

COORDINATION
COMPOUNDS

Molecular and Intracomplex Dioxomolybdenum(VI) Compounds
with *o*-Hydroxyazomethines, Derivatives of Salicylaldehydes
and 2-Furfurylamine: Crystal Structures of 3-Methoxysalicylidene-
2-furfurylamine (HL²) and the Binuclear Complex
[$\{\text{MoO}_2(\text{L}^2)(\text{MeOH})\}_2(\mu\text{-O})$]

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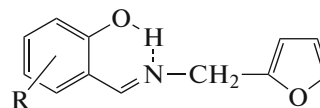
Abstract—The crystal structures of methoxysalicylidene-2-furfurylamine (HL²) and the related binuclear complex [$\{\text{MoO}_2(\text{L}^2)(\text{MeOH})\}_2(\mu\text{-O})$] (**I**) have been determined by single-crystal X-ray diffraction. In complex **I**, which lies on a crystallographic twofold axis passing through the bridging oxo ligand O(4), the Mo atom has a distorted octahedral coordination (facial isomer) with two terminal oxygen atoms (O(3), O(6)) and the bridging oxo ligand, the O(7) and N(1) atoms of the bidentate chelating ligand (L²)[−], and the O(5) atom of the monodentate methoxy ligand. In the HL² molecule, the intramolecular hydrogen bond O–H⋯N closes the six-membered H-ring HOC₃N.

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Previously, we have reported the synthesis of molecular complexes (MCs) and intracomplex compounds (ICCs) of dioxomolybdenum(VI) with *o*-hydroxyazomethines (Schiff bases) (HL), derivatives of substituted salicylaldehydes and aliphatic, aromatic, and heterocyclic amines [1–3], monoethanolamine [4, 5], and tris(hydroxymethyl)aminomethane [6–8]. It has been shown [9] that MCs are synthesized by the reaction of metal halides, in particular, MoO₂Cl₂, with HL in low-polarity or nonpolar solvents at room temperature. Several approaches are suitable for synthesis of ICCs: the ligand exchange between metal acetylacetonates and acetates, template synthesis [9], or the reaction of metal aldehydates, for example, MoO₂Sal₂ (HSal is salicylaldehyde), with a corresponding amine in alcohol under reflux, which is, in essence, a variant of template synthesis [2]. The structures of some dioxomolybdenum(VI) complexes have been determined on the basis of IR, UV, and ¹H NMR spectroscopy data and by single-crystal X-ray diffraction [10].

In continuation of our ongoing research on synthesis, structures, and properties of dioxomolybdenum(VI) compounds, we have studied the possibility of synthesis of dioxomolybdenum(VI) MCs and ICCs

with *o*-hydroxyazomethines containing an alkylheterocycle in the amine moiety:



HLⁿ: R = H (*n* = 1); 3-OCH₃ (*n* = 2); 5-Br (*n* = 3).

The structures of the Mo(VI) ICC with the (L²)[−] anion as a ligand (**I**) and free azomethine (HL²) have been determined by X-ray crystallography. In the course of structure determination, it has been found that complex **I** has a dimeric rather than monomeric structure.

EXPERIMENTAL

Dioxomolybdenum dichloride was synthesized by chlorination of a molybdenum dioxide powder at 200°C; molybdenyl acetylacetonate was prepared by boiling a MoO₃ powder in acetylacetone until complete dissolution with subsequent cooling of the solution. The MoO₂(Acac)₂ precipitate was purified by crystallization from acetylacetone.

Synthesis of HLⁿ. A solution of 1.94 g (0.01 mol) of 2-furfurylamine in 20 mL of ethanol was added to a hot solution of 0.01 mol of the corresponding aldehyde in 20 mL of ethanol; the resulting solution was heated under reflux for 30 min, evaporated to one-half, and left for 24 h for crystallization. HL¹ was a viscous liquid; therefore, it was purified by vacuum distillation. The other *o*-hydroxyazomethines were purified by crystallization from ethanol. The purity of the compounds was monitored by TLC. HL²: lemon crystals, mp 70–71°C; HL³: lemon crystals, mp 76–77°C.

