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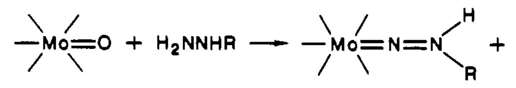
New Organonitrogen-Derivatized Polyoxomolybdate Anion Clusters. Syntheses and Characterization of Tetranuclear and Octanuclear Oxomolybdates Containing Coordinatively Bound Organohydrazido(2–) Units: $[Mo_4O_{10}(OCH_3)_2(NNPh_2)_2]^{2-}$ and $[Mo_8O_{16}(OCH_3)_6(NNMePh)_6]^{2-}$

Sir:

Although the perceived analogies of isopolymetalates to metal oxide surfaces provide a current focus of interest in these species,[1] the coordination chemistry of polymetalates with small organic molecules remains relatively undeveloped. Structurally characterized organooxygen derivatives of polymolybdate anions are limited to the methoxy species $[Mo_8O_{24}(OCH_3)_4]^{4-}$,[2] to the formylated derivative $[(HCO)_2Mo_8O_{28}]^{6-}$,[3] and to the "acetal"-containing anion $[CH_2Mo_4O_{15}H]^{3-}$.[4] A single example of an isopolymolybdate containing nitrogen-donating ligands, the pyridine derivative $[(C_5H_5N)_2Mo_8O_{26}]^{4-}$,[5] had been described prior to our recent reports of the extensive chemistry of isopolymolybdates with phenylhydrazine, to produce a variety of organodiazenido–polyoxomolybdate units: the tetranuclear derivatives $[Mo_4O_8(OR)_2(NNPh)_4]^{2-}$,[6] the hexanuclear species $[Mo_6O_{18}(NNAr)]^{3-}$,[7] and the octamolybdate anion $[Mo_8O_{20}(NNPh)_6]^{4-}$.[8]

The synthesis of the organodiazenido-derivatized clusters consists of a condensation reaction of a molybdenum–oxo center with a phenylhydrazine precursor, eq 1, followed by either an internal redox process or formation of a hydroxy intermediate via transfer of the third hydrazine proton.[9] In this paper, we report on the extension of these studies to the disubstituted organohydrazines H_2NNR_2, organic substrates that display reactivity patterns similar to phenylhydrazine with metal–oxo species,[10] but which function in a formal sense as four-electron-donating dianionic ligands, $(NNR_2)^{2-}$, in contrast to the three-electron diazenido donor, $(NNR)^+$.



$$-\mathrm{Mo}{=}\mathrm{O} + \mathrm{H_2NNHR} \longrightarrow -\mathrm{Mo}{=}\mathrm{N}{=}\mathrm{N}(\mathrm{H})\mathrm{R} + \mathrm{H_2O} \qquad (1)$$

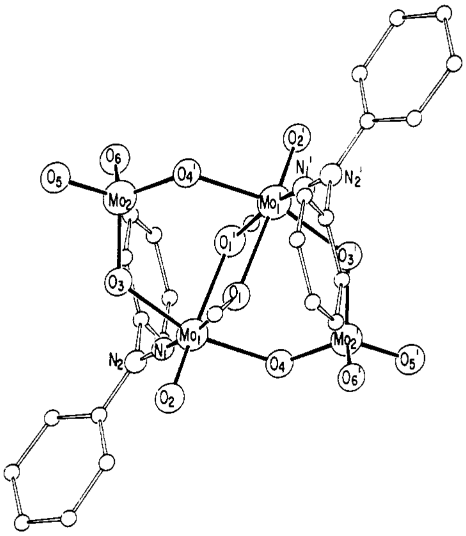


Figure 1. ORTEP view of the tetranuclear anion $[Mo_4O_{10}(OCH_3)_2(NNPh_2)_2]^{2-}$, showing the atom-labeling scheme and 50% probability surfaces.

