Synthesis, Structure and Characterization of Dinuclear Pentacoordinate Molybdenum(V) Complexes with Thiosemicarbazone Ligands

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Abstract. New dinuclear pentacoordinate molybdenum(V) complexes, $[Mo_2^{V}O_3L_2]$ [L = thiosemicarbazonato ligand: $C_6H_4(O)CH:NN:C(S)NHR'$ and $C_{10}H_6(O)CH:NN:C(S)NHR'$; $R' = H, CH_3, C_6H_5$) were obtained either by oxygen atom abstraction from $Mo^{VI}O_2L$ with triphenylphosphine or by using

Introduction

Oxomolybdenum compounds have been extensively studied as models for molybdoenzymes that catalyze oxygen atom transfer (OAT) [1–5]. It is known that OAT reactions proceed in steps: a) transfer of an oxygen atom from $Mo^{VI}O_2L$ to an appropriate substrate (PR₃) and formation of the corresponding $Mo^{IV}OL$ complex, and b) transfer of an oxo-group from an oxo-donor substrate (DMSO, pyridine *N*-oxide, or O₂) to $Mo^{IV}OL$ and regeneration of the initial $Mo^{VI}O_2L$ complex. The oxomolybdenum complexes of interest are those which can provide completion of the catalytic cycle. However, the OAT cycle is in some cases accompanied by the formation of a dinuclear oxo-bridged molybdenum(V) complex, usually inactive toward further oxo-transfer:

$$MoO^{2+} + MoO_2^{2+} \Leftrightarrow Mo_2O_3^{4+}$$

There are only rare examples of complexes with the $Mo_2O_3^{4+}$ core that take part in oxo-transfer reactions. They were found to have a labile bonded molecule *trans* to the terminal Mo=O bond [6–8].

Recently, we have published syntheses, as well as structural and spectral properties of several molybdenum(VI) complexes with thiosemicarbazones [9-12]. In the continuation of our research we report herein the synthesis and characterization of several pentacoordinate molybdenum(V) complexes, $[Mo_2O_3L_2]$, in which L represents a

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1242 InterScience

deprotonated thiosemicarbazonato ligand. Although a large number of molybdenum(V) complexes containing the $Mo_2O_3^{4+}$ core are known, only a few complexes containing pentacoordinate molybdenum have been synthesized and structurally characterized so far [13–16].

Results and Discussion

The molybdenum(V) complexes having the general formula $[Mo_2^{V}O_3L_2]$ (1–6) [L = thiosemicarbazonato ligand: $C_6H_4(O)CH:NN:C(S)NHR'$ and $C_{10}H_6(O)CH:NN:C(S)NHR'; R' = H, CH_3, C_6H_5]$ have been prepared by two alternative ways (Scheme 1). Either by oxygen atom abstraction from $[Mo^{VI}O_2L]_n$ (1a–6a) with triphenylphosphine in acetonitrile (*method A*) or by the reaction of $[Mo_2O_3(acac)_4]$ (acac = acetylacetonate ion) with the corresponding thiosemicarbazone ligands, H_2L (*method B*). Complexes prepared by either of the methods were of the same formula, as proven not only by comparison of their spectral and elemental analyses, but also by the X-ray powder diffraction.

Dark red-brown products were characterized as novel dinuclear five-coordinate molybdenum(V) complexes, with ligands coordinated to molybdenum as tridentate *ONS*-donors through phenolic-oxygen, imine-nitrogen and thiol-sulfur atoms. The existence of Mo^V instead of Mo^{IV} in the OAT process was proven by EPR spectroscopy [17]. For all complexes a similar spectrum was obtained and therefore just one representative example is given in Figure 1.

These compounds are very soluble in coordinating solvents D such as CH₃OH, dmf, dmso, picoline or py and only moderately soluble in acetonitrile. Their solutions are quite sensitive to traces of oxygen resulting in color change form dark red to orange. This change of the coloration is a consequence of oxidation of the $[Mo_2^{V}O_3L_2]$ complexes to

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Scheme 1.



Figure 1. EPR spectrum of molybdenum(V) complex 2.

the mononuclear $[Mo^{VI}O_2LD]$ (1b-6b) complexes, additionally coordinated by a solvent molecule D (Scheme 1). The molybdenum(VI) complexes $[Mo^{VI}O_2LD]$ obtained by this procedure are identical to those known from our previous investigations [9-12, 18].

