

Synthesis of Two Molybdenum(VI) Complexes Coordinated by Schiff Base Derivatives: *N*-Phenyl-2-hydroxy-1-naphthaldimine and *N*-Benzyl-2-hydroxy-1-naphthaldimine. Molecular and Crystal Structure of $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{OCH}_3)(2\text{-OC}_{10}\text{H}_6\text{CH}=\text{NHC}_6\text{H}_5)]$

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The synthesis of two monomeric molybdenum(VI) Schiff base complexes derived from *N*-phenyl-2-hydroxy-1-naphthaldimine and *N*-benzyl-2-hydroxy-1-naphthaldimine: $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{OCH}_3)(2\text{-OC}_{10}\text{H}_6\text{CH}=\text{NHC}_6\text{H}_5)]$ (**I**) and $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{OCH}_3)(2\text{-OC}_{10}\text{H}_6\text{CH}=\text{NHCH}_2\text{C}_6\text{H}_5)]$ (**II**) described in this paper are the first examples in which potentially bidentate Schiff bases are monodentately bonded to molybdenum as zwitterionic ligands. The structure of complex **I** was determined by X-ray analysis. Within the same ligand, the hydrogen atom attached to nitrogen forms an intramolecular hydrogen bond of 2.548(2) Å with the oxygen atom coordinated to molybdenum. The octahedral coordination of molybdenum is completed by two oxo-oxygens, two acetylacetonato oxygens and one methoxy oxygen. The compounds were characterized by chemical analysis, IR spectroscopy and single crystal structure determination.

INTRODUCTION

The numerous molybdenum(VI) Schiff base complexes have been extensively investigated for over twenty years. Owing to their importance in the domains of stereochemistry,¹ structural² and analytical chemistry³ and as model systems for the interaction of organic substrates with catalytic oxide surfaces,⁴ some of them are also interesting due to their ability to oxidize thiols, hydrazines, polyketones and tertiary phosphines.^{5,6,7} Their oxygen atom transfer properties play a significant role in investigating the functioning mechanism of molybdenum oxotransferase.^{8,9} Although a number of literature reports deal with the mononuclear dioxomolybdenum(VI) complexes

of bi-, tri- or tetradentate Schiff base ligands,^{1-5, 8-16} complexes containing monodentately coordinated Schiff base derivatives as zwitterionic ligands are extremely rare.⁴ In this paper we describe the first two examples of such mononuclear molybdenum(VI) complexes.

EXPERIMENTAL

Reagents and Apparatus

All chemicals were of reagent grade and used as purchased from commercial sources. The starting complex $[\text{MoO}_2(\text{acac})_2]$ was prepared as described in the literature.¹⁷

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TABLE I. Crystallographic data for compound **I**

I	
Chemical formula	MoO ₂ (C ₅ H ₇ O ₂)(OCH ₃)-(C ₁₇ H ₁₃ NO)
<i>M_r</i>	505.36
Crystal system	triclinic
Colour	yellow
Space group	<i>P</i> $\bar{1}$
<i>a</i> / Å	8.0478(19)
<i>b</i> / Å	10.2829(19)
<i>c</i> / Å	13.7790(12)
α / °	76.541(12)
β / °	82.295(18)
γ / °	77.4(2)
<i>V</i> / Å ³	1078.1(3)
<i>Z</i>	2
<i>T</i> / K	293
<i>D_c</i> / g cm ⁻³	1.557
μ / mm ⁻¹	0.648
F(000)	516
2 θ range for data collection / °	2.60 to 30.00
<i>h, k, l</i> range	-11 to 11, -13 to 14, 0 to 19
Scan type	ω
Data measured	6239
Unique data	6239
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	5061
Number of variables	285
Max/min $\Delta\rho$ / e ³ Å ⁻³)	0.501, -0.500
Extinction coefficient	0.0029(9)
<i>R</i> (<i>F_o</i>)	0.0329
<i>R_w</i> (<i>F_o</i> ²)	0.0805
Goodness of fit <i>F</i> ² , <i>S</i>	1.028
Maximum Δ / σ	0.006

