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Complexes with *cis*-MoO₂ unit of new isothiosemicarbazone

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A new 5-bromo-2-hydroxobenzaldehyde *S*-ethylisothiosemicarbazone hydroiodide free Schiff base (H₂L) is synthesized and a series of molybdenum(VI) complexes, Mo^{IV}O₂LD, have prepared where D can be DMF, DMSO and pyridine. The compounds are characterized with molar conductance, FT-IR, ¹H NMR, elemental analyses, and UV-Vis techniques. Structures of complexes are determined with X-ray analysis. All experimental results confirmed that H₂L is a tridentate bi-deprotonated ligand (ONN), coordinating through phenolic oxygen, azomethine nitrogen, and isothioamide nitrogen. The neutral complexes are distorted octahedral.

Keywords: Isothiosemicarbazone; Molybdenum(VI) complex; *cis*-MoO₂; Spectral study; Crystal structure

1. Introduction

Isothiosemicarbazides (ITSC) were first reported by Freund *et al.* in 1901 [1]. ITSC and its Schiff bases have been used as ligands for preparation of transition metal complexes [2, 3]. Derivatives of the salicylaldehyde *S*-alkyl-isothiosemicarbazone can be tridentate ONN-chelating agents *via* phenyl oxygen, imino nitrogen and isothioamide nitrogen as a doubly negative ligand [4, 5]. Coordination chemistry of molybdenum(VI) has relevance to several biological systems as an active site [6–10]. Molybdenum as a trace element is present in several oxidation states. Mo⁶⁺ is stabilized through formation of MoO₂²⁺ [11]. An important characteristic of coordination compounds containing MoO₂²⁺ is their ability to participate in reversible oxo-transfer reactions in aqueous aerobic media for nitrogenase, aldehyde oxidase, xanthine dehydrogenase, nitrate reductase, etc. [12–17]. This property has made them popular as oxidase or reductase catalyzers in industrial and biochemical process. Oxygen transfer reactions are

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catalyzed by Mo(VI)-cofactor-containing enzymes in many organisms and occur in DMSO reductase, sulfite oxidase, nitrate reductase, and aldehyde oxidoreductase reactions [18–20]. Synthesis and characterization of molybdenum(VI) compounds are important because they are relevant in industrial and biological research. We present here the results of the synthesis and characterization of 5-bromo-2-hydroxobenzaldehyde *S*-ethylisothiosemicarbazone hydroiodide (H_2L) as a new Schiff base and its MoO_2LD ($D = DMF, DMSO, \text{ and pyridine}$) complexes.

2. Experimental

2.1. Materials and instrumentation

All chemicals were of AR grade and obtained from commercial sources, unless otherwise specified. Elemental analyses (C, H, and N) were performed with a Thermo Finnigan Flash Elemental Analyzer 1112EA. Molar conductances of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ MeOH solutions of the complexes were measured with a Metrohm 712 Conductometer. IR spectra were obtained with a FT-IR 8400-SHIMADZU spectrophotometer using KBr pellets ($4000\text{--}400 \text{ cm}^{-1}$). ^1H NMR spectra in $DMSO\text{-}d_6$ were run on a Bruker BRX 100 AVANCE spectrometer. Electronic spectra were recorded in MeOH with a SHIMADZU model 2550 UV-Vis spectrophotometer (200–1100 nm).

