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Synthesis and Crystal Structures of Dioxomolybdenum(VI) Complexes With Similar Benzohydrazone Ligands

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Two new dioxomolybdenum(VI) complexes, [MoO₂L¹(EtOH)] (1) and $[MoO_2L^2(H_2O)]$ (2), where L^1 and L^2 are the dianionic forms of N'-(3-ethoxy-2-hydroxybenzylidene)-4-hydroxybenzohydrazide and N'-(3-ethoxy-2-hydroxybenzylidene)-2-methylbenzohydrazide, respectively, have been synthesized and characterized by elemental analysis, FT-IR spectra, and single-crystal X-ray determination. The crystal of (1) is triclinic: space group P-1, a =7.806(2), b = 9.947(2), c = 12.225(3)Å, $\alpha = 82.915(2), \beta = 89.845(2), \beta = 89.$ $\gamma = 78.063(2)^\circ, V = 921.4(4) \text{ Å}^3, Z = 2, R_1 = 0.0374, wR_2 = 0.1041.$ The crystal of (2) is monoclinic: space group $P2_1/c$, a = 8.120(2), $b = 25.848(2), c = 8.590(2) \text{ Å}, \beta = 95.247(2)^{\circ}, V = 1795.3(6) \text{ Å}^3,$ Z = 4, $R_1 = 0.0473$, $wR_2 = 0.0734$. Mo atoms in the complexes are coordinated by phenolic O, imino N, and enolic O atoms of the benzohydrazone ligand, oxo O atoms, and solvate O atom, forming octahedral coordination. In the crystal structure of (1), adjacent two molecules are linked through intermolecular O-H...N hydrogen bonds, forming dimers. The dimers are further linked through intermolecular O-H····O hydrogen bonds, forming 1D chains. In the crystal structure of (2), adjacent two molecules are linked through intermolecular O-H ... N and O-H ... O hydrogen bonds, forming dimers. The complexes have effective catalytic properties for sulfoxidation.

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Keywords benzohydrazone, catalytic property, crystal structure, dioxomolybdenum, hydrogen bonds

INTRODUCTION

Coordination chemistry of dioxomolybdenum complexes with multidentate ligands has received considerable attention structures.^[5-7] Benzohydrazone derivatives are a kind of special Schiff bases which have been used as interesting ligands in coordination chemistry.^[8-10] Hundreds of complexes of copper, iron, vanadium, manganese, and molybdenum derived from benzohydrazone derivatives have so far been reported. However, due to the best of our knowledge, dioxomolybdenum complexes with such ligands have seldom been reported. Some of these dioxomolybdenum complexes have been shown to possess oxygen atom transfer properties as they were found to oxidize thiols, hydrazine, polyketones, and tertiary phosphines.^[11–13] As an extension of work on the structures and catalytic properties of such complexes, we report in this article the synthesis, structures, and properties of two new dioxomolybdenum(VI) complexes, $[MoO_2L^1(EtOH)]$ (1) and $[MoO_2L^2(H_2O)]$ (2), where L^1 and L^2 are the dianionic forms of N'-(3-ethoxy-2hydroxybenzylidene)-4-hydroxybenzohydrazide (H_2L^1) and N'-(3-ethoxy-2-hydroxybenzylidene)-2-methylbenzohydrazide (H_2L^2) , respectively (Scheme 1).

in recent years for their catalytic properties^[1-4] and versatile



SCH. 1. The benzohydrazone ligands.

EXPERIMENTAL

Materials and Methods

3-Ethoxysalicylaldehyde, 4-hydroxybenzohydrazide, and 2methylbenzohydrazide were purchased from Fluka (Switzerland). Other reagents and solvents were analytical grade and used without further purification. Elemental (C, H, and N) analyses were made on a Perkin-Elmer Model 240B automatic analyzer (USA). IR spectra were recorded on an IR-408 Shimadzu

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568 spectrophotometer (Japan). ¹H NMR spectra were recorded on Bruker Avance 300 MHz spectrometer (Germany).

Synthesis of H₂L¹

3-Ethoxysalicylaldehyde (1.66 g, 0.01 mol) and 4-hydroxybenzohydrazide (1.52 g, 0.01 mol) were mixed in methanol (30 mL). The mixture was stirred at reflux for 30 min and three quarter of the solvent was evaporated, to give colorless solid product of H_2L^1 , which was collected by filtration and dried in vacuum containing anhydrous CaCl₂. The yield is 2.5 g (83%). Found (%): C, 63.8; H, 5.4; N, 9.4. C₁₆H₁₆N₂O₄ Anal. Calcd. (%): C, 64.0; H, 5.4; N, 9.3.

