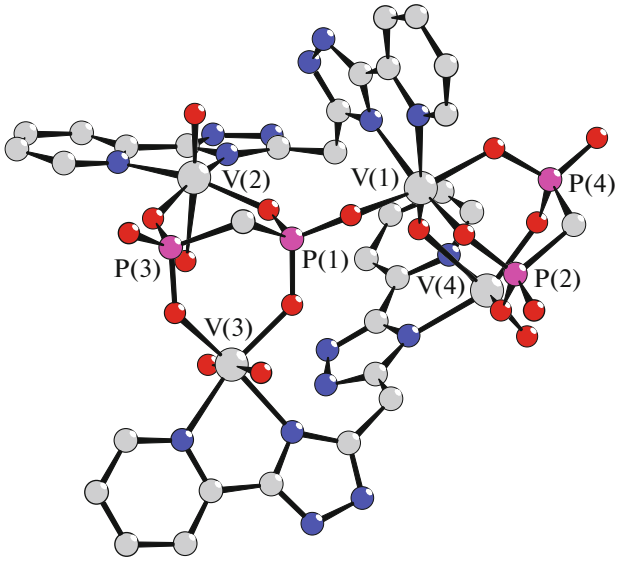


Fig. 1. General view of the complex molecule **I**. The hydrogen atoms and methyl and hydroxyl groups of the diphosphonate ligands are omitted for clarity.

water (10 mL), and the mixture was stirred at a temperature of 70–80°C until the reactants completely dissolved. A solution of $VOSO_4$ (0.137 g, 0.5 mmol) in water (5 mL) was added to the resulting solution, the mixture was cooled with stirring, and triethylamine (5 mmol) was slowly added until pH was 6–7. The precipitate was kept for 3 days under mother liquor at room temperature. The blue crystals that formed were collected on a filter and dried in air. The yield was 40% (based on oxovanadium(IV) sulfate).

For $C_{34}H_{42}N_{16}O_{24}P_4V_4$,			
Anal. calcd., %	C, 29.45	H, 3.05	N, 16.16
Found, %	C, 29.46	H, 3.15	N, 15.55

According to elemental analysis data, the composition of the complex was $[(VO)_4(H_2L)_2(EDP)_2(H_2O)_2]\cdot 4H_2O$ (**I**). A single crystal suitable for X-ray diffraction was taken from the precipitate of complex **I**.

The IR absorption spectra of complex **I**, apart from the absorption bands of spacered 2-pyridyl-1,2,4-triazole (1615, 1575, 1512, 1474, 1405, and 1294 cm^{-1}), exhibited broad bands with absorption maxima at 1094, 965, 794, 754, and 710 cm^{-1} due to stretching vibrations of vanadium and phosphorus bonds with oxygen atoms [8, 12]. The broad enveloping curve in the 3500–3000 cm^{-1} range covered the stretching bands of water, the bending mode of which was observed as a weak band with a maximum at 1645 cm^{-1}.

X-ray diffraction study was carried out on an Agilent Technologies SuperNova Dual diffractometer equipped with a CCD array detector at 100 K using monochromatic CuK_α radiation (λ = 1.54184 Å) by a standard procedure [13]. The unit cell parameters were refined by the least-squares method. The structure was solved by direct methods and refined using the SHELX program [14] included in the OLEX2 package by the full-matrix anisotropic approximation for all non-hydrogen atoms.

The crystallographic parameters and structure refinement details for **I**: $C_{34}H_{44}N_{16}O_{24}P_4V_4$, M = 1388.49, crystal size: 0.2 × 0.1 × 0.1 mm, blue crystals, T = 100(2) K, triclinic system, space group $\bar{P}$, a = 13.2081(3), b = 13.4290(2), c = 17.5381(3) Å, α = 91.4236(15)°, β = 101.3159(16)°, γ = 101.1159(17)°, V = 2986.71(10) Å^3, Z = 2, ρ = 1.544 g/cm^3, μ = 6.875 mm^{-1}, θ = 6.722°–153.04°, $-15 \le h \le 16$, $-16 \le k \le 16$, $-21 \le l \le 21$; totally 59468 reflections, 12358 unique reflections, 10648 reflections with $I \ge 2\sigma(I)$, R_{int} = 0.0748, T_{min}/T_{max} = 0.357/1.000, F = 1.058, R_1 = 0.0544, wR_2 = 0.1537 (for all data), R_1 = 0.0637, wR_2 = 0.1623 (for $I \ge 2\sigma(I)$), $\Delta\rho_{min}/\Delta\rho_{max}$ = –0.47/0.82 e Å^{-3}.

