

## Molybdenum(VI) Complexes with N-Substituted Hydroxylamines

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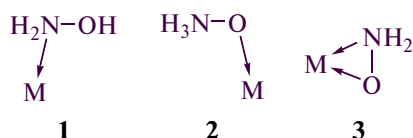
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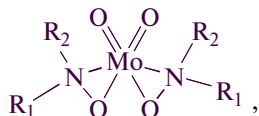
**Abstract**—New molybdenum(VI) complexes with N-monoalkylsubstituted hydroxylamines have been synthesized and studied. The structure of  $[\text{MoO}_2(\text{C}_2\text{H}_5\text{NHO})_2]$  and  $[\text{MoO}_2(i\text{-C}_3\text{H}_7\text{NHO})_2]$ , whose distinguishing feature is the bidentate chelate coordination of the ligand to molybdenum with the formation of the three-membered NMoO chelate ring, has been determined by X-ray diffraction.

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The presence of two active donating sites of different characters in a hydroxylamine molecule allows us to classify it with polydentate ligands, which are capable of adding to many complex-forming metals to realize different coordination modes, namely,



For example, hydroxylamine is coordinated to the central ion via the nitrogen atom (**1**) in platinum, cobalt, and nickel complexes and via the oxygen atom (**2**) in zinc, cadmium, calcium, barium, and manganese complexes [1]. The bidentate coordination of hydroxylamine and its derivatives (**3**) is more rarely encountered, mainly in complexes of Group V and VI metal oxocations. This coordination mode, which was first proved for complexes of uranyl [2] and tungsten(VI) [3], was further also discovered in complexes of molybdenum [4, 5], vanadium [6], and other metals using X-ray diffraction. However, the formation mechanisms of uranyl and molybdenum complexes with hydroxylamine are different. Exchange reactions are more typical for uranyl, whereas redox processes with the resulting formation of mixed molybdenum(IV) and vanadium(III) nitrosohydroxylamate complexes predominate for molybdenum(VI) and vanadium(V). Similar reactions between molybdenum(VI) compounds and N-substituted hydroxylamines, which are weaker reducers than hydroxylamine, proceed without any change in the oxidation state of the central atom to give mononuclear molybdenum dihydroxylamines  $[\text{MoO}_2(\text{R}_1\text{R}_2\text{NO})_2]$  [7–9]



which are mainly represented by complexes with N-dialkylsubstituted hydroxylamine derivatives. Such molybdenum(VI) complexes have certain bioactivity [10] and can also be used in olefin oxidation processes [9].

In this work, we have studied molybdenum(VI) complexes with N-ethyl- and N-isopropylhydroxylamines.

### EXPERIMENTAL

Nitromethane, nitroethane (both from Acros Organics), and 2-nitropropane (from Aldrich) were used in this study. The other reagents were of chemically pure or pure for analysis grade.

**N-methylhydroxylamine hydrochloride** was synthesized by the following method [1]. To a solution of nitromethane (50 g) and  $\text{NH}_4\text{Cl}$  (30 g) in water (400 mL), zinc dust (185 g) was added during 2–3 h under continuous stirring, maintaining the temperature within a range of 0–15°C. The mixture was then filtered out, and the filtrate was neutralized by hydrochloric acid and evaporated on a water bath until the residue solidified under cooling. The residue was dissolved in ethanol, thereupon the solution was separated out of the ammonium chloride precipitate, and ether was added. The settled precipitate was filtered out and twice recrystallized from ethanol with the addition of ether (1 : 1).

