# Synthesis and X-Ray Structural Characterization of Dioxomolybdenum(VI) Complexes with N'-(5-chloro-2-hydroxybenzylidene)-4-methylbenzohydrazide and N'-(2-hydroxybenzylidene)-4-methylbenzohydrazide<sup>1</sup>

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[MoO<sub>2</sub>(ClHm)(CH<sub>3</sub>OH)] Abstract—Two new dioxomolybdenum(VI) complexes, **(I)** and  $[MoO_2(Hm)(CH_3OH)]$  (II) with the hydrazone ligands  $H_2ClHm$  and  $H_2Hm$  derived from 4-methylbenzohydrazide with 5-chlorosalicylaldehyde and salicylaldehyde, respectively, have been synthesized and structurally characterized by physicochemical methods and single-crystal X-ray determination. The crystal of I crystallizes in the triclinic space group  $P\overline{1}$ , with a = 7.839(2), b = 9.656(3), c = 11.548(4) Å,  $\alpha = 88.885(3)^{\circ}$ ,  $\beta = 87.454(3)^{\circ}$ ,  $\gamma = 88.996(3)^\circ$ , V = 873.0(5) Å<sup>3</sup>, Z = 2,  $R_1 = 0.0292$ ,  $wR_2 = 0.0685$ , S = 1.092. The crystal of **H** crystallizes in the triclinic space group  $P\overline{1}$ , with a = 7.780(2), b = 10.584(3), c = 10.628(3) Å,  $\alpha = 91.462(3)^{\circ}$ ,  $\beta = 104.818(3)^{\circ}$ ,  $\gamma = 103.288(3)^{\circ}$ , V = 820.1(4) Å<sup>3</sup>, Z = 2,  $R_1 = 0.0403$ ,  $wR_2 = 0.0784$ , S = 1.065. An X-ray analysis indicates that the structures of both complexes are similar to each other. The molybdenum atom in each complex is in an octahedral coordination environment constructed by two oxo groups, an NO<sub>2</sub> donor set of the hydrazone ligand, and one methanol O atom.

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#### **INTRODUCTION**

The coordination chemistry of molybdenum(VI) has attracted considerable attention due to its biological importance [1-3] and application as catalysts in various oxidations reactions [4-6]. Recent reports indicate that the molybdenum(VI) complexes with hydrazone ligands possess the oxygen atom transfer properties as they were found to oxidize thiols, hydrazine, polyketones, and tertiary phosphines [7, 8]. Moreover, molybdate as a functional mimic for vanadium-haloperoxidase enzymes shows a higher catalytic activity as compared to vanadate [9]. However, in comparison with the oxovanadium complexes, the number of crystal structures of molybdenum complexes with hydrazone ligands is rather few. Herein, we report the synthesis and crystal structures of two new dioxomolybdenum(VI) complexes,  $[MoO_2(ClHm)(CH_3OH)]$  (I) and  $[MoO_2(hm)(CH_3OH)]$  (II), with similar tridentate hydrazone ligands N'-(5-chloro-2-hydroxybenzylidene)-4-methylbenzohydrazide (H<sub>2</sub>ClHm) and N'-(2-hydroxybenzylidene)-4-methylbenzohydrazide  $(H_2Hm)$ , respectively, as shown below:



X = Cl for  $H_2ClHm$ , X = H for  $H_2Hm$ .

## **EXPERIMENTAL**

**Materials.** Ammonium molybdate, acetylacetone, 5-chlorosalicylaldehyde, salicylaldehyde, and 4-me-thylbenzohydrazide were purchased from Aldrich.  $[MoO_2(Acac)_2]$  was prepared and purified as described previously [10]. All other reagents were used as received without further purification.

Synthesis of  $H_2$ ClHm. Hot methanol solutions of 5-chlorosalicylaldehyde and 4-methylbenzohydrazide (1 : 1, v/v) were stirred under reflux for 1 h and cooled to room temperature. The precipitate was then filtered, washed with methanol, and dried in vacuo. The yield was 93%.