The atom coordinates and other parameters of structure **I** are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2022772); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif.

The elemental analysis was carried out on a EURO Vector 3000A automated analyzer. IR spectra were measured on a Spectrum Two Fourier Transform IR spectrometer equipped with a single attenuated total internal reflection atachment (Perkin Elmer). The ESR spectra were recorded on an SpinscanX instrument (ADANI, Belarus).

RESULTS AND DISCUSSION

The complex has an intricate molecular structure composed of four crystallographically independent vanadium atoms, two H_2L molecules, and two bridging diphosphonate anions (Fig. 1).

The distances between the vanadium atoms are as follows: V(1)...V(2), 5.39 Å; V(1)...V(3), 6.01 Å; V(1)...V(4), 3.59 Å; V(2)...V(3), 4.76 Å; V(2)...V(4), 7.33 Å; V(2)...V(4), 6.76 Å. The lengths of the vanadium and phosphorus bonds with the donor ligand atoms are summarized in Table 1 and are typical of known oxovanadium(IV) complexes with phosphonate ligands [9, 10].

The spacered triazole molecules bind vanadium atoms in pairs, being coordinated to the nitrogen atoms of the pyridyl moiety and the triazole heterocycle. The bond lengths between the vanadium atoms and the triazole nitrogen atoms are similar and vary in the range of 2.100–2.109 Å; most of the bond lengths between vanadium atoms and pyridyl nitrogen atoms are in the 2.146–2.160 Å range, but the bond between the N(17) pyridyl nitrogen atom and the V(1) atom is

elongated to 2.327(3) Å. The triazole ring planes are rotated relative to each other by 60° and 68° (Fig. 2a).

The diphosphonate anions connect in pairs the V(1) and V(4) atoms and V(2) and V(3) atoms and function as bridging ligands; one diphosphonate anion binds V(1), V(2), and V(3) atoms, thus performing a μ_3-bridging function (Fig. 2b).

The phosphorus–oxygen bond lengths lie in a narrow range of 1.541–1.544 Å, while the P=O bond lengths are in the 1.497–1.507 Å range. The V(2) and V(3) atoms have a distorted octahedral environment, which is formed by two nitrogen atoms, two oxygen atoms of the bridging diphosphonate anion, an oxygen atom of the water molecule, and the oxo group.

The V=O bond length is 1.599–1.603 Å, the lengths of the bonds between vanadium and coordinated water molecule are 2.222(2) and 2.260(3) Å for V(2) and V(3), respectively. The V(1) and V(4) atoms are connected by the bridging oxygen atom of the V(1) oxo group; the bond lengths are 1.613(2) Å for V(1)–O(19) and 2.309(2) Å for V(4)–(19), and the V(1)O(19)V(4) bond angle is 131.5°. The chelate rings formed by the diphosphonate ligand and a vanadium atom are bent and have a boat conformation for V(2) and a chair conformation for V(1), V(3), and V(4).

In the crystal structure of **I**, one hydrogen atom is transferred from the triazole ring to the diphosphonate anion, and two complex molecules are connected into a centrosymmetric dimer via a disordered hydrogen bond, in which hydrogen atoms are located in two positions with occupancies of 1/2, the O(28)–H(28) and O(28)'–H(28) distances are 1.14 and 1.32 Å, the O(28)...O(28)' distances are 2.43 Å, and the O(28)H(28)O(28)' angle is 160°. The other hydrogen atoms are uniformly distributed between the four triazole rings. A partial ligand deprotonation and hydrogen atom delocalization between the triazole rings has been observed previously in complexes of spacered pyridyl-1,2,4-triazoles [11, 15]. The composition of complex **I** is actually described as $[(VO)_4\text{-}(H_2L)(HL)\text{-}(EDP)(HEDP)(H_2O)_2]_2\cdot 8H_2O$. The dimer formation via hydrogen bonding of phosphoryl groups has been described in a study of crystal structures of some diphosphonic acids and metal diphosphonates [2].

