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ORIGINAL PAPER

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

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Abstract Three dioxomolybdenum complexes namely dioxo(5-chlorosalicylaldehyde thiosemicarbazonato) dime thylsulfoxide molybdenum(VI) **(C1)**, dioxo(5-chlorosalicylaldehyde 2-ethylthiosemicarbazonato) dimethylsulfoxide molybdenum(VI) **(C2)** and dioxo(5-chlorosalicylal dehyde *N*-phenylthiosemicarbazonato) dimethylsulfoxide molybdenum(VI) **(C3)** were prepared. The compounds all crystallize in the triclinic space group P-1 with $a = 7.3184(3)$ Å, $b = 7.5035(3)$ Å, $c = 14.9713(6)$ Å, $\alpha = 85.005(2)°$, $\beta = 85.616(2)°$, $\gamma = 66.987(2)°$ for **C1,** $a = 8.2339(1)$ Å, $b = 10.1739(1)$ Å, $c = 10.4017(1)$ Å, $\alpha = 78.486(1)°$, $\beta = 89.312(1)°$, $\gamma = 81.730(1)°$ for **C2**, $a = 7.0591(1)$ Å, $b = 9.5603(1)$ Å, $c = 14.5762(2)$ Å, $\alpha = 76.280(1)°$, $\beta = 81.351(1)°$, $\gamma = 81.985(1)°$ for **C3**. In general, the overall geometry of these complexes can be regarded as a distorted octahedron with the tridentate thiosemicarbazonato ligands (L^{2-}) bonded to the MoO_2^{2+} core, with the imine nitrogen, phenoxyl oxygen, sulfur atom and one of the terminal oxygen atoms of the dioxomolybdenum occupying the equatorial position. The sixth coordination site is occupied by the dimethylsulfoxide (DMSO) solvent molecules. The adjacent molecules of **C1** are linked by N–H···N intermolecular hydrogen bonding, forming polymeric chains that run parallel to the *bc* plane. On the other hand, **C2** is a discrete molecule while the molecules of **C3** associate via weak N–H···O hydrogen bonding interaction to form a polymeric chain that runs along the *a*-axis.

Keywords Dioxomolybdenum(VI) complexes · Schiff base · Hydrogen bond · ONS donor atoms

Introduction

Dioxomolybdenum(VI) complexes with thiosemicarbazonato ligands have been investigated owing to their new chemical features for potential biological activities such as antitumor [1], antifungal [2] and antiviral [3] properties. The first study on the use of thiosemicarbazone ligands [(salicylaldehyde thiosemicarbazone (TSCsal) and salicylaldehyde 4-phenylthisemicarbazone (4-PhTSCsal)] in the modeling of molybdoenzyme binding site was carried out by Saktiprosad Ghosh [4]. Thereafter, a flurry of literatures on the structures and biological properties of the oxomolybdenum(VI) complexes with ONS donor systems have been reported [5–10].

Thiosemicarbohydrazone ligand has several potential donor sites which allow it to bind to the metal through sulfur atom, hydrazinic nitrogen atom and phenolic oxygen atom. The chemistry of thiosemicarbazones (mixed hard-soft nitrogen-sulfur chelating ligands) and the compounds formed with Mo moiety of higher oxidation states therefore is of current interest. Although the thiosemicarbazone, obtained by the condensation process with *o*-hydroxyl carbonyl compounds, shows antibacterial activity, but the metal complexes often manifest effect of a larger order of magnitude compared

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to the corresponding ligand [11]. In this context, molybdenum (VI) complexes of this type of ligands constitute an important class of compounds. As part of our studies on molybdenum (VI) complexes with oxygen, nitrogen, and/or sulfur donor ligands, we describe here the synthesis and structures of $MoO_2L(DMSO)$ complexes, where L is 5-chlorosalicylaldehyde thiosemicarbazide (**L1**), 5-chlorosalicylaldehyde 2-ethylthiosemicarbazide (**L2**) and 5-chlorosalicylaldehyde *N*-phenylthiosemicarbazide (**L3**) ligands.

Experimental

General Procedures

All the reagents and solvents employed were procured commercially and used without subsequent purification. The starting complex, bis(acetylacetato) dioxomolybdenum(VI), [MoO_2 (acac)$_2$] was prepared as described in the literatures [12, 13].