Synthesis of H₂L²

3-Ethoxysalicylaldehyde (1.66 g, 0.01 mol) and 2-methylbenzohydrazide (1.50 g, 0.01 mol) were mixed in methanol (30 mL). The mixture was stirred at reflux for 30 min and threequarters of the solvent was evaporated, to give colorless solid product of H_2L^2 , which was collected by filtration and dried in vacuum containing anhydrous CaCl₂. The yield is 2.3 g (77%). Found: C, 68.6; H, 6.0; N, 9.3. C₁₇H₁₈N₂O₃ Anal. Calcd. (%): C, 68.4; H, 6.1; N, 9.4.

Synthesis of [MoO₂L¹(EtOH)] (1)

 $MoO_2(acac)_2$ (0.1 mmol, 33 mg) in ethanol (10 mL) was added with stirring to H_2L^1 (0.1 mmol, 30.0 mg) in methanol (10 mL). The mixture was stirred at refluxed for 30 min to give an orange solution. The solution was left still at room temperature in air to give orange block-shaped single crystals, which were collected by filtration and dried in vacuum containing anhydrous CaCl₂. The yield is 21 mg (44%). Found (%): C, 45.6; H, 4.3; N, 6.1. C₁₈H₂₀MoN₂O₇ Anal. Calcd. (%): C, 45.8; H, 4.3; N, 5.9.

Synthesis of $[MoO_2L^2(H_2O)]$ (2)

 $MoO_2(acac)_2$ (0.1 mmol, 33 mg) in ethanol (10 mL) was added with stirring to H_2L^2 (0.1 mmol, 29.8 mg) in methanol (10 mL). The mixture was stirred at refluxed for 30 min to give an orange solution. The solution was left still at room temperature in air to give red block-shaped single crystals, which

	TABL	E 1		
Crystal and	structure refinem	ent data for	the comp	olexes

	(1)	(2)
Molecular formula	C ₁₈ H ₂₀ MoN ₂ O ₇	C ₁₇ H ₁₈ MoN ₂ O ₆
Molecular weight	472.3	442.3
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> –1	$P2_{1}/c$
a /Å	7.806(2)	8.120(2)
b /Å	9.947(2)	25.848(2)
c /Å	12.225(3)	8.590(2)
α /°	82.915(2)	90
βΙ°	89.845(2)	95.247(2)
γl°	78.063(2)	90
$V/Å^3$	921.4(4)	1795.3(6)
Ζ	2	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.702	1.636
Crystal dimensions (mm)	0.20 imes 0.18 imes 0.17	$0.20 \times 0.20 \times 0.18$
$\mu (\mathrm{mm}^{-1})$	0.757	0.767
Radiation λ	Μο Κα (0.71073 Å)	Mo Kα (0.71073 Å)
T_{\min}/T_{\max}	0.8634/0.8821	0.8618/0.8743
Reflections measured	7524	10053
Range/indices (h, k, l)	-9, 9; -12, 12; -15, 14	-7, 10; -33, 28; -10, 10
θ limit (°)	2.53-27.00	2.51-27.00
Unique reflections	$3924 [R_{int} = 0.0205]$	$3882 [R_{int} = 0.0457]$
Observed reflections $(I > 2\sigma(I))$	3483	2869
Parameters	258	243
Restraints	15	3
Goodness of fit on F^2	1.046	1.031
$R_1, wR_2 \ [I \ge 2\sigma(I)]^a$	0.0374, 0.1041	0.0473, 0.0733
R_1 , wR_2 (all data) ^a	0.0434, 0.1089	0.0744, 0.0805

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|, wR_{2} = [\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2}]^{1/2}.$

were collected by filtration and dried in vacuum containing anhydrous CaCl₂. The yield is 17 mg (38%). Found (%): C, 46.1; H, 4.2; N, 6.4. $C_{17}H_{18}MoN_2O_6$ Anal. Calcd. (%): C, 46.2; H, 4.1; N, 6.3.

X-Ray Diffraction

Data were collected from selected crystals mounted on glass fibers. The data for the complexes were processed with SAINT^[14] and corrected for absorption using SADABS.^[15] Multi-scan absorption corrections were applied with ψ scans.^[16] The structures of the complexes were solved by direct method using the SHELXS-97 program and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters.^[17] All non-hydrogen atoms were refined anisotropically. Water and ethanol hydrogen atoms were located from difference Fourier maps and refined isotropically, with O–H and H…H distances restrained to 0.85(1) and 1.37(2) Å, respectively. The remaining hydrogen atoms were placed at the calculated positions. Crystallographic data for the complexes are listed in Table 1. Selected bond lengths and angles are given in Table 2. Hydrogen bonds are listed in Table 3.

