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SYNTHESIS AND X-RAY CRYSTALLOGRAPHIC CHARACTERIZATION OF NEW DINUCLEAR BIS(PHENYLDIAZENIDO)MOLYBDENUM COMPLEXES $[\{Mo(C_6H_5N_2)_2X(\mu\text{-}OR)(C_6H_5NHNH_2)\}_2]$ (X = Cl, OR), $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OR)(C_6H_5CONHO)\}_2]$ AND $[\{Mo(C_6H_5N_2)_2Cl(\mu\text{-}OEt)(EtOH)\}_2]$

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Abstract—Polyoxomolybdates, monomeric chelated(O,O) oxomolybdenum(VI) and monomeric halogenooxomolybdenum(V) complexes reacted in alcohols with phenylhydrazine to yield dinuclear complexes of the following formulae noted (**1**), (**2**), (**3**), and (**4**): $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OR)(C_6H_5CONHO)\}_2]$, $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OR)(OR)(C_6H_5NHNH_2)\}_2]$, $[\{Mo(C_6H_5N_2)_2Cl(\mu\text{-}OR)(C_6H_5NHNH_2)\}_2]$ and $[\{Mo(C_6H_5N_2)_2Cl(\mu\text{-}OC_2H_5)(C_2H_5OH)\}_2]$; **a**: $R = CH_3$; **b**: $R = C_2H_5$; **c**: $R = C_3H_7$. **1b** crystallized in the triclinic space group $P\bar{1}$ $a = 9.728(3)$, $b = 11.154(1)$, $c = 12.720(2)$ Å, $\alpha = 97.92(1)°$, $\beta = 106.40(2)°$, $\gamma = 106.56(2)°$, $V = 1233$ Å^3, $Z = 1$. Refinement was based on 2549 reflections and converged at $R = 0.06$. **2a** crystallized in the monoclinic space group $P2_1/n$, $a = 11.404(2)$, $b = 11.998(1)$, $c = 16.778(4)$ Å, $\beta = 108.56(1)°$, $V = 2176$ Å^3, $Z = 2$. Refinement was based on 2481 reflections and converged at $R = 0.024$. Mixed crystals containing **2a** and **3a** in the same unit cell (70 : 30) are isomorphous with **2a**, $a = 11.443(3)$, $b = 11.826(4)$, $c = 16.785(4)$ Å, $\beta = 108.45(2)°$, $V = 2155$ Å^3, $Z = 2$. Refinement was based on 2623 reflections and converged at $R = 0.049$. **3c** crystallized in the triclinic space group $P\bar{1}$, $a = 9.534(3)$, $b = 12.057(2)$, $c = 12.751(3)$ Å, $\alpha = 98.90(1)°$, $\beta = 96.37(2)°$, $\gamma = 112.50(2)°$, $V = 1314$ Å^3, $Z = 1$. Refinement was based on 1615 reflections and converged at $R = 0.053$. **4** crystallized in the monoclinic space group $C2/m$, $a = 10.495(3)$, $b = 18.792(4)$, $c = 11.115(3)$ Å, $\beta = 101.91(1)°$, $V = 2145$ Å^3, $Z = 2$. Refinement was based on 1238 reflections and converged at $R = 0.055$. All these structures consist of discrete dinuclear units containing *cis*-bisdiazenido moieties $[Mo(C_6H_5N_2)_2]^{2+}$ bridged by two alkoxo groups. Molybdenum achieves six coordination either with a chelating bidentate ligand as in **1** or with two unidentate ligands as in **2**, **3** and **4**. A unique feature of **2** and **3** is the occurrence of phenylhydrazine and phenyldiazenido in the same coordination sphere.

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In view of the perceived analogies of isopolymetalates to metal oxide surfaces, the coordination chemistry of these species with small organic molecules is of current interest.[1] A number of organooxygen[2] and organonitrogen[3] derivatives of high valent polyoxomolybdates are known for which we have a continued interest. Zubieta *et al.* have recently reported the reaction of isopolymolybdates with phenylhydrazine yielding tetranuclear, hexanuclear, or octanuclear species, depending on reaction conditions.[4] Jeannin and co-workers have reported the reactions of $[MoO_2(acac)_2]$ with phenylhydrazine and acetamidoxime yielding, respectively, a dinuclear bis(phenyldiazenido)molybdenum complex[5] and a nitrosylmolybdenum(II) complex.[6] We report here the reactions of phenylhydrazine with various Mo^{VI} and Mo^{V} oxo complexes yielding dinuclear bis(phenyldiazenido)molybdenum complexes of the following types: $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OR)(C_6H_5CONHO)\}_2]$, (**1**); $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OR)(OR)(C_6H_5NHNH_2)\}_2]$, (**2**); $[\{Mo(C_6H_5N_2)_2Cl(\mu\text{-}OR)(C_6H_5NHNH_2)\}_2]$, (**3**); $[\{Mo(C_6H_5N_2)_2Cl(\mu\text{-}OC_2H_5)(C_2H_5OH)\}_2]$, (**4**); **a**: $R = CH_3$; **b**: $R = C_2H_5$; **c**: $R = C_3H_7$. The synthesis and the X-ray structure of one of these complexes (**2a**) were recently reported by Zubieta *et al.*[7]

