Reactivity of Acetone Oxime towards Oxomolybdenum(VI) Complexes. Part 2.[1] Syntheses, Crystal Structures and Reactivity of Molybdenum Nitrosyl Complexes†

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The complexes [Mo(NO)(acac)$_2$(Me$_2$CNO)] **1** (acac = acetylacetonate), [{Mo(NO)(OR)(Me$_2$CNO)$_2$}$_2$] (R = Me **2a** or Et **2b**) and [Mo$_2$(NO)$_2$(OR)$_2$Cl(Me$_2$CNO)$_3$(Me$_2$CNHO)] (R = Me **3a** or Et **3b**) have been obtained by reductive nitrosylation of [MoO$_2$(acac)$_2$], [NBu$^n_4$]$_2$[Mo$_6$O$_{19}$] and [NBu$^n_4$]$_2$[Mo$_4$O$_{12}$(Me$_2$CNO)$_2$], respectively, by acetone oxime in methanol or ethanol under reflux. Complex **2a** reacts with [NBu$^n_4$]$_2$[Mo$_2$O$_7$] to yield [NBu$^n_4$]$_2$[Mo$_4$O$_{10}$(NO)(OMe)(Me$_2$CNO)$_2$] **4**. This suggests that the reaction of molybdenum(II) nitrosyl complexes with polyoxomolybdates could be a route to a variety of oxonitrosyl species. Crystal structure determinations for **1**, **2b**, **3b** and **4** give further insight into the rich co-ordination chemistry of acetone oxime and reveal an unprecedented μ_3-κ*N*:κ^2*O* co-ordination mode.

In the preceding paper[1] we described the role of acetone oxime in the stabilization of molybdenum(VI) tetranuclear cores. We now turn to its role as a source of the nitrosyl ligand, demonstrated by the isolation and characterization of several molybdenum(II) nitrosyl complexes. Although the reductive nitrosylation of oxomolybdenum(VI) precursors by hydroxylamine is a well known and widely illustrated reaction,[2–7] little if any mention of such reactivity has been made for its organic derivatives.[8] The herein reported ability of acetone oxime is thus unprecedented and parallels that already established by our group for acetamide oxime.[9]

Interest in nitrosyl complexes arises in part from the diversity of their electronic structures: $\{Mo(NO)\}^n$‡ (n = 4,[2a c,3,4a,4c,5,6] 5[2c,4b] or 6[4b,8]) or $\{Mo(NO)_2\}^n$ (n = 4 or 6).[7,11] It also stems from their catalytic applications: oxidation of organic substrates, based on the NO_2–NO redox couple and oxygen-atom transfer,[12] polymerization[13a] or hydrogenation[13b] of olefins, but also from their possible involvement in atmospheric pollution control.[14] Nitrosyl species also provide structural and functional synthetic models for nitrite reductase active sites and the transformation of co-ordinated NO into NH_3[15] is therefore relevant to the assimilation process within the biological nitrogen cycle.[16]

We present here the syntheses of nitrosyl complexes containing the $\{Mo(NO)\}^4$ moiety: [Mo(NO)(acac)$_2$(Me$_2$CNO)] **1** (acac = acetylacetonate), [{Mo(NO)(OR)(Me$_2$CNO)$_2$}$_2$] (R = Me **2a** or Et **2b**), [Mo$_2$(NO)$_2$(OR)$_2$Cl(Me$_2$CNO)$_3$(Me$_2$CNHO)] (R = Me **3a** or Et **3b**). Single-crystal X-ray analyses will be described for **1**, **2b** and **3b**. Complexes **1** and **2b** contain side-on κ^2*N*,*O* acetone oximato-ligands while **3b** displays an end-on κ*O* zwitterionic acetone oxime ligand and both side-on κ^2*N*,*O* and bridging μ-κ*N*:*O* acetone oximato-ligands. The reactivity of the dimer **2a** towards [NBu$^n_4$]$_2$[Mo$_2$O$_7$] has also been investigated and shown to provide a route to nitrosyl complexes of higher nuclearity, a class of compounds much less documented.§ We will thus describe the synthesis and X-ray diffraction characterization of [NBu$^n_4$]$_2$[Mo$_4$O$_{10}$(NO)(OMe)(Me$_2$CNO)$_2$] **4**; the structure of this tetranuclear oxonitrosyl complex reveals the unprecedented μ_3-κ*N*:κ^2*O* co-ordination mode for one acetone oximato-ligand and the rather common κ^2*N*,*O* mode for the second.

Experimental

Acetone oxime and reagent grade solvents were obtained from Aldrich and used as received. A methanolic solution of hydrochloric acid was prepared by bubbling the gaseous acid through methanol. Its concentration was then determined by titration of an aliquot diluted in water. An approximately molar solution of NH_2OH in methanol was prepared by addition of a methanolic solution of sodium methoxide to a methanolic solution of [NH$_3$OH]Cl and subsequent removal of precipitated NaCl. The complexes [MoO$_2$(acac)$_2$],[19] [NBu$^n_4$]$_2$[Mo$_6$O$_{19}$][20] and [NBu$^n_4$]$_2$[Mo$_2$O$_7$][20] were synthesised according to published procedures, as were [NBu$^n_4$]$_2$[Mo$_4$O$_{12}$(Me$_2$CNO)$_2$] and [Mo$_4$O$_{10}$(OMe)$_4$(Me$_2$CNHO)$_2$].[1]

Infrared spectra were recorded from KBr pellets on a Perkin Elmer model 597 spectrophotometer. The elemental analyses were performed by the Service Central d'Analyse of the Centre National de la Recherche Scientifique (Vernaison, France).

Preparation of Complexes.—[Mo(NO)(acac)$_2$(Me$_2$CNO)] **1**. A mixture of [MoO$_2$(acac)$_2$] (1.63 g, 5 mmol) and Me$_2$CNOH (1.8 g, 25 mmol) in methanol (10 cm^3) was boiled under reflux for 5.5 h. The resulting yellow-orange solution was then allowed to stand at room temperature. A day later, large ill formed orange crystals of complex **1** were filtered off and air dried (0.11 g, 6% based on molybdenum). A further crop of smaller but better shaped crystals then grew from the filtrate within a few days, together with a white unidentified precipitate. These stick-shaped crystals were suitable for a X-ray analysis. IR: 1650s, 1575s, 1515s, 1435w, 1370s, 1280w, 1140w, 1020w, 945w, 680w and 490w cm^{-1} (Found: C, 39.65; H, 4.95; Mo, 24.30; N, 7.05. $C_{13}H_{20}MoN_2O_6$ requires C, 39.40; H, 5.10; Mo, 24.20; N, 7.05%).

[{Mo(NO)(OMe)(Me$_2$CNO)$_2$}$_2$] **2a**. *From* [NBu$^n_4$]$_2$[Mo$_6$O$_{19}$]. A mixture of [NBu$^n_4$]$_2$[Mo$_6$O$_{19}$] (1.36 g, 1 mmol) and Me$_2$CNOH (2.92 g, 40 mmol) in methanol (20 cm^3) was heated to reflux for 7 h, after which unreacted [NBu$^n_4$]$_2$[Mo$_6$O$_{19}$]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ The numerical exponent indicates the total number of valence electrons in d and π*(NO) orbitals (see ref. 10).

§ Polynuclear molybdenum nitrosyl complexes include a few 'classic' di-[4c] and tetra-nuclear species[2d] and an expanding class of oxonitrosyls.[17,18]

(and sometimes a small amount of a nitrosyl compound) was filtered off. During the following night, colourless crystals of $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ settled. They were discarded and the resulting filtrate provided light yellow stick-like crystals of complex **2a** within 1 d. The yield was very low. IR: 2960w, 2920w, 1625s, 1435w, 1380m, 1120w, 1060m, 955w, 620m, 535ms, 465m and 440m cm^{-1} (Found: C, 28.00; H, 5.15; Mo, 32.45; N, 13.20. $C_{14}H_{30}Mo_2N_6O_8$ requires C, 27.90; H, 5.00; Mo, 31.85; N, 13.95%).

From $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ *without* NH_2OH. To a suspension of $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ (0.8 g, 1 mmol) in methanol (10 cm^3) was added Me_2CNOH (2.92 g, 40 mmol). After 8 h of reflux, unreacted $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ was discarded and the yellow-orange filtrate allowed to stand at room temperature. Within a few days a few crystals of complex **2a** were formed.

From $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ *and additional* NH_2OH. To a suspension of $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ (1.2 g, 1.5 mmol) in methanol (10 cm^3) were added Me_2CNOH (2.4 g, 32.8 mmol) and NH_2OH (1 mol dm^{-3}, 6 cm^3, 6 mmol). The resulting orange mixture was heated to reflux for 2.5 h, during which time a yellow precipitate of complex **2a** deposited. It was filtered off and washed with diethyl ether (1.14 g, 63%).

