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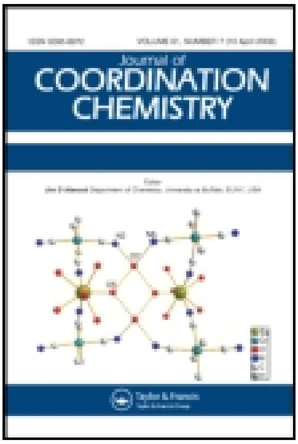

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Synthesis and crystal structures of N′-(3-ethoxy-2-hydroxybenzylidene)-3-methylbenzohydrazide and its dioxomolybdenum(VI) complex

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Synthesis and crystal structures of *N′*-(3-ethoxy-2-hydroxybenzylidene)-3-methylbenzohydrazide and its dioxomolybdenum(VI) complex

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A new hydrazone *N′*-(3-ethoxy-2-hydroxybenzylidene)-3-methylbenzohydrazide (H_2L), derived from condensation of 3-ethoxysalicylaldehyde with 3-methylbenzohydrazide, and its dioxomolybdenum(VI) complex [$MoO_2L(CH_3OH)$], have been prepared and characterized by physico-chemical methods and single crystal X-ray diffraction. The hydrazone coordinates to Mo through the phenolate O, imine N, and enolic O. The Mo is six-coordinate in a distorted octahedral geometry, with the three donors of L and one oxo defining the equatorial plane, and with one methanol and another oxo occupying the axial positions. The bond values especially for those related to the donors in the complex are different from those in H_2L.

Keywords: Hydrazone; Dioxomolybdenum complex; Crystal structure; Synthesis; Coordination compound

1. Introduction

Hydrazones and their complexes have been widely investigated for their structures and versatile applications in analytical, catalytic, and medicinal chemistry [1–3]. The hydrazones due to their facile keto-enol tautomerization and the availability of several potential donors can coordinate with metals in versatile ways [4–6]. The coordination chemistry of molybdenum(VI) has attracted considerable attention due to its catalytic properties in various oxidation reactions [7–9]. Recent reports indicate that the molybdenum(VI) complexes with hydrazones possess oxygen transfer properties as they were found to oxidize thiols, hydrazine, polyketones, and tertiary phosphines [10, 11]. In comparison with other complexes with hydrazones, the number of crystal structures of molybdenum complexes with hydrazones is rather few. As an extension of the work on the synthesis and coordination of molybdenum complexes with hydrazones, the author reports here the synthesis and characterization of a new hydrazone, *N′*-(3-ethoxy-2-hydroxybenzylidene)-3-methylbenzohydrazide (H_2L), and its dioxomolybdenum(VI) complex [$MoO_2L(CH_3OH)$] (scheme 1).

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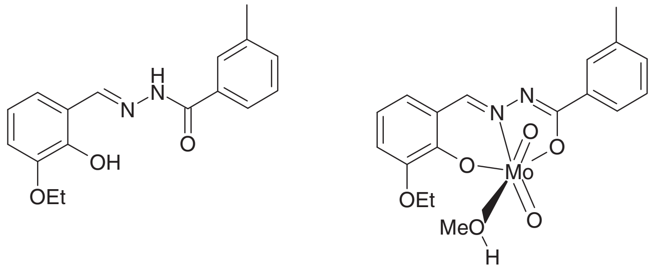

H_2L $[MoO_2L(CH_3OH)]$

Scheme 1. H_2L and $[MoO_2L(CH_3OH)]$.

2. Experimental

2.1. *Materials and methods*

High-purity 3-ethoxysalicylaldehyde (Aldrich, USA) and 3-methylbenzohydrazide (Lancaster, UK) were used as received. All other chemicals and solvents were of AR grade and used as received. $[MoO_2(acac)_2]$ was prepared according to the literature method [12]. Elemental analyses (carbon, hydrogen, and nitrogen) were performed on a Perkin Elmer 2400 elemental analyzer. IR spectra (KBr discs) were recorded using a JASCO FT-IR model 420 spectrometer. Molar conductance was measured using a DDS-11A conductivity meter and acetonitrile used as the solvent.