The advantage of pentacoordinated molybdenum(V) complexes is their capability of regenerating the initial dioxomolybdenum(VI) complexes so that catalytic cycle can be accomplished. It is reasonable to suppose that the arrangement around molybdenum gives the opportunity for a ready access to the sixth coordination place around the molybdenum atom by an appropriate substrate.

Infrared Spectra

In the polymeric complexes $[Mo^{VI}O_2L]_n$ (1a-6a) there are intense bands in the region 799-834 cm⁻¹ associated with the Mo=O···Mo interaction. In complexes

 $[Mo_2^{V}O_3L_2]$ (1-6), these bands are shifted to a single strong absorption in the region 763-746 cm⁻¹, indicative for Mo-O-Mo bridging [13, 19]. The molybdenum(V) complexes 1-6 exhibit a single strong absorption band around 960 cm⁻¹ assigned to terminal Mo=O groups. The $[Mo^{VI}O_2LD]$ (1b-6b) complexes obtained by the oxidation of $[Mo_2^{V}O_3L_2]$ were identified by the appearance of the $\tilde{v}_{asym}(MoO_2)$ and $\tilde{v}_{sym}(MoO_2)$ around 930 cm⁻¹ and 895 cm⁻¹, respectively, and by absence of the band indicative of metal-oxygen bridging [9-11, 20].

The stretching frequencies found at about 1545 cm⁻¹ and two strong bands at about 1595 and 1575 cm⁻¹ were attributed to C–O_{phenolic} and C=N, respectively. The remaining frequencies in the IR spectra were due to the vibrations within the ligand.

Thermal Analyses

Upon heating of the $[Mo_2^{V}O_3L_2]$ complexes in the atmosphere of pure oxygen weight gain occurred [in the range 173-200 °C (2); 195-201 °C (3); 174-192 °C (4); 192-198 °C (5); 173-199 °C (6)], that was related to the oxidation of molybdenum and formation of the molybdenum(VI) thiosemicarbazonato complexes. This thermal oxidation was followed on further heating by significant weight losses [in the range 237-460 °C (1); 248-569 °C (2); 228-540 °C (3); 219-499 °C (4); 206-555 °C (5); 247-569 °C (6)] that were indicative of complex decomposition resulting in the solid residue identified as MoO₃. The first step in the thermogravimetric curve of the $[Mo_2O_3{C_6H_4(O)CH:NN:C(S)NHC_6H_5}_2] \cdot CH_3CN$ (3)(weight loss within the range 60-170 °C) was related to the loss of solvent of crystallization. The other complexes were unsolvated or they were loosing their molecules of crystallization already at room temperature.

| Bond lengths /Å | | | Bond angles / ° | | |
|-----------------|------------|------------|-----------------|------------|------------|
| | x = 1 | x = 2 | | x = 1 | x = 2 |
| Mox - Sx | 2.3560(14) | 2.3573(14) | Sx-Mox-O1x | 139.48(10) | 137.02(12) |
| Mox - O1x | 1.977(3) | 1.964(3) | Sx-Mox-O2x | 107.07(11) | 109.35(14) |
| Mox - O2x | 1.669(3) | 1.683(4) | Sx-Mox-O3x | 89.15(10) | 88.70(10) |
| Mox - O3x | 1.851(4) | 1.872(4) | Sx-Mox-N1x | 78.22(12) | 78.07(12) |
| Mox - N1x | 2.140(4) | 2.146(4) | O1x - Mox - O2x | 112.15(14) | 112.39(18) |
| Sx - C3x | 1.753(5) | 1.767(5) | O1x - Mox - O3x | 87.93(14) | 87.16(14) |
| O1x - C5x | 1.342(6) | 1.351(6) | O1x - Mox - N1x | 84.33(15) | 83.91(16) |
| N1x - N2x | 1.401(6) | 1.395(6) | O2x - Mox - O3x | 108.48(17) | 109.13(18) |
| N1x - C1x | 1.311(7) | 1.296(7) | O2x - Mox - N1x | 101.55(16) | 101.75(17) |
| N2x-C3x | 1.319(7) | 1.316(7) | O3x - Mox - N1x | 149.72(16) | 148.97(16) |
| N4x - C3x | 1.361(7) | 1.341(7) | Mo1-O3-Mo2 | | 177.7(2) |
| N4x - C15x | 1.422(7) | 1.408(6) | | | |

Table 1. Selected bond lengths and angles for 3.