EXPERIMENTAL

Materials

Acetylacetone, benzohydroxamic acid and phenylhydrazine are commercially available. $(NBu_4)_2[Mo_6O_{19}]$,[8] α-$(NBu_4)_4[Mo_8O_{26}]$[9] and $[MoO_2(acac)_2]$[10] were prepared according to literature procedures. $(NEt_4)[MoOCl_4(H_2O)]$ and $(NH_4)_2[MoOBr_5]$ were prepared by reducing MoO_4^{2-} in concentrated hydrochloric or hydrobromic acid and adding $(NEt_4)Cl$ or NH_4Br.[11] $[MoO_2(C_6H_5CONHO)_2]\cdot CH_3OH$ was prepared from $[MoO_2(acac)_2]$ and PhCONHOH following a general procedure described by Murray and co-workers.[12]

Synthesis of $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OEt)(C_6H_5CONHO)\}_2]$ (**1b**)

$[MoO_2(C_6H_5CONHO)_2]\cdot CH_3OH$ (0.40 g, 0.92 mmol) was dissolved in C_2H_5OH (10 cm^3) and $C_6H_5NHNH_2$ (0.5 cm^3, 5.1 mmol) was added. A deep purple colour developed immediately and dark violet microcrystals of $[\{Mo(C_6N_2)_2(\mu\text{-}OC_2H_5)(C_6H_5CONHO)\}_2]\cdot 2C_2H_5OH$ (**1b**) began to deposit within 1 h. They were filtered off after 12 h, washed with C_2H_5OH and air dried. Yield: 0.35 g (71%). Found; C, 51.4; H, 4.8; N, 13.3. Calc. for $C_{46}H_{54}N_{10}Mo_2O_8$: C, 51.8; H, 5.1; N. 13.1%. The crystallization was slower when the reactant concentrations were lowered but keeping the same $C_6H_5NHNH_2/Mo$ ratio; crystals of a suitable size for X-ray work were obtained in this way. $[\{Mo(C_6H_5N_2)(\mu\text{-}OCH_3)(C_6H_5CONHO)\}_2]\cdot 2CH_3OH$ (**1a**) was prepared similarly to **1b** but with CH_3OH. Found: C, 49.8; H, 4.5; N, 14.1. Calc. for $C_{42}H_{46}N_{10}Mo_2O_8$: C, 49.9; H, 4.6; N, 13.9%.

Synthesis of $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OCH_3)(OCH_3)(C_6H_5NHNH_2)\}_2]$ (**2a**)

The preparation of **2a** has been given by Hsieh and Zubieta.[7] Two other methods are reported hereunder.

Method 1. From $(NBu_4)_4[Mo_8O_{26}]$ *or* $(NBu_4)_2[Mo_6O_{19}]$. A large excess of $C_6H_5NHNH_2$ (20 cm^3, 0.20 mol) was added to $(NBu_4)_4[Mo_8O_{26}]$ (1.1 g, 0.5 mmol) in MeOH (50 cm^3). The resulting mixture was stirred at room temperature for 15 min during which time all the solid dissolved, and a purple–red colour developed. Well-shaped purple–black crystals of **2a** separated upon standing. The crystals were filtered off after 3 days, washed with CH_3OH and air-dried. Successive crops were collected over a period of 10 weeks. Yield: 1.2 g (62%, based on Mo). Found: C, 50.4; H, 5.1; N, 17.6; Mo, 19.6. Calc. for $C_{40}H_{48}N_{12}Mo_2O_4$: C, 50.4; H, 5.1; N, 17.6; Mo, 20.1%.

The reaction of $(NBu_4)_2[Mo_6O_{19}]$ (0.5 g, 0.36 mmol) with various amounts of $C_6H_5NHNH_2$ (from 0.15 cm^3 up to 10 cm^3) in CH_3OH (25 cm^3) was also studied at room temperature. A crystalline precipitate was formed within a few days. Its chemical analysis and IR spectroscopic study showed that pure $(NBu_4)_2[Mo_4O_8(OCH_3)_2(C_6H_5N_2)_4]$ was obtained for low $C_6H_5NHNH_2/Mo$ ratios while essentially pure **2a** separated for high ratios. Mixtures of these two diazenido complexes were obtained for intermediate cases.

Method 2. *From* $[MoO_2(acac)_2]$. This synthesis was analogous to that used for $[\{Mo(C_6H_5N_2)_2(acac)(\mu\text{-}OCH_3)\}_2]$[5] but a larger $C_6H_5NHNH_2/Mo$ ratio was used: 10 cm^3 of $C_6H_5NHNH_2$ and 0.65 g (2 mmol) of $[MoO_2(acac)_2]$ in 40 cm^3 of CH_3OH. The product collected after 2 days was spectroscopically identical with that obtained from method 1. Yield: 0.3 g, 31%.

