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Dioxomolybdenum(VI) Complex with (1-Oxyethylidene)diphosphonic Acid in an Aqueous Medium: Synthesis and Crystal Structure

B. I. Petrov[a, *], V. V. Semenov[a], T. S. Pochekutova[a], N. M. Lazarev[a],
E. V. Baranov[a], and N. M. Khamaletdinova[a]

[a] *Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,*
Nizhny Novgorod, 603600 Russia
**e-mail: bip@iomc.ras.ru*

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Abstract—A new complex of hexaammonium bis(1-oxyethylidenediphosphonate)dioxomolybdenum tetrahydrate $(NH_4)_6[MoO_2(L)_2] \cdot 4H_2O$ (**I**) (H_4L is $H_2O_3P{-}C(OH)(CH_3){-}PO_3H_2$) is synthesized. Its molecular structure consisting of the complex anion $[MoO_2L_2]^{6-}$, six out-of-sphere ammonium cations NH_4^+, and four water molecules is determined by X-ray diffraction analysis (CIF file CCDC no. 813517). The solubility of complex **I** is studied. The changes in the IR absorption spectra upon complex formation are discussed.

Keywords: synthesis, dioxomolybdenum(VI) complex, X-ray diffraction analysis

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INTRODUCTION

Molybdenum is one of the main microelements in the feeding of people, animals, and plants. Molybdenum enters the composition of a series of enzymes involved in processes of nitrogen assimilation in plants. Legumes (soybean, haricot, pea, and vetch) and some vegetable cultures (lettuce, spinach, and tomato) experience the most demand in molybdenum fertilizers. The provision of plants with this element cannot always be determined by the content of total molybdenum in the soil, because the presence of the digestible form, being 5–20% of the overall content, is primarily important for plants. Ammonium molybdate and molybdenized superphosphate are used as molybdenum fertilizers [1]. Depending on the ligand, coordination compounds of metals can manifest substantially different agronomic efficiencies. A high efficiency of their use for the presowing treatment of seeds and foliar nutrition compared to the corresponding salt forms was shown [2] for the manganese, zinc, and copper compounds with (1-hydroxyethylidene)diphosphonic acid as examples. A low phytotoxicity relative to sulfate was established for the cobalt compounds [3].

The possibility to apply a compound in plant cultivation is determined, in particular, by its solubility in an aqueous medium. Unlike the compounds of manganese(II) [2], cobalt(II) [3], and iron(III) [4], the molybdenum(VI) compounds with (1-oxyethylidene)diphosphonic acid (OEDP) are fairly well soluble in water and precipitate as fine and medium-size crystals from saturated solutions. This property enables one to obtain pure forms of the compounds and to test their agrochemical properties. The copper and molybdenum compounds are most studied among all synthesized metal derivatives with OEDP [5, 6]. They form diverse crystalline forms depending on the pH of the medium and the presence of other cations (Na^+, K^+, or NH_4^+) in an aqueous solution.

The data on the new dioxomolybdenum(VI) complex obtained by the reaction of ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ with OEDP in an alkaline medium at the ratio $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$: OEDP = 1 : 2 are reported.

EXPERIMENTAL

Synthesis. Complex **I** was obtained in an aqueous solution using a described procedure [7]. A weighed sample of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (6.18 g, 0.005 mol) was dissolved in H_2O (50 mL), and 10 mL of aqueous ammonia (25%) were added to attain the necessary pH 8–9. (1-Oxyethylidene)diphosphonic acid (14.42 g, 0.001 mol) was dissolved in water (50 mL), and the solution was added by portions with stirring to the prepared solution of the molybdenum complex. The mixture became lemon-colored and was slightly warmed. The pH changed to 7–8. After 2 days of the spontaneous evaporation of water at room temperature, a white finely crystalline precipitate was formed, separated, and dried in air to a constant weight. The yield was 88%.

For $C_4H_{40}N_6O_{20}P_4Mo$

Anal. calcd., %	C, 6.74	H, 5.56	P, 17.39	Mo, 13.47
Found, %	C, 6.91	H, 5.61	P, 16.41	Mo, 12.71

Elemental analyses to C, H, and N were carried out on a EuroVector EA3000 elemental C,H,N-analyzer, and analyses to P and Mo were conducted on the pyrolytic decomposition setup.

IR absorption spectra were recorded on an FSM 1201 FT-IR spectrometer in a range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and a scan number of 32. The samples were prepared as a suspension in Nujol between potassium bromide windows.

