3996 *Inorg. Chem.* **1990**, *29*, 3996-4001

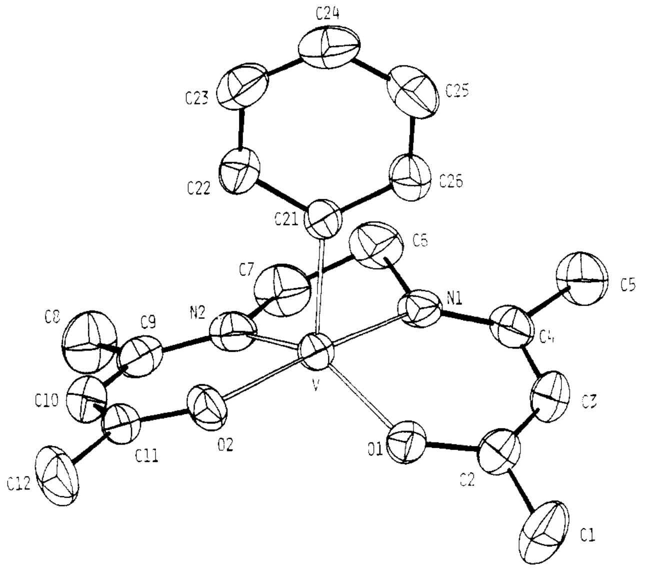

Figure 3. ORTEP drawing for complex **8** (50% probability ellipsoids).

formation of the [V(acacen)] moiety markedly different from that observed in the six-coordinated complexes **7** and [(THF)V(acacen)(Cl)][7] (**2**), as clearly indicated by the dihedral angle between the two O-V-N planes [40.4 (1)°] (Table VI). The V-O distances [V-O1 = 1.897 (3) Å; V-O2 = 1.952 (3) Å] are significantly different from each other, as well as the V-N distances [V-N1 = 2.056 (3) Å; V-N2 = 1.993 (5) Å]. This could be the result of an asymmetric interaction of the phenyl ligand with the Schiff base. In fact the aromatic ring, which is perpendicular to the mean plane through the N_2O_2 core [dihedral angle 89.5 (1)°], does not bisect the N-V-O angles, being oriented to form the shortest intramolecular contacts between its ortho hydrogen atoms and the O2 and N1 atoms, respectively (H22···O2 = 2.86 Å; H26···N1 = 3.01 Å). The basicity of the oxygen atom along with the geometry of the C-H···O group suggests this could be interpreted as an intramolecular hydrogen bond: C22···O2 = 3.298 (6) Å, C22-H22 = 1.04 Å, C22-H22···O2 = 106°. The vanadium-carbon distance [V-C21 = 2.064 (5) Å] is in good agreement with that observed in [(TMTAA)V(Mes)][21c] [2.085 (8) Å], where vanadium exhibits a very similar geometry. Vanadium is 0.130 (1) Å out from the plane through the phenyl ring.

The data in Table VI indicate that no part of the [M(acacen)] moieties is strictly planar. The N_2O_2 cores exhibit relevant twisting. All the six-membered chelation rings are folded along the N···O lines, albeit to different extents. The five-membered chelation rings have different conformation. In the six-coordinate complex **7** it shows a gauche conformation, while in the five-coordinate complexes **5** and **8** they are folded with respect to the N···N line with the C6 and C7 carbons upward on the same side as a consequence of the downward folding of the six-membered chelation rings.

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Supplementary Material Available: Listings of unrefined hydrogen coordinates (Tables SI-SIII), thermal parameters (Tables SIV-SVI), and nonessential bond distances and angles (Tables SVII-SIX) (9 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

Contribution from the Instituto de Quimica, Universidad Católica de Valparaiso, Valparaiso, Chile,
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Synthesis, Characterization, and Electrochemistry of *cis*-Dioxomolybdenum(VI) Complexes of Schiff Bases Derived from Carbohydrazide, Thiocarbohydrazide, and Salicylaldehyde. Crystal Structures of $[MoO_2(o\text{-}OC_6H_4CH{=}NN{=}CSNHN{=}CHC_6H_4OH\text{-}o)Me_2SO]$ and $[(MoO_2)_2(o\text{-}OC_6H_4CH{=}NN{=}CONN{=}CHC_6H_4O\text{-}o)(Me_2SO)_2]\cdot 0.5Me_2SO$

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Bis(acetylacetonato)dioxomolybdenum(VI), $[MoO_2(acac)_2]$, reacts with Schiff bases derived from thiocarbohydrazide and carbohydrazide $(o\text{-}HOC_6H_4CH{=}NNH)_2CX$, (X = S,O) and salicylaldehyde in methanol, to afford mono- and binuclear complexes respectively. These complexes have been characterized by elemental analysis and IR and ^1H NMR spectroscopy, and formulated as $[MoO_2(o\text{-}OC_6H_4CH{=}NN{=}CSNHN{=}CHC_6H_4OH\text{-}o)L]$, and $[(MoO_2)_2(o\text{-}OC_6H_4CH{=}NN{=}CONN{=}CHC_6H_4O\text{-}o)L_2]$ (L = MeOH, Me_2SO). All complexes exhibit an irreversible voltammetric peak that is attributed to an electron transfer centered at molybdenum (~-0.90 V vs SCE). Coulometric reduction at -0.95 V is either a two- or four-electron process depending on whether the complex is mono- or binuclear. The X-ray crystal structures of the title complexes are described. Crystals of the mononuclear complex (L = Me_2SO) are triclinic, space group group $P\bar{1}$, with a = 10.138 (2) Å, b = 13.489 (2) Å, c = 7.964 (1) Å, α = 106.80 (2)°, β = 100.00 (2)°, γ = 95.546 (2)°, and Z = 2. The structure was solved by using 2812 unique reflections, and refinement gave final R and R_w values of 0.038 and 0.047, respectively. The binuclear complex (L = Me_2SO) crystallizes in the space group $P2_1/c$ with a = 11.419 (4) Å, b = 8.390 (4) Å, c = 31.075 (9) Å, β = 92.09 (3)°, and Z = 4. The structure was solved using 2873 reflections, and refinement gave final R and R_w values of 0.067 and 0.087, respectively.