 Table 2. Hydrogen bonding arrangement in 3.

| D-H···· A | d(D-H)/Å | $d(\operatorname{H} \cdot \cdot \cdot A) / \operatorname{\AA}$ | $d(D \cdot \cdot \cdot A) / \mathring{A}$ | $\angle (D - \mathbf{H} \cdot \cdot \cdot A) /^{\circ}$ |
|-----------------------------|----------|--|---|---|
| N41-H41N····N5 | 0.88(3) | 2.13(3) | 3.006(7) | 172(4) |
| N42-H42N···O21 ⁱ | 0.85(3) | 2.23(4) | 3.017(5) | 153(4) |

Symmetry code: (i) -x, 2 - y, -z.

Crystal Structure of 3

An ORTEP plot of the asymmetric unit of **3** is shown in Figure 2 and the selected geometrical parameters are presented in Table 1. In compound **3**, molecules of the dinuclear molybdenum(V) complex $[Mo_2O_3\{C_6H_4(O)-CH:NNC(S)NHC_6H_5\}_2]$ co-crystallize with molecules of acetonitrile.



Figure 2. An asymmetric unit of 3 with the numbering scheme and displacement ellipsoids drawn at the 50 % probability level. A molecule of acetonitrile is connected to molecule of the dinuclear complex by the hydrogen bond represented by the dashed line.

The complex consists of an *anti*-Mo₂O₃⁴⁺ core with an oxo-bridge being almost linear $[\angle (Mo1-O3-Mo2) = 177.7(2)^{\circ}]$, but slightly asymmetrical [d(Mo1-O3) = 1.851(4) Å and d(Mo2-O3) = 1.872(4) Å]. Each Mo^V is coordinated by a bridging (O3) and one terminal (O2*x*; *x* = 1 or 2) oxo group and by the tridentate doubly deprotonated salicylaldehyde 4-phenylthiosemicarbazone ligand

 (H_2L^3) bonded through an oxygen atom (O1x) from the deprotonated phenolic group, imine nitrogen atom (N1x), and sulfur atom (Sx) from the deprotonated thiol group (Figure 2). The two thiosemicarbazonato ligands are bound in a quasi-centrosymmetrical mode regarding the bridging oxo group and each of them forms a five- and six-membered chelate ring with the Mo^V atom. The coordination arrangement around Mo^V is distorted tetragonal-pyramidal with the terminal oxo group in the apical position and with the other coordinating atoms defining the basal plane of the pyramid { $\tau_1 = 0.17$ and $\tau_2 = 0.20$; $\tau_x =$ $|\angle(Sx-Mox-O1x) - \angle(O3-Mox-N1x)|/60^{\circ}$ [21]}. The maximum deviation from the least-squares plane defined by Sx, N1x, O1x, O3 in both parts is that of O1x being 0.114(3) Å for x = 1 and 0.128(4) Å for x = 2. Mo1 and Mo2 are moved out of the corresponding basal plane by 0.6210(5) Å and 0.6505(5) Å, respectively. The molybdenum-donor bond lengths are similar to those observed for this type of complexes [15, 22].

Each thiosemicarbazonato ligand consists of three (nearly) planar parts: salicyl (atoms C1x, C5x-C10x and O1x), thiosemicarbazonyl (Sx, N1x, N2x, C3x and N4x) and N-phenyl (C15x-C20x) moiety. Dihedral angles between the least-squares planes of the salicyl and the thiosemicarbazonyl moieties are 5.14(18)° and 3.44(18)° for the ligand molecules bound to Mo1 and Mo2, respectively, thus allowing a high degree of π -electron delocalization throughout these parts (as observed in the values of bond lengths). Whereas the N-phenyl part in the ligand molecule coordinating Mo2 is basically coplanar with the thiosemicarbazonyl moiety [dihedral angle between the least-squares planes is $1.8(2)^{\circ}$ and thus extending the delocalized π -electron system, in the other ligand the N-phenyl moiety is inclined by 21.7(3)° in respect to the thiosemicarbazonyl part, so the π -electron delocalization between these two moieties

is slightly interrupted (cf. N4*x*-C3*x* bond lengths; Table 1). In contrast to the crystal structure of salicylaldehyde 4phenylthiosemicarbazone [23], in which molecules of the free ligand (three per asymmetric unit) are found in the thioketo tautomeric form with C=S distances in the range 1.662(3)-1.680(2) Å and C-N(amino) distances ranging from 1.347(3) to 1.356(3) Å, the analogous C3*x*-S*x* distances in **3** are much longer [1.753(5) and 1.767(5) Å], whereas C3*x*-N2*x* are shorter [1.319(7) and 1.316(7) Å] as consistent with the thiolate form. In comparison to the free thiosemicarbazone ligand [23], the formally double bonds in the bound ligand in **3** are significantly elongated, whereas the formally single bonds are significantly shortened thus suggesting a higher degree of π -electron delocalization in the complex.