Reaction of α-$[(C_4H_9)_4N]_4[Mo_8O_{26}]$ with H_2NNRR' ($R = R' = C_6H_5$; $R = C_6H_5$, $R' = CH_3$) in a rigorously dry 1:1 methanol/methylene chloride solution, at room temperature for 24 h, in a 1:6 molar ratio yields a light red solution, which affords lustrous orange crystals of $[(C_4H_9)_4N]_2[Mo_4O_{10}(OCH_3)_2(NNRR')_2]$ (I) upon addition of ether. The infrared spectrum of Ia, $R = R' = C_6H_5$, shows a strong N–N stretching vibration at 1590 cm^{-1} and bands associated with the presence of both terminal, 893 cm^{-1}, and bridging oxo groups, 786 and 765 cm^{-1}. The electronic spectrum exhibits intense absorptions at 337 and 274 nm ($\epsilon = 2.44 \times 10^4$ and 2.80×10^4 L mol^{-1} cm^{-1}, respectively), characteristic of the $[MoO(NNR_2)]^{2+}$ chromophore.

Upon exposure to the atmosphere, crystals of either Ia or Ib ($R = C_6H_5$, $R' = CH_3$) rapidly lose their luster. Furthermore, solutions of Ia or Ib in wet organic alcohols gradually turn dark red, depositing ca. 40% of the original molybdenum content as crystals of $[(C_4H_9)_4N]_4[Mo_8O_{26}]$. Upon filtering, dilution with petroleum ether/ether, and standing, the solution affords dark red crystals of $(Bu_4N)_2[Mo_8O_{16}(OCH_3)_6(NNRR')_6]$ (II) in 30% yield. The synthesis of II may be effected more directly by reaction of α-$[Mo_8O_{26}]^{4-}$ with disubstituted organohydrazines in methanol containing a 1:1 water:molybdenum ratio. The infrared spectrum of II displays the characteristic band at 1592 cm^{-1} associated with the N–N stretching vibration, suggesting monosubstituted molybdenum centers. The complex pattern in the 750–950-cm^{-1} region is characteristic of the presence of both terminal and bridging oxo groups.

The crystal structure of the centrosymmetric dianion of Ia is illustrated in Figure 1.[11] The structure of the tetranuclear unit

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Table I. Selected Bond Lengths (Å) and Angles (deg) for the Tetramolybdate and Octamolybdate Anions[a]

	$[Mo_4O_{10}(OCH_3)_2(NNPh_2)_2]^{2-}$		$[Mo_8O_{16}(OCH_3)_6(NNPhMe)_6]^{2-}$			
	Mo1	Mo2	Mo1	Mo2	Mo3	Mo4
Mo–O_t	1.707 (5)	1.721 (7) 1.708 (6)		1.66 (2)	1.69 (2)	1.64 (2)
Mo–O_b	2.026 (6) 2.054 (5)	1.816 (5) 1.833 (6)	2.20 (2), q 2.07 (2) 2.00 (2) 1.82 (1)	2.29 (1), q 2.17 (2), t 2.06 (2) 2.01 (2)	2.16 (2), t	2.35 (1), q 1.91 (1), t 1.84 (2) 1.83 (2)
Mo–$O(CH_3)$	2.158 (6) 2.204 (5)		2.01 (2)		2.21 (2) 2.11 (2) 1.98 (2)	2.12 (2)
Mo–N	1.780 (7)		1.71 (1)	1.75 (2)	1.82 (2)	
Mo–N–N	173.7 (6)		174.3 (16)	173.9 (18)	168.8 (22)	

[a] Abbreviations: O_t = terminal oxo group; O_b = bridging oxo group. Bridging groups are doubly bridging unless otherwise noted: q = quadruply bridging; t = triply bridging.