^{1}H and ^{13}C NMR spectra were measured in DMSO-d_6 on a JEOL Lambda and a ECA 400 MHz NMR spectrometers. IR spectra were measured in Nujol mulls in the range of 4000–400 cm^{-1} by using a Perkin-Elmer 2000 FTIR instrument. Elemental analysis was performed by the in-house microanalytical laboratory using a Perkin-Elmer 2400 Series II CHNS/O System. Single-crystal X-ray data collection was carried out at 100 K on a Bruker Smart Apex II diffractometer.

Synthesis of Ligands

*5-Chlorosalicylaldehyde thiosemicarbazone **(L1)***

5-Chlorosalicylaldehyde (0.156 g, 1.00 mmol) was dissolved in 20 mL methanol. The solution was then added to a 20.0 mL thiosemicarbazide (0.091 g, 1.00 mmol) solution. The reaction mixture was refluxed for 1 h. A precipitate was formed when the solution was allowed to cool at room temperature overnight. The yellow precipitate was filtered, washed with methanol and dried in air. m.p.: 138–140 °C (0.25 g, 82%) Calcd. for $C_8H_8ClN_3OS_1$: C, 41.56; H,3.90; N, 18.19%; Found: C, 41.02; H, 4.02; N, 18.41%; IR(KBr) (ν_{max}/cm^{-1}): 3411 (m, NH), 3245 (m, OH), 1613 (m, C=N), 1271 (s, C=S),; ^{1}H NMR (DMSO-d_6, ppm): 11.76 (1H, OH), 10.25 (1H, N–NH), 8.73 (1H, HC=N); ^{13}C NMR (DMSO-d_6, ppm): 159.89 (C=N), 178.51 (C=S).

Similar procedure was applied to the preparation of **L2** and **L3**.

*5-Chlorosalicylaldehyde 2-ethylthiosemicarbazone **(L2)***

m.p.: 112–114 °C (0.22 g, 79%) Calcd. for $C_{10}H_{12}ClN_3OS_1$: C, 46.51; H, 4.65; N, 16.28%; Found: C, 46.11; H, 4.82; N, 16.41%; IR(KBr) (ν_{max}/cm^{-1}): 3301 (m, NH), 3128 (m, OH), 1601 (m, C=N), 1269 (s, C=S),; ^{1}H NMR (DMSO-d_6, ppm): 11.39 (1H,OH), 10.33 (1H, N–NH), 8.62 (1H, HC=N); ^{13}C NMR (DMSO-d_6, ppm): 158.25 (C=N), 181.11 (C=S).

*5-Chlorosalicylaldehyde N-phenylthiosemicarbazone **(L3)***

m.p.: 145–147 °C (0.19 g, 73%) Calcd. for $C_{14}H_{12}ClN_3OS_1$: C, 54.90; H, 3.92; N, 13.73%; Found: C, 54.33; H, 4.02; N, 13.52%; IR(KBr) (ν_{max}/cm^{-1}): 3365 (m, NH), 3137 (m, OH), 1614 (m, C=N), 1327 (s, C=S),; ^{1}H NMR (DMSO-d_6, ppm): 12.41 (1H, OH), 11.05 (1H, N–NH), 8.57 (1H, HC=N); ^{13}C NMR (DMSO-d_6, ppm): 160.55 (C=N), 183.26 (C=S).

Synthesis of Complexes

*Dioxo(5-chlorosalicylaldehyde-thiosemicarbazinato)dimethylsulfoxide Molybdenum(VI)**(C1)***

A solution of L1 (0.231 g, 1.00 mmol), which was dissolved in 20.0 mL of ethanol was added to a solution of $MoO_2(acac)_2$ in 20.0 mL methanol. A reddish precipitate formed immediately DMSO was added dropwise until the precipitate was completely dissolved in the solution. The reaction mixture was then refluxed for 2 h and was allowed to stand at room temperature. Reddish crystals were formed after slow evaporation for 3 days. The products was filtered, washed with ethanol and dried in air.

m.p.: 208–210 °C (0.15 g, 46%) Calcd. for $C_{10}H_{12}ClMoN_3O_4S_2$: C, 27.71; H, 2.78; N, 9.59%; Found: C, 28.00; H, 2.51; N, 9.47%; IR(KBr) (ν_{max}/cm^{-1}): 1587 (s, C=N), 924, 895 (s,Mo=O). ^{1}H NMR (DMSO-d_6, ppm): 8.39 (1H, HC=N). ^{13}C NMR (DMSO-d_6, ppm): 166.65 (C=N).