2.2. Preparation of 5-bromo-2-hydroxobenzaldehyde *S*-ethylisothiosemicarbazone hydroiodide (H_2L)

A hot ethanolic solution (10 mL) of thiosemicarbazide (1.82 g, 20 mmol) was reacted with 5 mL hot solution of ethyl iodide (3.43 g, 22 mmol). The mixture was refluxed for 1 h at 90°C . Then, 5-bromo-2-hydroxobenzaldehyde (4.02 g, 20 mmol) was added and reflux continued for one more hour at the same temperature. A yellow precipitate separated, was filtered off, washed several times with cold ethanol and dried *in vacuo* over $CaCl_2$. Yield: 3.76 g, 75%; m.p.: 190°C . Anal. Calcd for $C_{10}H_{13}BrIN_3OS$ ($430.10 \text{ g mol}^{-1}$): C, 27.93; H, 3.05; N, 9.77. Found (%): C, 27.69; H, 3.08; N, 9.71. IR (KBr), cm^{-1} : $\nu_{as}(\text{NH}_2)$ 3267s; $\nu_s(\text{NH}_2)$ 3167s; $\nu(\text{O-H})$ 3105s; $\nu(\text{C-H})$ 2962, 2931, 2831m; $\nu(\text{C=N}) + \nu(\text{C=C}) + \delta(\text{NH}_2)$ 1624vs, 1586m, 1551s; $\nu(\text{C-O})$ 1176m; $\nu(\text{N-N})$ 1049m; $\delta_{\text{opb}}(\text{ring})$ 698. ^1H NMR (100 MHz, $DMSO\text{-}d_6$): $\delta = 11.4$ (s, 1H, $O^1\text{H}$; exchanges with D_2O), 9.7 (s, 2H, $N3H_2$; exchanges with D_2O), 8.6 (s, 1H, $C7\text{H}$), 8.3 (s, 1H, $C5$), 7.4 (dd, 1H, $C3$), 6.9 (d, 1H, $C2$), 3.2 (q, 2H, $C9$), 1.3 (t, 3H, $C10$). UV-Vis (methanol), λ_{max} , nm ($\log \epsilon$, $\text{L mol}^{-1} \text{ cm}^{-1}$): 224 (4.86), 292 (4.66), 340 (4.62).

2.3. Synthesis methods of complexes

2.3.1. *cis*-Dioxo-dimethylformamide-(5-bromo-2-hydroxobenzaldehyde *S*-ethylisothiosemicarbazonato-(N,N',O)molybdenum(VI) (I). Ethanolic solution (2 mL) of molybdenyl acetylacetonate (96 mg, 0.036 mmol) was added dropwise to 3 mL ethanolic solution of 5-bromo-2-hydroxobenzaldehyde *S*-ethylisothiosemicarbazone hydroiodide (150 mg, 0.036 mmol) under stirring. The clear solution was stirred about 1 h and yellow

precipitate appeared. The product was then filtered and washed with cold ethanol, and dried in air. The resulting compound was dissolved in 2 mL DMF and by slow evaporation of the solvent, red crystals of **1** appeared after 1 week. Yield: 83 mg, 74%; m.p.: 140°C decomposition. Molar conductivity (1.0×10^{-3} mol L⁻¹; methanol): $5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calcd for C₁₃H₁₇BrMoN₄O₄S (501.23 g mol⁻¹): C, 31.15; H, 3.42; N, 11.18. Found (%): C, 31.04; H, 3.44; N, 11.07. IR (KBr), cm⁻¹: $\nu(\text{N-H})$ 3321m; $\nu(\text{CH})_{\text{aromatic}} + \nu(\text{CH})_{\text{ethyl}}$ 2896–2962; $\nu(\text{C=C})_{\text{allyl}}$ 1640w; $\nu(\text{C=O})$ 1655vs; $\nu(\text{C=N})$ 1601vs; $\nu(\text{C=C})_{\text{aromatic}}$ 1539m; $\nu(\text{C-N})_{\text{DMF}}$ 1334vs; $\nu(\text{C-O})$ 1111m; $\nu(\text{N-N})$ 1022w; $\nu_{\text{s}}(\text{Mo=O})$ 933vs; $\nu_{\text{as}}(\text{Mo=O})$ 899vs; $\delta(\text{C-H})_{\text{opb}}$ 702w. ¹H NMR (100 MHz, DMSO-d₆): δ = 9.4 (s, 1H, N3H; exchanges with D₂O), 8.5 (s, 1H, C7H), 8.0 (s, 1H, C5), 7.75 (dd, 1H, C3), 6.9 (d, 1H, C2), 3.6 (s, 1H, C11H), 3.2 (q, 2H, C9), 3.0 (m, 6H, C12, C13), 1.3 (t, 3H, C10). UV-Vis (methanol), λ_{max} , nm (log ϵ , L mol⁻¹ cm⁻¹): 226 (4.44), 240 (4.42), 298 (4.30), 332 (4.14)sh, 398 (3.62), 432 (3.61)sh.

