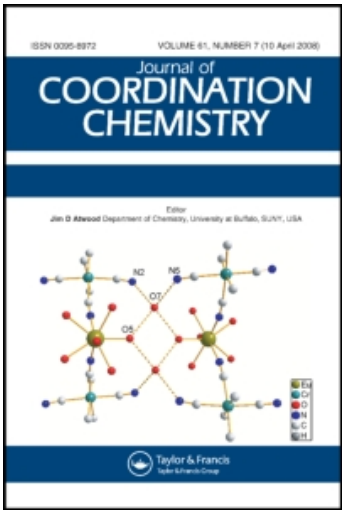

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Synthesis and characterization of new dioxomolybdenum(VI) complexes derived from benzophenone-thiosemicarbazone (H_2L). Crystal structure of [$MoO_2L(PrOH)$]

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Five mixed-ligand complexes of dioxomolybdenum(VI) [$MoO_2L(ROH)$], where L is dianionic form of the 2-hydroxybenzophenone *S*-methyl-4-phenyl-thiosemicarbazone (H_2L) and ROH are *n*-alcohols (C_nH_{2n+1}–OH; $n = 1 - 5$) were synthesized and characterized by elemental analysis, electronic, infrared and ^{1}H-NMR spectroscopies. The ligand is coordinated to the *cis*-MoO_2^{2+} core through ONN, while the sixth coordination site is occupied by alcohol. The crystal structure of [$MoO_2L(PrOH]$ complex was determined by single crystal X-ray diffraction method. Effect of the 4-phenyl substituent on conjugation of chelate rings was discussed.

Keywords: Dioxomolybdenum; Thiosemicarbazone; 2-Hydroxybenzophenone; Crystal structure

1. Introduction

Molybdenum compounds exhibit various catalytic activities in biological processes; molybdenum cofactor is an essential component of various enzymes such as nitrogenase, sulfite and xanthine oxidases [1–4] and some molybdenum compounds catalyze oxygen atom transfer mechanisms [5, 6]. Because the function of molybdenum core depends on the ligands [7], a number of molybdenum complexes were synthesized to model oxomolybdenum enzymes [8–13].

Various metal complexes of thiosemicarbazide derivatives have been the subject of interest due to their wide range of pharmacological properties [14–18]; some benzophenone thiosemicarbazones have biological activities such as bacteriostatic [19] and anticonvulsant effects [20]. However, structural studies on the benzophenone-thiosemicarbazones and their metal complexes are limited [21–24].

Most molybdenum(VI) complexes of thiosemicarbazones are thiosemicarbazones of 2-hydroxybenzaldehyde or naphthaldehyde derivatives. Coordination of thiosemicarbazones to dioxomolybdenum(VI) ion occurs through the ON^1N^4 [10, 25–27] or ON^1S [11, 13, 28–33] donor sets. In these articles, molybdenum-thiosemicarbazones

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have only one substituent either on N^4 or on sulfur, and octahedral coordination of the molybdenum atom is completed by an alcohol or nitrogen of heterocyclic compounds such as pyridine and picoline.

The present work comprises the synthesis and characterization of a new benzophenone-thiosemicarbazone ligand which is substituted both on N^4 and S atoms and its five dioxomolybdenum(VI) complexes; *n*-C_{3-5} alcohols complete the coordination of the molybdenum complexes, [$MoO_2L(ROH)$] (figure 1). The synthesized compounds were characterized by elemental analysis, molar conductivity, electronic, infrared and ^{1}H-NMR spectra. The crystal structure of [$MoO_2L(PrOH]$ was determined by single crystal X-ray diffraction.

2. Experimental

2.1. *Chemicals and apparatus*

All chemicals were of reagent grade and used as purchased without purification. Elemental analyses were determined on a Thermo Finnigan Flash EA 1112 Series Elementar Analyzer. IR spectra were recorded as KBr pellets with a Mattson 1000 FT-infrared spectrometer. UV–Visible spectra were obtained on a ATI-Unicam UV/Visible Spectrometer UV2 Series. ^{1}H-NMR spectra were recorded on a Varian UNITY INOVA 500 MHz spectrometer. The molar conductances of the compounds were measured in 10^{-3} M DMF solution at $25 \pm 1^{\circ}$C using a digital WPA CMD 750 conductivity meter.

