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$[MoO(NNPh_2)(acac)_2]$, a precursor of novel binuclear hydrazido(2−)molybdenum(VI) complexes containing bridging alkoxo ligands: $[\{MoO(NNPh_2)(acac)(\mu\text{-}OR)\}_2]$. Syntheses, characterization, reactivity and electrochemical studies. Crystal structure of $[\{MoO(NNPh_2)(acac)(\mu\text{-}OEt)\}_2]$

Carlos Bustos, Carolina Manzur, Hugo Gonzalez, Ricardo Schrebler, David Carrillo*
Instituto de Quimica, Universidad Catolica de Valparaiso, Brasil 2950, Valparaiso (Chile)

Claudette Bois, Yves Jeannin and **Pierre Gouzerh***
Laboratoire de Chimie des Métaux de Transition, URA-CNRS 419, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cédex 05 (France)

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Abstract

1,1-Diphenylhydrazine reacts with $[MoO_2(acac)_2]$ in methanol to yield either the mononuclear complex $[MoO(NNPh_2)(acac)_2]$ (**I**) or the binuclear complex $[\{MoO(NNPh_2)(acac)(\mu\text{-}OMe)\}_2]$ (**II**) depending on the temperature. In refluxing ROH, complex **I** transforms into $[\{MoO(NNPh_2)(acac)(\mu\text{-}OR)\}_2]$. (R = Me: **II**; R = Et: **III**; R = n-Pr: **IV**.) The crystal structure of **III** is reported. Crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions $a = 9.211(1)$, $b = 10.375(2)$, $c = 12.107(3)$ Å, $\alpha = 72.98(2)$, $\beta = 64.55(1)$, $\gamma = 70.10(1)°$ and $Z = 1$. The structure was solved using 5034 unique observed reflections; the refinement of 304 variables gave R and R_w values of 0.024 and 0.026, respectively. The lattice is made of discrete centrosymmetrical dinuclear molecules. The geometry of the hydrazido(2−) ligand (Mo–N = 1.784(1), N–N = 1.298(2) Å, Mo–N–N = 169.5(1)°) indicates extensive delocalization through the Mo–N–N unit. **II**, **III** and **IV** are representative members of a new family of dinuclear complexes which display the $[(Ph_2NN)OMo(\mu\text{-}OR)_2MoO(NNPh_2)]^{2+}$ core.

Introduction

The identification of the hydrazido(2−) species, NNH_2, as an intermediate in the conversion of coordinated dinitrogen into ammonia [1, 2], has stimulated extensive research in order to synthesize a variety of complexes containing the analogous organohydrazido(2−) ligand, NNR′R″, as stable possible models. Dioxomolybdenum(VI) complexes, $[MoO_2(LL)_2]$, where LL is a bidentate ligand having S,S [3–5], N,N [4], N,O [6] or S,O [7] donor atoms, have been widely used in synthesis of hydrazido(2−) complexes. They react with 1,1-disubstituted hydrazines, $R'R''NNH_2$, giving [hydrazido(2−)]oxo derivatives, $[MoO(NNR'R'')(LL)_2]$ and/or bis-[hydrazido(2−)] derivatives, $[Mo(NNR'R'')_2(LL)_2]$. In all cases both bidentate ligands are retained in the structure and consequently mononuclear complexes are obtained. The stability of these complexes has restricted their potential use in the synthesis of polynuclear derivatives. Besides these mononuclear species an asymmetrical binuclear hydrazido(2−)oxomolybdenum complex [8], and a number of organohydrazido-derivatized polyoxomolybdates [9–11] have been characterized by Zubieta and coworkers. Here we report the results of the reactions of diphenylhydrazine with $[MoO_2(acac)_2]$. The syntheses and properties of $[MoO(NNPh_2)(acac)_2]$ (**I**) and of $[\{MoO(NNPh_2)(acac)(\mu\text{-}OR)\}_2]$, where R = Me (**II**), Et (**III**) and n-Pr (**IV**), are reported, and the X-ray crystal structure of **III** is presented. After completion of this work, the results of reactions of diphenylhydrazine with a dioxomolybdenum(VI) hydroxamate complex were reported by Murray and co-workers [7].