TABLE II. Selected bond lengths and angles for **I**

Bond lengths / Å		Bond angles / Å	
Mo1–O1	1.6958(17)	O1–Mo1–O2	103.62(9)
Mo1–O2	1.7004(16)	O1–Mo1–O3	94.60(8)
Mo1–O3	2.0744(16)	O2–Mo1–O3	91.04(8)
Mo1–O4	2.2128(16)	O1–Mo1–O4	91.09(8)
Mo1–O5	2.2143(15)	O3–Mo1–O4	79.43(6)
Mo1–O6	1.8873(16)	O6–Mo1–O4	83.06(7)
O3–C2	1.287(3)	O2–Mo1–O5	89.60(7)
O4–C4	1.266(3)	O3–Mo1–O5	82.10(7)
O5–C6	1.293(2)	O4–Mo1–O5	75.41(6)
O6–C23	1.400(3)	O6–Mo1–O5	81.50(7)
N1–C16	1.312(3)	O1–Mo1–O6	98.11(9)
N1–C17	1.421(3)	O2–Mo1–O6	102.63(8)

The IR spectra were recorded in KBr with a FTIR 1600 Fourier-transform spectrophotometer in the 4500–450 cm⁻¹ region. Molybdenum was analytically determined according to the literature.¹⁸

Synthesis and Characterization of Complexes

General Procedure. – MoO₂(acac)₂ (1.00 mol) and *N*-phenyl-2-hydroxy-1-naphthaldimine (1.00 mol) or *N*-benzyl-2-hydroxy-1-naphthaldimine (1.00 mol) were refluxed in a mixture of dry methanol (10 mL) and dichloromethane (10 mL) for 1.5 h. When the solutions were concentrated under reduced pressure and left in a refrigerator overnight, the precipitated yellow crystalline products of [MoO₂(C₅H₇O₂)(OCH₃)(2-OC₁₀H₆CH=NHC₆H₅)] (**I**) and [MoO₂(C₅H₇O₂)(OCH₃)(2-OC₁₀H₆CH=NHC₆H₅)] (**II**) were isolated.

(**I**) Yield 0.2 g (64.3 %). IR (KBr) ν_{\max} /cm⁻¹: 1625(C=N), 1585, 1545(C=O), 1182(C–O), 927(O=Mo=O), 902(O=Mo=O).

Anal. Calcd. for C₂₃H₂₃MoNO₆: C, 54.66; H, 4.59; Mo, 18.98; N, 2.77 %. Found: C, 54.66; H, 4.55; Mo, 19.67; N, 2.70 %.

(**II**) Yield 0.26 g (81.5 %). IR (KBr) ν_{\max} /cm⁻¹: 1634(C=N), 1544, 1594(C=O), 1138(C–O), 928(O=Mo=O), 893(O=Mo=O).

Anal. Calcd. for C₂₄H₂₅MoNO₆: C, 55.50; H, 4.85; Mo, 18.47; N, 2.70 %. Found: C, 55.83; H, 4.81; Mo, 19.3; N, 2.79 %.

Crystal Structure Determination

Crystal parameters, data collection details and refinement results for compound **I** are summarized in Table I. Selected bond lengths and angles are listed in Table II.

Diffraction data for **I** were collected at room temperature on a Philips PW1100 diffractometer updated by STOE, with graphite-monochromated Mo-K α radiation (λ = 0.7107 Å). Unit cell parameters were obtained by the least-squares refinement from the settings of 30 reflections, 18 < 2 θ < 36°. Reference reflections were monitored periodically during data collection, every 90 minutes, and showed no significant

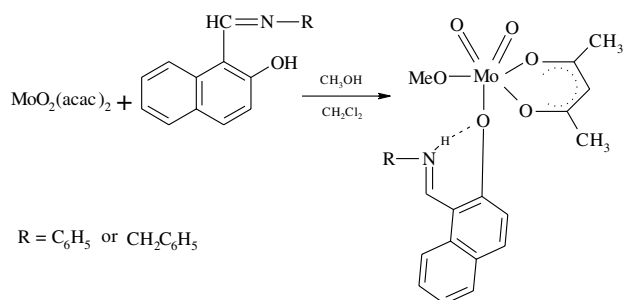


Figure 1. Synthesis reaction scheme for the complexes $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{OCH}_3)(2\text{-OC}_{10}\text{H}_6\text{CH}=\text{NHC}_6\text{H}_5)]$ (**I**) and $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{OCH}_3)(2\text{-OC}_{10}\text{H}_6\text{CH}=\text{NHCH}_2\text{C}_6\text{H}_5)]$ (**II**).

