

Co-ordination Complexes of Polyoxomolybdates with a Hexanuclear Core: Synthesis and Structural Characterization of $(\text{NBu}^n_4)_2[\text{Mo}_6\text{O}_{18}(\text{NNMePh})]$

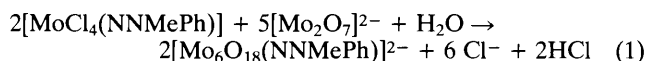
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Reaction of $[\text{MoCl}_4(\text{NNMePh})]$ with $(\text{Bu}^n_4\text{N})_2[\text{Mo}_2\text{O}_7]$ yields a co-ordination complex with the hexanuclear oxomolybdate core, $(\text{Bu}^n_4\text{N})_2[\text{Mo}_6\text{O}_{18}(\text{NNMePh})]$; the reaction is general with appropriate precursors in providing a ready entry into the class of co-ordination compounds of the types $[\text{Mo}_5\text{O}_{18}(\text{ML})]^{n-}$ and $[\text{W}_5\text{O}_{18}(\text{ML})]^{n-}$, with $\text{M} = \text{Mo}$ or W and $\text{L} = \text{NNR}_2$, NR , or N .

The interactions of isopolyanions with small organic molecules are of considerable interest in the development of models for the interactions of organic substrates with catalytic metal oxide surfaces.¹⁻³ In the course of a continuing investigation of polyoxomolybdate interactions with nitrogenous ligands,⁴ we have examined the reactions of disubstituted organohydrazines H_2NNR_2 with various polymolybdate precursors. Although tetranuclear and octanuclear species $[\text{Mo}_4\text{O}_{10}(\text{OR})_2(\text{NNR}_2)_2]^{2-}$ and $[\text{Mo}_8\text{O}_{16}(\text{OR})_6(\text{NNR}_2)_6]^{2-}$ were readily isolated from $\alpha\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ in alcoholic solutions,⁵ co-ordination complexes based upon the hexanuclear core $[\text{Mo}_6\text{O}_{19-n}(\text{NNR}_2)_n]^{2-}$ could not be prepared directly from $[\text{Mo}_6\text{O}_{19}]^{2-}$, owing to the nonbasic and unreactive nature of the oxo groups of this unit. However, it has been demonstrated that the aggregating tendencies of $[\text{Mo}_2\text{O}_7]^{2-}$ may be exploited to provide entry into the organotransition metal chemistry of complexes of the type $[(\text{C}_5\text{H}_5)_2\text{Ti}(\text{Mo}_5\text{O}_{18})]^{3-}$.⁶ In this paper we report an extension of this reaction chemistry to co-ordination compounds of the class $[\text{LM}(\text{Mo}_5\text{O}_{18})]^{n-}$ where $\text{L} = \text{NNR}_2$, NR , or N and $\text{M} = \text{Mo}$, and related tungstate derivatives.

Reaction of $[\text{MoCl}_4(\text{NNMePh})]_7$ with $(\text{Bu}^n_4\text{N})_2[\text{Mo}_2\text{O}_7]$ in wet methanol yields, upon addition of ether, black crystals of $(\text{NBu}^n_4)_2[\text{Mo}_6\text{O}_{18}(\text{NNMePh})]$ (**1**) [reaction (1)]. Alternatively, (**1**) may be prepared from the reaction of $[\text{Mo}_6\text{O}_{18}(\text{NNPh})]^{3-}$ (ref. 8) with methyl iodide in CH_2Cl_2 .



The i.r. spectrum of (**1**) displays strong bands at 1589 cm^{-1} associated with $\nu(\text{N}=\text{N})$, and at 943 and 780 cm^{-1} assigned to $\nu(\text{Mo}=\text{O}_t)$ and $\nu(\text{Mo}-\text{O}_b)$ ($t = \text{terminal}$, $b = \text{doubly bridging}$), respectively. The ^{17}O n.m.r. spectrum exhibits a pattern of resonances† consistent with $[(\text{Mo}_5\text{O}_{18})\text{ML}]^{n-}$ geometry.^{6,8} The structure of (**1**)‡ is illustrated in Figure 1, and the caption presents selected bond lengths and angles for the hexanuclear dianion. The structure is derived from that of the well known hexamolybdate cluster $[\text{Mo}_6\text{O}_{19}]^{2-}$ (ref. 9) by replacement of a terminal oxo group with the hydrazido(2-) ligand ($-\text{NNMePh}$). Alternatively, the structure may be viewed in terms of close-packed layers of oxide units with a single peripheral oxide group replaced by the hydrazido ligand, as shown in Figure 2.