Introduction

The presence of the *cis*-dioxomolybdenum(VI) cation, $[MoO_2]^{2+}$, in the oxidized forms of certain molybdoenzymes[2] has stimulated both the search for new structures in which this moiety is coordinated to ligands containing nitrogen, oxygen, and/or sulfur donors and also the study of their chemical, spectroscopic, electrochemical, and structural properties.[3] At present, a large number of *cis*-dioxomolybdenum(VI) complexes are known, some of which have been proposed as models for the active sites of oxo-transfer molybdoenzymes, viz. sulfite and aldehyde oxidase, xanthine oxidase/dehydrogenase, and nitrate reductase.[4-6]

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(1) (a) Universidad Católica de Valparaiso. (b) The University of Texas at Austin.

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Thiocarbohydrazide, $H_2NNHC(S)NHNH_2$, and its Schiff base complexes constitute interesting ligand systems because of the availability of several potential donor sites.[7-12] Thiocarbohydrazides, for example, usually behave as neutral or uninegative ligands and bind the metal through one sulfur atom and one hydrazinic nitrogen atom. Such behavior is a consequence of the tautomeric equilibrium between the thioketo and the thioenol forms. Several factors affect this equilibrium, namely the nature of the metal ion and its counterion, the reaction conditions, the nature of the solvent, and the pH of the medium. Interestingly, much less is known about the coordination behavior of the oxygen-analogous carbohydrazide,[13-17] $H_2NNHC(O)NHNH_2$, and its Schiff base derivatives.[12,13]

In the present paper, we describe the synthesis and spectroscopic characterization of new mono- and binuclear complexes of the *cis*-dioxomolybdenum(VI) cation with Schiff base ligands derived from salicylaldehyde and thiocarbohydrazide, $(o\text{-}HOC_6H_4CH{=}NNH)_2CS$ (**1**), or carbohydrazide, $(o\text{-}HOC_6H_4CH{=}NNH)_2CO$ (**2**). The electrochemical properties of these complexes have been investigated and X-ray analyses have been performed on $[MoO_2(o\text{-}OC_6H_4{=}NN{=}CSNHN{=}CHC_6H_4OH\text{-}o)Me_2SO]$ and $[(MoO_2)_2(o\text{-}OC_6H_4CH{=}NN{=}CONN{=}CHC_6H_4O\text{-}o)(Me_2SO)_2]\cdot 0.5Me_2SO$.

Experimental Section

Chemicals. Carbohydrazide, thiocarbohydrazide, salicylaldehyde, and tetraethylammonium perchlorate (TEAP) were procured commercially and used without subsequent purification. $[MoO_2(acac)_2]$ was prepared as described in the literature.[18] Reagent grade solvents were dried and distilled by standard methods prior to use.

Physical Measurements. Infrared spectra were recorded as KBr disks on a Perkin-Elmer 599 spectrophotometer. ^1H NMR spectra were measured on a Varian T-60 spectrometer. Cyclic voltammetry measurements were made with a homemade potentiostat of conventional design. A three-electrode cell was utilized. The working electrode was Pt, and the auxiliary electrode consisted of Pt wire. Saturated calomel was employed as the reference electrode. All measurements were carried out in dry and deairated DMF with 0.1 M TEAP as supporting electrolyte. A molybdenum complex concentration of 0.1 mM was employed. The range of potential scan rates was $0.005 \leq V \leq 0.2$ V s^{-1}. Controlled potential coulometry was performed by using a platinum mesh electrode and a molybdenum complex concentration of 0.1 mM. Magnetic measurements were made on a Cahn Ventron RTL Faraday balance, and $[Ni(en)_2]S_2O_3$ was used as calibrant. Melting points were determined by using a Kofler apparatus and were not corrected.

Preparation of 1,5-Bis(salicylidene)thiocarbohydrazide, $(o\text{-}HOC_6H_4CH{=}NNH)_2CS$ (1). Thiocarbohydrazide (10 mmol) was dissolved in 50 mL of methanol. Salicylaldehyde (20 mmol) was added to this solution, and the resulting reaction mixture was refluxed for 1.0 h. The pale yellow solid, which formed on cooling, was filtered, washed with cold methanol, dried in vacuo, and recrystallized from nitromethane. Yield: 68%. Mp: 191 °C. Anal. Calcd for $C_{15}H_{14}N_4O_2S$: C, 57.3; H, 4.5; N, 18.7. Found: C, 58.0; H, 4.2; N, 18.0.

Preparation of 1,5-Bis(salicylidene)carbohydrazide, $(o\text{-}HOC_6H_4CH{=}NNH)_2CO$ (2). This ligand was prepared from carbohydrazide and salicylaldehyde by a procedure similar to that described for the synthesis of **1**. Yield: 81%. Mp: 226 °C. Anal. Calcd for $C_{15}H_{14}N_4O_3$: C, 60.4; H, 4.7; N, 18.8. Found: C, 59.2; H, 4.5; N, 18.5.

Table I. Crystallographic Data for **4** and **6**

	complex **4**	complex **6**
formula	$C_{17}H_{18}N_4O_5S_2Mo$	$C_{19}H_{22}N_4O_9S_2Mo_2\cdot$ $0.5(C_2H_5OS)$
fw	518.43	745.48
space group	$P\bar{1}$	$P2_1/c$
syst abs	none	$(h0l)$, l odd; $(0k0)$, k odd
a, Å	10.138 (2)	11.419 (4)
b, Å	13.489 (2)	8.390 (4)
c, Å	7.964 (1)	31.075 (9)
α, deg	106.80 (2)	90
β, deg	100.00 (2)	92.09 (3)
γ, deg	95.55 (2)	90
V, Å^3	1014	2975
Z	2	4
d_{calcd}, g/cm^3	1.697	1.649
cryst size, mm	0.2 × 0.2 × 0.4	0.1 × 0.2 × 0.3
$F(000)$, e	524	1492
μ(Mo Kα), cm^{-1}	8.64	10.4
radiation	monochromated in Mo Kα (λ = 0.71069 Å) incident beam	
orientation reflcns: no.; range (2θ), deg	25; $28.0 < 2\theta < 30.0$	25; $28.0 < 2\theta < 30.0$
temp, °C	24 ± 1	24 ± 1
scan method	$\theta/2\theta$	$\theta/2\theta$
data collcn range (2θ), deg	$3.0 < 2\theta < 48.0$	$3.0 < 2\theta < 50.0$
tot. no. of reflcns measd	3177	5202
tot. no. of reflcns with $F_o^2 > 3\sigma(F_o^2)$	2812	2873
check reflcns	every 100	every 100
no. of params refined	262	335
transm factors: max; min	99.97; 95.86	99.94; 88.49
R^a	0.0382	0.067
$R_w{}^b$	0.0470	0.087
largest shifted/esd, final cycle	0.38	0.14
largest peak, e/Å^3	0.95	2.5