**N-ethyl- and N-isopropylhydroxylamine hydrochlorides** were synthesized by the same method from nitroethane and 2-nitropropane (the reduction temperature was 10–25 and 15–35°C, respectively). After neutralization with hydrochloric acid, the filtrate was evaporated on a water bath until  $\text{NH}_4\text{Cl}$  began to crystallize. The residue was diluted with ethanol and ether (4 : 1) and evaporated again after ammonium chloride was separated out. This operation was repeated several times. Strong N-ethyl- and N-isopropylhydroxylam-

**Table 1.** Crystallographic data and details of X-ray diffraction experiments for the structure of complexes I–III

Parameter	I	II	III
Bulk formula	C <sub>4</sub> H <sub>12</sub> MoN <sub>2</sub> O <sub>4</sub>	C <sub>6</sub> H <sub>16</sub> MoN <sub>2</sub> O <sub>4</sub>	C <sub>2</sub> H <sub>8</sub> MoN <sub>2</sub> O <sub>4</sub>
FW	248.10	276.15	220.04
Crystal size, mm	0.40 × 0.30 × 0.20	0.25 × 0.20 × 0.20	0.25 × 0.12 × 0.03
Symmetry system	Monoclinic	Orthorhombic	Monoclinic
Space group, <i>Z</i>	<i>C2/c</i> , 4	<i>Pbca</i> , 8	<i>P2<sub>1</sub>/c</i> , 4
Unit cell parameters			
<i>a</i> , Å	12.113(4)	10.2278(6)	8.991(1)
<i>b</i> , Å	9.191(3)	10.1560(6)	11.706(2)
<i>c</i> , Å	9.995(3)	22.5943(14)	6.360(2)
β, deg	124.932(4)	90	92.47(3)
<i>V</i> , Å <sup>3</sup>	912.3(5)	2346.9(2)	668.8(3)
ρ <sub>calcd</sub> , g/cm <sup>3</sup>	1.806	1.563	2.185
μ, mm <sup>-1</sup>	1.413	1.107	15.759
<i>F</i> (000)	496	1120	432
θ range, deg	3.02–28.00	2.69–28.00	4.92–69.93
Index ranges	–15 ≤ <i>h</i> ≤ 15 –12 ≤ <i>k</i> ≤ 12 –13 ≤ <i>l</i> ≤ 13	–13 ≤ <i>h</i> ≤ 13 –13 ≤ <i>k</i> ≤ 13 –29 ≤ <i>l</i> ≤ 29	–10 ≤ <i>h</i> ≤ 10 –14 ≤ <i>k</i> ≤ 1 –7 ≤ <i>l</i> ≤ 7
Reflections in total	4254	17441	2645
Independent reflections with <i>I</i> > 2σ( <i>I</i> )	1088 ( <i>R</i> <sub>int</sub> = 0.0369)	2829 ( <i>R</i> <sub>int</sub> = 0.0357)	1266 ( <i>R</i> <sub>int</sub> = 0.0595)
Number of variables	52	130	85
<i>R</i> <sub>1</sub> for <i>I</i> > 2σ( <i>I</i> )	0.0730	0.0207	0.0359
w <i>R</i> <sub>2</sub> (all data)	0.2639	0.0515	0.0959
GOOF	1.961	1.036	1.088
Δρ <sub>min</sub> /Δρ <sub>max</sub> , e/Å <sup>3</sup>	–3.128/3.715	–0.359/0.296	–1.060/0.855

monium solutions with admixture NH<sub>4</sub>Cl were used for synthesis.

**Synthesis of molybdenum(VI) dioxo-bis-N-ethylhydroxylamine (I).** To a suspension of MoO<sub>3</sub> (6 g) in water (40 mL), KOH (4.7 g) was added. To the resulting transparent solution, a strong N-ethylhydroxylamine hydrochloride solution (9 g) was added drop by drop under stirring (molar ratio Mo : OH<sup>-</sup> : C<sub>2</sub>H<sub>5</sub>NHOH · HCl = 1 : 2 : ~2). To the solution with a white precipitate, diluted ethanol (1 : 1, 60 mL) was added, thereupon it was heated under stirring almost to boiling, filtered out, and allowed to stay in air for crystallization. The resulting colorless crystals were filtered out, washed with a small amount of water and ethanol, and dried on a filter in an air flow. The yield was 4.86 g (47%).

For [MoO<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>NHO)<sub>2</sub>] anal. calcd. (%): Mo, 38.68; N, 11.29; C, 19.36.

Found (%): Mo, 38.89, 38.85; N, 11.06, 10.92; C, 19.83, 19.77.