Catalytic Oxidation

The dioxomolybdenum complexes (0.001 M) and phenyl methyl sulfide (0.1 M) were dissolved at room temperature in a mixture of CH₂Cl₂ and CH₃OH (6:4) together with 1,3,5-trimethoxybenzene (0.1 M) as internal standard. The resulting solution was cooled to 283 K and H₂O₂ (35% w/w) added dropwise (0.125 M). An aliquot of the reaction solution (2.0 mL) was quenched with 5 mL of a stock solution of Na₂SO₃ (0.1 M) and extracted with dichloromethane (three times 4 mL). From the collected organic phases the solvent was removed under reduced pressure to complete dryness and the residue redissolved in deuterated chloroform (0.6 mL) and analyzed by ¹H NMR to determine the yield with reference to the internal standard 1,3,5-trimethoxybenzene.

RESULTS AND DISCUSSION

Reaction of the benzohydrazone ligands with $MoO_2(acac)_2$ affords the orange products of complexes (1) and (2) (Scheme 2). The complexes are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile. We have attempted to grow diffraction quality crystals from various solvents. However, well-shaped single crystals suitable for X-ray diffraction were finally obtained from the mixture solvent of ethanol and methanol containing the complexes.

TABLE 2Selected bond lengths (Å) and angles (°) for the complexes

(1)						
Bond lengths						
Mo1-O1	1.908(2)	Mo1-O3	1.999(2)			
Mo1-O4	2.373 (3)	Mo1-O5	1.693 (3)			
Mo1-O6	1.710(2)	Mo1-N1	2.240(3)			
Bond angles						
O5-Mo1-O6	106.2(1)	O5-Mo1-O1	98.2(1)			
O6-Mo1-O1	102.4(1)	O5-Mo1-O3	96.5(1)			
O6-Mo1-O3	98.1(1)	O1-Mo1-O3	150.2(1)			
O5-Mo1-N1	97.2(1)	O6-Mo1-N1	155.4(1)			
O1-Mo1-N1	81.2(1)	O3-Mo1-N1	71.4(1)			
O5-Mo1-O4	172.1(1)	O6-Mo1-O4	80.9(1)			
O1-Mo1-O4	83.4(1)	O3-Mo1-O4	78.8(1)			
N1-Mo1-O4	75.3(1)					
	(2))				
Bond lengths						
Mo1-O2	1.918(2)	Mo1-O3	2.019(2)			
Mo1-O4	1.692(3)	Mo1-O6	1.713 (2)			
Mo1-O5	2.303 (3)	Mo1-N1	2.215 (3)			
Bond angles						
O4-Mo1-O6	106.0(1)	O4-Mo1-O2	98.3(1)			
O6-Mo1-O2	106.0(1)	O4-Mo1-O3	97.8(1)			
O6-Mo1-O3	95.1(1)	O2-Mo1-O3	148.7(1)			
O4-Mo1-N1	94.2(1)	O6-Mo1-N1	157.1(1)			
O2-Mo1-N1	81.1(1)	O3-Mo1-N1	71.0(1)			
O4-Mo1-O5	170.9(1)	O6-Mo1-O5	83.0(1)			
O2-Mo1-O5	79.5(1)	O3-Mo1-O5	80.4(1)			
N1-Mo1-O5	76.8(1)					

Crystal Structure Description of the Complexes

The molecular structures of the complexes are shown in Figures 1 and 2. The coordination geometry around Mo atom in each of the complexes is octahedrally distorted. The benzohydrazone ligand coordinates through phenolic O, imino N, and enolic O atoms to the MoO_2 moiety, forming a five- and a six-membered chelate rings with Mo atom. The sixth coordination is weakly coordinated by a solvate O atom. For the Mo1 coordination of complex (1), atoms O1, O3, N1, and O6 located at the equatorial plane show a high degree of planarity, with mean deviation from the plane of 0.061(3) Å. The Mo1 atom deviates from the least-squares plane defined by the four



SCH. 2. The preparation of the complexes. X = OH, Y = H for (1); X = H, Y = Me for (2).

Hydrogen geometries for the complexes						
D–H…A	<i>d</i> (<i>D</i> –H) (Å)	$d(H\cdots A)$ (Å)	$d(D\cdots A)$ (Å)	Angle $(D-H\cdots A)$ (°)		
(1)						
O4−H4A…N2 ⁱ	0.85(1)	1.93(2)	2.764(3)	167(5)		
O7−H7…O6 ⁱⁱ	0.82	1.95	2.773(3)	176		
		(2)				
$D5-H5B\cdots N2^{iii}$	0.85(1)	1.95(2)	2.769(4)	162(5)		
O5−H5A…O6 ^{iv}	0.85(1)	1.96(2)	2.792(4)	171(5)		

