$[M_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ (M = Mo or W), a Tetranuclear Complex with a μ_4-Acetamidoximate Ligand as an Unprecedented Bridge

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Salts of $[M_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ with M = Mo or W have been synthesized and characterised by *X*-ray diffraction.

In view of the perceived analogies between isopolymetalates and metal oxide surfaces, the co-ordination chemistry of isopolymetalates with small organic molecules is of current interest,[1] as demonstrated by reports on the anions $[Mo_8O_{24}(OMe)_4]^{4-}$,[2] $[(HCO)_2Mo_8O_{28}]^{6-}$,[3] $[(H_2CO_2)Mo_4O_{12}(OH)]^{3-}$,[4] (acac = pentane-1,4-dione) and $[(C_5H_5N)_2Mo_8O_{26}]^{4-}$.[5] We have recently observed the reaction of acetamidoxime with $[MoO_2(acac)_2]$, yielding the unexpected compound $[Mo(acac)_2NO\{MeC(NH_2)NO\}]$.[6] Looking for other reactions in which acetamidoxime could behave as a nitrosylating reagent, we found that acetamidoxime reacts with $[Mo_6O_{19}]^{2-}$ and with α-$[Mo_8O_{26}]^{4-}$ to yield the new polymolybdate $[Mo_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$; the same complex is obtained starting from $[W_6O_{19}]^{2-}$.

A solution of $(NBu_4)_4[Mo_8O_{26}]$ (4.305 g) and $MeC(NH_2)NOH$ (2.369 g) in MeCN (100 ml) was refluxed for 1.5 h. $(NBu_4)_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]$ (**1a**) was deposited as colourless parallelepiped crystals within 2 days in 90% yield (based on Mo). The reaction can also be carried out in methanol, leading to the solvat $(NBu_4)_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]\cdot 2MeOH$ (**1b**), which is also obtained from $(NBu_4)_2[Mo_6O_{19}]$ and acetamidoxime in methanol and from the slow reaction of $(NBu_4)_2[Mo_4O_8(OMe)_2(N_2C_6H_5)_4]$[7] with an excess of acetamidoxime in methanol.

The reaction of acetamidoxime with $[MoO_2(acac)_2]$ first produces orange crystals of $[Mo(acac)_2\{MeC(NH_2)NO\}(NO)]$, in *ca.* 30% yield.[6] After several days crystals of $[MeC(NH_2)NHOH]_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]$ (**1c**) are deposited (yield 8%). $[Mo_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ was also unexpectedly formed from the reaction of $(NBu_4)[MeC(NO)NO]$ (0.312 g) with $[MoO_2(acac)_2]$ (0.162 g) dissolved in methanol (10 ml). The brown solution progressively turned yellow-orange, and crystals of (**1b**) were deposited within 2 days.

Table 1. Principal bond lengths (Å) and angles (°).

	(**1a**)			
	Unit 1	Unit 2	(**1c**)	(**2**)
M(1)–O(1)	1.705(3)	1.719(3)	1.710(4)	1.747(9)
M(1)–O(2)	1.698(3)	1.700(3)	1.724(3)	1.726(8)
M(2)–O(3)	1.717(3)	1.701(3)	1.690(4)	1.738(8)
M(2)–O(4)	1.701(3)	1.705(3)	1.714(4)	1.712(8)
M(1)–O(5′)	1.899(3)	1.886(3)	1.887(4)	1.872(8)
M(1)–O(6)	1.936(3)	1.917(3)	1.926(3)	1.901(8)
M(2)–O(5)	1.900(3)	1.921(3)	1.891(4)	1.910(8)
M(2)–O(6)	1.925(3)	1.943(3)	1.957(3)	1.943(8)
M(1)–O(7)	2.200(2)	2.158(3)	2.202(3)	2.192(8)
M(2)–O(7)	2.215(2)	2.222(3)	2.202(3)	2.215(8)
M(1)–N(2′)	2.572(3)	2.758(3)	2.476(4)	2.54(1)
M(2)–N(2′)	2.578(3)	2.405(3)	2.598(4)	2.50(1)
N(2)–C(1)	1.298(5)	1.328(5)	1.328(7)	1.33(1)
N(2)–O(7)	1.420(4)	1.418(4)	1.428(5)	1.42(1)
C(1)–N(1)	1.334(5)	1.311(6)	1.312(7)	1.31(2)
C(1)–C(2)	1.490(6)	1.486(6)	1.487(8)	1.49(2)
O(1)–M(1)–O(2)	104.1(1)	104.1(1)	103.9(2)	102.8(4)
O(3)–M(2)–O(4)	105.0(1)	105.0(2)	105.0(2)	104.9(4)
O(6)–M(1)–O(5′)	143.5(1)	140.8(1)	145.3(1)	144.0(4)
O(6)–M(2)–O(5)	142.8(1)	145.2(1)	142.3(1)	141.6(3)

$[W_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ was prepared from $(NBu_4)_2[W_6O_{19}]$ (3.788 g) added to $MeC(NH_2)NOH$ (1.776 g) in MeOH (25 ml); the mixture was refluxed for 20 h. $(NBu_4)_2[W_4O_{12}\{MeC(NH_2)NO\}_2]\cdot 2MeOH$ (**2**) was produced in 60% yield (based on W).