2.2. *X-ray structure solution and refinement*

The diamagnetic molybdenum complexes **1**–**5** were obtained as bright orange solids. Single crystals of [$MoO_2L(PrOH)$] (**3**), suitable for X-ray diffraction, were obtained by recrystallization from propanol. It was not possible to obtain single crystals of the other molybdenum complexes suitable for crystallographic work.

A red crystal prism of $C_{24}H_{25}N_3O_4MoS$ having dimensions $0.50 \times 0.20 \times 0.20\,mm^3$ was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied, which resulted in transmission factors

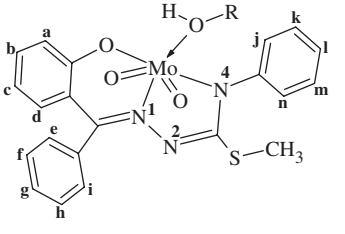

Figure 1. The dioxomolybdenum(VI) complexes. R: CH_3 (**1**); C_2H_5 (**2**); C_3H_7 (**3**); C_4H_9 (**4**); C_5H_{11} (**5**).

ranging from 0.79 to 1.00. Unique F^2 data (6958) were used in the final cycle of the full-matrix least-squares refinement of 323 variables. The structure was solved by direct methods using the program SIR92 [34]. Hydrogen atoms were refined using the riding model and the non-hydrogen atoms were refined anisotropically. All calculations were performed using the Crystal Structure crystallographic software package [35, 36].

2.3. *Synthesis of the ligand*

2-Hydroxybenzophenone *S*-methyl-4-phenylthiosemicarbazone (H_2L) and [$MoO_2(acac)_2$] were prepared with small modifications of general methods [37–39].

H_2L: light yellow, m.p. 93.8°C, yield 62%. Anal. Calcd. for $C_{21}H_{19}N_3OS$: C, 69.78; H, 5.30; N, 11.63; S, 8.87. Found: C, 69.58; H, 5.18; N, 11.55; S, 8.52%. FT-IR (KBr, cm^{-1}): ν(OH) 3553(s); ν(NH) 3179(s); $\nu(C{=}N^1)$ 1605(s); $\nu(N^2{=}C)$ 1589(m). ^{1}H-NMR (DMSO-d_6, 500 MHz, 25°C, δ ppm): 9.27 (s, 1H, O*H*), 8.48, 8.14 (*cis*/*trans* ratio: 2/3, s, 1H, N*H*), 7.60–7.48 (m, 3H, *k*, *l*, *m*), 7.39–7.34 (m, 4H, *e*, *f*, *h*, *i*), 7.30 (t, 1H, g), 7.00 (t, 2H, *j*, *n*), 6.96 (t, 1H, *d*), 6.90 (d, 1H, *c*), 6.87 (d, 1H, *a*), 6.84 (t, 1H, *b*), 2.64–2.56 (*cis*/*trans* ratio:1/1, s, 3H, S–CH_3).

2.4. *Synthesis of [MoO_2(L)CH_3OH] (1)*

The ligand (0.345 g, 1 mmol) was dissolved in absolute methanol (2 mL) by heating. The hot solution was treated with 2 mL of a methanolic solution of $MoO_2(acac)_2$ (0.325 g, 1 mmol), stirred for 5 h at 60 ± 2°C and allowed to stand at room temperature overnight. The orange precipitate was collected by filtration and washed twice by 2–4 mL of cold methanol. The product was dried for 12 h in air.

The molybdenum complexes, **2**–**5**, were synthesized by a similar procedure. The analytical, physical and IR data of **1**–**5** and ^{1}H-NMR data of ROH as a ligand are:

1: Orange, m.p. 233.6°C, yield 42%, Λ: 4.44 $\Omega^{-1}\,cm^2\,mol^{-1}$ (10^{-3} M DMF), Anal. Calcd. for $C_{22}H_{21}N_3O_4SMo$: C, 50.87; H, 4.07; N, 8.09; S, 6.17. Found: C, 50.58; H, 4.15; N, 8.05; S, 5.92%. FT-IR (KBr, cm^{-1}): ν(OH) 3422(s); $\nu(C{=}N^1)$ 1628(m); $\nu(N^2{=}C)$ 1593(m); $\nu(MoO_2)$ 889(m), 862(m); ν(CH) 2923(m), $\delta(CH_3)$ 1470 (s), $\delta(CH_2)$ 1362(m). ^{1}H-NMR (500 MHz, 25°C, δ ppm): 4.45 (t, 1H, O*H*), 3.45 (s, 3H, CH_3).