Synthesis of MCs. Molecular complexes were synthesized by the reaction of MoO₂Cl₂ with HLⁿ at the ratio metal : ligand = 1 : 2 in dry ethyl acetate at room temperature. A solution of 0.402 g (0.002 mol) of HL¹ was added dropwise to a stirred solution of 0.199 g (0.001 mol) of MoO₂Cl₂ in 10 mL of ethyl acetate. The resulting precipitate was filtered off on a Schott filter funnel equipped with calcium chloride tube, and dried in a dry argon flow and then in a vacuum desiccator over P₂O₅. MCs with other azomethines were synthesized analogously. The yield of the products was ~90% of the theoretical one.

Synthesis of ICCs. ICCs were synthesized by boiling methanol solutions of molybdenyl acetylacetonate and azomethines for 30 min. A portion of 0.326 g (0.001 mol) of MoO₂(Acac)₂ was dissolved in 20 mL of methanol on heating under reflux, and then 20 mL of a methanol solution containing 0.002 mol of HLⁿ was added. The reaction mixture was heated under reflux for 30 min, evaporated to 30 mL, and left for crystallization at 0°C for 24 h. The resulting crystals were filtered off on a filter, washed with cold methanol, and dried in a dry air flow. The yield of the products was 80–90% of the theoretical one.

In the course of the experiment, it was found that the composition of the dioxomolybdenum(VI) ICC with azomethine HL² depended noticeably on synthesis conditions. The reaction of MoO₂(Acac)₂ with HL² on cooling or at room temperature led to the formation of a fine orange powder of the MoO₂(L²)₂ composition. Boiling this reaction mixture in methanol led, within a few minutes, to the formation of a brown solution from which crystals of tentative composition [MoO₂(L²)(CH₃OH)]₂(μ-O) were precipitated on cooling; this composition was supported by X-ray crystallography data.

Molybdenum was quantified by calcining a weighed portion of the complex at 450°C to MoO₃ as a gravimetric form [11]. Chlorine was determined by the Volhard method after preliminary hydrolysis with an alkali solution. Nitrogen was quantified using the Dumas method [12].

Physicochemical and IR spectroscopy data for dioxomolybdenum(VI) MCs (II–IV) and ICCs (V–

VII) with R-salicylidene-2-furfurylamines are summarized in Table 1.

The IR spectra were recorded as Nujol mulls on an IKS-29 spectrophotometer.

X-ray crystallography. Experimental material for crystals of I and HL² was collected on an automated Enraf-Nonius CAD-4 diffractometer. In both cases, the structure was solved by direct methods (SHELXL-97) [13] and refined by least-squares calculation in the full-matrix anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [14]. The hydrogen atoms were introduced into geometrically calculated positions and refined as riding on their bonded atoms. The H(1) atoms in the structures of I and HL² were located from difference Fourier syntheses and refined isotropically. The unit cell parameters and key experimental details are presented in Table 2. Complete crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1481909 (I), 1481910 (HL²); <http://www.ccdc.cam.ac.uk/deposit/>).

RESULTS AND DISCUSSION

It has been experimentally demonstrated that, at any ratio of the reagents, the reaction of MoO₂Cl₂ with salicylidene-2-furfurylamines in low-polarity solvents (ethyl acetate, diethyl ether, tetrahydrofuran) gives MCs II–IV of only one composition, MoO₂Cl₂ · 2HLⁿ (Table 1), which are lemon or yellow amorphous powders readily soluble in alcohols, dimethylformamide, and dimethyl sulfoxide to form conducting solutions.

The ICCs have the composition MoO₂Lⁿ₂ (Table 1). In addition, the reaction with 3-methoxysalicylidene-2-furfurylamine leads to binuclear complex I. The synthesized ICCs are high-melting lemon to brown crystalline powders poorly soluble in cold methanol and moderately soluble in dimethylformamide and dimethyl sulfoxide to give non-conducting solutions.

