

# Crystal Structures of Dioxomolybdenum(VI) Complexes with ONS-Donor Ligands

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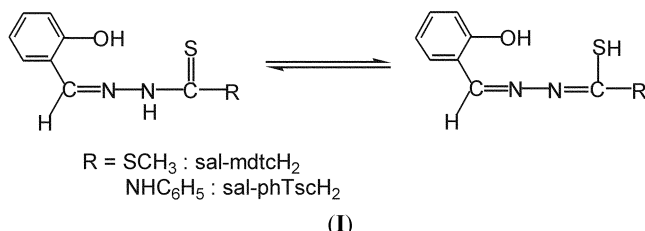
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Molybdenum chemistry has received the intense attention because of its relevance to the active sites of molybdoenzymes. The presence of the *cis*-dioxomolybdenum(VI) cation,  $[\text{MoO}_2]^{2+}$ , in the oxidized forms of certain molybdoenzymes has stimulated both the search for new structures in which this moiety is coordinated to ligands containing nitrogen, oxygen and/or sulfur donors and also the study of their chemical, spectroscopic, electrochemical and structural properties.<sup>1-7</sup>

Tridentate ONS-chelating ligands derived from thiosemicarbazide or dithiocarbamate of salicylaldehydes have been widely used for the preparation of transition metal complexes.<sup>8-10</sup> The tautomerism (I) of these ligands as well as the well known tendency of sulfur donors to act as bridging ligands allow various structural possibilities for the corresponding metal complexes.



Related complexes with tridentate ONS ligand have been reported to undergo reversible oxo-transfer reactions involving molybdenum(VI) and -(IV) species.<sup>11-16</sup> As part of our studies on molybdenum(VI) complexes with nitrogen, oxygen, and/or sulfur donor ligands, we have described the synthesis and spectroscopic and electrochemical properties for the molybdenum(VI) complexes with these ligand in previous paper,<sup>12</sup> but no crystal structure has been reported. In this paper, we report the crystal structures on the complexes.

## Experimental Section

**Synthesis.** The Schiff base ligands<sup>17</sup> and both complexes,<sup>12</sup>  $[\text{MoO}_2(\text{sal-mdtc})(\text{MeOH})]$  (**1**) (sal-mdtc = dibasic salicylaldehyde S-methylthiocarbamate ion) and  $[\text{MoO}_2(\text{sal-phTsc})(\text{MeOH})]\cdot\text{MeOH}$  (**2**) (sal-phTsc = dibasic salicylaldehyde N-phenylthiosemicarbazate ion) were prepared by

the procedure of literature reported previously, respectively. Analytical data are listed in *reference*.<sup>18</sup>

**Crystal structure determination of 1 and 2.** X-ray quality crystals of both complexes, **1** and **2** were obtained by slow evaporation of a saturated dichloromethane solution of the brown powder. Data were collected on a STOE STAD14<sup>19</sup> four-circle (**1**) and Bruker SMART<sup>20</sup> diffractometer (**2**) using graphite monochromatized Mo-K $\alpha$  radiation