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$.

Preparation of $[MoO_2(o\text{-}OC_6H_4CH{=}NN{=}CSNHN{=}CHC_6H_4OH\text{-}o)MeOH]$ (3). Ligand **1** (5.0 mmol) was dissolved in methanol (100 mL) and treated with 5.0 mmol of $[MoO_2(acac)_2]$. The resulting red reaction mixture was heated to reflux and stirred for 15 min. Filtration afforded red solid **3**, which was washed with cold methanol and dried in vacuo. Purification of **3** was accomplished by recrystallization from methanol. Yield: 88%. Mp: 160 °C dec. Anal. Calcd for $C_{16}H_{16}N_4O_5SMo$: C, 40.7; H, 3.4; Mo, 20.0. Found: C, 39.8; H, 3.6; Mo, 19.9.

Preparation of $[MoO_2(o\text{-}OC_6H_4CH{=}NN{=}CSNHN{=}CHC_6H_4OH\text{-}o)Me_2SO]$ (4). This complex was prepared by recrystallization of **3** from Me_2SO. The resulting red crystals were suitable for X-ray analysis. Mp: 155 °C. Anal. Calcd for $C_{17}H_{18}N_4O_5S_2Mo$: C, 39.4; H, 3.5; N, 10.8; Mo, 18.5. Found: C, 38.8; H, 3.6; N, 10.7; Mo, 17.9.

Preparation of $[(MoO_2)(o\text{-}OC_6H_4CH{=}NN{=}CONN{=}CHC_6H_4O\text{-}o)(MeOH)_2]$ (5). This red, crystalline complex was prepared by a procedure similar to that described for the synthesis of **3**. Purification was effected by recrystallization from methanol. Yield: 61%. Mp: 115 °C dec. Anal. Calcd for $C_{17}H_{18}N_4O_9Mo_2$: C, 33.2; H, 3.0; Mo, 31.2. Found: C, 33.7; H, 3.2; Mo, 30.6.

Preparation of $[(MoO_2)_2(o\text{-}OC_6H_4CH{=}NN{=}CONN{=}CHC_6H_4O\text{-}o)(Me_2SO)_2]$ (6). This red, crystalline complex was prepared by recrystallization of **5** from Me_2SO. The resulting crystals were suitable for X-ray analysis. Mp: 145 °C dec. Anal. Calcd for $C_{19}H_{22}N_4O_9S_2Mo_2\cdot 0.5Me_2SO$: C, 32.2; H, 3.4; N, 7.5; Mo, 25.7. Found: C, 32.2, H, 3.6; N, 7.6; Mo, 25.7.

X-ray Crystallography. The data sets for complexes **4** and **6** were collected on an Enraf-Nonius CAD-4 diffractometer (Table I). The general procedures have been described more fully elsewhere.[19] Both were corrected for the effects of Lorentz, polarization, and decay. Empirical absorption corrections were also applied to both data sets. Both structures were solved by direct methods and refined by using full-matrix least-squares methods. For **6**, half a molecule of Me_2SO co-crystallized

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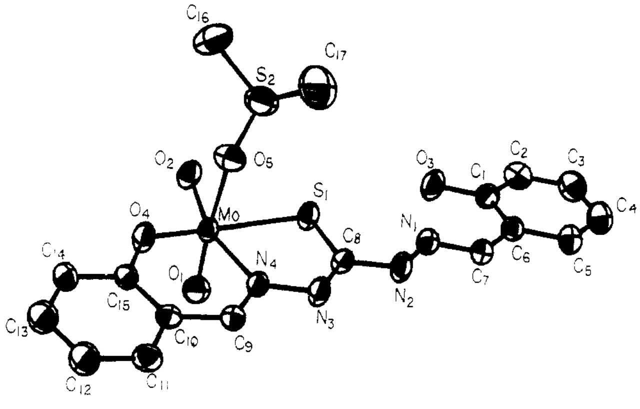


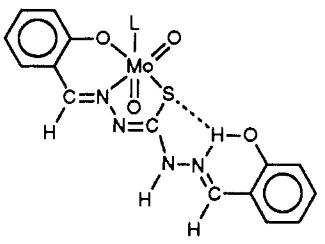
Figure 1. Molecular structure of complex **4** showing the atom-numbering scheme.

with each molecule of the complex. All programs used were from the SDP Plus program package.

Results and Discussion

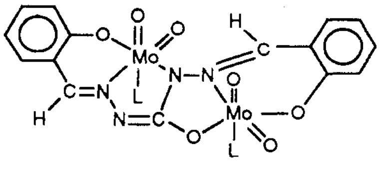
The new Schiff base ligands **1** and **2** (Scheme I) were prepared by treatment of salicylaldehyde with carbo- or thiocarbohydrazide in a 2:1 mole ratio in refluxing MeOH. These ligands are potentially quinquedentate in the keto (thioketo) form, A. However, as in the case of the parent hydrazides, keto–enol (thioketo–thioenol)tantomerism is possible.[7-13] Moreover, the enol and thioenol tautomers can exist as syn (B) or anti (B′) geometric isomers as a consequence of the double bond character of the central N–C linkage. In the anti form, B′, the ligands are potentially hexadentate with two sets of nonequivalent coordination sites, viz. ONN and XNO.