To determine the type of the complexes and location of coordinate bond, we studied their spectra of compounds II–VII. Changes in the spectra in the range of azomethine bond absorption are of greatest interest. Formation of ICCs leads to a low-frequency shift of the ν(C=N) absorption band by 8–10 cm⁻¹, which indicates that the nitrogen atom of the C=N group is involved in donor–acceptor interaction. In the spectra of MCs, the same range displays a strong band at ~1650 cm⁻¹; by analogy with MCs of MoO₂Cl₂ with other salicylideneimines [1, 3, 10], this band should be assigned to the red-shifted C=O absorption of the quinoid tautomer of *o*-hydroxyazomethines. This is supported by the appearance of the N–H stretching vibration band at 3170–3190 cm⁻¹ in the spectra of MCs.

A strong doublet in the range 900–950 cm⁻¹ is due to symmetric and antisymmetric stretching vibrations of the *cis*-MoO₂ group [3]. A broad and strong absorp-

Table 1. Physicochemical and IR spectroscopy data for dioxomolybdenum(VI) complexes with *R*-salicylidene-2-furfurylamines

Complex	Empirical formula	T_m , °C	Content, % (found/calculated)			IR spectrum, cm^{-1}			
			Mo	N	Cl	ligand	complex	complex	
$\text{MoO}_2\text{Cl}_2 \cdot 2\text{HL}^1$ (II)	$\text{C}_{24}\text{H}_{22}\text{Cl}_2\text{MoN}_2\text{O}_6$	194–196	15.83/15.96	4.75/4.66	11.72/11.79	$\nu(\text{C}=\text{N})$ 1630	$\nu(\text{C}=\text{N})$ 1630	$\nu(\text{C}=\text{O})$ 1645	$\nu(\text{Mo}=\text{O})$ 908, 932
$\text{MoO}_2\text{Cl}_2 \cdot 2\text{HL}^2$ (III)	$\text{C}_{26}\text{H}_{26}\text{Cl}_2\text{MoN}_2\text{O}_8$	183–185	14.47/14.51	4.32/4.24	10.60/10.72	$\nu(\text{C}=\text{N})$ 1632	$\nu(\text{C}=\text{N})$ 1632	$\nu(\text{C}=\text{O})$ 1652	$\nu(\text{Mo}=\text{O})$ 905, 931
$\text{MoO}_2\text{Cl}_2 \cdot 2\text{HL}^3$ (IV)	$\text{C}_{24}\text{H}_{20}\text{Br}_2\text{Cl}_2\text{MoN}_2\text{O}_6$	195–197	12.80/12.64	3.62/3.69	9.27/9.34	$\nu(\text{C}=\text{N})$ 1632	$\nu(\text{C}=\text{N})$ 1632	$\nu(\text{C}=\text{O})$ 1650	$\nu(\text{Mo}=\text{O})$ 907, 930
MoO_2L_2^1 (V)	$\text{C}_{24}\text{H}_{20}\text{MoN}_2\text{O}_6$	227–228	18.30/18.16	5.24/5.30	—	$\nu(\text{C}=\text{N})$ 1630	$\nu(\text{C}=\text{N})$ 1620	—	$\nu(\text{Mo}=\text{O})$ 903, 929
MoO_2L_2^2 (VI)	$\text{C}_{26}\text{H}_{24}\text{MoN}_2\text{O}_8$	180–182	16.42/16.31	4.65/4.76	—	$\nu(\text{C}=\text{N})$ 1632	$\nu(\text{C}=\text{N})$ 1625	—	$\nu(\text{Mo}=\text{O})$ 900, 930
MoO_2L_2^3 (VII)	$\text{C}_{24}\text{H}_{18}\text{Br}_2\text{MoN}_2\text{O}_6$	229–230	13.85/13.98	4.15/4.08	—	$\nu(\text{C}=\text{N})$ 1632	$\nu(\text{C}=\text{N})$ 1624	—	$\nu(\text{Mo}=\text{O})$ 905, 928
$[\text{MoO}_2(\text{L}^2)(\text{CH}_3\text{OH})_2]_2(\text{O})$ (I)	$\text{C}_{28}\text{H}_{32}\text{Mo}_2\text{N}_2\text{O}_{13}$	184–186	24.18/24.09	3.70/3.52	—	$\nu(\text{C}=\text{N})$ 1632	$\nu(\text{C}=\text{N})$ 1626	—	$\nu(\text{Mo}=\text{O})$ 902, 928