The geometry of the hexanuclear core of molybdenum atoms is distorted from the idealized octahedral symmetry displayed by the $[\text{Mo}_6\text{O}_{19}]^{2-}$ prototype as a consequence of hydrazido(2-) co-ordination at $\text{Mo}(6)$. The $\text{Mo}(6)-\text{O}(10)$ bond distance of $2.161(5)\text{ \AA}$ is significantly shorter than the average of all other $\text{Mo}-\text{O}(10)$ bond distances [$2.351(7)\text{ \AA}$]. The $\text{Mo}(6)-\text{O}(10)$ bond contraction is compensated by lengthening of the $\text{Mo}(6)$ -doubly bridging oxo group distances: $1.960(6)$ vs. $1.924(11)\text{ \AA}$ for the average of all other $\text{Mo}-\text{O}_b$ distances. The $\text{Mo}(6)$ -hydrazido moiety presents metrical parameters consistent with the hydrazido(2-) description of the ligand and extensive delocalization throughout the $[\text{MoNN}]$ unit.¹⁰

The complex (**1**) is electrochemically active, displaying successive reversible one-electron reductions at -0.35 and -0.63 V . Controlled potential electrolysis at -0.40 V produces the paramagnetic species $[\text{Mo}_6\text{O}_{18}(\text{NNR}_2)]^{3-}$, the e.p.r. spectrum of which at 77 K exhibits a shape characteristic of an axial crystal field with $g_{\perp} = 1.935$ and $g_{\parallel} = 1.922$, and

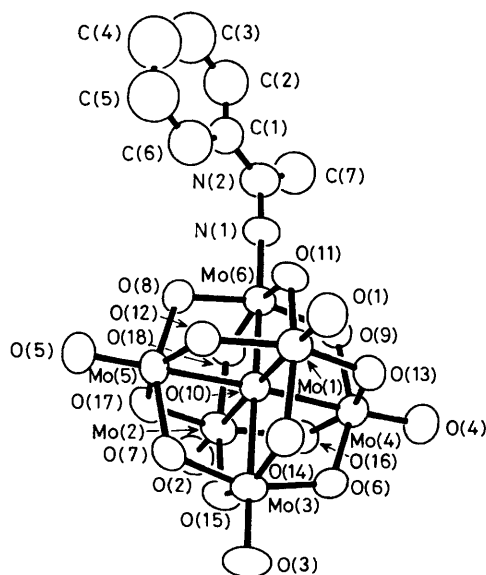


Figure 1. ORTEP view of the structure of $[\text{Mo}_6\text{O}_{18}(\text{NNPhMe})]^{2-}$, showing the atom-labelling scheme. Selected bond lengths (\AA) and angles ($^\circ$): $\text{Mo}(6)-\text{O}(8)$, $1.968(5)$; $\text{Mo}(6)-\text{O}(9)$, $1.917(5)$; $\text{Mo}(6)-\text{O}(10)$, $2.161(5)$; $\text{Mo}(6)-\text{O}(11)$, $1.982(6)$; $\text{Mo}(6)-\text{O}(18)$, $1.971(6)$; $\text{Mo}(6)-\text{N}(1)$, $1.769(6)$; $\text{N}(1)-\text{N}(2)$, $1.318(10)$; $\text{Mo}-\text{O}_t$ (av.), $1.685(9)$; $\text{Mo}-\text{O}_b$ (av.), $1.924(11)$; $\text{Mo}-\text{O}_c$ (av.), $2.351(7)$; $\text{Mo}-\text{N}(1)-\text{N}(2)$, $173.9(6)$. Abbreviations: O_t , terminal oxo group; O_b , doubly bridging oxo group; O_c , central oxo group $\text{O}(10)$. Average bond lengths are for unsubstituted Mo sites only, $\text{Mo}(1)$ to $\text{Mo}(5)$.