In the crystal structure of **3**, a molecule of acetonitrile is bonded to a molecule of the dinuclear complex by the N41-H41N····N5 hydrogen bond (Figure 2; Table 2). Two molecules of the complex are mutually connected by N42-H42N····O21 (-x, 2-y, -z) hydrogen bonds (Figure 3; Table 2) thus forming a centrosymmetrical dimer and a ring described by a graph-set notation as $R_2^2(16)$.

NMR Spectroscopy

Assignments of proton and carbon chemical shifts in $[D_6]DMSO$ were made by using standard one- (¹H and APT) and two-dimensional (COSY, HMQC and HMBC) NMR experiments. Chemical shifts of the ligands $H_2L^{1}-H_2L^{6}$ (Scheme 2) as well as their Mo^V complexes 1-6 are given in Table 3 and Table 4.

The ¹H and ¹³C chemical shift values are similar to those previously reported for the related ligands and their Mo^{VI} complexes [10, 11, 24]. A relatively broad OH resonance was observed for all ligands at approximately 10 ppm, re-



Figure 3. The crystal packing in **3**. Hydrogen atoms bound to carbon atoms are omitted for clarity. Hydrogen bonds are shown by the dashed lines. Symmetry code: (i) -x, 2-y, -z.

flecting intramolecular hydrogen bonding interactions that was consistent with the previous results. According to the chemical shifts, all ligands exist in the hydroxy-thione tautomeric form in $[D_6]DMSO$ as found in the solid state.

The absence of OH and NH-2 protons observed for compounds 1-6 corroborates the formation of complexes. As a consequence, the NH-4 protons experience an up-field shift of approximately 1 ppm. The coordination-induced chemical shifts are more profound for carbon atoms. The largest change was observed for carbons C-1, C-3 being the two most effected interacting sites. These effects are down-field (up to 14.55 ppm) for the former and up-field (up to 15.32 ppm) for the later site. The observed shielding and deshielding effects are a consequence of electron redistribution upon complexation. The total effect at C-3 is a superposition of a coordination-induced effect and the formation of an imine instead of a thiocarbonyl bond.



Scheme 2.

| | H_2L^1 | | 1 | | $H_2L^2 *$ | | 2 | | $H_2L^3 *$ | | 3 | |
|------|----------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|
| atom | ¹ H | ¹³ C | $^{1}\mathrm{H}$ | ¹³ C |
| 1 | 8.39 | 139.55 | 8.45 | 150.82 | 8.37 | 139.09 | 8.57 | 151.68 | 8.48 | 139.95 | 8.81 | 154.50 |
| 2 | 11.39 | _ | _ | _ | 11.47 | _ | _ | _ | 11.75 | _ | _ | _ |
| 3 | _ | 177.56 | _ | 166.18 | _ | 177.68 | _ | 164.60 | _ | 175.61 | _ | 161.08 |
| 4 | 8.17 / 7.92 | _ | 7.14 | _ | 8.42 | _ | 7.45 | _ | 10.03 | _ | 9.69 | _ |
| 5 | _ | 156.28 | _ | 158.82 | _ | 156.46 | _ | 158.67 | _ | 156.49 | _ | 158.83 |
| 6 | 6.88 | 115.92 | 6.85 | 118.00 | 6.87 | 116.16 | 6.85 | 118.01 | 6.88 | 115.92 | 6.87 | 117.98 |
| 7 | 7.22 | 130.97 | 7.40 | 133.27 | 7.22 | 131.09 | 7.41 | 133.31 | 7.23 | 131.20 | 7.47 | 133.95 |
| 8 | 6.83 | 119.15 | 6.98 | 120.84 | 6.83 | 119.32 | 6.98 | 120.83 | 6.84 | 119.10 | 7.03 | 120.85 |
| 9 | 7.92 | 126.65 | 7.58 | 133.48 | 7.95 | 126.72 | 7.60 | 133.52 | 8.08 | 129.96 | 7.69 | 133.95 |
| 10 | _ | 120.22 | _ | 121.22 | _ | 120.62 | _ | 121.19 | _ | 120.15 | _ | 120.69 |
| 11 | | | | | 3.01 | 30.96 | 2.81 | 30.89 | _ | 139.04 | _ | 140.52 |
| 12 | | | | | | | | | 7.57 | 125.56 | 7.75 | 119.64 |
| 13 | | | | | | | | | 7.36 | 127.90 | 7.31 | 128.54 |
| 14 | | | | | | | | | 7.19 | 125.04 | 7.01 | 122.35 |
| 15 | | | | | | | | | 7.36 | 127.90 | 7.31 | 128.54 |
| 16 | | | | | | | | | 7.57 | 125.56 | 7.75 | 119.64 |
| OH | 9.88 | _ | _ | _ | 9.87 | _ | _ | _ | 9.96 | _ | _ | _ |

