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Dinuclear organohydrazido(2−)molybdenum(VI) complexes containing bridging alkoxo ligands: [{MoO(NNMePh)(acac)(μ-OR)}$_2$]. Crystal structures of [MoO(NNMePh)(acac)$_2$] and [{MoO(NNMePh)(acac)(μ-OPr-n)}$_2$]

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Abstract

1-Methyl-1-phenylhydrazine reacts with [MoO$_2$(acac)$_2$] in ROH (R = Me, Et, n-Pr) at room temperature, to yield [MoO(NNMePh)(acac)$_2$] (I). In refluxing ROH under argon, complex I transforms into [{MoO(NNMePh)(acac)(μ-OR)}$_2$] (R = Me(II), Et(III), n-Pr(IV)). The crystal structures of I and IV are reported. Crystals of I are monoclinic, space group $P2_1/c$, with unit cell dimensions a = 8.442(1), b = 16.090(1), c = 13.875(1) Å, β = 94,86(1)° and Z = 4. The structure was solved using 2529 unique observed reflections. The refinement of 226 variables gave R and R_w values of 0.024 and 0.026, respectively. The lattice is made of discrete mononuclear molecules. Crystals of IV are monoclinic, space group $P2_1/n$, with a = 8.917(2), b = 21.728(3), c = 9.351(1) Å, β = 107.83(2)° and Z = 2. The final refinement of 200 variables gave R = 0.036 and R_w = 0.039 for 2700 observed reflections. The lattice is made of discrete centrosymmetric dinuclear molecules. The geometries of the *cis*-[MoO(NNMePh)]$^{2+}$ cores in I and IV are similar and indicative of multiple bonding. In I, Mo–O = 1.701(2), Mo–N = 1.789(3), N–N = 1.281(4) Å, Mo–N–N = 175.6(2), O–Mo–N = 102.8(1)°; in IV, Mo–O = 1.693(3), Mo–N = 1.780(4), N–N = 1.292(6) Å, O–Mo–N = 101.8(2)°.

Introduction

The organohydrazido(2−) ligand NNR′R″ is of current interest as a potential model of the hydrazido(2−) species NH$_2$, which has been identified as an intermediate in the conversion of coordinated dinitrogen into ammonia and is also postulated to be involved in enzymatic nitrogen fixation [1–5]. Organohydrazido(2−) complexes have been synthesized by a variety of processes, including alkylation of organodiazenido complexes [1, 2, 4, 5] and reaction of arylhydrazines with oxomolybdenum complexes via a condensation type reaction [6]. Both the *cis*-[Mo(NNR′R″)$_2$]$^{2+}$ and *cis*-[MoO(NNR′R″)]$^{2+}$ units are known. The former is present in a number of mononuclear complexes containing ancillary (S,S) [7, 8], (N,N) [8] and (O,S) [9] chelated ligands, while the later is found in a number of mononuclear complexes containing monodentate thiolate ligands [10] or (O,O) [9], (O,S) [9], (S,S) [11], (N,O) [12], (N,S) [13], (S,O,S) [14], (S,S,S) [14], (S,N,S) [15] and (S,N,N,S) [16] chelated coligands. An asymmetrical binuclear molybdenum complex [17] and some organohydrazido-derivatized polyoxomolybdates [18–20] have also been characterized. The [Mo(NNR′R″)]$^{4+}$ unit is also known [14, 21].

[MoO$_2$(acac)$_2$] has proved to be a useful precursor in the synthesis of a number of molybdenum complexes owing to the lability of the acetylacetonate ligands. The reactions of [MoO$_2$(acac)$_2$] with hydrazines [22] and aroylhydrazines [23–25] have been previously studied. Our studies on the reactions of 1,1-diphenylhydrazine with [MoO$_2$(acac)$_2$] [22] have now been extended to 1-methyl-1-phenylhydrazine.

Experimental

Chemicals

1-Methyl-1-phenylhydrazine, (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, acetylacetone and high-purity solvents were commercial

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samples and were used as received. Tetrabutylammonium tetrafluoborate, NBu_4BF_4 (Aldrich), was recrystallized twice from H_2O and dried at 100 °C *in vacuo*. $[MoO_2(acac)_2]$ was prepared as described in the literature [26].