$[\{Mo(NO)(OEt)(Me_2CNO)_2\}_2]$ **2b**. *From* $[NBu^n_4]_2[Mo_6O_{19}]$. The procedure was similar to that described above for complex **2a**, using ethanol instead of methanol. After a few days a mixture of colourless crystals of $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ and pale yellow stick-shaped crystals of **2b** was isolated from the filtrate and air dried. They were mechanically sorted. IR: 2920w, 2870w, 1625s, 1435w, 1380m, 1120w, 1100m, 1040m, 955w, 900w, 620m, 530ms, 460m and 440m cm^{-1} (Found: C, 30.85; H, 5.70; Mo, 30.15; N, 13.20. $C_{16}H_{34}Mo_2N_6O_8$ requires C, 30.50; H, 5.45; Mo, 30.45; N, 13.35%).

$[Mo_2(NO)_2(OMe)_2Cl(Me_2CNO)_3(Me_2CNHO)]$ **3a**. A solution of $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ (1.2 g, 1 mmol), Me_2CNOH (1.46 g, 20 mmol) and HCl (12 mol dm^{-3}, 0.4 cm^3, 0.48 mmol) in methanol (10 cm^3) was boiled under reflux for 5 h, after which a small amount of $[NBu^n_4]_2[Mo_6O_{19}]$ was filtered off. Allowing the filtrate to cool to room temperature resulted in the formation of thin plate-like yellow crystals of complex **3a** during the following night. They were filtered off and air dried (0.43 g, 33%). IR: 3040w, 2920w, 1640s, 1435w, 1380w, 1130m, 1050m, 985m, 700w, 620w, 510ms and 420m cm^{-1} (Found: C, 26.55; H, 5.10; Cl, 5.75; Mo, 30.40; N, 12.65. $C_{14}H_{31}ClMo_2N_6O_8$ requires C, 26.30; H, 4.90; Cl, 5.55; Mo, 30.05; N, 13.15%).

$[Mo_2(NO)_2(OEt)_2Cl(Me_2CNO)_3(Me_2CNHO)]$ **3b**. The procedure was as described above for complex **3a**, using ethanol instead of methanol. IR: 3040w, 2920w, 1640s, 1435w, 1380m, 1130m, 1050m, 990m, 900w, 700w, 620w, 510ms and 420m cm^{-1} (Found: C, 28.65; H, 5.20; Cl, 5.20; Mo, 29.80; N, 12.30. $C_{16}H_{35}ClMo_2N_6O_8$ requires C, 28.80; H, 5.30; Cl, 5.30; Mo, 8.80; N, 12.60%).

$[NBu^n_4]_2[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]$ **4**. To $[\{Mo(NO)(OMe)(Me_2CNO)_2\}_2]$ **2a** (0.3 g, 0.5 mmol) in methanol (10 cm^3) was added $[NBu^n_4]_2[Mo_2O_7]$ (1.57 g, 2 mmol) and the resulting mixture was heated to reflux for 2.5 h, during which a reddish colour appeared. The clear solution was then cooled to room temperature. A few days later it was concentrated and then afforded yellow plate-shaped crystals of complex **4**, which were isolated and air dried. Further crystals grew from the filtrate but they were contaminated by $[NBu^n_4]_3[Mo_6O_{18}(NO)]$, probably a decomposition product of the former. IR: 2960m, 2880w, 1630s, 1485w, 1380w, 1020w, 940m, 910s, 840m, 785s, 730s and 635m cm^{-1} (Found: C, 38.35; H, 6.95; Mo, 31.10; N, 5.60. $C_{39}H_{87}Mo_4N_5O_{14}$ requires C, 37.95; H, 7.10; Mo, 31.10; N, 5.70%).

Crystal Structure Determinations.—Relevant crystal data, data collection and refinement parameters for complexes **1**, **2b**, **3b** and **4** are summarized in Table 1. The intensity data were collected at room temperature on a CAD4 Enraf-Nonius diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) for **1**, **2b** and **4** and, owing to the small size of the crystal, on a CAD4 Enraf-Nonius diffractometer equipped with a rotating copper anode (λ = 1.5418 Å) for **3b**. The lattice parameters and the orientation matrix were obtained from a least-squares fit of 25 automatically centred reflections of high θ. Intensities were corrected for Lorentz and polarization effects and only those with $I > 3\sigma(I)$ were used in subsequent calculations. The structures were solved by Patterson (**1**, **2b** and **3b**) or direct[21] (**4**) methods and subsequent Fourier syntheses. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref. 22. An empirical absorption correction was applied using DIFABS.[23] The C–C distances within the two ethoxy bridges of **3b** were constrained to 1.5 Å. Disorder was also encountered for one tetrabutylammonium cation in **4** but up to now we have failed to model it. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on Fourier difference maps for **1** and **2b**; they were refined and then introduced as fixed contributions in the final refinement. Only 17 of them were found in the case of **3b**, including that on N(6) (see below) and thus they were not retained. As for **4**, they were not theoretically generated. Final least-squares refinements were carried out in full matrix for **1**, **2b** and **3b** but in a large-block approximation for **4**. All computations were performed on a MicroVax II computer, using the CRYSTALS system.[24] Final atomic coordinates of non-hydrogen atoms are listed in Tables 2–5, selected bond lengths and angles in Tables 6–9.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The reaction of acetone oxime with various oxomolybdenum(VI) complexes in methanol or ethanol, under reflux, leads to the formation of nitrosyl complexes of three types: $[Mo(NO)(acac)_2(Me_2CNO)]$ **1**, $[\{Mo(NO)(OR)(Me_2CNO)_2\}_2]$ (R = Me **2a** or Et **2b**) and $[Mo_2(NO)_2(OR)_2Cl(Me_2CNO)_3(Me_2CNHO)]$ (R = Me **3a** or Et **3b**). Synthetic procedures for these so-called nitrosylation reactions are summarized in Scheme 1. Whereas $[MoO_2(acac)_2]$, $[NBu^n_4]_2[Mo_6O_{19}]$ and $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ or $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ can equally be employed as starting reagents (irrespective of the distinctive features of each nitrosyl complex), the use of $[NBu^n_4]_4[\alpha\text{-}Mo_8O_{26}]$ only affords $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$.[1] In an attempt to rationalize the synthetic procedures, we note that: (*i*) monomer **1** is isolated when starting with the mononuclear $[MoO_2(acac)_2]$, whereas symmetric (**2**) and dissymmetric (**3**) dinuclear complexes are formed when starting with polynuclear compounds, *i.e.* $[NBu^n_4]_2[Mo_6O_{19}]$ or $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ for **2** and $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ for **3**; (*ii*) the formation of **3**, instead of **2**, under the reported conditions is not surprising in view of the additional presence of HCl. The formation of **1** requires heating under reflux, since the reaction of Me_2CNOH with $[MoO_2(acac)_2]$ at room temperature gives the tetranuclear complex $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$. Since $[NBu^n_4]_2[Mo_6O_{19}]$ yields a mixture of $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ and $[\{Mo(NO)(OR)(Me_2CNO)_2\}_2]$ **2**, $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$, which reacts more selectively, is preferred. Carrying out the reaction between Me_2CNOH and $[NBu^n_4]_2[Mo_6O_{19}]$ in acetonitrile results in the formation of $[MeC(NH_2)_2]_2[Mo_4O_{12}(Me_2CNO)_2]$ **5**[*] together with a yet

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[*] Characterized by X-ray diffraction: space group *Pbca*, *a* = 9.022(9), *b* = 15.344(3), *c* = 17.681(2) Å, *U* = 2447.6(5) Å^3, *R* = 0.030 for 1980 reflections with $I > 3\sigma(I)$. The structure of the $[Mo_4O_{12}(Me_2CNO)_2]^{2-}$ anion in **5** is quite similar to that observed in $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$.[1]

Table 1 Crystal data, data collection and refinement parameters for the structures of $[Mo(NO)(acac)_2(Me_2CNO)]$ **1**, $[\{Mo(NO)(OEt)(Me_2CNO)_2\}_2]$ **2b**, $[Mo_2(NO)_2(OEt)_2Cl(Me_2CNO)_3(Me_2CNHO)]$ **3b** and $[NBu^n_4]_2[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]$ **4**

