Reactivity of Acetone Oxime towards Oxomolybdenum(VI) Complexes. Part 1. Syntheses and Crystal Structures of Tetranuclear Molybdenum(VI) Complexes†

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Reaction of acetone oxime with $[NBu^n_4]_4[\alpha\text{-}Mo_8O_{26}]$ in refluxing methanol yielded $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ **1** while that with $[MoO_2(acac)_2]$ (acac = acetylacetonate) at room temperature resulted in the formation of $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2**. The crystal structures of **1** and **2** have been determined [**1**, space group $P\bar{1}$, $a = 9.009(1)$, $b = 17.860(1)$, $c = 16.769(1)$ Å, $\alpha = 91.624(5)$, $\beta = 101.158(7)$, $\gamma = 91.983(7)°$, $R = 0.037$ for 7429 reflections with $I > 3\sigma(I)$; **2**, space group $P2_1/c$, $a = 9.437(1)$, $b = 8.827(1)$, $c = 13.727(3)$ Å, $\beta = 92.15(1)°$, $R = 0.029$ for 2821 reflections with $I > 3\sigma(I)$]. The anion of **1** displays a cyclic $(MoO_2)_4(\mu\text{-}O)_4$ ring while **2** displays a $Mo^{VI}_4(\mu_3\text{-}OMe)_2$ central core. The $\mu_4\text{-}\kappa^2N{:}\kappa^2O$ co-ordination mode exhibited by the acetone oximate in **1** is unprecedented for such a ligand, so is the end-on co-ordination mode of zwitterionic acetone oxime in **2**. The reactivity of **1** and **2** respectively towards hydrochloric acid and tetrabutylammonium hydroxide was studied.

The recent but rapidly expanding development of polyoxometalate co-ordination chemistry[1] arises from the perceived analogies between polyoxometalates and metal oxide surfaces[2,3] and their own catalytic activity towards organic substrate molecules.[4] Selected examples include methoxo-,[5,6] alkoxo-,[7] formyl,[8] acetal,[9] pyridine,[10a] pyrazole,[10b] imidazole,[10c] thiocyanato,[10d] cyclopentadienyl,[11] imido-,[12] hydrazido-[13] or diazenido-[14] derivatives of polyoxometalates. Beyond the understanding of catalyst-to-substrate interactions and the modelling of industrial (methanol oxidation,[15] ammoxidation of propene[16]) or biological (nitrogen fixation[17]) processes, this approach also aims to achieve the stabilization of still unknown species. One of the most striking examples is that of the V_6O_{19} core with branched polyhydroxylic ligands.[7]

In the course of our investigation of polyoxomolybdate co-ordination chemistry with amide oximes we have characterized the new anion $[Mo_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$, which displays a cyclic Mo_4O_{12} core capped by two acetamide oximate ligands linked in a $\mu_4\text{-}\kappa^2N{:}\kappa^2O$ unprecedented fashion.[18] Assuming that the oxime function was sufficient to ensure stabilization of the Mo_4O_{12} ring, we then turned to the acetone oxime ligand. We report here the synthesis and characterization of $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ **1** and $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2**. Their molecular structures, determined by single-crystal X-ray analysis, will be discussed in relation to those of $[NBu^n_4]_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]$[18] and $[NBu^n_4]_2[Mo_4O_{10}(OMe)_6]$.[5] They reveal two new co-ordination modes of the acetone oxime ligand and, together with the structures of the nitrosyl complexes to be described in the following paper,[19] they emphasize the versatility and potential of this ligand.

Experimental

Acetone oxime, dimethylhydroxylamine hydrochloride, 1 mol dm $^{-3}$ methanolic tetrabutylammonium hydroxide and reagent grade solvents were obtained from Aldrich and used as supplied. The complexes $[MoO_2(acac)_2]$ (acac = acetylacetonate)[20] and $[NBu^n_4]_4[\alpha\text{-}Mo_8O_{26}]$[21] were prepared as described in the literature. Methanolic solutions of hydrochloric acid were obtained by bubbling HCl(g) in methanol. Their concentrations were subsequently determined by titration of an aliquot diluted in water. The IR spectra were recorded from KBr pellets on a Perkin Elmer 597 spectrometer. Elemental analyses were performed by the Service Central d'Analyse of the Centre National de la Recherche Scientifique (Vernaison, France).

Preparation of Complexes.—$[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ **1**. *From* $[NBu^n_4]_4[\alpha\text{-}Mo_8O_{26}]$. To a suspension of $[NBu^n_4]_4[\alpha\text{-}Mo_8O_{26}]$ (10.75 g, 5 mmol) in methanol (50 cm^3) was added Me_2CNOH (7.3 g, 100 mmol). The resulting mixture was stirred and boiled under reflux for 4 h, after which the pink clear solution was filtered to remove any solid particles and allowed to stand at room temperature. Within a few hours, colourless crystals of complex **1**·*x*MeOH deposited as thin plates (10 g, 83% based on Mo). They were filtered off and found to decompose rapidly outside their mother-liquor, probably by loss of solvent of crystallization. Air-stable crystals, more convenient for X-ray analysis, were obtained by reaction in ethanol {in this case, some yellow $[NBu^n_4]_2[Mo_6O_{19}]$ was discarded after reflux}. IR: 2960m, 2880m, 1610w, 1485m, 1380w, 935s, 910s, 780s and 700s cm^{-1} (Found: C, 38.3; H, 7.0; Mo, 31.7; N, 4.7. $C_{38}H_{84}Mo_4N_4O_{14}$ requires C, 37.9; H, 7.0; Mo, 31.9; N, 4.7%).

From $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2**. To a solution of complex **2** (0.045 g, 0.056 mmol) and Me_2CNOH (0.08 g, 1.12 mmol) in methanol (5 cm^3) was added dropwise a 1 mol dm^{-3} solution of NBu^n_4OH in methanol (0.11 cm^3, 0.11 mmol) and the resulting mixture heated to reflux for 2.5 h. After concentration and standing at room temperature it yielded colourless crystals of **1**, which were filtered off and washed with diethyl ether.