For $C_{15}H_{13}ClN_2O_2$			
anal. calcd., %:	C, 62.4;	Н, 4.5;	N, 9.7.
Found, %:	C, 62.2;	Н, 4.6;	N, 9.8.

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Synthesis of  $H_2Hm$  was similar to that of  $H_2ClHm$  except that salicylaldehyde was used instead of 5-chlorosalicylaldehyde. The yield was 91%.

For $C_{15}H_{14}N_2O_2$			
anal. calcd., %:	C, 70.8;	Н, 5.6;	N, 11.0.
Found, %:	C, 70.5;	Н, 5.6;	N, 11.2.

Synthesis of I. To a stirred solution of  $H_2$ ClHm (0.29 g, 1 mmol) in 50 ml of methanol was added  $MoO_2(Acac)_2$  (0.33 g, 1 mmol). The resulting mixture was refluxed for 1 h. The orange reaction solution was filtered, and the solvent was removed under reduced pressure, yielding a red solid of the complex. The yield was 87%. Red single crystals suitable for X-ray diffraction were obtained by the recrystallization of the solid from methanol.

For C <sub>16</sub> H <sub>15</sub> ClMoN <sub>2</sub> O <sub>5</sub>			
anal. calcd., %:	C, 43.0;	Н, 3.4;	N, 6.3.
Found, %:	C, 43.3;	Н, 3.5;	N, 6.2.

Synthesis of II and its crystallization were similar to that of I except that  $H_2Hm$  (0.25 g, 1 mmol) was used instead of  $H_2ClHm$ . The yield was 83%.

For $C_{16}H_{16}MoN_2O_5$			
anal. calcd., %:	C, 46.6;	Н, 3.9;	N, 6.8
Found, %:	C, 46.4;	Н, 3.9;	N, 6.7

**Physical measurements.** Infrared spectra (4000–400 cm<sup>-1</sup>) were recorded as KBr discs with a FTS-40 BioRad FT-IR spectrophotometer. Electronic spectra were recorded on a Shimadzu UV 3101 spectrophotometer. Microanalyses (C, H, and N) of the ligands and the complexes were carried out on a Carlo-Erba 1106 elemental analyzer. Solution electrical conductivity was measured at 298 K using a DDS-11 conductivity meter.

X-ray crystallography. Crystallographic data of complexes I and II were collected on a Bruker SMART CCD area diffractometer with graphitemonochromated Mo $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å) at 298(2) K. Absorption corrections were applied by using the multi-scan program [11]. The structures were solved by direct methods and successive Fourier difference syntheses (SHELXS-97), and anisotropic thermal parameters for all nonhydrogen atoms were refined by a full-matrix least-squares procedure against  $F^2$  (SHELXL-97) [12]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in the calculated positions and refined by a riding model with a common thermal parameter. H atoms for the methanol molecules were located in difference Fourier map and refined isotropically with O-H distances restrained to 0.85 Å. The crystallographic data and experimental details for the structure analysis are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Supplementary material for structure I and II has been deposited with the Cambridge Crystallographic Data Centre (nos. 807009 (I) and 807010 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc. cam.ac.uk).

## **RESULTS AND DISCUSSION**

The two hydrazone compounds are readily prepared by the Schiff base condensation reaction of 4-methylbenzohydrazide with 5-chlrosalicylaldehyde and salicylaldehyde, respectively, in methanol:



X = Cl for  $H_2ClHm$ , X = H for  $H_2Hm$ .

The stoichiometric reactions of the hydrazone ligands with  $MoO_2(Acac)_2$  as a molybdenum source in refluxing methanol yielded the corresponding dioxomolybdenum(VI) complexes I and II:



The reaction progress is accompanied by an immediate color change of the solution from slight yellow to orange. We have attempted to prepare and grow diffraction quality crystals of the complexes from various solvents; however, only methanol is suitable. The molar conductance values of the complexes measured in absolute methanol at a concentration of  $10^{-3}$  mol  $1^{-1}$  is