is characterized by a planar Mo1–Mo1′–O1–O1′ rhombus, inclosed within a slightly puckered Mo_4O_4 heterocycle. The overall geometry may be described as two *cis*-$[MoO(NNR_2)]^{2+}$ units bridged by two methoxy groups and two $[MoO_4]^{2-}$ units, functioning as bidentate bridging ligands. The bridging $[MoO_4]^{2-}$ units display tetrahedral geometry about the molybdenum atoms, with unexceptional bonding parameters. The hydrazido-coordinated Mo centers enjoy distorted octahedral geometry through ligation to the bridging oxygen atoms of the methoxy groups, to the bridging oxo groups of the $[MoO_4]^{2-}$ units, to the terminal oxo groups, and to the terminal hydrazido(2–) ligand, with bond distances of 2.181 (8) (av), 2.040 (7) (av), 1.707 (5), and 1.780 (7) Å, respectively. The short Mo–N bond distance, together with the N–N bond distance of 1.32 (1) Å and the Mo–N–N bond angle of 173.7 (6)°, is suggestive of extensive delocalization throughout the $[Mo(N_2R_2)]$ unit and consistent with the description of the organonitrogen ligand as a four-electron-donating organohydrazido(2–) species. The structure of Ia is similar to that previously reported for $[Mo_4O_8(OR)_2(NNPh)_4]^{2-}$,[6] with the exception that in the latter case the derivatized Mo centers display the *cis*-bis(diazenido)molybdenum core $[Mo(NNR)_2]^{2+}$, in contrast to the oxo–hydrazido molybdenum unit $[MoO(NNR_2)]^{2+}$ of Ia. The electronic requirements of the metal prevent further substitution of hydrazido groups for oxo ligands, since a $[Mo(NNR_2)_2]^{2+}$ unit would generate a 20-electron structure in the absence of considerable structural rearrangement.[12]

The structure of the complex dianion $[Mo_8O_{16}(OCH_3)_6(NNPhMe)_6]^{2-}$ (II),[13] crystallized as the $(Ph_3PCH_3)^+$ salt, is displayed in Figure 2 and shown to consist of two centrosymmetrically related $[Mo_4O_8(OCH_3)_3(NNPhMe)_3]^-$ units connected through the doubly and quadruply bridging oxo groups O3 and O1, respectively. Of the six methoxy groups, two are terminal and four doubly bridging. Six terminal hydrazido(2–) groups ligated to six of eight molybdenum centers, together with terminal, doubly bridging, and triply bridging oxo groups, complete the pseudooctahedral coordination adopted by all molybdenum centers. Selected structural parameters for the crystallographically unique Mo centers of II are presented in Table I and compared to those observed for Ia. The presence of four chemically and structurally distinct molybdenum sites is a most unusual feature of the structure.

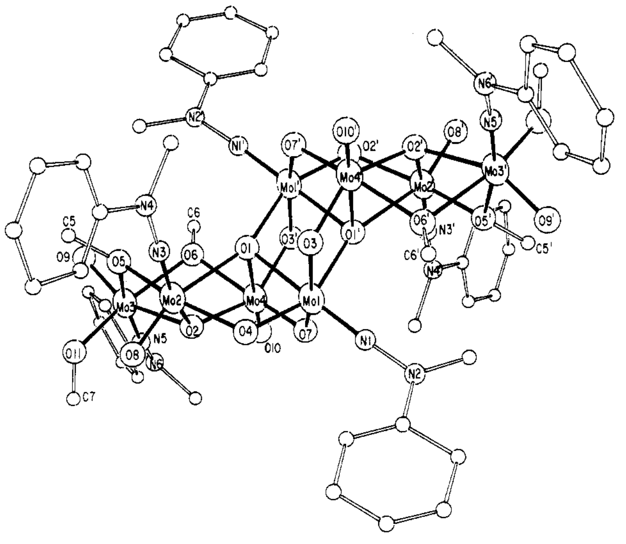

Figure 2. Perspective view of the octanuclear dianion $[Mo_8O_{16}(OCH_3)_6(NNPhMe)_6]^{2-}$, showing the atom-labeling scheme and 50% probability ellipsoids for the molybdenum atoms.