	1	**2b**	**3b**	**4**
Molecular formula	$C_{13}H_{20}MoN_2O_6$	$C_{16}H_{34}Mo_2N_6O_8$	$C_{16}H_{35}ClMo_2N_6O_8$	$C_{39}H_{87}Mo_4N_5O_{14}$
M	396.25	630.36	663.83	1233.91
Crystal dimensions/mm	0.13 × 0.18 × 0.45	0.17 × 0.16 × 0.38	0.16 × 0.25 × 0.25	0.25 × 0.38 × 0.42
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Pcab$
a/Å	9.166(1)	8.119(1)	8.221(2)	19.869(5)
b/Å	12.242(1)	16.912(3)	10.825(2)	22.405(5)
c/Å	15.662(3)	10.121(1)	16.022(5)	24.78(1)
α/°			75.04(2)	
β/°	100.94(1)	111.6(1)	75.38(2)	
γ/°			81.70(2)	
U/Å^3	1725(4)	1292(6)	1328.0(6)	11 032(6)
Z	4	2	2	8
F(000)	608	640	676	508
μ(Mo-Kα)/cm^{-1}	7.67	9.94	92.71	9.24
D_c/g cm^{-3}	1.53	1.622	1.67	1.49
2θ range/°	2–50	2–56	2–133	2–50
Scan width/°	0.8 + 0.34 tan θ	0.12 + 0.34 tan θ	0.8 + 0.15 tan θ	0.8 + 0.34 tan θ
Scan speed/° min^{-1}	1–10.1	1.7–20.1	1.8–20.1	1.7–20.1
Scan mode	ω–2θ	ω–2θ	ω–2θ	ω–2θ
Range *hkl* collected	±10, 0–14, 0–18	−10 to 9, 0–22, 0–13	±9, ±12, 0–19	0–23, 0–26, 0–28
No. of reflections collected	3225	3273	5011	9680
No. of unique reflections	3031	3107	4654	9678
Merging R factor	0.021	0.036	0.037	—
No. of reflections with $I > 3\sigma(I)$	2017	2342	2762	4656
Least-squares parameters	200	146	299	561
Goodness-of-fit index S	1.1	2.9	4.6	2.8
R	0.026	0.024	0.067	0.050
R' (w = 1)	0.028	0.026	0.079	0.056

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$.

Table 2 Fractional atomic coordinates* for $[Mo(NO)(acac)_2(Me_2CNO)]$ **1**

Atom	x	y	z
Mo(1)	0.263 67(4)	0.180 31(3)	0.201 42(2)
O(2)	0.275 0(3)	0.081 9(2)	0.094 1(2)
N(3)	0.188 3(3)	0.034 9(3)	0.144 5(2)
C(4)	0.118 7(5)	−0.055 0(4)	0.128 6(3)
C(5)	0.027 3(7)	−0.093 2(5)	0.190 4(4)
C(6)	0.126 2(7)	−0.119 9(5)	0.049 3(4)
O(7)	0.400 8(3)	0.273 2(2)	0.138 5(2)
C(8)	0.542 9(5)	0.270 7(4)	0.151 4(3)
C(9)	0.633 4(5)	0.199 8(4)	0.206 2(4)
C(10)	0.590 3(5)	0.119 4(4)	0.258 3(3)
O(11)	0.457 1(3)	0.097 9(2)	0.264 2(2)
C(12)	0.611 0(6)	0.356 2(5)	0.102 4(4)
C(13)	0.706 9(6)	0.053 9(5)	0.317 2(4)
O(14)	0.338 1(3)	0.302 2(2)	0.290 7(2)
C(15)	0.349 9(4)	0.305 9(4)	0.372 6(3)
C(16)	0.286 9(5)	0.231 3(4)	0.419 8(3)
C(17)	0.200 3(5)	0.144 2(3)	0.384 0(3)
O(18)	0.170 7(3)	0.120 3(2)	0.303 3(2)
C(19)	0.434 3(6)	0.400 8(5)	0.416 1(3)
C(20)	0.124 9(5)	0.073 5(4)	0.440 4(3)
N(21)	0.104 0(4)	0.251 3(3)	0.150 6(2)
O(22)	−0.002 5(4)	0.301 3(3)	0.114 9(2)

* Estimated standard deviations in the least significant digits are given in parentheses.

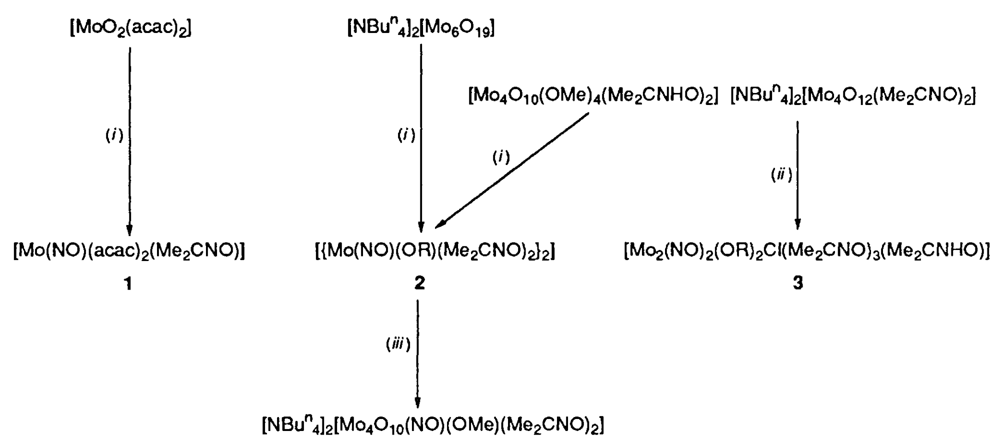
Table 3 Fractional atomic coordinates* for $[\{Mo(NO)(OEt)(Me_2CNO)_2\}_2]$ **2b**

Atom	x	y	z
Mo(1)	0.107 48(3)	0.068 81(1)	0.119 25(3)
N(1)	0.272 7(3)	0.071 4(2)	0.289 7(2)
O(1)	0.385 0(3)	0.071 2(2)	0.407 6(2)
O(2)	−0.052 9(3)	0.153 7(1)	0.153 2(2)
N(2)	−0.099 6(3)	0.082 3(2)	0.194 3(3)
C(1)	−0.216 8(4)	0.077 5(2)	0.249 4(3)
C(2)	−0.313 1(5)	0.147 9(3)	0.271 8(4)
C(3)	−0.258 4(6)	−0.002 2(3)	0.291 9(4)
O(3)	0.283 2(3)	0.078 7(1)	0.011 4(2)
N(3)	0.220 9(3)	0.150 3(2)	0.029 9(3)
C(4)	0.256 2(4)	0.216 0(2)	−0.015 0(3)
C(5)	0.378 0(5)	0.221 6(2)	−0.094 1(4)
C(6)	0.169 6(5)	0.288 1(2)	0.009 7(4)
O(4)	0.094 6(3)	−0.049 7(1)	0.089 9(2)
C(7)	0.216 1(5)	−0.107 1(2)	0.175 6(4)
C(8)	0.177 2(7)	−0.127 4(3)	0.304 9(5)

* Estimated standard deviations in the least significant digits are given in parentheses.

unidentified nitrosyl complex. In addition to absorptions assigned to the acetylacetonato- or acetone oximato-ligands (respectively strong and weak), the IR spectra of complexes **1**–**3** display a very strong band around 1600 cm^{-1}, attributed to the ν(N=O) stretching vibration (see Table 10). This value is consistent with those reported in the literature.[2–7] Complexes **2** and **3** are further characterized by ν(C–O) stretching vibrations in the range 1000–1100 cm^{-1}.

At this stage we shall raise the question of the reductive nitrosylation mechanism or, more precisely, that of the true nature of the nitrosylating agent, since free hydroxylamine, released by prior hydrolysis of the organic ligand, could alternatively be involved. From the formation of an acetamidinium cation in acetonitrile, which should arise from hydroxylamine attack on solvent molecules, we infer that hydrolysis of acetone oxime may occur under the experimental conditions reported here. It is also to be noted that the yield of **2** from $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ is dramatically increased by addition of hydroxylamine, although acetone oxime is already present in excess. The reductive nitrosylation of oxomolybdenum(VI) complexes by hydroxylamine has been extensively studied in water[2–7] and the mechanism in equations



Scheme 1 Synthetic procedures for complexes **1**–**4**. (*i*) Me_2CNOH, reflux in ROH (R = Me or Et); (*ii*) Me_2CNOH, HCl, reflux in ROH (R = Me or Et); (*iii*) $[NBu^n{}_4]_2[Mo_2O_7]$, reflux in MeOH

Table 4 Fractional atomic coordinates* for $[Mo_2(NO)_2(OEt)_2Cl(Me_2CNO)_3(Me_2CNHO)]$ **3b**