2.3.2. cis-Dioxo-dimethylsulfoxide-(5-bromo-2-hydroxobenzaldehyde S-ethylisothiosemicarbazonato-(N,N',O)-molybdenum(VI) (2). Compound **2** was prepared in a similar method as for **1**, but DMSO was used instead of DMF. The product was crystallized after 1 week and red crystals were obtained. Yield: 94 mg, 84%; m.p.: 180°C (dec). Molar conductivity (1.0×10^{-3} mol L⁻¹; methanol): $6.7 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calcd for C₁₂H₁₆BrMoN₃O₄S₂ (506.27 g mol⁻¹): C, 28.47; H, 3.19; N, 8.30. Found (%): C, 28.38; H, 3.22; N, 8.21. IR (KBr) cm⁻¹: $\nu(\text{N-H})$ 3282m; $\nu(\text{CH})_{\text{aromatic}} + \nu(\text{CH})_{\text{ethyl}}$ 2866–2966; $\nu(\text{C=C})_{\text{allyl}}$ 1640w; $\nu(\text{C=N})$ 1600vs; $\nu(\text{C=C})_{\text{aromatic}}$ 1539m; $\nu(\text{C-O})$ 1130m; $\nu(\text{N-N})$ 1018w; $\nu(\text{S=O})$ 1006s; $\nu_{\text{s}}(\text{Mo=O})$ 930vs; $\nu_{\text{as}}(\text{Mo=O})$ 887vs; $\delta(\text{C-H})_{\text{opb}}$ 702w. ¹H NMR (100 MHz, DMSO-d₆): δ = 9.3 (s, 1H, N3H; exchanges with D₂O), 8.5 (s, 1H, C7H), 7.8 (s, 1H, C5), 7.5 (dd, 1H, C3), 6.7 (d, 1H, C2), 3.4 (s, 6H, C11, C12), 3.0 (q, 2H, C9), 1.3 (t, 3H, C10). UV-Vis (methanol), λ_{max} , nm (log ϵ , L mol⁻¹ cm⁻¹): 228 (4.62), 248 (4.60), 300 (4.47), 338 (4.28)sh, 402 (3.82), 444 (3.61)sh.

2.3.3. cis-Dioxo-(5-bromo-2-hydroxobenzaldehyde S-ethylisothiosemicarbazonato-(N,N',O)-pyridine-molybdenum(VI) (3). A solution of molybdenyl acetylacetonate (39 mg, 0.012 mmol) in 2 mL of methanol was added dropwise to 3 mL methanol solution containing H₂L (52 mg, 0.012 mmol). The mixture was stirred for 30 min and 1 mL pyridine was then added to the solution and stirring was continued for 1 h. On standing one week, the clear solution yielded red crystals which were filtered, washed with cold ethanol, and dried in air. Yield: 32 mg, 54%; m.p.: 153°C (dec). Molar conductivity (1.0×10^{-3} mol L⁻¹; methanol): $7 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. Anal. Calcd for C₁₅H₁₅BrMoN₄O₃S (507.23 g mol⁻¹): C, 35.52; H, 2.98; N, 11.05. Found (%): C, 35.36; H, 3.01; N, 11.12. IR (KBr), cm⁻¹: $\nu(\text{N-H})$ 3333m; $\nu(\text{CH})_{\text{pyridine}}$ 3193m; $\nu(\text{CH})_{\text{aromatic}} + \nu(\text{CH})_{\text{ethyl}}$ 2985, 2931; $\nu(\text{C=C})_{\text{allyl}}$ 1640w; $\nu(\text{C=N})$ 1597vs; $\nu(\text{C=C})_{\text{aromatic}}$ 1550m; $\nu(\text{C-O})$ 1126m; $\nu(\text{N-N})$ 1018w; $\nu_{\text{sy}}(\text{Mo=O})$ 935vs; $\nu_{\text{as}}(\text{Mo=O})$ 895vs; $\delta(\text{C-H})_{\text{opb}}$ 702w; $\delta_{\text{opb}}(\text{Py})$ 640 m. ¹H NMR (100 MHz, DMSO-d₆): δ = 9.3 (s, 1H, N3H; exchanges with D₂O), 8.6 (d, 1H, C13H), 8.5 (s, 1H, C7H), 7.9–7.7 (m, 3H, C11, C15), 7.7–7.2 (m, 3H, C12, C14), 6.7 (d, 1H, C2), 3.0 (q, 2H, C9), 1.3 (t, 3H, C10). UV-Vis (methanol), λ_{max} , nm (log ϵ , L mol⁻¹ cm⁻¹): 230 (4.43), 248 (4.43), 300 (3.26), 336 (4.08)sh, 412 (3.44), 440 (3.38)sh.

