

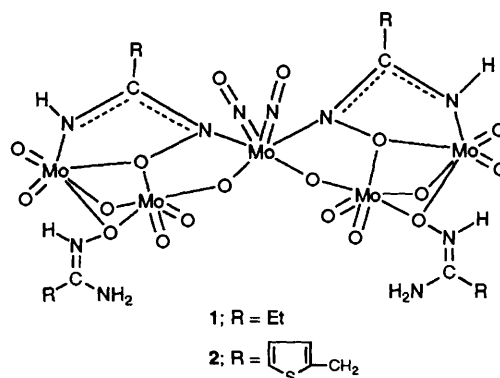
## Oxo–Nitrosyl Polymetalates containing $[M(NO)_2]^{2+}$ Units ( $M = Mo, W$ )

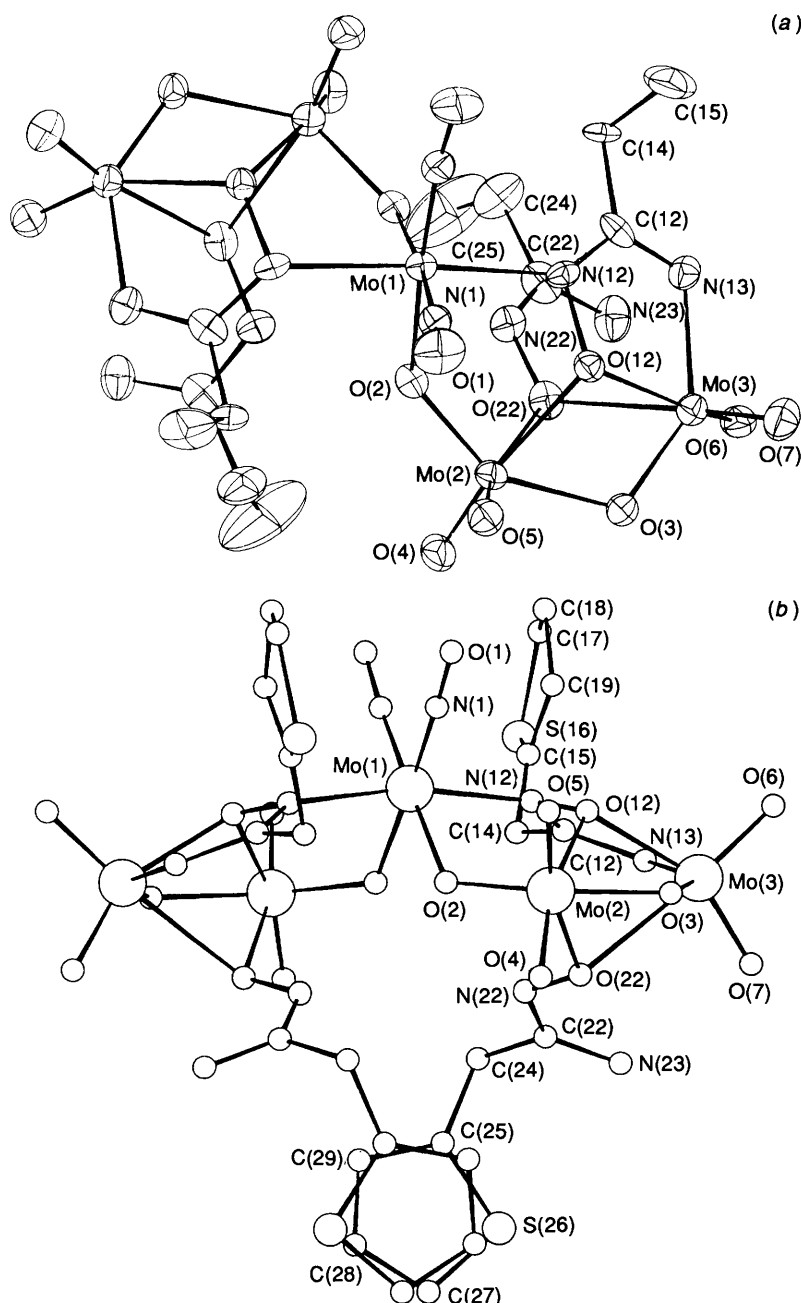
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Oxo–nitrosyl complexes of the type  $[M_4O_{12}M'(NO)_2\{RC(NH)NO\}_2\{RC(NH_2)NHO\}_2]^{2-}$  ( $M = M' = Mo, R = Me, Et$  (**1**),  $PhCH_2$  or 2-thienylmethyl (**2**);  $M = M' = W, R = Me$ ;  $M = W, M' = Mo, R = Me$ ) have been prepared; **1** and **2** have been characterized by X-ray diffraction.