Atom	*x*	*y*	*z*
Mo(1)	0.042 0(2)	0.327 0(1)	0.289 95(8)
Mo(2)	0.207 7(2)	0.071 4(1)	0.217 81(8)
Cl	0.165 7(6)	0.489 7(4)	0.159 4(3)
N(1)	−0.155(2)	0.417(1)	0.298 1(9)
O(1)	−0.288(2)	0.479(1)	0.301(1)
O(2)	0.070(1)	0.313(1)	0.415 2(7)
N(2)	0.140(1)	0.419(1)	0.361 4(8)
C(1)	0.222(2)	0.490(1)	0.388(1)
C(2)	0.298(2)	0.605(2)	0.321(1)
C(3)	0.249(2)	0.453(2)	0.482(1)
O(3)	0.051(1)	0.037 6(8)	0.340 1(6)
N(3)	−0.047(1)	0.142(1)	0.365 4(7)
C(4)	−0.171(2)	0.108(2)	0.434(1)
C(5)	−0.293(2)	0.213(2)	0.474(1)
C(6)	−0.202(2)	−0.031(2)	0.477(1)
N(4)	0.362(2)	−0.049(1)	0.247(1)
O(4)	0.470(2)	−0.131(1)	0.270(1)
O(5)	0.151(2)	0.017(1)	0.114 6(8)
N(5)	0.064(2)	−0.049(1)	0.190 6(9)
C(7)	−0.044(2)	−0.135(2)	0.202(2)
C(8)	−0.122(2)	−0.204(2)	0.291(1)
C(9)	−0.079(3)	−0.157(2)	0.118(2)
O(6)	0.398(2)	0.152(1)	0.110 1(8)
N(6)	0.349(2)	0.265(1)	0.061 1(9)
C(10)	0.418(2)	0.293(2)	−0.022(1)
C(11)	0.531(3)	0.203(2)	−0.069(2)
C(12)	0.366(3)	0.426(2)	−0.075(1)
O(7)	0.027(1)	0.238 7(9)	0.195 3(6)
C(13)	−0.120(3)	0.240(2)	0.164(1)
C(14)	−0.078(5)	0.293(4)	0.069(2)
O(8)	0.272(1)	0.206 2(9)	0.268 6(7)
C(15)	0.432(3)	0.239(2)	0.270(2)
C(16)	0.509(5)	0.144(4)	0.327(3)

* Estimated standard deviations in the least significant digits are given in parentheses.

(1) and (2), based on intramolecular electron transfers, is

$$[Mo^{VI}O]^{4+} + NH_2OH \longrightarrow [Mo^{VI}(NH_2O)O]^{3+} + H^+ \quad (1)$$

$$[Mo^{VI}(NH_2O)O]^{3+} \longrightarrow [Mo^{II}(NO)]^{3+} + H_2O \quad (2)$$

generally accepted[25] [we will later discuss the question of oxidation states within the Mo(NO) moiety]. Nevertheless, whatever the real nitrosylating agent, acetone oxime acts as the only source of NO in most of the present reactions.

The complex $[NBu^n{}_4]_2[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]$ **4** can be viewed as the result of a condensation reaction between $[\{Mo(NO)(OMe)(Me_2CNO)_2\}_2]$ **2a** and $[NBu^n{}_4]_2[Mo_2O_7]$, in refluxing methanol. However, a more precise study of the reactivity of **2a** shows that the nature of the final product depends largely on the ratio *r* of $[NBu^n{}_4]_2[Mo_2O_7]$ to **2a**. Complex **4** has actually been isolated for *r* between 3 and 4:1, whereas $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ and $[Mo_6O_{18}(NO)]^{3-}$ anions[17] are formed respectively with *r* values of 2 and 5:1. Complex **4** is likely to be only one representative of a larger family, even if attempts to enlarge it have so far failed. Its IR spectrum indicates a polynuclear core with bands in the ranges 940–910 and 840–730 cm^{-1} respectively assigned to ν(Mo=O) and ν(Mo–O–Mo) vibrations. It further displays a strong absorption at 1630 cm^{-1} attributed to the nitrosyl ligand.

From the composition of complexes **1**–**4** it can be inferred that all display a $[Mo(NO)]^{3+}$ unit, commonly referred to by the $\{Mo(NO)\}^4$ notation, where the exponent *n* represents the whole number of electrons in d and π*(NO) orbitals.[10] This is by far the most widespread situation among mononitrosyl complexes of molybdenum, even if some examples of $\{Mo(NO)\}^5$ [refs. 2(*c*) and 4(*b*)] or $\{Mo(NO)\}^6$ [refs. 4(*b*) and 8] configurations have also been reported. The whole range of *n* values is covered by the series $[Mo(NO)(CN)_5]^{2-}$,[3a,7c] $[Mo(NO)(CN)_5]^{3-}$ [ref. 2(*c*)] and $[Mo(NO)(CN)_5]^{4-}$.[8] The electronic description of a non-innocent[26] ligand such as NO is often problematical. However, according to theoretical studies,[27] a $\{Mo(NO)\}^4$ configuration would imply a linear geometry of the Mo(NO) fragment, and thus a formal NO^+ ligand and a formal molybdenum(II) centre. The linear geometry of the Mo(NO) units in complexes **1**–**4** has been confirmed by X-ray analyses (see Table 10). Therefore, **1**–**3** should be described as containing only molybdenum(II) centres, whereas **4** should contain three Mo^{VI} and one Mo^{II}. However, the electron density on these formally molybdenum(II) centres is significantly depleted by the strong retrodonation revealed by the rather low ν(NO) stretching vibrations and short Mo=N distances (see Table 10).

The structures of complexes **1**, **2b** and **3b** are depicted in Figs. 1, 2 and 3 respectively; **2b** is located at a crystallographic centre of symmetry, so that the asymmetric unit only contains the half-molecule '$Mo(NO)(OEt)(Me_2CNO)_2$'. Final fractional atomic coordinates and selected bond lengths and angles are given in Tables 2–4 and 6–8 respectively. Complexes **1**, **2b** and **3b** exhibit common features. (*i*) The formal +II oxidation state can be assigned to all molybdenum atoms (see above). All molybdenum centres have a pentagonal-bipyramidal environment with the nitrosyl ligand in one apical position and at least one (two in **2b**) κ^2N,O co-ordinated acetone oximato-ligand. They thus achieve an eighteen-electron count. The co-ordination sphere consists of one nitrosyl-, one acetone oximato- and two acetylacetonato-ligands in $[Mo(NO)(acac)_2(Me_2CNO)]$ **1**, of one nitrosyl-, two acetone oximato- and two bridging ethoxo-

Table 5 Fractional atomic coordinates* for $[NBu^n_4]_2[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]$ **4**

Atom	*x*	*y*	*z*
Mo(1)	0.301 77(5)	0.150 49(4)	0.552 35(4)
Mo(2)	0.369 65(6)	0.119 59(5)	0.427 07(4)
Mo(3)	0.230 21(5)	0.023 09(4)	0.447 34(4)
Mo(4)	0.172 43(5)	0.061 76(4)	0.562 23(4)
N(21)	0.358 8(5)	0.166 9(5)	0.602 4(4)
O(22)	0.399 6(5)	0.180 3(5)	0.636 8(4)
O(7)	0.287 1(4)	0.237 5(4)	0.525 0(4)
N(2)	0.244 7(6)	0.224 4(4)	0.563 6(4)
C(1)	0.200 0(8)	0.262 4(6)	0.582 4(6)
C(2)	0.154 9(8)	0.238 2(7)	0.627 6(7)
C(3)	0.188 3(9)	0.323 6(6)	0.558 8(7)
O(12)	0.373 6(4)	0.154 5(4)	0.492 3(3)
O(14)	0.234 9(3)	0.107 6(3)	0.598 9(3)
O(134)	0.229 3(3)	0.120 3(3)	0.490 5(3)
C(134)	0.187 3(7)	0.163 8(5)	0.461 8(5)
O(1)	0.334 1(6)	0.167 9(5)	0.382 7(4)
O(2)	0.448 1(5)	0.103 4(5)	0.405 6(4)
O(23)	0.322 1(4)	0.050 2(3)	0.429 5(3)
O(3)	0.242 2(4)	−0.049 3(3)	0.432 8(3)
O(4)	0.191 2(4)	0.052 2(4)	0.392 3(3)
O(34)	0.156 5(3)	0.018 9(3)	0.495 0(3)
O(5)	0.153 6(4)	0.008 7(3)	0.608 9(3)
O(6)	0.104 4(4)	0.108 0(3)	0.560 3(3)
O(17)	0.271 1(3)	0.022 6(3)	0.531 2(3)
N(12)	0.328 6(4)	0.054 9(4)	0.544 8(3)
C(11)	0.383 4(6)	0.022 9(6)	0.545 6(5)
C(12)	0.449 2(6)	0.052 9(6)	0.560 4(5)
C(13)	0.383 6(7)	−0.043 4(6)	0.531 9(6)
N(46)	0.284 7(5)	0.563 8(5)	0.248 4(4)
C(47)	0.311 5(7)	0.521 2(6)	0.204 3(5)
C(48)	0.358 2(9)	0.472 0(7)	0.225 0(7)
C(49)	0.384(1)	0.438 0(9)	0.175 4(8)
C(50)	0.433(1)	0.390(1)	0.192(1)
C(51)	0.241 0(7)	0.609 5(6)	0.217 5(5)
C(52)	0.209 3(8)	0.655 7(8)	0.257 1(6)
C(53)	0.172(1)	0.701(1)	0.220(1)
C(54)	0.114(2)	0.677(1)	0.201(1)
C(55)	0.342 4(6)	0.592 2(7)	0.279 9(5)
C(56)	0.386 9(8)	0.633 2(8)	0.243 9(6)
C(57)	0.444 8(9)	0.653 6(9)	0.278 5(7)
C(58)	0.482(1)	0.704(1)	0.247(1)
C(59)	0.243 7(7)	0.529 7(6)	0.290 7(5)
C(60)	0.182 4(7)	0.496 2(8)	0.268 4(6)
C(61)	0.140 2(9)	0.475 0(9)	0.316 5(6)
C(62)	0.078(1)	0.445(1)	0.303 4(8)
N(29)	0.930 1(6)	0.650 1(6)	0.011 2(5)
C(30)	0.969(1)	0.593(1)	0.030 5(8)
C(31)	0.978(1)	0.587 1(9)	0.085(1)
C(32)	1.018 2(8)	0.529 6(7)	0.100 2(7)
C(33)	1.019(1)	0.523(1)	0.159 2(8)
C(34)	0.871(1)	0.671 9(9)	0.056(1)
C(35)	0.828(2)	0.633(1)	0.054(1)
C(36)	0.770(1)	0.655(1)	0.105(1)
C(37)	0.787(2)	0.665(1)	0.159(1)
C(38)	0.972(1)	0.705(1)	0.004 6(9)
C(39)	1.005(1)	0.731(1)	0.026(3)
C(40)	1.042(1)	0.787(1)	0.016(2)
C(41)	1.074(2)	0.795(1)	0.070(1)
C(42)	0.915(1)	0.628 9(9)	−0.048(1)
C(43)	0.891(2)	0.658(1)	−0.084(1)
C(44)	0.882(1)	0.626(1)	−0.140 4(7)
C(45)	0.838(1)	0.665(1)	−0.171 8(9)