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*Authors to whom correspondence should be addressed.

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Experimental

Chemicals

1,1-Diphenylhydrazine hydrochloride, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, acetylacetone and triethylamine are commercially available. High-purity solvents were used as received. $[MoO_2(acac)_2]$ was prepared as described in the literature [12].

Physical measurements

^{1}H NMR spectra were recorded in $CDCl_3$ by using either a Varian T-60 spectrometer or a General Electric QE-300 spectrometer or a Bruker WM 250 spectrometer. IR spectra were obtained on a Perkin-Elmer 599 spectrophotometer as KBr disks. Absorption spectra were recorded in CH_3CN solutions on a Cary 219 spectrophotometer. Magnetic measurements were performed at 20 ± 2 °C by the Faraday method using a Cahn Ventron RTL magnetic balance and $[Ni(en)_2]S_2O_3$ as a standard. Melting points were determined by using a Kofler apparatus and were not corrected. Cyclic voltammetry (CV) measurements were made with a home made potentiostat of conventional design using a three-electrode cell with platinum working and auxiliary electrodes and a saturated calomel electrode (SCE) as the reference. All measurements were made at ambient temperature (20 ± 2 °C) in either CH_2Cl_2, CH_3CN or dimethylformamide (DMF) with 0.1 M tetrabutylammonium tetrafluoroborate, NBu_4BF_4, tetrabutylammonium hexafluorophosphate, NBu_4PF_6, or tetraethylammonium perchlorate, NEt_4ClO_4, as the supporting electrolyte.

TABLE 1. Crystal data

Formula	$C_{38}H_{44}Mo_2N_4O_8$
Formula weight	876.7
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.211(1)
b (Å)	10.375(2)
c (Å)	12.107(3)
α (°)	72.98(2)
β (°)	64.55(1)
γ (°)	70.10(1)
V (Å^3)	967.6
Z	1
ρ_{calc} (g cm^{-3})	1.5
Crystal dimensions (mm)	0.65 × 0.40 × 0.30
$F(000)$	448
Systematic absences	none
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
Linear absorption coefficient (cm^{-1})	6.6
Transmission factor range	1.0–1.13
Scan type	$\theta/2\theta$
Scan range (°)	$1.2 + 0.345\mathrm{tg}\theta$
θ limits (°)	1.5–30
Octants collected	$-h+h,\ -k+k,\ +l$
No. unique data collected	5981
No. unique data used	5034 $(F_o)^2 > 3\sigma(F_o{}^2)$
Final discrepancy factors	
$R = \Sigma(\lVert F_o\rvert - \lvert F_c\rVert)/\Sigma\lvert F_o\rvert$	0.024
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.026

X-ray data collection and structure determination

An air-stable crystal was mounted on a thin glass fiber on a Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation. Lattice parameters were obtained from a least-squares refinement of the setting angles of 25 automatically centered reflections ($15 < \theta < 16°$). The cell constants and other parameters including conditions of data collection are summarized in Table 1.

Two reflections were monitored every hour and no significant intensity fluctuations were observed. Intensities were corrected for Lorentz and polarization effects, and for absorption by using an empirical method based or the Ψ scans of two reflections.

The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. Computations were performed on a Micro VAX2 using the CRYSTALS system [13]. The structure was solved by conventional heavy-atom methods. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All the hydrogen atoms were located on difference electron density maps and were included in the refinements; their coordinates and an overall isotropic thermal parameter were refined. Correction was made for extinction. Final refinement of 304 parameters in two blocks gave $R = 0.024$ and $R_w = 0.026$. The weighting scheme was based on a three-term Chebyshev series: $w = w'[1 - \{\Delta F/6\sigma(F)\}^2]^2$ with $w' = 1/[8.617t_0(x) - 2.715t_1(x) + 6.835t_2(x)]$ where $x = F_0/F_0(\max)$ and t_n is the polynomial function. Scattering factors and corrections for anomalous dispersion were taken from ref. 14. A final difference electron density map was featureless. Atomic positional parameters for non-hydrogen atoms are given in Table 2. Selected intramolecular bond distances and angles are given in Table 3. An ORTEP [15] representation of the molecular structure with the atom labeling scheme is shown in Fig. 1.