Similar procedure was applied to the preparation of **C2** and **C3**.

*Dioxo(5-chlorosalicylaldehyde 2-Ethylthiosemicarbazinato)dimethylsulfoxide Molybdenum(VI) **(C2)***

m.p.: 200–202 °C (0.17 g, 45%) Calcd. for $C_{12}H_{17}ClMoN_3O_4S_2$: C, 31.17; H, 3.68; N, 9.09%; Found: C, 30.79; H, 3.56; N, 9.17%; %; IR(KBr) (ν_{max}/cm^{-1}): 1588 (s, C=N), 939, 905 (s,Mo=O). ^{1}H NMR (DMSO-d_6, ppm): 8.39 (1H, HC=N). ^{13}C NMR (DMSO-d_6, ppm): 166.65 (C=N).

*Dioxo(5-chlorosalicylaldehyde N-phenylthiosemicarbazinato)dimethylsulfoxide molybdenum(VI) **(C3)***

m.p.: 240–242 °C (0.21 g, 51%) Calcd. for $C_{16}H_{16}ClMoN_3O_4S_2$: C, 37.64; H, 3.14; N, 8.24%; Found: C, 37.49; H,

3.36; N, 8.17%; IR(KBr) (ν_{max}/cm^{-1}): 1594 (s, C=N), 929, 889 (s,Mo=O). ^{1}H NMR (DMSO-d$_6$, ppm): 9.73 (1H, NH,) 8.73 (1H, HC=N). ^{13}C NMR (DMSO-d$_6$, ppm): 161.65 (C=N).

X-Ray Structural Analysis

Crystallographic data are given in Table 1. The X-ray data for **C1**, **C2** and **C3** were collected on a Bruker Smart Apex II diffractometer using Mo–Kα ($\lambda = 0.71073$ Å) radiation at 100(2) K. Data reduction and cell refinement was performed using *SAINT* (Bruker 2008) [14]. The data sets

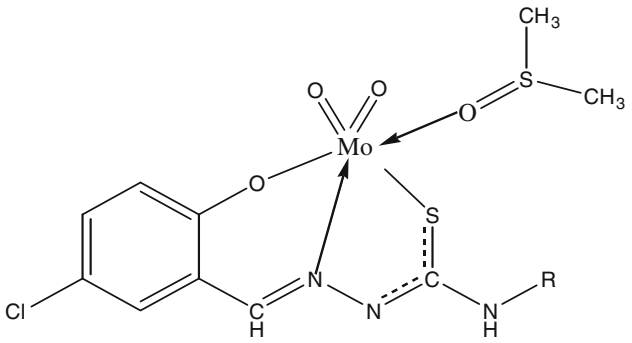

Chart 1 Structural diagram of [$MoO_2L(DMSO)$], L1: R = H, L2: R = CH_2CH_3 and L3 = C_6H_5