	Value		
Parameters	Ι	Ш	
Formula	C <sub>16</sub> H <sub>15</sub> ClMoN <sub>2</sub> O <sub>5</sub>	C <sub>16</sub> H <sub>16</sub> MoN <sub>2</sub> O <sub>5</sub>	
Formula weight	446.7	412.2	
Crystal system	Triclinic	Triclinic	
Space group	PĪ	$P\overline{1}$	
<i>a</i> , Å	7.839(2)	7.780(2)	
b, Å	9.656(3)	10.584(3)	
<i>c</i> , Å	11.548(4)	10.628(3)	
$\alpha$ , deg	88.885(3)	91.462(3)	
β, deg	87.454(3)	104.818(3)	
γ, deg	88.996(3)	103.288(3)	
<i>V</i> , Å <sup>3</sup>	873.0(5)	820.1(4)	
Ζ	2	2	
Crystal size, mm	$0.27 \times 0.27 \times 0.23$	$0.30 \times 0.28 \times 0.27$	
$ ho_{calcd}$ , g cm <sup>-3</sup>	1.699	1.669	
$\mu_{Mo}, mm^{-1}$	0.933	0.828	
Scan mode	Multiscan	Multiscan	
<i>F</i> (000)	448	416	
$\theta$ Range, deg	2.11-27.00	2.68-26.98	
hkl Range	$-10 \le h \le 8$ $-12 \le k \le 12$ $-13 \le l \le 14$	$-10 \le h \le 8$ $-10 \le h \le 8$ $-10 \le h \le 8$	
Reflections collected	5724	6135	
Independent reflections $(R_{int})$	3669	3453	
Number of reflections with $I > 2\sigma(I)$	3280	2845	
Parameters	231	222	
Restraints	1	1	
Goodness-of-fit on $F^2$	1.092	1.065	
$R$ indices $(I > 2\sigma(I))$	$     R_1 = 0.0292 \\     wR_2 = 0.0685 $	$R_1 = 0.0403$ $wR_2 = 0.0784$	
<i>R</i> indices (all data)	$R_1 = 0.0341$ $wR_2 = 0.0708$	$R_1 = 0.0536$ $wR_2 = 0.0833$	
Largest different peak and hole, $e \text{ Å}^{-3}$	0.344 and $-0.600$	0.417  and  -0.687	

Table 1. Crystallographic data and experimental details for complex I and II  $% \mathcal{I}$ 

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Bond	I	п	
Dona	<i>d</i> , Å		
Mo(1)-O(1)	1.920(2)	1.921(2)	
Mo(1)-O(2)	1.996(2)	2.007(2)	
Mo(1)–O(3)	1.690(2)	1.685(3)	
Mo(1)–O(4)	1.694(2)	1.693(2)	
Mo(1)-O(5)	2.365(2)	2.389(3)	
Mo(1)-N(1)	2.249(2)	2.237(3)	
Angle	ω, deg		
O(3)Mo(1)O(1)	98.6(1)	98.8(1)	
O(4)Mo(1)O(1)	101.4(1)	102.1(1)	
O(1)Mo(1)O(2)	150.3(1)	150.0(1)	
O(1)Mo(1)N(1)	81.4(1)	81.2(1)	
O(1)Mo(1)O(5)	82.4(1)	82.0(1)	
O(3)Mo(1)O(2)	96.5(1)	97.1(1)	
O(4)Mo(1)O(2)	98.8(1)	97.7(1)	
O(2)Mo(1)N(1)	71.4(1)	71.4(1)	
O(2)Mo(1)O(5)	78.9(1)	79.0(1)	
O(3)Mo(1)O(4)	106.1(1)	106.1(1)	
O(3)Mo(1)N(1)	97.0(1)	98.0(1)	
O(3)Mo(1)O(5)	171.0(1)	172.1(1)	
O(4)Mo(1)N(1)	155.9(1)	154.6(1)	
O(4)Mo(1)O(5)	82.4(1)	81.3(1)	
N(1)Mo(1)O(5)	74.2(1)	74.2(1)	

Table 2. Selected bond (Å) and angles (deg) for I and II

17.2 and 21.5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, indicating the nonelectrolytic nature of the complexes in methanol [13].