Physical measurements

IR spectra (KBr pellets) were obtained on a Perkin-Elmer 599 spectrophotometer. ^1H NMR spectra were recorded in $CDCl_3$ at room temperature (20 ± 2 °C) using an Hitachi Perkin-Elmer R-24B spectrometer. Absorption spectra were recorded in CH_2Cl_2 solution on a CARY 219 spectrophotometer. Magnetic measurements were performed at room temperature by the Faraday method using a Cahn Ventron RTL magnetic balance and $[Ni(en)_3]S_2O_3$ as a standard. Cyclic voltammetry was carried out on a PAR model 273 instrument. A standard three-electrode cell was used, which consisted of platinum working and auxiliary electrodes and a saturated calomel reference electrode (SCE). Measurements were made at room temperature at a concentration complex of 1.0×10^{-3} M in deaerated DMF with 0.1 M NBu_4BF_4 as the supporting electrolyte.

Preparation of complexes

Bis(acetylacetonato)oxo[1-methyl-1-phenylhydrazido(2−)]molybdenum(VI), [MoO(NNMePh)(acac)₂] (I)

1-Methyl-1-phenylhydrazine (10 mmol) was added to a solution of $[MoO_2(acac)_2]$ (10 mmol) in methanol (30 ml). The reaction mixture was stirred for 1.0 h at room temperature. The resulting orange precipitate was filtered off and washed with cold methanol. Suitable crystals of **I** were obtained by recrystallization from acetonitrile. Yield 79%.

Anal. Calc. for $C_{17}H_{22}MoN_2O_5$: C, 47.5; H, 5.2; N, 6.5; Mo, 22.3. Found: C, 47.4; H, 5.0; N, 6.2; Mo, 22.3%.

Di-μ-methoxo-bis[(acetylacetonato)oxo{1-methyl-1-phenylhydrazido(2−)}molybdenum(VI)], [{MoO(NNMePh)(acac)(μ-OMe)}₂] (II)

Complex **I** (2.0 mmol) was dissolved in methanol (25 ml) and refluxed for 1.0 h under argon. A yellow crystalline solid was obtained. The solid was collected, washed with cold methanol, recrystallized from hot methanol and dried *in vacuo*. Yield 69%.

Anal. Calc. for $C_{26}H_{36}Mo_2N_4O_8$: C, 43.1; H, 5.0; N, 7.7; Mo, 26.5. Found: C, 43.5; H, 5.0; N, 7.5; Mo, 25.8%.

Di-μ-ethoxo-bis[(acetylacetonato)oxo{1-methyl-1-phenylhydrazido(2−)}molybdenum(VI)], [{MoO(NNMePh)(acac)(μ-OEt)}₂] (III)

Complex **III** was similarly obtained from **I** refluxed in ethanol for 1.0 h under argon. The crystalline yellow solid was filtered off, washed with cold ethanol, recrystallized from hot ethanol and dried *in vacuo*. Yield 78%.

Anal. Calc. for $C_{28}H_{40}Mo_2N_4O_8$: C, 44.7; H, 5.4; N, 7.4; Mo, 25.5. Found: C, 44.9; H, 5.3; N, 7.3; Mo, 25.2%.

Di-μ-(n-propoxo)-bis[(acetylacetonato)oxo{1-methyl-1-phenylhydrazido(2−)}molybdenum(VI)], [{MoO(NNMePh)(acac)(μ-OPr-n)}₂] (IV)

Complex **IV** was similarly synthesized from **I** refluxed in n-propanol for 1.0 h under argon. A microcrystalline yellow solid was obtained. It was filtered off, washed with diethyl ether. Suitable crystals for an X-ray structure determination were obtained by recrystallization from hot n-propanol. Yield 95%.

Anal. Calc. for $C_{30}H_{44}Mo_2N_4O_8$: C, 46.2; H, 5.7; N, 7.2. Found: C, 46.2; H, 5.5; N, 6.8%.

X-ray data collection and structure determination

Diffraction measurements were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromatized Mo Kα radiation. Unit cell parameters and an orientation matrix were calculated from the setting angles of 25 carefully centered reflections. Crystal data are given in Table 1. The intensities of two reflections were monitored every hour of exposure and showed insignificant variations. All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made by using the program DIFABS [27].

All computations were performed on a micro VAX2 using the CRYSTALS system [28]. The structures were solved by using the Patterson method and difference Fourier syntheses, and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized was $\Sigma(w|F_o|-|F_c|)^2$ where $w=1$. The neutral atom scattering factors and anomalous dispersion coefficients were taken from standard sources [29]. Hydrogen atoms were located on difference Fourier maps; they were introduced in structure factor calculations but not refined. Atomic positional parameters for non-hydrogen atoms are given in Tables 2 and 3. Selected intramolecular bond distances and angles are given in Tables 4 and 5. Drawings [28, 30] of compounds **I** and **IV** are shown in Figs. 1 and 2, respectively.