$[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2**. *From* $[MoO_2(acac)_2]$. A mixture of $[MoO_2(acac)_2]$ (1.63 g, 5 mmol) and Me_2CNOH (1.8 g, 25 mmol) in methanol (10 cm^3) was stirred at room temperature for 7 h. After 1 d the cloudy yellow solution was clarified by passage over a filter-paper. Orange-red ill shaped crystals of complex **2** then slowly grew from the filtrate within 3 weeks. They were filtered off and washed with diethyl ether (0.3 g, 30%). IR: 3150w, 1135m, 1035w, 980m, 940s, 920s, 880s, 700s,

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

680s and 560 cm^{-1} (Found: C, 14.6; H, 3.4; Mo, 45.8; N, 3.6. $\mathrm{C_{10}H_{26}Mo_4N_2O_{16}}$ requires C, 14.7; H, 3.2; Mo, 47.1; N, 3.4%).

From $[\mathrm{NBu^n_4}]_2[\mathrm{Mo_4O_{12}(Me_2CNO)_2}]$ **1**. To a mixture of complex **1** (1.2 g, 1 mmol) and $\mathrm{Me_2CNOH}$ (1.46 g, 20 mmol) in methanol (10 cm^3) was added dropwise a 12 mol dm^{-3} solution of HCl in methanol (0.5 cm^3, 6 mmol). Stirring at room temperature for 7 h afforded **2** as a white precipitate, which was filtered off and washed with diethyl ether (0.8 g, 98%).

$[\mathrm{NBu^n_4}]_2[\mathrm{Mo_4O_{10}(OMe)_4Cl_2}]$ **3**.—*From* $[\mathrm{NBu^n_4}]_2[\mathrm{Mo_4O_{12}(Me_2CNO)_2}]$ **1**. A mixture of complex **1** (1.2 g, 1 mmol) and 10 mol dm^{-3} methanolic hydrochloric acid (1 cm^3, 10 mmol) in methanol (10 cm^3) was boiled under reflux for 3 h, after which a white solid was filtered off. Within a few days, light yellow crystals of **3** deposited from the green filtrate. They were identified by IR spectroscopy, microanalysis and lattice parameter determinations. IR: 2960m, 2880m, 1485m, 1380w, 1025m, 995m, 945w, 920s, 905s, 745 (sh), 710s and 550m cm^{-1} (Found: C, 35.6; H, 7.0; N, 2.3. Calc. for $\mathrm{C_{36}H_{84}Cl_2Mo_4N_2O_{14}}$: C, 35.5; H, 6.9; N, 2.3%).

From $[\mathrm{NBu^n_4}]_4[\alpha\text{-}\mathrm{Mo_8O_{26}}]$. A mixture of $[\mathrm{NBu^n_4}]_4[\alpha\text{-}\mathrm{Mo_8O_{26}}]$ (2.15 g, 1 mmol) and $[\mathrm{Me_2NHOH}]\mathrm{Cl}$ (1.91 g, 20 mmol) in methanol (15 cm^3) was heated under reflux until a clear yellow-green solution was obtained. Upon allowing the solution to cool slowly to room temperature, crystals of complex **3** were deposited within 2–3 h (1.35 g, 55%).

X-Ray Crystallography.—Crystal data, data collection and refinement parameters for complexes **1** and **2** 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). The lattice parameters and the orientation matrix were obtained from a least-squares fit of the setting angles of 25 automatically centred reflections in the range $15.5 < \theta < 16.5°$ for **1** and in the range $17 < \theta < 18°$ for **2**. 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 either by direct[22] (compound **1**) or Patterson (**2**) methods and subsequent Fourier syntheses. Neutral-atom scattering factors and anomalous dispersion correction were taken from ref. 23. An empirical absorption correction was applied using DIFABS.[24] The hydrogen atoms of the anion of **1** and those of complex **2** were located on Fourier difference maps, but those of the tetrabutylammonium cations of **1** were placed in idealized positions (C–H 0.95 Å). All hydrogen atoms were introduced in fixed positions in the final full-matrix least-squares refinement. All non-hydrogen atoms were anisotropically refined. Computations were performed on a MicroVax II computer, using the CRYSTALS system.[25] Final atomic coordinates of non-hydrogen atoms are presented in Tables 2 and 3, selected bond lengths and angles in Tables 4 and 5.

Table 1 Summary of crystallographic data for $[\mathrm{NBu^n_4}]_2[\mathrm{Mo_4O_{12}(Me_2CNO)_2}]$ **1** and $[\mathrm{Mo_4O_{10}(OMe)_4(Me_2CNHO)_2}]$ **2**

	1	**2**
Molecular formula	$\mathrm{C_{38}H_{84}Mo_4N_4O_{14}}$	$\mathrm{C_{10}H_{26}Mo_4N_2O_{16}}$
M	1204.87	814.08
Crystal dimensions/mm	0.18 × 0.41 × 0.43	0.22 × 0.28 × 0.33
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	9.009(1)	9.437(1)
b/Å	17.860(1)	8.827(1)
c/Å	16.769(1)	13.727(3)
α/°	91.624(5)	90.0
β/°	101.158(7)	92.15(1)
γ/°	91.983(7)	90.0
U/Å^3	2643(4)	1142.6(6)
Z	2	2
$F(000)$	1240	792
μ(Mo-Kα)/cm^{-1}	9.61	21.70
D_c/g cm^{-3}	1.51	2.37
2θ range/°	2–50	2–60
Scan width ω–2θ/°	$0.8 + 0.345 \tan\theta$	$1.2 + 0.345 \tan\theta$
Scan speed/° min^{-1}	1.5–6.7	2.2–6.7
Range *hkl* collected	±10, ±21, 0–19	±13, 0–12, 0–19
No. of reflections collected	9654	3650
No. of unique reflections	9302	3326
Merging R factor	0.013	0.024
No. of reflections with $I > 3\sigma(I)$	7429	2821
No. least-squares parameters	542	146
Goodness-of-fit index S	2.7	3.2
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.037	0.029
$R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w F_o^{\,2}]^{\frac{1}{2}}$ (w = 1.0)	0.041	0.031