The perspective views of complexes I and II are shown in Figs. 1 and 2, respectively. The two complex-

es are very similar to each other. The hydrazone ligand in each complex is nearly planar with a dihedral angle between the two benzene rings of  $6.2(1)^{\circ}$  for I and  $5.5(1)^{\circ}$  for **II**. The hydrazone ligand coordinates in a dianionic fashion forming five- and six-membered chelate rings with the Mo atom. This is evident from the N(2)-C(8) and O(2)-(8) bond lengths with values of about 1.305(4) and 1.315(4) Å, respectively, which are indicative of the presence of the enolate form of the ligand amide groups. The coordination around the Mo atom in each of the complexes is distorted octahedral. The hydrazone ligand coordinates through one phenolate O, one imine N, and one ethanolic O atoms to the  $MoO_2$  moiety, and the sixth weaker coordination comes from the O atom of the methanol molecule. The equatorial donor atoms O(1), O(2), O(4), and N(1) form a high degree of planarity mean deviations from the least-squares planes of 0.055(2) Å for I and 0.058(2) Å for II. The Mo atoms are displaced by 0.334(2) Å for I and 0.347(2) Å for II toward the axial oxo O atoms from the least-squares planes defined by the equatorial donor atoms. The Mo-O and Mo-N bonds in both structures are comparable to each other. The Mo=O bond lengths are within the previously reported ranges [4, 7, 14]. The rather long Mo-O<sub>methanol</sub> bonds and consequently weak bonding are due to the trans influence of the oxo groups. The distortion of the octahedral coordination of both structures can also be observed from the bond angles related to the Mo atoms. The N(1)Mo(1)O(2) bond angles are much less than ideal values of 90° as a result of the strain created by the five-membered chelate rings Mo(1)-N(1)-N(2)-C(8)-O(2).

In the crystal structures of complexes I and II, the molecules are linked *via* intermolecular O-H…N hy-



Fig. 1. ORTEP diagram of complex I (30% thermal ellipsoid).



Fig. 2. ORTEP diagram of complex II (30% thermal ellipsoid).



Fig. 3. Dimeric structures of complex I linked by the O-H…N hydrogen bonds.

drogen bonds to form dimers, as shown in Figs. 3 and 4, respectively.

The weak bands centered at about  $3330 \text{ cm}^{-1}$  in the IR spectra of both complexes may be attributed to the v(OH) vibrations of the coordinated methanol molecules. The hydrazone ligands show stretching bands attributed to C=O, C=N, C–OH, and NH at about 1669, 1637, 1155, 1223, and 3278 cm<sup>-1</sup>, respectively. The Mo=O stretching modes occur as a pair of sharp strong bands at 938 and 912 cm<sup>-1</sup>, assigned to the antisymmetric and symmetric stretching modes of the dioxomolybdenum(VI) moieties. The bands due to v(C=O) and v(NH) were absent in the complexes, and new C–O stretches appear at 1270 cm<sup>-1</sup>. This suggests the occurrence of keto–imine tautomerization of the hydrazone ligands during the coordination. The strong bands indicative of the C=N–N=C groups in the two complexes are shifted to 1603 cm<sup>-1</sup> for I and 1602 cm<sup>-1</sup> for II. The v(C=N) band appear at 1623 cm<sup>-1</sup> in both complexes. The three new peaks observed at about 815, 721, and 683 cm<sup>-1</sup> may be attributed to the Mo–O bonds in the complexes. The



Fig. 4. Dimeric structures of complex II linked by the O-H…N hydrogen bonds.

comparison of the IR spectra of the free ligands and the dioxomolybdenum(VI) complexes confirms the enolate coordination mode of the hydrazone ligands.

The electronic spectra for the complexes recorded in absolute methanol displayed absorption maxima in the ranges 396–410, 306–312, and 260–267 nm. The bands at 306–308 and 260–263 nm can be attributed to the internal ligand transitions. The absorption maxima at 396–410 nm could be assigned to the ligand-tometal Mo( $d\pi$ )  $\leftarrow$  O( $\pi$ ) charge-transfer (LMCT) transition. This is in the range usually observed for the MoO<sub>2</sub> complexes [15].

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