Table 2. Crystal data and key experimental details for the structures of **I** and HL²

	I	HL ²
FW	398.12	231.24
Color, shape	Pink, prism	Yellow, block
Crystal size, mm	0.19 × 0.18 × 0.13	0.15 × 0.10 × 0.08
Symmetry system, space group	Orthorhombic, <i>Pbcn</i>	Monoclinic, <i>P2₁/c</i>
Unit cell parameters:		
<i>a</i> , Å	10.468(1)	9.083(1)
<i>b</i> , Å	15.925(1)	12.535(1)
<i>c</i> , Å	18.123(1)	11.301(1)
β, deg	90	113.19(1)
<i>V</i> , Å ³	3021.2(4)	1182.7(2)
<i>Z</i>	4	4
ρ _{calc} , g/cm ³	0.893	1.293
μ _{Mo} , mm ⁻¹	0.453	0.765
<i>F</i> (000)	820	484
<i>T</i> , K	293(2)	
Radiation (λ, Å)	MoK _α (0.71073)	CuK _α (1.54178)
graphite monochromator		
Scan mode	ω	
θ range, deg	2.25–27.97	5.30–69.86
Index ranges	0 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 21, –1 ≤ <i>l</i> ≤ 23	–1 ≤ <i>h</i> ≤ 11, –15 ≤ <i>k</i> ≤ 15, –13 ≤ <i>l</i> ≤ 13
Total number of reflections/unique reflections	3819/3604 [<i>R</i> (int) = 0.1136]	5188/2236 [<i>R</i> (int) = 0.0210]
Completeness for θ = 27.97° (I), 69.86° (HL ²)	99.0%	100.0%
Number of reflections with <i>I</i> ≥ 2σ(<i>I</i>)	1006	1769
Number of refined parameters	209	159
GOOF on <i>F</i> ²	0.871	1.412
<i>R</i> [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0502, <i>wR</i> 2 = 0.1176	<i>R</i> 1 = 0.0486, <i>wR</i> 2 = 0.1654
Extinction coefficient	0000(3)	0.017(3)
Residual electron density (max/min), e/Å ³	0.982/–1.304	0.530/–0.194

tion band at 800–700 cm⁻¹ in the spectrum of **I** corresponds to vibrations of the Mo–O–Mo bridging bond [15]. At low frequencies, new absorption bands appear in the spectra of complexes, arising from Mo–O_{HL} stretching vibrations (580–590 cm⁻¹) (for MCs) or Mo–N_L (530–540 cm⁻¹) and Mo–O_L (480–490 cm⁻¹) stretching vibrations (for ICCs).

Thus, the above data allow us to conclude that the MCs and ICCs of dioxomolybdenum(VI) with salicylidene-2-furfurylamines **II–VII** have a monomeric octahedral structure with two multiply bonded *cis* oxo atoms. The other octahedron vertices in MCs are occupied by two carbonyl oxygen atoms of the quinoid tautomeric form of azomethines *trans* to the terminal O(oxo) in accord to the “self-consistency rule” [16, 17] and two chlorine atoms *trans* to each other. For

ICCs, the octahedron vertices are occupied, in addition to the terminal oxygen atoms, by two donor nitrogen atoms *trans* to the oxo ligands and two oxygen atoms of the deprotonated hydroxyl groups of salicyl-alimines *trans* to each other.