Table 1 Crystallographic data for **C1**, **C2** and **C3**

Compounds	**C1**	**C2**	**C3**
Chemical formula	$C_{10}H_{12}ClMoN_3O_4S_2$	$C_{12}H_{16}ClMoN_3O_4S_2$	$C_{16}H_{16}ClMoN_3O_4S_2$
M_r	433.76	461.81	509.85
Crystal colour, habit	Red, block	Red, block	Red, block
Crystal size (mm)	0.40 × 0.30 × 0.20	0.10 × 0.10 × 0.10	0.40 × 0.30 × 0.20
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
Unit cell dimension			
a(Å)	7.3148(3)	8.23390(10)	7.05910(10)
b(Å)	7.5035(3)	10.17390(10)	9.56030(10)
c(Å)	14.9713(6)	10.40170(10)	14.5762(2)
α(°)	85.005(2)	78.4860(10)	76.2800(10)
β(°)	85.616(2)	89.3120(10)	81.3510(10)
γ(°)	66.987(2)	81.7320(10)	81.9850(10)
V(Å^3)	752.65(5)	844.825(15)	939.24(2)
Z	2	2	2
T(K)	296(2)	100(2)	100(2)
D_{calc} (gcm^{-3})	1.914	1.815	1.803
μ(Mo–Kα) mm^{-1}	1.343	1.202	1.116
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{min}	0.7620	0.887	0.6730
T_{max}	0.8937	0.887	0.7457
F(0 0 0)	432	464	584
Total data	5693	5984	8954
Unique data	2925	3305	4298
R_{int}	0.0154	0.0144	0.0134
Observed data [$I > 2\sigma(I)$]	2806	3092	4199
Number of parameter	197	211	246
R indices [$I > 2\sigma(I)$]	$R1 = 0.0291$	$R1 = 0.0213$	$R1 = 0.0201$
	$wR2 = 0.1260$	$wR2 = 0.0591$	$wR2 = 0.0602$
R indices[all data]	$R = 0.0303$	$R1 = 0.0233$	$R1 = 0.206$
	$wR2 = 0.1286$	$wR2 = 0.0602$	$wR2 = 0.0607$
S	1.174	1.035	1.116
$\Delta\rho_{max}$(e Å^{-3})	0.955	0.623	0.360
$\Delta\rho_{min}$(e Å^{-3})	−0.927	−0.465	−0.729
CCDC number	825059	825057	825058

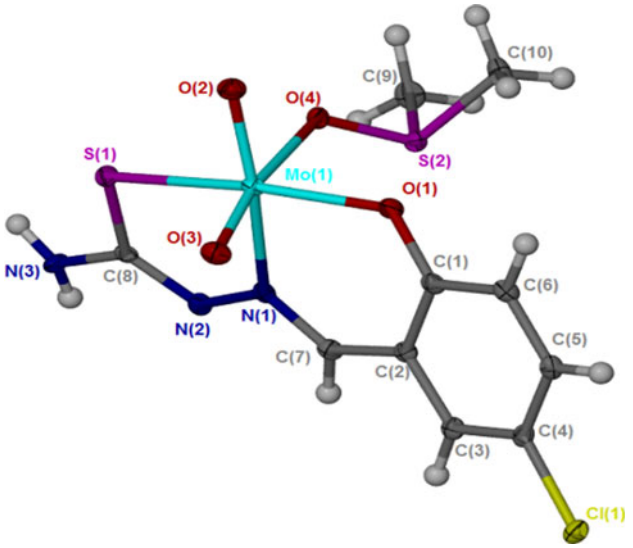

Fig. 1 Molecular structure of **C1** with numbering scheme. Displacement ellipsoids are drawn at the 50%-level

were corrected for absorption effects based on multiple scans. The structures were solved and refined using SHELXS97 (Sheldrick, 2008) [15]. The molecular graphic were drawn using the XSeed program [16].

Result and Discussion

The dioxomolybdenum(VI) complexes, **C1**, **C2,** and **C3** were obtained by the reaction of $[MoO_2(acac)_2]$ with a stoichiometric amount of **L1**, **L2,** and **L3**, respectively in ethanol. In the presence of DMSO, the reactions yielded red mononuclear $[MoO_2L(DMSO)]$ complexes shown in Chart 1. The IR spectra of the dioxomolybdenum(VI) complexes show two strong absorption bands in the region