Organodiazenido-derivatives of polyoxomolybdates have been obtained by condensation-type reactions of organohydrazines with oxomolybdenum complexes or polyoxomolybdates in non-aqueous solvents. A number of tetranuclear species<sup>1</sup> and one octanuclear<sup>2</sup> compound containing  $[Mo(NNAr)_2]^{2+}$  units have been characterized. In addition, there have been two reports of Linqvist-type derivatives containing  $[Mo(NNAr)]^{3+}$  units.<sup>3</sup> On the grounds of the analogy between the diazenido and nitrosyl ligands,<sup>4</sup> we expected that nitrosyl derivatives of polyoxomolybdates could be prepared. Indeed we have found that oxo–nitrosyl molybdenum complexes containing  $[Mo(NO)]^{3+}$  units can be obtained by reductive nitrosylation of polyoxomolybdates in alcohols.<sup>5</sup> We have now succeeded in preparing oxo–nitrosyl molybdenum complexes containing  $[Mo(NO)_2]^{2+}$  units. The





**Fig. 1** (a) Molecular drawing<sup>9</sup> of the anion of **1**, showing the atom labelling scheme and the organization of the two 'Mo<sub>2</sub>O<sub>5</sub>' moieties. (b) Molecular drawing of the anion of **2**, showing the atom labelling scheme and the environment of the central Mo atom. Selected bond lengths (Å) and angles (°) for **1** and **2** (in brackets): Mo(1)–N(1) 1.80(2) [1.82(2)], Mo(1)–O(2) 2.065(9) [2.04(1)], Mo(1)–N(12) 2.18(1) [2.12(2)], N(1)–O(1) 1.19(1) [1.15(2)], Mo(2)–O(2) 1.861(9) [1.90(1)], Mo(2)–O(3) 2.024(9) [1.98(1)], Mo(2)–O(4) 1.71(1) [1.71(1)], Mo(2)–O(5) 1.71(1) [1.69(1)], Mo(2)–O(12) 2.285(9) [2.28(1)], Mo(2)–O(22) 2.36(1) [2.32(2)], Mo(3)–O(3) 1.844(9) [1.80(1)], Mo(3)–O(6) 1.72(1) [1.70(1)], Mo(3)–O(7) 1.72(1) [1.73(1)], Mo(3)–O(12) 2.145(9) [2.15(1)], Mo(3)–N(13) 2.05(1) [2.08(2)], Mo(3)–O(22) 2.48(1) [2.51(1)], Mo(1)–N(1)–O(1) 173.2(12) [176.7(14)], N(1)–Mo(1)–N(1') 83.8(8) [81.4(10)], O(2)–Mo(1)–N(1) 97.4(4) [98.8(6)], O(2)–Mo(1)–N(1') 175.5(5) [177.9(7)], O(2)–Mo(1)–O(2') 81.7(5) [81.1(7)], N(12)–Mo(1)–N(1) 96.2(5) [93.2(7)], N(12)–Mo(1)–N(1') 94.0(5) [96.1(7)], O(2)–Mo(1)–N(12) 81.6(4) [81.8(5)], N(12)–Mo(1)–O(2') 88.0(4) [88.9(6)], N(12)–Mo(1)–N(12') 166.2(6) [167.8(9)]. The coordinates of the halves of the molecule are related via the transformation  $[x', y', z'] = [-x, y, \frac{1}{2} - z]$ .

success of our approach relies in part on the unique ligating properties of amide oximes.

Although the reductive nitrosylation of  $[\alpha\text{-Mo}_8\text{O}_{26}]^{4-}$  and  $[\text{Mo}_4\text{O}_{12}\{\text{RC}(\text{NH}_2)\text{NO}\}_2]^{2-}$  (R = Me, Et,  $\text{N}\equiv\text{CCH}=\text{CH}$ ) in methanol provides a convenient route to the  $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$  anion,<sup>5</sup> this reaction is dependent upon the  $\text{NH}_2\text{OH}:\text{Mo}$  ratio. Indeed, reaction of 1 equiv. of  $(\text{Bu}^n_4\text{N})_4[\alpha\text{-Mo}_8\text{O}_{26}]$  with 4–6 equiv. of  $\text{RC}(\text{NH}_2)\text{NOH}$  (R =

phenyl, *p*-tolyl, 2-thienyl, 2-thienylmethyl)<sup>†</sup> and 4 equiv. of  $\text{NH}_2\text{OH}$  in refluxing MeOH produced brown solutions from which green crystals were obtained upon standing at room temperature. The IR spectra of these compounds exhibit two

