Synthesis and Characterization of Oxomolybdate Clusters Containing Co-ordinatively Bound Diazenido Units. The Crystal and Molecular Structure of the Octanuclear Oxomolybdate $(NHEt_3)_2(NBu_4)_2[Mo_8O_{20}(NNPh)_6]$.

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Treatment of α-$(NR_4)_4[Mo_8O_{26}]$ with an excess of phenylhydrazine in ethanol and fractional crystallization yielded a tetranuclear species, $[Mo_4O_8(OEt)_2(NNPh)_4]^{2-}$, with bridging ethoxy groups, and an octanuclear complex, $[Mo_8O_{20}(NNPh)_6]^{4-}$, structurally related to the α-$[Mo_8O_{26}]^{4-}$ precursor, as determined by *X*-ray crystallography; the structure of the Mo_8 precursor is reported.

Although the co-ordination chemistry of polymolybdates with small organic molecules is of interest in the development of models for the interaction of organic substrates with catalytic oxide surfaces,[1,2] relatively few examples of organic derivatives of polymolybdates have been documented.[3—5] We have extended this chemistry to the organodiazenido group, -NNR, a ligand which forms robust complexes with molybdenum, often displacing *cis* oxo groups *via* a condensation type reaction,[6,7] equation (1). In the course of these investigations, the chemistry of $(NR_4)_2[Mo_8O_{26}]$ with phenylhydrazine in various organic solvents has been studied.[7]

$$cis\text{-}[MoO_2L_4] + 2H_2NNHR \rightarrow cis\text{-}[Mo(NNR)_2L_4] + 2H_2O + H_2 \qquad (1)$$

Reaction of $(NBu_4)_2[Mo_8O_{26}]$ with an excess of phenylhydrazine and triethylamine in ethanol yields an intensely coloured purple solution. Over a period of two weeks, lustrous dark hexagonal crystals, compound (**2**), were isolated; subsequently, purple–black irregular crystals, (**1**), grew from the reaction mixture. While compound (**1**) behaved as a 2 : 1 electrolyte in acetonitrile solution, compound (**2**) exhibited properties consistent with a 4 : 1 electrolyte. The i.r. spectra of

$$[Mo_4O_8(OEt)_2(NNPh)_4]^{2-}$$
(**1**)

$$[Mo_8O_{20}(NNPh)_6]^{4-}$$
(**2**)

the compounds confirmed the presence of co-ordinated phenyldiazenido units ($\nu_{N-N'}$ 1550—1650 cm^{-1}) and were nearly identical with the exception of the appearance of a medium intensity band at 921 cm^{-1} in the spectrum of (**1**). The *X*-ray crystallographic study of (**1**) revealed a tetranuclear polyoxmolybdate unit, previously described,[7] while the structure of (**2**) consists of an octanuclear polyoxomolybdate tetra-anion incorporating the diazenido units in the $[Mo_8O_{20}(NNPh)_6]^{4-}$ framework.

Crystal data: $C_{80}H_{134}Mo_8N_{16}O_{20}$, (**2**), M = 2415.6, monoclinic, space group $P2_1/c$, a = 18.456(3), b = 26.620(4), c = 21.350(3) Å, β = 95.24(1)°; U = 10445.5(13) Å^3, Z = 4, based on the octanuclear formulation, to give D_c = 1.54 g cm^{-3}, 5928 reflections of 7568 collected were used in the structural analysis (Mo-K_α radiation, R = 0.089, error of fit 1.45).†

$(Bu^n{}_4N)_4[Mo_8O_{26}]$, $C_{64}H_{144}Mo_8N_4O_{26}$, M = 2153.4, monoclinic space group $P2_1/n$, a = 15.093(2), b = 16.011(2), c = 18.519(3) Å, β = 91.36(1)°; U = 4474.0(8) Å^3, Z = 2, to give D_c = 1.60 g cm^{-3}; 3274 reflections of 6600 collected were used in the structural analysis (Mo-K_α, R = 0.039, error of fit 1.36).†

The *X*-ray structure of (**2**) confirms the presence of discrete octanuclear units incorporating co-ordinatively bound phenyldiazenido groups, $[Mo_8O_{20}(NNPh)_6]^{4-}$, as illustrated in Figure 1. The overall geometry consists of a crown of six oxo-bridged molybdenum centres, alternating oxomolybdate units $[MoO_4]^{2-}$ and *cis*-bisdiazenido molybdenum moieties $[Mo(NNPh)_2]^{2+}$, capped above and below by oxomolybdate