**Table 1.** Crystal data and structure refinement for complexes **1** and **2**

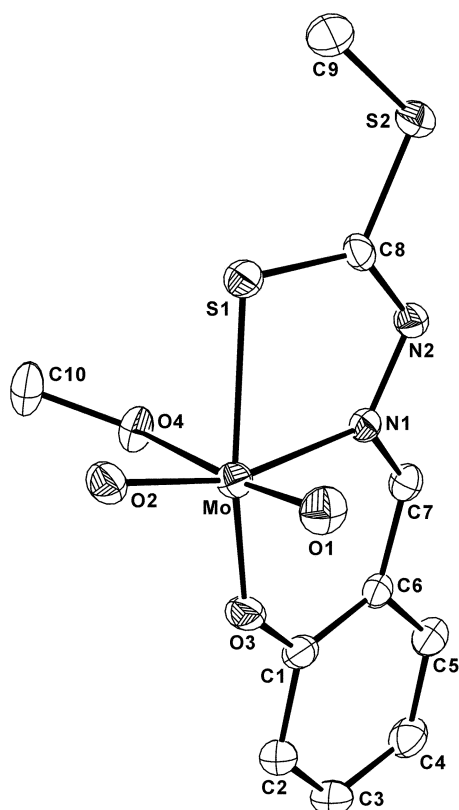
	Complex 1	Complex 2
Empirical formula	C <sub>10</sub> H <sub>12</sub> MoN <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>16</sub> H <sub>16</sub> MoN <sub>3</sub> O <sub>5</sub> S
Fw	384.28	461.34
Temp (K)	293(2)	173(2)
$\lambda$ (Å)	0.71069	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/n
a (Å)	12.934(3)	6.8259(3)
b (Å)	14.119(3)	7.5881(3)
c (Å)	7.568(2)	35.928(2)
$\alpha$ (°)	90	90
$\beta$ (°)	95.13(3)	95.102(1)
$\gamma$ (°)	90	90
V(Å <sup>3</sup> )	1376.5(6)	1853.5(2)
Z	4	4
D <sub>calc</sub> (Mg/m <sup>3</sup> )	1.854	1.653
$\mu$ (mm <sup>-1</sup> )	1.266	0.852
F(000)	768	936
Crystal size (mm)	0.30 × 0.15 × 0.10	0.5 × 0.40 × 0.20
Theta range	1.58-27.51°	1.14-28.25°
Index ranges	<i>h</i> 0 → 16, <i>k</i> -18 → 0, <i>l</i> -9 → 9	<i>h</i> -9 → 9, <i>k</i> -8 → 9, <i>l</i> -47 → 33
Reflections/unique	3144/3144 [Rint=0.0000]	11456/4294 [Rint=0.0444]
Completeness to theta	99.4%	93.7%
Data/restraints	3144/0/173	4294/0/235
/parameters		
<i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.0517, <i>wR</i> <sub>2</sub> =0.0925	<i>R</i> <sub>1</sub> =0.0363, <i>wR</i> <sub>2</sub> =0.0940
<i>R</i> (all data)	<i>R</i> <sub>1</sub> =0.0927, <i>wR</i> <sub>2</sub> =0.1131	<i>R</i> <sub>1</sub> =0.0405, <i>wR</i> <sub>2</sub> =0.1013
G.O.F. on F <sup>2</sup>	1.127	1.219
Largest diff. peak and hole	0.624 and -0.605 eÅ <sup>-3</sup>	0.779 and -1.041 eÅ <sup>-3</sup>

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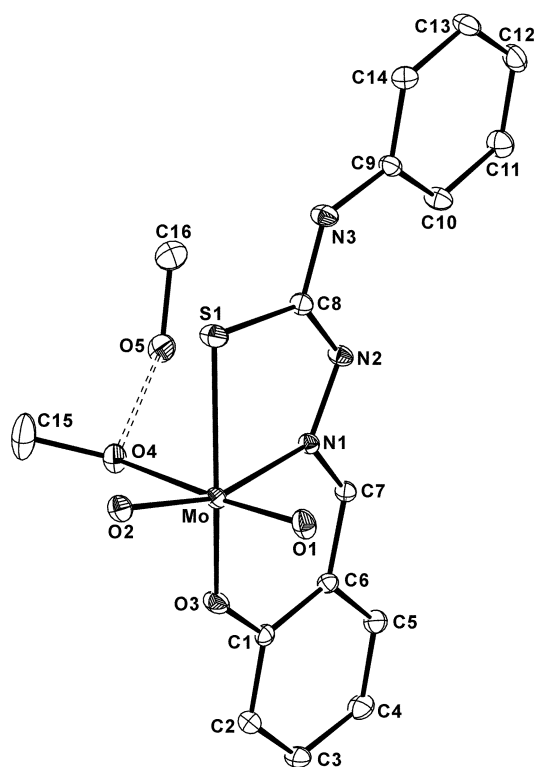
by  $\omega$ -2 $\theta$  (1) and  $\pi$ - $\omega$  (2) scans, respectively. In each case, unit cell parameters were determined by least-squares fit of 31 (1) and 7908 (2) reflections having  $\theta$  values in the ranges of 9.5-10.3 (1) and 2.28-28.22 (2). Intensities of three check reflections were measured after every 1 h during the data collection to monitor the crystal stability for 1 and there was no significant change in the intensities of the check reflections. A numerical absorption correction for complex 1 was made: the transmission factor was 0.8128 (min.) and 0.8692 (max.), while complex 2 was not made. The structures were solved by direct method<sup>21</sup> and refined on  $F^2$  by full-matrix least-squares procedures.<sup>22</sup> All non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions by using riding model, but not refined. The data collection and structure solution parameters are listed in Table 1, together with standard discrepancy indices,  $R$  and  $wR$ .