Results and discussion

Synthesis of complexes

In methanol, ethanol or n-propanol, 1-methyl-1-phenylhydrazine reacts on $[MoO_2(acac)_2]$ at room temperature to give the mononuclear complex **I** (eqn. (1)).

TABLE 1. Crystal data for compounds **I** and **IV**

	I	**IV**
Formula	$C_{17}H_{22}MoN_2O_5$	$C_{30}H_{44}Mo_2N_4O_8$
Formula weight	430.31	780.58
System	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	8.442(1)	8.917(2)
b (Å)	16.090(1)	21.728(3)
c (Å)	13.875(1)	9.351(1)
α (°)	90.0	90.0
β (°)	94.86(1)	107.83(2)
γ (°)	90.0	90.0
V (Å^3)	1878	1725
Z	4	2
μ (Mo Kα) (cm^{-1})	7.08	7.58
ρ_{calc}(g cm^{-3})	1.52	1.50
Diffractometer	CAD4F	CAD4F
2θ range (°)	$2\leqslant 2\theta\leqslant 50$	$2\leqslant 2\theta\leqslant 56$
Scan type	$\omega/2\theta$	$\omega/2\theta$
Scan width (°)	$1.0+0.345\mathrm{tg}\theta$	$1.0+0.345\mathrm{tg}\theta$
Scan speed (° min^{-1})	variable	variable
Octants collected	$-h+h,+k,+l$	$-h+h,+k,+l$
No. reflections collected	3559	4511
No. unique reflections	3280	4152
No. reflections with $I\geqslant 3\sigma(I)$	2529	2700
Absorption corrected by	DIFABS	DIFABS
R^a	0.024	0.036
$R_w{}^b$	0.026	0.039
Weighting scheme	$w=1$	$w=1$
No. variables	226	200

$^aR=\Sigma||F_c|-|F_o||/\Sigma|F_o|$. $^bR_w=[\Sigma w(|F_c|-|F_o|)^2/\Sigma wF_o{}^2]^{1/2}$.

TABLE 2. Positional and thermal U_{eq} parameters for [MoO(NNMePh)(acac)$_2$] (**I**)

Atom	x/a	y/b	z/c	U_{eq}
Mo(1)	0.15033(3)	0.15492(2)	0.35686(2)	0.0352
O(1)	0.3111(3)	0.1938(1)	0.3060(2)	0.0483
O(3)	−0.0177(3)	0.1879(1)	0.2476(2)	0.0460
O(4)	−0.0649(3)	0.1338(1)	0.4334(2)	0.0470
O(13)	0.2573(3)	0.1323(1)	0.4922(2)	0.0426
O(14)	0.1015(3)	0.2765(1)	0.4104(2)	0.0467
N(1)	0.1469(3)	0.0487(2)	0.3184(2)	0.0416
N(2)	0.1387(3)	−0.0254(2)	0.2847(2)	0.0409
C(1)	0.2523(4)	−0.0524(2)	0.2218(2)	0.0354
C(2)	0.3737(4)	0.0010(2)	0.2003(2)	0.0437
C(3)	0.4830(5)	−0.0245(2)	0.1383(3)	0.0556
C(4)	0.4745(5)	−0.1028(3)	0.0989(3)	0.0596
C(5)	0.3564(5)	−0.1561(2)	0.1201(2)	0.0539
C(6)	0.2431(4)	−0.1317(2)	0.1816(2)	0.0458
C(7)	0.0052(5)	−0.0779(3)	0.3082(3)	0.0611
C(13)	−0.2415(5)	0.1925(3)	0.1355(3)	0.0703
C(14)	−0.1650(4)	0.1691(2)	0.2329(2)	0.0454
C(15)	−0.2537(4)	0.1333(2)	0.2997(3)	0.0551
C(16)	−0.2041(4)	0.1194(2)	0.3975(3)	0.0454
C(17)	−0.3197(5)	0.0884(3)	0.4647(3)	0.0682
C(23)	0.3800(4)	0.1484(3)	0.6497(2)	0.0539
C(24)	0.2862(4)	0.1846(2)	0.5626(2)	0.0382
C(25)	0.2398(4)	0.2660(2)	0.5641(2)	0.0489
C(26)	0.1493(4)	0.3076(2)	0.4907(2)	0.0434
C(27)	0.1038(5)	0.3966(3)	0.5062(3)	0.0637

TABLE 3. Positional and thermal U_{eq} parameters for [{MoO(NNMePh)(acac)(μ-OPr-n)}$_2$] (**IV**)