Table 3. ¹H and ¹³C chemical shifts /ppm of ligands $H_2L^1-H_2L^3$ and their molybdenum(V) complexes 1–3.

* The ¹H and ¹³C chemical shift values for H_2L^2 and H_2L^3 are taken from ref. [11] and [24], respectively.

Table 4. ¹H and ¹³C chemical shifts /ppm of ligands $H_2L^4 - H_2L^6$ and their molybdenum(V) complexes 4–6.

| | H_2L^4 | | 4 | | H_2L^5 | | 5 | | $H_{2}L^{6} *$ | | 6 | |
|------|------------------|-----------------|------------------|-----------------|----------------|-----------------|------------------|-----------------|------------------|-----------------|------------------|-----------------|
| atom | $^{1}\mathrm{H}$ | ¹³ C | $^{1}\mathrm{H}$ | ¹³ C | ¹ H | ¹³ C | $^{1}\mathrm{H}$ | ¹³ C | $^{1}\mathrm{H}$ | ¹³ C | $^{1}\mathrm{H}$ | ¹³ C |
| 1 | 9.05 | 143.18 | 9.26 | 146.09 | 9.05 | 142.59 | 9.31 | 147.00 | 9.20 | 143.65 | 9.59 | 150.11 |
| 2 | 11.39 | — | _ | _ | 11.40 | _ | _ | — | 11.79 | _ | _ | - |
| 3 | _ | 178.20 | _ | 165.64 | _ | 177.28 | _ | 164.45 | _ | 175.85 | _ | 160.53 |
| 4 | 8.21 | _ | 7.22 | _ | 8.34 | _ | 7.49 | _ | 10.11 | _ | 9.71 | _ |
| 5 | _ | 156.75 | _ | 159.46 | _ | 156.24 | _ | 159.33 | _ | 156.78 | _ | 159.98 |
| 6 | 7.20 | 118.49 | 7.14 | 119.81 | 7.21 | 118.29 | 7.14 | 119.87 | 7.25 | 118.63 | 7.19 | 119.36 |
| 7 | 7.88 | 132.62 | 8.00 | 133.67 | 7.89 | 132.25 | 7.99 | 133.74 | 7.92 | 132.73 | 8.05 | 134.76 |
| 8 | - | 128.21 | _ | 128.53 | - | 128.01 | _ | 128.56 | _ | 128.19 | _ | 128.62 |
| 9 | 7.85 | 128.82 | 7.91 | 128.55 | 7.86 | 128.61 | 7.91 | 128.85 | 7.87 | 128.87 | 7.93 | 128.95 |
| 10 | 7.38 | 123.54 | 7.45 | 124.08 | 7.39 | 123.38 | 7.45 | 1224.11 | 7.39 | 123.62 | 7.46 | 124.35 |
| 11 | 7.56 | 128.02 | 7.60 | 127.99 | 7.57 | 127.74 | 7.60 | 128.00 | 7.60 | 127.95 | 7.65 | 128.19 |
| 12 | 8.51 | 123.59 | 8.26 | 121.13 | 8.45 | 122.58 | 8.30 | 121.29 | 8.51 | 122.62 | 8.45 | 121.59 |
| 13 | _ | 131.66 | _ | 132.02 | _ | 131.50 | _ | 132.08 | _ | 131.76 | _ | 132.33 |
| 14 | - | 110.10 | _ | 112.02 | - | 109.74 | _ | 112.11 | _ | 109.83 | _ | 111.98 |
| 15 | | | | | 3.04 | 31.15 | 2.88 | 30.82 | _ | 139.32 | _ | 140.63 |
| 16 | | | | | | | | | 7.62 | 125.22 | 7.88 | 119.76 |
| 17 | | | | | | | | | 7.41 | 128.33 | 7.36 | 128.69 |
| 18 | | | | | | | | | 7.21 | 125.22 | 7.03 | 122.36 |
| 19 | | | | | | | | | 7.41 | 128.33 | 7.36 | 128.69 |
| 20 | | | | | | | | | 7.62 | 125.22 | 7.88 | 119.76 |
| OH | 10.49 | _ | _ | _ | 10.51 | _ | _ | _ | 10.68 | _ | _ | _ |