* Estimated standard deviations in the least significant digits are given in parentheses.

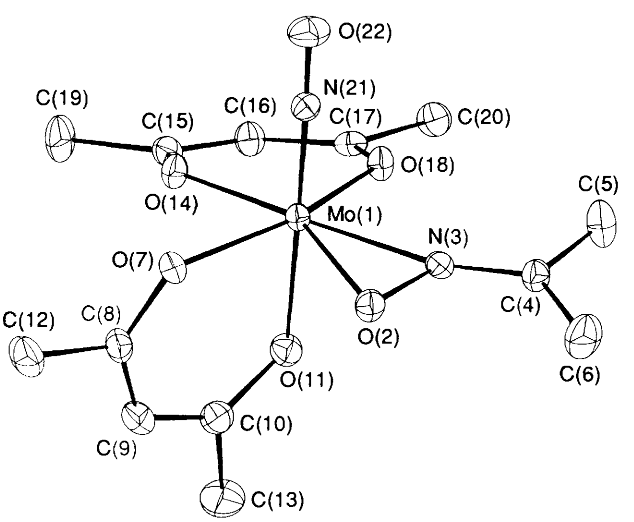


Fig. 1 Perspective view of $[Mo(NO)(acac)_2(Me_2CNO)]$ **1** showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity in this and all other Figures

ligands in $[\{Mo(NO)(OEt)(Me_2CNO)_2\}_2]$ **2b**. The molecular structure of $[Mo_2(NO)_2(OEt)_2Cl(Me_2CNO)_3(Me_2CNHO)]$ **3b** is more complicated: two 'Mo(NO)(Me$_2$CNO)' fragments are held together by two ethoxo- and one acetone oximato-bridges. The co-ordination sphere of the molybdenum centres is then completed by one chloro-ligand for Mo(1) and one end-on ligated acetone oxime ligand for Mo(2). Although the zwitterionic identity of the latter could have been deduced from its co-ordination mode, this was further supported by the location of the hydrogen atom on N(6). This was shown to be involved in an hydrogen bond with Cl(1) [H · · · Cl(1) 2.213 Å and N(6)–H(1) · · · Cl(1) 173.6°]. The molecular structure of **1** is closely related to those of $[Mo(NO)(acac)_2\{MeC(NH_2)NO\}]$[9] and $[PPh_4]_2[Mo(NO)(NCS)_4(Me_2CNO)]$.[2a] The side-on *N*,*O* co-ordination mode of the acetone oximato-ligand in **1**–**3** is quite similar to that of amide oximato-,[9] hydroxylaminato(1 −)-[3b,28] and hydroxylaminato(2 −)-[3c] ligands. Complex **2b** is a symmetrical dimer: a few other dinuclear nitrosyl complexes containing a central $[Mo^{II}_2(\mu\text{-}OR)_2]^{2+}$ core have been reported.[29] Complex **3b** is highly dissymmetric and displays organic ligands in three different co-ordination modes:

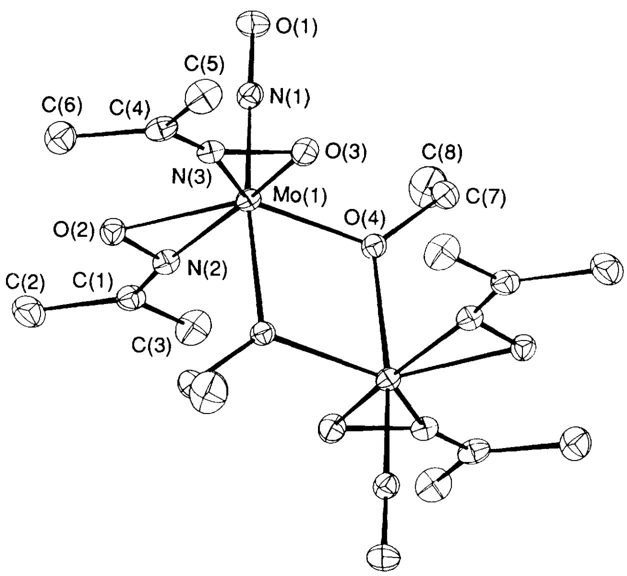


Fig. 2 Perspective view of $[\{Mo(NO)(OEt)(Me_2CNO)_2\}_2]$ **2b** showing the atom labelling scheme

Table 6 Selected bond lengths (Å) and angles (°) for [Mo(NO)(acac)$_2$(Me$_2$CNO)] **1**

Mo(1)–O(2)	2.086(3)	Mo(1)–N(3)	2.051(3)
Mo(1)–O(7)	2.077(3)	Mo(1)–O(11)	2.113(3)
Mo(1)–O(14)	2.070(3)	Mo(1)–O(18)	2.080(3)
Mo(1)–N(21)	1.758(4)		
O(2)–N(3)	1.350(4)	N(3)–C(4)	1.273(5)
C(4)–C(5)	1.471(7)	C(4)–C(6)	1.488(7)
O(7)–C(8)	1.280(5)	C(8)–C(9)	1.381(7)
C(8)–C(12)	1.502(7)	C(9)–C(10)	1.383(7)
C(10)–O(11)	1.269(5)	C(10)–C(13)	1.504(7)
O(14)–C(15)	1.268(5)	C(15)–C(16)	1.369(6)
C(15)–C(19)	1.486(6)	C(16)–C(17)	1.384(6)
C(17)–O(18)	1.275(5)	C(17)–C(20)	1.497(6)
N(21)–O(22)	1.197(4)		
N(3)–Mo(1)–O(2)	38.1(1)	O(7)–Mo(1)–O(2)	78.9(1)
O(7)–Mo(1)–N(3)	116.9(1)	O(11)–Mo(1)–O(2)	86.2(1)
O(11)–Mo(1)–N(3)	88.4(1)	O(11)–Mo(1)–O(7)	87.3(1)
O(14)–Mo(1)–O(2)	154.2(1)	O(14)–Mo(1)–N(3)	163.7(1)
O(14)–Mo(1)–O(7)	77.0(1)	O(14)–Mo(1)–O(11)	83.7(1)
O(18)–Mo(1)–O(2)	120.3(1)	O(18)–Mo(1)–N(3)	82.7(1)
O(18)–Mo(1)–O(7)	158.5(1)	O(18)–Mo(1)–O(11)	84.5(1)
O(18)–Mo(1)–O(14)	82.3(1)	N(21)–Mo(1)–O(2)	94.9(1)
N(21)–Mo(1)–N(3)	92.8(1)	N(21)–Mo(1)–O(7)	92.3(1)
N(21)–Mo(1)–O(11)	178.8(1)	N(21)–Mo(1)–O(14)	95.1(1)
N(21)–Mo(1)–O(18)	95.5(1)		
N(3)–O(2)–Mo(1)	69.5(2)	O(2)–N(3)–Mo(1)	72.4(2)
C(4)–N(3)–Mo(1)	161.9(3)	C(4)–N(3)–O(2)	125.6(4)
C(5)–C(4)–N(3)	118.2(4)	C(6)–C(4)–N(3)	121.6(4)
C(6)–C(4)–C(5)	120.2(4)	C(8)–O(7)–Mo(1)	126.9(3)
C(9)–C(8)–O(7)	125.9(4)	C(12)–C(8)–O(7)	114.3(5)
C(12)–C(8)–C(9)	119.8(4)	C(10)–C(9)–C(8)	127.5(4)
O(11)–C(10)–C(9)	125.2(4)	C(13)–C(10)–C(9)	119.5(5)
C(13)–C(10)–O(11)	115.2(5)	C(10)–O(11)–Mo(1)	126.9(3)
C(15)–O(14)–Mo(1)	131.6(3)	C(16)–C(15)–O(14)	123.9(4)
C(19)–C(15)–O(14)	115.4(4)	C(19)–C(15)–C(16)	120.7(4)
C(17)–C(16)–C(15)	124.3(4)	O(18)–C(17)–C(16)	125.2(4)
C(20)–C(17)–C(16)	120.0(4)	C(20)–C(17)–O(18)	114.7(4)
C(17)–O(18)–Mo(1)	129.7(3)	O(22)–N(21)–Mo(1)	178.4(3)