Treatment of ligand **1** with an equimolar quantity of $[MoO_2(acac)_2]$ in refluxing MeOH results in complex **3**. In turn, **3** is converted into **4** by recrystallization from Me_2SO. The structure of **4** was established by X-ray analysis (vide infra). The spectroscopic and analytical data for **3** and **4** are consistent with the view that these compounds possess virtually identical skeletal structures.



3 (L = MeOH)
4 (L = Me_2SO)

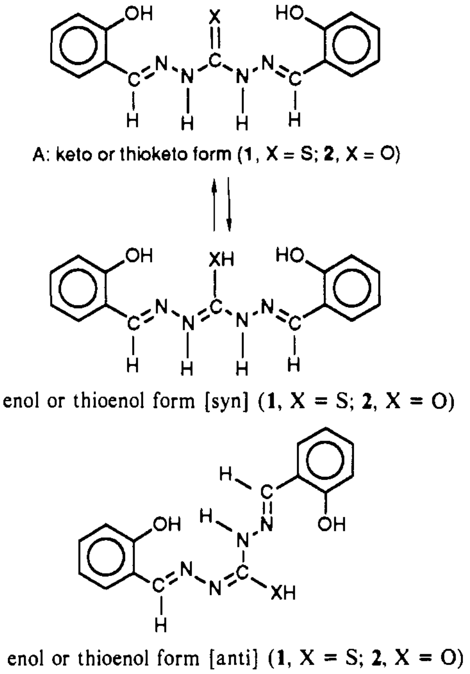
Interestingly, the reaction of ligand **2** with $[MoO_2(acac)_2]$ in equimolar ratios results only in ill-defined heterogeneous solids. However, use of a 3:1 Mo:ligand reactant ratio permits the isolation of the dinuclear complex **5**, which is converted to **6** by recrystallization from Me_2SO. The structure of **6** was determined by X-ray diffraction, and as in the case of the mononuclear complexes, **5** and **6** are different solvates of the same basic structure.



5 (L = MeOH)
6 (L = Me_2SO)

Structural Studies. The X-ray analysis of **4** establishes that in this mononuclear complex, **1** serves as a doubly negative ligand in the thioenolate (syn, B) form. A view of **4** is presented in Figure 1 and the atomic coordinates are listed in Table II. important bond distances and angles are summarized in Table III. Ligand **1** bonds to a *cis*-MoO_2 moiety through S(1), N(4), and O(4) and is thus tridentate. The sixth coordination site around Mo is occupied by a solvent (Me_2SO) molecule, thereby achieving the customary requirement[20] of Mo(VI) hexacoordination. In general, the structure of **4** resembles that of the *cis*-dioxomolybdenum(VI)

Scheme I



A: keto or thioketo form (**1**, X = S; **2**, X = O)

B: enol or thioenol form [syn] (**1**, X = S; **2**, X = O)

B′: enol or thioenol form [anti] (**1**, X = S; **2**, X = O)

Table II. Atomic Coordinates and Their Estimated Standard Deviations for **4**

atom	*x*	*y*	*z*	*B*,[a] Å²
Mo	0.39286 (4)	0.23199 (3)	0.25618 (6)	2.047 (9)
S(1)	0.2874 (1)	0.3400 (1)	0.4814 (2)	2.80 (3)
S(2)	0.2978 (2)	0.1024 (1)	0.5265 (2)	4.21 (4)
O(1)	0.4056 (4)	0.3149 (3)	0.1332 (5)	3.18 (9)
O(2)	0.2430 (4)	0.1512 (3)	0.1564 (5)	3.02 (9)
O(3)	0.0205 (4)	0.4907 (3)	0.7001 (5)	3.7 (1)
O(4)	0.5260 (4)	0.1468 (3)	0.1787 (3)	2.95 (9)
O(5)	0.4166 (4)	0.1348 (3)	0.4516 (5)	3.31 (9)
N(1)	0.2886 (4)	0.5128 (3)	0.7954 (6)	2.6 (1)
N(2)	0.5835 (5)	0.5086 (4)	0.2220 (6)	3.0 (1)
N(3)	0.5575 (4)	0.4072 (3)	0.6215 (6)	2.7 (1)
N(4)	0.5727 (4)	0.3283 (3)	0.4732 (5)	2.16 (9)
C(1)	0.9714 (6)	0.4307 (4)	0.1455 (7)	2.7 (1)
C(2)	1.0914 (6)	0.4001 (5)	0.1008 (8)	3.2 (1)
C(3)	1.0869 (6)	0.3205 (5)	−0.0530 (8)	3.7 (1)
C(4)	0.9635 (6)	0.2683 (5)	−0.1681 (8)	3.7 (1)
C(5)	0.8431 (6)	0.2992 (4)	−0.1246 (7)	3.1 (1)
C(6)	0.8449 (5)	0.3809 (4)	0.0312 (7)	2.4 (1)
C(7)	0.7160 (6)	0.4110 (4)	0.0661 (7)	2.6 (1)
C(8)	0.5674 (5)	0.5848 (4)	0.3693 (7)	2.3 (1)
C(9)	0.6985 (5)	0.3233 (4)	0.4655 (7)	2.3 (1)
C(10)	0.7449 (5)	0.2453 (4)	0.3329 (7)	2.2 (1)
C(11)	0.8869 (5)	0.2523 (4)	0.3483 (8)	2.9 (1)
C(12)	0.9414 (6)	0.1784 (5)	0.2319 (9)	3.6 (1)
C(13)	0.8556 (6)	0.0957 (5)	0.0968 (9)	3.6 (1)
C(14)	0.7152 (5)	0.0875 (4)	0.0792 (7)	2.7 (1)
C(15)	0.6615 (5)	0.1611 (4)	0.1971 (7)	2.2 (1)
C(16)	0.2793 (9)	−0.0378 (5)	0.462 (1)	5.7 (2)
C(17)	0.372 (1)	0.1267 (8)	0.758 (1)	9.3 (3)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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Table III. Selected Bond Lengths (Å) and Angles (deg) for **4**