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

Results and Discussion

Reaction of acetone oxime with $[\mathrm{NBu^n_4}]_4[\alpha\text{-}\mathrm{Mo_8O_{26}}]$ in methanol affords $[\mathrm{NBu^n_4}]_2[\mathrm{Mo_4O_{12}(Me_2CNO)_2}]$ **1** in good yield. In addition to the features characteristic of tetrabutylammonium cations, its IR spectrum displays absorbances attributed to Mo=O (935 and 910 cm^{-1}) and Mo–O–Mo groups (780 and 700 cm^{-1}). The weak band at 1610 cm^{-1} can be assigned to the ligand ν(C=N) stretching vibration. Starting from $[\mathrm{NBu^n_4}]_2[\mathrm{Mo_6O_{19}}]$ results in a mixture of **1** and $[\{\mathrm{Mo(NO)(\mu\text{-}OMe)(Me_2CNO)_2}\}_2]$, while the reaction of $[\mathrm{MoO_2(acac)_2}]$ and $\mathrm{Me_2CNOH}$ in methanol at room temperature gives $[\mathrm{Mo_4O_{10}(OMe)_4(Me_2CNHO)_2}]$ **2** in poor yield. When $[\mathrm{MoO_2(acac)_2}]$ and $\mathrm{Me_2CNOH}$ are heated to reflux only the nitrosyl complex $[\mathrm{Mo(NO)(acac)_2(Me_2CNO)}]$ is obtained.[19] That **2** also belongs to the polyoxometalate family can be inferred from its IR spectrum, which exhibits a pattern of bands compatible with the presence of Mo=O (940, 920 cm^{-1}) and Mo–O–Mo units (700, 680 and 560 cm^{-1}). It further presents absorbances at 1035 and 980 cm^{-1}, which can be assigned to ν(O–C) stretching vibrations. Finally, the weak band at 3150 cm^{-1} can be attributed to the ν(N–H) stretching vibration, which supports the zwitterionic formulation of the ligand (see below).

Since complexes **1** and **2** are related by a simple acid–base equilibrium (1), we anticipated that the yield of **2** could be improved by using **1** as a precursor. However, acidification of a methanolic solution of **1** and subsequent reflux leads to the already known compound $[\mathrm{NBu^n_4}]_2[\mathrm{Mo_4O_{10}(OMe)_4Cl_2}]$ **3**.[5] The present procedure thus provides an alternative to that described in the literature. Compound **3** itself reacts with acetone oxime in methanol to give $[\{\mathrm{Mo(NO)(\mu\text{-}OMe)(Me_2CNO)_2}\}_2]$, while the reaction of **1** with hydrochloric acid and acetone oxime under reflux yields $[\mathrm{Mo_2(NO)_2(OMe)_2Cl(Me_2CNO)_3(Me_2CNHO)}]$.[19] It is only at room temperature that this latter route stops at complex **2** according to equation (1). The reverse reaction, *i.e.* from **2** to **1**, was achieved by boiling

$$[\mathrm{NBu^n_4}]_2[\mathrm{Mo_4O_{12}(Me_2CNO)_2}] + 2\mathrm{HCl} + 4\mathrm{MeOH} \rightleftharpoons [\mathrm{Mo_4O_{10}(OMe)_4(Me_2CNHO)_2}] + 2\mathrm{NBu^n_4Cl} + 2\mathrm{H_2O} \quad (1)$$

under reflux a solution of **2**, acetone oxime and $\mathrm{NBu^n_4OH}$. In the absence of the organic ligand, only $[\mathrm{NBu^n_4}]_4[\alpha\text{-}\mathrm{Mo_8O_{26}}]$ is isolated. The interrelationships between compounds **1**–**3** and the synthetic procedures are summarized in Scheme 1.

The formation of the nitrosyl complexes, $[\mathrm{Mo(NO)(acac)_2(Me_2CNO)}]$, $[\{\mathrm{Mo(NO)(\mu\text{-}OMe)(Me_2CNO)_2}\}_2]$ and $[\mathrm{Mo_2(NO)_2(OMe)_2Cl(Me_2CNO)_3(Me_2CNHO)}]$ described in

Table 2 Fractional atomic coordinates* for $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ **1**