2: Orange, m.p. 230.7°C, yield 25%, Λ: 0.12 $\Omega^{-1}\,cm^2\,mol^{-1}$ (10^{-3} M DMF), Anal. Calcd. for $C_{23}H_{23}N_3O_4SMo$: C, 51.78; H, 4.35; N, 7.88; S, 6.01. Found: C, 51.58; H, 4.26; N, 8.12; S, 5.72%. FT-IR (KBr, cm^{-1}): ν(OH) 3480(s); $\nu(C{=}N^1)$ 1620(m); $\nu(N^2{=}C)$ 1593(m); $\nu(MoO_2)$ 888(m), 865(m); ν(CH) 2925(m), 2975(m), $\delta(CH_3)$ 1470(s), $\delta(CH_2)$ 1366(m). ^{1}H-NMR (500 MHz, 25°C, δ ppm): 4.32 (t, 1H, O*H*), 3.44 (m, 2H, C^1H_2), 1.05 (t, 3H, C^2H_3).

3: Orange, m.p. 234.0°C, yield 50%, Λ: 0.09 $\Omega^{-1}\,cm^2\,mol^{-1}$ (10^{-3} M DMF), Anal. Calcd. for $C_{24}H_{25}N_3O_4SMo$: C, 52.65; H, 4.60; N, 7.68; S, 5.86. Found: C, 52.85; H, 4.82; N, 7.45; S, 5.68%. FT-IR (KBr, cm^{-1}): ν(OH) 3395(s); $\nu(C{=}N^1)$ 1632(m); $\nu(N^2{=}C)$ 1597(m); $\nu(MoO_2)$ 888(m), 862(m); ν(CH) 2929(m), 2956(m), 2968(m); $\delta(CH_3)$ 1466(s), $\delta(CH_2)$ 1364(m). ^{1}H-NMR (500 MHz, 25°C, δ ppm): 4.32 (t, 1H, O*H*), 3.34 (m, 2H, C^1H_2), 1.39–1.43 (m, 2H, C^2H_2), 0.83 (t, 3H, C^3H_3).

4: Orange, m.p. 232°C, yield 35%, Λ: 0.55 $\Omega^{-1}\,cm^2\,mol^{-1}$ (10^{-3} M DMF), Anal. Calcd. for $C_{25}H_{27}N_3O_4SMo$: C, 53.48; H, 4.85; N, 7.48; S, 5.71. Found: C, 53.35; H, 4.78; N, 7.45; S, 5.42%. FT-IR (KBr, cm^{-1}): ν(OH) 3408(s); $\nu(C{=}N^1)$ 1647(w); $\nu(N^2{=}C)$ 1593(m); $\nu(MoO_2)$ 889(m), 869(m); ν(CH) 2925(m), 2956(m); $\delta(CH_3)$ 1478(s), $\delta(CH_2)$ 1366(m). ^{1}H-NMR (500 MHz, 25°C, δ ppm): 4.28 (t, 1H, OH), 3.37 (m, 2H, C^1H_2), 1.37–1.39 (m, 2H, C^2H_2), 1.28–1.30 (m, 2H, C^3H_2), 0.86 (t, 3H, C^4H_3).

