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Synthesis and Properties of Mo(VI), Mo(V), Mo(IV) and Mixed Valence Mo(V)–Mo(IV) Complexes with a Binucleating Schiff's Base. X-ray Structure of the Mononuclear *cis*-Dioxo-aquo[1,4-dihydrazinophthalazine-bis(salicylidene-iminato)]molybdenum(VI) Acetone Solvate

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Abstract

The chemistry of the hexadentate, potentially binucleating N_2O_4 ligand 1,4-dihydrazinophthalazine-bis(salicylideneimine), LH_2, with molybdenum in the VI, V, and IV oxidation states is reported.

In the case of Mo(VI) only mononuclear species of the type MoO_2L, or $MoO_2L\cdot D$, where D is a donor molecule, were obtained. However, depending on the experimental conditions, Mo(V) gives either a mononuclear complex, or the trinuclear mixed oxidation state compound [Mo(V)OCl(Mo(IV)OLCl)$_2$]. Further reduction of this compound in the presence of PhSH gives the binuclear Mo(IV) complex [(MoO)$_2$L(OEt)Cl]. Spectroscopic evidence shows that the metal sites in the mixed valence trimer are quite different, so that it is a class I compound in the Robin–Day classification.

The X-ray structure of the Mo(VI) compound $[MoO_2L(H_2O)]\cdot CH_3COCH_3$ is reported. The complex forms dark red monoclinic crystals with a = 11.676(3), b = 10.725(4), c = 21.255(5) Å, and β = 105.66(2)°. The space group is $P2_1/n$ with Z = 4. The structure, refined to an R value of 0.053, shows a planar ligand molecule with two tridentate coordination sites, one of which is occupied by the metal ion.

The distorted octahedral coordination is completed by the two oxygens of the *cis*-dioxo grouping and by an apical water molecule.

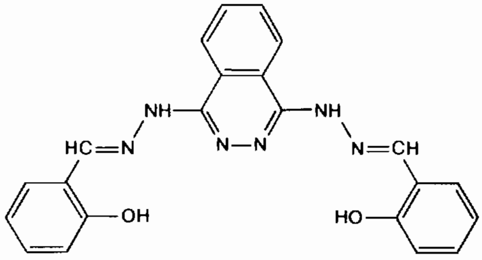
Introduction

Homo- and heterobinuclear transition metal complexes are currently an active area of research in the field of coordination chemistry. The investigation of magnetic exchange interactions [1], as well the synthesis of simple models for metallo bio-molecules [2] or multi-metal centered catalysts [3], are the main objectives for this kind of work.

One general approach has been the use of suitable multidentate ligands which hold the metals in a rigid arrangement, leaving vacant or labile bridging sites so as to allow the binding and possibly the activation of different molecular species [4–6].

Similar studies have involved a number of different metals, but we are not aware of any example concerning molybdenum ions. A reason for this may be the fact that the chemistry of Mo, especially in its high oxidation states, is already dominated by the presence of bi- or polynuclear species [7]. These systems usually contain strongly coupled, fairly unreactive metal core structures with one to three single-atom bridges generally formed by oxo, sulfido, or chloro ligands. The synthesis of binuclear Mo complexes incorporating more labile bridging ligands could enhance the reactivity of these systems, allowing displacement and binding of different substrate molecules.

With this aim we investigated the Mo coordination chemistry with the Schiff's base ligand 1,4-dihydrazinophthalazine-bis(salicylideneimine), LH_2 (Scheme 1). LH_2, as well as the parent base 1,4-dihydrazinophthalazine, dhph, and other related ligands, have already been used to obtain several binuclear metal complexes, mainly with Cu(II) and Ni(II) [8–11]. In our case the title ligand was chosen primarily to achieve a metal–metal distance larger than that imposed by single atom bridging.



LH_2

Besides, LH_2 has an extensive, conjugated π-system which might contribute to the stabilization of the Mo ion in a range of different oxidation states.

This report deals with the synthesis and characterization of the Mo(VI), Mo(V) and Mo(IV) complexes of the above ligand. The crystal and molecular structure of the mononuclear complex $[MoO_2L \cdot H_2O]CH_3COCH_3$ has been solved and is presented here.

Experimental

All syntheses and manipulations involving Mo(V) and Mo(IV) species were carried out under dry, oxygen-free nitrogen, using Schlenk-tube techniques. Solvents were distilled under N_2 from CaH_2 and were degassed immediately before use. $(NH_4)_2MoOCl_5$ [12] and $MoO_2Cl_2(dmf)_2$ [13] were prepared according to the literature. All other materials were obtained commercially and used as supplied.

Synthesis of Ligands

The synthesis of dhph, briefly reported some time ago [14], was modified as follows.

1,4-Dihydrazinophthalazine

$N_2H_4 \cdot H_2O$ (62 g, 1.24 mol) was dissolved in 32 ml of $AcOH:H_2O$ 1:1 and added to a suspension of phthalodinitrile (51.2 g, 0.40 mol) in 100 ml of 1,4-dioxane. The mixture was mechanically stirred and refluxed for 3 h. After cooling the mother liquors were decanted and the dark orange precipitate, still wet, was crystallized from boiling HCl (250 ml, 3 N) to give 45% of dhph·2HCl in the form of yellow crystals. *Anal.* Calcd. for $C_8H_{12}N_6Cl_2$: C, 36.51; H, 4.60; N, 31.94. Found: C, 36.97; H, 4.65; N, 30.71. Recrystallization from water yields the monohydrate derivative. *Anal.* Calcd. for $C_8H_{14}N_6OCl_2$: C, 34.17; H, 5.02; N, 29.89; Cl, 12.61. Found: C, 34.20; H, 4.81; N, 30.14; Cl, 12.25%.