Synthesis of $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OC_2H_5)(OC_2H_5)(C_6H_5NHNH_2)\}_2]$ (**2b**)

An excess of $C_6H_5NHNH_2$ (5 cm^3, 51 mmol) was added to $(NH_4)_2[MoOBr_5]$ (1.1 g, 2 mmol) in

C_2H_5OH (100 cm^3) and the mixture was stirred at room temperature for 15 min. The colour changed from red–brown to purple–red and **2b**, purple–black crystals, slowly separated upon standing. Yield: 0.8 g, 79%. Found: C, 51.8; H, 5.6; N, 16.5. Calc. for $C_{44}H_{56}N_{12}Mo_2O_4$: C, 52.4; H, 5.6; N, 16.7%.

Synthesis of [{Mo($C_6H_5N_2$)$_2$(μ-OC_3H_7)(OC_3H_7)($C_6H_5NHNH_2$)}$_2$] (**2c**)

This synthesis was performed analogously to method 2 for **2a**. A large excess of $C_6H_5NHNH_2$ (20 cm^3) was added to [MoO_2(acac)$_2$] (0.65 g, 2 mmol) in 1-propanol (25 cm^3) and the mixture was stirred for 10 min at room temperature. A dark purple crystalline solid began to deposit after several weeks; it was filtered off after 3 months and washed with 1-propanol and ether. Yield: 0.55 g, 52%. Found; C, 54.2; H, 6.1; N, 15.6. Calc. for $C_{48}H_{64}N_{12}Mo_2O_4$; C, 54.1; H, 6.1; N, 15.8%.

Synthesis of [{Mo($C_6H_5N_2$)$_2$Cl(μ-OR)($C_6H_5NHNH_2$)}$_2$] (**3a**: R = CH_3; **3b**: R = C_2H_5)

$C_6H_5NHNH_2$ (5 cm^3, 51 mmol) was added to (NEt_4)[$MoOCl_4$(H_2O)] (1 g, 2.5 mmol) and the mixture was refluxed for 1 h. The resulting purple suspension was filtered and the filtrate was allowed to stand at room temperature yielding single crystals within 2 days. The IR spectra of the precipitate and of crystals were nearly identical and both samples were shown to be mixtures of **2a** and **3a**. Moreover it was shown by X-ray diffraction that **2a** and **3a** actually form mixed crystals, i.e. the unit cell contains both **2a** and **3a**. Analysis of a crystalline sample calculated for a mixture of 65% of $C_{40}H_{48}N_{12}Mo_2O_4$ and 35% of $C_{38}H_{42}N_{12}Cl_2Mo_2O_2$: C, 49.4; H, 4.8; N, 17.6; Cl, 2.6; Mo, 20.1. Found: C, 48.7; H, 4.8; N, 178.6; Cl, 2.6; Mo. 20.0%. This ratio was suggested by the chemical analysis and by the X-ray structure determination. Similar results were obtained if the whole reaction was carried out at room temperature.

Attempts to prepare **3b** similarly by the reaction of $C_6H_5NHNH_2$ with (NEt_4)[$MoOCl_4$(H_2O)] in C_2H_5OH either at room temperature or under reflux yielded mixtures of **2b** and **3b**.

Synthesis of [{Mo($C_6H_5N_2$)$_2$(μ-OC_3H_7)(Cl)($C_6H_5NHNH_2$)}$_2$]·2C_3H_7OH (**3c**)

The synthesis was performed following a modification of the method used for **3a** and **3b**. $C_6H_5NHNH_2$ (4 cm^3) was added to (NEt_4)[$MoOCl_4$(H_2O)] (0.5 g) suspended in 1-propanol (50 cm^3). The resulting mixture was stirred at room temperature for 5 h; the solution was purple and a grey–white precipitate separated. It was filtered off and was identified as $C_6H_5NHNH_2HCl$ by IR spectroscopy. Large dark purple needles were recovered from the mother solution after standing for 48 h at room temperature. Yield: 0.28 g, 39%. Found: C, 51.1; H, 5.4; N, 15.1; Cl, 5.9; Mo, 17.0. Calc. for $C_{48}H_{66}N_{12}Cl_2Mo_2O_4$: C, 50.7; H, 5.8; N, 14.8; Cl, 6.2; Mo, 16.9%.

Synthesis of [{Mo($C_6H_5N_2$)$_2$Cl)(μ-OEt)(EtOH)}$_2$] (**4**)

(NBu_4)$_2$[Mo_4O_8($C_6H_5N_2$)$_4$]^{4a} (1.0 g, 0.66 mmol) was dissolved in CH_3CN/CH_2Cl_2 (10 cm^3/10 cm^3) and an excess of 12 N HCl (0.5 cm^3, 6.0 mmol) was added. Dark violet crystals of [{Mo($C_6H_5N_2$)$_2$Cl(μ-OEt)(EtOH)}$_2$] (**4**) deposited after standing for 3 weeks at room temperature. Yield: 0.39 g (74%). Found: C, 48.1; H, 5.1; N, 13.8. Calc. for $C_{32}H_{42}N_8Cl_2Mo_2O_4$: C, 48.4; H, 5.3; N, 14.1%.