X-ray diffraction analysis of compound I was carried out on a Bruker D8 Quest diffractometer (ω scan mode, MoK_α radiation, $\lambda = 0.71073$ Å). Experimental sets of intensities were integrated using the SAINT program [8]. The structure was solved by a direct method and refined by least squares for F^2_{hkl} in the anisotropic approximation for all non-hydrogen atoms. The hydrogen atoms of the methyl groups were placed in the geometrically calculated positions and refined isotropically by the riding model. Other hydrogen atoms were revealed from the difference Fourier synthesis and refined isotropically. The calculations were performed using the SHELXTL program package [9–11]. The SADABS utility was used to apply an absorption correction [12]. The main crystallographic data and the X-ray diffraction experimental and refinement parameters for the structure of compound **I** are presented in Table 1.

The structure was deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 813517; https://www.ccdc.cam.ac.uk/structures).

RESULTS AND DISCUSSION

A complicated broad band caused by the superposition of the absorption bands of stretching vibrations of the NH bonds and hydroxyl groups of the coordinated water molecule is observed in the IR spectrum of complex **I** in a range of 3600–2500 cm^{-1}. The low-intensity bands with frequencies of 1690 and 1610 cm^{-1} correspond to bending vibrations of the N–H bonds.

In the spectrum of the initial OEDP acid, the ν(P=O) stretching vibrations of the P=O bond are characterized by intense absorption bands with frequencies of 1173 and 1109 cm^{-1}. One band with a maximum at 1126 cm^{-1} is observed in this range in the spectrum of complex **I**. The following set of bands corresponds to the ν(POH) stretching vibrations of the P–O bond: 1026, 960, 911, and 877 cm^{-1}. As compared to the spectrum of OEDP, in the IR spectrum of complex **I** these bands change the shape and are shifted to the low-frequency range, which confirms the coordination of the metal atom with the ligand [13].

The IR spectrum of compound **I** exhibits no bands at 1054 and 935 cm^{-1} ($\nu_{as}(P(OH)_2)$ and $\nu_{as}(P(OH)_2)$, respectively) that are observed in the spectrum of OEDP, and the band at 1084 cm^{-1} is manifested and can be assigned to asymmetric vibrations of the O–P–O fragment of the PO_3H^- group [14]. The absorption band with a frequency of 814 cm^{-1} is caused by the ν(P–C) stretching vibrations. This band is present in both the spectrum of compound **I** and the spectrum of OEDP. In the spectrum of compound **I**, the absorption bands with frequencies of 583 and 560 cm^{-1} correspond to the $\delta(PO_3)$ bending vibrations [15].

The single crystals of complex **I** suitable for X-ray diffraction analysis were isolated by recrystallization from an aqueous solution with drying of the obtained crystalline precipitate in air followed by vacuum pumping out to a constant weight.

According to the X-ray diffraction data, compound **I** consists of the complex anion $[MoO_2L_2]^{6-}$ and six out-of-sphere ammonium cations NH_4^+. Four solvate water molecules are located in the external sphere. The structure of the complex anion (Fig. 1) is identical to the structures of the earlier studied dioxomolybdenum complexes with OEDP [7, 16–18]. The molybdenum atom is coordinated by two oxygen oxo atoms and two chelate oxyethylidenediphosphonic ligands in the *cis* positions. The coordination polyhedron of Mo(1) is a distorted octahedron. The Mo(1)–O(1,2) distances are nearly (1.7158(15), 1.7047(14) Å). The Mo(1)–O(3,4) and Mo(1)–O(10,11) bond lengths differ appreciably being 2.1594(14), 1.9745(14) and 2.1771(14), 1.9824(14) Å, respectively. The P–O distances also differ. The P–O bond lengths of the chelate oxygen atoms O(3,4,10,11) vary in a narrow range of 1.5545(14)–1.5672(14) Å. Similar P–O distances to the terminal oxygen atoms O(5,6,8,9,12,13,15,16) are somewhat shorter and close to each other (1.5021(15)–1.5283(14) Å). It is most likely that these distances are equalized due to the redistribution of the negative charge over the P=O and $P-O^-$ bonds (Table 2).

Numerous intra- and intermolecular hydrogen bonds are observed in the crystal of compound **I** (Fig. 2). The complex anions form layers along the *b*0*a* plane, and the ammonium cations and water molecules are arranged between the layers (Fig. 2b).