The free base was obtained by dissolving 15 g of dhph·2HCl in 110 ml of water. The solution was filtered and the stoichiometric amount of KOH in water was added (6 g, 20 ml). The yellow-pink precipitate was filtered and crystallized from water (220 ml) to give 70% of crystalline $dhph(H_2O)_{1.5}$. *Anal.* Calcd. for $C_8H_{13}N_6O_{1.5}$: C, 44.23; H, 6.03; N, 38.69; H_2O, 12.44. Found: C, 44.20; H, 6.11; N, 38.51; H_2O, 13.0%.

1,4-Dihydrazino-bis(salicylideneimine)

An excess of salicylaldehyde (3.5 g, 28.7 mmol) was dissolved in EtOH (120 ml) and added to a suspension of $dhph(H_2O)_{1.5}$ (2 g, 9.2 mmol) in water (120 ml). After reflux (1 h) and cooling the yellow Schiff-base was filtered in almost quantitative yield. 1 g of the crude compound was dissolved in 200 ml of boiling EtOH. Addition of water (160 ml) and overnight refrigeration yielded 90% of crystalline $LH_2(H_2O)_{1.5}$. *Anal.* Calcd. for $C_{22}H_{21}N_6O_{3.5}$: C, 62.10; H, 4.98; N, 19.75; H_2O, 6.3. Found: C, 61.84; H, 4.70; N, 19.76; H_2O, 6.0%.

If the synthesis is carried out in the presence of a stoichiometric amount of aldehyde, a mixture of the di- and monosubstituted Schiff-base is obtained. This latter can be easily prepared in pure form using a 1:1 ratio of $dhph(H_2O)_{1.5}$ and salicylaldehyde.

Synthesis of Complexes

$MoO_2L(H_2O)_3$, 1

Solid $MoO_2(acac)_2$ (615 mg, 1.89 mmol) was added to a clear hot solution of $LH_2(H_2O)_{1.5}$ (400 mg, 0.94 mmol) in EtOH (80 ml). The mixture was refluxed for 0.5 h and then cooled to give around 550 mg of dark green needle crystals. *Anal.* Calcd. for $C_{22}H_{22}N_6O_7Mo$: C, 45.68; H, 3.83; N, 14.53; Mo, 16.59; H_2O, 9.3. Found: C, 45.88; H, 3.17; N, 14.47; Mo, 16.95; H_2O, 8.5%. The compound is easily soluble in many common solvents, apart from lower alcohols. Crystallization usually affords solvate species, sometimes together with variable amounts of the original hydrate. The preparation of three of these solvates is reported below.

Heating *in vacuo* of the trihydrate (85 °C, 3 h) yields the anydrous air-stable MoO_2L.

$[MoO_2L(H_2O)]CH_3COCH_3$, 2

Slow evaporation (*ca.* 10 days) of a solution of the hydrate in hot acetone (100 mg, 80 ml) yielded large prismatic, dark-red crystals of the acetone solvate. *Anal.* Calcd. for $C_{25}H_{24}N_6O_6Mo$: C, 50.01; H, 4.03; N, 14.00. Found: C, 49.50, H, 3.99; N, 13.84%.

$[MoO_2L(dmf)]H_2O$, 3

200 mg of 1 were dissolved in dmf (3 ml). After addition of EtOH (10 ml) the solution was stoppered and set aside to give, after 24 h, 80 mg of the product in dark red microcrystalline form. Evaporation of the solution yielded, in a few days, a further crop of large prismatic crystals. *Anal.* Calcd. for $C_{25}H_{25}N_7O_6Mo$: C, 48.79; H, 4.09; N, 15.93. Found: C, 48.72; H, 4.04; N, 15.72%.

$MoO_2L(py)$, 4

200 mg of 1 were dissolved in 4 ml of pyridine. Addition of EtOH (12 ml) and overnight refrigeration yielded small crystals of the monopyridine derivative. *Anal.* Calcd. for $C_{27}H_{21}N_7O_4Mo$: C, 53.74; H, 3.51; N, 16.25. Found: C, 53.66; H, 3.74; N, 16.12%.

$[MoO(LH)Cl_2]$, 5

Solid $(NH_4)_2MoOCl_5$ (825 mg, 2.54 mmol) was added, under nitrogen, to a hot solution of $LH_2(H_2O)_{1.5}$ (540 mg, 1.27 mmol) in 100 ml of anhydrous, N_2 purged EtOH. After refluxing for 1 h the microcrystalline brown product was filtered from the hot solution and washed with EtOH. Yield 75%. *Anal.* Calcd. for $C_{22}H_{17}N_6O_3Cl_2Mo$: C, 45.53; H, 2.95; N, 14.48; Cl, 12.22; Mo, 16.53. Found: C, 46.53; H, 3.11; N, 14.68; Cl, 12.68; Mo, 17.05%. The compound is appreciably soluble only in solvents such as dmf, dmso or py. The solutions are oxygen and water sensitive, whereas the dry solid is stable in air for weeks.