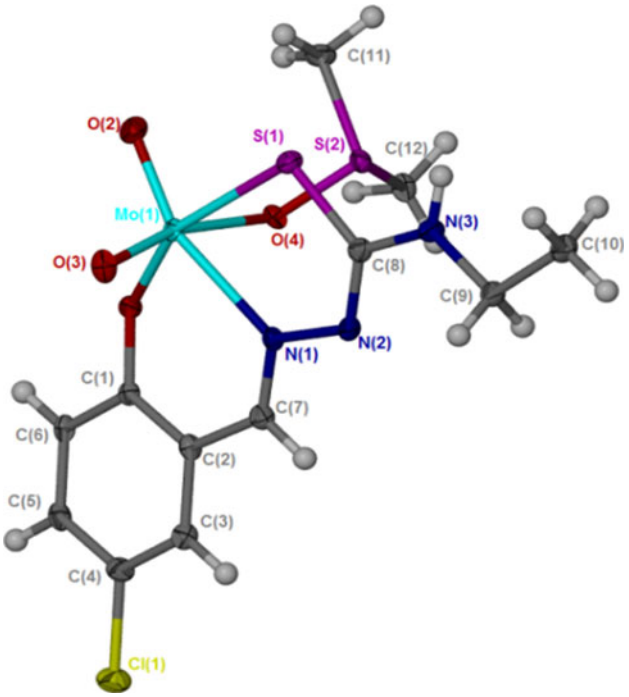

Fig. 3 Molecular structure of C1 with numbering scheme. Displacement ellipsoids are drawn at the 50%-level

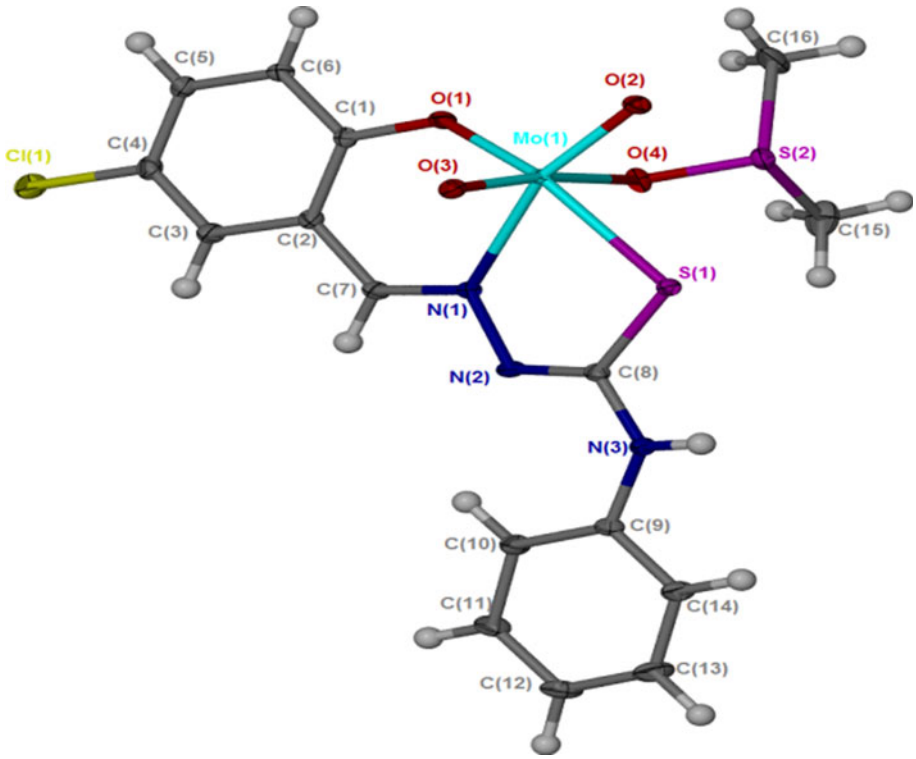

Fig. 2 Molecular structure of **C2** with numbering scheme. Displacement ellipsoids are drawn at the 50%-level