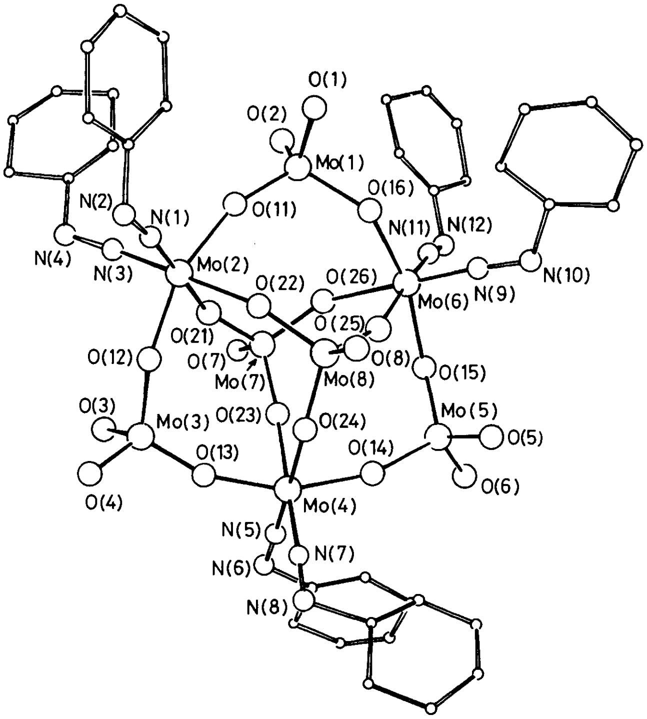

Figure 1. ORTEP view of $[Mo_8O_{20}(NNPh)_6]^{4-}$ (**2**) showing the atom labelling scheme. Selected bond lengths (Å) and angles (°): Mo(1)–O(1) 1.62(2), Mo(1)–O(2) 1.66(2), Mo(1)–O(11) 1.76(2), Mo(1)–O(16) 1.76(2), Mo(2)–O(11) 2.00(2), Mo(2)–O(12) 1.99(2), Mo(2)–O(21) 2.18(2), Mo(2)–O(22) 2.15(2), Mo(2)–N(1) 1.83(2), Mo(2)–N(3) 1.82(2), N(1)–N(2) 1.23(3), N(3)–N(4) 1.19(3), Mo(7)–O(7) 1.72(1), Mo(7)–O(21) 1.74(2), Mo(7)–O(23) 1.73(2), Mo(7)–O(25) 1.77(1); O(1)–Mo(1)–O(2) 93.1(9), O(1)–Mo(1)–O(11) 113.2(8), O(1)–Mo(1)–O(16) 116.9(9), O(2)–Mo(1)–O(11) 107.4(8), O(2)–Mo(1)–O(16) 103.1(8), O(11)–Mo(1)–O(16) 118.7(7), O(11)–Mo(2)–O(12) 160.3(6), O(21)–Mo(2)–N(1) 176.7(7), O(22)–Mo(2)–N(3) 176.7(8), O(7)–Mo(7)–O(21) 107.6(7), O(7)–Mo(7)–O(23) 110.0(7), O(7)–Mo(7)–O(25) 107.9(7), O(21)–Mo(7)–O(23) 110.7(8), O(21)–Mo(7)–O(25) 110.6(7), O(23)–Mo(7)–O(25) 110.0(7), Mo(2)–N(1)–N(2) 174.8(17), Mo(2)–N(3)–N(4) 177.3(17). Parameters for Mo(3) and Mo(5) are similar to those for Mo(1); those for Mo(4) and Mo(6) are similar to values for Mo(2); Mo(7) and Mo(8) display similar co-ordination environments.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