[Mo(V)OCl(Mo(IV)OLCl)$_2$], 6

Clean lithium metal (13.5 mg, 1.95 mmol) was dissolved in 80 ml of hot EtOH. Addition of the ligand (410 mg, 0.96 mmol) gave a clear yellow solution. Solid $(NH_4)_2MoOCl_5$ (625 mg, 1.92 mmol) was then added and the dark suspension refluxed for 1 h. 500 mg of an almost black crystalline precipitate were filtered from the hot solution and washed with EtOH. *Anal.* Calcd. for $C_{44}H_{32}N_{12}O_7Cl_3Mo_3$: C, 42.79; H, 2.61; N, 13.61; Cl, 8.61; Mo, 23.31. Found: C, 43.49; H, 2.83; N, 13.46; Cl, 8.77; Mo, 23.20%. The air-stable compound dissolves easily in CH_2Cl_2 to give dark green solutions, from which impure samples of the brown mononuclear Mo(V) complex **5** rapidly re-precipitate. Under N_2 the decomposition is slower but difficult to eliminate.

[Mo$_2$(IV)O$_2$L(OEt)Cl], 7

The above reaction was carried out as already described, but the addition of the Mo(V) salt was followed by a threefold excess of thiophenol (635 mg, *ca.* 0.6 ml, 5.76 mmol). After refluxing for 20 h the solution was refrigerated for two days to give a low yield of black microcrystals (230 mg). *Anal.* Calcd. for $C_{24}H_{21}N_6O_5ClMo_2$: C, 41.13; H, 3.02; N, 11.99; Cl, 5.06; Mo, 27.38. Found: C, 41.22; H, 2.92; N, 11.78; Cl, 5.48; Mo, 27.10%. The product is an air-stable solid, but shows the same solution behavior described for compound **6**.

Physical Measurements

Elemental analyses were performed by the Servizio Microanalitico, Area della Ricerca di Roma del CNR and by A. Bernhardt Anal. Lab., Elbach, West Germany. TGA and DTA analyses were carried out under anhydrous N_2 on a DuPont 950 thermal analyzer. IR and optical reflectance spectra were recorded respectively on a Perkin-Elmer 983 G and on a Beckman DK2A spectrophotometer. Magnetic susceptibilities were measured by the Gouy method. X-band EPR spectra were measured on a Varian E-9 spectrometer. The X-ray photoelectron spectra were recorded on the VG ESCA 3Mk2 of the Servizio ESCA, Area della Ricerca di Roma del CNR. The exciting source was the Al-$K_{\alpha 1,2}$ radiation.

X-ray Data Collection

A crystal of the title compound was wedged into a thin walled glass capillary. Preliminary rotation and Weissenberg photographs indicated monoclinic symmetry with systematic absences consistent with the space group $P2_1/n$. The lattice constants were determined by least-squares refinement of the setting angles of 15 computer-centered reflections ($2\theta >$ 25°). A summary of crystal data and intensity collection is reported in Table I. Intensities were measured at room temperature, by a Nicolet $P2_1$ automated diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å). The data were reduced in the conventional manner with corrections for Lorentz and polarization factors. Given the low value of μ and the crystal size, the effects of absorption were not compensated for.

TABLE I. Summary of Crystal Data, Data Collection Parameters and Least Squares Residuals for $[MoO_2L(H_2O)]\cdot CH_3COCH_3$.

Formula	$C_{25}H_{24}N_6O_6Mo$
Formula weight	600.46
Space group	$P2_1/n$
a (A)	11.676(3)
b (A)	10.725(4)
c (A)	21.255(5)
β (deg)	105.66(2)
V (A^3)	2563
ρ (calcd) (g cm^{-3})	1.546
ρ (obsd) (g cm^{-3})	1.54(2)
Crystal size (mm)	0.10 × 0.15 × 0.50
Crystal colour	Dark-red
Diffractometer	Syntex $P2_1$
Radiation	MoKα
μ (cm^{-1})	5.17
2θ scan range (deg)	$3 \leq 2\theta \leq 70$
Scan technique	$\theta - 2\theta$
Data collected	7000
Unique data	2843
with $I \geq 3\sigma(I)$	2252
weighting factor w	$1.0/(\sigma^2(F_o^2) + 0.000418F_o^2)$
L.S. parameters	225
Data/parameters	10
R (% (F_o))	5.29
R_w (%)	5.18

Solution and Refinement of the Structure

The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least-squares techniques with the SHELX-76 system of crystallographic computer programs [15]. All the hydrogen atoms belonging to the ligand were included at idealized positions as fixed contributions to the structure factor calculations. Neutral-atom scattering factors were applied to non-hydrogen atoms [16]. Hydrogen scattering factors were those tabulated by Stewart [17]. Anisotropic thermal parameters were used for all non-hydrogen atoms and a fixed isotropic value for the hydrogen atoms.

The final residual (R) and weighted residual (R_w), defined as $R = \Sigma||F_o| - |F_c||/|F_o|$ and $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w(F_o)^2]^{1/2}$, w is given in Table I, are 0.053 and 0.052 respectively. Thermal parameters and structure factors are available as supplementary material.

