

## STRUCTURAL AND SPECTROSCOPIC CHARACTERIZATION OF DIOXOMOLYBDENUM(VI) COMPLEXES WITH SCHIFF BASES DERIVED FROM ISONICOTINOYLHYDRAZIDE

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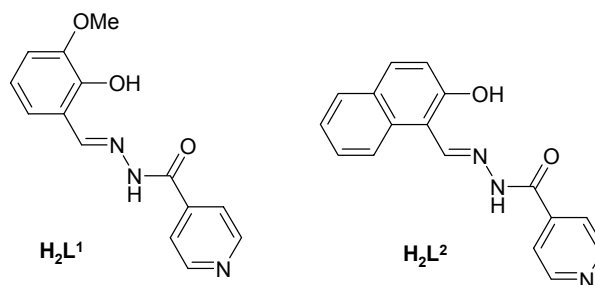
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New dioxomolybdenum(VI) complexes were obtained by the reaction of  $[\text{MoO}_2(\text{acac})_2]$  with isonicotinoylhydrazone ligands derived from 2-hydroxy-3-methoxybenzaldehyde ( $\text{H}_2\text{L}^1$ ) or 2-hydroxy-1-naphthaldehyde ( $\text{H}_2\text{L}^2$ ). Isonicotinoylhydrazone ligands are coordinated to molybdenum as tridentate ONO-donors. Octahedral coordination of each molybdenum atom is completed by methanol (in **1**) or by DMSO molecule (in **2**). The complexes were characterized by means of chemical analyses, IR spectroscopy and NMR measurements. The molecular structures of the complexes  $[\text{MoO}_2\text{L}^1(\text{CH}_3\text{OH})]$  (**1**) and  $[\text{MoO}_2\text{L}^2(\text{DMSO})]$  (**2**) have been determined by single crystal X-ray crystallography.

### INTRODUCTION

The coordination chemistry of molybdenum(VI) has assumed special importance due to its biochemical significance<sup>1-3</sup> as well as for the involvement of Mo(VI) compounds as catalysts in several industrial processes such as amoxidation of propene, epoxidation of olefins, olefin metathesis and isomerization of allylic alcohols.<sup>4-6</sup> Mo(VI) complexes of some selected ONO donor ligands may mimic the active sites of some oxotransfer molybdoenzymes and hence it is of great interest in bioinorganic chemistry.

Here we describe the preparation and characterization of new mononuclear *cis*-dioxo molybdenum(VI) complexes, containing the tridentate Schiff base ligands derived from 2-hydroxy-3-methoxybenzaldehyde and 2-hydroxy-1-naphthaldehyde and isonicotinic hydrazide (Scheme 1).



Scheme 1 – Tridentate isonicotinoylhydrazone Schiff base ligands.

### RESULTS AND DISCUSSION

#### 1. Synthesis and characterization of molybdenum complexes

Molybdenum complexes  $[\text{MoO}_2(\text{L}^1)(\text{MeOH})]$  (**1**) and  $[\text{MoO}_2(\text{L}^2)(\text{DMSO})]$  (**2**) were prepared by combination of molybdenum(VI) acetylacetonate with the appropriate ligand in methanol and

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methanol-DMSO mixture as the reaction medium. Both complexes are red-orange coloured non-hygroscopic solids and stable in air. They are soluble in methanol, ethanol, DMF, DMSO solvents.

### Spectroscopic characterization

In the IR spectra of the ligands there are two bands at about 3100–3200 and 1680–1690  $\text{cm}^{-1}$ , associated with the N–H and C=O stretches, respectively. Their absence in the spectra of the complexes is consistent with enolization and coordination through deprotonated enolic-oxygen atom. This is additionally supported by the appearance of a new band in the region 1330–1350  $\text{cm}^{-1}$  assigned to the C–O(enolic). The stretching frequencies found at 1602 and 1575  $\text{cm}^{-1}$  ( $\text{H}_2\text{L}^1$ ) and 1603 and 1565  $\text{cm}^{-1}$  ( $\text{H}_2\text{L}^2$ ) attributed to C=N(imine) and C–O(phenolic), respectively, are shifted to ca. 1600  $\text{cm}^{-1}$  and 1580  $\text{cm}^{-1}$  in the spectra of all of the complexes.<sup>7</sup> IR spectra of the compounds exhibit also two bands in the regions 930–900  $\text{cm}^{-1}$  and 920–890  $\text{cm}^{-1}$ , due to the  $\nu_{\text{asym}}(\text{MoO}_2)$  and  $\nu_{\text{sym}}(\text{MoO}_2)$  stretches, respectively, thus confirming the formation of mononuclear molybdenum(VI) complexes.