Preparation of complexes

Bis(acetylacetonato)oxo[diphenylhydrazido(2 −)]-molybdenum(VI), [MoO(NNPh₂)(acac)₂], (I)

Triethylamine (7.23 mmol) was added to a suspension of 1,1-diphenylhydrazine hydrochloride (7.23 mmol) in methanol (20 ml). The resulting solution was added to $[MoO_2(acac)_2]$ (7.23 mmol) dissolved

TABLE 2. Atomic and thermal parameters for the non-hydrogen atoms of [{MoO(N_2Ph_2)(μ-OEt)(acac)}$_2$]

Atom	x/a	y/b	z/c	U_{eq}
Mo(1)	0.08907(1)	−0.02767(1)	−0.148824(9)	0.0335
O(1)	−0.0762(1)	0.0470(1)	−0.1929(1)	0.0451
O(2)	−0.0083(1)	−0.12196(9)	0.02780(9)	0.0374
O(3)	0.2239(1)	0.0990(1)	−0.2958(1)	0.0473
O(4)	0.3113(1)	−0.0702(1)	−0.1018(1)	0.0498
N(1)	0.1833(2)	−0.1826(1)	−0.2149(1)	0.0410
N(2)	0.2257(2)	−0.2915(1)	−0.2644(1)	0.0415
C(1)	0.3654(2)	−0.4018(2)	−0.2539(1)	0.0429
C(2)	0.4365(2)	−0.4038(2)	−0.1737(2)	0.0570
C(3)	0.5717(3)	−0.5124(3)	−0.1628(2)	0.0715
C(4)	0.6353(3)	−0.6166(3)	−0.2312(3)	0.0744
C(5)	0.5665(3)	−0.6116(3)	−0.3134(3)	0.0732
C(6)	0.4319(4)	−0.5048(2)	−0.3265(2)	0.0596
C(7)	0.1339(2)	−0.2915(2)	−0.3352(1)	0.0440
C(8)	0.1224(3)	−0.1826(2)	−0.4315(2)	0.0586
C(9)	0.0419(4)	−0.1821(3)	−0.5052(3)	0.0769
C(10)	−0.0286(4)	−0.2865(4)	−0.4816(3)	0.0876
C(11)	−0.0242(5)	−0.3919(5)	−0.3838(4)	0.0968
C(12)	0.0603(4)	−0.3970(3)	−0.3092(3)	0.0768
C(13)	0.4253(4)	0.1962(4)	−0.4650(3)	0.0823
C(14)	0.3769(2)	0.0997(2)	−0.3431(2)	0.0590
C(15)	0.4913(3)	0.0249(3)	−0.2895(2)	0.0735
C(16)	0.4529(2)	−0.0552(2)	−0.1698(2)	0.0540
C(17)	0.5893(3)	−0.1250(3)	−0.1198(3)	0.0769
C(18)	−0.0075(2)	−0.2655(1)	0.0686(1)	0.0443
C(19)	−0.1350(3)	−0.2971(3)	0.0408(2)	0.0661

TABLE 3. Selected interatomic distances (Å) and angles (°) with e.s.d.s in parentheses (primed numbers refer to atoms generated by an inversion center)