Results and Discussion

The synthesis of dhph and LH_2 is straightforward. However, it is of some interest to point out that reaction of salicylaldehyde with the two hydrazino residues of dhph occurs in two well-separated steps. Reaction of dhph and aldehyde in 1:1 molar ratio in hydroalcoholic medium and crystallization of the crude product from EtOH gives the pure monosubstituted Schiff's base*. Reaction of the second hydrazino moiety requires an excess of aldehyde and/or longer refluxing times. Such behavior is interesting in that it should allow synthesis of asymmetrically substituted ligands, so as to obtain different environments for the two coordination sites.

Mo(VI) Complexes

LH_2 easily reacts with $MoO_2(acac)_2$ in an alcoholic medium to give the mononuclear hydrate **1**. Several attempts to introduce a second Mo ion were carried out, using either Mo(VI) or Mo(V) salts. In the first case the starting complex was recovered unchanged, whereas using Mo(V) salts ion exchange occurred and the mononuclear complex **5** was obtained. In spite of this, preliminary experiments have shown that **1** easily reacts with other metal ions, like copper or iron, to give the corresponding heterobinuclear compounds [18].

Thermogravimetric curves show that **1** easilylooses the three H_2O molecules in two different steps, which are complete at 70–75 °C, and give the air-stable anhydrous compound MoO_2L. Apart from lower alcohols **1** dissolved in most organic solvents. Crystallization usually affords solvate species or causes coordinated water to be substituted by solvent molecules. Three of these species, namely those containing acetone, dmf and py have been isolated. Complex **2** easily gives the anhydrous species (*ca.* 90 °C), whereas partial decomposition occurs upon solvent elimination from **3** and **4**.

All the above compounds are typical diamagnetic *cis*-MoO_2^{2+} complexes. Apart from typical ligand absorptions the IR spectra display strong doublets at 935–920 and 905–885 cm^{-1}, characteristic of the symmetric and asymmetric stretches of the *cis*-dioxo grouping. The region around 700 cm^{-1} is masked by strong ligand absorptions, but there is no evidence of bands due to dimeric μ-oxo core structures [19]. A medium intensity sharp band between 3300 and 3230 cm^{-1} (free ligand 3270) is assigned to the N–H stretching vibration. Compound **1** displays two other absorptions in this region: a broad one around 3280 cm^{-1} and a sharp one at 3600 cm^{-1}, which probably arise from the stretchings of coordinated and lattice water.

The diffuse reflectance spectra of the Mo(VI) complexes are reported in Table II. The general assignment of the bands as charge-tranfer transitions is likely, but no detailed analysis has been attempted.

In summary these compounds appear as *cis*-dioxo Mo(VI) derivatives of the doubly deprotonated ligand, which behaves as a tridentate molecule. The sixth coordination position of the Mo(VI) ion is labile and allows easy coordination and displacement of different donor molecules. A similar situation has been proposed for the Mo(VI) complexes of truly tridentate dianionic ligands [20]. However, in the case of tridentate monoanionic molecules [21], structural evidence indicates that a

TABLE II. Magnetic and Electronic Spectral Data for the Complexes.

Compound		μ_{eff} (BM)	ν (cm^{-1})^a
$[MoO_2L(H_2O)](H_2O)_2$	1	diam.	17900, 27400
$[MoO_2L(H_2O)]CH_3COCH_3$	2	diam.	17900, 27400
$[MoO_2L(dmf)]H_2O$	3	diam.	18200, 27000
$[MoO_2L(py)]$	4	diam.	16100, 27000
$[MoO(LH)Cl_2]$	5	1.64	8000, 13300, (18000), (23250), (28600)
$[Mo^VOCl(Mo^{IV}OLCl)_2]$	6	1.01	8000, 15900, (23250), (28600)
$[(MoO)_2L(OEt)Cl]$	7	0.48	15900, (23250), (28600)

^{a}Frequencies in brackets represent shoulders.

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*Apparently this compound (m.p. 208–210 °C) corresponds to the unidentified yellow powder (m.p. 214–218 °C) isolated by Robichaud *et al.* [11] during the synthesis of LH_2.

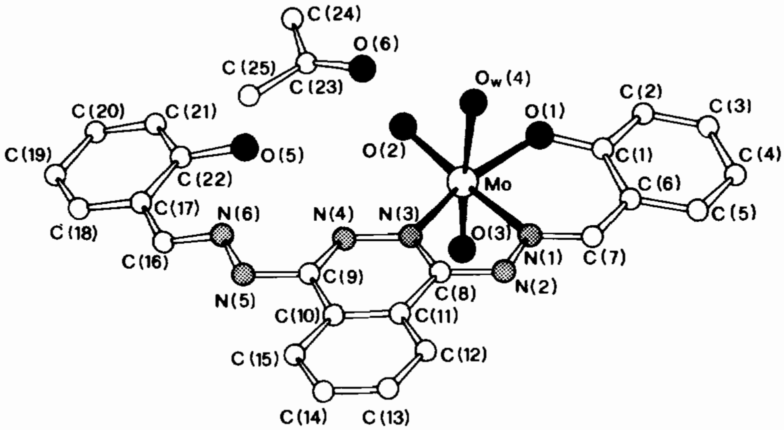


Fig. 1. Structure of [$MoO_2L(H_2O)$]·CH_3COCH_3, **2**.