2.4. X-ray crystal structure determination

Data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection, cell refinement, data reduction and absorption correction were performed using multiscan methods with Bruker software [21]. The structures were solved by direct methods using SIR2004 [22]. The non hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL [23]. All hydrogen atoms were placed at calculated positions and constrained to ride on their parent atoms. Details concerning collection and analysis are reported in table 1.

3. Results and discussion

3.1. Spectral properties

In the infrared spectrum of H₂L, the asymmetric and symmetric stretching vibrations of isothioamide NH₂ are observed at 3267 and 3167 cm⁻¹ as distinct peaks with equal intensity [24]. Strong band at 3105 cm⁻¹ is characteristic of $\nu(\text{O-H})$. The $\nu(\text{C-H})$ of the aromatic ring and ethyl moieties are at 2827–2962 cm⁻¹ [25]. The peak at 698 cm⁻¹ is attributed to the out of plane bending of the aromatic ring [26]. Combination modes of two C=N, aromatic C=C stretching and bending vibrations of NH₂ and OH are intense peaks at 1624, 1586, and 1551 cm⁻¹ [27]. Finally, the N–N and C–O bond stretching are at 1049 and 1176 cm⁻¹, respectively [28]. In spectra of **1**, **2**, and **3**, only one peak is observed for N3H at 3321, 3282, and 3333 cm⁻¹, respectively, indicating the NH₂ of H₂L is coordinated through isothioamide nitrogen after deprotonation [29]. The C–H bonds of aromatic ring and ethyl moieties show no significant change after coordination. Coordination of azomethinic nitrogen to Mo(VI) in **1**, **2**, and **3** are identified by peaks at 1601, 1600, and 1597 cm⁻¹, respectively, which correspond to C=N vibration, shifting to lower frequencies (blue shift) after coordination [30–33]. At 1111, 1130, and 1126 cm⁻¹ stretches of C–O blue shift with respect to free ligand, evidence of coordination of H₂L to Mo(VI) *via* phenolic oxygen for **1–3** [34]. The symmetric and asymmetric vibrations of *cis*-MoO₂ are assigned at 933, 899; 930, 887; and 935, 895 for **1**; **2**; and **3**, respectively [35]. The absorbance in **1** at 1655 cm⁻¹ is attributed to C=O coordinated DMF [36]. In **2**, the peak at 1006 cm⁻¹ is from S=O stretch of DMSO. The red shift of this value compared with S=O of free DMSO at 1040 cm⁻¹ verifies oxygen of DMSO coordinated to metal [37]. The breathing of pyridine in **3** is at 640 cm⁻¹, indicating coordination of pyridine [38].

Electronic spectrum of ligand shows three bands in the ultraviolet region. One at 244 nm is attributed to $\pi \rightarrow \pi^*$ transition of aromatic ring and 292 and 340 nm are $n \rightarrow \pi^*$ transitions of azomethine and isothioamide [39].

In electronic spectra of **1–3** in methanol $\pi \rightarrow \pi^*$ transition of aromatic rings do not show a shift but $n \rightarrow \pi^*$ transitions shift a little from the ligand spectrum. Electron transfer from HOMO to LUMO as O($p\pi$)–Mo($d\pi$) and N($p\pi$)–Mo($d\pi$) transitions make LMCT bands in the complexes, 398–412, 240–248, and 432–440 nm, attributed to LMCT charge transfer of phenyl oxygen, azomethine nitrogen, and oxygen of coordinated solvent, respectively. These bands are evidence of coordination of ligand and solvent. The molybdenum(VI) 4d⁰ has no d–d transitions [40].

Table 1. Crystal data and structure refinement for 1–3.