Mo(1)–Mo(1)′	3.3906(2)	N(1)–N(2)	1.298(2)	C(14)–O(3)	1.274(2)
Mo(1)–O(1)	1.690(1)	N(2)–C(1)	1.426(2)	C(16)–O(4)	1.242(2)
Mo(1)–O(2)	2.0146(9)	N(2)–C(7)	1.440(2)	C(13)–C(14)	1.501(3)
Mo(1)–O(2)′	2.1722(9)			C(14)–C(15)	1.367(3)
Mo(1)–O(3)	2.069(1)			C(15)–C(16)	1.404(3)
Mo(1)–O(4)	2.224(1)			C(16)–C(17)	1.499(3)
Mo(1)–N(1)	1.784(1)				
O(1)–Mo(1)–O(2)	103.92(5)	O(1)–Mo(1)–O(2)′	92.26(5)		
O(2)–Mo(1)–O(2)′	71.90(4)	O(1)–Mo(1)–O(3)	90.08(5)		
O(2)–Mo(1)–O(3)	157.89(5)	O(3)–Mo(1)–O(2)′	90.80(2)		
O(1)–Mo(1)–O(4)	165.34(5)	O(4)–Mo(1)–O(2)	83.74(4)		
O(1)–Mo(1)–N(1)	103.12(6)	O(4)–Mo(1)–O(3)	79.16(5)		
N(1)–Mo(1)–O(4)	88.22(5)	O(2)–Mo(1)–N(1)	96.17(5)		
N(1)–Mo(1)–O(2)′	162.60(5)	O(3)–Mo(1)–N(1)	97.20(5)		
Mo(1)–N(1)–N(2)	169.5(1)				

in methanol (20 ml). The reaction mixture was stirred for 2.0 h at room temperature. The resulting orange precipitate was filtered off, washed with cold methanol, recrystallized from acetonitrile and dried *in vacuo*. Yield 66%. Additional product was obtained by cooling the filtrate to −10 °C. Complex **I** was similarly obtained in ethanol and n-propanol in 65% and 83% yield, respectively.

Anal. Calc. for $C_{22}H_{24}N_2MoO_5$: C, 53.7; H, 4.9; N, 5.7. Found: C, 53.8; H, 5.2; N, 5.8%.

Di-μ-methoxo-bis[(acetylacetonato)oxo{diphenylhydrazido(2−)}molybdenum(VI)], [{MoO(NNPh$_2$)(acac)(μ-OMe)}$_2$] (II)

Method 1. The preparation was carried out as described above, but the reaction mixture was refluxed for 1 h. The resulting yellow precipitate (complex **II** with a small amount of complex **I**) was filtered off, washed with cold methanol, recrystallized from hot methanol, and dried *in vacuo*. Yield 63%. The

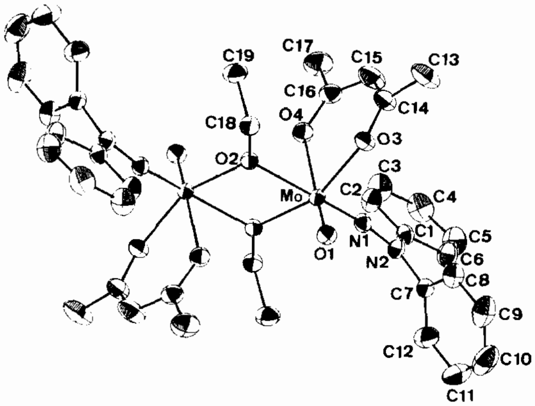


Fig. 1. ORTEP drawing of the molecule [{MoO($NNPh_2$)(acac)(μ-OEt)}$_2$] (**III**) showing the atom-labeling scheme.

red–brown filtrate was cooled to −10 °C affording the orange mononuclear complex **I** as a by-product. Yield 12%.

Method 2. Complex **I** (1.0 g) was dissolved in methanol (20 ml) and refluxed for 30 min. The orange solution turned yellow and a crystalline solid was formed. The solid was collected, washed with cold methanol, recrystallized from hot methanol and dried *in vacuo*. Yield 92%.

Anal. Calc. for $C_{36}H_{40}N_4Mo_2O_8$: C, 51.0; H, 4.8; N, 6.6. Found: C, 51.1; H, 5.0; N, 6.6%.

Di-μ-ethoxo-bis[(acetylacetonato)oxo{diphenylhydrazido(2−)}molybdenum(VI)], [{MoO($NNPh_2$)(acac)(μ-OEt)}$_2$] (III)

Complex **III** was similarly obtained from **I** refluxed in ethanol for 1 h. The microcrystalline yellow solid was filtered off, washed with cold ethanol, recrystallized from hot ethanol and dried *in vacuo*. Yield 84%. *Anal.* Calc. for $C_{38}H_{44}N_4Mo_2O_8$: C, 52.1; H, 5.1; N, 6.4. Found: C, 52.3; H, 5.3; N, 6.4%.