TABLE 3 Hydrogen geometries for the complexe

Symmetry codes: i) 2 - x, -y, 1 - z; ii) 2 - x, 1 - y, 1 - z; iii) 1 - x, 1 - y, 1 - z; iv) -x, 1 - y, 1 - z.

equatorial donor atoms by 0.334(2) Å in the direction of the axial atom O5. For the Mo1 coordination of complex (2), atoms O2, O3, N1, and O6 located at the equatorial plane show a high degree of planarity, with mean deviation from the plane of 0.014(3) Å. The Mo1 atom deviates from the least-squares plane defined by the four equatorial donor atoms by 0.325(2)Å in the direction of the axial atom O4. The Mo-Ooxo bonds in each of the complexes are almost equal. The remaining coordinate bond lengths in both complexes are similar to each other, and also comparable to those observed in dioxomolybdenum(VI) complexes with benzohydrazone ligands.^[18,19] The angular distortion in the octahedral coordination comes from the bites O3-Mo1-N1 taken by the benzohydrazone ligands. The dihedral angles between the benzene rings are $1.9(4)^{\circ}$ in complex (1), and $10.3(4)^{\circ}$ in complex (2). In the crystal of complex (1), adjacent two $[MoO_2L^1]$ moieties are linked through intermolecular O-H...N hydrogen bonds, to form dimers. The dimers are further linked through intermolecular O-H···O hydrogen bonds, to form 1D chains (Figure 3). In the crystal of complex (2), adjacent two [MoO₂L²] moieties are linked through intermolecular O-H...N and O-H...O hydrogen bonds, to form dimers (Figure 4).



FIG. 1. Molecular structure of complex (1) at 30% probability displacement.



FIG. 2. Molecular structure of complex (2) at 30% probability displacement.

Infrared Spectra

In the infrared spectra of the free benzohydrazone ligands, there showed stretching bands attributed to C=O, C=N, C-OH, and NH at about 1660, 1635, 1180, and 3255 cm⁻¹, respectively. In addition, strong bands indicative of the -C=N-N=C- groups are observed at about 1625 cm⁻¹. In the spectra of the complexes, there showed two prominent bands at about 952 and 893 cm⁻¹ for complex (1), and 940 and 888 cm⁻¹ for complex (2), which attributed to *cis*-dioxomolybdenum groups. The bands due to $\nu_{C=O}$ and ν_{NH} are absent in the complexes, and



FIG. 3. The hydrogen bonds linked 1D chain structure of complex (1).



FIG. 4. The hydrogen bonds linked dimeric structure of complex (2).

the formation of new C–O absorption at about 1253 cm⁻¹ for complex (1) and 1264 cm⁻¹ for complex (2). This suggests occurrence of keto-imino tautomerization of the ligands during complexation.^[18] The -C=N-N=C- absorptions observed in the free ligands are shifted to lower wave numbers in the complexes, 1611 cm⁻¹ for complex (1) and 1608 cm⁻¹ for complex (2). The weak and broad bands centered at 3439 cm⁻¹ for complex (1) and 3357 cm⁻¹ for complex (2) were attributed to the O–H vibrations. The weak bands in the low wave numbers are assigned to the Mo–O and Mo–N vibrations. The similar absorptions in the spectra indicate similar structures of the complexes.

Catalytic Sulfoxidation

Catalytic oxidation test of the complexes on the oxidation of sulfides under homogeneous conditions in solution using methyl phenyl sulfide (thioanisol) as substrate was shown as Scheme 3. As oxidant hydrogen peroxide was used in a slight excess of 1.25 equivalents based on the sulfide substrate. Reactions were run with 1 mol% of catalyst based on the substrate at a temperature of 10° C. NMR technique has been used to monitor the formation



SCH. 3. The sulfoxidation process.

of the sulfoxides with 1,3,5-trimethoxybenzene (TMB) as internal standard to determine the yields. The reaction was started by the addition of hydrogen peroxide. A control reaction under the same condition without any complex present leads to less than 1% sulfide conversion within 4 h. In the presence of the complexes conversions of about 72% for (1) and 86% for (2) of sulfide to the corresponding sulfoxide within 60 min reaction time were observed. After about 2 h in all cases the conversions of total amount of sulfide were complete. Under the given conditions no over oxidation to the sulfone could be detected. Both complexes show catalytic properties for the sulfoxidation.

CONCLUSION

In summary, two new dioxomolybdenum(VI) complexes with similar benzohydrazone ligands have been synthesized and characterized. The benzohydrazone ligands coordinate to the Mo atom through enolic forms by using phenolic O, imino N, and enolic O atoms. Both complexes have effective catalytic properties for the sulfoxidation of sulfides.

SUPPLEMENTARY MATERIALS

CCDC-892776 (1) and 892777 (2) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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