X-ray structures

Crystals were mounted on glass fibers with epoxy cement and were studied by precession and Weissenberg methods. Cell constants and data collection were measured at room temperature with Mo-K_α radiation ($\lambda = 0.71069$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. Unit cell dimensions were determined by a least-squares fit of the setting angles of 25 reflections. Data were corrected for Lorentz and polarization effects and an empirical absorption correction based upon Ψ-scan was applied. Structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares using CRYSTALS program package.[13] Neutral atom form factors including anomalous dispersion were taken from *International Tables*.[14] Extinction was corrected. Crystallographic data are summarized in Table 1. Only specific points are quoted below for each case.

1b—Hydrogen atoms were included in refinement as fixed contributions. Carbon and oxygen atoms of the solvent molecule were constrained with the usual bond distances and with an overall isotropic thermal parameter; solvent hydrogen atoms were omitted.

2a—This structure was solved first by Hsieh and Zubieta[7] and independently by Jeannin and coworkers. Results are in agreement.

Mixed crystals of **2a** and **3a**—During refinement, it became apparent that the coordination site *trans* to $C_6H_5NHNH_2$ was disordered, being occupied either by a methoxo group or by a chlorine atom,

Table 1. Crystal data

	Compound **1b**	Compound **2a**	Compound **2a**/**3a**	Compound **3c**	Compound **4**
Formula	$C_{46}H_{54}N_{10}Mo_2O_8$	$C_{40}H_{48}N_{12}Mo_2O_4$	0.7 $C_{40}H_{48}N_{12}Mo_2O_4$: 0.3 $C_{38}H_{42}N_{12}Cl_2Mo_2O_2$	$C_{42}H_{50}N_{12}Cl_2Mo_2O_4$[c]	$C_{32}H_{42}N_8Cl_2Mo_2O_4$
Molecular weight	1066.87	952.78		1017.72	865.52
Crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$C2/m$
a (Å)	9.728(3)	11.404(2)	11.443(3)	9.534(3)	10.495(3)
b (Å)	11.154(1)	11.998(1)	11.826(4)	12.057(2)	18.792(4)
c (Å)	12.720(2)	16.778(4)	16.785(4)	12.751(3)	11.115(3)
α (°)	97.92(1)	90.00	90.00	98.90(1)	90.00
β (°)	106.40(2)	108.56(1)	108.45(2)	96.37(2)	101.91(1)
γ (°)	106.56(2)	90.00	90.00	112.50(2)	90.00
V (Å^3)	1233	2176	2155	1314	2145
Z	1	2	2	1	2
$d_{calc.}$ (g cm^{-3})	1.44	1.45	1.47	1.29	1.34
$F(000)$	548	976	976	588	812
μ, Mo-K_α (cm^{-1})	5.65	6.24	6.64	6.27	7.32
Crystal dimensions (mm)	0.42 × 0.14 × 0.09	0.24 × 0.22 × 0.18		0.30 × 0.14 × 0.10	0.43 × 0.37 × 0.29
Diffractometer	CAD4	CAD4	CAD4	CAD4	R3m
Temperature (°C)	20	20	20	20	20
Radiation	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
Scan mode	θ–2θ	θ–2θ	θ–2θ	θ–2θ	θ–2θ
θ range (°)	1.5–25	1.5–25	1–25	1–23	2–23
Reflections collected	4317	3827	4187	3641	2569
Reflections used	2549	2481	2623	1615	1238
Criteria	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Number parameters ref.	282	336	321	279	110
R[a]	0.0596	0.0245	0.0495	0.0533	0.0553
R_w[b]	0.0664	0.0252	0.0562	0.0587	0.0598
Weighting scheme	w = 1.0	w = 1.0	w = 1.0	w = 1.0	w = 1.0
rms (shift/esd)	0.08	0.15	0.09	0.01	0.02
Largest residue (e Å^{-3})	1.9	0.3	0.7	0.6	0.8

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.

[b] $R_w = \{\Sigma w(F_o - F_c)^2/\Sigma w F_o^2\}^{1/2}$.

[c] Excluding solvent.

indicating mixed crystals; occupancy factors converged to 0.72 and 0.31, and were fixed at 0.7 and 0.3 in the final refinement. Hydrogen atoms were located on a difference Fourier map and all but five were refined with an overall isotropic thermal parameter. Only the hydrogen atoms of the terminal OCH_3 groups were omitted.