Di-μ-(n-propoxo)-bis[(acetylacetonato)oxo{diphenylhydrazido(2−)}molybdenum(VI)], [{MoO($NNPh_2$)(acac)(μ-OPr^n)}$_2$] (IV)

Complex **IV** was similarly obtained from **I** heated for 1 h in n-propanol at 60 °C under nitrogen. The yellow solid was washed with diethylether, recrystallized from 1/3 (vol./vol.) n-propanol/diethylether and dried *in vacuo*. Yield 81%.

Anal. Calc. for $C_{40}H_{48}N_4Mo_2O_8$: C, 53.1; H, 5.3; N, 6.2. Found: C, 53.3; H, 5.5; N, 6.3%.

Results and discussion

Synthesis and reactivity of complexes

In methanol 1,1-diphenylhydrazine reacts on [MoO_2(acac)$_2$] to give the mononuclear complex **I** at room temperature or the binuclear complex **II** under reflux. Complex **I** similarly transforms into the binuclear complexes **III** and **IV** when heated in ethanol or n-propanol. Complexes **III** and **IV** can alternatively be obtained by reacting [MoO_2(acac)$_2$] with 1,1-diphenylhydrazine in the appropriate alcohol at 60–80 °C. Consequently complex **I** is recrystallized in acetonitrile.

The displacement of ancillary ligands in the reaction of mononuclear oxomolybdenum(VI) complexes with substituted hydrazines is not exceptional. The expected mononuclear bis(phenyldiazenido)-molybdenum complex [Mo($NNPh$)$_2$(acac)$_2$] was not obtained from the reaction of $PhNHNH_2$ on [MoO_2(acac)$_2$] in alcohol; instead binuclear alkoxo-bridged complexes were obtained [16]. However mononuclear complexes [Mo($(C_6H_5N_2)_2$)$_2$(LL)$_2$] are formed from (N,O), (N,S) and (S,S) chelates. 1,1-Diphenylhydrazine behaves similary: dimerization via alkoxo bridging occurs when LL is acac, i.e. a (O,O) ligand, but is not observed with (S,S) [3–5], (N,N) [4], (N,O) [6], and (S,O) [7] ligands. Clearly solvent basicity competes with ligand basicity.

Complex **I** is recovered when complexes **II**, **III** and **IV** are heated in acetylacetone. This indicates that the binuclear complex is in equilibrium with the mononuclear species and that reaction (1) can be shifted back and forth.

$$2[\mathrm{MoO(NNPh_2)(acac)_2}] + 2\mathrm{ROH} \rightleftharpoons [\{\mathrm{MoO(NNPh_2)(acac)}(\mu\text{-OR})\}_2] + 2\mathrm{Hacac} \quad (1)$$

Likewise substitution of the bridging alkoxo ligand OR can be achieved by refluxing [{MoO($NNPh_2$)(μ-OR)}$_2$] in the appropriate alcohol R′OH.

$$[\{\mathrm{MoO(NNPh_2)(acac)}(\mu\text{-OR})\}_2] + 2\mathrm{R'OH} \rightleftharpoons [\{\mathrm{MoO(NNPh_2)(acac)}(\mu\text{-OR'})\}_2] + 2\mathrm{ROH} \quad (2)$$

Attempts to obtain the mononuclear bis[diphenylhydrazido(2−)] complex from [MoO_2-(acac)$_2$] and Ph_2NNH_2 (1:2.5), or from complex **I** and Ph_2NNH_2 (1:1), in methanol at room temperature and in refluxing dichloromethane or acetonitrile were unsuccessful. Ph_2NNH_2 also failed to react with complex **II** in refluxing methanol or acetonitrile.

The new oxo[diphenylhydrazido(2−)]molybdenum complexes **I**, **II**, **III** and **IV** are air-stable diamagnetic crystalline yellow to orange compounds. **I** is fairly soluble while **II**, **III** and **IV** are only slightly soluble in common organic solvents; moreover, the latter dissolve slowly. DMF or CH_3CN solutions are stable while solutions in chlorinated solvents slowly turn darker on standing in air.