The uncoordinated water molecules occupy the crystal lattice voids and are linked by strong hydrogen bonds to one another. The crystal structure of the complex has an intricate system of hydrogen bonds involving water molecules, heterocyclic nitrogen atoms, and diphosphonate oxygen atoms (Table 2). An interesting feature of the crystal structure is the proximity of the oxygen atoms connected to V(2) and V(3); the O(21)...O(41) distance is 2.811 Å.

The ESR spectrum of the polycrystalline complex (Fig. 3) exhibits a single broadened line with *g*-factor

Table 1. Selected bond lengths involving vanadium and phosphorus in structure **I**

Bond	*d*, Å	Bond	*d*, Å
V(1)–N(2)	2.108(3)	V(2)–N(36)	2.146(3)
V(1)–N(17)	2.327(3)	V(2)–N(47)	2.101(3)
V(1)–O(3)	2.004(2)	V(2)–O(13)	1.957(2)
V(1)–O(6)	1.989(2)	V(2)–O(24)	1.599(2)
V(1)–O(11)	1.958(2)	V(2)–O(41)	2.222(3)
V(1)–O(19)	1.614(2)	V(2)–O(7)	1.987(2)
V(3)–N(18)	2.109(3)	V(4)–N(26)	2.100(3)
V(3)–N(25)	2.160(3)	V(4)–N(63)	2.151(4)
V(3)–O(1)	1.971(2)	V(4)–O(8)	1.984(2)
V(3)–O(4)	2.260(2)	V(4)–O(14)	1.591(3)
V(3)–O(10)	1.978(2)	V(4)–O(16)	1.957(3)
V(3)–O(21)	1.603(2)	V(4)–O(19)	2.309(2)
P(5)–O(1)	1.527(2)	P(6)–O(5)	1.506(2)
P(5)–O(6)	1.517(2)	P(6)–O(8)	1.531(2)
P(5)–O(13)	1.522(2)	P(6)–O(11)	1.544(2)
P(7)–O(7)	1.518(2)	P(8)–O(3)	1.543(2)
P(7)–O(10)	1.521(2)	P(8)–O(15)	1.496(3)
P(7)–O(28)	1.535(2)	P(8)–O(16)	1.541(3)

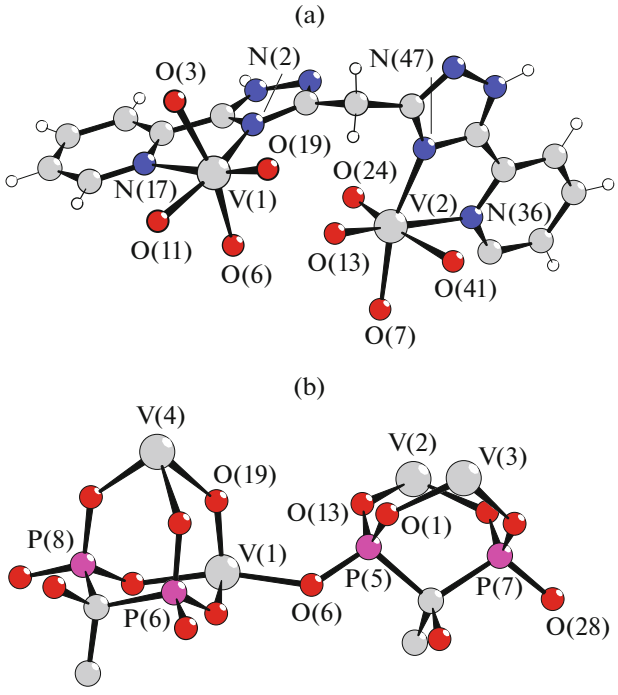


Fig. 2. Binding mode of (a) spacered 2-pyridyl-1,2,4-triazole and (b) diphosphonate anions in the structure of **I** (the methyl hydrogen atoms are omitted for clarity).

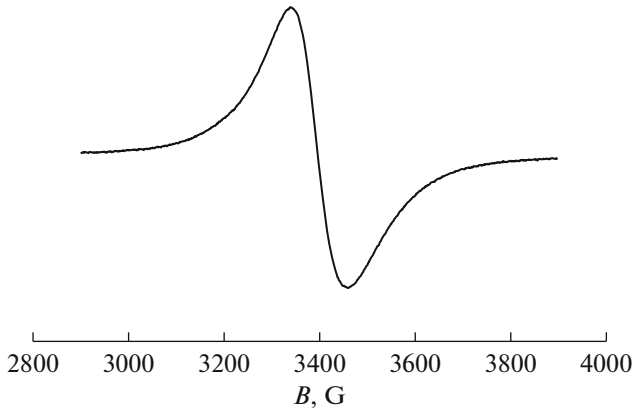


Fig. 3. ESR spectrum of the polycrystalline sample of complex **I** at room temperature.