Atom	x/a	y/b	z/c	U_{eq}
Mo(1)	0.03933(5)	0.07264(2)	0.06466(4)	0.0348
O(1)	−0.1437(4)	0.0936(2)	0.0640(4)	0.0500
O(2)	0.0006(3)	0.0221(1)	−0.1232(3)	0.0347
O(3)	0.1293(4)	0.0955(2)	0.2896(4)	0.0459
O(4)	0.2790(4)	0.0330(2)	0.1181(4)	0.0459
N(1)	0.1061(5)	0.1404(2)	−0.0040(5)	0.0446
N(2)	0.1178(5)	0.1936(2)	−0.0612(5)	0.0509
C(1)	0.2566(6)	0.2096(2)	−0.0974(6)	0.0469
C(2)	0.3844(7)	0.1703(3)	−0.0555(6)	0.0572
C(3)	0.5191(8)	0.1861(4)	−0.0921(8)	0.0734
C(4)	0.5237(9)	0.2397(4)	−0.1680(9)	0.0801
C(5)	0.397(1)	0.2774(4)	−0.2087(9)	0.0821
C(6)	0.2619(8)	0.2629(3)	−0.1745(8)	0.0689
C(7)	−0.0154(9)	0.2364(3)	−0.0902(9)	0.0779
C(13)	0.2785(9)	0.1288(3)	0.5282(7)	0.0685
C(14)	0.2675(7)	0.0994(2)	0.3804(6)	0.0469
C(15)	0.4004(6)	0.0764(4)	0.3531(6)	0.0591
C(16)	0.3989(6)	0.0427(3)	0.2263(6)	0.0526
C(17)	0.5496(7)	0.0167(4)	0.2153(8)	0.0780
C(18)	0.0380(6)	0.0381(3)	−0.2563(5)	0.0466
C(19)	−0.1003(9)	0.0581(4)	−0.3820(7)	0.0750
C(20)	−0.172(1)	0.1136(5)	−0.356(1)	0.1037

$$[MoO_2(acac)_2]+PhMeNNH_2 \longrightarrow [MoO(NNMePh)(acac)_2]+H_2O \quad (1)$$

A similar reaction occurs with 1,1-diphenylhydrazine in methanol [22]. In refluxing methanol, ethanol or n-propanol under argon, complex **I** transforms into binuclear compounds **II**, **III** and **IV**, respectively (eqn. (2)).

$$2[MoO(NNMePh)(acac)_2]+2ROH \longrightarrow [\{MoO(NNMePh)(acac)(\mu\text{-}OR)\}_2]+2Hacac \quad (2)$$

Compounds **II**, **III** and **IV** can be obtained directly by refluxing a mixture of [MoO$_2$(acac)$_2$] and 1-methyl-1-phenylhydrazine in the appropriate alcohol under argon. Slow degradation of the compounds was observed when the reactions were carried out in the presence of air, especially when the solvent was n-propanol.

Displacement of one acac ligand and subsequent dimerization via alkoxo bridging was also observed in the reactions of [MoO$_2$(acac)$_2$] with 1,1-diphenylhydrazine [22]. As a rule, organohydrazines react with dioxomolybdenum complexes to give mononuclear diazenido- or hydrazido-molybdenum complexes. However either mononuclear complexes of the type [Mo(NNC$_6$H$_4$R-p)$_2$(acac)$_2$] (R = H, Me, OMe, F or NO$_2$) [31] or binuclear alkoxo-bridged bis(phenyldiazenido) molybdenum complexes [32–34] were obtained in the

TABLE 4. Distances (Å) and angles (°) for [MoO(NNMePh)(acac)$_2$] (I)