2.2. *Synthesis of $H_2L \cdot H_2O$*

To a stirred methanolic solution (20 mL) of 3-ethoxysalicylaldehyde (1.67 g, 0.01 mol), a methanolic solution (20 mL) of 3-methylbenzohydrazide (1.50 g, 0.01 mol) was added. The mixture was stirred at reflux for 30 min. Afterwards, the mixture was cooled to room temperature, and the product formed was collected by filtration. The solid product was washed with cold methanol and dried over silica gel. Yield: 78%. Anal. Calcd (%) for $C_{17}H_{18}N_2O_3$: C, 68.4; H, 6.1; and N, 9.4. Found (%): C, 68.2; H, 6.1; and N, 9.3. Selected IR data (KBr, cm^{-1}): 3542 (m, H_2O), 3425 (m, O–H), 3235 (w, N–H), 1646 (vs, C=O), and 1607 (s, C=N). Single crystals suitable for X-ray diffraction were formed by recrystallization of the product from 95% ethanol.

2.3. *Synthesis of $[MoO_2L(CH_3OH)]$*

To a stirred methanolic solution (15 mL) of $MoO_2(acac)_2$ (0.33 g, 1.0 mmol), a methanolic solution (15 mL) of H_2L (0.30 g, 1.0 mmol)was added, which resulted in an instant color change to yellow. The mixture was stirred at room temperature for 1 h and filtered. The filtrate was left at room temperature to slowly evaporate the solvent for a few days, yielding yellow block single crystals of the complex, suitable for X-ray diffraction. Yield: 37%. Anal. Calcd (%) for $C_{18}H_{20}MoN_2O_6$: C, 47.4; H, 4.4; and N, 6.1. Found (%): C, 47.6; H, 4.5; and N, 6.0. Selected IR data (KBr, cm^{-1}): 3422 (br, w, OH), 1611 (s, C=N), 1257 (s, C–O, enolic), 1224 (w, C–O, phenolate), 1086 (w, N–N), 946, and 918 (s, MoO_2). $\Lambda_M = 9.5\ \Omega^{-1}\ cm^2\ mol^{-1}$ in acetonitrile.

Table 1. Crystallographic and experimental data for the compounds.

Compound	$H_2L \cdot H_2O$	$[MoO_2L(CH_3OH)]$
Empirical formula	$C_{17}H_{20}N_2O_4$	$C_{18}H_{20}MoN_2O_6$
Formula weight	316.3	456.3
Temperature, T (K)	298(2)	298(2)
Wavelength, λ (Mo-Kα) (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
Unit cell dimensions (Å, °)		
a	6.526(1)	10.023(2)
b	13.507(3)	10.900(2)
c	18.656(4)	17.198(3)
β	90	95.892(2)
Volume, V (Å^3), Z	1644.5(6), 4	1869.0(6), 4
Absorption coefficient (Mo-Kα) (cm^{-1})	0.092	0.739
Crystal size (mm^3)	0.23 × 0.20 × 0.20	0.30 × 0.27 × 0.23
Max. (T_{max}) and min. (T_{min}) transmission	0.979 and 0.982	0.809 and 0.848
Measured reflections	13,236	10,684
Unique reflections	3519	4027
Observed reflections	1747	3266
Parameters/restraints	220/4	250/1
Goodness-of-fit on F^2	1.035	1.090
Final R indices $[I \geq 2\sigma(I)]$[a]	$R_1 = 0.0897$, $wR_2 = 0.1239$	$R_1 = 0.0274$, $wR_2 = 0.0646$
R indices (all data)[a]	$R_1 = 0.1933$, $wR_2 = 0.1530$	$R_1 = 0.0398$, $wR_2 = 0.0727$

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

2.4. *X-ray structural determination*

Suitable single crystals were mounted on a Bruker SMART CCD diffractometer equipped with a graphite monochromator and Mo-Kα ($\lambda = 0.71073$ Å) radiation. Diffraction data were measured using the ω-scan mode. Crystal data and data collection parameters are listed in table 1. The intensity data were corrected for Lorentz and polarization effects and the absorption correction was employed using SAINT [13] and SADABS [14]. The structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELXTL [15]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The water and amino hydrogens in $H_2L \cdot H_2O$ and methanol hydrogen in the complex were located from difference Fourier maps and refined isotropically, with N–H, O–H, and H $\cdots$ H distances restrained to 0.90(1), 0.85(1), and 1.37(2) Å, respectively. The remaining hydrogens were placed in calculated positions. Selected bond lengths and angles for the compounds are listed in table 2. Hydrogen bonding information is summarized in table 3.