Atom	*x*	*y*	*z*
Mo(1)	−0.107 49(5)	0.040 05(3)	−0.137 53(3)
Mo(2)	−0.105 11(5)	0.111 16(2)	0.042 80(3)
O(1)	−0.006 8(4)	0.090 0(2)	−0.196 2(2)
O(2)	−0.272 2(4)	0.013 4(2)	−0.202 3(2)
O(3)	−0.275 2(4)	0.121 7(2)	0.071 5(2)
O(4)	−0.009 3(4)	0.194 1(2)	0.073 3(3)
O(5)	0.008 5(4)	−0.046 3(2)	−0.124 1(2)
O(6)	−0.153 4(4)	0.123 1(2)	−0.073 2(2)
O(7)	−0.168 0(4)	0.000 5(2)	−0.025 3(2)
N(2)	0.128 6(4)	0.070 6(2)	−0.002 8(3)
C(1)	0.231 0(6)	0.106 8(3)	−0.031 1(3)
C(2)	0.201 5(7)	0.183 0(3)	−0.061 8(4)
C(3)	0.381 1(7)	0.075 6(4)	−0.033 6(5)
Mo(21)	−0.431 66(5)	0.370 33(2)	−0.521 61(3)
Mo(22)	−0.598 23(6)	0.492 42(3)	−0.642 76(3)
O(21)	−0.539 2(5)	0.293 8(2)	−0.505 0(2)
O(22)	−0.265 4(5)	0.334 2(2)	−0.534 1(3)
O(23)	−0.516 5(5)	0.521 1(2)	−0.720 7(2)
O(24)	−0.784 9(5)	0.477 2(2)	−0.686 9(2)
O(25)	−0.392 3(4)	0.415 1(2)	−0.415 6(2)
O(26)	−0.541 1(4)	0.390 0(2)	−0.629 1(2)
O(27)	−0.385 9(4)	0.485 7(2)	−0.551 8(2)
N(22)	−0.325 8(5)	0.541 1(2)	−0.492 4(3)
C(21)	−0.203 5(6)	0.572 4(3)	−0.504 0(3)
C(22)	−0.127 1(7)	0.632 8(3)	−0.444 2(4)
C(23)	−0.132 9(8)	0.550 2(4)	−0.574 2(4)
N(30)	−0.540 4(5)	0.215 2(2)	0.235 3(3)
C(31)	−0.634 0(7)	0.249 1(3)	0.160 6(3)
C(32)	−0.681 8(8)	0.328 6(4)	0.172 3(4)
C(33)	−0.774 4(9)	0.355 6(4)	0.093 8(4)
C(34)	−0.821(1)	0.435 6(5)	0.102 0(6)
C(35)	−0.500 3(7)	0.137 5(3)	0.209 6(4)
C(36)	−0.413 4(8)	0.092 7(4)	0.277 2(4)
C(37)	−0.348 1(9)	0.024 8(4)	0.242 1(5)
C(38)	−0.270(1)	−0.024 2(5)	0.304 8(7)
C(39)	−0.630 3(7)	0.211 5(3)	0.303 6(4)
C(40)	−0.779 2(9)	0.166 8(4)	0.282 3(5)
C(41)	−0.846(1)	0.159 2(6)	0.357 4(7)
C(42)	−0.911(5)	0.095(1)	0.401(2)
C(43)	−0.397 9(7)	0.263 6(3)	0.268 5(3)
C(44)	−0.287 4(8)	0.271 3(4)	0.210 9(4)
C(45)	−0.151 6(9)	0.323 5(5)	0.248 1(6)
C(46)	−0.184(1)	0.399 5(6)	0.255 1(7)
N(50)	−0.652 9(5)	0.733 9(3)	0.243 8(3)
C(51)	−0.643 8(8)	0.740 7(4)	0.154 8(4)
C(52)	−0.616(1)	0.667 9(5)	0.112 2(5)
C(53)	−0.622(1)	0.674 7(5)	0.024 1(5)
C(54)	−0.605(1)	0.599 9(7)	−0.017 3(6)
C(55)	−0.768 4(7)	0.672 4(4)	0.253 8(4)
C(56)	−0.926 4(8)	0.679 0(4)	0.202 6(4)
C(57)	−1.024 4(9)	0.610 6(5)	0.212 1(6)
C(58)	−1.180(1)	0.610 3(6)	0.159 8(6)
C(59)	−0.501 4(7)	0.710 2(4)	0.293 1(4)
C(60)	−0.372 4(8)	0.766 5(4)	0.298 5(5)
C(61)	−0.236 5(9)	0.739 1(6)	0.358 6(6)
C(62)	−0.108(1)	0.791 1(7)	0.378 0(8)
C(63)	−0.694 4(8)	0.809 0(4)	0.274 5(4)
C(64)	−0.690 4(9)	0.816 4(5)	0.346 9(5)
C(65)	−0.723(1)	0.895 2(5)	0.389 3(5)
C(66)	−0.712(2)	0.904 5(8)	0.479 3(7)

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

Table 3 Fractional atomic coordinates* for $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2**

Atom	*x*	*y*	*z*
Mo(1)	0.252 40(4)	−0.117 65(4)	0.094 63(2)
Mo(2)	0.046 98(4)	0.179 32(4)	0.062 36(2)
O(1)	0.313 8(3)	−0.273 7(4)	−0.007 2(2)
O(2)	0.399 5(3)	−0.011 7(4)	0.074 5(2)
O(3)	−0.034 6(4)	0.286 5(3)	0.145 7(2)
O(4)	0.187 8(3)	0.283 6(3)	0.029 3(2)
O(5)	0.134 9(3)	0.031 5(3)	0.146 9(2)
O(6)	−0.062 5(3)	0.242 7(3)	−0.061 7(2)
O(7)	0.296 2(3)	−0.225 1(4)	0.193 8(2)
O(8)	−0.127 2(3)	0.018 0(3)	0.037 7(2)
N(1)	0.426 5(4)	−0.258 8(4)	−0.063 1(3)
C(1)	0.459 9(4)	−0.364 4(5)	−0.121 3(3)
C(2)	0.377 1(6)	−0.504 5(6)	−0.124 9(4)
C(3)	0.581 1(5)	−0.344 0(7)	−0.184 5(3)
C(6)	−0.029 4(6)	0.373 9(6)	−0.117 5(4)
C(8)	−0.198 1(5)	−0.026 9(5)	0.125 2(3)

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

the following paper,[19] reveals that acetone oxime can also act as a nitrosylating agent towards oxomolybdenum(VI) complexes. Such behaviour has previously been observed for acetamide oxime.[26]