Mo(1)–O(1)	1.701(2)	Mo(1)–O(3)	2.056(2)
Mo(1)–O(4)	2.207(2)	Mo(1)–O(13)	2.047(2)
Mo(1)–O(14)	2.145(2)	Mo(1)–N(1)	1.789(3)
O(3)–C(14)	1.280(4)	O(4)–C(16)	1.258(4)
O(13)–C(24)	1.296(4)	O(14)–C(26)	1.256(4)
N(1)–N(2)	1.281(4)	N(2)–C(1)	1.419(4)
N(2)–C(7)	1.468(4)	C(1)–C(2)	1.389(4)
C(1)–C(6)	1.391(4)	C(2)–C(3)	1.377(5)
C(3)–C(4)	1.373(5)	C(4)–C(5)	1.366(5)
C(5)–C(6)	1.391(5)	C(13)–C(14)	1.495(5)
C(14)–C(15)	1.368(5)	C(15)–C(16)	1.404(5)
C(16)–C(17)	1.492(5)	C(23)–C(24)	1.505(4)
C(24)–C(25)	1.367(5)	C(25)–C(26)	1.392(5)
C(26)–C(27)	1.502(5)		
O(3)–Mo(1)–O(1)	97.1(1)	O(4)–Mo(1)–O(1)	167.0(1)
O(4)–Mo(1)–O(3)	81.34(9)	O(13)–Mo(1)–O(1)	98.1(1)
O(13)–Mo(1)–O(3)	161.05(9)	O(13)–Mo(1)–O(4)	81.30(8)
O(14)–Mo(1)–O(1)	89.5(1)	O(14)–Mo(1)–O(3)	83.05(9)
O(14)–Mo(1)–O(4)	77.50(9)	O(14)–Mo(1)–O(13)	85.83(9)
N(1)–Mo(1)–O(1)	102.8(1)	N(1)–Mo(1)–O(3)	91.9(1)
N(1)–Mo(1)–O(4)	90.2(1)	N(1)–Mo(1)–O(13)	95.7(1)
N(1)–Mo(1)–O(14)	167.3(1)		
C(14)–O(3)–Mo(1)	131.1(2)	C(16)–O(4)–Mo(1)	128.2(2)
C(24)–O(13)–Mo(1)	128.0(2)	C(26)–O(14)–Mo(1)	127.9(2)
N(2)–N(1)–Mo(1)	175.6(2)	C(1)–N(2)–N(1)	119.5(3)
C(7)–N(2)–N(1)	118.3(3)	C(7)–N(2)–C(1)	122.1(3)
C(2)–C(1)–N(2)	119.4(3)	C(6)–C(1)–N(2)	120.7(3)
C(6)–C(1)–C(2)	119.9(3)	C(3)–C(2)–C(1)	119.6(3)
C(4)–C(3)–C(2)	120.6(3)	C(5)–C(4)–C(3)	120.3(3)
C(6)–C(5)–C(4)	120.5(3)	C(5)–C(6)–C(1)	119.1(3)
C(13)–C(14)–O(3)	115.1(3)	C(15)–C(14)–O(3)	124.8(3)
C(15)–C(14)–C(13)	120.0(3)	C(16)–C(15)–C(14)	126.0(3)
C(15)–C(16)–O(4)	123.0(3)	C(17)–C(16)–O(4)	117.0(3)
C(17)–C(16)–C(15)	120.0(3)	C(23)–C(24)–O(13)	113.9(3)
C(25)–C(24)–O(13)	126.7(3)	C(25)–C(24)–C(23)	119.3(3)
C(26)–C(25)–C(24)	126.1(3)	C(25)–C(26)–O(14)	124.9(3)
C(27)–C(26)–O(14)	116.1(3)	C(27)–C(26)–C(25)	119.0(3)

reactions of substituted hydrazines with [MoO$_2$(acac)$_2$], depending on the conditions. Thus it appears that the products of the condensation reaction between organohydrazines and dioxomolybdenum complexes in alcohols depend on subtle changes in the reactants as well as on the experimental conditions.

(Bis(phenylmethylhydrazido(2 −)] complexes were not obtained, even on prolonged treatment of [MoO$_2$(acac)$_2$] or oxo[phenylmethylhydrazido(2 −)] complexes **I**, **II**, **III** and **IV** with a large excess of 1-methyl-1-phenylhydrazine. The reaction pathway is dependent on the basicity of the hydrazine [8] and, possibly, on the electronic requirement of the molybdenum centre (*vide infra*).

It must be added that oxo[hydrazido(2 −)] complexes were not obtained upon treatment of [MoO$_2$(acac)$_2$], with dimethylhydrazine. A pink solid of unknown composition was obtained by reacting Me$_2$NNH$_2$ with [MoO$_2$(acac)$_2$] in acetonitrile at room temperature,

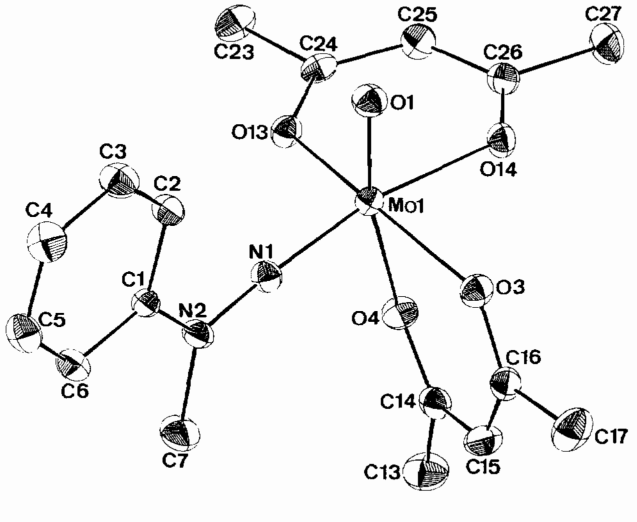

Fig. 1. Structure of MoO(NNMePh)(acac)$_2$] (I) showing 20% probability thermal ellipsoids and the atom labelling scheme (hydrogen atoms omitted for clarity).