* The ¹H and ¹³C chemical shift values for H_2L^6 are taken from ref. [10].

Experimental Section

Thiosemicarbazones $H_2L^1-H_2L^6$ were prepared analogously to the procedure described by *Purohit* et al. [20]. The starting complex $[Mo_2O_3(acac)_4]$ was prepared as described in the literature [25, 26]. The $[MoO_2L]_n$ complexes (1a-6a) were synthesized by the reaction of $[MoO_2(acac)_2]$ with the appropriate ligands H_2L in acetonitrile, or by dissolving of $[MoO_2L(CH_3OH)]$ in acetonitrile [9, 11, 18]. Acetonitrile was dried with P_2O_5 .

C, H, N and S analyses were provided by the Analytical Services Laboratory of Rudjer Bošković Institute, Zagreb. Infrared spectra were recorded in KBr with the Perkin–Elmer 502 spectrophotometer in the 4500-450 cm⁻¹ region. Thermogravimetric (TG)

analyses were measured with a Mettler TG 50 thermobalance using aluminum crucibles under oxygen atmosphere within the temperature range from 25 to 600 °C. All experiments were recorded with a heating rate of 5 °C min⁻¹ in a dynamic atmosphere with a flow rate of 200 cm³ min⁻¹. The results were developed by applying the Mettler STAR° 6.1 program. EPR spectra were measured at 293 K with a Varian E-109 spectrometer operating at 100 kHz modulation, equipped with dual sample cavity. As a *g*-factor standard 2,2-diphenyl-1-picrylhydrazyl (DPPH, *g* = 2.0036) was used. X-ray diffraction powder data were obtained using Cu- K_{α} radiation ($\lambda = 1.5406$ Å) with a Philips X^{PERT} PW 3710 diffractometer. Data were collected in the 5 < 2 θ < 70° range, in the θ -2 θ step scan mode with $\Delta 2\theta = 0.02^{\circ}$ and t = 12 s.



Synthesis of the Molybdenum(V) Complexes $[Mo_2O_3L_2]$

All syntheses were performed under dry argon atmosphere by the following methods:

Method A. $[MoO_2L]_n$ (0.25 mmol) was suspended in dry acetonitrile and PPh₃ (0.1 g, 0.38 mmol) was added. The solution was warmed up for 5 h during which a dark red-brown microcrystalline product deposited. It was collected by filtration, washed with acetonitrile and dried.

Method B. $[Mo_2O_3(acac)_4]$ (0.15 mmol) was dissolved in dry acetonitrile (25 mL) and appropriate thiosemicarbazone ligand H_2L (0.3 mmol) was added. The mixture was warmed for 5 h. A dark red-brown product obtained from the solution was filtered off, washed with acetonitrile and dried.

Synthesis of $[Mo_2O_3\{C_6H_4(O)CH:NN:C(S)NH_2\}_2]$ (1)

Yield: 0.05 g, 20 % (*method A*, obtained from **1a**). Yield: 0.06 g, 43 % (*method B*, obtained from the reaction of $[Mo_2O_3(acac)_4]$ with **H₂L¹**). C₁₆H₁₄Mo₂N₆O₅S₂ ($M_r = 626.331$): C 30.68; H 2.25; N 13.42; S 10.24; Found: C 30.25; H 2.44; N 13.28; S 10.13. TG: 46.01 % MoO₃ (calcd. 45.96 %). Selected IR data: $\tilde{v} = 1601, 1582$ (C=N), 1546 (C-O), 962 (Mo = O), 760 (Mo-O-Mo) cm⁻¹.