3c—The centrosymmetric dinuclear unit $[\{Mo(C_6H_5N_2)_2Cl(\mu\text{-}OC_3H_7)(C_6H_5NHNH_2)\}_2]$ was easily located and refined; however refinement revealed high thermal motion with temperature factors ranging from 5 Å^2 for molybdenum up to 22 Å^2 for the terminal carbon atom of the propanolato bridge which contains an unusually short C—C distance. This could arise from disorder or from departure from centrosymmetry. Attempts to refine in non-centrosymmetric *P*1 space group were not successful. The propanolato bridge was loosely constrained in further refinement. Hydrogen atoms were included as fixed contributions. Then at this stage, a difference Fourier series revealed weak diffuse residual peaks located around the inversion centre (1/2, 1/2, 1/2) suggesting the presence of solvent. The disorder was not solved. The best decrease of *R* was obtained with six carbon atoms introduced with 0.5 occupancy so that *R* dropped from 8.5 to 5.3. Despite these difficulties the structure of $[\{Mo(C_6H_5N_2)_2Cl(\mu\text{-}OC_3H_7)(C_6H_5NHNH_2)\}_2]$ seems reliable in view of its comparison with those of **2a**, **3a** and **4**.

4—The general conditions of data collection and the methodologies used in this structure were similar to those employed for structures **1b**–**3a**, except that data were collected on a Nicolet R3m diffractometer and the SHELXTL[13b] program package was used in the structure solution and refinement. The choice of the centric space group *C*2/*m* yielded a centrosymmetric binuclear unit $[\{Mo(C_6H_5N_2)_2Cl(\mu\text{-}OC_2H_5)(C_2H_5OH\}_2]$ with the Mo, Cl, O(2), and C(3) atoms located on the mirror plane through $y = 0$. The oxygen atom O(1) and the methylene carbon C(1) of the bridging ethoxy group are located on the two-fold axis through $x = 0.5$, $z = 0.5$. As a consequence of this disposition of the binuclear unit, C(4) of the terminal ethoxy group is disordered about the mirror plane while C(2) of the bridging ethoxo group is disordered about the two-fold axis. Refinement in the acentric space group *C*2 produced no significant improvement in the residuals and resulted in temperature factors of 18–21 Å^2 for the terminal carbon atoms. The centric alternative *C*2/*m* was assumed to be the correct choice.

Atomic positional and thermal parameters for **1b**, **2a**, mixed **2a**–**3a**, **3c** and **4**, and complete listings of bond angles and distances are available as supplementary material and from authors. Selected interatomic distances and bond angles showing a comparison between those five compounds are listed in Table 2.

Spectral measurements

IR spectra were determind as KBr or RbI pellets with a Perkin–Elmer 597 spectrophotometer. Absorption spectra were obtained with a Beckman 5240 spectrophotometer.

RESULTS AND DISCUSSION

Some general trends of the reaction of phenylhydrazine with Mo^{VI} oxo-compounds can be inferred from our synthetic work and from the work of other groups,[15,16] although reaction conditions are not strictly identical since phenylhydrazine hydrochloride was sometimes used by other groups and triethylamine was sometimes added to the reaction mixture:

—the main products of $C_6H_5NHNH_2$ reaction with polyoxomolybdates in alcohols are the tetranuclear species, $[Mo_4O_8(OR)_2(C_6H_5N_2)_4]^{2-}$,[4a] and dinuclear compounds, $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OR)(OR)(C_6H_5NHNH_2)\}_2]$, depending on the $C_6H_5NHNH_2$/Mo ratio; aside from these compounds two complexes with different stoichiometries, $[Mo_8O_{26}(C_6H_5N_2)_6]^{4-}$[4d] and $[Mo_4O_{10}(OCH_3)_2(C_6H_5N_2)_2]^{2-}$[4c] have been characterized by Zubieta and co-workers;

—the reaction of $C_6H_5NHNH_2$ with $[MoO_2L_2]$ complexes yields dinuclear species $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OR)L\}_2]$ or $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OR)(C_6H_5NHNH_2)\}_2]$ when L is an (O,O)-chelate; this contrasts with the behaviour of (N,O)-, (N,S)-, and (S,S)-chelates which yield mononuclear $[Mo(C_6H_5N_2)_2L_2]$ complexes.[15,16] Compounds **1** are only slightly soluble in common solvents. Complexes **2** and **3** are more soluble, especially in chlorohydrocarbon solvents, but these solutions were found to be relatively unstable, even if dry solvents were used.

The IR spectra of complexes **1**, **2**, **3** and **4** show the characteristic pattern of singly-bent diazenido ligands in the range 1480–1650 cm^{-1}.[4a,15c,17,18] The visible absorption spectra of these complexes in solution are characterized by an intense band at *ca* 520 nm ($\varepsilon = 8 \times 10^{-4}$ mol^{-1} dm^3 cm^{-1} per Mo). These features are typical of the *cis*-$[Mo(C_6H_5N_2)_2]^{2+}$ unit.[4a]

The IR spectra of **2** and **3** show weak bands at 3220 and 3380 cm^{-1} assigned to ν(N—H). However, clear characterization of the hydrazine ligand by ^{1}H NMR in $CDCl_3$ was hampered by

Table 2. Selected interatomic distances (Å) and angles (°) with standard deviations in parentheses