	1	2	3
Compound	C ₁₃ H ₁₇ BrMoN ₄ O ₄ S	C ₁₂ H ₁₆ BrMoN ₃ O ₄ S ₂	C ₁₅ H ₁₅ BrMoN ₄ O ₃ S
Empirical formula			
Formula weight	501.22	506.25	507.22
Temperature (K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	C2/c
Unit cell dimensions (Å, °)			
<i>a</i>	9.2025(2)	9.3975(2)	16.8134(4)
<i>b</i>	9.6624(2)	9.7928(2)	7.95410(10)
<i>c</i>	11.0471(2)	11.3864(3)	28.5872(5)
α	106.9440(10)	109.2090(10)	90
β	105.3820(10)	112.2370(10)	106.835(2)
γ	94.3710(10)	93.7690(10)	90
Volume (Å ³), <i>Z</i>	893.35(3), 2	893.97(4), 2	3659.27(12), 8
Calculated density (Mg m ⁻³)	1.863	1.881	1.841
Absorption coefficient (mm ⁻¹)	3.112	3.222	3.037
<i>F</i> (000)	496	500	2000
Crystal size (mm ³)	0.26 × 0.09 × 0.05	0.22 × 0.12 × 0.08	0.18 × 0.10 × 0.09
θ range for data collection (°)	2.95–28.08	2.91–27.58	2.53–29.12
Limiting indices	–12 ≤ <i>h</i> ≤ 12; –12 ≤ <i>k</i> ≤ 12; –14 ≤ <i>l</i> ≤ 14	–12 ≤ <i>h</i> ≤ 12; –12 ≤ <i>k</i> ≤ 12; –14 ≤ <i>l</i> ≤ 14	–22 ≤ <i>h</i> ≤ 22; –10 ≤ <i>k</i> ≤ 10; –39 ≤ <i>l</i> ≤ 39
Reflections collected	15,255	16,594	68,908
Independent reflection	4334 [<i>R</i> (int) = 0.0197]	4125 [<i>R</i> (int) = 0.0213]	4912 [<i>R</i> (int) = 0.0324]
Completeness to θ	(28.08°) 99.7%	(27.58°) 99.6%	(29.12°) 99.9%
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	4334/1/221	4125/1/212	4912/1/231
Goodness-of-fit on <i>F</i> ²	1.073	1.054	1.036
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0239, <i>wR</i> ₂ = 0.0636	<i>R</i> ₁ = 0.0223, <i>wR</i> ₂ = 0.0558	<i>R</i> ₁ = 0.0240, <i>wR</i> ₂ = 0.0545
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0275, <i>wR</i> ₂ = 0.0654	<i>R</i> ₁ = 0.0261, <i>wR</i> ₂ = 0.0577	<i>R</i> ₁ = 0.0310, <i>wR</i> ₂ = 0.0570
Largest difference peak and hole (e Å ⁻³)	0.933 and –0.898	1.180 and –1.049	0.625 and –0.681

Table 2. Selected bond lengths and angles of **1–3**.

Distances (Å)	Distances (Å)			Angles (°)	Angles (°)		
	1	2	3		1	2	3
Mo1–N1	2.257(2)	2.251(2)	2.254(2)	N1–Mo1–N3	70.84(7)	70.95(7)	70.70(6)
Mo1–N3	2.033(2)	2.031(2)	2.019(2)	N3–Mo1–O3	95.62(8)	94.85(8)	96.61(7)
Mo1–O1	1.937(2)	1.932(2)	1.935(1)	O3–Mo1–O1	104.93(8)	105.03(8)	104.18(7)
Mo1–O2	1.690(2)	1.691(2)	1.694(2)	O1–Mo1–N1	81.37(7)	81.78(7)	81.99(6)
Mo1–O3	1.704(2)	1.709(2)	1.705(1)	N1–Mo1–O4/N4	80.20(6)	76.39(6)	79.27(5)
Mo1–O4/N4	2.416(2)	2.395(1)	2.491(2)	N3–Mo1–O4/N4	80.76(7)	79.81(7)	81.54(6)
C1–O1	1.334(3)	1.336(4)	1.331(2)	O3–Mo1–O4/N4	80.64(8)	83.70(7)	83.33(7)
C7–N1	1.284(3)	1.287(4)	1.288(2)	O1–Mo1–O4/N4	78.09(7)	77.92(7)	76.95(6)
N1–N2	1.399(2)	1.399(2)	1.402(2)	N1–Mo1–O2	94.06(8)	94.21(8)	92.31(7)
N2–C8	1.303(3)	1.303(3)	1.306(2)	N3–Mo1–O2	98.69(9)	98.62(9)	99.75(8)
C8–N3	1.349(3)	1.349(3)	1.346(3)	O3–Mo1–O2	105.25(9)	105.80(9)	105.68(8)
C8–S1	1.741(2)	1.734(2)	1.747(2)	O1–Mo1–O2	99.83(8)	99.59(9)	97.87(7)
				C6–C7–N1	124.3(2)	124.2(2)	124.9(2)
				C7–N1–N2	115.1(2)	114.9(2)	115.8(1)
				N1–N2–C8	108.8(2)	108.4(2)	107.9(1)
				N2–C8–S1	120.8(2)	121.2(2)	121.5(1)
				N2–C8–N3	122.9(2)	123.2(2)	123.1(2)
				N3–C8–S1	116.3(2)	115.6(2)	115.4(1)