The structure of $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ **1** consists of discrete $[Mo_4O_{12}(Me_2CNO)_2]^{2-}$ anions, located at crystallographic inversion centres, and of tetrabutylammonium cations. The asymmetric unit contains two independent $[Mo_2O_6(Me_2CNO)]^-$ half-anions and two tetrabutylammonium cations. Final fractional atomic coordinates and selected bond lengths and angles are listed in Tables 2 and 4 respectively; a perspective view[27] of the centrosymmetrical $[Mo_4O_{12}(Me_2CNO)_2]^{2-}$ anion is depicted in Fig. 1. It can be viewed as a Mo_4O_{12} ring, based on four *cis*-MoO_2 units linked by four doubly bridging oxo-ligands and capped above and below by an acetone oximato-ligand. The latter is bound to the four molybdenum centres in a μ_4-κ^2N:κ^2O co-ordination fashion involving both its nitrogen and oxygen atoms. This co-ordination mode is unprecedented in the chemistry of the acetone oximato-ligand for which only the κ^2N,O[28] and μ-κN:O[29] co-ordination modes have been previously described. It results in the formation of two-electron three-centre Mo–N–Mo bonds. However, the Mo(1)–N(2) and Mo(2)–N(2) distances of 2.798 and 2.535 Å respectively (average values) reveal the dissymmetry in the organic ligand bonding. This is further reflected, but to a lesser extent, in the Mo(1)–O(7) and Mo(2)–O(7) distances of 2.184 and 2.233 Å (average values) respectively. As expected, the Mo–N distances are longer than that observed in amine derivatives: 2.34–2.39 Å for example in $[Mo_4O_{12}(C_{12}H_{30}N_4S_2)_2]$.[30] Finally, the N(2)–O(7) and N(2)–C(1) bond lengths of 1.400 and 1.275 Å (average values), compared to 1.36 and 1.29 Å for the free oxime,[31] are consistent with a single and a double bond respectively. Each molybdenum centre displays a MoO_5N pseudo-octahedral environment and the typical two short (to the terminal oxo-ligands), two intermediate (to the doubly bridging oxo-ligands) and two long (to the acetone oximato-ligands) bond pattern observed in isopolymolybdates. The polyhedral description[32] of the structure corresponds to two pairs of face-sharing octahedra connected through two corners as shown in Fig. 2. The overall geometry of the $[Mo_4O_{12}(Me_2CNO)_2]^{2-}$ anion is similar to that of $[M_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ (M = Mo or W).[18]

A perspective view[27] of $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2** is shown in Fig. 3; final fractional atomic coordinates and selected bond lengths and angles are listed in Tables 3 and 5 respectively. The species is situated on a crystallographic centre of symmetry and is based on a ring of alternate *cis*-MoO_2 units and doubly bridging oxo- or methoxo-ligands. The co-ordination sphere of Mo(1) is completed by a zwitterionic acetone oxime ligand and

Table 4 Selected bond lengths (Å) and angles (°) for $[NBu^n{}_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ **1**