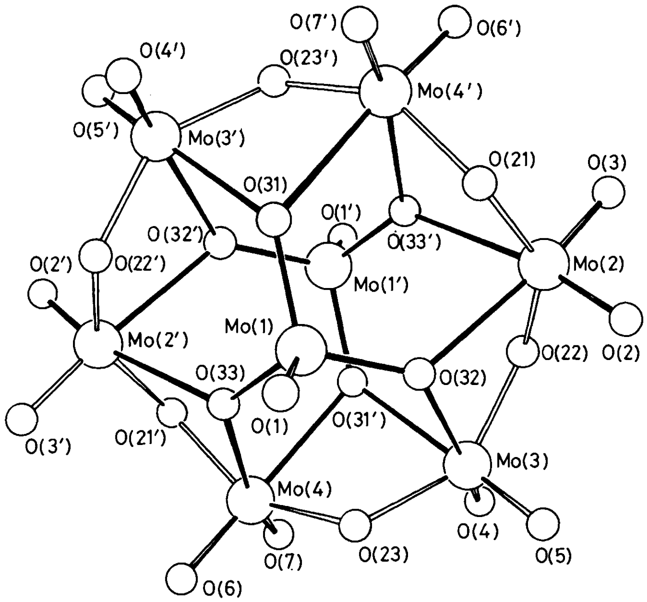

Figure 2. ORTEP view of the structure of α-$[Mo_8O_{26}]^{4-}$, [ref. 8(b)]. The capping $MoO_4{}^{2-}$ units display two types of Mo–O bond (Å): Mo–O(terminal) 1.711(6) Mo–O(bridging) 1.778(6). The pseudo-octahedrally co-ordinated Mo atoms in the equatorial girdle display three distinct Mo–oxo interactions (Å): Mo–O(terminal) 1.692(8) aver., Mo–O(equatorial bridge) 1.905(8) aver., Mo–O(triply bridging to capping group) 2.451(8) aver.

fragments. Thus, there are three structurally unique molybdenum centres: tetrahedral oxomolybdate units bridging through two oxo groups and occupying positions in the Mo_6O_6 crown, distorted octahedral *cis*-bisdiazenido molybdenum centres which alternate with the oxomolybdate units in the crown, and the pseudo-tetrahedral oxomolybdate centres which cap the crown and bridge through three oxo groups. Examination of the structure of (**2**) reveals the relationship to the α-$[Mo_8O_{26}]^{4-}$ structure, which is shown in Figure 2.[8] Compound (**2**) is derived from the α-$[Mo_8O_{26}]^{4-}$ structure by replacement of two terminal oxo groups on each of three alternate molybdenum atoms in the Mo_6O_6 crown by two phenyldiazenido groups and rotation of the capping $[MoO_4]^{2-}$ units so as to shorten the Mo–O distance to the diazenido-co-ordinated molybdenum atoms [Mo(2), Mo(4), Mo(6)] at the expense of the interaction between the oxo-groups of the capping unit and the molybdenum–oxo units of the crown [Mo(1), Mo(2), Mo(3)]. Whereas three oxo-groups of each capping $[MoO_4]^{2-}$ unit of α-$[Mo_8O_{26}]^{4-}$ form weak bridging interactions with each of two adjacent molybdenum centres in the crown with an average Mo–O distance of 2.425 Å, in (**2**) the bridging oxo-groups of the capping $[MoO_4]^{2-}$ units interact exclusively with the diazenido-co-ordinated Mo atoms of the crown at an average distance of 2.13(2) Å, with no significant interaction with the molybdenum–oxo centres of the crown (Mo–O, 3.5—4.1 Å). This observation supports arguments[8] that the capping $[MoO_4]^{2-}$ units of the α-$[Mo_8O_{26}]^{4-}$ structure are weakly interacting and may be reoriented with only slight deformations of geometry. The potential lability with respect to dissociation of the capping $[MoO_4]^{2-}$ units in (**2**) suggests that it may serve as an intermediate in the formation of compound (**1**). Indeed, addition of an excess of phenylhydrazine to an ethanol solution of (**2**) yields (**1**) in nearly quantitative amounts.

The structures of both (**1**) and (**2**) reveal that $[Mo(NNPh)_2]^{2+}$ represents a robust chemical moiety that persists in the structural chemistry of molybdenum. Since the structural parameters associated with the capping $[MoO_4]^{2-}$ units and with the $[MoO_4]^{2-}$ groups in the crown are similar to those observed for $Na_2MoO_4 \cdot 2H_2O$,[9] the formal oxidation state of these Mo-centres is assigned as Mo^{VI}. The linear Mo–N–N linkage, together with the short Mo–N and N–N distances, is consistent with the description of the phenyldiazo linkage as the three-electron donating $-N_2R^+$ structure.[10] Hence, the Mo-centres of the $[Mo(NNPh)_2]^{2+}$ units may be described in a formal sense as Mo^0, suggesting the 'non-innocent' nature of the phenyldiazo ligand.‡

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‡ All oxidation state formalisms are to some extent artificial, especially when the complexes being considered contain strong π-bonding ligands. The system adopted by us conforms to that used in ref. 10. However, European authors appear to prefer the aryldiazenido(1−) formalism, $-N_2R^-$, which appears artificial in terms of the ligand electronic structure but which does produce more reasonable metal oxidation states for thiolate and dithioacid derivatives, ref. 11.