The recrystallization of ICC MoO₂(L²)₂ (**VI**) from methanol led to compound **I**; its composition and structure have been determined by X-ray crystallography.

Complex **I**, [{MoO₂(L²)(MeOH)}₂(μ-O)] (Fig. 1), is a dimer. The molecule lies on a crystallographic twofold axis passing through the bridging O(4) atom. The Mo atom has an octahedral coordination (facial isomer) with two terminal (t) oxo ligands (O(3), O(6)) and the bridging (br) oxo ligand (O(4)), the N(1) and O(7) atoms of the bidentate chelating ligand (L²)⁻, and the O(5) atom of the terminal MeOH ligand. Like

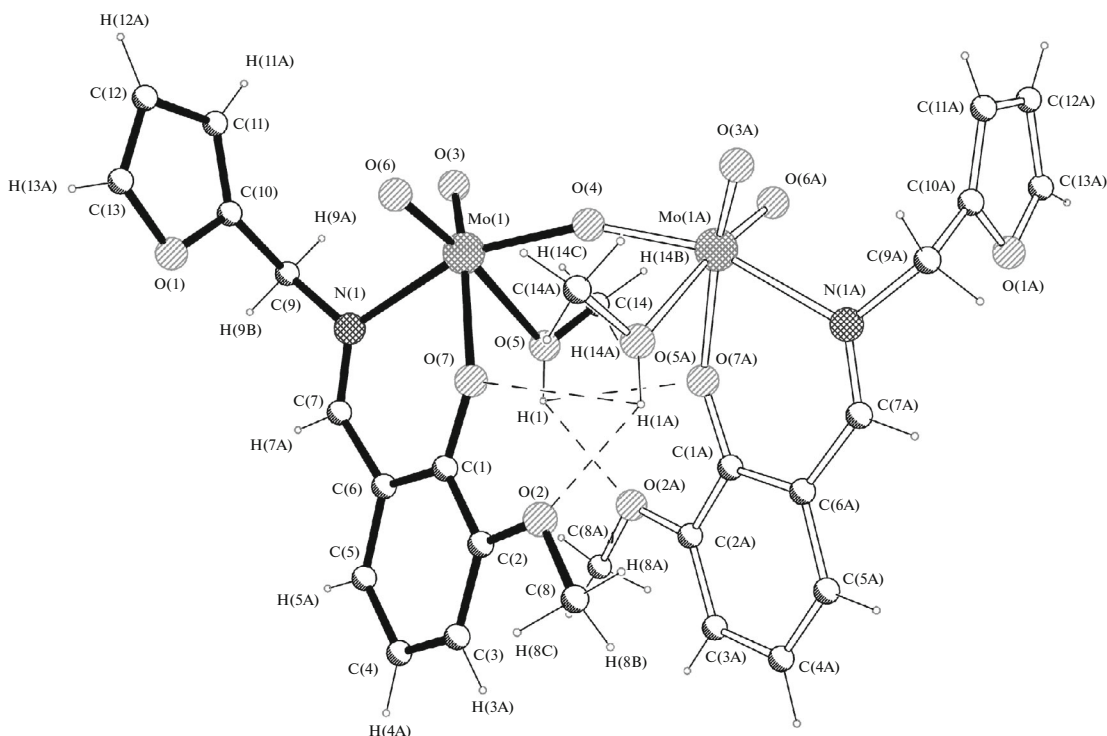


Fig. 1. Structure of dimeric complex I. Hydrogen bonds are shown by dashed lines.