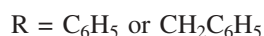
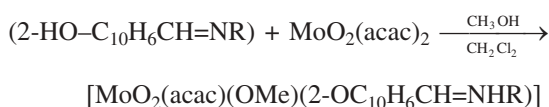
variation in intensities. The data were corrected for the Lorentz and polarization effects by the X-RED programme.¹⁹ The structure of complex **I** was solved by the Patterson and Fourier methods using SHELXS-97,²⁰ and refined by the full-matrix least-squares method based on F^2 values against all reflections assuming anisotropic temperature factors for all non-H atoms using the SHELXL-97 programme.²¹

The positions of hydrogen atoms bonded to carbon atoms were geometrically optimized applying the riding model ($\text{C}_{\text{aro}}\text{-H}$ and $\text{C}_{\text{sp}^3}\text{-H}$ 0.93 and 0.96 Å, respectively, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}_{\text{aro}})$, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C}_{\text{sp}^3})$). Hydrogen atom H1, belonging to the nitrogen atom N1, was located in a difference Fourier map with the N1-H1 distance of 0.86 Å, and was included in the structure factor calculation at a fixed position.

All attempts to prepare crystals of **II** suitable for X-ray structure analysis failed. Nevertheless, the structure obtained and refined up to $R = 0.134$ from the X-ray data collected from a very thin plate crystal ($0.03 \times 0.20 \times 0.22$ mm) essentially confirmed the analogy between the structures of **I** and **II**. Preliminary crystal data of **II** are as follows: monoclinic, $P2_1/n$, $a = 13.142(3)$, $b = 11.080(2)$, $c = 16.011(3)$ Å, $\beta = 102.84(2)^\circ$, $Z = 4$, $V = 2273.1(8)$ Å³, $D_c = 1.52$ g cm⁻³.

RESULTS AND DISCUSSION

The synthesis of the molybdenum complexes reported can be achieved *via* the ligand substitution reaction of $\text{MoO}_2(\text{acac})_2$ with the appropriate Schiff base in a mixture of methanol and dichloromethane. Instead of the expected deprotonation of the Schiff base, the reaction occurred by the deprotonation of methanol:



Both molybdenum complexes are yellow crystalline solids that appeared to be air and moisture stable. They exhibit two $\nu(\text{O}=\text{Mo}=\text{O})$ vibrations at about 930 (ν_{asym}) and

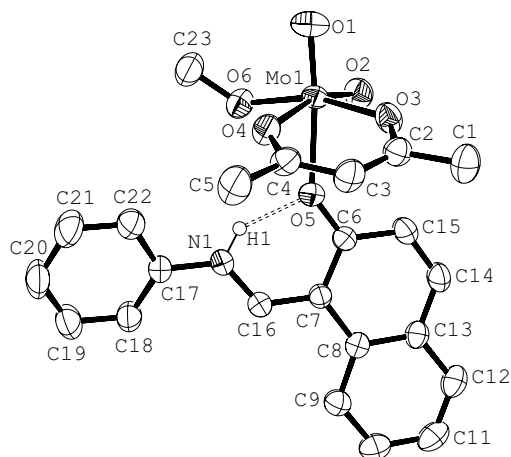


Figure 2. ORTEP³¹ representation of $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{OCH}_3)(2\text{-OC}_{10}\text{H}_6\text{CH}=\text{NHC}_6\text{H}_5)]$ (**I**) with the atom numbering scheme. Thermal ellipsoids are at 50 % probability level. Hydrogen atoms, except for H1 forming the intramolecular hydrogen bond, are omitted for clarity.

890–900 cm^{-1} (ν_{sym}), confirming the presence of a *cis*- MoO_2 structure. The $\nu(\text{C}=\text{N})$, $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})_{(\text{alcoholic})}$ strong to medium bands appeared at about 1634–1625, 1590–1545 and 1182–1138 cm^{-1} , respectively. The peaks observed at 835 cm^{-1} **I** and 836 cm^{-1} **II** may be attributed to the $\text{Mo}-\text{OCH}_3$ vibration.²²

The crystal structure of **I** is built up of mononuclear molecules with the MoO_2^{2+} core as shown in Figure 2. The molybdenum atom is octahedrally coordinated by six oxygen atoms: two oxo-ligands, two oxygens from acetylacetonato ligand, one from the *N*-phenyl-2-hydroxy-1-naphthalaldimine and one from the methoxy group. The octahedral coordination is considerably distorted with the angles at Mo atom ranging from 75.41(6) to 103.62(9)°. The $\text{Mo}=\text{O}$ distances of 1.6958(17) and 1.7004(16) Å and the $\text{O}=\text{Mo}=\text{O}$ angle of 103.62(9)° are in the usual range for such complexes.²³