3. Results and discussion

The hydrazone $H_2L \cdot H_2O$ was readily prepared by condensation of 3-ethoxysalicylaldehyde with 3-methylbenzohydrazide in methanol, followed by recrystallization from ethanol. The dioxomolybdenum(VI) complex was prepared by reacting $[MoO_2(acac)_2]$ with H_2L in methanol. The ligand adopts an enolic tautomeric form on complexation. Both the ligand and complex are stable in air for an extended period of time and soluble

Table 2. Selected bond lengths (Å) and angles (°) for the compounds.

$H_2L \cdot H_2O$			
C7–N1	1.278(5)	N1–N2	1.373(5)
N2–C8	1.349(5)	C8–O3	1.240(5)
C2–O1	1.359(5)		
C7–N1–N2	117.8(4)	N1–N2–C8	118.7(4)
N2–C8–C9	118.3(4)	N2–C8–O3	120.3(5)
$MoO_2L(CH_3OH)$			
Mo1–O1	1.937(2)	Mo1–O3	2.022(2)
Mo1–O4	2.370(2)	Mo1–O5	1.697(2)
Mo1–O6	1.683(2)	Mo1–N1	2.242(2)
C7–N1	1.285(3)	N1–N2	1.406(3)
N2–C8	1.311(3)	C8–O3	1.308(3)
C2–O1	1.345(3)		
O1–Mo1–O3	149.2(1)	O1–Mo1–N1	81.6(1)
O5–Mo1–O1	103.3(1)	O5–Mo1–O3	96.8(1)
O5–Mo1–N1	156.6(1)	O3–Mo1–N1	71.0(1)
O6–Mo1–O1	99.3(1)	O6–Mo1–O3	97.3(1)
O6–Mo1–O5	106.0(1)	O6–Mo1–N1	95.6(1)
O6–Mo1–O4	170.1(1)	O5–Mo1–O4	83.1(1)
O1–Mo1–O4	81.8(1)	O3–Mo1–O4	77.6(1)
N1–Mo1–O4	74.8(1)	C7–N1–N2	117.6(2)
N1–N2–C8	108.8(2)	N2–C8–C9	120.5(2)
N2–C8–O3	122.9(2)		

Table 3. Hydrogen bonding for the compounds.

D–H ··· A	$d(D$–H) (Å)	d(H ··· A) (Å)	$d(D \cdots A)$ (Å)	$\angle(D$–H ··· $A)$ (°)
$H_2L \cdot H_2O$				
O1–H1 ··· N1	0.82	1.88	2.599(5)	146
N2–H2 ··· O7^{i}	0.90(1)	2.08(3)	2.911(5)	153(5)
O7–H7B ··· O3^{ii}	0.85(1)	1.93(2)	2.756(5)	163(5)
O7–H7A ··· O2	0.85(1)	2.16(3)	2.930(4)	152(5)
$MoO_2L(CH_3OH)$				
O4–H4 ··· N2^{iii}	0.84(1)	2.04(1)	2.868(3)	170(4)

Symmetry codes: $^{i}1-x, -1/2+y, 1/2-z$; $^{ii}1+x, y, z$; $^{iii}2-x, 2-y, -z$.

in DMF, DMSO, chloroform, dichloromethane, acetonitrile, methanol, and ethanol, and insoluble in water and diethyl ether. Elemental analyses of the compounds are in agreement with theoretical expectation. The low conductivity in acetonitrile suggests non-electrolyte complex in solution [16].

3.1. *IR spectra*

The middle absorption band at 3235 cm^{-1} in the spectrum of $H_2L \cdot H_2O$, attributed to the N–H stretch, is absent in the spectrum of the dioxomolybdenum(VI) complex, indicating coordination of L through the enolic tautomeric form. This type of coordination mode of L has been confirmed by X-ray analysis of the complex. Weak coordination of methanol *trans* to the oxo is not uncommon in oxomolybdenum complexes with tridentate ligands when these are synthesized or crystallized in methanol