TABLE 5. Distances (Å) and angles (°) for [{MoO(NNMePh)(acac)(μ-OPr-n)}$_2$] (**IV**)

Mo(1)–O(1)	1.693(3)	Mo(1)–O(2)	2.010(3)
Mo(1)–O(2′)	2.187(3)	Mo(1)–O(3)	2.069(3)
Mo(1)–O(4)	2.215(3)	Mo(1)–N(1)	1.780(4)
O(2)–C(18)	1.427(5)	O(3)–C(14)	1.267(6)
O(4)–C(16)	1.244(6)	N(1)–N(2)	1.292(6)
N(2)–C(1)	1.423(6)	N(2)–C(7)	1.466(8)
C(1)–C(2)	1.382(8)	C(1)–C(6)	1.372(8)
C(2)–C(3)	1.389(8)	C(3)–C(4)	1.37(1)
C(4)–C(5)	1.35(1)	C(5)–C(6)	1.379(9)
C(13)–C(14)	1.498(7)	C(14)–C(15)	1.380(8)
C(15)–C(16)	1.391(8)	C(16)–C(17)	1.489(8)
C(18)–C(19)	1.485(8)	C(19)–C(20)	1.42(1)
O(2)–Mo(1)–O(1)	103.7(1)	O(2′)–Mo(1)–O(1)	91.4(1)
O(2)–Mo(1)–O(2′)	72.9(1)	O(3)–Mo(1)–O(1)	90.7(2)
O(3)–Mo(1)–O(2)	158.3(1)	O(3)–Mo(1)–O(2′)	90.8(1)
O(4)–Mo(1)–O(1)	165.5(2)	O(4)–Mo(1)–O(2)	83.1(1)
O(4)–Mo(1)–O(2′)	78.3(1)	O(4)–Mo(1)–O(3)	79.5(1)
N(1)–Mo(1)–O(1)	101.8(2)	N(1)–Mo(1)–O(2)	97.1(2)
N(1)–Mo(1)–O(2′)	165.2(2)	N(1)–Mo(1)–O(3)	95.7(2)
N(1)–Mo(1)–O(4)	89.8(2)		
Mo(1)–O(2)–Mo(1′)	107.1(1)	C(18)–O(2)–Mo(1)	127.3(3)
C(18)–O(2)–Mo(1′)	123.2(3)	C(14)–O(3)–Mo(1)	133.8(3)
C(16)–O(4)–Mo(1)	130.3(4)	N(2)–N(1)–Mo(1)	165.5(4)
C(1)–N(2)–N(1)	120.2(5)	C(7)–N(2)–N(1)	118.7(5)
C(7)–N(2)–C(1)	121.0(5)	C(2)–C(1)–N(2)	118.9(5)
C(6)–C(1)–N(2)	120.3(5)	C(6)–C(1)–C(2)	120.8(5)
C(3)–C(2)–C(1)	118.6(6)	C(4)–C(3)–C(2)	120.2(7)
C(5)–C(4)–C(3)	120.4(7)	C(6)–C(5)–C(4)	120.7(7)
C(5)–C(6)–C(1)	119.3(7)	C(13)–C(14)–O(3)	115.0(5)
C(15)–C(14)–O(3)	124.4(5)	C(15)–C(14)–C(13)	120.5(5)
C(16)–C(15)–C(14)	124.4(5)	C(15)–C(16)–O(4)	124.3(5)
C(17)–C(16)–O(4)	116.7(5)	C(17)–C(16)–C(15)	119.0(5)
C(19)–C(18)–O(2)	113.7(5)	C(20)–C(19)–C(18)	114.9(6)

while a blue solution was obtained when dimethylhydrazine chlorhydrate was used.

Spectroscopic and electrochemical studies

Oxo[hydrazido(2−)]molybdenum complexes **I**, **II**, **III** and **IV** are air-stable diamagnetic yellow crystalline solids which are soluble in common organic solvents. They have been characterized by chemical analysis and by spectroscopic methods. The IR spectra display strong bands at *c.* 1600 and 915 cm^{-1} characteristic of ν(N=N) and ν(M=O), respectively. In addition, those of the binuclear complexes show a doublet near 560 cm^{-1} assigned to the Mo–O–Mo bridges.

