Complexes with the Di-μ-alkoxy-tetrakisphenyldiazenido-dimolybdenum Core, $[Mo_2(NNPh)_4(OR)_2]^{2+}$. The Synthesis and Structural Characterization of the Phenylhydrazino-derivative, $[Mo_2(NNPh)_4(OMe)_4(H_2NNHPh)_2]$

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The organodiazenido-group, –NNR, is of intrinsic chemical interest as a model for understanding the chemistry of metal-bound dinitrogen and NO [1]. The organodiazenido-group is known to form robust complexes with molybdenum, often displacing oxo-groups to give the *cis*-$[Mo(NNR)_2]^{2+}$ structural unit [2]. We have recently extended this chemistry to the polyoxomolybdates with the characterization of species of the type $[Mo_4O_8(OR)_2(NNR)_4]^{2-}$ [3]. At the time, we speculated on the potential utility of the $[Mo_2(NNR)_4(OR)_2]^{2+}$ unit of this species as a core for further synthetic and structural studies. Immediately thereafter, details of the synthesis and structural characterization of $[Mo_2(NNPh)_4(OMe)_2(acac)_2]$ were reported [4]. Although the synthetic approach to this latter complex varied from that employed in our studies, it did suggest the potential for varied chemistry for the $[Mo_2(NNPh)_4(OR)_2]^{2+}$ unit. We report herein the synthesis and structural characterization of $[Mo_2(NNPh)_4(OMe)_4(H_2NNHPh)_2]$, a species containing this core and exhibiting molybdenum–hydrazino coordination, to our knowledge the first example of a molybdenum–diazenido–hydrazino complex.

Reaction of $(Bu^n{}_4N)_2[Mo_4O_8(OMe)_2NNPh)_4]$ with phenylhydrazine in methanol yields lustrous black crystals of $[Mo_2(NNPh)_4(OMe)_4(H_2NNHPh)_2]$. The infrared spectrum shows bands at 1605 and 1565 cm^{-1} characteristic of ν(N–N) for *cis* coordination of the diazenido groups. The band at 2815 cm^{-1} is associated with ν(C–H) for the bridging methoxy-groups and the medium intensity bands at 3210 and 3385 cm^{-1} are assigned for ν(N–H) for the coordinated H_2NNHPh ligand. The complex may also be synthesized by reaction of $[MoO_2(2,3\text{-butanediolate})_2]\cdot$2butane-2,3-diol [5] with excess phenylhydrazine in methanol. Analogous reactions in ethanol/chloroform yield the species $[Mo_2(NNPh)_4(OEt)_2Cl_2(HOEt)_2]$ [6].

Crystal Data: $[Mo_2(NNPh)_4(OMe)_4(H_2NNHPh)_2]$, monoclinic space group $P2_1/n$, $a = 11.437(2)$, $b = 12.004(2)$, $c = 16.756(3)$ Å, $\beta = 108.45(1)°$, $V = 2182.2(6)$ Å^3, $Z = 2$ to give $D_c = 1.45$ g cm^{-1}. Structure solution and refinement based on 2009 reflections with $I_o \geqslant 3\sigma I_o$ converged at $R = 0.047$, with a goodness of fit of 1.657.

The structure of $[Mo_2(NNPh)_4(OMe)_4(H_2NNHPh)_2]$, illustrated in Fig. 1 consists of binuclear molecular units lying on a center of symmetry, with two chemically and crystallographically related $[Mo(NNPh)_2(OCH_3)(H_2NNHPh)]$ moieties linked by two bridging methoxy-groups. The coordination geometry about the molybdenum is distorted octahedral, generated by ligation to the α-N donors of two phenyldiazenido units, to the two bridging methoxy and the one terminal methoxy groups, and to the α-N of the phenylhydrazino-ligand, H_2NNHPh. The location of a center of symmetry on the mid-point of the Mo–Mo′ vector imposes planarity on the Mo–O2–Mo′–O2′ rhombus. The entire $[Mo_2(OCH_3)_2(NN\text{–})_4]$ moiety of the central core is essentially planar, such that the complex $[Mo_2(NNPh)_4(OMe)_4(H_2NNHPh)_2]$ is structurally related to the $\{[Mo_2(NNPh)_4(OMe)_2][MoO_4]_2\}^{2-}$ precursors, that is $[Mo_4O_8(OMe)_2(NNPh)_4]^{2-}$, by substitution of the capping $[MoO_4]^{2-}$ units by two terminal methoxy groups and two phenylhydrazino-ligands.