Compounds (**1a—c**), and (**2**) gave satisfactory analytical results; (**1a**) and (**1c**) are air-stable but the methanol addition compounds (**1b**) and (**2**) slowly lose methanol.

$(NBu_4)_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]$
(**1a**)

$(NBu_4)_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]\cdot 2MeOH$
(**1b**)

$[MeC(NH_2)NHOH]_2[Mo_4O_{12}\{MeC(NH_2)NO\}_2]$
(**1c**)

$(NBu_4)_2[W_4O_{12}\{MeC(NH_2)NO\}_2]\cdot 2MeOH$
(**2**)

The complexes (**1a**), (**1c**), and (**2**) all contain similar centrosymmetrical tetranuclear $[M_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ anions.† The structure of these tetrametalates is based upon a

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† Determinations of cell constants and data collection were carried out at room temperature with Mo-K_α radiation with a Nonius CAD4 diffractometer equipped with a graphite monochromator. Unit cell dimensions were obtained by a least-squares fit of 25 reflections in the range $14 < \theta < 17$ °C. Data were recorded by θ–2θ scan in the range $1.0 < \theta < 25$ °C and were corrected for Lorentz-polarization effects; an empirical absorption correction based upon ψ scan was applied. In the case of (**2**), data were corrected for decay. All calculations were performed with the program CRYSTALS.[18]

Crystal data: (**1a**) $C_{36}H_{82}N_6O_{14}Mo_4$, $M = 1206.84$, triclinic, $P\bar{1}$, $a = 8.902(4)$, $b = 18.052(2)$, $c = 16.546(3)$ Å, $\alpha = 92.60(1)$, $\beta = 102.32(2)$, $\gamma = 93.08(2)°$, $U = 2590(2)$ Å^3, $Z = 2$; 8121 independent reflections measured, 6426 with $I > 3\sigma(I)$, $R = 0.031$, $R_w = 0.033$.

(**1c**) $C_8H_{24}N_8O_{16}Mo_4$, $M = 872.08$, triclinic, $P\bar{1}$, $a = 7.709(3)$, $b = 8.819(5)$, $c = 9.665(2)$ Å, $\alpha = 75.29(2)$, $\beta = 86.98(2)$, $\gamma = 67.69(3)°$, $U = 587.3(1)$ Å^3, $Z = 1$; 2067 independent reflections measured, 1651 with $I > 3\sigma(I)$, $R = 0.039$, $R_w = 0.037$.

(**2**) $C_{38}H_{90}N_6O_{16}W_4$, $M = 1622.56$, monoclinic, $P2_1/c$, $a = 8.955(1)$, $b = 19.414(2)$, $c = 15.585(2)$ Å, $\beta = 91.24(1)°$, $U = 2708.9(9)$ Å^3, $Z = 2$; 5104 independent reflections measured, 3298 with $I > 3\sigma(I)$, $R = 0.038$, $R_w = 0.040$.

Structures were solved by Patterson and Fourier methods. Hydrogen atoms were located on difference Fourier maps. They were isotropically refined [overall refined thermal parameters in (**1c**); arbitrarily fixed thermal parameters in (**1b**) and (**2**)]. Refinement was performed by full-matrix least-squares techniques for (**1c**) and (**2**), in two blocks for (**1b**).

