

Synthesis and Structure of a Mixed-valence Tetramolybdate containing a Binucleating Diazene Ligand

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Reaction of $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ (dmf = dimethylformamide) with 1,4-dihydrazinophthalazine (dhphH_6) gives $[\text{Et}_3\text{NH}]_2[\text{Mo}_4\text{O}_{11}\text{dhphH}_2]$, which is shown by an X-ray crystal structure analysis to be a binuclear, oxo-bridged, formally Mo^{IV} , diazene complex with bridging molybdate groups; upon acidification the complex reversibly converts into a Mo^{VI} derivative of the fully protonated, parent hydrazine.

At present the co-ordination chemistry of polyoxoanions is being actively pursued with the aim of developing understanding of the interactions between small organic molecules and catalytic oxide surfaces.¹ Recent work shows the possibility of extending the chemistry of polyoxoanions to organic and organotransition metal reagents.^{2,3} The synthesis of diazenido polymolybdates^{4,5} has provided an entry into the vast field of organodinitrogen ligands and opens new perspectives for the reactivity of these species.

We have now obtained the novel tetranuclear diazene compound $[\text{Et}_3\text{NH}]_2[\text{Mo}_4\text{O}_{11}\text{dhphH}_2]$, (1), by treating $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ (dmf = dimethylformamide) and 1,4-dihydrazinophthalazine, (dhphH_6)⁶ (molar ratio 2:1) in cold EtOH containing excess of Et_3N . Black, rod-shaped crystals of the diamagnetic air-stable compound (1) have been grown from MeNO_2 .†

Figure 1 shows the essential features of (1) which can be described as a strictly planar (maximum deviation 0.07 Å), binuclear oxo-bridged, formally Mo^{IV} complex with bridging MoO_4^{2-} ions. These anions exhibit, as expected, a co-ordination geometry close to tetrahedral (the O–Mo–O angles range from 102.8 to 115.8°) slightly affected by weak interactions with the central oxo ligand [O(1)–Mo(3) and O(1)–Mo(4) distances are 2.581(7) and 2.810(7) Å]. One of the two MoO_4^{2-} groups is strongly hydrogen bonded to one of the two Et_3NH^+ cations [O(11)–N(8) is 2.74(2) Å] and this accounts for the different metal–oxygen bond distances in the two molybdates.

The Mo(1) and Mo(2) atoms display six-co-ordinated, strongly distorted octahedral geometries. In-plane bond angles range from 68.5(3) to 117.7(3)°. These large distortions are essentially due to ligand constraints. They are the result of the large metal–metal distance imposed by the ligand, 3.47 Å, suggesting that direct interaction, if any, is negligible, and the exceedingly small chelating bite of 2.358 Å. Within the chelate rings bond distances are intermediate between single and double bonds and, together with the strict planarity of the rings and the quasi sp^2 hybridization of the nitrogens, are indicative of extensive charge delocalization.

From a comparison of the literature data on chelating substituted hydrazines these distances can be correlated with the degree of protonation of the ligands.^{7,8} In our case these data strongly support a quadruply deprotonated, oxidized diazene formulation of the ligand which can be described by the two canonical forms (I) and (II).

The shortening of the N–N bond distance compared with literature values suggests that the canonical form (I) has a large contribution to the overall structure of the ligand.

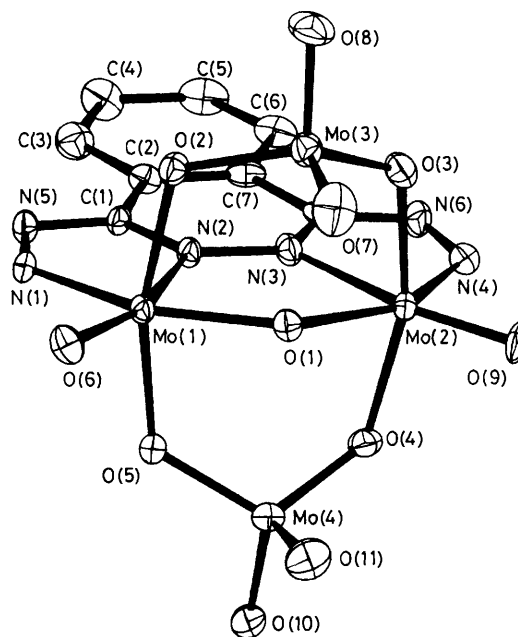
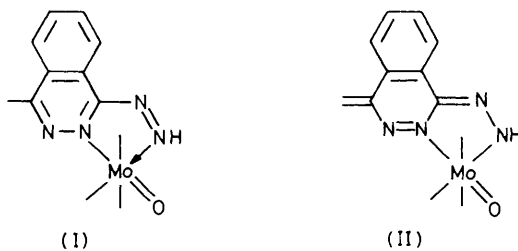