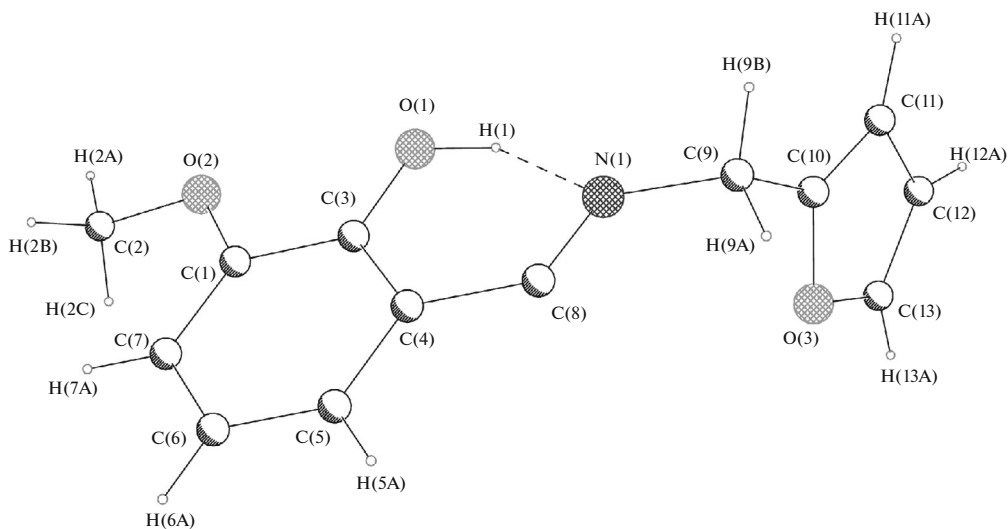


Fig. 2. Structure of HL^2 . The hydrogen bond is shown by the dashed line.

in the other mono- and binuclear trioxo complexes of Group V–VII metals d^0-M^{5+n} ($n = 0-2$; $M = V^{5+}$, Nb^{5+} , Mo^{6+} , W^{6+} , Tc^{7+} , Re^{7+}), the $O_3(t)$ or $O_2(t)$ and $O(br)$ oxygen atoms are *cis* to each other (on the common face of an octahedron). In structure I, the MoO_5N octahedron is strongly distorted: three $O(oxo)MoO(oxo)$ angles are noticeably increased, while the $N(1)MoO(5)$, $N(1)MoO(7)$, and $O(5)MoO(7)$ angles are equally decreased as compared with the angle 90° in a regular octahedron

(respectively, $100.6(3)^\circ-102.7(3)^\circ$ and $76.8(3)^\circ-79.3(3)^\circ$). The molybdenum atom is at a distance of $+0.777$ and -1.303 Å from the $O(3)O(4)O(6)$ and $N(1)O(5)O(7)$ planes, respectively; i.e., it is 0.263 Å out of the octahedron center toward the plane of the trioxo ligands.

The coordination of the L^2 ligand to the metal atom closes a six-membered chelate ring $MoNC_3O$ in a sofa conformation: the Mo atom is 0.494 Å out of the plane