The acetylacetonato ligand is bidentately coordinated to the molybdenum atom with $\text{Mo}-\text{O}_{\text{acac}}$ distances of 2.074(2) and 2.214(2) Å, which are close to the values already observed in previously determined structures of Mo(VI) complexes with β -diketones.^{24–26} The *N*-phenyl-2-hydroxy-1-naphthalaldimine is unexpectedly coordinated in monodentate manner as a zwitterionic ligand through the oxygen atom O5 from the naphthalaldimine part of the molecule. The $\text{Mo}-\text{O5}$ bond length of 2.2143(15) Å is relatively long, due to the *trans* influence of the multiply bonded oxo-ligand.²⁷ Methoxy group is coordinated to molybdenum in *cis* position with respect to oxo-oxygens, with the $\text{Mo}-\text{O6}$ distance of 1.8873(16) Å. This value is significantly shorter than those found in complexes with the methanol molecule coordinated as a neutral ligand in spite of being *trans* to terminal oxygen.^{1,28}

The C6–O5 [1.293(2) Å] and N1–C16 [1.312(3) Å] bonds correspond to the values observed for the ketoamino

TABLE III. π stacking and C–H... π contact parameters

π stacking rings ^(a)	(1)...(1) ⁱ	(1)...(2) ⁱ	(3)...(3) ⁱⁱ
Ct...Ct/Å ^(b)	4.22	4.52	4.20
\angle P–P/ ^(c)	0	2.0	0
Ct...P/Å ^(d)	3.49	3.42	3.58
\angle P–CCt/ ^(e)	34.1	38.9	31.5
C–H... π contact	C1–H3...Ct(1) ⁱⁱⁱ	C1–H4...Ct(2) ⁱⁱⁱ	C11–H11...Ct(3) ^{iv}
H...Ct/Å ^(f)	2.89	3.31	3.19
H...P/Å	2.86	3.19	3.16
\angle C–H...Ct/ ^(g)	137.1	123.7	121.6

^(a) Ring (1) is defined with atoms C6, C7, C8, C13, C14 and C15, ring (2) with C8, C9, C10, C11, C12 and C13, ring (3) with C17, C18, C19, C20, C21 and C22. Symmetry code: i = 1–x, 1–y, 2–z; ii = 1–x, 1–y, 1–z; iii = –x, 2–y, 2–z; iv = –x, 1–y, 2–z. ^(b) Ct...Ct = distance between ring centroids. ^(c) \angle P–P = dihedral angle between the ring centroids. ^(d) Ct...P = perpendicular distance from the centroid to the other ring plane. ^(e) \angle P–CCt = angle between the Ct...Ct vector and the normal to the ring plane. ^(f) H...Ct = distance between the hydrogen atom and the ring centroid. ^(g) H...P = perpendicular distance from the hydrogen atom to the ring plane.

(NH) tautomers of the Schiff bases derived from 2-hydroxy-1-naphthaldehyde.^{29–30} Protonation of the imino group in the *N*-phenyl-2-hydroxy-1-naphthalimine is supported also by locating the hydrogen atom H1 in a difference map, involved in a strong intramolecular hydrogen bond N1–H1...O5 [N1–H1 fixed at 0.86 Å, H1...O5 1.81 Å, N1...O5 distance of 2.548(2) Å and the angle N1–H1...O5 of 142.4°] reinforced by π -delocalization along the atoms in the ligand molecule. A torsion flexibility of *N*-substituent induced by twisting around the single N_{sp2}–C_{sp2}(N1–C17) bond is established by C16–N1–C17–C18, torsion angle –24.8(4)°. The dihedral angle between the two planes defined by the carbon ring atoms [C(6)–C(15) and C(17)–C(22)] is 23.92(11)°. (Figure 2). Crystal packing appears to be mostly controlled by π stacking between the aromatic rings of *N*-phenyl-2-hydroxy-1-naphthalimine. Aromatic rings show the typical

parallel-displaced π interactions with its centrosymmetric pairs (Figure 3). Parameters for the π stacking and additional C–H... π contacts are listed in Table III.