	Bond Lengths		
Mo-O(1)	1.696 (5)	C(8)-N(3)	1.294 (7)
Mo-O(2)	1.699 (3)	N(3)-N(4)	1.385 (6)
Mo-S(1)	2.437 (2)	N(4)-C(9)	1.295 (7)
Mo-N(4)	2.269 (3)	C(9)-C(10)	1.439 (7)
Mo-O(4)	1.924 (4)	C(10)-C(15)	1.400 (6)
Mo-O(5)	2.305 (5)	C(15)-O(4)	1.345 (6)
S(1)-C(8)	1.737 (5)	C(8)-N(2)	1.364 (6)
		N(2)-N(1)	1.377 (7)
	Bond Angles		
S(1)-Mo-O(1)	97.7 (1)	O(4)-Mo-N(4)	83.0 (1)
S(1)-Mo-O(2)	90.9 (1)	O(5)-Mo-N(4)	77.5 (2)
S(1)-Mo-O(4)	153.9 (1)	S(1)-C(8)-N(3)	127.7 (4)
S(1)-Mo-O(5)	82.9 (1)	S(1)-C(8)-N(2)	117.8 (4)
S(1)-Mo-N(4)	76.7 (1)	C(8)-N(3)-N(4)	111.1 (4)
O(1)-Mo-O(2)	105.1 (2)	C(8)-N(2)-N(1)	119.8 (4)
O(1)-Mo-O(4)	99.2 (2)	N(3)-C(8)-N(2)	114.5 (4)
O(1)-Mo-O(5)	169.1 (2)	N(3)-N(4)-Mo	122.2 (3)
O(1)-Mo-N(4)	92.1 (2)	N(3)-N(4)-C(9)	112.8 (4)
O(2)-Mo-O(4)	103.6 (2)	N(2)-N(1)-C(7)	115.4 (4)
O(2)-Mo-O(5)	85.7 (2)	N(4)-C(9)-C(10)	125.0 (4)
O(2)-Mo-N(4)	160.1 (2)	N(1)-C(7)-C(6)	120.9 (4)
O(4)-Mo-O(5)	76.8 (2)		

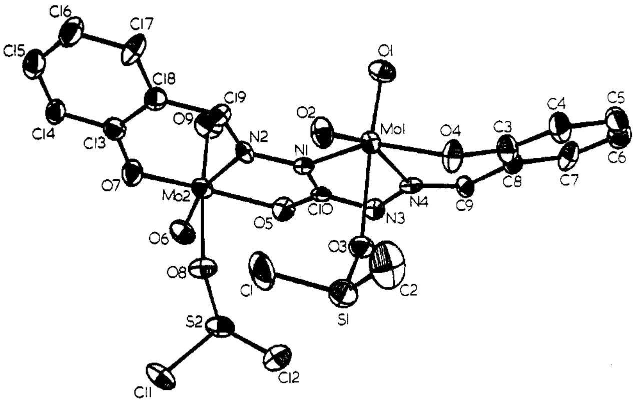

Figure 2. Molecular structure of complex **6** showing the atom-numbering scheme.

complex of the tridentate 2-(salicylideneamino)benzenethiolato(2−) ligand.[21] The geometry around Mo is distorted octahedral. Cis bond angles range from 76.7 (1)° for N(4)-Mo-S(1) to 105.1 (2)° for O(1)-Mo-O(2) and the range of trans bond angles extends from 153.9 (1)° for O(4)-Mo-S(1) to 169.1 (2)° for O(5)-Mo-O(1). To a large extent these distortions stem from the incorporation of Mo into a five-membered ring. The average Mo-O bond length (1.697 (5) Å) and the O-Mo-O bond angle (105.1 (2)°) are comparable to other such data reported for the MoO$_2$ group.[22-26] The Mo-S(4) and Mo-N(4) bond lengths and other metric parameters for the Mo-S(1)-C(8)-N(3)-N(4) ring are similar to those reported for other five-membered rings of this general type (Table IV). The most significant variations are observed for the N-Mo bond length. It has been established previously that this bond length is quite susceptible to charge delocalization.[28,31] The N(2)-C(8) (1.364 (6) Å) and N(3)-C(8) (1.296 (7) Å) distances indicate that these correspond to single and double bonds respectively. The coplanarity of the Mo-S(1)-C(8)-N(3)-N(4) ring and the atoms N(1), N(2), C(7), O(3), and C(1)-C(6) can be explained by the presence of a phenolic proton on O(3), which is hydrogen bonded to N(1) and S(1).[27] Finally, the metric parameters for the six-membered ring Mo-N(4)-C(9)-C(10)-C(15)-O(4) are unexceptional and do not warrant further comment.[33,34]

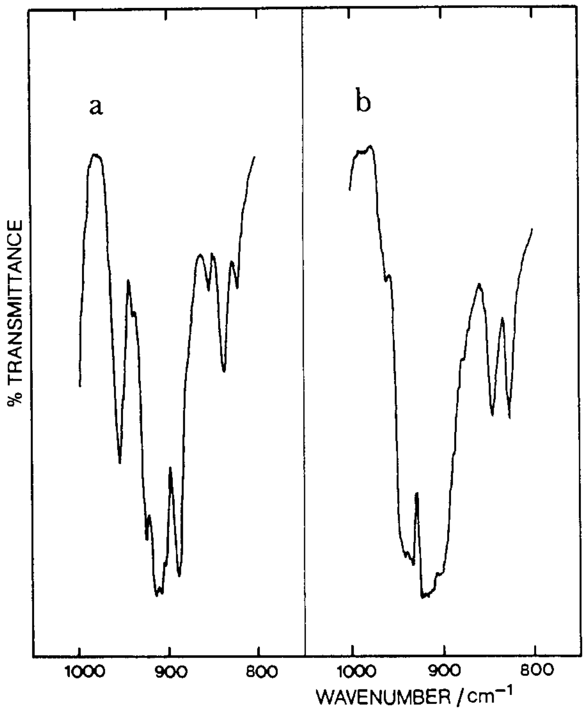

Figure 3. IR stretching frequencies for the MoO$_2$ units in (a) complex **5** and (b) complex **6**.