**Synthesis of molybdenum(VI) dioxo-bis-N-isopropylhydroxylamine (II).** To a suspension of MoO<sub>3</sub> (6 g) in water (40 mL), KOH (4.7 g) was added. To the resulting transparent solution, a strong N-isopropylhydroxylamine hydrochloride solution (10 g) was added drop by drop under stirring (molar ratio Mo : OH<sup>-</sup> : *i*-C<sub>3</sub>H<sub>7</sub>NHOH · HCl = 1 : 2 : ~2). To the solution with a white precipitate, dilute ethanol (1 : 1, 100 mL) was added, thereupon it was heated under stirring almost to boiling, filtered out, and allowed to stay in air for crystallization. The resulting colorless crystals were filtered out, washed with water and a small amount of ethanol, and dried on a filter in an air flow. The yield was 7.12 g (62%).

For [MoO<sub>2</sub>(*i*-C<sub>3</sub>H<sub>7</sub>NHO)<sub>2</sub>] anal. calcd. (%): Mo, 34.75; N, 10.14; C, 26.09.

Found (%): Mo, 34.72, 34.69; N, 10.56, 10.32; C, 26.43, 26.38.

NMR <sup>1</sup>H(*d*<sub>6</sub>-DMSO) (ppm): CH<sub>3</sub>, 1.08, 1.25; CH, 2.85; H, 8.7.

**Table 2.** Selected bond lengths (Å) and bond angles (deg) in the coordination polyhedron of a molybdenum atom in complexes I–III and other molybdenum(VI) complexes with N-alkyl-substituted hydroxylamines

Complex	Mo=O		O=Mo=O	Mo–O		Mo–N		N–O	
[MoO <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> NHO) <sub>2</sub> ] (I)	1.728(7)		118.4(5)	1.967(7)		2.118(9)		1.426(11)	
[MoO <sub>2</sub> ( <i>i</i> -C <sub>3</sub> H <sub>7</sub> NHO) <sub>2</sub> ] (II)	1.723(1)	1.725(1)	118.84(7)	1.951(1)	1.952(13)	2.119(2)	2.120(2)	1.424(2)	1.426(2)
[MoO <sub>2</sub> (CH <sub>3</sub> NHO) <sub>2</sub> ] (III)	1.701(3)	1.739(3)	114.5(2)	1.960(3)	1.972(3)	2.128(4)	2.132(3)	1.418(5)	1.424(4)
[MoO <sub>2</sub> (CH <sub>3</sub> NHO) <sub>2</sub> ] [3]	1.709	1.728	113.7	1.961	1.964	2.119	2.130	1.428	1.431
[MoO <sub>2</sub> {(CH <sub>3</sub> ) <sub>2</sub> NO} <sub>2</sub> ] [9]	1.699	1.714	116.0	1.957	1.957	2.127	2.146	1.416	1.425
[MoO <sub>2</sub> {(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NO} <sub>2</sub> ] [8]	1.713	1.714	116.6	1.970	1.971	2.141	2.145	1.427	1.428

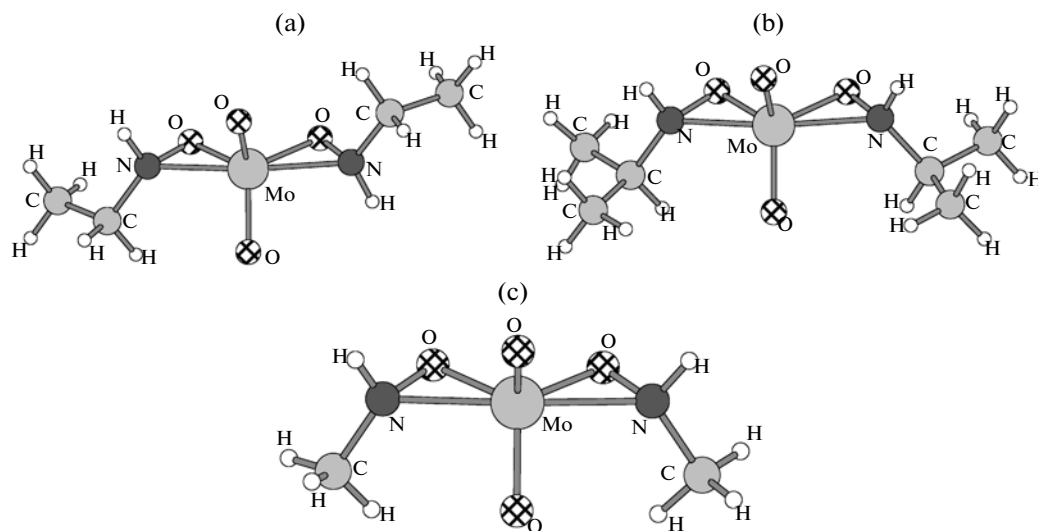
<sup>13</sup>C{H} (ppm): CH<sub>3</sub>, 18.44, 18.50; CH, 52.73, 52.65.