5: Orange, m.p. 233.5°C, yield 25%, Λ: 0.12 $\Omega^{-1}\,cm^2\,mol^{-1}$ (10^{-3} M DMF), Anal. Calcd for $C_{26}H_{29}N_3O_4SMo$: C, 54.26; H, 5.08; N, 7.30; S, 5.57. Found: C, 54.09; H, 5.20; N, 7.15; S, 5.42%. FT-IR (KBr, cm^{-1}): ν(OH) 3410(s); $\nu(C{=}N^1)$ 1632(w); $\nu(N^2{=}C)$ 1593(m); $\nu(MoO_2)$ 888(m), 865(m); ν(CH) 2929(m), 2956(m), 2968(m); $\delta(CH_3)$ 1471(s), $\delta(CH_2)$ 1362(m). ^{1}H-NMR (500 MHz, 25°C, δ ppm): 4.29 (t, 1H, OH), 3.36 (m, 2H, C^1H_2), 1.39–1.42 (m, 2H, C^2H_2), 1.23–1.26 (m, 4H, $C^{3,4}H_2$), 0.86 (t, 3H, C^5H_3).

3. Results and discussion

3.1. *Electronic spectra*

Electronic absorption bands of the compounds in 10^{-3} M DMF solution, given in table 1, showed $\pi \rightarrow \pi^*$ transitions of the aromatic rings in the range 238–268 nm. Two bands at *ca.* 313 and 342 nm are probably $n \rightarrow \pi^*$ transitions of the azomethine and thioamide moieties of the ligand [40]. In the spectra of the complexes, these bands shift to lower or higher frequencies because of the metal-ligand bond formation, but the changes are not regular.

The spectra of **1**–**5** showed a broad band at 439–440 nm which is assignable to the lowest empty Mo(dπ) orbital as a LMCT [41, 42]. The bands of the complexes from 610–633 are assigned to $d_{x^2-y^2} \rightarrow d_{z^2}$ transitions corresponding to a square planar structure consisting of the ON^1N^4 donor set and alcohol. Even though the electronic transitions of the complexes look like spectra of a planar structure, **1**–**5** have octahedral geometry due to the oxo-groups of MoO_2. The relatively low intensity of these d–d bands can be accepted as evidence for octahedral geometry.

Table 1. The λ_{max} (nm) values and molar extinction coefficients (log ε) of the compounds in DMF.

Comp.	$\pi \rightarrow \pi^*$		$n \rightarrow \pi^*$		LMCT	d–d	
L	238 (4.91)	262 (4.34)	313 (4.26)	342 (4.39)			
1	238 (4.26)	267 (4.34)	312 (4.05)	352 (4.28)	439 (3.65)	582 (3.05)	633 (2.80)
2	238 (4.52)	268 (4.26)	317 (4.27)	337 (4.25)	440 (3.40)	581 (3.10)	610 (2.74)
3	238 (4.18)	268 (4.24)	316 (4.44)	350 (4.27)	439 (3.61)	592 (3.00)	625 (2.66)
4	246 (4.21)	267 (4.24)	318 (4.25)	338 (4.23)	421 (3.44)	598 (3.06)	616 (2.82)
5	236 (4.90)	267 (4.37)	313 (4.33)	344 (4.26)	440 (3.59)	597 (3.15)	614 (2.95)

3.2. *IR spectra*

In ligand spectra the stretching vibrations of the OH, N^4H, $C{=}N^1$ and $N^4{=}C$ groups were clearly observed. The ν(OH) and $\nu(N^4H)$ bands disappear in spectra of **1–5** due to coordination of the deprotonated phenolate and N^4 nitrogen. The vibrations of the $\nu(C{=}N^1)$ and $\nu(N^4{=}C)$ groups of the ligand shifted by *ca.* 4–27 cm^{-1} to higher frequencies by coordination.

The spectra of **1–5** contain the characteristic OH and aliphatic CH vibrations of alcohol. The slightly broad ν(OH) bands of ROH are between 3480 and 3395 cm^{-1}. Medium bands in ranges of 1452–1478 cm^{-1} and 1362–1366 cm^{-1} are assigned to aliphatic CH_3 and CH_2 groups of the alcohols and S–CH_3 group. In the spectra of all molybdenum complexes the ν_s and ν_{as} bands of *cis*-MoO_2 group can be observed at 862–869 and 888–889 cm^{-1}, respectively.

3.3. *^{1}H-NMR spectra*

Ligand protons showed the expected chemical shift values. Besides the *S*-methyl and N^4H protons, the ligand displayed a systematic pattern of *cis* and *trans* isomers at 2.56/2.64 and 8.48/8.14 ppm, respectively [22].