$^1\text{H}$  NMR spectra of complex **1** and **2** are in agreement with the proposed formula, they confirm the dianionic coordination of the ligands by the loss of the signals for the OH and NH protons. The azomethine proton ( $-\text{CH}=\text{N}$ ) is upfield shifted by around 0.4 ppm, with respect to

the corresponding free ligands. The aromatic protons appear in the expected region, with slight shifts in their positions.

### Crystal structure determination of **1** and **2**

The single crystals for X-ray study of both complexes were selected from initial syntheses. The molecular structures of the complexes **1** and **2** are shown in Fig. 1 and 2, respectively. Selected bond lengths and angles are listed in Table 2. Both compounds crystallize with two crystallographically independent molecules, **A** and **B**, in the asymmetric part of the unit cell. The values of the bond lengths and angles for both **A** and **B** components of the structure are in well agreement with each other and with values observed for the similar earlier studied compounds.<sup>7,8</sup> The tridentate Schiff base ligands are bonded to the *cis*- $[\text{Mo}(\text{VI})\text{O}_2]^{2+}$  core through the phenolate-O, the imine-N, which is trans to an oxo group, and the deprotonated enolate-O atoms forming one five- and one six-membered chelating ring. The sixth coordination site around Mo is occupied by a solvent methanol (in **1**) or DMSO (in **2**) molecule, providing a distorted octahedral coordination environment around Mo in which the coordinated MeOH and DMSO occupy *trans* coordination position to another oxo group. In general the structures resembles that of the *cis*-dioxomolybdenum(VI) complex with tridentate Schiff base ligand of isonicotinoylhydrazone of salicylaldehyde.<sup>8</sup>

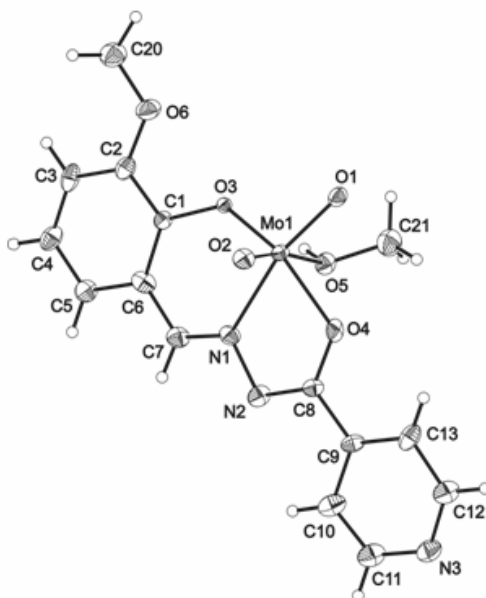


Fig. 1 – Molecular structure of  $[\text{MoO}_2(\text{L}^1)(\text{MeOH})]$  (**1**). Thermal ellipsoids are drawn at the 50% probability level.