Synthesis of $[Mo_2O_3\{C_6H_4(0)CH:NN:C(S)NHCH_3\}_2]$ (2)

Yield: 0.07 g, 42 % (*method A*, obtained from **2a**). Yield: 0.07 g, 66 % (*method B*, obtained from the reaction of $[Mo_2O_3(acac)_4]$ with H_2L^2). $C_{18}H_{18}Mo_2N_6O_5S_2$ (M_r = 654.381): C 33.04; H 2.77; N 12.84; S 9.80; Found: C 33.28; H 2.25; N 13.38; S 10.24. TG: 43.59 % MoO_3 (calcd. 43.99 %). Selected IR data: \tilde{v} = 1598, 1580 (C=N), 1548 (C-O), 972 (Mo=O), 763 (Mo-O-Mo) cm⁻¹.

Synthesis of

$[Mo_2O_3\{C_6H_4(O)CH:NN:C(S)NHC_6H_5\}_2] \cdot CH_3CN(3)$

Yield: 0.06 g, 31 % (*method A*, obtained from **3a**). Yield: 0.084 g, 73 % (*method B*, obtained from the reaction of $[Mo_2O_3(acac)_4]$ with **H₂L³**). C₃₀H₂₅Mo₂N₇O₅S₂ ($M_r = 819.57$): C 43.96; H 3.07; N 11.96; S 7.83. Found: C 43.40; H 2.85; N 11.79; S 8.24. TG: 4.79 % CH₃CN (calcd. 5.01 %); 34.98 % MoO₃ (calcd. 35.13 %). Selected IR data: $\tilde{\nu} = 1599$, 1579 (C=N), 1543 (C-O), 967 (Mo=O), 755 (Mo-O-Mo) cm⁻¹.

Synthesis of $[Mo_2O_3\{C_{10}H_6(0)CH:NN:C(S)NH_2\}_2]$ (4)

Yield: 0.09, 47 % (*method A*, obtained from **4a**). Yield: 0.04 g, 36 % (*method B*, obtained from the reaction of $[Mo_2O_3(acac)_4]$ with H_2L^4). $C_{24}H_{18}Mo_2N_6O_5S_2$ ($M_r = 726.449$): C 39.68; H 2.50; N 11.57; S 8.83; Found: C 39.20; H 2.75; N 11.39; S 8.45. TG: 39.38 % MoO_3 (calcd. 39.63 %). Selected IR data: $\tilde{v} = 1594$, 1575 (C=N), 1543 (C-O), 959 (Mo = O), 746 (Mo-O-Mo) cm⁻¹.

Synthesis of $[Mo_2O_3\{C_{10}H_6(O)CH:NN:C(S)NHCH_3\}_2]$ (5)

Yield: 0.08 g, 43 % (*method A*, obtained from **5a**). Yield: 0.07 g, 62 % (*method B*, obtained from the reaction of $[Mo_2O_3(acac)_4]$ with

 $\begin{array}{l} \textbf{H_2L^5}\text{). } C_{26}\textbf{H}_{22}\textbf{Mo}_2N_6\textbf{O}_5\textbf{S}_2 \ (\textit{M}_r = 754.502)\text{: } C \ 41.39\text{; } H \ 2.94\text{; } N \\ 11.14\text{; } S \ 8.50\text{; } Found\text{: } C \ 41.18\text{; } H \ 2.85\text{; } N \ 11.29\text{; } S \ 8.31\text{. } TG\text{: } 37.89 \ \% \\ \textbf{MoO}_3 \ (\text{Calcd. } 38.15 \ \%)\text{. } \text{Selected IR } \text{data: } \tilde{\nu} = 1594\text{, } 1575 \ (\text{C=N})\text{, } \\ 1547 \ (\text{C-O})\text{, } 959 \ (\text{Mo} = \text{O})\text{, } 747 \ (\text{Mo-O-Mo}) \ \text{cm}^{-1}\text{.} \end{array}$

Synthesis of $[Mo_2O_3\{C_{10}H_6(O)CH:NN:C(S)NHC_6H_5\}_2]$ (6)

Yield: 0.09 g, 42 % (*method A*, obtained from **6a**). Yield: 0.07 g, 51 % (*method B*, obtained from the reaction of $[Mo_2O_3(acac)_4]$ with H_2L^6). $C_{36}H_{26}Mo_2N_6O_5S_2$ ($M_r = 878.64$): C 49.21; H 2.98; N 9.56; S 7.30, Found: C 49.58; H 2.96; N 10.07; S 7.11. TG: 32.28 % MoO_3 (Calcd. 32.76 %). Selected IR data: $\tilde{v} = 1593$, 1573 (C=N), 1540 (C-O), 959 (Mo = O), 752 (Mo-O-Mo) cm⁻¹.