X-ray crystallographic data for **6** establish that in this complex ligand **2** acts as a tetranegative anion in the enolate (B′ anti) form. A view of **6** is presented in Figure 2 and atomic coordinates are listed in Table V. Important bond lengths and angles have been compiled in Table VI. Note that half a molecule of Me$_2$SO cocrystallizes with each molecule of the complex. The binucleating ligand coordinates to Mo(1) and Mo(2) through the donor sets O(4)-N(4)-N(1) and O(7)-N(2)-O(8), respectively, thus forming six- and five-membered chelate rings around the *cis*-MoO$_2$ moieties. The sixth coordination site of each molybdenum is occupied by a molecule of Me$_2$SO. Note that both Me$_2$SO molecules are perpendicular to the near-planar system containing the Mo atoms and that they adopt a mutually cis orientation. As in the case of complex **4**, the geometry at each Mo is distorted octahedral. For example, the cis angles range from 70.8 (4)° for N(1)-Mo(1)-N(4) to 105.3 (5)° for O(1)-Mo(1)-O(2) at Mo(1) and from 72.2 (4)° for O(5)-Mo(2)-N(2) to 104.6 (6)° for O(6)-Mo(2)-O(9) at Mo(2). Comparable variations are observed for the trans angles. Both sets of Mo=O bond lengths are identical with those found for the MoO$_2$ moiety in **4**. Furthermore, with the exception of Mo(1)-N(1) (2.12 (1) Å) and Mo(2)-O(5) (1.99 (1) Å) all other distances at the two molybdenum sites are either very similar or are identical within experimental error. Finally, it is interesting to compare the differences in the N(2)-C(8) and N(3)-C(8) bond lengths in **4** (0.7 Å) with the

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Table IV. Comparison of Structural Parameters[a] of Five-Membered Rings of the Type $\overline{\mathrm{MoSCNN}}$ and Related Ligands

	distances					angles					
compd	Mo–S	S–C	C–N	N–N	N–Mo	Mo–S–C	S–C–N	C–N–N	N–N–Mo	N–Mo–S	ref
$NH_2CSNHNH_2$	*b*	1.685	1.337	1.399	*b*	*b*	121.5	122.5	*b*	*b*	29, 30
$[Mo_2O(S_2CNEt_2)_2(ClC_6H_4CSN_2)_2]$[c]	2.398 (7)	1.73 (2)	1.29 (2)	1.39 (2)	1.91 (2)	99.5 (8)	119.7 (17)	111.5 (16)	134.3 (11)	75.8 (6)	28
$[Mo(C_6H_5CSNNH)_3]$[d]	2.400 (5)	1.69 (2)	1.35 (2)	1.32 (2)	2.03 (1)	98.2 (7)	119.5 (14)	114.8 (15)	126.3 (13)	76.3 (14)	31
$[Mo(Me_2CNNC(S)SMe)N_2C(S)SMe)MeSC(S)NNC(S)SMe)]$[f]	2.440 (2)	1.732 (2)	1.287 (10)	1.416 (9)	2.239 (6)	*e*	*e*	*e*	*e*	*e*	32
	2.516 (2)	*e*	1.345 (10)	1.323 (8)	1.791 (6)	95.3 (3)	*e*	*e*	142.1 (5)	*e*	
	2.456 (2)	*e*	1.306 (11)	1.361 (9)	2.132 (6)	*e*	*e*	*e*	*e*	*e*	
$[MoO_2(o\text{-}OC_6H_4CHNNCSNHNCHC_6H_4O\text{-}o)Me_2SO]$ (**4**)	2.437 (2)	1.737 (5)	1.294 (7)	1.385 (6)	2.269 (3)	99.1 (2)	127.7 (4)	111.1 (4)	122.2 (3)	76.7 (1)	*g*

[a] Distances in Å; angles in deg. [b] Nonexistent. [c] Average parameter for the two ligands in the pseudoprismatic coordination site. [d] Average parameters for three ligands. [e] Not reported. [f] The heptacoordinated molybdenum complex has three different five-membered rings. [g] This work.