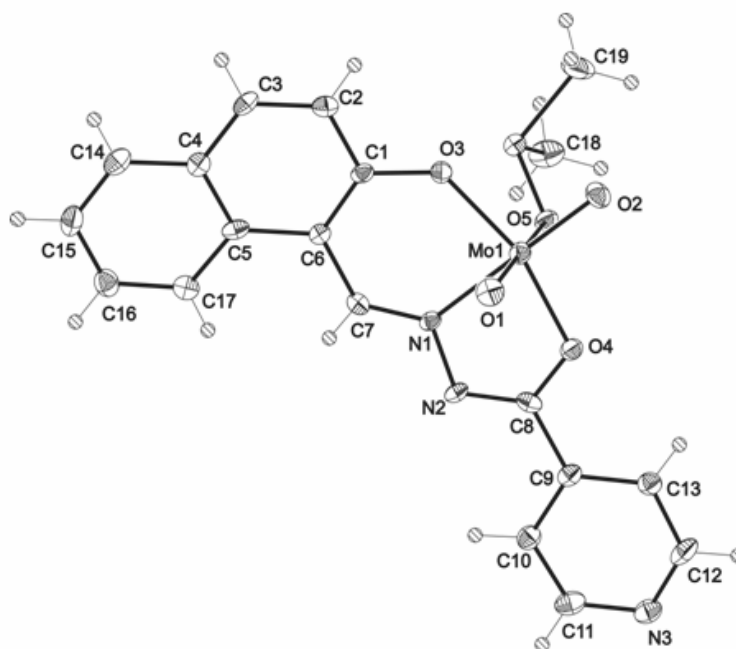


Fig. 2 – Molecular structure of  $[\text{MoO}_2(\text{L}^2)(\text{DMSO})]$  (**2**). Thermal ellipsoids are drawn at the 50% probability level.

Table 1

Crystallographic data and structure refinement parameters for complexes **1** and **2**

Compound	<b>1</b>	<b>2</b>
empirical formula	$\text{C}_{15}\text{H}_{15}\text{MoN}_3\text{O}_6$	$\text{C}_{19}\text{H}_{17}\text{MoN}_3\text{O}_5\text{S}$
fw	429.24	495.36
space group	$\text{P}2_1/\text{c}$	$\text{P}\bar{1}$
$a$ , Å	13.5636(4)	12.8275(10)
$b$ , Å	17.2847(6)	12.9045(9)
$c$ , Å	14.1626(4)	13.2944(6)
$\alpha$ , deg	90	76.963(5)
$\beta$ , deg	90.587(2)	75.667(5)
$\gamma$ , deg	90	64.666(7)
$V$ , Å <sup>3</sup>	3320.14(18)	1909.0(2)
$Z$	8	4
$T$ , K	100	100
$\rho_{\text{calcd}}$ , Mg m <sup>-3</sup>	1.717	1.724
crystal size, mm	0.25×0.15×0.15	0.25×0.15×0.15
$\mu$ , cm <sup>-1</sup>	6.819	0.834
$R1^a$	0.0735	0.0358
$wR2^b$	0.2028	0.0541
GOF <sup>c</sup>	1.011	1.043
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ , eÅ <sup>3</sup>	4.166 and -1.298	0.591 and -0.549

<sup>a</sup>  $R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ , <sup>b</sup>  $wR2 = \{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}\}^{1/2}$ .

<sup>c</sup>  $\text{GOF} = \{\frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)}\}^{1/2}$ , where  $n$  is the number of reflections and  $p$  is the total number of parameters refined.