The ^1H NMR spectrum of H_2L in DMSO-d_6 shows two downfield broad signals at 11.4 and 9.7 ppm due to O1H and N3H_2 groups, respectively. Both signals disappear in the presence of D_2O , proving their exchangeability. These downfield signals confirm the deshielding caused by hydrogen bonds of ligand and DMSO . The N3H_2 as a singlet for two equivalent protons verifies the presence of isothioamide in solution. The azomethine proton (C7H) is a singlet at 8.6 ppm [41]. Protons on C5 , C3 , and C2 are assigned at 8.3, 7.4, and 6.9 ppm as singlet, doublet of doublets, and doublet, respectively. The quartet and triplet signals with 2 and 3 protons are detected at 3.2 and 1.3 ppm from C9H_2 and C10H_3 of ethyl, respectively.

In ^1H NMR spectra of the complexes in DMSO-d_6 a signal for one proton is assigned for N3H at 9.3–9.4 ppm. The upfield shift and integration of N3H and O1H disappearing prove ligand deprotonation and complex formation *via* isothioamide nitrogen and phenolic oxygen. The azomethine proton in complexes does not show significant shift. Similarly, in both ligand and complexes, the aromatic ring (5-bromo-2-hydroxobenzaldehyde) and ethyl protons do not shift. The C11 proton at 3.6 ppm and C12 and C13 proton signals at 3.0 ppm in **1** and C11 and C12 proton signals at 3.4 ppm in **2** reveal DMF and DMSO as ligand. In **3**, pyridine protons appear from 8.6 to 6.7 ppm.

3.2. Crystallographic description of complexes

Selected bond distances and angles are given in table 2. ORTEP views of the complexes are shown in figures 1–3. Two *cis* and *trans* configurations can be considered for free ligand, where N1 and N3 are *cis* and *trans* toward each other; *cis* configuration is seen in complexes. In **1–3**, N1 with respect to N3 and S1 is *trans* and *cis*, respectively.

In the complexes, the doubly deprotonated tridentate ligand coordinates to molybdenum *via* isothioamide nitrogen (N3), azomethine nitrogen (N1), and

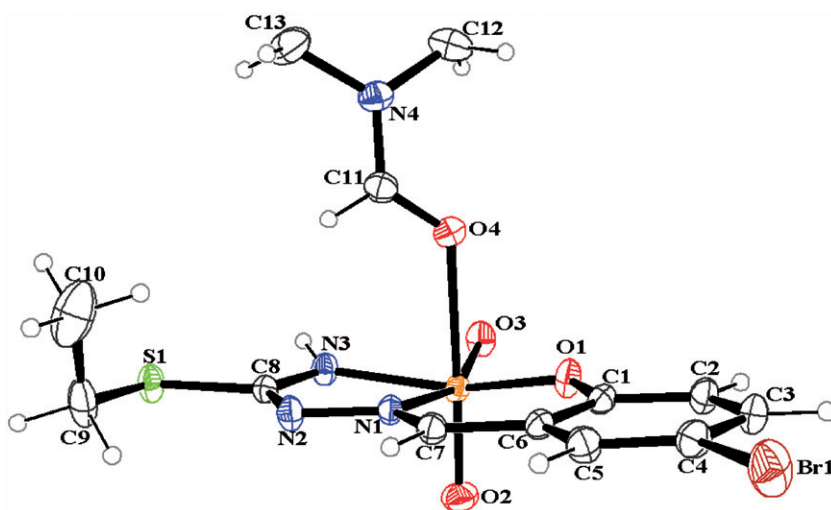


Figure 1. ORTEP drawing of **1** with atom numbering. Thermal ellipsoids are shown at 30% probability.