† Satisfactory elemental analyses were obtained. ^{17}O N.m.r. (CDCl_3 ; δ [assignment]) -13 [$\text{O}(10)$]; 553 , 572 , and 594 [doubly bridging O]; 922 [$\text{O}(3)$]; and 944 [$\text{O}(1)$, $\text{O}(2)$, $\text{O}(4)$, and $\text{O}(5)$].

‡ *Crystal data:* $\text{C}_{39}\text{H}_{80}\text{Mo}_6\text{N}_4\text{O}_{18}$, triclinic, space group $P\bar{1}$, $a = 11.712(3)$, $b = 12.477(3)$, $c = 20.615(4)\text{ \AA}$, $\alpha = 103.7(1)^\circ$, $\beta = 105.93(1)^\circ$, $\gamma = 91.66(1)^\circ$, $U = 2802.1(10)\text{ \AA}^3$, $Z = 2$, $D_c = 1.74\text{ g cm}^{-3}$. Structure solution and refinement based on 5999 reflections with $F_o \geq 6.0 \sigma(F_o)$ ($\text{Mo}-\text{K}\alpha$; $\lambda = 0.71073\text{ \AA}$) converged at a conventional R factor of 0.0541 . 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.

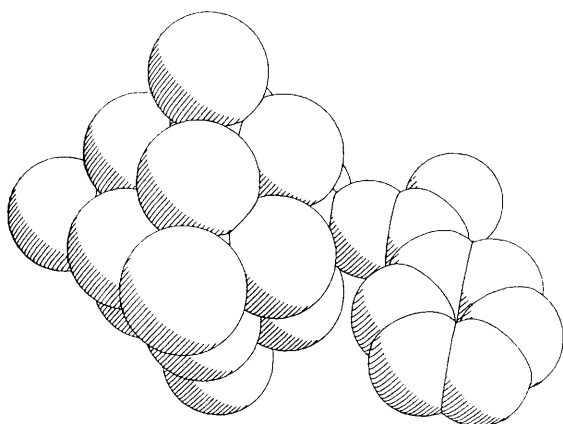


Figure 2. The structure of $[\text{Mo}_6\text{O}_{18}(\text{NNMePh})]^{3-}$ shown as a space-filling model where the oxygen centres are drawn as shaded spheres having van der Waals radii of 1.4 Å.

several weaker peaks due to hyperfine interactions of the unpaired electron with the $I = 5/2$ nuclear species of the molybdenum isotopes.

The synthesis of **(1)** via the displacement of labile chloride ligands from a hydrazido-containing precursor by oxo groups of polyoxometalate anions $(\text{M}_x\text{O}_y)^{n-}$, followed by aggregation, appears to represent a general methodology for the synthesis of the type $[\text{M}_5\text{O}_{18}(\text{M}'\text{L})]^{n-}$, where $\text{M} = \text{Mo}$ or W , $\text{M}' = \text{Mo}$ or W , and $\text{L} = \text{NNR}_2$, NR , or N . Thus, reaction of $[\text{MoCl}_4(\text{NNR}_2)]$ with $[\text{WO}_4]^{2-}$ under similar conditions yields $[\text{W}_5\text{O}_{18}\text{Mo}(\text{NNR}_2)]^{2-}$. Similarly, reactions of $[\text{MoCl}_4(\text{NR})(\text{thf})]^{11}$ and $[\text{MoNCl}_4]^{2-}$ (ref. 12) with $[\text{Mo}_2\text{O}_7]^{2-}$

yield, respectively, $[\text{Mo}_5\text{O}_{18}(\text{MoNR})]^{2-}$ and $[\text{Mo}_5\text{O}_{18}(\text{MoN})]^{3-}$, the structures and properties of which will be discussed in future publications.

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