Mo(1) ··· Mo(2)	3.2425(7)	Mo(21) ··· Mo(22)	3.2297(6)	Mo(2)–O(5′)	1.913(4)	Mo(22)–O(25′)	1.909(3)
Mo(1)–O(1)	1.710(4)	Mo(21)–O(21)	1.708(4)	Mo(2)–O(6)	1.928(4)	Mo(22)–O(26)	1.925(3)
Mo(1)–O(2)	1.705(4)	Mo(21)–O(22)	1.699(4)	Mo(2)–O(7)	2.253(3)	Mo(22)–O(27)	2.212(4)
Mo(1)–O(5)	1.887(3)	Mo(21)–O(25)	1.892(3)	Mo(2)–N(2′)	2.498(4)	Mo(22)–N(22′)	2.571(5)
Mo(1)–O(6)	1.913(4)	Mo(21)–O(26)	1.928(3)	O(7)–N(2)	1.400(5)	O(27)–N(22)	1.401(5)
Mo(1)–O(7)	2.188(3)	Mo(21)–O(27)	2.180(3)	N(2)–C(1)	1.280(6)	N(22)–C(21)	1.270(7)
Mo(1)–N(2′)	2.813(4)	Mo(21)–N(22′)	2.783(5)	C(1)–C(2)	1.484(7)	C(21)–C(22)	1.504(8)
Mo(2)–O(3)	1.708(3)	Mo(22)–O(23)	1.703(4)	C(1)–C(3)	1.488(7)	C(21)–C(23)	1.492(8)
Mo(2)–O(4)	1.703(4)	Mo(22)–O(24)	1.710(4)				
O(2)–Mo(1)–O(1)	104.3(2)	O(22)–Mo(21)–O(21)	104.0(2)	O(7)–Mo(2)–O(4)	159.4(2)	O(27)–Mo(22)–O(24)	158.6(2)
O(5)–Mo(1)–O(1)	99.3(2)	O(25)–Mo(21)–O(21)	99.3(2)	O(7)–Mo(2)–O(5′)	81.2(1)	O(27)–Mo(22)–O(25′)	81.6(1)
O(5)–Mo(1)–O(2)	105.9(2)	O(25)–Mo(21)–O(22)	105.4(2)	O(7)–Mo(2)–O(6)	68.3(1)	O(27)–Mo(22)–O(26)	69.1(1)
O(6)–Mo(1)–O(1)	97.0(2)	O(26)–Mo(21)–O(21)	97.3(2)	N(2′)–Mo(2)–O(3)	169.3(2)	N(22′)–Mo(22)–O(23)	169.0(2)
O(6)–Mo(1)–O(2)	106.3(2)	O(26)–Mo(21)–O(22)	106.2(2)	N(2′)–Mo(2)–O(4)	86.9(2)	N(22′)–Mo(22)–O(24)	86.9(2)
O(6)–Mo(1)–O(5)	138.8(2)	O(26)–Mo(21)–O(25)	139.3(1)	N(2′)–Mo(2)–O(5′)	74.1(1)	N(22′)–Mo(22)–O(25′)	73.4(1)
O(7)–Mo(1)–O(1)	156.8(2)	O(27)–Mo(21)–O(21)	156.7(2)	N(2′)–Mo(2)–O(6)	77.0(1)	N(22′)–Mo(22)–O(26)	76.5(1)
O(7)–Mo(1)–O(2)	98.0(2)	O(27)–Mo(21)–O(22)	98.4(2)	N(2′)–Mo(2)–O(7)	73.9(1)	N(22′)–Mo(22)–O(27)	73.1(1)
O(7)–Mo(1)–O(5)	80.7(1)	O(27)–Mo(21)–O(25)	80.8(1)	Mo(2′)–O(5′)–Mo(1)	142.0(2)	Mo(22′)–O(25′)–Mo(21)	142.6(2)
O(7)–Mo(1)–O(6)	69.9(1)	O(27)–Mo(21)–O(26)	69.8(1)	Mo(2)–O(6)–Mo(1)	115.2(2)	Mo(22)–O(26)–Mo(21)	113.9(2)
N(2′)–Mo(1)–O(1)	89.1(2)	N(22′)–Mo(21)–O(21)	88.5(2)	Mo(2)–O(7)–Mo(1)	93.8(1)	Mo(22)–O(27)–Mo(21)	94.7(1)
N(2′)–Mo(1)–O(2)	166.5(2)	N(22′)–Mo(21)–O(22)	167.6(2)	N(2)–O(7)–Mo(1)	120.9(3)	N(22)–O(27)–Mo(21)	122.3(3)
N(2′)–Mo(1)–O(5)	73.3(1)	N(22′)–Mo(21)–O(25)	72.3(1)	N(2)–O(7)–Mo(2)	126.7(3)	N(22)–O(27)–Mo(22)	125.6(3)
N(2′)–Mo(1)–O(6)	69.4(1)	N(22′)–Mo(21)–O(26)	71.2(1)	Mo(2)–N(2)–Mo(1)	75.0(1)	Mo(22)–N(22)–Mo(21)	74.1(1)
N(2′)–Mo(1)–O(7)	68.6(1)	N(22′)–Mo(21)–O(27)	69.2(1)	O(7)–N(2)–Mo(1)	103.8(3)	O(27)–N(22)–Mo(21)	105.0(3)
O(4)–Mo(2)–O(3)	103.4(2)	O(24)–Mo(22)–O(23)	103.7(2)	O(7)–N(2)–Mo(2)	111.0(3)	O(27)–N(22)–Mo(22)	109.1(3)
O(5′)–Mo(2)–O(3)	101.1(2)	O(25′)–Mo(22)–O(23)	101.6(2)	C(1)–N(2)–Mo(1)	105.1(3)	C(21)–N(22)–Mo(21)	119.0(4)
O(5′)–Mo(2)–O(4)	101.2(2)	O(25′)–Mo(22)–O(24)	100.3(2)	C(1)–N(2)–Mo(2)	132.1(3)	C(21)–N(22)–Mo(22)	128.8(4)
O(6)–Mo(2)–O(3)	103.1(2)	O(26)–Mo(22)–O(23)	104.0(2)	C(1)–N(2)–O(7)	115.1(4)	C(21)–N(22)–O(27)	113.3(4)
O(6)–Mo(2)–O(4)	100.4(2)	O(26)–Mo(22)–O(24)	99.2(2)	C(2)–C(1)–N(2)	119.6(5)	C(22)–C(21)–N(22)	118.5(5)
O(6)–Mo(2)–O(5′)	142.6(1)	O(26)–Mo(22)–O(25′)	142.8(1)	C(3)–C(1)–N(2)	122.4(5)	C(23)–C(21)–N(22)	121.9(5)
O(7)–Mo(2)–O(3)	96.1(2)	O(27)–Mo(22)–O(23)	96.7(2)	C(3)–C(1)–C(2)	118.0(5)	C(23)–C(21)–C(22)	119.5(5)