The benzophenone thiosemicarbazone (H_2L) acts as a tridentate ligand coordinating through phenolic oxygen, and N^1 and N^4. Coordination of the phenolic oxygen and thioamide nitrogen (N^4) can be easily monitored by the ^{1}H-NMR spectra due to the absence of the OH and N^4H signals after chelating.

In the ^{1}H-NMR spectra of **1–5**, the chemical shift values of the protons on thiosemicarbazone are in approximately the same positions, 7.55–7.49 (m, 3H, *f*, *g*, *h*), 7.42 (t, 1H, *d*), 7.38 (d, 2H, *e*, *i*), 7.33 (t, 2H, *j*, *n*), 7.21–7.18 (m, 3H, *k*, *l*, *m*), 6.95 (d, 1H, *a*), 6.91 (d, 1H, *c*), 6.86 (t, 1H, *b*) and 1.96 (s, 3H, S–CH_3) ppm. These chemical shifts are 0.01 and 0.6 ppm, different compared to the free ligand. Some of the aromatic protons, *d* and *j*–*n*, showed shifts *ca.* 0.3 and 0.5 ppm to higher or lower fields. The isomer signals of the S–CH_3 protons disappeared upon chelation, observed as a singlet at 1.96 ppm shifted to lower frequencies by 0.6 ppm. These changes indicate the altering chemical environment of aromatic protons because of the conjugated backbone of the new complex system. Proton signals of the coordinated alcohols are clearly observed except for OH proton of methanol.

3.4. *Crystal structure of [MoO_2(L)PrOH] (3)*

The basic crystal data and structure refinement parameters for [MoO_2(L)PrOH] are shown in table 2 and selected bond distances and angles are presented in table 3.

The MoO_2 unit has *cis*-MoO_2^{2+} structure with the angle 106.03(4)°; Mo=O bond lengths have the expected values (table 3) [13, 27]. Chelation of the doubly deprotonated benzophenone-thiosemicarbazone to *cis*-MoO_2 is in approximately planar form coordinating through O1, N1 and N3. The fourth and fifth coordination sites of molybdenum are occupied by two oxo groups. Octahedral coordination is completed by PrOH, which is weakly coordinated with a Mo–O distance of 2.37 Å (figure 2).

Considering the O4–Mo1–O2 of **3** as *z* axis of an octahedron, the coordination geometry of molybdenum can be described as distorted octahedral. Axial Mo1–O2

Table 2. Crystal data and structure refinement parameters for $[MoO_2(L)PrOH]$.

Empirical formula	$C_{24}H_{25}N_3O_4MoS$
Formula weight	547.48
Crystal color, habit	Red, prism
Crystal dimensions (mm^3)	$0.50 \times 0.20 \times 0.20$
Crystal system	Monoclinic
Space group	$P2_1/n$ (#14)
Lattice type	Primitive
Unit cell dimensions (Å, °)	
a	12.2027(4)
b	15.1188(4)
c	13.3379(4)
α/β	90.00/94.883(2)
Z/V (Å^3)/D_{Calcd} (g cm^{-3})	4/2451.78(13)/1.483
$F(000)$	1120
μ (Mo-Kα) (cm^{-1})	6.54
Radiation (Å)	0.71070
Pixel size/$2\theta_{max}$ [mm(°)$^{-1}$]	0100/60.3
Refinement collected/unique reflections	141012/7466
R_{int}	0.028
R [$I > 3.00\sigma(I)$]	0.058
Rw [$I > 3.00\sigma(I)$]	0.008
Max/min. peak in final diff. map (e Å^{-3})	0.62/−0.74
Goodness of fit indicator on F^2	1.153

Table 3. Selected bond distances and angles of **3**.