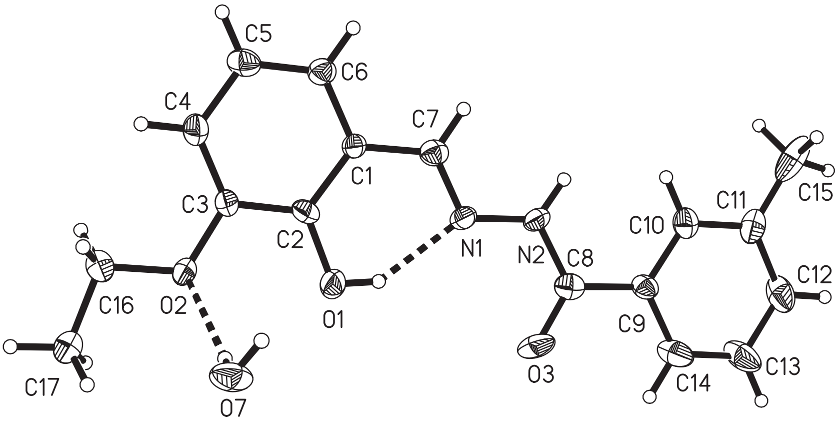

Figure 1. ORTEP of $H_2L \cdot H_2O$ with 30% thermal ellipsoids. Hydrogen bonds are drawn as dashed lines.

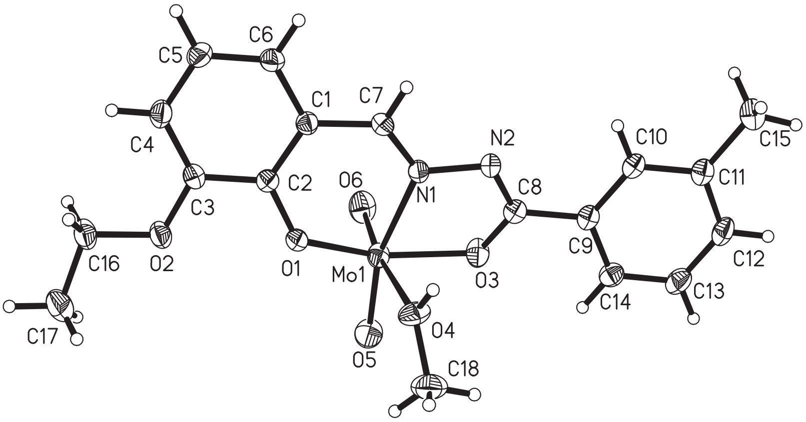

Figure 2. ORTEP of $[MoO_2L(CH_3OH)]$ with 30% thermal ellipsoids.

[17, 18]. Weak and broad absorptions at 3425 and 3422 cm^{-1} in spectra of ligand and complex prove the existence of O–H stretches of phenol of $H_2L \cdot H_2O$ and methanol ligand of the complex. The ligand showed C=O, C=N, and C–OH stretches at 1646, 1607, and 1249 cm^{-1}, respectively. The complex showed two prominent bands at 946 and 918 cm^{-1} attributed to *cis*-dioxomolybdenum. Bands due to $\nu_{C=O}$ and ν_{NH} were absent in the complex, and a new C–O stretch appeared at 1257 cm^{-1}, suggesting occurrence of keto-imine tautomerization of the ligand during complexation. The –C=N– vibration in the complex is at 1611 cm^{-1}. New bands at 830, 731, 684, and 615 cm^{-1} may be attributed to Mo–O and Mo–N bonds.

3.2. *Molecular structures of the hydrazone and the dioxomolybdenum(VI) complex*

Figures 1 and 2 give perspective views of the monohydrate form of the hydrazone and the dioxomolybdenum(VI) complex. The hydrazone crystallizes in the orthorhombic space group $P2_12_12_1$ and the complex in the monoclinic space group $P2_1/n$.