Table 5 Selected bond lengths (Å) and angles (°) for $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2**

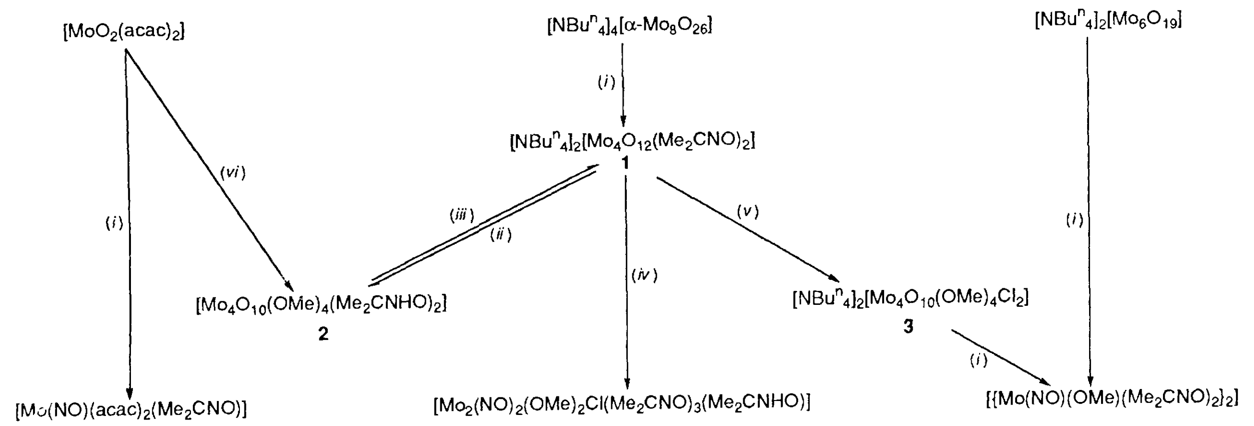
Mo(1)–O(1)	2.061(3)	Mo(1)–O(2)	1.705(3)
Mo(1)–O(5)	1.881(3)	Mo(1)–O(6)	2.139(3)
Mo(1)–O(7)	1.697(3)	Mo(1)–O(8)	2.304(3)
Mo(2)–O(3)	1.692(3)	Mo(2)–O(4)	1.693(3)
Mo(2)–O(5′)	1.915(3)	Mo(2)–O(6)	2.037(3)
Mo(2)–O(8′)	2.192(3)	Mo(2)–O(8)	2.360(3)
O(1)–N(1)	1.341(4)	O(6)–C(6)	1.429(5)
N(1)–C(1)	1.275(5)	C(1)–C(2)	1.463(7)
O(8)–C(8)	1.452(4)	C(1)–C(3)	1.472(6)
O(2)–Mo(1)–O(1)	90.3(1)	O(5)–Mo(1)–O(1)	155.7(1)
O(5)–Mo(1)–O(2)	100.0(1)	O(6)–Mo(1)–O(1)	76.5(1)
O(6)–Mo(1)–O(2)	158.4(1)	O(6)–Mo(1)–O(5)	86.6(1)
O(7)–Mo(1)–O(1)	96.0(2)	O(7)–Mo(1)–O(2)	105.2(2)
O(7)–Mo(1)–O(5)	102.4(1)	O(7)–Mo(1)–O(6)	93.3(1)
O(8)–Mo(1)–O(1)	82.5(1)	O(8)–Mo(1)–O(2)	93.4(1)
O(8)–Mo(1)–O(5)	75.0(1)	O(8)–Mo(1)–O(6)	68.28(9)
O(8)–Mo(1)–O(7)	161.4(1)		
O(4)–Mo(2)–O(3)	105.0(2)	O(5′)–Mo(2)–O(3)	99.7(1)
O(5′)–Mo(2)–O(4)	101.9(1)	O(6)–Mo(2)–O(3)	100.5(1)
O(6)–Mo(2)–O(4)	90.3(1)	O(6)–Mo(2)–O(5′)	152.7(1)
O(8)–Mo(2)–O(3)	96.3(1)	O(8)–Mo(2)–O(4)	154.7(1)
O(8)–Mo(2)–O(5′)	87.5(1)	O(8)–Mo(2)–O(6)	72.3(1)
O(8′)–Mo(2)–O(3)	166.0(1)	O(8′)–Mo(2)–O(4)	88.5(1)
O(8′)–Mo(2)–O(5′)	73.1(1)	O(8′)–Mo(2)–O(6)	83.1(1)
O(8)–Mo(2)–O(8′)	71.7(1)		
N(1)–O(1)–Mo(1)	124.9(3)	Mo(2′)–O(5)–Mo(1)	119.6(1)
Mo(2)–O(6)–Mo(1)	115.4(1)	C(6)–O(6)–Mo(1)	120.2(3)
C(6)–O(6)–Mo(2)	123.8(3)	Mo(2)–O(8)–Mo(1)	103.5(1)
Mo(2)–O(8)–Mo(1)	89.39(9)	Mo(2)–O(8)–Mo(2)	108.3(1)
C(8)–O(8)–Mo(1)	121.2(2)	C(8)–O(8)–Mo(2)	114.5(2)
C(8)–O(8)–Mo(2)	116.6(2)	C(1)–N(1)–O(1)	120.4(4)
C(2)–C(1)–N(1)	119.6(4)	C(3)–C(1)–N(1)	119.7(4)
C(3)–C(1)–C(2)	120.6(4)		

one of the two triply bridging methoxo-ligands, while that of Mo(2) is completed by both triply bridging methoxo-ligands; the distorted octahedra share exclusively edges (Fig. 4). The usual pattern of two short (to the terminal oxo-ligands), two intermediate [Mo(1)–O(5), Mo(1)–O(1), Mo(2)–O(5) and Mo(2)–O(6)] and two long (to the remaining methoxo-ligands) bonds is less pronounced than for **1**.

The various structural types of molybdenum tetranuclear cores have recently been discussed in terms of the junction of the four co-ordination polyhedra.[1] Compound **2** belongs to the most widespread type, which consists of a compact assembly of four edge-sharing octahedra. The $[W_4O_{16}]^{8-}$ anion[33] is the prototype of this family of complexes. Although its molybdenum analogue is still unknown, a number of related derivatized tetramolybdates have been described, among them $[Mo_4O_{10}(OMe)_4X_2]^{2-}$ (X = OMe or Cl), $[Mo_4O_{10}(OMe)_2(OC_6H_4O\text{-}o)_2]^{2-}$,[5] $[Mo_4O_{10}(OMe)_2(PhCONO)_2]^{2-}$ [34a] and $[Mo_4O_8(OEt)_2\{MeC(CH_2O)_3\}_2]$.[35] A similar geometry is observed for the asymmetric units present in $[\beta\text{-}Mo_8O_{26}]^{4-}$,[36] $[Mo_8O_{26}X_2]^{n-}$ (X = HCO_2,[8] pyridine,[10a] pyrazole,[10b] imidazole[10c] or NCS[10d]; *n* = 4 or 6) and $[Mo_8O_{24}(OMe)_4]^{4-}$ (ref. 6) and also for $[V_4O_4(OH)_2\{Me_2C(CH_2O)_2\}_4Cl_2]$.[37]

The cyclic $(MO_2)_4(\mu\text{-}O)_4$ ring present in the anion of complex **1** is also rather common. However the type of junction of the co-ordination polyhedra depends on the bridging capacity of the capping ligands. A cyclic assembly of four alternately face- and corner-sharing octahedra is exhibited by $[M_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ (M = Mo or W),[18] $[Mo_4O_{12}(Me_2CNO)_2]^{2-}$ (anion of **1**) and $[W_4O_{12}(NCHCHNO_2)_2]^{4-}$,[38] while that of four edge-sharing octahedral is displayed only by the peroxo species[39] $[Mo_4O_{12}(O_2)_2]^{4-}$. A number of tetramolybdates, among them $[Mo_4O_{12}(OH)(H_2CO_2)]^{3-}$,[9] $[Mo_4O_{12}(OH)(Me_2AsO_2)]^{2-}$ (ref. 40) and $[Mo_4O_{12}F_3]^{3-}$,[41] display a cyclic set of four alternatively face- and edge-sharing octahedra. Finally, in $[Mo_4O_{12}(C_{12}H_{30}N_4S_2)_2]$,[30] the four octahedra are connected only by corners. The M_4O_{12} ring also occurs in polyoxovanadate chemistry, *e.g.* in metavanadate[42] and in metavanadate-supported organometallic complexes.[43]