Mo1–O1	1.9342(6)	O1–Mo1–O2	97.03(3)
Mo1–O2	1.6904(8)	O2–Mo1–O3	106.03(4)
Mo1–O3	1.7136(8)	O3–Mo1–O4	82.56(4)
Mo1–O4	2.3726(8)	O4–Mo1–O1	77.13(3)
Mo1–N1	2.2542(9)	O4–Mo1–N1	77.51(3)
Mo1–N3	2.0600(6)	O4–Mo1–N3	80.24(3)
O1–C1	1.3460(1)	O3–Mo1–N3	93.66(3)
C1–C2	1.4060(1)	O3–Mo1–O1	105.64(3)
C2–C7	1.4690(1)	O2–Mo1–N1	94.67(4)
C7–N1	1.3130(1)	O3–Mo1–N1	157.04(4)
N1–N2	1.3960(1)	O2–Mo1–N3	102.12(4)
N2–C14	1.3050(1)	O4–Mo1–O2	170.80(4)
C14–N3	1.3480(1)	O1–Mo1–N1	81.02(3)
C19–N3	1.4420(1)	O1–Mo1–N3	147.83(3)
C19–C20	1.3770(2)	N1–Mo1–N3	71.94(3)
C14–S1	1.7597(8)	C1–O1–Mo1	127.48(6)
C15–S1	1.795(2)	N2–N1–Mo1	116.40(6)

bond has a length of 1.6904(6) Å, and the equatorial Mo1–O3 bond is longer, 1.7136(8) Å. Bond lengths in the chelate rings of **3** indicate that localized π electrons are in N1–C7 and N2–C14 bonds with lengths 1.313(1) and 1.305(1) Å, respectively. The positions of double bonds are the same as analogous molybdenum complexes of *S*-methyl-4-phenyl-thiosemicarbazone [43]. However, in the molybdenum complex obtained from S-methyl-thiosemicarbazone with no substituent on N^4-nitrogen, $[MoO_2(L)CH_3OH]$ (complex **I** in reference 27), the double bond is between N1 and N2 of the five-membered chelate ring. The electron localization of thiosemicarbazone of **3** has been influenced by the phenyl substituents on N3 and also C7.

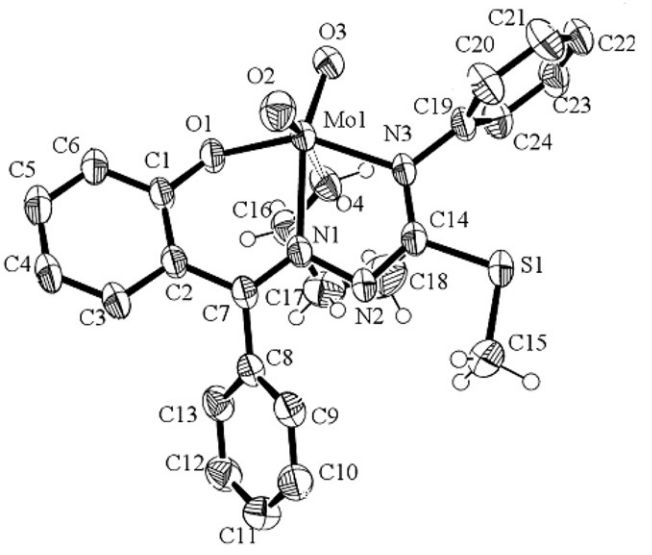

Figure 2. ORTEP diagram and atom numbering scheme for **3**. Aromatic hydrogens are excluded for clarity.

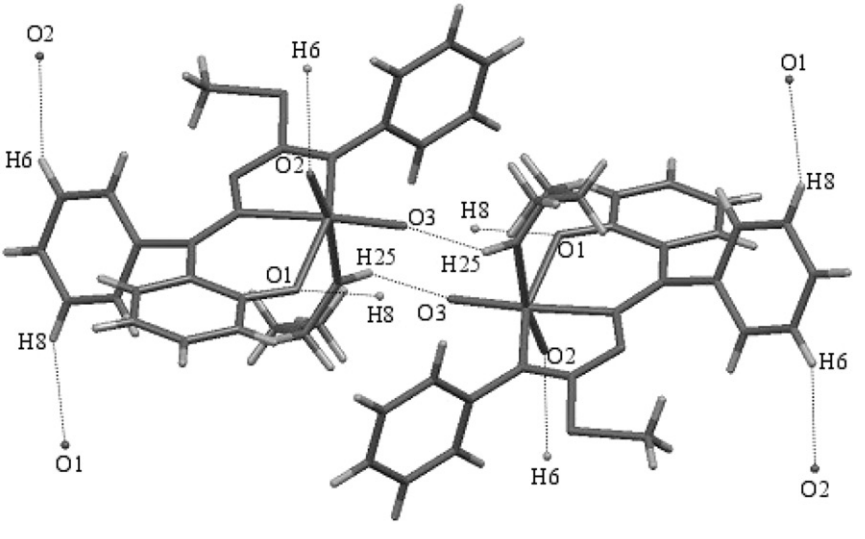

Figure 3. Stick scheme of **3** indicating H-bonding interactions between the molecules.