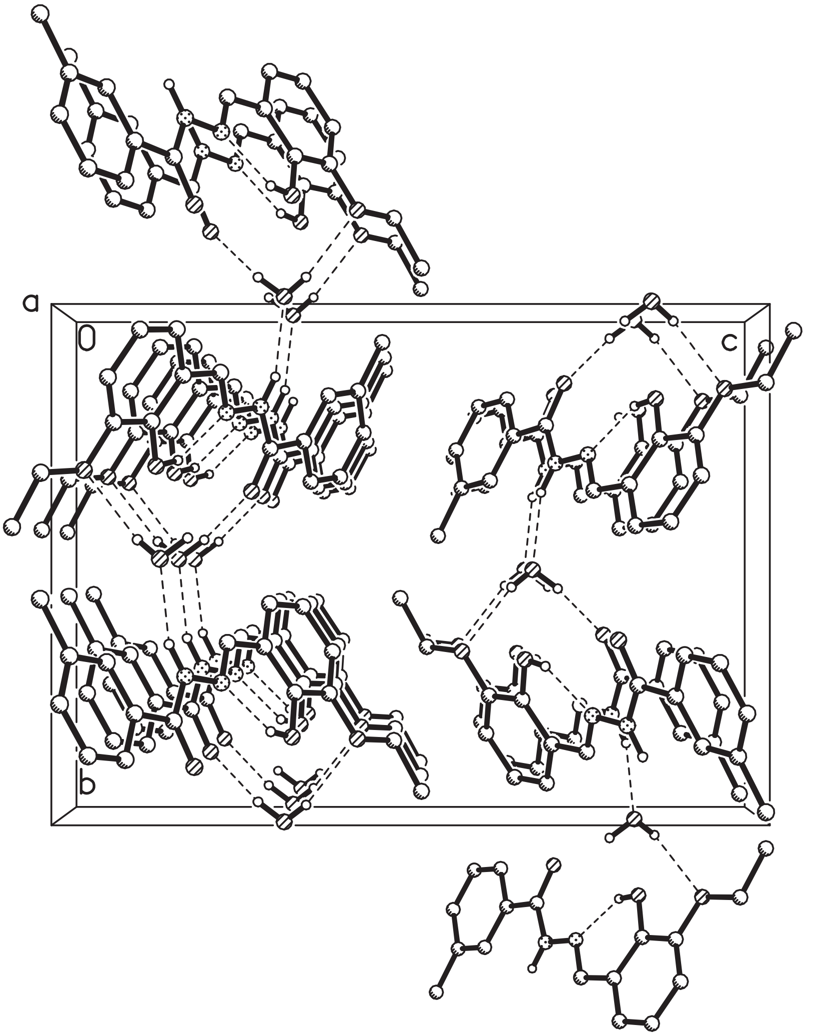

Figure 3. Molecular packing of $H_2L \cdot H_2O$. Hydrogen bonds are drawn as dashed lines.

The hydrazone crystallizes as a monohydrate with water linked to the hydrazone through O–H ··· O and N–H ··· O hydrogen bonds. In the hydrazone molecule, there is an intramolecular O1–H1 ··· N1 hydrogen bond, which contributes to the planarity of the molecule. The dihedral angle between the two benzene rings is 6.4(2)°. The complex is a mononuclear dioxomolybdenum(VI) compound. The ligand forms one five-membered ring and one six-membered chelate ring with bite angles of 71.0(1)° and 81.6(1)°. Mo is in a distorted octahedral O_5N coordination sphere. The phenolate O1, imine N1, enolic O3 of L, and the oxo O5 constitute the equatorial plane of the octahedral coordination. The two axial positions of the octahedral coordination are occupied by oxo O6 and methanol O4. Displacement of Mo from the equatorial plane toward the axial oxo group is 0.339(2) Å. The *cis* bond angles are in the range 71.0(1)–106.0(1)° and the *trans* bond angles in the range 149.2(1)–170.1(1)°. The Mo–O and