**Synthesis of molybdenum(VI) dioxo-bis-N-methyl-hydroxylamine (III)** was performed by a known method [4] to compare the structure and properties of the separated complexes. Its single crystals were subjected to repeated X-ray diffraction analysis.

**X-ray diffraction analysis.** The collection of experimental data was performed on a Bruker SMART APEX II automatic diffractometer (MoK<sub>α</sub> radiation, λ = 0.71073 Å, graphite monochromator) at 160 K for complexes I and II and on a Enfras-Nonius CAD4 four-circle diffractometer (CuK<sub>α</sub> radiation, λ = 1.54178 Å, graphite monochromator) at room temperature for complex III. Absorption was taken into account via equivalent reflection intensities [11, 12]. The structures of complexes I–III were solved by direct methods and refined by full-matrix anisotropic least-squares on *F*<sup>2</sup> for all non-hydrogen atoms

(SHELXTL-Plus, [12]). All hydrogen atoms in the structures of complexes I and III were placed in calculated positions and refined as “riding.” The H1 and H2 amine atoms in the structure of complex II were found from the Fourier difference synthesis and refined isotropically, and the other hydrogen atoms were placed in calculated positions and refined as “riding.” Crystallographic data, characteristics of X-ray diffraction experiments, and refinement details for the structures of complexes I–III are compiled in Table 1, and selected bond lengths and bond angles are listed in Table 2. The structures of complexes I–III were deposited with the Cambridge Structure Database (nos. 947259, 947260, and 947261, respectively).

**IR spectra** of the complexes were recorded on an INFRALUM FT-02 IR Fourier-transform spectrometer (Lumex, Russia) in the region of 4000–400 cm<sup>-1</sup> with a resolution of 1 cm<sup>-1</sup>. Samples were prepared as Nujol mull (Aldrich).