The $\delta+$ effect of phenyl ring on N3 may cause longer bond lengths between N3 and molybdenum. While Mo–N3 bond length of **I** (see [27]) is 1.9418(11) Å, this bond of **3** has a length of 2.0600(6) Å. Other bond lengths of thioamide group are different compared to the complex where the double bond is localized in N1–N2 [25–27]. The bond lengths of **3**/comp. **I** (see [27]) are *ca.* 1.34/1.37, 1.76/1.64 and 1.79/1.90 Å, N3–C14, C14–S1 and S1–C15, respectively.

The Mo1 centered angles indicate that the five- and six-membered chelate rings are inclined to the oxygen of PrOH. The torsion angles of Mo1–N3–C19–C20/C24 and

N1–C7–C8–C9/C13 are 83.8/−96.2 and 53.7/53.5°, respectively, indicating that the 4-phenyl and unsubstituted benzophenone phenyl rings are not coplanar with the chelate rings.

The crystal structure of **3** showed intermolecular hydrogen bonding between O4 as proton donor and O3 of the neighboring molecule as proton acceptor with the following parameters: O4–H25 0.95, H25 ··· O3^{i} 1.996, O4 ··· O3 2.763 Å and <O4–H25 ··· O3 136.40°, (i) $1-x,-y,1-z$. Pairs of these hydrogen bonds connect two molecules into a dimer and the chelate ring planes of two molecules become approximately parallel (figure 3). Other interactions are formed by O1 and O2 giving longer hydrogen bonds. These hydrogen bond parameters are C10−H6 0.95, H6 ··· O2^{ii} 2.419, C10 ··· O2 3.234, <O2–H6–C10 143.60°, (ii) x, y, $1+z$ and C12−H8 0.95, H8 ··· O1^{iii} 2.658, C12 ··· O1 3.532, <O1–H8–C12 133.18°, (iii) $3/2-x$, $-1/2+y$, $1/2-z$. The dimer structure repeats itself through these H-bonding interactions in the form of a bifurcated arrangement.

4. Conclusion

Syntheses of [MoO_2(L)L′] have been realized by using the sulfur or N^4-nitrogen of substituted thiosemicarbazone derivatives [–C(SR)–N^4H_2 or –C(SH)–N^4HR]. The ON^1N^4 chelates were prepared using only *S*-substituted thiosemicarbazones in all studies except our previous article [26]. In reaction of the NH_2–SR group with $MoO_2(acac)_2$, a Mo–N^4 bond (Mo–NH–SR bond) forms by losing a proton of thioamide.

As part of our studies on thiosemicarbazones, we report chelation of the disubstituted thioamide group, –C(SR^2)–N(R^1)–H, and formation of a –C(SR^2)–N(R^1)–Mo system for new ON^1N^4 molybdenum chelates synthesized from benzophenone thiosemicarbazones.

Structural properties of the **3** suggest different conjugation of the ON^1N^4 chelate rings in comparison to [MoO_2(L)CH_3OH] (L: 2-hydroxy-1-naphthaldehyde-*S*-methyl-thiosemicarbazone) [27].

The *cis*-MoO_2 center shows a bio-catalytic function in oxo-transfer reactions. A large number of *cis*-MoO_2 complexes of various ligands which have ONO [3, 45, 46], ONS [9], ONNO [47] or SNNS [2, 8, 47] donor sets and some thiosemicarbazones [47] as ONS ligands have been synthesized, and the significant results on their catalytic activities for oxygen atom transfer (OAT) were reported. It can be suggested that the synthesized *cis*-MoO_2 complexes (**1**–**5**) would be suitable structures for metal-catalyzed OAT reactions.

Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 659903 for [MoO_2(L)PrOH]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from

the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk).

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