		Compound **1b**	Compound **2a**	Compound **2a**:**3a**	Compound **3c**	Compound **4**
Phenyldiazenido ligands						
No. 1	Mo—N(21)	1.817(8)	1.830(3)	1.822(6)	1.79(1)	1.830(6)
	N(21)—N(22)	1.24(1)	1.227(4)	1.225(8)	1.23(1)	1.235(9)
	Mo—N(21)—N(22)	171.6(7)	170.3(3)	171.0(5)	166.0(1)	173.8(5)
	N(21)—N(22)—C(23)	118.3(8)	117.3(3)	119.0(6)	119.0(1)	119.1(6)
No. 2	Mo—N(31)	1.841(8)	1.832(3)	1.817(7)	1.84(2)	
	N(31)—N(32)	1.26(1)	1.231(4)	1.227(8)	1.24(2)	
	Mo—N(31)—N(32)	175.7(7)	161.2(3)	163.2(6)	170.0(1)	
	N(31)—N(32)—C(33)	118.2(9)	121.4(3)	121.8(6)	118.0(2)	
Phenylhydrazine ligand						
	Mo—N(11)		2.267(3)	2.248(6)	2.22(1)	
	N(11)—N(12)		1.423(4)	1.413(9)	1.41(1)	
	Mo—N(11)—N(12)		115.5(2)	115.8(5)	118.3(8)	
	N(11)—N(12)—C(13)		119.2(3)	118.5(6)	119.0(1)	
Benzohydroxamato ligand						
	Mo—O(2)	2.114(6)				
	Mo—O(3)	2.050(5)				
	C(3)—O(2)	1.29(1)				
	C(3)—N(1)	1.33(1)				
	N(1)—O(3)	1.375(9)				
	O(2)—C(3)—N(1)	118.8(9)				
	C(3)—N(1)—O(3)	119.3(8)				
Bridging alkoxo ligands						
	Mo—O(1)	2.157(5)	2.112(2)	2.105(5)	2.094(8)	2.113(4)
	Mo—O(1′)	2.020(5)	2.127(2)	2.115(5)	2.108(9)	2.113(4)
Terminal methoxo ligand						
	Mo—O(2)		1.986(2)	2.04(1)		
Chloro ligand						
	Mo—Cl			2.36(1)	2.421(4)	2.441(3)
Ethanol ligand						
						2.143(7)

rather low solubility and by some instability of the solutions as mentioned above.

The IR spectrum of **3** shows a band at *ca* 290 cm^{-1} which is not present in the spectrum of **2** and is therefore assigned to stretching ν(Mo—Cl) consistently with published data.[19]

The molecular structures of the centrosymmetrical dinuclear complexes of **1b**, **2a**, **3a**, **3c** and **4** are shown in Figs 1, 2, 3, 4 and 5. All complexes contain the $[\{MO(C_6H_5N_2)_2(\mu\text{-}OR)\}_2]^{2+}$ unit which has already been found in a number of compounds.[4a,5] In this unit, the molybdenum atom is ligated to two bridging alkoxo and two phenyldiazenido groups; it achieves six coordination either by a chelating bidentate ligand as in **1**, or by two unidentate ligands as in **2**, **3** and **4**. In the first case, the geometry around molybdenum is forced by the chelate ring. In the second case, two different geometries are conceivable according to whether the unidentate ligands are mutually *cis* or *trans*. However, only the latter has been ever found. As a consequence of the *trans* influence of the phenyldiazenido, the bridge is dissymmetrical for **1** while it is nearly symmetrical for **2** and **3**.

The overall geometry of $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OC_2H_5)(C_6H_5CONHO)\}_2]$ is similar to that of $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OCH_3)(acac)\}_2]$ while those of complexes **2**, **3** and **4** are similar. In **4** the Mo—O(2) distance 2.113(4) Å is outside the range for terminal alkoxides;[20] it clearly indicates that the ligand is ethanol.

A unique feature of compounds **2** and **3** is the occurrence of phenylhydrazine and phenyldiazenido ligands in the same coordination sphere. There was no example of this kind of molybdenum complexes until the recent report

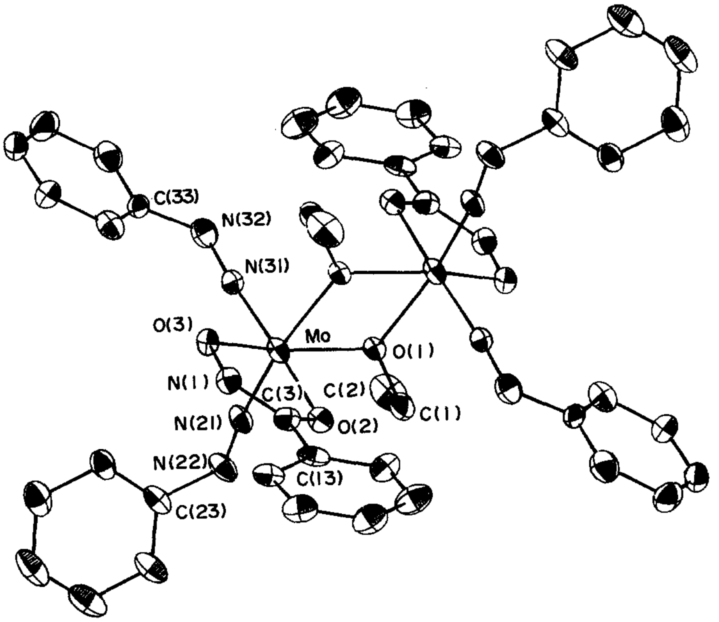

Fig. 1. Molecular structure and labelling scheme for $[Mo(C_6H_5N_2)_2(\mu\text{-}OC_2H_5)(C_6H_5CONHO)\}_2]$ (**1b**) with 20% thermal ellipsoids.