TABLE III. Final Atomic Coordinates ($\times 10^4$) with e.s.d.s in Parentheses.

Atom	*x*	*y*	*z*
Mo	2156(1)	2349(1)	5073(0)
O(1)	1089(5)	3461(5)	5335(3)
O(2)	2435(6)	3073(5)	4418(3)
O(3)	3385(5)	2524(5)	5707(3)
$O_w(4)$	346(5)	1856(5)	4294(3)
O(5)	4747(7)	2939(6)	3711(4)
O(6)	591(10)	897(11)	3131(5)
N(1)	1288(6)	926(5)	5561(3)
N(2)	1438(6)	−331(5)	5444(3)
N(3)	2580(5)	561(5)	4832(3)
N(4)	3437(6)	515(6)	4475(4)
N(5)	4616(6)	−620(6)	3985(4)
N(6)	4973(7)	525(6)	3799(4)
C(1)	566(8)	3501(7)	5824(5)
C(2)	200(8)	4662(8)	6004(5)
C(3)	−368(10)	4711(9)	6485(6)
C(4)	−570(10)	3654(10)	6815(5)
C(5)	−207(9)	2511(9)	6653(5)
C(6)	365(7)	2412(8)	6149(4)
C(7)	693(8)	1172(7)	5985(5)
C(8)	2159(8)	−451(6)	5068(5)
C(9)	3799(8)	−577(7)	4351(5)
C(10)	3426(7)	−1749(6)	4573(4)
C(11)	2575(7)	−1686(7)	4925(5)
C(12)	2165(8)	−2776(6)	5147(4)
C(13)	2574(8)	−3913(7)	4998(5)
C(14)	3408(9)	−3995(7)	4657(6)
C(15)	3825(8)	−2925(7)	4431(5)
C(16)	5860(8)	564(8)	3552(5)
C(17)	6247(9)	1767(11)	3367(5)
C(18)	7193(10)	1812(14)	3104(6)
C(19)	7651(13)	2952(21)	2957(8)
C(20)	7120(18)	4062(17)	3050(10)
C(21)	6175(14)	3996(12)	3287(8)
C(22)	5702(10)	2892(11)	3450(6)
C(23)	1327(17)	1066(16)	2818(7)
C(24)	1554(27)	2306(16)	2650(14)
C(25)	1954(14)	11(15)	2555(9)

dimeric $Mo_2O_5^{2+}$ core structure is preferred. In our case different structural arrangements were possible and, in addition, the role of the second phenolic oxygen was not clear. Therefore the crystal and molecular structure of one of the above compounds, *i.e.* **2**, were determined.

Description of the Structure

A perspective view of $MoO_2L(H_2O)$·CH_3COCH_3 is shown in Fig. 1, with final atomic coordinates given in Table III, and bond distances and angles in Table IV. The structure consists of discrete molecular units among which only Van der Waals contacts exist, as reported in Table V. The ligand molecule is planar and presents two equivalent tridentate coordination sites, of which only one is occupied by a metal ion, forming two rings with five and six members. Molybdenum has six neighbours in a distorted octahedral coordination, *i.e.* two *cis* oxygen atoms from the MoO_2^{2+} group, an apical water molecule, a phenolic oxygen and two nitrogen atoms from the ligand. The two Mo–O bond distances and the O–Mo–O angle within the MoO_2^{2+} group, of 1.700(7) and 1.694(6) Å, and 107.0(3)° respectively, are comparable with those found in other Mo(VI) compounds [22–24]. The distances between Mo and the coordinated nitrogen atoms are significantly different, 2.237(2) Å for Mo–N(1) and 2.079(6) Å for Mo–N(3), such difference arising from a *trans* effect due to the oxo O(2) atom, the same effect, by O(3), influencing the Mo–O_w(4) distance of 2.366(5) Å.

Comparison of the coordinated and uncoordinated parts of L^{2-} shows that formation of the six-membered coordination ring does not affect the ligand bond distances, whereas small but significant differences are present in the more strained five-membered ring. The N(2)–C(8) and N(3)–C(8) distances are, respectively, 1.31(1) and 1.34(1) Å, whereas the corresponding N(5)–C(9) and N(4)–C(9) are 1.38(1) and 1.30(1) Å.

TABLE IV. Bond Distances (Å) and Selected Bond Angles (°), with e.s.d.s in Parentheses.