### Results and Discussion

The reaction of  $\text{MoO}_2(\text{acac})_2$  with the Schiff base ligands derived from salicylaldehyde and S-methyldithiocarbamate<sup>17</sup> or 4-phenylthiosemicarbazide in methanol solution gave a monomeric molybdenum(VI) complex 1 and 2, respectively. Both complexes were identified by physicochemical methods and the resulting data were compared to the values of the



**Figure 1.** OrtepIII<sup>23</sup> drawing of 1. Displacement ellipsoids are drawn at 30% probability level and H atoms have been omitted for clarity.



**Figure 2.** OrtepIII<sup>23</sup> drawing of 2. Displacement ellipsoids are drawn at 30% probability level and H atoms have been omitted for clarity.

literature.<sup>12,16</sup>

The solid state molecular structures of the complex 1 and 2 are shown in Figure 1 and 2, respectively. Selected bond lengths and angles are listed in Table 2 and 3, respectively. The tridentate Schiff base ligand is bonded to the *cis*- $[\text{Mo}(\text{VI})\text{O}_2]^{2+}$  core on a meridional plane through the phenolate-O, the imine-N, which is trans to an oxo group, and the deprotonated thiolate-S atoms forming one five- and

**Table 2.** Selected bond lengths (Å) for complexes 1 and 2

Bond lengths	Complex 1	Complex 2
Mo-O1	1.687(4)	1.702(2)
Mo-O2	1.690(4)	1.723(2)
Mo-O3	1.929(4)	1.923(2)
Mo-N1	2.268(4)	2.260(2)
Mo-S1	2.456(2)	2.425(1)
Mo-O4	2.352(4)	2.344(2)
C8-S1	1.721(6)	1.759(3)
C8-N2	1.296(7)	1.296(4)
N2-N1	1.407(6)	1.404(3)
N1-C7	1.294(7)	1.297(3)
C7-C6	1.434(8)	1.445(4)
C6-C1	1.406(8)	1.405(4)
C1-O3	1.339(7)	1.344(3)
O4-H17		0.820
H17...O5		1.830
O4...O5		2.642(3)

**Table 3.** Selected bond angles ( $^{\circ}$ ) for complexes **1** and **2**

Angles	Complex 1	Complex 2
O1-Mo-O2	105.3(2)	105.1(1)
O1-Mo-O3	99.8(2)	99.9(1)
O1-Mo-O4	171.8(2)	171.2(1)
O1-Mo-N1	95.6(2)	92.4(1)
S1-Mo-O1	94.9(2)	98.1(1)
S1-Mo-O2	90.4(2)	89.6(1)
S1-Mo-O3	154.8(1)	153.0(1)
S1-Mo-O4	82.5(1)	81.3(1)
S1-Mo-N1	76.2(1)	75.9(1)
O2-Mo-O3	105.4(2)	104.8(1)
O2-Mo-O4	82.6(2)	83.7(1)
O2-Mo-N1	156.1(2)	158.8(1)
O3-Mo-O4	80.1(2)	77.8(1)
O4-Mo-N1	76.3(2)	78.9(1)
C7-N1-Mo	126.5(4)	124.3(2)
C7-N1-N2	112.7(4)	112.4(2)
O4-H17...O5		169.8

one six-membered chelate ring. The sixth coordination site around Mo is occupied by a solvent methanol molecule, thereby providing a distorted octahedral coordination environment around Mo in which the coordinated MeOH lie *trans* to another oxo group. In general the structure resembles that of the *cis*-dioxomolybdenum(VI) complex with tridentate Schiff base ligand of thiocarbodihydrazone of salicylaldehyde.<sup>10</sup>