<sup>†</sup> Amide oximes were prepared by adding a solution of free hydroxylamine in MeOH to 1 equiv. of the appropriate nitrile in MeOH.<sup>6</sup>

bands at *ca.* 1630 and 1750  $\text{cm}^{-1}$ , characteristic of the *cis*-[Mo(NO)<sub>2</sub>]<sup>2+</sup> unit. In addition, they display a pattern of bands in the range 600–1000  $\text{cm}^{-1}$ , attributable to Mo–O stretching modes. A number of by-products, including (Bu<sup>n</sup><sub>4</sub>N)<sub>2</sub>[Mo<sub>5</sub>O<sub>13</sub>(OMe)<sub>4</sub>(NO){Na(MeOH)}]·3MeOH,<sup>5</sup> and (Bu<sup>n</sup><sub>4</sub>N)<sub>2</sub>[Mo<sub>4</sub>O<sub>12</sub>{RC(NH<sub>2</sub>)NO}<sub>2</sub>] (R = 2-thienyl methyl)<sup>‡</sup> were also isolated in the course of these reactions. We found that the yield of the green oxo–nitrosyl complexes could be increased by addition of [Mo(NO)<sub>2</sub>(acac)<sub>2</sub>]<sup>§</sup> (Hacac = pentane-2,4-dione) to the reactant mixture. In a typical experiment, a mixture of (NBu<sup>n</sup><sub>4</sub>)<sub>4</sub>[α-Mo<sub>8</sub>O<sub>26</sub>] (0.5 mmol), propionamide oxime (8 mmol), [Mo(NO)<sub>2</sub>(acac)<sub>2</sub>] (1 mmol), and hydroxylamine (2 mmol)<sup>§</sup> in methanol (25 ml) was refluxed for 16 h. Green crystals of (Bu<sup>n</sup><sub>4</sub>N)<sub>2</sub>[Mo<sub>5</sub>O<sub>12</sub>(NO)<sub>2</sub>{EtC(NH)NO}<sub>2</sub>{EtC(NH<sub>2</sub>)NHO}<sub>2</sub>] **1** were obtained on cooling at room temperature {yield: 0.63 g, 40% based on [Mo(NO)<sub>2</sub>(acac)<sub>2</sub>]}. The 2-thienylmethyl derivative **2** was similarly obtained in 32% yield from 2-thienylacetamide oxime.<sup>§</sup> The structures of **1** and **2** have been determined by X-ray crystallography.<sup>¶</sup>

Both compounds **1** and **2** contain [Mo<sub>5</sub>O<sub>12</sub>(NO)<sub>2</sub>{RC(NH)NO}<sub>2</sub>{RC(NH<sub>2</sub>)NHO}<sub>2</sub>]<sup>2-</sup> ions (Fig. 1),<sup>9</sup> which contain two [Mo<sup>VI</sup>O<sub>5</sub>]<sup>2+</sup> cores and a central [Mo<sup>0</sup>(NO)<sub>2</sub>]<sup>2+</sup> unit. Alternatively, these anions may be viewed in terms of an open [Mo<sub>5</sub>O<sub>12</sub>(NO)<sub>2</sub>]<sup>2+</sup> core which derives from the parent [Mo<sub>5</sub>O<sub>14</sub>]<sup>2+</sup> core by replacing the terminal oxo groups of the central Mo atom by nitrosyl ligands. The unique Mo<sup>0</sup> centre lies on a two-fold axis. Each of the two symmetry-equivalent [Mo<sub>2</sub>O<sub>5</sub>{RC(NH)NO}{RC(NH<sub>2</sub>)NHO}] units is linked to the {Mo<sup>0</sup>(NO)<sub>2</sub>]<sup>2+</sup> unit by its hydroxylamino nitrogen atom and by an additional bridging oxo ligand. The [Mo<sub>2</sub>O<sub>5</sub>{RC(NH)NO}{RC(NH<sub>2</sub>)NHO}] units are quite similar to the anionic dinuclear moiety present in the [Mo<sub>4</sub>O<sub>11</sub>{RC(NH)NHO}{RC(NH)NO}{RC(NH<sub>2</sub>)NHO}<sub>2</sub>]<sup>-</sup> ion.<sup>10</sup> Although the hydrogen atoms could not be located in the anions of **1** and **2**, the protonation states of the two crystallographically independent ligands are unequivocally revealed by their coordination modes. To the best of our knowledge, the parent [Mo<sub>5</sub>O<sub>14</sub>]<sup>2+</sup> core has not been yet characterized although the class of compounds with an open [Mo<sub>n</sub>O<sub>3n-1</sub>]<sup>2+</sup> core is steadily expanding. A large number of dinuclear complexes<sup>11</sup> and a few examples with *n* = 3,<sup>12</sup> 4,<sup>10,13,14</sup> and 6<sup>15</sup> are known.