of Hsieh and Zubieta about the structure of **2a**.[7] This **2a** structure is the archetype of a new family of complexes with the general formula $[\{Mo(C_6H_5N_2)_2X(\mu\text{-}OR)(C_6H_5NHNH_2)\}_2]$ ($X = OR$, Cl; $R = CH_3$, C_2H_5, $n\text{-}C_3H_7\ldots$) which are readily formed when polyoxometalates, monomeric oxomolybdenum(VI), or monomeric halogenomolybdenum(V) complexes are treated with an excess of phenylhydrazine in ROH. The vanadium complex $[VCl_2\{C_6H_5(CH_3)N_2\}\{C_6H_5(CH_3)NNH_2\}]^+$ is the only other case of a complex containing hydrazine residues in more than one protonated state which was obtained by reacting a metal compound with a substituted hydrazine.[21] Compounds **2** and **3** also appear to be the first molybdenum complexes where end-on hydrazine coordination is crystallographically supported; this coordination is likely to occur in complexes

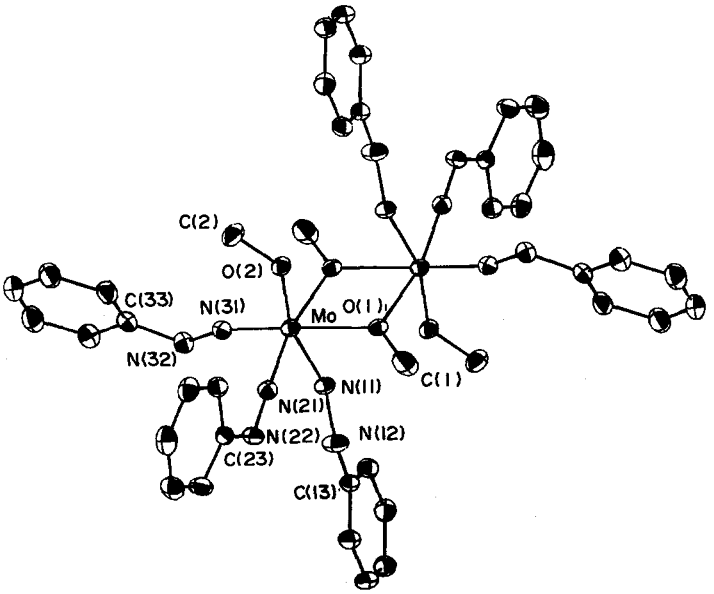

Fig. 2. ORTEP drawing of $[\{Mo(C_6H_5N_2)_2(\mu\text{-}OCH_3)(OCH_3)(C_6H_5NHNH_2)\}_2]$ (**2a**) with 20% thermal ellipsoids.

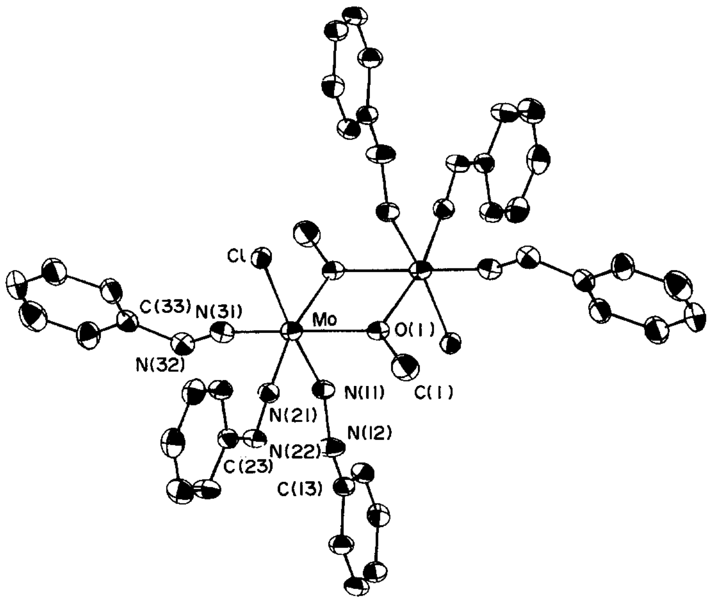

Fig. 3. ORTEP drawing of [{Mo($C_6H_5N_2$)$_2$Cl(μ-OCH_3)($C_6H_5NHNH_2$)}$_2$] occurring in mixed crystals (**2a**/**3a**) with 20% thermal ellipsoids.

such as [Mo(CO)$_5$($C_6H_5NHNH_2$)][22] and [Mo(η^5-C_5H_5)I_2(NO)($C_6H_5NHNH_2$)][23] studied by IR spectroscopy. The occurrence of neutral phenylhydrazine in **2** and **3** is consistent with electron count requirements; it is also supported by the appearance of NH_2 and NH hydrogen atoms in Fourier maps, their successful refinement, and the Mo—NH_2—NH—C_6H_5 geometry: the Mo—N and N—N distances 2.267(3) and 1.423(4) Å in **2a** are indicative of single bonds. The environment of the NH_2 nitrogen atom is roughly tetrahedral and the configuration about the N—N bond is *gauche*.