In both the complexes **1** and **2**, the *cis*-bond angles around Mo range from 75.9(1) $^{\circ}$  to 76.2(1) $^{\circ}$  for N1-Mo-S1 to 105.1(1) $^{\circ}$ -105.3(2) $^{\circ}$  for O1-Mo-O2, while the range of *trans*-bond angles extends from 153.0(1) $^{\circ}$  to 154.8(1) $^{\circ}$  for O3-Mo-S1 and 171.2(1) $^{\circ}$ -171.8(2) $^{\circ}$  for O1-Mo-O4.<sup>10</sup> To a large extent these distortions stem from the incorporation of Mo into a five-membered ring. The Mo-O bond length [1.689(4) Å for **1** and 1.713(2) Å for **2**] and the O-Mo-O bond angle [105.3(2) for **1** and 105.1(1) for **2**] are comparable to other such data reported for the MoO<sub>2</sub> group.<sup>13,24,25</sup> The Mo-S1 and Mo-N1 bond lengths and other metric parameters for Mo-S1-C8-N2-N1 ring are similar to those reported for other five-membered rings of this general type.<sup>8</sup> The N1-C7 [1.294(7) Å-1.297(3) Å] and N2-C8 [1.296(4) Å-1.296(7) Å] distances indicate that these correspond to double bonds (normal single bond is 1.364 Å).<sup>8</sup> The Mo-O4 [2.352(4) Å in **1** and 2.344(2) Å in **2**] bond length is relatively long due to the *trans* effect<sup>26</sup> of the terminal oxide ligands and the coordinated solvent molecule (CH<sub>3</sub>OH) is labile. The metric parameters for the six-membered rings Mo-O3-C1-C6-C7-N1 for **1** and **2** are unexceptional and compare closely to those in related molecules.<sup>8</sup> Both of the five- and six-membered rings which are formed upon coordination of ligand are almost plane; for the complex of **1**, the mean deviations of the planes Mo-S1-C8-N2-N1 and Mo-N1-C7-C6-C1-O3 from the least-square plane are 0.0829 and 0.0035 Å, respectively, and each of the dihedral angles of the Mo-S1-C8-N2, Mo-O3-C1-C6, and Mo-N1-C7-C6 to the

plane, Mo-S1-C8-N2-N1 is 3.77 (0.09), 11.27 (0.16), and 11.37 (0.19) $^{\circ}$ . Also, both planes in complex **2** are nearly plane with the magnitude of the Mo-S1-C8-N2, Mo-O3-C1-C6, and Mo-N1-C7-C6 dihedral angles to the plane, Mo-S1-C8-N2-N1 (mean deviation is 0.0764 Å) of 3.3 (0.1), 14.4 (0.1), and 7.0 (0.1) $^{\circ}$ , respectively.

In case of **2**, the unit cell contains one methanol solvent molecule per molecule, which is hydrogen-bonded to the molybdenum-bound methanol molecule. The O4...O5 separation and the O4-H...O5 angle are 2.642(3) Å and 169.8, respectively.<sup>27</sup>

## Conclusions

Two dioxomolybdenum(VI) complexes with the ONS-donor ligands, salicylaldehyde S-methylthiocarbamate and salicylaldehyde S-phenylthiosemicarbazate have been synthesized and characterized. In both complexes, the structure consists of molybdenyl moiety, one tridentate Schiff base ligand, and a solvent methanol molecule that occupies the sixth metal coordination site. The geometry around Mo is distorted octahedral. The tridentate ligand is bonded to the *cis*-MoO<sub>2</sub> core on a meridional plane through phenolated-O, deprotonated-S, and an imine nitrogen atom forming one five- and one six-membered chelate ring. The molecules of these two display essentially similar coordination geometry.

**Supporting information available.** Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition No. CCDC-232954 (**1**) and 232953 (**2**)). The data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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18. Analytical data for (1). Yield: 0.227 g (59%), mp 248-250 °C. Anal. Calcd. for  $C_{10}H_{12}N_2O_4S_2Mo$ : C, 31.26; H, 3.15; N, 7.29; S, 16.69. Found: C, 31.34; H, 3.01; N, 7.50; S, 16.72. Significant infrared bands ( $cm^{-1}$ ): 902 ( $\nu_{Mo=O, asym}$ ), 932 ( $\nu_{Mo=O, sym}$ ), 1600 ( $\nu_{C=N}$ ).  $^1H$ NMR (200 MHz,  $DMSO-d_6$ ): 2.60 (s, 3H, S-CH<sub>3</sub>), 3.18 (d, 3H, CH<sub>3</sub>OH), 4.14 (q, 1H, CH<sub>3</sub>OH), 6.95-7.77 (m, 4H, ArH), 8.93 (s, 1H, N=CH). (2). Yield: 0.277 g (60%), mp 205-208 °C. Anal. Calcd. for  $C_{16}H_{19}N_3O_5SMo$ : C, 41.66; H, 4.15; N, 9.11; S, 6.95. Found: C, 41.23; H, 4.35; N, 9.25; S, 7.02. Significant infrared bands ( $cm^{-1}$ ): 920 ( $\nu_{Mo=O, sym}$ ), 931 ( $\nu_{Mo=O, asym}$ ), 1604 ( $\nu_{C=N}$ ).  $^1H$ NMR (200 MHz,  $DMSO-d_6$ ):  $\delta$  3.16 (d, 6H, CH<sub>3</sub>OH), 4.12 (q, 2H, CH<sub>3</sub>OH), 6.89-7.77 (m, 9H, ArH), 8.82 (s, 1H, N=CH), 9.70 (s, 1H, NH).
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