Spectroscopic characterization

Complexes have been characterized by chemical analysis and spectroscopic methods. The IR spectra show strong bands in the 900–930 cm^{-1} region assigned to $\nu(Mo{=}O)$. In addition, those of the dinuclear complexes show a more or less resolved doublet near 550 cm^{-1} assigned to the MoOMo bridges.

The solution absorption spectra of complexes in CH_3CN have two bands at *c.* 350 nm ($\epsilon = 8 \times 10^3$ l mol^{-1} cm^{-1} per Mo) and 280 nm ($\epsilon = 2 \times 10^4$ l mol^{-1} cm^{-1} per Mo). In addition, the spectrum of **I** has a shoulder at 310 nm ($\epsilon = 1.5 \times 10^4$ l mol^{-1} cm^{-1}). The bands at 350 and 280 nm are characteristic of the MoN_2Ph_2 chromophore [9] while the band at 310 nm could arise from a π–π^* transition within acetylacetonate [17, 18].

The ^1H NMR spectrum of **I** in $CDCl_3$ at room temperature shows singlets at 1.602, 2.116, 2.118 and 2.135 ppm for the four inequivalent methyl groups, and at 5.295 and 5.652 ppm for the two inequivalent ring protons. This is consistent with the *cis* arrangement of the oxo and the diphenylhydrazido(2−) ligands and indicates stereochemical rigidity. The ^1H NMR spectra of the dinuclear complexes in $CDCl_3$ were more complicated. First, they displayed the characteristic resonances of **I**, although a careful examination of the dinuclear crystalline solids prior to dissolution did not reveal any contamination by **I**. Second, three ring proton signals at 4.86, 5.09 and 5.38 ppm were observed for **III**, indicating that at least two isomers were present in solution although only the C_i isomer occurs in the crystals (*vide infra*).

Electrochemical studies

The complex $[MoO(N_2Ph_2)(acac)_2]$ was examined by cyclic voltammetry at a platinum electrode in various conditions. The following description applies to DMF 0.1 M NBu_4BF_4.

The complex is oxidized and is reduced respectively at potentials near +1.20 and −1.70 V versus SCE (Fig. 2). CV data for the primary oxidation process were consistent with a diffusion-controlled quasi-reversible one-electron charge-transfer reaction. The number of electrons transferred in this step was estimated to be 1 by comparison to the ferrocene oxidation in the same conditions. Scans gave constant values of $i_{pa}/v^{1/2}$ over the range 0.1–1.0 V s^{-1}. The peak separation ($\Delta E_p = 100$ mV at $v = 1$ V s^{-1} was only marginally larger than that for the ferrocene oxidation ($\Delta E_p = 80$ mV in the same conditions).

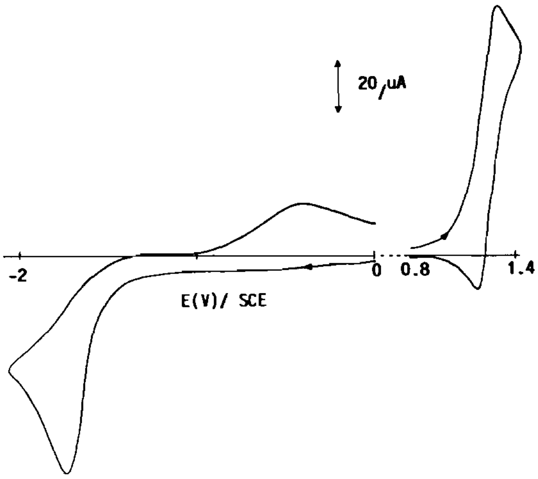


Fig. 2. Cyclic voltammograms of $[MoO(NNPh_2)(acac)_2]$ (**I**) in DMF at a platinum electrode (1 mmol l^{-1} **I**, 0.1 mol l^{-1} NBu_4BF_4, scan rate 1 V s^{-1}).

There were, however, certain deviations from reversibility: the ratio of the reverse (cathodic) current to the forward (anodic) current fell below unity at the slower scan rates; also the cathodic peak near +1.20 V decreased in intensity when the potential was held at the switching value for 20 s prior to scan reversal, while two new cathodic peaks appeared at +0.1 and −0.3 V. This behaviour shows that the oxidized species $[MoO(N_2Ph_2)(acac)_2]^+$ is somewhat unstable in solution at ambient temperature, its half-live being in the order of a few seconds.