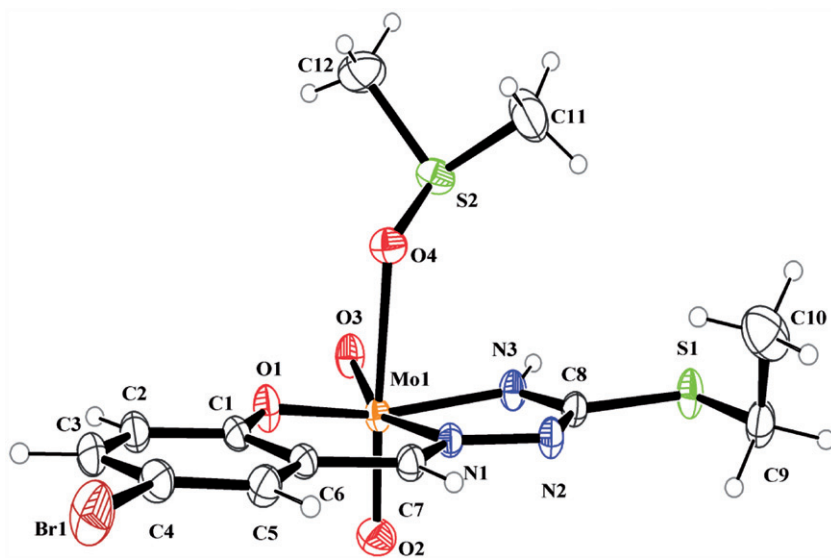


Figure 2. ORTEP drawing of **2** with atom numbering. Thermal ellipsoids are shown at 30% probability.

deprotonated phenolic oxygen (O1) in a meridional configuration. Coordination results in one five-membered and one six-membered chelate ring. The fourth and fifth sites have two oxygen atoms (*cis*-MoO₂ moiety) and the remaining site has DMF (O4), DMSO (O4) or pyridine (N4) in **1**, **2**, and **3**, respectively.

In **1**, **2**, and **3**, maximum deviation from mean plane of isothiosemicarbazone (C7N1N2C9N3S1) is 0.037, 0.043, and 0.037 Å for N2, respectively. The torsion angle of the mean plane of five- and six-coordination rings is about 10° for the complexes. Molybdenum deviates toward axial oxygen by 0.339, 0.342, and 0.322 Å from the mean plane of equatorial donors for **1**, **2**, and **3**, respectively, common in many *cis*-MoO₂

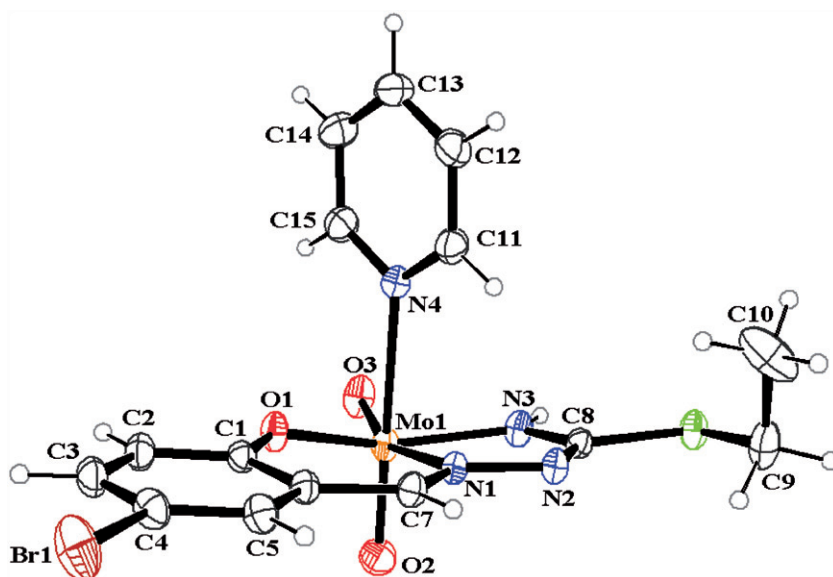


Figure 3. ORTEP drawing of **3** with atom numbering. Thermal ellipsoids are shown at 30% probability.