Table 7 Selected bond lengths (Å) and angles (°) for [{Mo(NO)(OEt)(Me$_2$CNO)$_2$}$_2$] **2b**

Mo(1)–N(1)	1.753(2)	O(1)–N(1)	1.206(3)
Mo(1)–O(4)	2.023(2)	Mo(1)–O(4′)	2.173(2)
O(4)–C(7)	1.428(4)	C(7)–C(8)	1.494(6)
Mo(1)–O(2)	2.050(2)	Mo(1)–O(3)	2.098(2)
Mo(1)–N(2)	2.097(2)	Mo(1)–N(3)	2.044(2)
O(2)–N(2)	1.376(3)	O(3)–N(3)	1.352(3)
N(2)–C(1)	1.270(4)	N(3)–C(4)	1.273(4)
C(1)–C(2)	1.486(5)	C(4)–C(5)	1.486(5)
C(1)–C(3)	1.491(5)	C(4)–C(6)	1.473(5)
O(3)–Mo(1)–O(2)	128.82(8)	O(4)–Mo(1)–O(2)	135.79(8)
O(4′)–Mo(1)–O(2)	88.24(8)	O(4)–Mo(1)–O(3)	85.38(8)
O(4′)–Mo(1)–O(3)	90.60(8)	O(4)–Mo(1)–O(4′)	74.31(8)
N(1)–Mo(1)–O(2)	96.9(1)	N(1)–Mo(1)–O(3)	95.1(1)
N(1)–Mo(1)–O(4)	98.6(1)	N(1)–Mo(1)–O(4′)	172.9(1)
N(2)–Mo(1)–O(2)	38.73(9)	N(2)–Mo(1)–O(3)	165.81(9)
N(2)–Mo(1)–O(4)	98.97(9)	N(2)–Mo(1)–O(4′)	87.15(9)
N(2)–Mo(1)–N(1)	93.8(1)	N(3)–Mo(1)–O(2)	91.11(9)
N(3)–Mo(1)–O(3)	38.07(9)	N(3)–Mo(1)–O(4)	127.60(9)
N(3)–Mo(1)–O(4′)	88.35(8)	N(3)–Mo(1)–N(1)	96.4(1)
N(3)–Mo(1)–N(2)	129.7(1)	N(2)–O(2)–Mo(1)	72.5(1)
N(3)–O(3)–Mo(1)	68.8(1)	Mo(1)–O(4)–Mo(1′)	105.69(8)
C(7)–O(4)–Mo(1)	126.7(2)	C(7)–O(4)–Mo(1)	126.5(2)
O(1)–N(1)–Mo(1)	178.2(3)	O(2)–N(2)–Mo(1)	68.8(1)
C(1)–N(2)–Mo(1)	169.2(3)	C(1)–N(2)–O(2)	121.6(3)
O(3)–N(3)–Mo(1)	73.2(1)	C(4)–N(3)–Mo(1)	160.8(2)
C(4)–N(3)–O(3)	126.0(3)	C(2)–C(1)–N(2)	122.5(3)
C(3)–C(1)–N(2)	118.0(3)	C(3)–C(1)–C(2)	119.5(3)
C(5)–C(4)–N(3)	122.0(3)	C(6)–C(4)–N(3)	118.5(3)
C(6)–C(4)–C(5)	119.5(3)	C(8)–C(7)–O(4)	111.6(3)

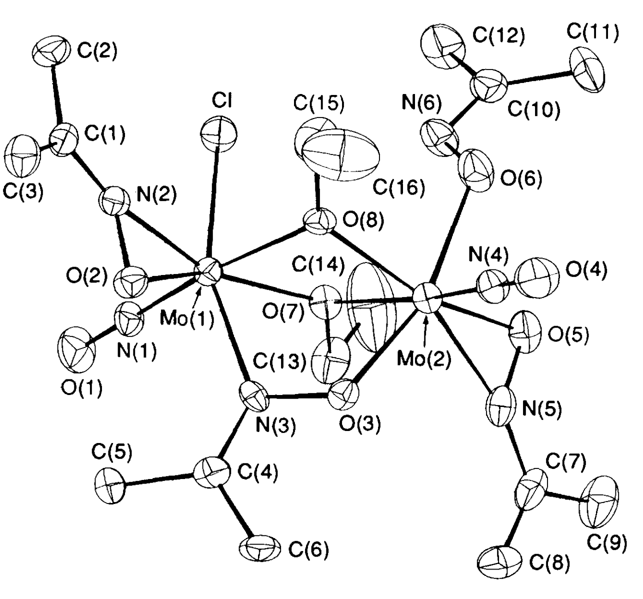


Fig. 3 Perspective view of [Mo$_2$(NO)$_2$(OEt)$_2$Cl(Me$_2$CNO)$_3$(Me$_2$CNHO)] **3b** showing the atom labelling scheme

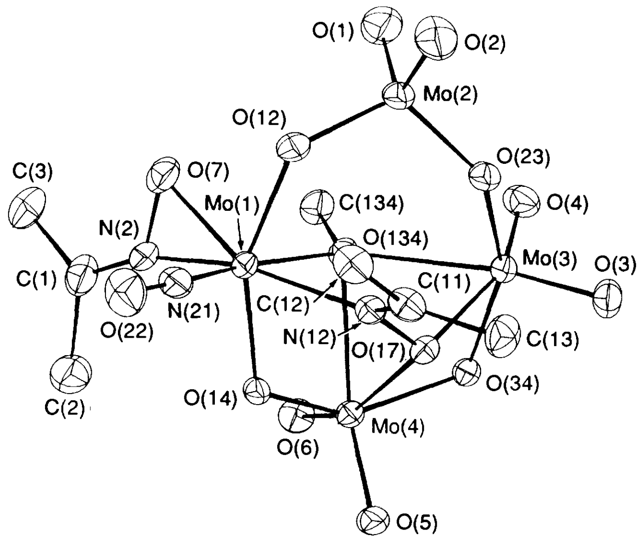


Fig. 4 Perspective view of the anion in [NBu$^n{}_4$]$_2$[Mo$_4$O$_{10}$(NO)(OMe)(Me$_2$CNO)$_2$] **4** showing the atom labelling scheme

although each of them has been previously observed separately [see refs. 2(*a*) and 30 for the κ^2*N*,*O* mode, ref. 31 for the μ-κ*N*:*O* mode and ref. 1 for the end-on mode] they are for the first time contained within the same species. The Mo ··· Mo distances of 3.3450(5) and 3.258(2) Å, respectively in **2b** and **3b** are non-bonding distances, in agreement with electronic considerations. (*ii*) All three complexes display, as expected, a linear Mo(NO) moiety, characterized by relatively short Mo=N bond lengths. The relevant values are listed in Table 10, together with the ν(NO) vibrational frequencies. (*iii*) Finally, the strong electron-withdrawing effect of the nitrosyl ligand is reflected in a bond lengthening in the *trans* position: 2.113(3) Å for Mo(1)–O(11) *versus* a mean value of 2.078 Å for the three other distances involving the remaining oxygen atoms of the acetylacetonato-ligands in **1**, 2.173(2) Å for Mo(1)–O(4′) *versus* 2.023(2) Å for Mo(1)–O(4) in **2b** and 2.027(9) Å [Mo(1)–O(7)] *versus* 2.144(9) Å [Mo(1)–O(8)] and 2.186(9) Å [Mo(2)–O(7)] *versus* 2.03(1) Å [Mo(2)–O(8)] in **3b**.