The solution absorption spectra in CH_2Cl_2 are similar to those of the analogous oxo[diphenylhydrazido(2−)] complexes [22]. They exhibit intense bands at 360 nm ($\epsilon \sim 7.8 \times 10^3$ l mol^{-1} cm^{-1} per Mo) and 278 nm ($\epsilon \sim 1.9 \times 10^4$ l mol^{-1} cm^{-1}) characteristic of the [MoO(NNMePh)]$^{2+}$ chromophore [18]. Additional features are observed at *c.* 320 nm ($\epsilon \sim 1.3 \times 10^4$ l mol^{-1} cm^{-1}) and 240 nm ($\epsilon = 1.3 \times 10^4$ l mol^{-1} cm^{-1}).

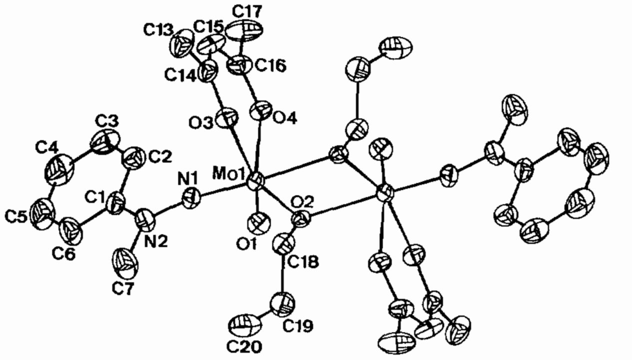

Fig. 2. Structure of [{MoO(NNMePh)(acac)(μ-OPr-n)}$_2$] (**IV**) showing 30% probability thermal ellipsoids and the atom labelling scheme (hydrogen atoms omitted for clarity).

The ^{1}H NMR spectrum of **I** in $CDCl_3$ shows two singlets at 1.97 (3H) and 2.07 (9H) ppm for the four acac methyl groups, a singlet at 3.97 ppm for the methyl group of the hydrazido ligand, two singlets at 5.40 and 5.52 ppm for the two inequivalent acac ring protons and a complex multiplet in the range 6.60–7.43 ppm for the phenyl group. A similar spectrum was obtained in CD_3CN except that three singlets at 1.90 (3H), 2.00 (6H) and 2.07 (3H) ppm were observed for the acac methyl groups. These results are consistent with the crystal structure (*vide infra*) and indicate stereochemical rigidity. The ^1H NMR spectra of **II**, **III** and **IV** in $CDCl_3$ show the same complexity as those of the analogous diphenylhydrazido dinuclear complexes [22].

The electrochemical behaviour of **I** is similar to that of $[MoO(NNPh_2)(acac)_2]$ [22]. In DMF, **I** undergoes a quasi-reversible one-electron oxidation at +1.04 V versus SCE.

Description of the structures of I and IV

The molecular structure of **I** (Fig. 1) is very similar to those previously reported for mononuclear oxo[hydrazido(2−)]molybdenum complexes containing bidentate chelated ligands [9, 11–13]. The structure exhibits the anticipated *cis* oxo[hydrazido(2−)] geometry which maximizes the overlap of these strongly π-bonding groups with the Mo t_{2g} orbitals. The strong *trans* influence exerted by these ligands is revealed by the lengthening of the Mo–O(4) and Mo–O(14) bonds which are *trans* to the oxo and hydrazido(2−) ligands, respectively, with respect to the Mo–O(3) and Mo–O(13) bonds which are *trans* to each other. The Mo–O(4) bond (2.207(2) Å) is significantly longer than the Mo–O(14) bond (2.145(2) Å), indicating that the effect of the oxo group is greater than that of the hydrazido(2−) ligand. The distortion of the coordination geometry from the octahedral limit (Mo–O vary from 1.701(2) to 2.207(2) Å, *cis* bond angles from 77.50(9) to 102.8(1)° and *trans* bond angles from 161.05(9) to 167.3(1)°) arises mainly from the effects associated with the two terminal multiple-bonded ligands and from non-bonding interaction in the coordination sphere of the Mo atom. The edge lengths in the $[N_2O_4]$ polyhedron show only little variation from 2.726(3) to 2.855(3) Å.