The primary one-electron reduction process was found to be irreversible at scan rates as high as 10 V s^{-1}. Three more or less resolved peaks were observed near −0.6, −0.2 and +0.5 V on the return scan. This indicates that $[MoO(N_2Ph_2)(acac)_2]^-$, the product of the initial reduction at −1.70 V, is unstable. In the same conditions, the parent complex $[MoO_2(acac)_2]$ is reversibly reduced ($E_{1/2} = -1$ V versus SCE). The primary and secondary anodic and cathodic peaks appear in the stabilized cyclic voltammogram of **I** shown in Fig. 3.

The electrochemical behaviour of **I** is similar to that of the related complexes $[Mo(N_2RR')(S_2CNMe_2)_2X_2]$ (X = 1/2O, Cl, $1/2N_2RR'$) for which it was concluded that the HOMO and LUMO are associated with the MoNNRR' group [19]. The instability of the initial oxidation and reduction products is believed to arise from reaction with the solvent. However the nature of the decomposition products remains elusive.

In the broad lines, the electrochemical behaviour of the dinuclear complexes is similar to that of **I** (Fig. 3).

Description of the structure of III

III crystallizes as discrete centrosymmetrical dinuclear molecules; the two chemically equivalent and

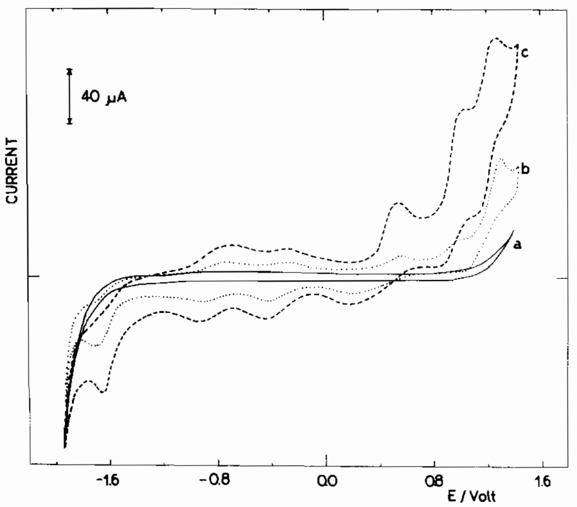
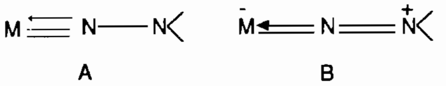


Fig. 3. Stabilized voltammetric profiles of $[MoO(NNPh_2)(acac)_2]$ (**I**) and $[\{MoO(NNPh_2)(acac)(\mu\text{-}OMe)\}_2]$ (**II**) in DMF at a platinum electrode. a, 0.1 mol l^{-1} NEt_4ClO_4; b, 1 mmol l^{-1} **I**; c, 1 mmol l^{-1} **II**. Scan rate 0.2 V s^{-1}.

crystallographically related $[MoO(NNPh_2)(acac)]$ units are bridged by two ethoxo ligands. The structure is similar to that previously reported for $[\{Mo(NNPh)_2(acac)(\mu\text{-}OMe)\}_2]$ [16] but in the latter case the Mo centre displays the *cis*-bis(phenyldiazenido) = molybdenum core in contrast to the *cis*-(hydrazido)oxomolybdenum core of **III**.

The Mo centre has a distorted octahedral environment made of the terminal oxo group, the terminal diphenylhydrazido ligand, the two acetylacetonate O(3) and O(4) atoms, and the two ethoxo bridging O(2) and O(2)′ atoms.

The overall geometry of the (hydrazido)-oxomolybdenum core is similar to that of other (hydrazido)oxomolybdenum complexes (Table 4). The short Mo–N and N–N bond distances of 1.784(1) and 1.298(2) Å, respectively, together with the Mo–N–N bond angle of 169.5(1)° indicate extensive delocalization through the Mo–N–N unit and is consistent with the description of the organonitrogen ligand as the four-electron donating diphenylhydrazido(2–) species.