Table 2 Selected bond distances (Å) and angles (°) for **C1**, **C2** and **C3**

	C1	C2	C3
Bond distances			
Mo–O1	1.954(2)	1.9507(16)	1.9260(14)
Mo–O2	1.711(2)	1.7115(17)	1.7176(14)
Mo–O3	1.695(2)	1.7021(17)	1.6966(14)
Mo–O4	2.312(2)	2.2628(19)	2.3366(15)
Mo–N1	2.284(3)	2.2897(19)	2.2699(16)
Mo–S1	2.4372(8)	2.4156(6)	2.4458(5)
C7–N1	1.295(4)	1.287(3)	1.297(3)
C8–S1	1.749(3)	1.759(2)	1.760(2)
C8–N2	1.309(4)	1.307(3)	1.296(3)
N1–N2	1.395(3)	1.397(2)	1.393(3)
Bond angles			
O2–Mo–O3	105.53(11)	105.17(9)	106.34(7)
O2–Mo–O1	96.74(10)	96.79(7)	99.00(7)
O3–Mo–O1	107.63(10)	106.43(7)	105.50(6)
O2–Mo–S1	89.50(8)	88.48(6)	90.23(5)
O3–Mo–S1	100.40(8)	99.81(6)	96.72(5)
O1–Mo–S1	151.51(7)	153.91(5)	153.51(5)
O2–Mo–N1	159.40(10)	160.19(7)	159.33(6)
O3–Mo–N1	91.10(10)	89.84(8)	90.49(6)
O1–Mo–N1	81.76(9)	84.05(6)	83.00(6)
S1–Mo–N1	75.36(6)	76.05(5)	75.66(4)
O2–Mo–O4	85.20(9)	88.60(7)	85.53(6)
O3–Mo–O4	168.94(9)	165.64(7)	168.13(6)
O1–Mo–O4	77.07(8)	74.96(6)	77.25(6)

between 890 and 930 cm^{-1}, which is indicative of symmetrical and anti-symmetrical stretching vibration of the two doubly-bonded oxygen atoms at the molybdenum core which are *cis* to each other [17, 18]. The IR spectra of the ligands exhibit a few ligand bands at the region 3100–3200 cm^{-1} [υ(OH)], 3400–3300 cm^{-1} [υ(NH)], 1200–1400 cm^{-1} [υ(C=S)]. Upon coordinating with MoO_2^{2+}, these absorption bands vanished as were observed in the spectra of the complexes.

The ^{1}H NMR spectra of the ligands exhibits a phenolic (OH) proton resonance at 11.76, 11.39, and 12.45 ppm, respectively. Upon coordination to the Mo atom, the signal for the OH disappeared, indicating the deprotonation of phenolic OH in order to coordinate with the dioxomolybdenum(VI) cation. The ^{13}C NMR spectra of the three ligands, **L1, L2** and **L3** exhibit C–S chemical shift at 178.51, 181.11 and 183.26 ppm, respectively.

Molecular Structures of C1, C2, and C3

The molecular structures of **C1**, **C2**, and **C3** shows that the Schiff base behave as a tridentate ligand, and reacted with the dioxomolybdenum anion to give a six coordinated molybdenum(VI) structure. As shown in the Figs. 1, 2 and 3, the imine nitrogen, one of the phenoxyl oxygen and the sulfur atom are involved in the coordination with molybdenum atom. The overall geometry can be regarded as a distorted octahedron, with the equatorial plane formed by the imine nitrogen, phenoxyl oxygen, sulfur atom and one of the terminal oxygen atoms of the dioxomolybdenum. The other terminal oxygen and the oxygen atom from the solvent occupy the apical position. In this case, the ligand which coordinates to Mo atom formed six- and five-member chelate rings around the *cis*-MoO_2 centre.

The selected bond distances and angles are summarized in Table 2. The Mo=O bond lengths and the O=M=O angles have values which are in the expected range for *cis*-dioxomolybdenum(VI) complexes [19–22]. The bond distance between the Mo and the oxygen atom from DMSO [2.312(2) Å (**C1**), 2.2628(19) Å (**C2**), 2.3366(15) Å (**C3**)] suggested that DMSO binds firmly to the MoO_2^{2+} moiety Tables 3 and 4.

The equatorial bases formed by S1, O2, O1 and N1 in the complexes are non planar. The Mo atom of **C1** and **C2** are shifted 0.2507 and 0.2359 Å, respectively out from the basal plane towards the solvent oxygen donor atom, O4, while the Mo atom of **C3** show a 0.2466 Å displacement towards the apical oxo-oxygen atom, O3.