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

D–H···A contact	Distance, Å			DHA angle, deg	Coordinates of A atoms
	D–H	H···A	D···A		
O(4)–H(4A)···O(48)	0.86	1.86	2.643(4)	152	$-1+x, y, z$
O(4)–H(4B)···N(25)	0.85	2.32	2.881(4)	124	x, y, z
O(9)–H(9)···O(4)	0.82	2.01	2.824(3)	172	x, y, z
N(20)–H(20)···O(29)	0.86	1.82	2.667(4)	169	$-x, -y, 1-z$
O(22)–H(22A)···O(6)	0.85	2.39	2.900(3)	119	$-x, -y, 1-z$
O(22)–H(22A)···O(11)	0.85	1.98	2.806(3)	164	$1+x, y, z$
O(22)–H(22B)···O(9)	0.85	2.18	3.023(4)	175	$1+x, y, z$
O(28)–H(28)···O(28)'	1.14	1.32	2.432(3)	160	x, y, z
O(29)–H(29B)···O(3)	0.91	2.06	2.967(3)	179	$1+x, y, z$
N(40)–H(40)···O(5)	0.86	1.71	2.567(4)	171	$-1-x, 1-y, -z$
O(48)–H(48A)···N(31)	0.85	2.02	2.860(4)	172	$-x, 1-y, -z$
O(61)–H(61B)···O(5)	0.85	2.00	2.819(4)	164	$1+x, y, z$
O(48)–H(48B)···O(22)	0.84	1.95	2.767(4)	165	x, y, z
O(61)–H(61A)···O(22)	0.84	2.06	2.809(5)	147	x, y, z

of 1.96, typical of oxovanadium(IV) complexes ($S = 1/2$) [16].

The results of this study indicate that joint coordination of spacered 1,2,4-triazole and diphosphonate anion in the bridging position gives rise to a non-trivial molecular and crystal structure, which can be used to design new hybrid materials.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Maeda, K., *Microporous and Mesoporous Mater.,* 2004, vol. 73, p. 47.
2. Matczak-Jon, E. and Videnova-Adrabinska, V., *Coord. Chem. Rev.,* 2005, vol. 249, p. 2458.
3. Fu, R., Hu, S., and Wu, X., *Cryst. Growth Des.,* 2014, vol. 14, p. 6197.
4. Mao, J.-G., *Coord. Chem. Rev.,* 2007, vol. 251, p. 1493.
5. Bao, S.-S. and Zheng, L.-M., *Coord. Chem. Rev.,* 2016, vol. 319, p. 63.
6. Ma Yu-Juan, Hu Ji-Xiang, Han Song-De, et al., *J. Am. Chem. Soc*., 2020, vol. 142, p. 2682.
7. Pan Jie, Ma Yu-Juan, Han Song-De, et al., *Cryst. Growth Des.*, 2019, vol. 19, p. 2919.
8. Rocha, J., Paz, F.A.A., Shi Fa-Nian, et al., *Eur. J. Inorg. Chem*., 2009, vol. 2009, p. 4931.
9. Aleksandrov, G.G., Sergienko, V.S., and Afonin, E.G., *Cryst. Rep.*, 2001, vol. 46, no. 1, p. 46.
10. Ban, R., Liang, Y., Ma, P., et al., *Inorg. Chem. Commun.,* 2016, vol. 71, p. 65.
11. Gusev, A.N., Shul'gin, V.F., Ryush, I.O., et al., *Eur. J. Inorg. Chem.,* 2017, p. 704.
12. Pan Ling-ling, Yuan Yi-xuan, Xiao, Y., et al., *J. Mol. Struct.,* 2008, vol. 892, p. 272.
13. *SMART (control) and SAINT (integration) Sofware. Version 5.0*, Madison: Bruker AXS Inc., 1997.
14. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
15. Gusev, A.N., Shul'gin, V.F., and Kiskin, M.A., *J. Struct. Chem.*, 2019, vol. 60, no. 3, p. 335.
16. Kuska, H.A. and Rogers, M.T., *Electron Spin Resonnance of First Row Transition Metal Complex Ions*, New York: Interscience, 1968.

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