A survey of the reactivity of acetone oxime towards common



Scheme 1 Synthetic procedures for complexes **1**–**3** and interplay reactions. (*i*) Me_2CNOH, reflux in MeOH; (*ii*) Me_2CNOH, HCl; (*iii*) Me_2CNOH, NBu^n_4OH, reflux in MeOH; (*iv*) Me_2CNOH, HCl, reflux in MeOH; (*v*) HCl, reflux in MeOH; (*vi*) Me_2CNOH

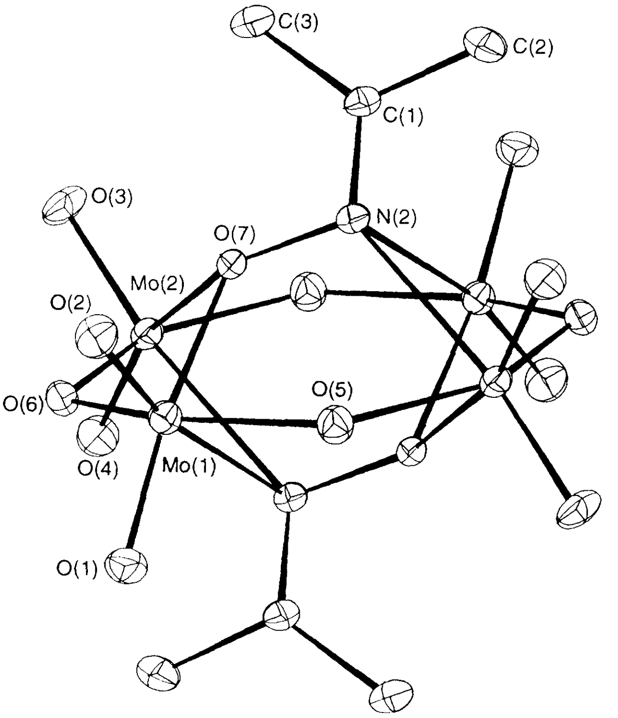


Fig. 1 Perspective view[27] of the anion $[Mo_4O_{12}(Me_2CNO)_2]^{2-}$ in **1**, showing the atom labelling scheme. Hydrogen atoms omitted for clarity

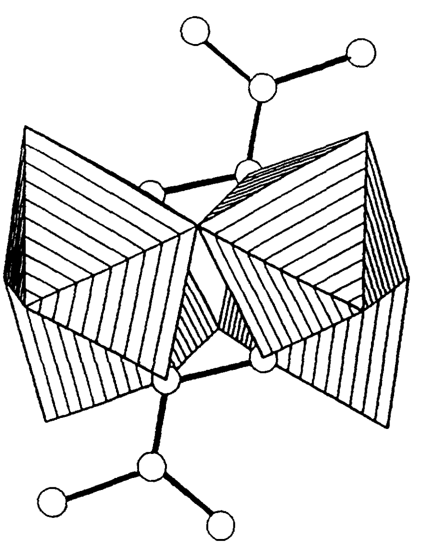


Fig. 2 Polyhedral[32] representation of the anion $[Mo_4O_{12}(Me_2CNO)_2]^{2-}$ in complex **1**

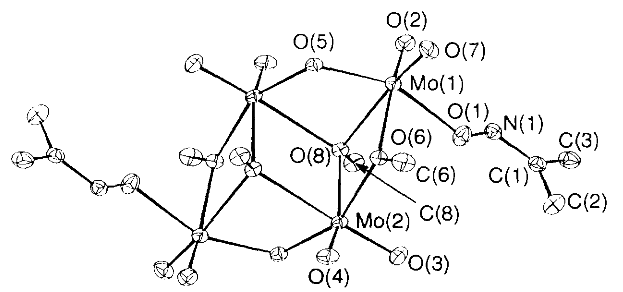


Fig. 3 Perspective view[27] of $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2**, showing the atom labelling scheme. Hydrogen atoms omitted for clarity

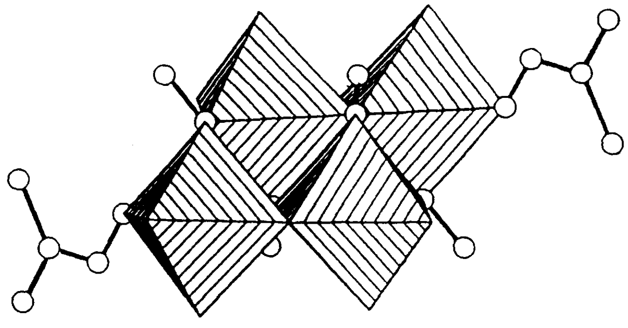


Fig. 4 Polyhedral[32] representation of $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2**

oxomolybdenum(VI) complexes has shown that it closely resembles that of acetamide oxime: this is nicely illustrated by the two similar $[Mo_4O_{12}(Me_2CNO)_2]^{2-}$ and $[Mo_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ anions. However, $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2** is as yet without any equivalent in the co-ordination chemistry of acetamide oxime,* even though the end-on co-ordination mode of zwitterionic acetamide oxime has been demonstrated in mononuclear uranyl complexes.[44] Of course, the NH_2 function brings further diversity in the co-ordination chemistry of amide oximes with respect to that of oximes.[45] Acid–base interconversion reactions between $[NBu^n_4]_2[Mo_4O_{12}(Me_2CNO)_2]$ **1** and $[Mo_4O_{10}(OMe)_4(Me_2CNHO)_2]$ **2** proved to be possible under appropriate conditions. Both compounds are useful precursors for the synthesis of nitrosyl complexes.[19]

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* Note, however, that $[Mo_4O_{10}(OMe)_2\{SC_4H_3C(NH)NO\}_2]^{2-}$, which displays a geometry similar to that of $[Mo_4O_{10}(OMe)_2(PhCONO)_2]^{2-}$,[34a] has been characterized with thiophene-2-carboxamide oxime.[34b]

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