Single-Crystal X-ray Structural Analysis

The X-ray diffraction data from the single crystal of 3 were collected at 295(2) K with the Oxford Diffraction Xcalibur 3 CCD diffractometer with graphite-monochromated Mo- K_{α} radiation $(\lambda = 0.71073 \text{ Å})$. Crystallographic data for 3: C₃₀H₂₅Mo₂N₇O₅S₂, $M_{\rm r} = 819.57$, red plate, $0.40 \times 0.06 \times 0.02$ mm, triclinic, $P\bar{1}$ (no. 2), a = 10.0221(12) Å, b = 12.2577(12) Å, c = 14.1225(13) Å, $\alpha =$ 74.333(8)°, $\beta = 83.969(9)°$, $\gamma = 77.162(10)°$, $V = 1626.8(3) \text{ Å}^3$, Z =2, $D_{\text{calc}} = 1.673 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 0.950 \text{ mm}^{-1}$, $\theta_{\text{max}} = 25.0^{\circ}$, 13939 measured reflections, 5637 unique reflections, $-11 \le h \le 11, -14$ $\leq k \leq 14, -16 \leq l \leq 16, 3359$ reflections with $I > 2\sigma(I), 422$ parameters refined, $R_1 = 0.0425 [I > 2\sigma(I)]$ and 0.0869 (all data), $wR_2 = 0.0895 [I > 2\sigma(I)]$ and 0.1031 (all data), S = 0.925, the largest difference peak and hole 1.40 and $-0.49 \text{ e}\cdot\text{\AA}^{-3}$. The data reduction (including the multi-scan absorption correction: $T_{\min} =$ 0.690, $T_{\text{max}} = 0.981$) was performed using the CrysAlis software package [27]. Solution, refinement and analysis of the structure were done using the programs integrated in WinGX system [28]. The structures were solved by the direct methods (SHELXS) [29] and refined by the full-matrix least-squares method based on F^2 against all reflections (SHELXL-97) [30]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier maps; those bound to nitrogen atoms were refined using restraints on the N-H distances, whereas others were refined using the riding model. All hydrogen atoms were assigned isotropic thermal parameters, $U_{iso}(H) = 1.2U_{eq}$ (parent atom). Geometrical calculations were performed using PLATON [31] and the structural figures were made using PLATON and ORTEP-3 [32].

NMR Spectroscopy

One- and two-dimensional (¹H, APT, gCOSY, gHSQC and gHMBC) NMR spectra were recorded at ambient temperature with the Avance DRX500 spectrometer using a 5 mm diameter inverse detection probe with *z*-gradient. The spectra were recorded in $[D_6]DMSO$ and $CDCl_3$ with the sample concentration of 20 mg mL⁻¹ and TMS as the internal standard.

Typical spectral conditions for one-dimensional ¹H and ¹³C (APT) spectra were as follows. The spectra were recorded using 64K data points and spectral widths of 6200 Hz and 20000 Hz for proton and carbon (APT) experiments, respectively. Digital resolution was 0.10 Hz and 0.30 Hz per point, respectively. The number of scans was 8-16 for ¹H and 1000-3000 for APT spectra.

2D gradient selected COSY spectra were acquired with a sweep width of 6000 Hz in both dimensions into 2 K data points with 256 increments. Spectra were zero-filled in the fl dimension to 1 K and processed using an unshifted sine bell window function. Digital resolution was 3.91 Hz per point in both dimensions.

The gradient selected inverse ${}^{1}H{-}{}^{13}C$ correlation experiments, gHSQC and gHMBC were recorded at 125.77 MHz using the acquisition matrix of 1 K x 256 with 32 scans and processed with 2 K × 1 K transformed matrix. The sweep width was 7500 Hz in f2 dimension and 31500 Hz in f1 dimension for both experiments. Spectra were processed with a shifted sine bell window function and linear prediction. Digital resolution was 3.25 Hz per point and 30.70 Hz per point in f2 and f1, respectively. HMBC spectra were recorded using transfer delay for the evolution of long range C–H couplings of 60 ms.

CCDC-683830 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre by www.ccdc.cam.ac.uk/ data_request/cif.

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