The molecular structure of the binuclear complex **IV** (Fig. 2) exhibits similar feature to that of $[\{MoO(NNPh_2)(acac)(\mu\text{-}OEt)\}_2]$ [22]. It contains two chemically equivalent and crystallographically related $[MoO(NNMePh)(acac)]^+$ units bridged by two n-propoxo ligands. This results in a centrosymmetrical edge-sharing bioctahedral molecule. The Mo–Mo′ separation of 3.376(1) Å is indicative of the absence of a significant interaction. It is noteworthy that one oxygen atom of the acac ligand, which is a weaker π-bonding ligand than the alkoxo group, is located *trans* to the oxo group.

The geometries of the acac rings are not unusual. One of the acac ring in **I** is nearly planar with maximum deviation of 0.03 Å from the least-squares plane defined by O(13), O(14) and C(23) to C(27); the Mo atom lies 0.14 Å out of this plane. Greater deviations from planarity are observed for the other ring in **I** (maximum deviation of 0.10 Å, Mo 0.20 Å out of the mean plane) and in **IV** (maximum deviation of 0.07 Å, Mo 0.42 Å out of the mean plane).

The geometries of the *cis*-$[MoO(NNMePh)]^{2+}$ units present in complexes **I** and **IV** are quite similar. The hydrazido(2−) ligand in **I** is nearly planar with maximum deviation of 0.02 Å from the least-squares plane through all nine non-hydrogen atoms. The Mo atom lies 0.20 Å out of this plane. The dihedral angle between the hydrazido ligand plane and the mean plane defined by Mo, O(4), O(14), O(1) and N(1) is 7.9°. The hydrazido ligand shows larger deviation from planarity in **IV** than in **I**. The N(2) surrounding is still planar (maximum deviation from the N(1)–N(2)–C(1)–C(7) plane is 0.006 Å) but it is twisted out of the phenyl ring by 6.8°. The dihedral angle between the N(1)–N(2)–C(1)–C(7) plane and the mean plane through Mo, N(1), O(1), O(2) and O(4), is 8.8°.

The metrical parameters for the $[MoNNMePh]^{4+}$ unit in **I** and **IV** are quite similar to that for other oxo[hydrazido(2−)]molybdenum(VI) complexes. The nearly linear Mo–N–N linkage (Mo–N(1)–N(2) =175.6(2)° for **I**; 165.5(4)° for **IV**) and the short Mo–N(1) (1.789(3) Å for **I**; 1.780(4) Å for **IV**) and N(1)–N(2) bonds (1.282(4) Å for **I**; 1.292(6) Å for **IV**) reflect extensive delocalization throughout the Mo–N–N unit and significant multiple bond character of the Mo–N and N–N bonds. The N–N–C bond angles (118.3(3)° in **I**; 120.2(5)° in **IV**) reflect the appropriate sp^2 hybridization for N(2). These features are consistent with the formal assignment of coordinated hydrazido(2−) groups as dinegative six-electron-donor ligands. Although the validity of the 18-electron rule in such high oxidation complexes may be questioned, the electronic requirement of the metal could have been occasionally put forward in order to account for the lack of reactivity of the oxo group, the bending of the MoNN group in some cases [12] or for the unusual tripodal coordination of a potentially tetradentate ligand [15]. A qualitative molecular orbital explanation has been proposed to rationalize the bonding in formally 20-electron six-coordinate bis[hydrazido(2−)]molybdenum complexes [8]. In any case, the electron count does not appear as the exclusive reason for the observed stereochemistry.

Conclusions

1,1-Disubstituted hydrazines $R'R''NNH_2$ ($R' = Me$, $R'' = Ph$; $R' = R'' = Ph$) react with $[MoO_2(acac)_2]$ to give oxo[hydrazido(2−)] derivatives [MoO(NNRR′)(acac)$_2$] which transform into binuclear complexes [{MoO(NNR′R″)(acac)(μ-OR)}$_2$] in refluxing alcohol ROH (R = Me, Et, n-Pr). 1,1-Dimethylhydrazine does not react similarly to 1,1-diphenylhydrazine and 1-methyl-1-phenylhydrazine. The structural characteristics of the *cis*-[MoO(NNR′R″)]$^{2+}$ cores are quite similar, irrespective of R′ and R″ and of the nuclearity. In view of the lability of the acetylacetonate ligand, these complexes are suitable precursors for the synthesis of new hydrazido(2−)- and hydrazido(1−)molybdenum complexes. These reactions will be discussed in forthcoming publications.

Supplementary material

Tables of atomic positional parameters for hydrogen atoms (S7 and S10), anisotropic thermal parameters for non-hydrogen atoms (S6 and S9), full lists of bond distances and angles (S8 and S11), and lists of observed and calculated structure factors are available from P. Gouzerh on request.

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