The linkage of octahedra in II is distinct from but related to those of β-$[Mo_8O_{26}]^{4-}$ and of the derived structures of the type $[(X)_2Mo_8O_{26}]^{2n-4}$.[2,4,14-16] The latter species are related to the β-$[Mo_8O_{26}]^{4-}$ structure by translation of one set of Mo_4 octahedra 1 octahedral edge length parallel to the second Mo_4-asymmetric unit. A second translation in the perpendicular direction produces the framework observed for II.

The details of the mechanisms of the formation of I and II and of their interconversion are not yet known. Although I is hydrolytically unstable, controlled addition of aqueous acid yields II and α-$[Mo_8O_{26}]^{4-}$ according to the stoichiometry shown in eq 2. We are currently studying the details of this interconversion

$$4[Mo_4O_{10}(OCH_3)_2(NNR_2)_2]^{2-} + 2H_2O + 2H^+ \rightarrow [Mo_8O_{26}]^{4-} + [Mo_8O_{16}(OCH_3)_6(NNR_2)_6]^{2-} + 2CH_3OH + 2H_2NNR_2 \quad (2)$$

and the effects of solvent and reaction conditions on the degree of oligomerization and on the nature of the hydrazido-derivatized products.

The anions I and II provide useful synthetic precursors for the introduction of the $[MoO(NNR_2)]^{2+}$ core. Reaction with arenethiolate ligands yields species of the type $[MoO(NNR_2)$-

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(11) Crystal data for $C_{58}H_{98}Mo_4N_6O_{12}$ (Ia): Nicolet R3m diffractometer, 21 °C, using a crystal of dimensions 0.16 × 0.20 × 0.15 mm; $a = 20.847$ (3) Å, $b = 13.384$ (2) Å, $c = 27.003$ (4) Å, $\beta = 104.78$ (1)°; space group $A2/a$, $Z = 4$; $d_{calcd} = 1.33$ g/cm³, $\mu = 7.14$ cm⁻¹, $2° \leq 2\theta \leq 45°$(Mo $\lambda(K\alpha)$, 0.71069 Å); no. of unique reflections 4987, no. used in refinement 3264 with $I_o \geq 3\sigma(I_o)$; reflections uncorrected for absorption; merging R value 0.024; final R value 0.069. Non-hydrogen atoms of the anion cluster only were refined anisotropically.

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(13) Crystal data for $C_{86}H_{102}Mo_8N_{12}O_{22}P_2$(II): Nicolet R3m diffractometer, 21 °C, using a crystal of dimensions 0.11 × 0.22 × 0.14 mm; $a = 13.305$ (2) Å, $b = 22.128$ (4) Å, $c = 19.088$ (3) Å, $\beta = 108.87$ (1)°; space group $P2_1/c$, $Z = 2$; $d_{calcd} = 1.55$ g/cm³, $\mu = 9.85$ cm⁻¹, $2° \leq 2\theta = 45°$(Mo $\lambda(K\alpha)$, 0.71069 Å); no. of unique reflections 5864, no. used in refinement 2743 with $I_o \geq 3\sigma(I_o)$; data uncorrected for absorption; merging R value 0.029; final R value 0.081. Molybdenum and phosphorus atoms only refined anisotropically.

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$(SAr)_3]^-$,[17] while bidentate ligands displace oxo groups to give species of the general types $[MoO(NNR_2)(LL)_2]$ and $[Mo_2O_2(NNR_2)_2(\mu\text{-}OR)_2(LL)_2]$. Synthetic studies are in progress to exploit the potential of I as a precursor and to test the persistence of the *cis*-$[MoO(NNR_2)]^{2+}$ unit, a moiety with structural and chemical characteristics related to those of the well-characterized *cis*-dioxomolybdate $[MoO_2]^{2+}$ core.