Table 3. Bond lengths (*d*) and bond angles (ω) in structure **I**

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Mo(1)–O(3)	1.690(7)	O(5)–H(1)	0.90(10)
Mo(1)–O(6)	1.710(8)	O(7)–C(1)	1.325(11)
Mo(1)–O(4)	1.895(2)	C(1)–C(6)	1.404(13)
Mo(1)–O(7)	2.035(6)	C(1)–C(2)	1.406(14)
Mo(1)–N(1)	2.242(9)	C(2)–C(3)	1.383(13)
Mo(1)–O(5)	2.397(8)	C(3)–C(4)	1.382(16)
N(1)–C(7)	1.253(13)	C(4)–C(5)	1.378(16)
N(1)–C(9)	1.492(13)	C(5)–C(6)	1.412(15)
O(1)–C(10)	1.365(13)	C(6)–C(7)	1.441(14)
O(1)–C(13)	1.363(14)	C(9)–C(10)	1.477(15)
O(2)–C(2)	1.341(12)	C(10)–C(11)	1.321(15)
O(2)–C(8)	1.429(14)	C(11)–C(12)	1.441(17)
O(5)–C(14)	1.445(12)	C(12)–C(13)	1.323(17)
Angle	ω , deg	Angle	ω , deg
O(3)Mo(1)O(6)	102.7(3)	C(6)C(1)C(2)	120.0(9)
O(3)Mo(1)O(4)	100.6(3)	O(2)C(2)C(3)	126.0(10)
O(6)Mo(1)O(4)	102.5(3)	O(2)C(2)C(1)	115.4(9)
O(3)Mo(1)O(7)	155.0(3)	C(3)C(2)C(1)	118.6(10)
O(6)Mo(1)O(7)	97.0(3)	C(4)C(5)C(6)	121.2(11)
O(4)Mo(1)O(7)	89.9(3)	Mo(1)O(5)H(1)	115(7)
O(3)Mo(1)N(1)	83.8(3)	C(1)O(7)Mo(1)	138.2(6)
O(6)Mo(1)N(1)	96.5(3)	O(7)C(1)C(6)	121.8(9)
O(4)Mo(1)N(1)	158.9(3)	O(7)C(1)C(2)	118.1(9)
O(7)Mo(1)N(1)	78.7(3)	C(6)C(1)C(2)	120.0(9)
O(3)Mo(1)O(5)	82.5(3)	O(2)C(2)C(3)	126.0(10)
O(6)Mo(1)O(5)	173.0(3)	O(2)C(2)C(1)	115.4(9)
O(4)Mo(1)O(5)	80.9(2)	C(3)C(2)C(1)	118.6(10)
O(7)Mo(1)O(5)	76.8(3)	C(4)C(3)C(2)	122.6(11)
N(1)Mo(1)O(5)	79.3(3)	C(5)C(4)C(3)	118.7(11)
C(7)N(1)C(9)	116.1(10)	C(4)C(5)C(6)	121.2(11)
C(7)N(1)Mo(1)	127.2(8)	C(1)C(6)C(5)	118.7(10)
C(9)N(1)Mo(1)	116.4(7)	C(1)C(6)C(7)	120.0(10)
C(10)O(1)C(13)	106.0(10)	C(5)C(6)C(7)	121.1(10)
C(2)O(2)C(8)	117.3(8)	N(1)C(7)C(6)	129.2(11)
Mo(1)O(4)Mo(1A)	157.0(5)	C(10)C(9)N(1)	110.2(10)
C(14)O(5)Mo(1)	120.6(6)	C(11)C(10)O(1)	109.5(12)
C(14)O(5)H(1)	108(7)	C(11)C(10)C(9)	133.5(13)
O(1)C(10)C(9)	117.0(11)	C(10)C(11)C(12)	108.2(12)
C(13)C(12)C(11)	104.3(13)	C(12)C(13)O(1)	112.1(13)

Symmetry codes for the atoms labeled with A: $-x, y, -z + 3/2$.

of the other five atoms (coplanar within ± 0.005 – 0.040 Å).

The Mo–O(5) bond involving the oxygen atom of the neutral methoxy ligand *trans* to Mo–O(6)_{oxo} is significantly elongated, to 2.397(8) Å, due to the structural manifestation of the *trans* influence (SMTI) of the multiply bonded oxo ligand. This bond is 0.357 Å longer than the standard (ST) bond, Mo–O(ST) 2.04 Å [18]. At the same time, the Mo–O(7) bond *trans* to Mo–O(3)_{oxo} involving the deprotonated oxygen atom of the L² ligand (2.035(6) Å) is comparable in length with Mo–O(ST); i.e., in this case, the SMTI of the oxo ligand is almost absent. The Mo–N(1) bond, 2.242(9) Å (involving the neutral nitrogen atom of the L² ligand), *trans* to the bridging O(4) atom is 0.132 Å longer than Mo–N(ST), 2.11 Å [18]. The Mo–O(oxo)_t (1.700(8) ± 0.010 Å) and Mo–O_{br} (1.895(2) Å) bond lengths and the MoO_{br}Mo angle (157.3(5)°) in structure **I** are within the ranges found for 37 dimeric d⁰-Mo(VI) complexes [O₂Mo–O–MoO₂]²⁺ (CCDC, version 5.37, February 2016 [19]): Mo–O_t, 1.66–1.72 Å; Mo–O_{br}, 1.86–1.93 Å; MoO_{br}Mo angles, 136°–180°. In particular, in the binuclear complex [{MoO₂(L⁴)(EtOH)}₂(μ-O)] (**VIII**) [20] (HL⁴ is *N*-hydroxyhomoazaadamantanone), containing the [{MoO₂(ROH)}₂(μ-O)]²⁺ moiety similar to that in **I**, the geometric parameters (av. Mo–O_{oxo}, 1.701 ± 0.003 Å; Mo–O_{br}, 1.887 Å; MoO_{br}Mo angle, 165.3°) are similar to those in structure **I**. The geometric parameters of the Mo–O(HOR) moiety in structure **I** (R = Me) and **VIII** (R = Et) are also close to each other: Mo–O(ROH), 2.397 and 2.397 Å; O–C, 1.429 and 1.444 Å; MoOC, 120.6° and 124.3°, respectively.