Mo–O(1)	1.913(6)	O(1)–Mo–O(2)	103.8(3)
Mo–O(2)	1.700(7)	O(1)–Mo–O(3)	100.2(3)
Mo–O(3)	1.694(6)	O(1)–Mo–O$_w$(4)	79.3(2)
Mo–O$_w$(4)	2.366(5)	O(1)–Mo–N(1)	83.0(2)
Mo–N(1)	2.237(7)	O(1)–Mo–N(3)	149.8(3)
Mo–N(3)	2.079(6)	O(2)–Mo–O(3)	107.0(3)
O(1)–C(1)	1.34(1)	O(2)–Mo–O$_w$(4)	82.0(2)
O(5)–C(22)	1.37(2)	O(2)–Mo–N(1)	154.5(3)
O(6)–C(23)	1.24(2)	O(2)–Mo–N(3)	96.2(3)
N(1)–N(2)	1.390(8)	O(3)–Mo–O$_w$(4)	170.6(3)
N(1)–C(7)	1.31(1)	O(3)–Mo–N(1)	95.6(3)
N(2)–C(8)	1.31(1)	O(3)–Mo–N(3)	95.2(3)
N(3)–N(4)	1.41(1)	O$_w$(4)–Mo–N(1)	75.0(2)
N(3)–C(8)	1.34(1)	O$_w$(4)–Mo–N(3)	81.3(2)
N(4)–C(9)	1.30(1)	N(1)–Mo–N(3)	69.7(3)
N(5)–C(9)	1.38(1)	Mo–O(1)–C(1)	135.6(5)
N(5)–N(6)	1.39(1)	Mo–N(1)–N(2)	119.0(6)
N(6)–C(16)	1.28(1)	Mo–N(1)–C(7)	125.1(5)
C(1)–C(2)	1.40(1)	N(1)–N(2)–C(8)	109.7(6)
C(1)–C(6)	1.41(1)	Mo–N(3)–C(8)	121.2(6)
C(2)–C(3)	1.36(2)	N(4)–N(3)–C(8)	123.8(6)
C(3)–C(4)	1.39(2)	N(3)–N(4)–C(9)	117.3(7)
C(4)–C(5)	1.37(2)	N(6)–N(5)–C(9)	115.9(7)
C(5)–C(6)	1.41(2)	N(5)–N(6)–C(16)	118.9(7)
C(6)–C(7)	1.45(1)	O(1)–C(1)–C(6)	121.6(8)
C(8)–C(11)	1.47(1)	C(1)–C(6)–C(7)	123.6(9)
C(9)–C(10)	1.45(1)	N(1)–C(7)–C(6)	125.0(8)
C(10)–C(11)	1.40(1)	N(2)–C(8)–N(3)	120.5(7)
C(10)–C(15)	1.41(1)	N(3)–C(8)–C(11)	118.4(9)
C(11)–C(12)	1.39(1)	N(4)–C(9)–N(5)	117.1(8)
C(12)–C(13)	1.38(1)	N(6)–C(16)–C(17)	118.9(9)
C(13)–C(14)	1.36(2)	O(5)–C(22)–C(17)	122.0(11)
C(14)–C(15)	1.38(1)	O(5)–C(22)–C(21)	119.4(12)
C(16)–C(17)	1.46(2)	O(6)–C(23)–C(24)	118.5(20)
C(17)–C(18)	1.37(2)	O(6)–C(23)–C(25)	124.0(16)
C(17)–C(22)	1.40(2)	C(24)–C(23)–C(25)	117.4(20)
C(18)–C(19)	1.40(3)		
C(19)–C(20)	1.38(3)		
C(20)–C(21)	1.33(3)		
C(21)–C(22)	1.39(2)		
C(23)–C(24)	1.42(3)		
C(23)–C(25)	1.53(3)		

TABLE V. Closest Intermolecular Contacts (Å) in [MoO$_2$L-(H$_2$O)]·CH$_3$COCH$_3$, within 3.5 Å.

O(3)–N(5)	[1 – x, –y, 1 – z]	3.04
O(3)–H(N(5))	[1 – x, –y, 1 – z]	2.21
O$_w$(4)–O(6)		2.76
O$_w$(4)–N(2)	[–x, –y, 1 – z]	2.82
O$_w$(4)–H(N(2))	[–x, –y, 1 – z]	1.84

The other ligand bond distances are as expected and can be compared with those found for a Ni(II) complex with a ligand containing the dhph skeleton [9].

Concerning the second, non-coordinated, phenolic oxygen O(5), its C(22)–O(5) bond distance of 1.37(2) Å, not significantly different from the analogous C(1)–O(1) distance of 1.34(1) Å, is slightly shorter than a single bond. This, together with the fact that O(5) is not involved in any interaction below 3.5 Å, is a strong indication of a partial delocalization of the residual negative charge over the whole ligand π-system.

Mo(V) and Mo(IV) Complexes

Reaction of LH$_2$ with an excess of (NH$_4$)$_2$MoOCl$_5$ in EtOH again gives a mononuclear species. The analyses are consistent with the formulation [MoO-(LH)Cl$_2$], thus implying that the ligand is in its monoanionic form. DTA and TGA curves show that thermal processes or weight losses do not occur before decomposition at *ca.* 250 °C. The solid compound is stable in air for weeks and is sparingly soluble in common organic solvents, apart from dmf, dmso and py.

Synthesis of a Mo(V) derivative of the fully deprotonated ligand was attempted in the presence of a stoichiometric amount of LiOEt. However, the green-black crystalline solid which was isolated showed an unexpected stoichiometry which, on the basis of elemental and thermogravimetric analyses, corresponds to [(MoO)$_3$L$_2$Cl$_3$], **6**, thus suggesting that we are in the presence of a mixed-valence species. Charge balance would require the presence of formally Mo(IV) and Mo(V) ions in a 2:1 ratio. Compound **6** is easily soluble in chlorinated solvents. However, its dark green solutions decompose, even in inert atmosphere, and deposit a brown solid which we identify as impure compound **5** (IR spectrum).