**Fig. 1.** Structure of complexes (a) I, (b) II, and (c) III.

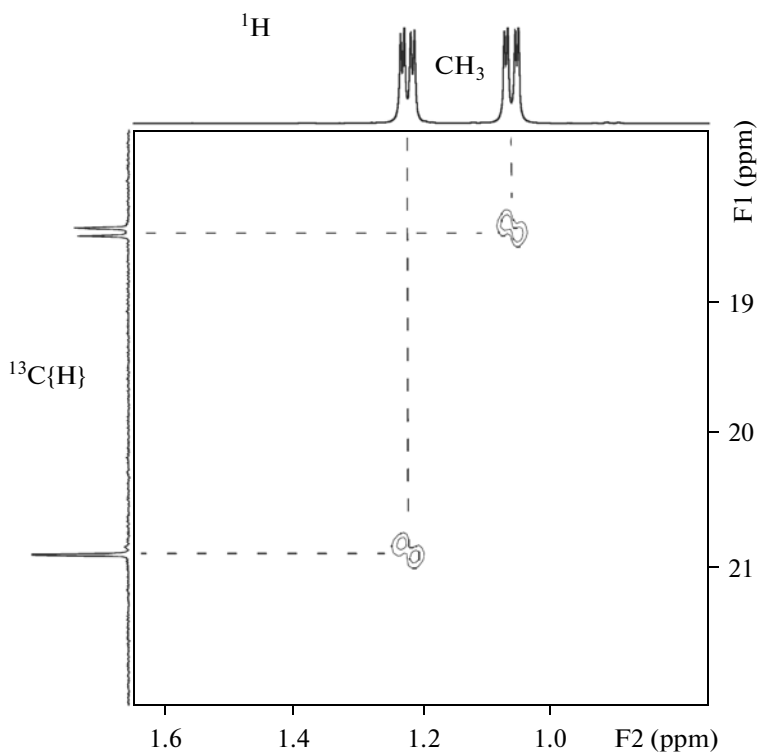


Fig. 2. Fragment of the 2D  $^{13}\text{C}$ ,  $^1\text{H}$ -HMQC NMR spectrum of a complex **II** solution in  $d_6$ -DMSO at 298 K.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV 400 spectrometer with working frequencies of 400.13 and 100.61 MHz, respectively, and a deuterated internal standard at room temperature (298 K). The chemical shifts of  $^1\text{H}$  and  $^{13}\text{C}$  signals are given with respect to tetramethylsilane (TMS).  $d_6$ -DMSO dried over 4 Å molecular sieves was used as a solvent.

To assign the signals of the  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  groups of the organic ligand in  $^{13}\text{C}$  NMR spectra, the spectra were recorded by the DEPT method using 45-, 90-, and 135-degree decoupling pulses [13].

The assignment of signals in the proton and carbon NMR spectra was performed by two-dimensional  $^{13}\text{C}$ ,  $^1\text{H}$ -HMQC (heteronuclear multiple quantum correlation) experiment.

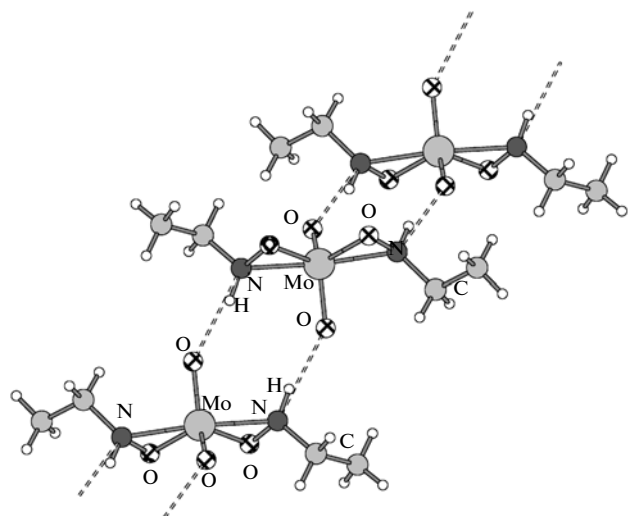
## RESULTS AND DISCUSSION

Complexes **I–III** have discrete structures. The surrounding of a molybdenum atom incorporates two oxygen oxoatoms ( $\text{Mo–O}$ , 1.701–1.739 Å) and the two oxygen atoms and two nitrogen atoms of two bidentate hydroxylamine ligands ( $\text{Mo–O}$ , 1.951–1.972 Å;  $\text{Mo–N}$ , 2.118–2.135 Å). Hence, the coordination number of the molybdenum atoms in complexes **I–III** is 6, and the coordination polyhedron may be considered as a distorted tetrahedron (considering the hydroxylamine ligand as occupying a single coordination position).

It is noteworthy that the alkyl substituents in complex **I** occupy the *trans*-position with respect to the

Table 3. Parameters of hydrogen bonds in the structure of complexes **I–III**

D–H...A	Symmetrycodes	$d(\text{D–H})$ , Å	$d(\text{H...A})$ , Å	$d(\text{D...A})$ , Å	$\angle(\text{DHA})$ , deg
<b>I</b>					
N(1)–H(1)...O(2A)	$-x + 1/2, -y + 1/2, -z$	0.93	1.91	2.821(11)	165
<b>II</b>					
N(1)–H(1)...O(4A)	$-x + 1/2, y - 1/2, z$	0.84(2)	2.01(2)	2.846(2)	169.8(18)
N(2)–H(2)...O(3A)	$1 - x, 1 - y, -z$	0.81(2)	2.04(2)	2.848(2)	175(2)
<b>III</b>					
N(1)–H(1)...O(3A)	$-x, 1 - y, 2 - z$	0.91	2.01	2.873(4)	157
N(2)–H(2)...O(3A)	$x, -y + 3/2, z - 1/2$	0.91	2.26	3.028(5)	142