The geometry of the *cis*-[Mo($C_6H_5N_2$)$_2$]$^{2+}$ unit ensures maximum π-interaction between the diazenido ligand π^*-orbitals and the molybdenum t_{2g} orbitals.[24] This is supported by the

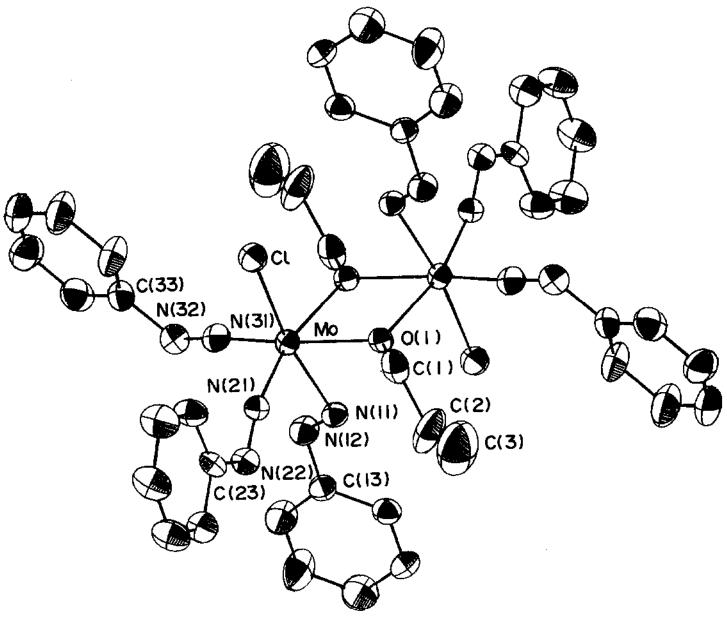

Fig. 4. ORTEP drawing of [{Mo($C_6H_5N_2$)$_2$Cl(μ-OC_3H_7)($C_6H_5NHNH_2$)}$_2$] (**3c**) with 15% thermal ellipsoids.

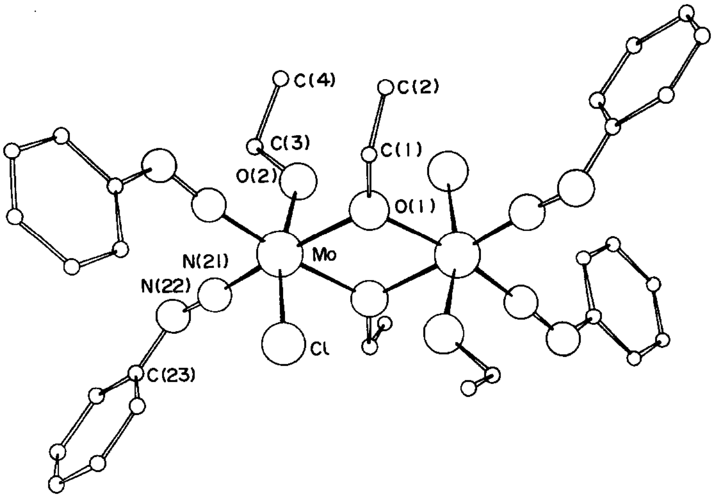

Fig. 5. Perspective drawing of $[\{Mo(C_6H_5N_2)_2Cl(\mu\text{-}OC_2H_5)(C_2H_5OH)\}_2]$ (**4**).

short Mo—N(diazenido) distances (1.82 Å average) and the wide angle of the Mo—N—N unit for the diazenido ligand (169° average).

Although there is obviously no π requirement for the phenylhydrazine ligand, its phenyl ring is not far from being coplanar with one diazenido ligand in both **2a** and **3c**; however the orientation of this phenyl ring in **3a** and **3c** with respect to the rest of the molecule is different while both $C_6H_5N_2$ groups are similarly orientated in both compounds.

Structural features of the benzohydroxamate ligand in **1b** are very similar to those of the hydroxamate ligand in $[MoO\{(CH_3)_2NO\}(C_6H_5CONHO)(C_6H_5CONO)]$[25] and in other hydroxamatomolybdenum complexes.[26] In **1b** crystals, an intermolecular hydrogen bond stretches between the NH group and the ethanol oxygen atom (N(1)···O(4) = 2.82(1) Å; N(1)—H(1)—O(4) = 153.3°).

Compounds **1**, **2**, **3** and **4** contain the $[Mo(C_6H_5N_2)_4(\mu\text{-}OR)_2]^{2+}$ unit which proves to be a robust core able to ligate various types of other ligands.

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