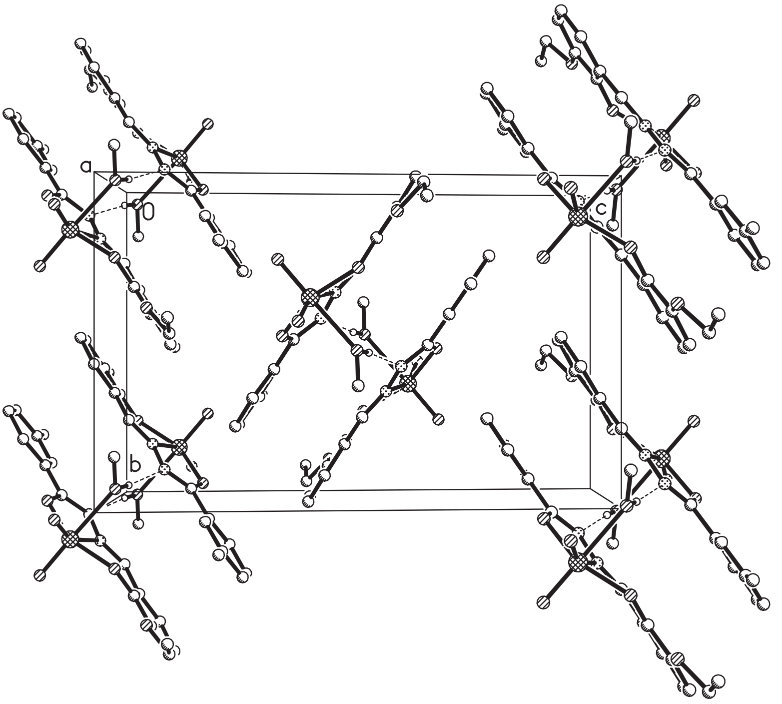

Figure 4. Molecular packing of [$MoO_2L(CH_3OH)$]. Hydrogen bonds are drawn as dashed lines.

Mo–N bond lengths in the complex are comparable with those observed in other oxomolybdenum complexes with hydrazones [17–20]. As commonly observed in analogous species, the elongated Mo1–O4 bond *trans* to oxo O6 indicates weak coordination of O4 at the axial position. The dihedral angle between the two benzene rings in the complex is 3.2(2)°.

The hydrazone coordinates to Mo through phenolate O1, imine N1, and enolic O3, which is consistent with those reported in the literature [17–20]. The bond lengths of C7=N1 [1.285(3) Å] and N1–N2 [1.406(3) Å] in the complex are longer than those [1.278(5) and 1.373(5) Å] in the free ligand, indicating that the imine is coordinated to Mo. The distance between C8 and N2 [1.311(3) Å] in the complex is shorter than that [1.349(5) Å] in the free ligand, and the distance between C8 and O3 [1.308(3) Å] in the complex longer than that [1.240(5) Å] in the free ligand, indicating the enolization of the N2–C8–O3 group in the complex.

In the crystal structure of the hydrazone, the hydrazone and water are linked through intermolecular N–H$\cdots$O and O–H$\cdots$O hydrogen bonds, forming layers parallel to the *ab* plane (figure 3). In the crystal structure of the complex, adjacent molecules are linked through two intermolecular O–H$\cdots$N hydrogen bonds, forming a dimer (figure 4).

Molybdenum complexes with Schiff bases or hydrazones usually adopt octahedral coordination [21–28]. The octahedral coordination of complexes **1**–**11** listed in table 4 consists of three donors of the ligand, one MoO_2 core, and an oxygen of a solvent, usually methanol or ethanol.

Table 4. The coordination geometry around the Mo center and the ligands for several molybdenum complexes.

Complex	Coordination geometry	Ligand	Reference
1	Octahedral	*N*′-(2-hydroxybenzylidene)-2-hydroxybenzohydrazide	[21]
2	Octahedral	*N*′-(2-hydroxybenzylidene)-2-hydroxybenzohydrazide	[22]
3	Octahedral	*N*′-(2-hydroxybenzylidene)isonicotinohydrazide	[23]
4	Octahedral	*N*′-(2-hydroxybenzylidene)isonicotinohydrazide	[24]
5	Octahedral	*N*′-[trimethylammoniomethyl(hydroxy)methyleneamino]-salicylaldimine	[25]
6–9	Octahedral	*N*′-(5-bromo-2-hydroxybenzylidene)-2-methyl-4-pyrazoloylhydrazone; *N*′-(2-hydroxybenzylidene)-2-methyl-4-pyrazoloylhydrazone; *N*′-[1-(2-hydroxyphenyl)ethylidene]-2-methyl-4-pyrazoloylhydrazone; *N*′-(2-hydroxy-5-nitrobenzylidene)-2-methyl-4-pyrazoloylhydrazone	[26]
10	Octahedral	*N*′-(2-hydroxynaphthylidene)benzohydrazide	[27]
11	Octahedral	*N*′-(2-hydroxybenzylidene)benzohydrazide	[28]

4. Conclusion

A new hydrazone was prepared by the condensation of 3-ethoxysalicylaldehyde with 3-methylbenzohydrazide. Using the hydrazone, a new dioxomolybdenum(VI) complex was prepared and structurally characterized. The hydrazone coordinates to Mo through phenolate O, imine N, and enolic O.

Supplementary material

CCDC 828385 for $H_2L \cdot H_2O$ and 828386 for $[MoO_2L(CH_3OH)]$ contain the supplementary crystallographic data. These data can be obtained free of charge *via* http://www.ccdc.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.

Acknowledgments

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