According to analytical and IR data, oxo–dinitrosyl pentanuclear compounds similar to **1** and **2** are also formed where R = Me (**3**), HOCH<sub>2</sub>CH<sub>2</sub> (**4**) and PhCH<sub>2</sub> (**5**). Although compounds obtained for R = 2-thienyl (**6**), phenyl (**7**) and *p*-tolyl (**8**) do contain a [Mo(NO)<sub>2</sub>]<sup>2+</sup> core, their analytical data are at variance with the above formula. The fast decay of crystals due to solvent loss has so far prevented the determination of their composition by X-ray crystallography.

<sup>‡</sup> This compound has been identified on the basis of analytical and IR data by comparison with similar compounds containing the [Mo<sub>4</sub>O<sub>12</sub>] core.<sup>7</sup>

<sup>§</sup> All compounds gave satisfactory analyses.

<sup>¶</sup> *Crystal data*: **1**, monoclinic, space group *C2/c*, *a* = 26.112(7), *b* = 14.091(9), *c* = 22.387(10) Å, β = 125.87(8)°, *U* = 6957 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.49 g cm<sup>-3</sup>; structure solution and refinement based on 1694 reflections with *I* > 3σ(*I*) [λ(Mo-Kα) = 0.71069 Å] converged at a conventional discrepancy index, *R*, of 0.042. **2**: monoclinic, space group *C2/c*, *a* = 26.471(3), *b* = 14.180(2), *c* = 24.661(2) Å, β = 125.87(8)°, *U* = 7501 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.63 g cm<sup>-3</sup>; structure solution and refinement based on 1648 reflections with *I* > 3σ(*I*) (Mo-Kα) converged at a conventional discrepancy index, *R*, of 0.072. One thiophene ring is clearly disordered between two possible orientations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The synthesis of the tungsten analogue (Bu<sup>n</sup><sub>4</sub>N)<sub>2</sub>[W<sub>5</sub>O<sub>12</sub>(NO)<sub>2</sub>{MeC(NH)NO}<sub>2</sub>{MeC(NH<sub>2</sub>)NHO}<sub>2</sub>]·*x*MeOH **9** was similarly achieved from [W(NO)<sub>2</sub>(acac)(MeCN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, (Bu<sup>n</sup><sub>4</sub>N)<sub>2</sub>[W<sub>6</sub>O<sub>19</sub>], NH<sub>2</sub>OH and MeC(NH<sub>2</sub>)NOH in refluxing methanol. When [Mo(NO)<sub>2</sub>(acac)<sub>2</sub>] was used in place of [W(NO)<sub>2</sub>(acac)(MeCN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, (Bu<sup>n</sup><sub>4</sub>N)<sub>2</sub>[W<sub>4</sub>O<sub>12</sub>Mo(NO)<sub>2</sub>{MeC(NH)NO}<sub>2</sub>{MeC(NH<sub>2</sub>)NHO}<sub>2</sub>] **10** was obtained.

All compounds **1–10** display an open [M<sub>*n*-1</sub>O<sub>3*n*-3</sub>M'(NO)<sub>2</sub>]<sup>2+</sup> core which is stabilized by additional ligands. In an attempt to get oxo nitrosyl molybdenum complexes without additional ligands, [Mo(NO)<sub>2</sub>(acac)<sub>2</sub>] was reacted with (Bu<sup>n</sup><sub>4</sub>N)<sub>2</sub>[Mo<sub>2</sub>O<sub>7</sub>] in MeCN. Only the known (Bu<sup>n</sup><sub>4</sub>N)<sub>3</sub>[Mo<sub>6</sub>O<sub>18</sub>(NO)]<sup>5</sup> was isolated from this reaction. (Bu<sup>n</sup><sub>4</sub>N)<sub>3</sub>[Mo<sub>5</sub>O<sub>18</sub>W(NO)] **11** was similarly obtained from [W(NO)<sub>2</sub>(acac)(MeCN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and (Bu<sup>n</sup><sub>4</sub>N)<sub>2</sub>[Mo<sub>2</sub>O<sub>7</sub>]. Recrystallization of **6** from acetone also afforded (Bu<sup>n</sup><sub>4</sub>N)<sub>3</sub>[Mo<sub>6</sub>O<sub>18</sub>(NO)]. The conversion of a [Mo(NO)<sub>2</sub>]<sup>2+</sup> unit into a [Mo(NO)]<sup>3+</sup> unit has already been reported.<sup>17,18</sup>

We are currently pursuing studies of the potential application of [Mo(NO)<sub>2</sub>(acac)<sub>2</sub>] and [W(NO)<sub>2</sub>(acac)(MeCN)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> in the synthesis of oxo–nitrosyl metalates.

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|| This compound was obtained in *ca.* 25% yield by dissolution of [W(NO)<sub>2</sub>(MeCN)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> (*ca.* 5 mmol)<sup>16</sup> in pentane-2,4-dione (25 ml), followed by addition of diethyl ether (*ca.* 100 ml).