The identification of **6** as a trinuclear Mo(IV)–Mo(V) complex (see below) suggested that complete reduction to Mo(IV) could be achieved in the presence of a suitable reducing agent. Therefore the reaction between LH$_2$ and (NH$_4$)$_2$MoOCl$_5$ was again carried out in the presence of both LiOEt and a threefold excess of C$_6$H$_5$SH to give a low yield of the green black Mo(IV) complex [(MoO)$_2$-L(OEt)Cl], 7. Both in the solid state and in solution the stability of 7 is very similar to that displayed by **6**.

Compound 7 does not exhibit any OH stretching in the IR spectrum and behaves as a non-electrolyte in dichloroethane solution. Furthermore, removal of the ethanol molecule by heating under vacuum does not occur before decomposition. Taken together these facts strongly support a binuclear formulation with a bridging ethoxide group. The results of conductivity measurements suggest that the chloride ion is also coordinated, although it is not clear whether it acts as a bridging ligand or not.

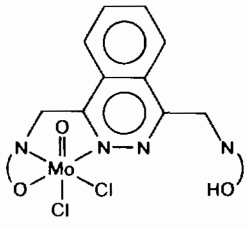
Besides typical ligand absorptions the IR spectra of the three compounds described above, *i.e.* **5**, **6**,

TABLE VI. X-band EPR Parameters for the Mo(V) and Mo(IV)–Mo(V) Complexes.[a]

Compound	Medium	$g_\parallel$	g_{iso}	$g_\perp$	$A_\parallel$	A_{iso}	$A_\perp$
$[MoO(LH)Cl_2]$ **5**	Pure	1.926		1.963			
	Solution		1.950			44.2	
	Fr. solution	1.929		1.958	72.3		32.0
$[Mo(V)OCl(Mo(IV)OLCl)_2]$ **6**	Pure	1.926		1.962			
	Solution		1.950			44.2	
	Fr. solution	1.929		1.958	72.5		32.0

[a]Measured in dmso solution. Hyperfine data are in units of 10^{-4} cm^{-1}.

and 7, display strong bands assignable to the Mo–O stretching (Mo(V) 970 cm^{-1}, Mo(IV) 946 cm^{-1}). Both bands are present in the mixed valence complex **6** and their relative intensity agrees satisfactorily with the expected 2:1 ratio of Mo(IV) and Mo(V). A sharp medium intensity band at 3290 cm^{-1} is present only in the spectrum of **5**, and confirms that this is the only compound in the series which contains the singly deprotonated ligand LH$^-$. Mo–Cl stretchings appear at 354, 326 and 311 cm^{-1} in the spectra of **5** and **6**, but are not easy to locate in the spectrum of **7**. This would support the presence of bridging Cl in this compound. Finally a medium intensity band at *ca.* 620 cm^{-1} in the spectrum of **7** is tentatively assigned to ν_{as} (MoOEtMo). No pertinent examples can be taken from the literature. However this band is in the expected frequency range, *i.e.* somewhat lower than the vibration of μ-oxo bridges in related compounds [7, 19].



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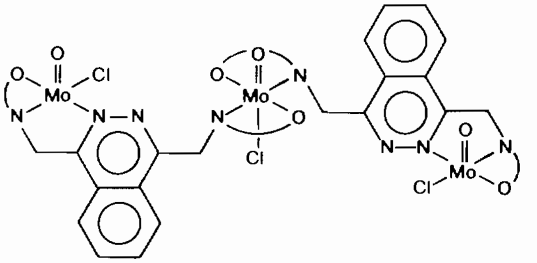

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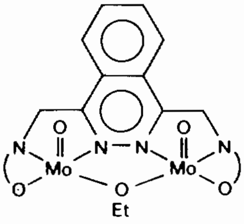

7

Fig. 3. Proposed structures for complexes **5**, **6** and **7**. In the case of complex **7** the chloro ligand, whose coordination site is uncertain, has been omitted.

The magnetic and EPR properties are summarized in Tables II and VI. Compound **5** is paramagnetic with μ_{eff} = 1.64 BM and an EPR spectrum typical of mononuclear Mo(V) complexes. The measured parameters are very close to those reported for Mo(V) species with similar sets of donor atoms [25], and support the structure sketched in Fig. 3. Compound **7** is diamagnetic and EPR-silent. Its magnetic moment (0.48 BM per Mo(IV) ion) is in the range of values reported for low-spin oxomolybdenum(IV) complexes and is probably due to temperature-independent paramagnetism [26]. Therefore, alternative explanations such as spin pairing between high-spin Mo(IV) ions interacting within the dimeric structure are unlikely.