octahedral complexes [42]. MoO₂ bond lengths and angles are 1.690(2)–1.709(2) Å and 105.25(9)–105.80(9)°, respectively. The repulsion between two oxygen atoms of *cis*-MoO₂ in the complexes show greater angles than 90° (table 2). The distances of Mo1–O4 (2.416(2) Å), Mo1–O4 (2.395(1) Å) and Mo1–N4 (2.491(2) Å) for **1**, **2**, and **3**, respectively, are the longest in the coordination sphere of Mo, revealing that DMF, DMSO, and pyridine have the weakest bond with molybdenum. The Mo1–N3 distance in **3** is longer than the related bond in **1** and **2**. Other important bonds in these complexes have no significant difference with each other. The *trans* influence of O2 and O3 result in elongation of equatorial and axial bonds [43]. The five-membered heterocyclic Mo1N3CN2N1 has equal bond lengths in **1** and **2**. Ethyl is located on the same side of DMF, DMSO, and py. In **3**, hydrogen bonds are formed by O3 and N3. The O3···H–N3 hydrogen bond distances is 2.915(2) Å and link two molecules as a dimer with R₂²(8) graph set (figure 4).

Thirty-three isothiosemicarbazone molybdenum complex structures have so far been determined by X-ray crystallography. The bond lengths Mo1–O2, Mo1–O3, Mo1–O1, Mo1–N1, Mo1–N3, and Mo1–O4/N4 in **1**–**3** increase in that order, as in similar reported compounds [44, 45]. The bond distances of Mo1–O1 (1.932(2)–1.937(2) Å), Mo1–O3 (1.704(2)–1.709(2) Å), and Mo1–N1 (2.251(2)–2.257(2) Å) are shorter, equal, and longer to those found in other oxo-molybdenum(VI) complexes of isothiosemicarbazone [46, 47].

4. Conclusion

MoO₂LDMF, MoO₂LDMSO, and MoO₂LPy (py: pyridine) with new 5-bromo-2-hydroxybenzaldehyde *S*-ethylisothiosemicarbazone hydroiodide ligand (H₂L) have

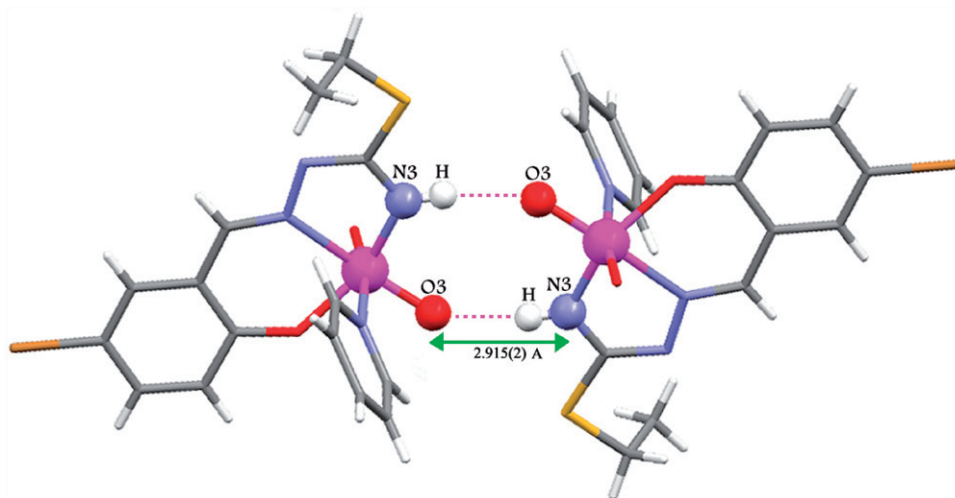


Figure 4. Dimer of two molecules of **3** showing hydrogen bond with $R_2^2(8)$ graph set.

been prepared. Molar conductance, FT-IR, ¹H NMR, elemental analyses, and UV-Vis are used for characterization. X-ray crystallography showed ligand coordinated to metal *via* deprotonated phenolic oxygen, azomethine nitrogen, and deprotonated isothioamide nitrogen in distorted octahedral geometries.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 870968–870970 for **1–3**, respectively. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

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