Figure 1. A perspective view of the tetranuclear anion $[\text{Mo}_4\text{O}_{11}\text{dhphH}_2]^{2-}$ of (1). Selected bond distances (Å) and angles (°) are: Mo(1)–O(1) 1.972(6), Mo(1)–O(2) 2.054(6), Mo(1)–O(5) 2.041(6), Mo(1)–O(6) 1.697(6), Mo(1)–N(1) 1.996(7), Mo(1)–N(2) 2.187(6), Mo(3)–O(2) 1.863(6), Mo(3)–O(3) 1.830(7), Mo(3)–O(7) 1.701(9), Mo(3)–O(8) 1.691(8), Mo(4)–O(4) 1.818(6), Mo(4)–O(5) 1.807(6), Mo(4)–O(10) 1.698(7), Mo(4)–O(11) 1.731(8), N(1)–N(5) 1.330(11), N(5)–C(1) 1.366(10), C(1)–N(2) 1.325(11), N(2)–N(3) 1.369(9), Mo(1) \cdots Mo(2) 3.47; O(1)–Mo(1)–O(6) 117.7(3), O(6)–Mo(1)–N(1) 92.0(3), N(1)–Mo(1)–N(2) 68.5(3), N(2)–Mo(1)–O(1) 81.8(2), O(2)–Mo(1)–O(1) 81.8(2), O(2)–Mo(1)–O(6) 96.9(3), O(2)–Mo(1)–N(1) 95.1(3), O(2)–Mo(1)–N(2) 86.0(2), O(5)–Mo(1)–O(1) 82.6(2), O(5)–Mo(1)–O(6) 95.1(3), O(5)–Mo(1)–N(1) 95.7(3), O(5)–Mo(1)–N(2) 86.5(3), Mo(1)–O(1)–Mo(2) 134.6(3). The O–Mo–O angles around Mo(3) and Mo(4) range from 102.8(3) to 115.8(3). Parameters for Mo(2) are similar to those listed for Mo(1).

† Crystal data: $\text{C}_{20}\text{H}_{38}\text{N}_8\text{O}_{11}\text{Mo}_4$, $M = 950.35$, monoclinic, space group $P2_1/n$, $a = 13.223(6)$, $b = 23.134(6)$, $c = 10.896(2)$ Å, $\beta = 104.17(2)^\circ$, $U = 3231.7(5)$ Å³, $D_c = 1.954$ g cm⁻³, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 15.13$ cm⁻¹, $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å. The final R value was 0.050 for 3277 reflections of the 8462 total reflections collected, 5838 of which were unique.

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, 1986.



However, a direct crystallographic location of the diazene protons was not possible.

Spectroscopic results are also in agreement with this formulation. The ^1H n.m.r. spectrum (200 MHz) shows a broad singlet at δ 8.44, which accounts for the two NH protons, in addition to two quartets at δ 8.28 and 7.86 for the aromatic protons, and multiplets associated with the triethylammonium cations. A sharp band at 3203 cm^{-1} in the i.r. spectrum is assigned to the stretching of the diazene protons. Absorptions assignable to the diazene groupings are difficult to locate; below 1000 cm^{-1} the spectrum displays typical, complex patterns centred at 920 and 750 cm^{-1} due to both terminal and bridging oxo ligands. The u.v.-visible spectrum in dmf shows three bands (λ/nm , ϵ) at 535 , 2.55×10^3 ; 400 , 1.55×10^3 ; 310 , 16.0×10^3 . The mixed valence formulation of the anion has been confirmed by X-ray photoelectron data.

Complex (1) easily undergoes a reversible protonation reaction. Addition of concentrated HCl to an ethanolic suspension of (1) yields a new compound analytically and spectroscopically consistent with the formulation $[\text{Mo}_2\text{O}_5\text{dphphH}_6]\text{Cl}_2(\text{EtOH})_{0.5}$. This binuclear Mo^{VI} deriva-

tive of the parent, fully protonated hydrazine ligand could also be obtained directly by treating $\text{MoO}_2\text{Cl}_2(\text{dmf})_2$ with dphphH_6 in the absence of added base.

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