Table V. Atomic Coordinates and Their Estimated Standard Deviations for **6**

atom	*x*	*y*	*z*	*B*,[a] Å^2
Mo(1)	0.2237 (1)	0.4354 (2)	0.88273 (4)	2.48 (2)
Mo(2)	0.6448 (1)	0.2000 (2)	0.90039 (5)	2.95 (3)
S(1)	0.1129 (4)	0.0429 (6)	0.8918 (2)	4.6 (1)
S(2)	0.5194 (4)	−0.1082 (5)	0.9442 (1)	3.74 (9)
O(1)	0.270 (1)	0.625 (1)	0.8739 (4)	3.6 (2)
O(2)	0.202 (1)	0.354 (1)	0.8329 (3)	3.8 (3)
O(3)	0.177 (1)	0.189 (1)	0.9083 (4)	3.6 (2)
O(4)	0.0691 (9)	0.485 (2)	0.9021 (4)	3.9 (3)
O(5)	0.5377 (9)	0.268 (1)	0.9461 (3)	3.3 (2)
O(6)	0.738 (1)	0.095 (1)	0.9334 (4)	4.3 (3)
O(7)	0.670 (1)	0.115 (2)	0.8445 (4)	4.3 (3)
O(8)	0.521 (1)	−0.011 (1)	0.9023 (3)	3.7 (3)
O(9)	0.713 (1)	0.378 (2)	0.8938 (4)	4.8 (3)
N(1)	0.393 (1)	0.340 (1)	0.8950 (4)	2.2 (2)
N(2)	0.479 (1)	0.295 (1)	0.8675 (4)	2.5 (2)
N(3)	0.371 (1)	0.375 (2)	0.9698 (4)	2.6 (3)
N(4)	0.268 (1)	0.450 (2)	0.9533 (4)	2.6 (2)
C(1)	0.186 (2)	−0.022 (3)	0.8435 (7)	6.3 (6)
C(2)	−0.021 (2)	0.116 (3)	0.8657 (9)	8.0 (7)
C(3)	0.033 (1)	0.586 (2)	0.9315 (5)	3.6 (4)
C(4)	−0.074 (2)	0.666 (2)	0.9245 (6)	4.7 (4)
C(5)	−0.112 (2)	0.773 (2)	0.9557 (6)	4.2 (4)
C(6)	−0.047 (2)	0.801 (2)	0.9932 (6)	4.7 (4)
C(7)	0.059 (1)	0.719 (2)	1.0010 (5)	4.1 (4)
C(8)	0.102 (1)	0.612 (2)	0.9706 (5)	2.8 (3)
C(9)	0.210 (1)	0.526 (2)	0.9807 (5)	2.7 (3)
C(10)	0.433 (1)	0.329 (2)	0.9367 (5)	2.3 (3)
C(11)	0.542 (2)	−0.310 (2)	0.9271 (6)	4.7 (4)
C(12)	0.366 (2)	−0.118 (3)	0.9569 (6)	5.0 (5)
C(13)	0.649 (1)	0.173 (2)	0.8046 (5)	3.3 (4)
C(14)	0.723 (1)	0.130 (2)	0.7718 (5)	3.7 (4)
C(15)	0.699 (2)	0.183 (2)	0.7303 (6)	4.6 (4)
C(16)	0.602 (2)	0.276 (3)	0.7194 (5)	4.7 (5)
C(17)	0.528 (1)	0.322 (3)	0.7514 (5)	4.1 (4)
C(18)	0.548 (1)	0.270 (2)	0.7946 (5)	3.1 (3)
C(19)	0.462 (1)	0.319 (2)	0.8262 (5)	2.9 (3)
S	0.129	0.321	0.222	5.9 (3)*
O	0.068 (2)	0.202 (3)	0.1987 (8)	4.4 (5)*
C(20)	0.068 (4)	0.496 (6)	0.212 (1)	3 (1)*
C(21)	0.250	0.332	0.207	8 (1)*

[a] Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as in Table II.

differences in the N(1)–C(10) and N(3)–C(10) bond lengths in **6** (0.3 Å). This suggests an increased delocalization of the π system in **6**.

IR and ^{1}H NMR Studies. Ligands **1** and **2** exhibit broad bands of medium intensity at 3170 and 3230 cm^{-1}, respectively, and are attributable to N–H stretching frequencies (Table VII). The additional medium-intensity feature at 3360 cm^{-1} in **2** is presumably due to the presence of an enolic OH group. As expected on the basis of the X-ray structures, ν_{N-H} is still detectable in **3** and **4**, but is absent in **5** and **6**. Likewise, the very strong $\nu_{C=X}$ (X = S, O) bands at 1290 and 1690 cm^{-1} in **1** and **2**, respectively, disappear upon complex formation. The very strong bands at 1265 cm^{-1} in the free ligands are assigned to $\nu_{C=N}$. The presence of three such bands in **3** and **4** is consistent with the three C=N environments that are evident in the X-ray structure of **4**, viz. an uncoordinated C=N group created by thioenolization of the

Table VI. Selected Bond Lengths (Å) and Angles (deg) for **6**

Bond Lengths			
Mo(1)–O(1)	1.70 (1)	Mo(2)–O(9)	1.70 (1)
Mo(1)–O(2)	1.70 (1)	Mo(2)–N(2)	2.27 (1)
Mo(1)–O(3)	2.28 (1)	O(5)–C(10)	1.33 (2)
Mo(1)–O(4)	1.93 (1)	N(1)–C(10)	1.36 (2)
Mo(1)–N(1)	2.12 (1)	N(1)–N(2)	1.37 (2)
Mo(1)–N(4)	2.24 (1)	N(2)–C(19)	1.31 (2)
Mo(2)–O(5)	1.99 (1)	N(3)–C(10)	1.33 (2)
Mo(2)–O(6)	1.70 (1)	N(3)–N(4)	1.41 (2)
Mo(2)–O(7)	1.91 (1)	N(4)–C(9)	1.27 (2)
Mo(2)–O(8)	2.27 (1)		
Bond Angles			
O(1)–Mo(1)–O(2)	105.3 (1)	O(2)–Mo(1)–O(4)	105.3 (5)
O(1)–Mo(1)–O(3)	168.4 (4)	O(2)–Mo(1)–N(1)	96.7 (5)
O(1)–Mo(1)–O(4)	98.3 (5)	O(2)–Mo(1)–N(4)	159.2 (5)
O(1)–Mo(1)–N(1)	95.5 (4)	O(3)–Mo(1)–O(4)	81.8 (5)
O(1)–Mo(1)–N(4)	92.8 (5)	O(3)–Mo(1)–N(1)	79.4 (5)
O(2)–Mo(1)–O(3)	85.8 (4)	O(3)–Mo(1)–N(4)	75.7 (4)
O(4)–Mo(1)–N(1)	149.8 (4)	O(6)–Mo(2)–O(8)	87.4 (5)
O(4)–Mo(1)–N(4)	81.8 (4)	O(6)–Mo(2)–O(9)	104.6 (9)
N(1)–Mo(1)–N(4)	70.8 (4)	O(6)–Mo(2)–N(2)	161.8 (6)
O(5)–Mo(2)–O(6)	96.0 (6)	O(7)–Mo(2)–O(8)	81.3 (5)
O(5)–Mo(2)–O(7)	150.8 (5)	O(7)–Mo(2)–O(9)	97.7 (6)
O(5)–Mo(2)–O(8)	78.7 (4)	O(7)–Mo(2)–N(2)	82.7 (5)
O(5)–Mo(2)–O(9)	97.3 (5)	O(8)–Mo(2)–O(9)	167.7 (5)
O(5)–Mo(2)–N(2)	72.2 (4)	O(8)–Mo(2)–N(2)	76.9 (4)
O(6)–Mo(2)–O(7)	104.2 (6)	O(9)–Mo(2)–N(2)	90.9 (5)

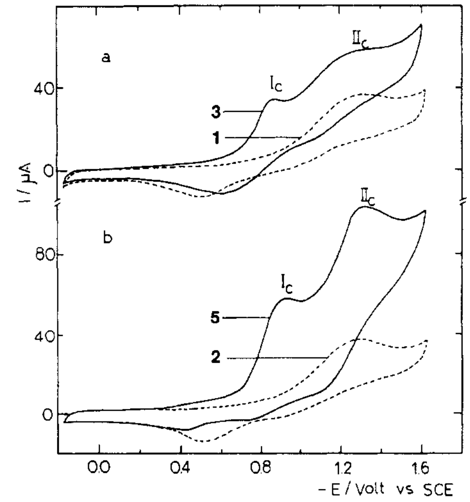

Figure 4. Cyclic voltammograms for ligands **1** and **2** and complexes **3** and **5** in DMF solution. Scan rate: 0.05 V s^{-1}.