Table 8 Selected bond lengths (Å) and angles (°) for $[Mo_2(NO)_2(OEt)_2Cl(Me_2CNO)_3(Me_2CNHO)]$ **3b**

Mo(1)–Cl	2.460(4)	Mo(1)–N(1)	1.76(1)	C(1)–C(2)	1.51(2)	C(1)–C(3)	1.51(2)
Mo(1)–O(2)	2.04(1)	Mo(1)–N(2)	2.06(1)	O(3)–N(3)	1.38(1)	N(3)–C(4)	1.31(2)
Mo(1)–N(3)	2.17(1)	Mo(1)–O(7)	2.027(9)	C(4)–C(5)	1.56(2)	C(4)–C(6)	1.51(2)
Mo(1)–O(8)	2.144(9)			N(4)–O(4)	1.22(2)		
Mo(2)–O(3)	2.030(9)	Mo(2)–N(4)	1.74(1)	O(5)–N(5)	1.33(2)	N(5)–C(7)	1.33(2)
Mo(2)–O(5)	2.06(1)	Mo(2)–N(5)	2.07(1)	C(7)–C(8)	1.47(3)	C(7)–C(9)	1.52(3)
Mo(2)–O(6)	2.11(1)	Mo(2)–O(7)	2.186(9)	O(6)–N(6)	1.34(2)	N(6)–C(10)	1.29(2)
Mo(2)–O(8)	2.03(1)			C(10)–C(11)	1.46(3)	C(10)–C(12)	1.53(3)
N(1)–O(1)	1.19(2)			O(7)–C(13)	1.42(2)	C(13)–C(14)	1.45(3)
O(2)–N(2)	1.35(1)	N(2)–C(1)	1.31(2)	O(8)–C(15)	1.42(2)	C(15)–C(16)	1.38(2)
N(1)–Mo(1)–Cl	90.7(4)	O(2)–Mo(1)–Cl	124.0(3)	O(1)–N(1)–Mo(1)	177.7(13)		
O(2)–Mo(1)–N(1)	98.0(5)	N(2)–Mo(1)–Cl	85.7(3)	N(2)–O(2)–Mo(1)	71.5(7)	O(2)–N(2)–Mo(1)	70.0(7)
N(2)–Mo(1)–N(1)	96.7(5)	N(2)–Mo(1)–O(2)	38.4(4)	C(1)–N(2)–Mo(1)	166.6(12)	C(1)–N(2)–O(2)	122.5(13)
N(3)–Mo(1)–Cl	157.7(3)	N(3)–Mo(1)–N(1)	97.9(5)	C(2)–C(1)–N(2)	117.3(15)	C(3)–C(1)–N(2)	120.6(15)
N(3)–Mo(1)–O(2)	75.3(4)	N(3)–Mo(1)–N(2)	113.5(4)	C(3)–C(1)–C(2)	122.0(15)		
O(7)–Mo(1)–Cl	82.0(3)	O(7)–Mo(1)–N(1)	98.3(5)	N(3)–O(3)–Mo(2)	116.6(7)	O(3)–N(3)–Mo(1)	114.7(7)
O(7)–Mo(1)–O(2)	149.0(4)	O(7)–Mo(1)–N(2)	160.6(4)	C(4)–N(3)–Mo(1)	133.1(10)	C(4)–N(3)–O(3)	112.1(12)
O(7)–Mo(1)–N(3)	76.4(4)	O(8)–Mo(1)–Cl	89.0(3)	C(5)–C(4)–N(3)	119.5(14)	C(6)–C(4)–N(3)	122.7(16)
O(8)–Mo(1)–N(1)	172.6(5)	O(8)–Mo(1)–O(2)	88.3(4)	C(6)–C(4)–C(5)	117.7(14)		
O(8)–Mo(1)–N(2)	90.6(4)	O(8)–Mo(1)–N(3)	79.8(4)	O(4)–N(4)–Mo(2)	177.8(14)		
O(8)–Mo(1)–O(7)	74.3(4)			N(5)–O(5)–Mo(2)	71.5(8)	O(5)–N(5)–Mo(2)	71.0(8)
N(4)–Mo(2)–O(3)	94.9(5)	O(5)–Mo(2)–O(3)	120.5(4)	C(7)–N(5)–Mo(2)	161.2(14)	C(7)–N(5)–O(5)	127.7(16)
O(5)–Mo(2)–N(4)	101.6(6)	N(5)–Mo(2)–O(3)	84.8(5)	C(8)–C(7)–N(5)	120.0(17)	C(9)–C(7)–N(5)	116.5(21)
N(5)–Mo(2)–N(4)	94.9(5)	N(5)–Mo(2)–O(5)	37.5(5)	C(9)–C(7)–C(8)	123.5(19)		
O(6)–Mo(2)–O(3)	159.9(4)	O(6)–Mo(2)–N(4)	86.5(6)	N(6)–O(6)–Mo(2)	114.5(10)	C(10)–N(6)–O(6)	118.2(15)
O(6)–Mo(2)–O(5)	78.7(5)	O(6)–Mo(2)–N(5)	115.2(6)	C(11)–C(10)–N(6)	124.0(19)	C(12)–C(10)–N(6)	116.5(17)
O(7)–Mo(2)–O(3)	82.0(4)	O(7)–Mo(2)–N(4)	170.5(5)	C(12)–C(10)–C(11)	119.4(19)		
O(7)–Mo(2)–O(5)	87.7(4)	O(7)–Mo(2)–N(5)	93.7(4)	Mo(2)–O(7)–Mo(1)	101.2(4)	C(13)–O(7)–Mo(1)	125.6(10)
O(7)–Mo(2)–O(6)	93.5(4)	O(8)–Mo(2)–O(3)	79.7(4)	C(13)–O(7)–Mo(2)	124.2(10)	C(14)–C(13)–O(7)	106.9(23)
O(8)–Mo(2)–N(4)	97.4(5)	O(8)–Mo(2)–O(5)	150.6(4)	Mo(2)–O(8)–Mo(1)	102.5(4)	C(15)–O(8)–Mo(1)	124.6(11)
O(8)–Mo(2)–N(5)	160.9(5)	O(8)–Mo(2)–O(6)	80.2(4)	C(15)–O(8)–Mo(2)	131.2(11)	C(16)–C(15)–O(8)	111.2(26)
O(8)–Mo(2)–O(7)	73.3(4)						

Table 9 Selected bond lengths (Å) and angles (°) for $[NBu^n{}_4]_2[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]$ **4**