Acknowledgment. This research was supported by a grant from the National Science Foundation (No. CHE8514634).

Supplementary Material Available: Tables of experimental details for the data collections, atomic positional parameters, bond lengths, bond angles, and anisotropic temperature factors for Ia and II and a table of calculated hydrogen atom positions for $[Bu_4N]_2[Mo_4O_{10}(OCH_3)_2(NNPh_2)_2]$ (19 pages); tables of observed and calculated structure factors for Ia and II (37 pages). Ordering information is given on any current masthead page.

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Structure of a Monomeric Phosphinoborane: Synthesis and X-ray Crystal Structure of (Diphenylphosphino)dimesitylborane

Sir:

A recent report from this laboratory has detailed the synthesis and structural characterization of the complexes $[Li(Et_2O)_2PRBMes_2]$ (**1**) and $[Li(12\text{-crown-}4)_2][RPBMes_2]$ (**2**) (Mes = $2,4,6\text{-}Me_3C_6H_2$; R = Ph, C_6H_{11}, or Mes), which were formulated to have a large degree of double bonding between boron and phosphorus with B–P distances of 1.82–1.83 Å.[1] This disclosure begs the following question. Would a molecule of formula R'_2BPR_2 (R or R′ = alkyl or aryl group) also have a double bond between boron and phosphorus? If this is the case, then such a molecule should have a B–P distance similar to **1** and **2** and a planar geometry at phosphorus in addition to a substantial B–P rotation barrier. In effect the structure should be very close to those seen for similar aminoborane compounds such as Me_2BNMe_2, which has a planar C_2BNC_2 array with a short BN bond.[2] The closest approaches to such a compound are the recently published structures of the aminophosphinoboranes $[\{MesPB(tmp)\}_2]$[3] (**3**), $[Mes(H)PB(Cl)(tmp)]$[3] (**4**), and $[\{Et_3CPB(tmp)\}_2]$[4] (**5**) (tmp = 2,2,6,6-tetramethylpiperidine). However in these compounds the competitive dative interaction to boron is dominated by the nitrogen ligand tmp. This gives rise to short B–N distances, pyramidal phosphorus centers, and B–P bond lengths of 1.916 (3) Å for **3**, 1.948 (3) Å for **4**, and 1.933 (2) and 1.916 (2) Å for **5**, consistent with B–P single bonds. For $R_2'BPR_2$ compounds, substituted by essentially noninteracting alkyl or aryl substituents, ring structures of formula $[(R_2'BPR_2)_n]$ are generally found[5] with n having a value of 2, 3, or 4. In order to study the P–B dative interaction in the absence of oligomerization or significantly competitive ligands the monomeric compound Mes_2BPPh_2 (**6**) has been synthesized and characterized by ^{31}P and ^{11}B NMR spectroscopy[6] in addition to X-ray crystallography.[7]

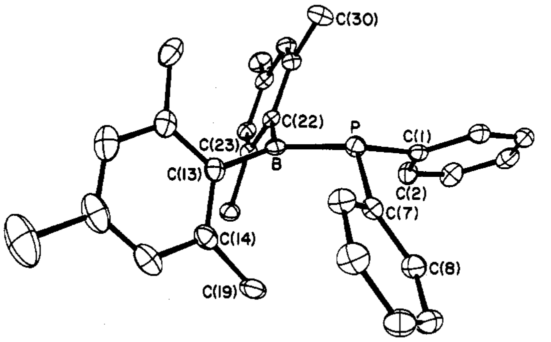

Figure 1. Computer-generated thermal ellipsoid plot of Mes_2BPPh_2. Important bond distances (Å) and angles (deg): B–P = 1.859 (3), B–C(13) = 1.584 (4), B–C(22) = 1.580 (4), P–C(1) = 1.811 (3), P–C(7) = 1.815 (3); C(1)PC(7) = 106.9 (1), C(1)PB = 116.0 (1), C(7)PB = 116.5 (1), PBC(13) = 116.2 (2), PBC(22) = 117.9 (2), C(13)BC(22) = 125.2 (2).