The magnetic behavior of **6** confirms its mixed valence nature. The experimental molar susceptibility (12.9 × 10^{-4} cgs units) agrees very well with the value calculated assuming two equivalent Mo(IV)

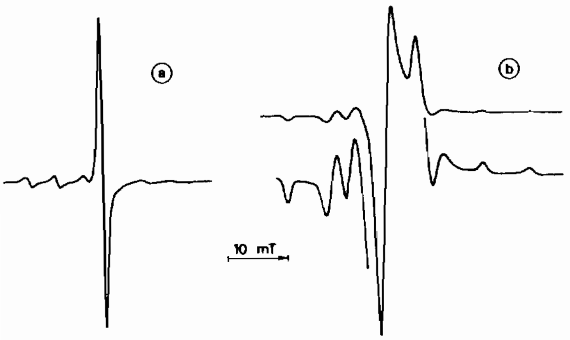

Fig. 2. X-band EPR spectra of $[Mo(V)OCl(Mo(IV)OLCl)_2]$ in dmso solution at: (a) RT and (b) 110 K.

for each Mo(V) ion. Using the χ_M values measured for compounds **5** and **7** the calculated χ_M for **6** is 13.07×10^{-4} cgs units. The EPR spectrum of compound **6**, both pure or in solution, see Fig. 2, is almost identical to that of the mononuclear complex **5**, suggesting that the two Mo(V) ions are present in similar environments and that no detectable magnetic interactions are present.

The low solution stability of **6** hampered molecular weight measurements, but definitive evidence concerning the molybdenum oxidation states was obtained through XPS spectroscopy. Figure 4 shows the Mo $3d_{5/2,3/2}$ region of the X-ray photoelectron spectrum of compound **6**. Also shown are the results of a peak fitting procedure carried out assuming the contribution of two gaussian peaks with a full width at half maximum of 1.8–2.0 eV. The intensity ratio of the two components is close to 2 and the Mo $3d_{5/2}$ orbital exhibits binding energies of respectively 231.3 and 232.7 eV (internally referenced to a C 1s energy of 285.0 eV). The $3d_{3/2}$ orbital is about 3.0 eV higher in energy.

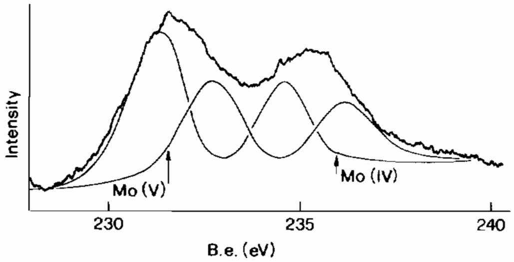

Fig. 4. X-ray photoelectron spectrum and deconvolution of the Mo $3d_{5/2,3/2}$ doublet in $[Mo(V)OCl(Mo(IV)OLCl)_2]$, **6**.

As a check we measured the Mo 3d region of the related Mo(IV) and Mo(V) complexes **7** and **5**. In spite of partial decomposition, which occurred mainly with compound **5**, we measured b.e. of 231.85 and 233.25 eV, which confirm the presence of localized oxidation states IV and V in complex **6**.

On the basis of the above information this compound is formulated as a trimer in which two mononuclear Mo(IV) units coordinate a Mo(V) ion, *i.e.* $[Mo(V)OCl(Mo(IV)OLCl)_2]$. Higher molecular weight formulations, although possible, are unlikely on the basis of the magnetic and EPR properties. Of course different structures can be envisaged for such a trimer. A possible formulation, in agreement with the experimental data, is proposed in Fig. 3. It accounts for the close similarity of the EPR spectra of compounds **5** and **6**.

In addition the gross chemical inequivalence and the large distance between the metal sites suggest complete localization of the oxidation states. This is in agreement with the optical spectrum, which results from the pure superposition of the absorptions shown by the Mo(IV) and Mo(V) complexes **7** and **5** (see Fig. 5). Therefore the properties of **6** support its classification as a class I compound in the Robin–Day scheme [27, 28].

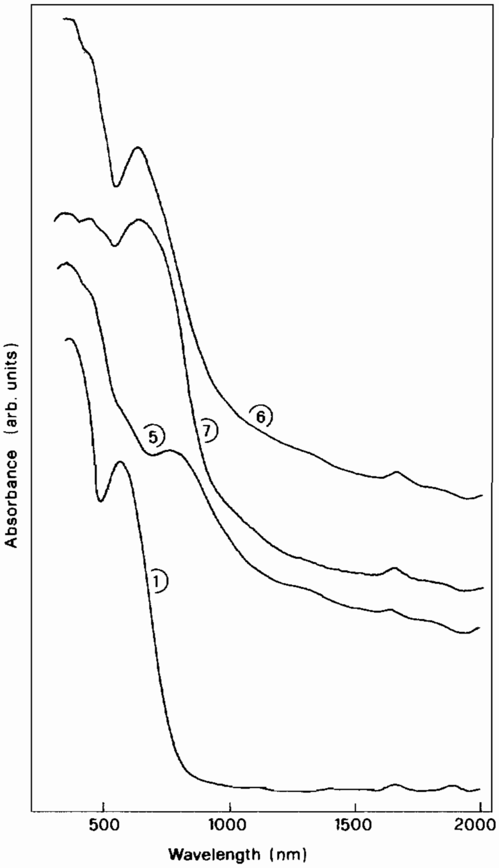

Fig. 5. Optical reflectance spectra of complexes $[MoO_2\text{-}L(H_2O)](H_2O)_2$, **1**; $[MoO(LH)Cl_2]$, **5**; $[Mo(V)OCl(Mo\text{-}(IV)OLCl)_2]$, **6**; and $[(MoO)_2L(OEt)Cl]$, **7**.

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