Table VII. IR and ^{1}H NMR Data for Ligands and Complexes

	IR,[a] cm^{-1}					^{1}H NMR,[b] ppm					
compd	ν(NH)	ν(OH)	ν(C=X)[c]	ν(C=N)	ν(MoO_2)	arom protons	–CH=N–	–NH–	–OH arom	–CH_3[d]	–OH[e]
1	3170 (m, br)	*f*	1290 (vs)	1265 (vs)	*g*	6.60–7.80 m (8)	8.60 s (2)	10.1–10.9 s (2)	11.0–11.4 s (2)	*g*	*g*
2	3230 (m, br)	3360 (m)	1690 (vs)	1625 (vs)	*g*	6.50–7.80 m (8)	8.35 s (2)	10.6 s (2)	10.8 s (2)	*g*	*g*
3	3220 (m, br)	*f*	*f*	1630 (m)	950 (vs)	6.75–7.80 m (8)	8.34 s (1)	10.8 s (1)	12.0 s (1)	3.10–3.20 d (3)[h]	3.90–4.30 s (1)
				1610 (vs) 1600 (sh)	915 (vs)		8.66 s (1)				
4	3240 (m)	*f*	*f*	1625 (m)	930 (vs)	6.70–8.00 m (8)	8.37 s (1)	10.9 s (1)	12.0 s (1)	2.60 s (6)	*g*
				1610 (vs) 1600 (vs)	905 (vs)		8.68 s (1)				
5	*f*	*f*	*f*	1610 (sh)	950, 940	6.80–7.90 m (8)	8.62 s (1)	*f*	*f*	3.11 s[i]	3.40 s[i]
				1605 (vs)	930, 920 (vs) 910 (sh)		8.68 s (1)				
6	*f*	*f*	*f*	1620 (vs)	940, 930	6.80–8.00 m (8)	8.68 s (1)	*f*	*f*	2.0 s (12)	*g*
				1605 (vs)	920, 915 900 (vs)		8.73 s (1)				

[a] Abbreviations: vs, very strong; s, strong; m, medium; sh, shoulder. [b] Recorded in Me_2CO-d_6 (compound **1**) and Me_2SO-d_6 (compound **2–6**). Abbrebiations: s, singlet; d, doublet; m, multiplet. [c] X = S (compound **1**); X = O (compound **2**). [d] Methyl protons corresponding to bonded MeOH or Me_2SO. [e] OH proton of bonded MeOH. [f] Not observed. [g] Nonexistent. [h] Doublet attributed to MeOH/Me_2SO-d_6 ligand exchange. [i] Integration not possible.

Table VIII. Cyclic Voltammetric Peak Potential Data (V vs SCE) in DMF Solution

	E_p, V		
compd[a]	Ic	IIc	n_{Ic}
1		1.28	
2		1.30	
3	0.86	1.25–1.35	1.95 ± 0.05
5	0.93	1.32	4.00 ± 0.05

ligand. We attribute the fact that two C=N bands are observed in the binuclear complexes **5** and **6** to the near equivalence of the two coordinated azomethine groups and the presence of a central C=N unit. The *cis*-MoO_2 moiety exhibits symmetric and asymmetric Mo=O stretching frequencies in the mononuclear complexes **3** and **4**. The Mo=O stretching region for dinuclear species **5** and **6** is somewhat more complex (Figure 3). It is clear from the X-ray analysis of **6** that this is due to the nonequivalence of the two MoO_2 groups.

^{1}H NMR data for the free ligands and complexes are summarized in Table VII. Note that in ligands **1** and **2** the azomethine protons are equivalent while in complexes **3–6** two different CH=N signals are detected. This observation is consistent with the interpretation of the IR spectra presented above, viz. the occupancy of only one coordination site in **3** and **4** and the near equivalence of two of the azomethine sites in **5** and **6**. As expected, NH and OH resonances are evident in **3** and **4** but absent in **5** and **6**. Finally, note that partial substitution of MeOH by Me_2SO was detected in the ^{1}H NMR spectrum of **3**. Substitution reactions of this type at MoO_2 centers have been described previously,[20] and a qualitative order of donor ability has been established.

Electrochemical Studies. Cyclic voltammetry (CV) studies of DMF solutions of **1**, **2**, **3**, and **5** were carried out with Pt electrodes. The CV data are summarized in Table VIII and the *E*/*I* profiles are presented in Figure 4. The free ligands exhibit reversible electrochemical behavior; however, complexes **3** and **5** both undergo irreversible reduction as observed for similar complexes.[35] The second cathodic contribution for both complexes (IIC) falls in the same region as that for the free ligands; hence, only the more positive potential values (IC) are attributable to reduction at the molybdenum centers. Coulometric measurements at constant potential (–0.95 V) indicate a two-electron reduction in the case of **3** and a four-electron reduction in the case of **5**. In both complexes, therefore, Mo(VI) is reduced to Mo(IV). The electrochemical behavior of **4** and **6** is virtually identical with that of **3** and **5**.

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Supplementary Material Available: Tables of all bond lengths, bond angles, and anisotropic thermal parameters for **4** and **6** (8 pages); listings of observed and calculated structure factors for **4** and **6** (24 pages). Ordering information is given on any current masthead page.

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