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

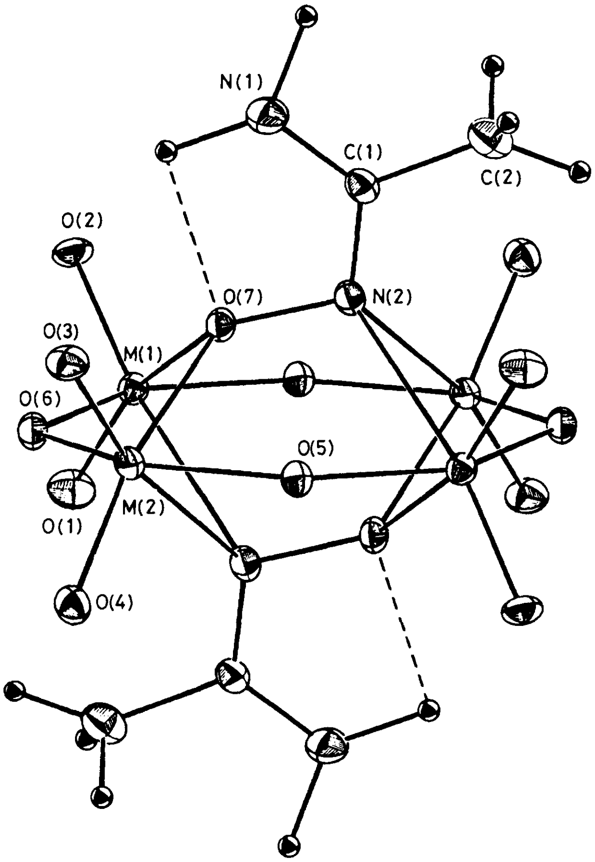

Figure 1. ORTEP drawing of $[W_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ (**2**) showing 20% probability thermal ellipsoids. Hydrogen thermal parameters have been constrained to isotropy: $B = 1.0$ Å^2.

ring of four corner-shared MoO_4 tetrahedra; to this ring, two bridging acetamidoxime ligands are added so that each metal atom becomes octahedrally surrounded. Such a ring has been found in $[(H_2CO_2)Mo_4O_{12}(OH)]^{3-}$,[4] in $[\{Me_2AsO_2\}Mo_4O_{12}(OH)]^{3-}$,[8] and in $[Mo_4O_{12}(O_2)_2]^{4-}$;[9] however such a structure seems unprecedented for tungsten although few tetranuclear tungsten species have been described.[10,11]

A unique feature of the present structures is the bonding of the acetamidoxime ligand. Such μ_4-bonding by the oxime group with N and O ligated to two metal atoms is novel not only with amidoximes but also with oximes. Indeed oximate groups are known to bridge two metal atoms,[12,13] but no example is known with four metal atoms. The oxime nitrogen atom is in a rather unusual situation. The two C–N distances within the ligand are approximately equal and indicate some double-bond character (average C–N = 1.319 Å; see Table 1), while the N–O distance is typical of a single bond (average N–O = 1.421 Å; see Table 1). Thus the oxime nitrogen atom seems too electron-deficient to form two Mo–N bonds (average Mo–N = 2.553 Å; see Table 1). Typical Mo–N distances are in the range 2.34—2.39 Å; for example in $[Mo_4O_{12}(C_{12}H_{30}N_4S_2)]$.[14]

The complexes (**2**) and (**1b**) are isostructural; precession photographs show that lattice constants and unit cell symmetry are the same.

Structure (**1a**) reveals a surprising feature: the unit cell contains two crystallographically independent tetranuclear units. One of them has a pseudo-mirror plane perpendicular to the Mo_4O_4 ring; the second has not. Consequently Mo–N and Mo–O distances become asymmetric in the second; the situation is similar in (**1c**) although not so marked.

In all these tetrametalates, the acetamidoximate ligand is nearly planar, with the exception of the CH_3 hydrogen atoms. This favours a weak intramolecular N(1)H(11) ... O(7) interaction, which also occurs in free amidoximes[15,16] and in other complexes of acetamidoxime.[6,17] A similar interaction also exists in the cation $[MeC(NH_2)NHOH]^+$ of (**1c**); incidentally, the cation structure reveals that amidoxime protonation occurs on the oxime nitrogen atom. There are also intermolecular hydrogen bonds. In (**1c**), anions and cations are connected by one OH ... O and two NH ... O hydrogen bonds; each cation is linked to three different tetranuclear units [O(47) ... O(2) 2.702(6) Å, N(42) ... O(6) 2.804(6) Å, N(41) ... O(1) 2.813(7) Å]. In (**1b**) and (**2**), the shortest intermolecular contacts are between the nitrogen NH_2 atom and an M=O oxygen atom of another tetranuclear unit [N(1) ... O(3) 2.968(5) Å and N(21) ... O(21) 2.842(5) Å in (**1b**), N(1) ... O(3) 2.89(1) Å in (**2**)]. The location of the hydrogen atoms is consistent with these hydrogen bonds.

The noteworthy stability of the $[Mo_4O_{12}\{MeC(NH_2)NO\}_2]^{2-}$ ion is illustrated by the various reactions which yield it. Among them, the most unusual is that of $[MoO_2(acac)_2]$ with $MeC(NO)NO^-$; the reduction mechanism is not clear.

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