The molecule of **I** has two pairs of intramolecular bifurcated hydrogen bonds O(5)–H(1)⋯O(2A) ($(-x + 1, y, -z + 3/2)$) (O(5)–H(1), 0.90(10) Å; H(1)⋯O(2A), 1.91(9) Å; O(5)⋯O(2A), 2.758(10) Å; O(5)H(1)O(2A), 157(10)°) and O(5)–H(1)⋯O(7A) ($(-x + 1, y, -z + 3/2)$) (H(1)⋯O(7A), 2.37(10) Å; O(5)⋯O(7A), 2.953(10) Å, O(5)H(1)O(7A), 123(8)°) between the methoxy ligand, one of the O(oxo) ligands, and the oxygen atom of the L² ligand of the two halves of the dimer.

The structure of the organic HL² molecule is shown in Fig. 2. It is worth noting that upon the coordination to the molybdenum atom, the geometric parameters of the deprotonated ligand (L²)[–] in structure **I** remain roughly the same as in the structure of HL²: the difference in lengths of corresponding N–C, O–C, and C–C bonds in two structures does not exceed 2σ for structure **I** (Tables 3, 4). The strong intramolecular hydrogen bond O(1)–H(1)⋯N(1) (O(1)–H(1), 0.99(3) Å; H(1)⋯N(1), 1.65(3) Å; O(1)⋯N(1), 2.5711(18) Å; O(1)H(1)N(1), 153(2)°) closes a planar six-membered H-ring HOC₃N (Fig. 2). The central 12-atom moiety of the HL² molecule—

Table 4. Selected bond lengths (d) and bond angles (ω) in the structure of HL²

Bond	d , Å
O(1)–C(3)	1.3520(18)
O(1)–H(1)	0.99(3)
O(2)–C(1)	1.3694(19)
O(2)–C(2)	1.416(2)
O(3)–C(13)	1.351(2)
O(3)–C(10)	1.359(2)
N(1)–C(8)	1.275(2)
N(1)–C(9)	1.464(2)
Angle	ω , deg
C(3)O(1)H(1)	103.5(13)
C(1)O(2)C(2)	118.00(15)
C(13)O(3)C(10)	107.48(16)
C(8)N(1)C(9)	118.58(16)
C(7)C(1)O(2)	125.51(15)
O(2)C(1)C(3)	114.65(14)
O(1)C(3)C(4)	121.77(14)
O(1)C(3)C(1)	118.59(14)
N(1)C(8)C(4)	121.82(15)
N(1)C(9)C(10)	111.05(15)
C(11)C(10)O(3)	108.95(17)

N(1), O(1), O(2), H(1), C(1), C(3)–C(9)—is also planar within ± 0.004 – 0.043 Å (the average deviation of the atoms from the mean plane of this moiety is 0.015 Å).

The structures of **I** and HL² have no short intermolecular contacts shorter than the sums of the van der Waals radii of the corresponding atoms.

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