The short Mo–N(diazenido) distances, 1.823(6) Å (average), together with the average N–N distance of 1.243(9) Å and the essentially linearity of the Mo–N–N unit for the two diazenido ligands, are

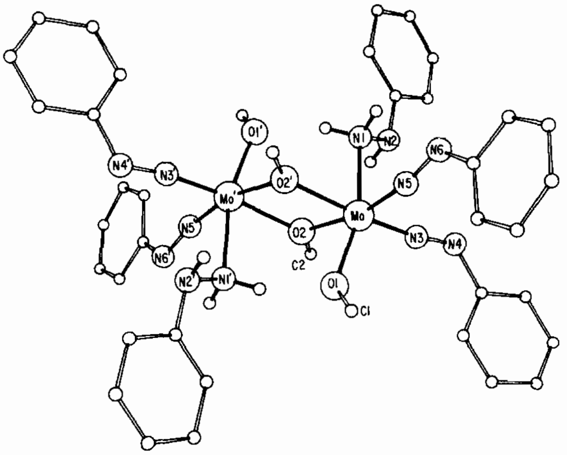

Fig. 1. ORTEP view of the structure of $[Mo_2(NNPh)_4(OMe)_4(H_2NNHPh)_2]$, showing the atom labelling scheme. Relevant bond lengths (Å) and angles (°): Mo–O1, 1.990(5); Mo–O2, 2.110(4); Mo–N1, 2.265(5); Mo–N3, 1.816(6); Mo–N5, 1.829(6); Mo–O2′, 2.125(4); N1–N2, 1.445(9); N3–N4, 1.242(8); N5–N6, 1.243(9); N1–Mo–O1, 163.9(2); N3–Mo–O2′, 167.4(2); N5–Mo–O2, 166.8(2); O2–Mo–O2′, 72.9(2); Mo–N1–N2, 115.4(3); Mo–N3–N4, 170.9(5); Mo–N5–N6, 161.0(5).

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TABLE I. Comparison of Structural Parameters for Complexes Possessing the $[Mo_2(NNPh)_4(OR)_2]^{2+}$ Core, of the Types $[Mo_2(NNPh)_4(OR)_2X_2L_2]^{n-}$ and $[Mo_2(NNPh)_4(OR)_2(LL)_2]^{n-}$ [a]

Complex	Mo–Mo (Å)	Mo–N(diazenido) (Å)	Mo–O(bridge) (Å)	Mo–X or Mo–L[b] (Å)
$\{[Mo_2(NNPh)_4(OMe)_2][MoO_4]_2\}^{2-}$	3.465(2)	1.823(9) (ave.)	2.140(8) (ave.)	2.063(8) (O)
$[Mo_2(NNPh)_4(OMe)_4(H_2NNHPh)_2]$	3.406(1)	1.823(7) (ave.)	2.118(6) (ave.)	1.990(5) (O) 2.265(5) (N)
$[Mo_2(NNPh)_4(OEt)_2(HOEt)_2Cl_2]$	3.407(1)	1.825(6) (ave.)	2.109(4)	2.440(2) (Cl) 2.148(5) (O)[c]
$[Mo_2(NNPh)_4(OMe)_2(acac)_2]$	3.296(3)	1.806(14) (ave.)	2.089(11)	2.055(8) (O) 2.167(7) (O)

[a] X = monoanionic ligand; L = neutral ligand; LL = bidentate ligand. [b] X and L refer to fifth and sixth ligands coordinated to each Mo-center of the $[Mo_2(NNPh)_4(OR)_2]^{2+}$ core. Donor atom is identified in parenthesis. [c] Refers to oxygen donor of terminally coordinated ethanol ligand.

common to this grouping and indicative of extensive delocalization throughout the unit. The Mo–N1-(phenylhydrazine) distance of 2.265(5) Å is consistent with a molybdenum–nitrogen single bond, while the N1–N2 distance of 1.445(9) Å is similar to that observed for N–N single bonds in organohydrazines.

Although the $[Mo_2(NNPh)_4(OR)_2]^{2+}$ core is common to the structures of $[Mo_4O_8(OR)_2(NNPh)_4]^{2-}$, $[Mo_2(NNPh)_4Cl_2(OEt)_2(HOEt)_2]$, $[Mo_2(NNPh)_4(OMe)_4(H_2NNHPh)_2]$ and $[Mo_2(NNPh)_4(OMe)_2(acac)_2]$, two distinct structural forms are observed. While the first three examples exhibit a planar $[Mo_2(OR)_2(NN-)_4]^{2+}$ moiety, the latter example presents a $[Mo_2(OMe)_2(NNPh)_4]^{2+}$ core with one phenyldiazenido-group on each Mo center rotated 90° to occupy a position axial to the plane of the $[Mo_2(NNPh)_2(OMe)_2]$ unit, in order to accommodate the terminally coordinated planar bidentate acac ligands. Table I compares bonding parameters for the four structures.

These observations suggest that the $[Mo_2(NNPh)_4(OR)_2]^{2+}$ unit provides a chemically robust and structurally flexible core, which may be prevalent in structures of the general types $[Mo_2(NNPh)_4(OR)_2X_2L_2]^{n-}$ and $[Mo_2(NNPh)_4(OR)_2(LL)_2]^{n-}$ ($n = 0$ or -2, depending on the nature of the coligands X, L or LL). In future publications, we will discuss the details of the syntheses and structural characteristics of this growing class of complexes, representatives of a general type with chemistry potentially as extensive as that of the well-known μ-oxo-tetraoxodimolybdenum core, $[Mo_2O_5]^{2+}$.

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