Mo(1)–N(21)	1.72(1)	Mo(1)–O(7)	2.085(8)	Mo(4)–O(14)	1.850(6)	Mo(4)–O(134)	2.481(7)
Mo(1)–N(2)	2.03(1)	Mo(1)–O(12)	2.063(7)	Mo(4)–O(34)	1.948(6)	Mo(4)–O(5)	1.699(7)
Mo(1)–O(14)	2.004(7)	Mo(1)–O(134)	2.209(7)	Mo(4)–O(6)	1.704(7)	Mo(4)–O(17)	2.282(7)
Mo(1)–N(12)	2.216(9)			N(21)–O(22)	1.21(1)		
Mo(2)–O(12)	1.798(8)	Mo(2)–O(1)	1.70(1)	O(7)–N(2)	1.31(1)	N(2)–C(1)	1.32(2)
Mo(2)–O(2)	1.686(9)	Mo(2)–O(23)	1.820(7)	C(1)–C(2)	1.53(2)	C(1)–C(3)	1.51(2)
Mo(3)–O(134)	2.426(7)	Mo(3)–O(23)	1.974(7)	O(134)–C(134)	1.47(1)		
Mo(3)–O(3)	1.678(8)	Mo(3)–O(4)	1.700(8)	O(17)–N(12)	1.39(1)	N(12)–C(11)	1.30(1)
Mo(3)–O(34)	1.884(7)	Mo(3)–O(17)	2.230(7)	C(11)–C(12)	1.52(2)	C(11)–C(13)	1.52(2)
O(7)–Mo(1)–N(21)	97.3(4)	N(2)–Mo(1)–N(21)	95.4(5)	O(34)–Mo(4)–O(134)	73.9(2)	O(5)–Mo(4)–O(14)	101.7(3)
N(2)–Mo(1)–O(7)	37.1(3)	O(12)–Mo(1)–N(21)	93.1(4)	O(5)–Mo(4)–O(134)	163.1(3)	O(5)–Mo(4)–O(34)	101.6(3)
O(12)–Mo(1)–O(7)	79.7(3)	O(12)–Mo(1)–N(2)	116.8(4)	O(6)–Mo(4)–O(14)	102.1(3)	O(6)–Mo(4)–O(134)	91.1(3)
O(14)–Mo(1)–N(21)	97.2(4)	O(14)–Mo(1)–O(7)	122.9(3)	O(6)–Mo(4)–O(34)	98.5(3)	O(6)–Mo(4)–O(5)	105.7(4)
O(14)–Mo(1)–N(2)	86.7(3)	O(14)–Mo(1)–O(12)	153.3(3)	O(17)–Mo(4)–O(14)	78.6(3)	O(17)–Mo(4)–O(134)	64.5(2)
O(134)–Mo(1)–N(21)	174.4(4)	O(134)–Mo(1)–O(7)	88.3(3)	O(17)–Mo(4)–O(34)	70.2(3)	O(17)–Mo(4)–O(5)	98.6(3)
O(134)–Mo(1)–N(2)	89.0(3)	O(134)–Mo(1)–O(12)	87.9(3)	O(17)–Mo(4)–O(6)	155.0(3)		
O(134)–Mo(1)–O(14)	79.7(2)	N(12)–Mo(1)–N(21)	96.3(4)	O(22)–N(21)–Mo(1)	177.8(10)		
N(12)–Mo(1)–O(7)	155.6(3)	N(12)–Mo(1)–N(2)	159.5(4)	N(2)–O(7)–Mo(1)	69.0(6)	O(7)–N(2)–Mo(1)	73.9(6)
N(12)–Mo(1)–O(12)	79.3(3)	N(12)–Mo(1)–O(14)	75.2(3)	C(1)–N(2)–Mo(1)	162.9(10)	C(1)–N(2)–O(7)	123.2(11)
N(12)–Mo(1)–O(134)	78.5(3)			C(2)–C(1)–N(2)	115.1(13)	C(3)–C(1)–N(2)	123.7(14)
O(1)–Mo(2)–O(12)	108.9(4)	O(2)–Mo(2)–O(12)	109.7(4)	C(3)–C(1)–C(2)	120.9(14)		
O(2)–Mo(2)–O(1)	108.5(6)	O(23)–Mo(2)–O(12)	111.4(3)	Mo(2)–O(12)–Mo(1)	126.8(4)	Mo(4)–O(14)–Mo(1)	115.4(3)
O(23)–Mo(2)–O(1)	110.5(4)	O(23)–Mo(2)–O(2)	107.9(4)	Mo(3)–O(134)–Mo(1)	125.2(3)	Mo(4)–O(134)–Mo(1)	87.8(2)
O(23)–Mo(3)–O(134)	80.2(3)	O(3)–Mo(3)–O(134)	164.4(4)	Mo(4)–O(134)–Mo(3)	81.1(2)	C(134)–O(134)–Mo(1)	120.2(6)
O(3)–Mo(3)–O(23)	96.8(4)	O(4)–Mo(3)–O(134)	90.4(3)	C(134)–O(134)–Mo(3)	112.8(6)	C(134)–O(134)–Mo(4)	116.0(6)
O(4)–Mo(3)–O(23)	97.1(4)	O(4)–Mo(3)–O(3)	105.2(4)	Mo(3)–O(23)–Mo(2)	138.6(4)	Mo(4)–O(34)–Mo(3)	112.7(3)
O(34)–Mo(3)–O(134)	76.3(3)	O(34)–Mo(3)–O(23)	151.0(3)	Mo(4)–O(17)–Mo(3)	90.0(2)	N(12)–O(17)–Mo(3)	121.4(5)
O(34)–Mo(3)–O(3)	101.4(4)	O(34)–Mo(3)–O(4)	99.7(3)	N(12)–O(17)–Mo(4)	115.0(5)	O(17)–N(12)–Mo(1)	109.0(6)
O(17)–Mo(3)–O(134)	66.2(2)	O(17)–Mo(3)–O(23)	82.7(3)	C(11)–N(12)–Mo(1)	136.9(8)	C(11)–N(12)–O(17)	113.8(9)
O(17)–Mo(3)–O(3)	98.2(4)	O(17)–Mo(3)–O(4)	156.3(3)	C(12)–C(11)–N(12)	118.7(11)	C(13)–C(11)–N(12)	122.3(11)
O(17)–Mo(3)–O(34)	72.5(3)			C(13)–C(11)–C(12)	119.0(11)		
O(134)–Mo(4)–O(14)	75.7(2)	O(34)–Mo(4)–O(14)	143.3(3)				

The asymmetric unit of complex **4** contains one $[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]^{2-}$ anion and two tetrabutylammonium cations. Final fractional atomic coordinates and selected bond lengths and angles are listed in Tables 5 and 9 respectively. The structure of the anion is depicted in Fig. 4. It displays a cyclic Mo_4O_4 ring capped by one triply bridging methoxo-ligand and one acetone oximato-ligand in a hitherto unknown μ_3-κN:$\kappa^2 O$ co-ordination mode. One of the most

Table 10 Relevant vibrational and structural data for the nitrosyl complexes $[Mo(NO)(acac)_2(Me_2CNO)]$ **1**, $[\{Mo(NO)(OEt)(Me_2CNO)_2\}_2]$ **2b**, $[Mo_2(NO)_2(OEt)_2Cl(Me_2CNO)_3(Me_2CNHO)]$ **3b** and $[NBu^n{}_4]_2[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]$ **4**

Complex	$\tilde{\nu}$(NO)/cm^{-1}	Mo–N/Å	N–O/Å	Mo–N–O/°
1	1650	1.758(4)	1.197(4)	178.4(3)
2b	1625	1.753(2)	1.206(3)	178.2(3)
3b	1640	1.76(1)	1.19(2)	177.7(13)
		1.74(1)	1.22(2)	177.8(14)
4	1630	1.72(1)	1.21(1)	177.8(10)

salient features of this structure is the diversity in molybdenum atom environments, since Mo(1) and Mo(2) are respectively seven- and four-co-ordinated, whereas Mo(3) and Mo(4) are six-co-ordinated. The co-ordination sphere of Mo(1) is highly reminiscent of that observed in the precursor **2a** with respect to the nitrosyl and methoxo-ligands and the $\kappa^2 N,O$ side-on co-ordinated acetone oximato-ligand. It is completed by two bridging oxo-ligands. Atom Mo(2) displays a tetrahedral geometry associated with two terminal and two bridging oxo-groups and evidenced by a mean value of 109.5° for the surrounding angles. Anyway, the Mo(2) ··· N(12) distance of 3.36 Å definitively rules out any significant interaction between Mo(2) and the capping acetone oximato-ligand. Atoms Mo(3) and Mo(4) exhibit similar environments consisting of the methoxo-ligand, the oxygen atom of the capping oximato-ligand, two terminal and two bridging oxo-ligands. Complex **4** therefore shares common structural features with **1**–**3** and with $[NBu^n{}_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ and $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ as well.[1] It can also be viewed as a link between classic molybdenum nitrosyl complexes such as **1**–**3** and oxonitrosyl derivatives of polyoxometalates such as $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ [refs. 17(*a*), (*b*)] or $[Mo_6O_{18}(NO)]^{3-}$ anions[17a,c] which do not necessarily contain any additional organic ligand. The former have generally a low nuclearity, most being mononuclear while a few di-[4c,29] and tetranuclear[2d] complexes have been reported. On the contrary, the latter include some quite large discrete molecular species.[18] Judging from the diversity in molybdenum environments, from the coexistence of two different localized oxidation states, II and VI, and from the characterization of a novel co-ordination mode for the acetone oximato-ligand, $[NBu^n{}_4]_2[Mo_4O_{10}(NO)(OMe)(Me_2CNO)_2]$ **4** is obviously an outstanding oxonitrosyl complex.

A general survey of the reactivity of acetone oxime towards oxomolybdenum(VI) complexes has allowed us to characterize, beside the already described $\kappa^2 N,O$ and μ-$\kappa N:O$ modes, three unprecedented co-ordination modes of the oxime function: the end-on κO mode for the zwitterionic acetone oxime ligand and the μ_3-$\kappa N:\kappa^2 O$ and μ_4-$\kappa^2 N:\kappa^2 O$ modes {the latter in $[NBu^n{}_4]_2[Mo_4O_{12}(Me_2CNO)_2]$[1]} for the acetone oximato-ligand. We have also established that acetone oxime can act as a source of NO and thus provided a new route for the synthesis of nitrosyl complexes. Moreover, condensation reactions between classical nitrosyl species and oxomolybdenum(VI) complexes appear to be an attractive and promising alternative to the hydroxylamine nitrosylation for the design of novel oxonitrosyl complexes. Another example of the ability of molybdenum(II) nitrosyl complexes to act as sources of the $[Mo(NO)]^{3+}$ unit is provided by the synthesis of the Keggin derivative $[PMo_{11}O_{39}\{Mo(NO)\}]^{4-}$ by reaction of **2a** with $[PMo_{11}O_{39}]^{7-}$, which was generated *in situ* by base degradation of the parent Keggin anion $[PMo_{12}O_{40}]^{3-}$.[32]

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