Table 2

Selected bond lengths (Å) and angles (°) for **1** and **2**

Bond	Compound			
	<b>1</b>		<b>2</b>	
	mol A	mol B	mol A	mol B
Mo-O1	1.699(4)	1.700(4)	1.693(2)	1.702(2)
Mo-O2	1.705(4)	1.704(4)	1.710(2)	1.698(2)
Mo-O3	1.934(7)	1.922(4)	1.937(2)	1.938(2)
Mo-O4	2.005(4)	2.016(4)	1.990(2)	1.996(2)
Mo-O5	2.343(4)	2.339(4)	2.312(2)	2.3297(19)
Mo1-N1	2.222(5)	2.236(5)	2.240(3)	2.228(3)
C1-C2	1.407(8)	1.420(8)	1.415(4)	1.418(4)
C1-C6	1.394(8)	1.400(8)	1.389(4)	1.389(4)
C1-O3	1.41(3)	1.348(7)	1.351(4)	1.345(3)
C2-C3	1.379(8)	1.358(8)	1.362(4)	1.362(4)
C3-C4	1.360(9)	1.383(8)	1.415(4)	1.412(4)
C4-C5	1.383(8)	1.358(9)	1.423(4)	1.420(4)
C5-C6	1.438(8)	1.424(8)	1.447(4)	1.443(4)
C6-C7	1.411(8)	1.427(8)	1.449(4)	1.442(4)
C7-N1	1.273(8)	1.292(7)	1.299(4)	1.292(3)
N1-N2	1.438(7)	1.396(7)	1.402(3)	1.395(3)
N2-C8	1.306(8)	1.306(7)	1.290(4)	1.293(4)
C8-O4	1.326(7)	1.317(7)	1.327(3)	1.327(3)
C8-C9	1.470(8)	1.468(8)	1.480(4)	1.485(4)
C9-C10	1.431(8)	1.400(8)	1.392(4)	1.382(4)
C10-C11	1.350(9)	1.360(8)	1.381(4)	1.380(4)
C11-N3	1.351(8)	1.362(8)	1.342(4)	1.343(4)
N3-C12	1.345(8)	1.346(8)	1.317(4)	1.318(4)
C12-C13	1.397(9)	1.412(9)	1.378(4)	1.381(4)
C13-C9	1.378(9)	1.386(8)	1.387(4)	1.390(4)
C2-O6	1.366(7)	1.389(7)		
O6-C20	1.421(8)	1.402(7)		
O5-C21	1.435(8)	1.433(7)		
C4-C14			1.399(5)	1.387(4)
C14-C15			1.368(4)	1.366(5)
C15-C16			1.390(4)	1.397(4)
C16-C17			1.368(5)	1.355(4)
C17-C5			1.416(4)	1.418(4)
O5-S1			1.5350(19)	1.523(2)
S1-C18			1.773(3)	1.729(3)
S1-C19			1.776(3)	1.924(10)
Angle	<b>1</b>		<b>2</b>	
	mol A	mol B	mol A	mol B
O1-Mo1-O2	105.1(2)	105.2(2)	104.28(10)	105.61(10)
O2-Mo1-O3	98.4(7)	99.41(17)	99.72(9)	98.28(9)
O1-Mo1-O3	99.0(9)	103.63(17)	99.63(10)	101.01(10)
O2-Mo1-O4	95.13(17)	96.37(17)	102.34(10)	97.93(9)
O1-Mo1-O4	97.50(16)	96.27(16)	97.43(9)	100.07(10)
O3-Mo1-O4	147.3(9)	150.24(17)	147.73(8)	148.76(8)
O2-Mo1-N1	95.23(19)	95.33(19)	92.09(10)	92.32(10)
O1-Mo1-N1	158.2(2)	157.5(2)	163.41(10)	161.42(10)
O3-Mo1-N1	81.9(5)	81.45(17)	79.80(9)	80.71(9)
O4-Mo1-N1	72.59(17)	72.06(17)	72.37(9)	72.11(9)
O2-Mo1-O5	169.82(17)	169.70(18)	168.27(9)	168.28(9)
O1-Mo1-O5	83.75(18)	84.31(18)	86.90(9)	85.86(9)
O3-Mo1-O5	75.5(15)	81.75(15)	81.62(8)	81.51(8)
O4-Mo1-O5	78.49(15)	78.42(15)	76.39(7)	77.30(8)
N1-Mo1-O5	75.37(17)	74.66(16)	76.60(8)	76.06(8)

## EXPERIMENTAL

All solvents and chemicals were of analytical grade and have been used as received. Elemental analyses (C, H, N) were performed on a Vario EL III CHNOS Elemental Analyzer. IR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer. NMR spectra were performed on a Bruker 400 spectrometer in DMSO-*d*<sub>6</sub> solution using TMS as internal reference. [MoO<sub>2</sub>(acac)<sub>2</sub>] and isonicotinoylhydrazone ligands (H<sub>2</sub>L<sup>1</sup>, H<sub>2</sub>L<sup>2</sup>) were prepared as described in the literature.<sup>9,11</sup>

**X-ray crystallography.** X-ray diffraction data for **1** and **2** were collected with an Oxford Diffraction XCALIBUR CCD diffractometer using graphite-monochromated Mo K<sub>α</sub> radiation. The crystals were placed 50 mm from the CCD detector. Coverage of the unique set is 99.9% complete up to 2θ = 130° and 99.8% up to 2θ = 52° for **1** and **2**, respectively. The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction.<sup>12</sup> Intensity data were corrected for Lorentz and polarization effects. All structures were solved by direct methods using SHELXS-97<sup>13</sup> and refined by full-matrix least squares on *F*<sup>2</sup> with SHELXL-97.<sup>14</sup> with anisotropic displacement parameters for non-hydrogen atoms. All hydrogen atoms attached to carbon were introduced in idealized positions (d<sub>CH</sub> = 0.96 Å) using the riding model with their isotropic displacement parameters fixed at 120% of their riding atom.