The planarity of N(2) surrounding (maximum deviation from the N(1)–N(2)–C(1)–C(7) plane is 0.021 Å) indicates that the canonical form B is most dominant. The C(1) ↔ C(6) and C(7) ↔ C(13) phenyl groups are twisted out of the plane of the hydrazido ligand (N(1)–N(2)–C(1)–C(7)) by 10.1 and 57.0°, respectively.

The electronic requirement of the metal presumably hinders further substitution of the oxo ligand by a diphenylhydrazido group since a $[Mo(NNPh_2)_2]^{2+}$ unit would generate a 20-electron structure [4]. However a number of molybdenum bis(hydrazido(2 –) complexes are known [4, 7].

The Mo–O(4) bond distance of 2.224(1) Å is significantly greater than the Mo–O(3) bond distance of 2.069(1) Å. That is consistent with a structural *trans* influence on O(4) from the multiply bonded terminal oxygen O(1). Similarly the Mo–O(2)′ bond distance (*trans* to the multiply bonded hydrazido ligand is significantly greater than the Mo–O(2) bond distance *trans* to the oxygen atom of the acetylacetonate, which has a negligible *trans* influence. The

TABLE 4. Comparison of geometries for oxo[hydrazido(2 –)]molybdenum complexes

Compound	Mo–N (Å)	N–N (Å)	Mo–N–N (°)	Reference
$[\{MoO(NNPh_2)(acac)(\mu\text{-}OEt)\}_2]$	1.784(1)	1.298(2)	169.5(1)	this work
$[MoO(NNMePh)(acac)_2]$	1.789(3)	1.281(4)	175.6(2)	22
$[MoO(NNPh_2)\{S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2S\}]$	1.778(3)	1.309(4)	172.9(2)	20
$[MoO(NNPh_2)\{PhC(O)N(Me)O\}_2]$	1.781(6) 1.763(6)	1.314(8) 1.315(8)	169.4(6) 172.2(5)	7 7
$[MoO(NNPh_2)\{PhC(S)N(Me)O\}_2]$	1.779(3)	1.309(4)	176.2(3)	7
$[MoO(NNMe_2)(S_2CNMe_2)_2]$	1.799(8)	1.29(1)	168.0(7)	5
$[\{MoO(NNPh_2)(\mu\text{-}MoO_4)\}_2]^{2-}$	1.780(7)	1.32(1)	173.7(6)	9
$[\{MoO(NNMePh)(\mu\text{-}MoO_4)\}_2]^{2-}$	1.71(1)	1.34(2)	170.0(13)	10
$[MoO(NNMePh)\{(SCH_2CH_2)_2NCH_2CH_2NMe_2\}]$	1.787(8)	1.30(1)	164.8(7)	21
$[Mo_2O_4(NNMePh)\{SCH_2CH_2NHCH_2CH_2NMe_2\}_2]$	1.808(4)	1.314(5)	169.3(3)	8

acetylacetonate ring has a slight envelope conformation with the Mo atom 0.48 Å out of the O(3)–C(14)–C(15)–C(16)–O(4) plane.

Conclusions

Complexes **II**, **III** and **IV** are the first members of a new class of symmetrical dinuclear [hydrazido(2−)]oxomolybdenum complexes with the general formula $[(LL)(R'R''NN)OMo(\mu\text{-}OR)_2MoO(NNR'R'')(LL)]$ were LL is a bidentate chelating ligand. The $[(R'R''NN)OMo(\mu\text{-}OR)_2MoO(NNR'R'')]^{2+}$ core has previously been found in two centrosymmetrical tetranuclear molybdenum(VI) coordination compounds [9, 10]. It is also present in dinuclear $[\{MoO(NNMePh)(acac)(\mu\text{-}OR)\}_2]$ complexes obtained in the reaction of PhMeNNH with $[MoO_2(acac)_2]$. These complexes will be described in a forthcoming publication [22].

Supplementary material

Tables of atomic positional parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, full list of bond distances and angles and list of observed and calculated structure factors are available on request to P. Gouzerh.

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