The molecular structure of **II** shows the same molecular pattern as structure **I** but because of the poor quality of collected data, only the bond lengths around molybdenum are worth discussing. Molybdenum atom is analogously octahedrally coordinated by six oxygen atoms, with the bond lengths very similar to those observed in compound **I**: two terminal oxygens [1.690(12) and 1.739(11) Å], two oxygens from acetylacetonato ligand [2.070(12) and 2.182(11) Å], one oxygen from *N*-benzyl-2-hydroxy-1-naphthalimine [2.188(11) Å] and one from methoxy group [1.870(12) Å].

Supplementary Materials. – CCDC 194588 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.

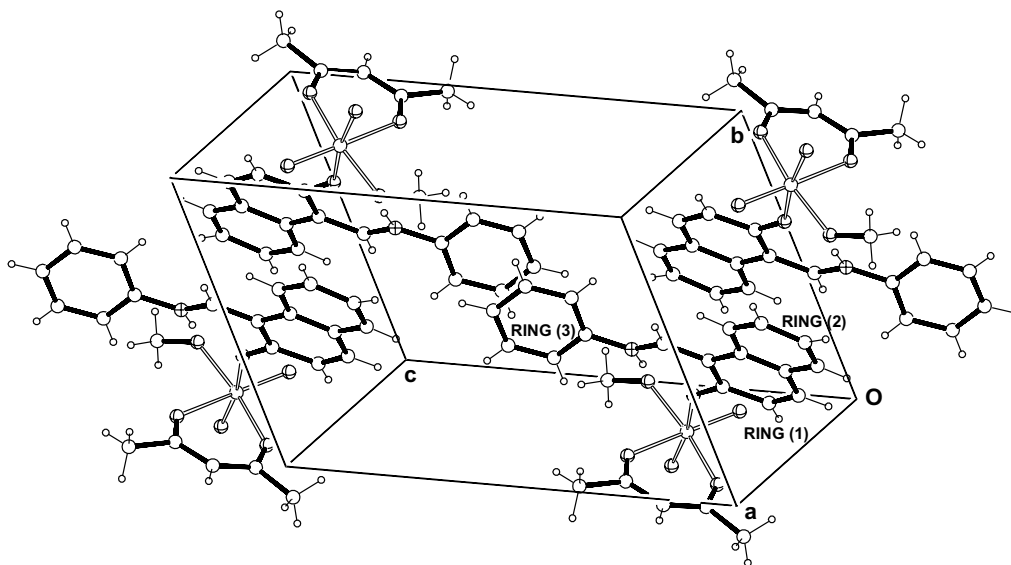


Figure 3. Unit cell packing diagram for compound **I** showing π stacking between the aromatic rings of *N*-phenyl-2-hydroxy-1-naphthalimine.

cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk)

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SAŽETAK

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Sinteza i karakterizacija dvaju kompleksa molibdena(VI) koordiniranih derivatima Schiffovih baza: *N*-fenil-2-hidroksi-1-naftaldiminom i *N*-benzil-2-hidroksi-1-naftaldiminom.

Molekularna i kristalna struktura [MoO₂(C₅H₇O₂)(OCH₃)(2-OC₁₀H₆CH=NHC₆H₅)]

U ovom radu je opisana sinteza dva nova monomerna kompleksa molibdena(VI) s derivatima Schiffovih baza: *N*-fenil-2-hidroksi-1-naftaldiminom i *N*-benzil-2-hidroksi-1-naftaldiminom molekularnih formula MoO₂(C₅H₇O₂)(OCH₃)(2-OC₁₀H₆CH=NHC₆H₅) (**I**) i [MoO₂(C₅H₇O₂)(OCH₃)(2-OC₁₀H₆CH=NHC₂C₆H₅)] (**II**). To su ujedno i prvi primjeri gdje su potencijalne didentatne Schiffove baze vezane kao monodentatni dvopolni (zwitter ionski) ligandi. Struktura kompleksa (**I**) određena je metodom rentgenske strukturne analize. Atom molibdena oktaedarski je koordiniran kisikovim atomima, i to: dva terminalna, dva iz acetilacetona, jedan iz Schiffove baze te jednim iz metokso skupine. Ustanovljena je prisutnost intramolekularne vodikove O...H-N veze duljine 2.548(2) Å i to između NH skupine i kisikovog atoma Schiffove baze koji je ujedno koordiniran i na atom molibdena.