It is known that the degree of deprotonation of OEDP is related to the pH of the solution [5]. In our case, the

Table 1. Crystallographic data and the experimental and refinement parameters for compound **I**

Parameter	Value
Empirical formula	$C_4H_{40}N_6O_{20}P_4Mo$
FW	712.24
Crystal system	Monoclinic
Space group	$P2_1$
Temperature, K	100(2)
a, Å	9.1965(2)
b, Å	15.2728(4)
c, Å	9.2328(2)
β, deg	97.972(1)
V, Å^3	1284.27(5)
Z	2
ρ_{calcd}, g/cm^3	1.842
μ, mm^{-1}	0.853
F(000)	736
Crystal size, mm	0.40 × 0.30 × 0.20
Range of measurements over θ, deg	2.60–30.00
Index ranges	$-12 \le h \le 12$ $-21 \le k \le 21$ $-12 \le l \le 12$
Total number of reflections	17828
Independent reflections (R_{int})	7415 (0.0153)
Absorption correction (max/min)	SADABS (0.8291/0.7110)
Number of refined parameters	453
GOOF (F^2)	1.037
R_1/wR_2 ($I > 2\sigma(I)$)	0.0176/0.0464
R_1/wR_2 (all reflections)	0.0177/0.0465
Absolute structure parameter	0.005(5)
$\Delta_{max}/\Delta_{min}$, e/Å^3	0.406/–1.324

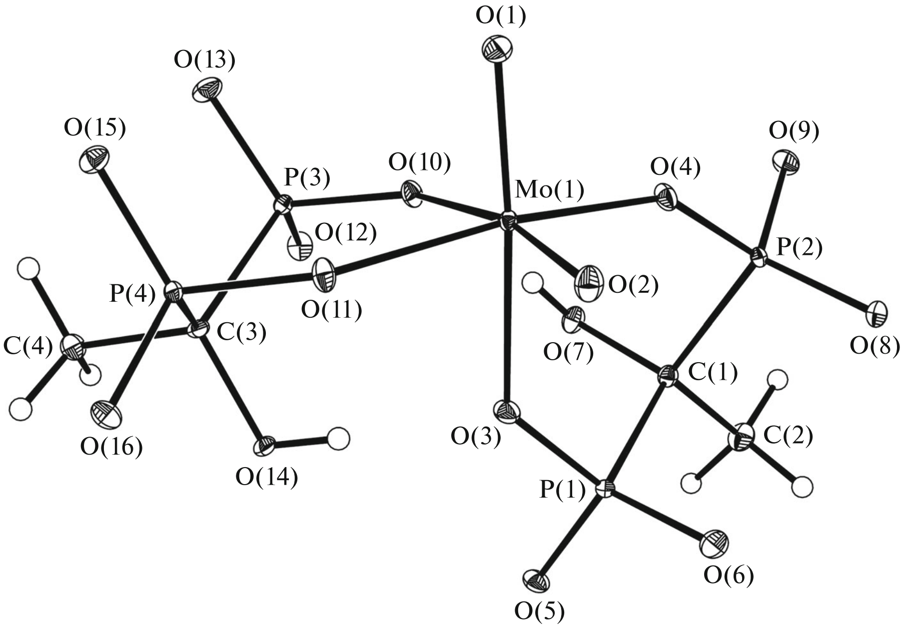

Fig. 1. Structure of the complex anion MoO_2L_2 with 50% probability ellipsoids.

Table 2. Selected bond lengths (Å) and angles (deg) in compound **I**

Bond	*d*, Å	Bond	*d*, Å
Mo(1)–O(1)	1.7158(15)	P(2)–O(8)	1.5094(15)
Mo(1)–O(2)	1.7047(14)	P(2)–O(9)	1.5131(15)
Mo(1)–O(3)	2.1594(14)	P(3)–O(10)	1.5545(14)
Mo(1)–O(4)	1.9745(14)	P(3)–O(12)	1.5255(14)
Mo(1)–O(10)	2.1771(14)	P(3)–O(13)	1.5066(15)
Mo(1)–O(11)	1.9824(14)	P(4)–O(11)	1.5672(14)
P(1)–O(3)	1.5558(15)	P(4)–O(15)	1.5108(15)
P(1)–O(5)	1.5283(14)	P(4)–O(16)	1.5086(15)
P(1)–O(6)	1.5021(15)	C(1)–O(7)	1.446(2)
P(2)–O(4)	1.5665(14)	C(3)–O(14)	1.450(2)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(1)Mo(1)O(10)	90.07(6)	O(1)Mo(1)O(3)	166.56(7)
O(10)Mo(1)O(3)	76.74(5)	O(2)Mo(1)O(10)	167.43(6)
O(3)Mo(1)O(2)	91.04(6)	O(4)Mo(1)O(11)	164.99(5)
O(2)Mo(1)O(1)	102.25(7)		