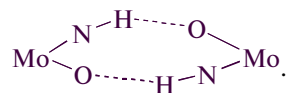


**Fig. 3.** Fragment of the structure of  $[\text{MoO}_2(\text{C}_2\text{H}_5\text{NHO})_2]$  (**I**). Here and in Figs. 4 and 5, hydrogen bonds are denoted by dashed lines.

bisecting plane of the  $\text{O}=\text{Mo}=\text{O}$  angle (Fig. 1a), while these substituents in complexes **II** and **III** occupy the *cis*-position (Figs. 1b, 1c).

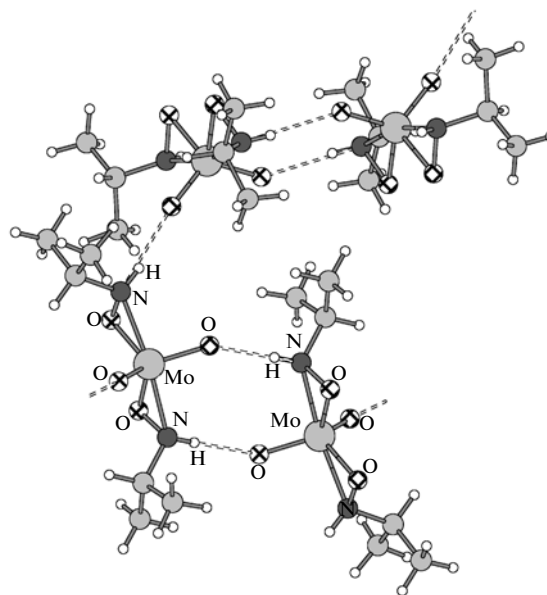
Noteworthy, two equally stable isomers with *cis*- and *trans*-substituents are likely to exist in a solution for all separated complexes, thus producing, for example, additional signals in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of complex **II** (Fig. 2). However, some NMR signals in a solution may be observed to split due to the diastereotopic surrounding of the substituents, so without additional experiments, it is currently impossible to make any unambiguous conclusion about the two variants that explain the splitting of signals in NMR spectra.

Molecules in the structures of the complexes are linked by intermolecular hydrogen bonds between oxygen oxoatoms and N-monoalkylhydroxylamine nitrogen atoms to form the moiety (Table 3)



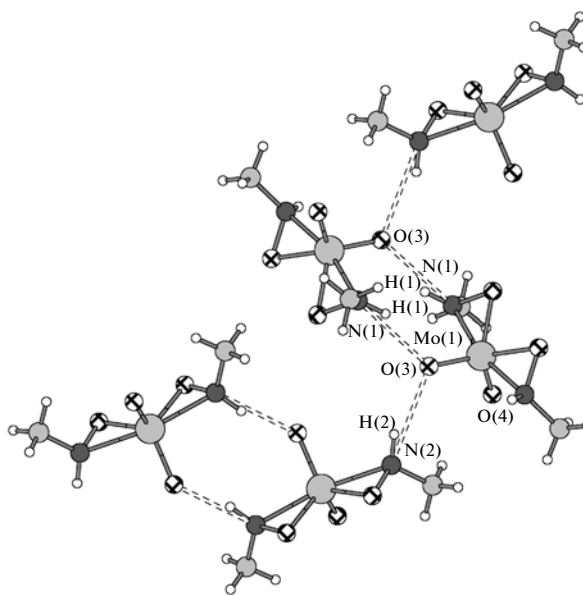
This produces chains running along the *ac* diagonal in complex **I** (Fig. 3) and hydrogen-bonded double layers lying perpendicular to the *c* crystallographic axis in complex **II** (Fig. 4), and a crystal of complex **III** contains hydrogen-bonded double layers which are perpendicular to the *a* crystallographic axis (Fig. 5).