Table 3 Hydrogen bonds for **C1**

D–H···A	d(D–H) Å	d(H···A) Å	d(D···A) Å	<(DHA) (o)	Symmetry operation
N(3)–H(2)···N(2)	0.77	2.25	3.000(4)	163.5	−x + 2, −y, −z + 1
N(3)–H(1)···O(4)	0.83(4)	2.08(4)	2.897(3)	167(4)	−x + 2, −y + 1, −z + 1

Table 4 Hydrogen bonds for C3

D–H···A	d(D–H) Å	d(H···A) Å	d(D···A) Å	<(DHA) (°)	Symmetry operation
N(3)–H(3)···O(4)	0.88	2.41	3.231(2)	154.9	x − 1, y, z

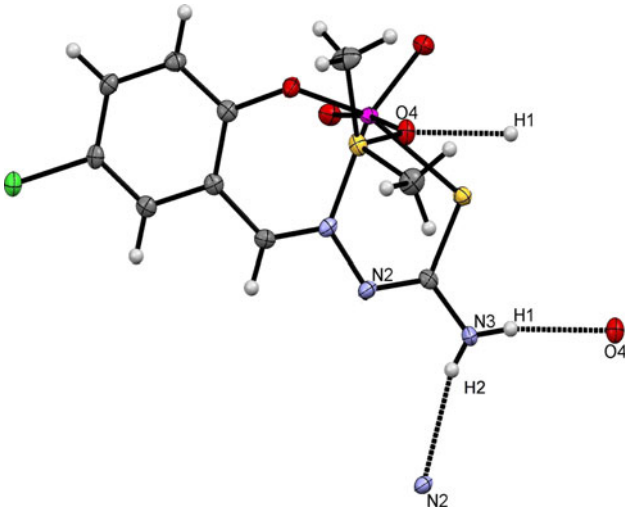

Fig. 4 **C1** molecules are linked into a layer by N3–H2···N2 and N3–H1···O4 hydrogen bonds

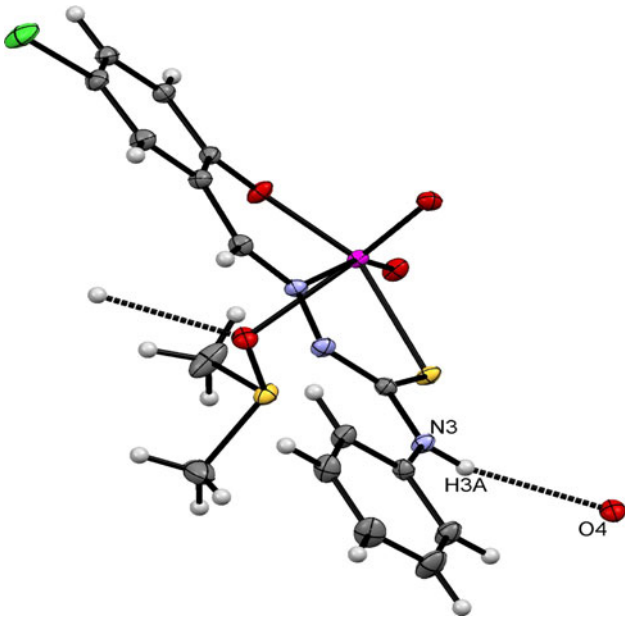

Fig. 5 **C3** molecules are joined into a long chain by N3–H3···O4 hydrogen bonds

In the crystal structures of **C1** and **C3**, the molecules are arranged in polymeric networks that are parallel to the *bc* and *ab* crystallographic plane, respectively as shown in Figs. 4 and 5. The **C1** molecules are held more firmly by two hydrogen bonds via N(3)–H(2)···N(2) [3.000 Å] and N(3)–H(1)···O(4) [0.2897 Å], whereas in the case of **C3** the molecules are merely connected by a rather weak N(3)–H(3)···O(4) hydrogen bond indicated by its bond length, d(D···A) of 3.23 Å. As a result, the molecules forms infinite chain that runs along the *a*-axis.

Conclusions

Three new dioxomolybdenum(VI) complexes with 5-chlorosalicylaldehyde thiosemicarbazate, 5-chlorosalicylaldehyde 2-ethylthiosemicabazate and 5-chlorosalicylaldehyde *N*-phenylthiosemicarbazate tridentate ligands have been prepared and characterized. The octahedral coordination of each of the molybdenum atom is completed by DMSO molecule. **C1** and **C3** molecules formed polymeric chains, respectively, through hydrogen bonds interaction, while **C2** molecule exists as discrete molecule.

Supplementary Material

CCDC 825057, CCDC 825058 and CCDC 825059 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_resquest/cif.

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