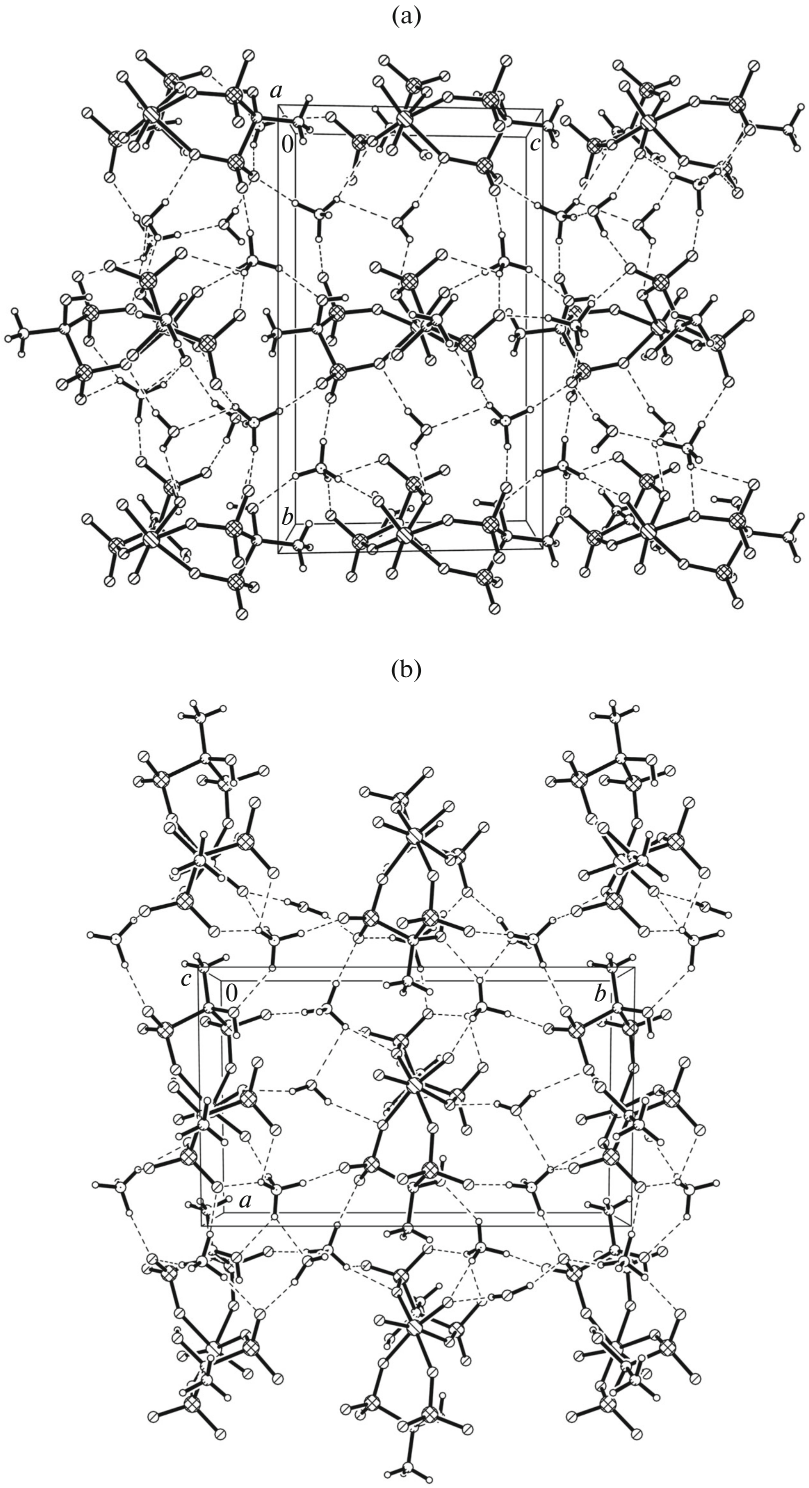

Fig. 2. Fragment of the crystal packing in the projection on the planes (a) *c*0*b* and (b) *b*0*a*.

organic ligand is completely deprotonated at pH 8–9. The reaction performed affords the complex anion containing the completely deprotonated chelate fragment, which is confirmed by the X-ray diffraction data (Fig. 1).

A fairly high solubility of compound **I** correlates with the layered character of the crystal packing and the presence of water molecules in the interlayer space (Figs. 2a, 2b). The solubility of oxo complex **I** is

0.28 mol/L, and the determination error is not higher than ±2%.

Thus, the synthesized molybdenum complex (I) is highly soluble, which enables one to use it as microfertilizers.

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