**Synthesis of complexes:** A suspension of the appropriate ligand (0.3 mmol) and MoO<sub>2</sub>(acac)<sub>2</sub> (0.1 g, 0.3 mmol) in 15 mL of methanol (for **1**) or 15 ml of methanol:DMSO (3:1) mixture (for **2**) was stirred for 10 min at 50°C. The solutions were left at room temperature for 1 day, and the obtained crystalline precipitate were filtered off, washed with methanol and dried in air.

**(1)** [MoO<sub>2</sub>(L<sup>1</sup>)(CH<sub>3</sub>OH)]: Yield. 70%. Anal. Calcd. for: C<sub>15</sub>H<sub>15</sub>MoN<sub>3</sub>O<sub>6</sub>; C, 41.97; H, 3.52; N, 9.79%; Found: C, 42.29; H, 3.98; N, 9.87%. Significant infrared bands (cm<sup>-1</sup>): 895 (ν<sub>Mo=O</sub>, asym), 923 (ν<sub>Mo=O</sub>, sym), 1593(ν<sub>C=N</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) = 3.82 (s, 3 H, OCH<sub>3</sub>), 7.06 (t, 1H, benzaldehyde ring proton), 7.28 (d, 1H, benzaldehyde ring proton), 7.34 (d, 1H, benzaldehyde ring proton), 7.87 (d, 2H, meta py), 8.76 (d, 2H, ortho py), 9.01 (s, 1H, CH=N).

**(2)** [MoO<sub>2</sub>(L<sup>2</sup>)(DMSO)]: Yield. 85%. Anal. Calcd. for: C<sub>19</sub>H<sub>17</sub>MoN<sub>3</sub>O<sub>3</sub>S; C, 49.25; H, 3.70; N, 9.07%. Found: C, 49.83; H, 3.45; N, 9.39%. Significant infrared bands (cm<sup>-1</sup>): 903 (ν<sub>Mo=O</sub>, asym), 919 (ν<sub>Mo=O</sub>, sym), 1599(ν<sub>C=N</sub>). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ (ppm) = 7.23 (d, 1H, naphthaldehyde ring proton), 7.52 (t, 1H, naphthaldehyde ring proton), 7.63 (t, 1H, naphthaldehyde ring proton), 7.89 (d, 2H, meta py), 7.91 (d, 1H, naphthaldehyde ring proton), 8.16 (d, 1H, naphthaldehyde ring proton), 8.53 (d, 1H, naphthaldehyde ring proton), 8.79 (d, 2H, ortho py), 9.82 (s, 1H, CH=N).

**Supporting information available:** CCDC-778760 (for **1**) and -778761 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/datarequest/cif](http://www.ccdc.cam.ac.uk/datarequest/cif).

## CONCLUSIONS

Two dioxomolybdenum(VI) complexes with ONO donor ligands, 2-hydroxy-3-

methoxybenzaldehyde isonicotinoylhydrazone and 2-hydroxy-1-naphthaldehyde isonicotinoylhydrazone have been synthesized and characterized by means of chemical analysis, IR spectroscopy and X-Ray crystallography. In both complexes, the structure consists of dioxomolybdenum(VI) moiety, one tridentate Schiff base ligand, bonded as tridentate ONO-donors and a solvent molecule that occupies the sixth metal coordination site. The geometry around Mo is distorted octahedral. Octahedral coordination of each Mo atom in [MoO<sub>2</sub>L<sup>1</sup>(CH<sub>3</sub>OH)] (**1**) and [MoO<sub>2</sub>L<sup>2</sup>(DMSO)] (**2**) in solid state was determined by X-ray crystallography and all complexes were in detail characterized. In DMSO-*d*<sub>6</sub> solution NMR spectra of complexes **1-2** revealed distinct differences in comparison with corresponding free ligands.

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