The selected bond length and bond angles in the coordination polyhedra of complexes **I–III** are close (Table 2). The only exception is the distorted geometric parameters of the molybdenyl moiety in complex **III** ( $\text{Mo}-\text{O}(1)$ , 1.701 Å;  $\text{Mo}-\text{O}(2)$ , 1.739 Å;  $\text{OMoO}$ ,  $114.5^\circ$ ), which is manifested as the splitting of the  $\nu(\text{Mo}=\text{O})$  band in the IR spectra of



**Fig. 4.** Fragment of the structure of  $[\text{MoO}_2(i\text{-C}_3\text{H}_7\text{NHO})_2]$  (**II**).

$[\text{MoO}_2(\text{CH}_3\text{NHO})_2]$  (Table 4). This is likely due to the nonparticipation of the O(1) oxoatom in this structure in hydrogen bonds, whereas the O(2) oxoatom forms a bifurcated hydrogen bond with the nitrogen atoms of neighboring molecules (Table 3).



**Fig. 5.** Fragment of the structure of  $[\text{MoO}_2(\text{CH}_3\text{NHO})_2]$  (**III**).

**Table 4.** Assignment of some absorption bands ( $\nu$ ,  $\text{cm}^{-1}$ ) in the IR spectra of molybdenum(VI) complexes with N-substituted hydroxylamines

Complex	$\nu(\text{Mo}=\text{O})$	$\nu(\text{NO})$	$\nu(\text{NH})$
$[\text{MoO}_2(\text{C}_2\text{H}_5\text{NHO})_2]$ (I)	917	891	3095
$[\text{MoO}_2(i\text{-C}_3\text{H}_7\text{NHO})_2]$ (II)	915	892	3087
$[\text{MoO}_2(\text{CH}_3\text{NHO})_2]$ (III)	930 891	860 870	3202 3108
$[\text{MoO}_2\{(\text{CH}_3)_2\text{NO}\}_2]$ [9]	~919 b	910	–
$[\text{MoO}_2\{(\text{C}_2\text{H}_5)_2\text{NO}\}_2]$ [8]	914	898	–

#### ACKNOWLEDGMENTS

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#### REFERENCES

1. Yu. Ya. Kharitonov and M. A. Sarukhanov, *The Chemistry of Metal Complexes with Hydroxylamine* (Nauka, Moscow, 1977) [in Russian].
2. A. Van Tets and H. W. W. Adrian, *J. Inorg. Nucl. Chem.* **39**, 1607 (1977).
3. Yu. A. Buslaev, S. G. Sakharov, Yu. V. Kokunov, and I. I. Moiseev, *Dokl. Akad. Nauk SSSR* **240**, 338 (1978).
4. K. Wiegardt, W. Holzbach, J. Weiss, et al., *Angew. Chem.* **91**, 582 (1979).
5. K. Wiegardt and W. Holzbach, *Angew. Chem.* **91**, 583 (1979).
6. K. Wiegardt, U. Quilitzsch, B. Nuber, and J. Weiss, *Angew. Chem.* **90**, 381 (1978).
7. K. Wiegardt, E. Hofer, W. Holzbach, et al., *Inorg. Chem.* **19**, 2927 (1980).
8. K. Wiegardt, M. Hahn, J. Weiss, and W. Swiridoff, *Z. Anorg. Allg. Chem.* **492**, 164 (1982).
9. L. Saussine, H. Mimoun, A. Mitschler, and J. Fisher, *Nouv. J. Chim.* **4**, 235 (1980).
10. D. C. Crans, J. J. Smee, E. G. Gaidamauskiene, et al., *J. Inorg. Biochem.* **98**, 1837 (2004).
11. G. M. Sheldrick, SADABS. Program for Scaling and Correction of Area Detector Data (Univ. of Göttingen, Göttingen, 1997).
12. G. M. Sheldrick, *Acta Crystallogr., Sect. A* **64** (1), 112 (2008).
13. D. T. Pegg and M. R. Bendall, *J. Magn. Res.* **60**, 347 (1984).

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