The molecular structure of **6** is shown in Figure 1. It can be seen that the molecule is monomeric with planar boron and pyramidal phosphorus coordination. The main features of interest concern the B–P bond length, 1.859 (3) Å, and the degree of pyramidicity at phosphorus, which are the most sensitive indications of the nature of the B–P bond. The bond length may be compared to 1.82–1.83 Å seen in complexes **1** and **2**,[1,8] distances indicative of multiple bonds and to 1.93–1.96 Å for a B–P single bond. The sum of the angles at phosphorus is 339.4°. However, this is significantly greater than the sum of the angles in PPh_3 (ca. 310°)[9] or in **4** (ca. 307°). Even in the very crowded and distorted diphosphaboretane **3** the sum of the angles at P is ca. 329°. The twist angle between the BP C(13)C(22) plane and the C(1)PC(7) plane is 1.6°, and the dihedral angle is 140.2°. The configuration Mes_2BPPh_2 therefore conveys a bonding picture intermediate between a totally planar B–P system with maximized P→B dative bonding and an alternative arrangement that has relatively acute angles at phosphorus and a smaller interaction between its lone pair and the acceptor p orbital on boron.

This view of the bonding receives some support from dipole moment data[10] and a theoretical study of the hypothetical molecule BH_2PH_2.[11] These calculations reveal a bond distance of 1.83 Å

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[6] The synthesis of the title compound was straightforward. Solid Mes_2BF (1.04 g, 3.9 mmol) was added slowly to a solution of $LiPPh_2$ formed from the addition of n-BuLi (2.4 mL of a 1.63 M n-hexane solution) to $PHPh_2$ (0.73 g, 3.9 mmol) in Et_2O (20 mL). The resultant orange yellow solution was stirred for 2 h, and the volatiles were removed in vacuo. The residue was redissolved in toluene (10 mL), and the yellow solution was filtered, reduced to ca. 5 mL, and cooled to −20 °C, which afforded the product as yellow crystals in ca. 40% yield (0.7 g), mp 172–174 °C. ^{31}P NMR: $\delta = 30.2$. ^{11}B NMR: $\delta = 51.7$.

[7] Mes_2BPPh_2, $C_{30}H_{32}PB$. Crystal data at 130 K: yellow needles, 0.15 × 0.30 × 0.50 mm, $a = 13.341$ (6) Å, $b = 9.689$ (4) Å, $c = 20.311$ (5) Å, $\beta = 106.21$ (5)°, monoclinic, $P2_1/c$, $Z = 4$. Data collection: Syntex $P2_1$ diffractometer, graphite monochromator, Mo Kα radiation, $0° < 2\theta < 50°$, $+h,+k,\pm l$; 4934 reflections collected of which 4449 were unique, $R(\text{merge}) = 0.024$; $\mu = 1.1$ cm^{-1}, absorption correction applied (program XABS). The structure was solved by direct methods, with 3207 data with $I > 2\sigma(I)$ in final refinement, 307 parameters for 32 non-hydrogen atoms (anisotropic), and 32 hydrogen atoms riding on the bonded carbon; $R = 0.049$.

[8] See: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 289. This reference suggests that the covalent radius of boron is not well-defined but probably lies between 0.85 and 0.90 Å. Huheey (Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; Table 6.1, p 258) gives 0.9 Å as the radius of boron. Using 1.1 Å as the radius of phosphorus and assuming the range of 0.85–0.90 Å for B, we may estimate a P–B single-bond length to be 1.94–1.98 Å. With an 8–9% reduction for double bonding, a P–B double bond is predicted to be 1.79–1.84 Å. These methods also predict a value of ca. 1.74–1.77 Å for a B–P multiple bond, which might be possible in a monomer of formula RPBR.

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