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Organonitrogen Derivatized Polyoxomolybdate Anion Clusters. Synthesis and Characterization of a Tetranuclear Oxomolybdate Containing a Single *cis*-Bisphenyldiazenido-molybdenum Unit: $[Mo_4O_{10}(OCH_3)_2(NNC_6H_5)_2]^{2-}$

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The perceived analogies of isopolymetalates to metal oxide surfaces provide one focus of interest in these species [1]. Despite the long history of these unusual species, there are relatively few examples of the coordination chemistry of polyoxometalates with small organic molecules [2–4]. For the specific case of organonitrogen derivatives, a single example, the pyridine complex $[(C_5H_5N)_2Mo_8O_{26}]^{4-}$ [5], had been described prior to our recent reports of the extensive chemistry of isopolymolybdates with arylhydrazines and disubstituted organohydrazine derivatives [6–9]. In this paper we report the preparation and characterization of the unusual tetranuclear dianion $[Mo_4O_{10}(OCH_3)_2(NNC_6H_5)_2)_2]^{2-}$.

Reaction of $[Bu^n_4N]_2[Mo_4O_{10}(OCH_3)_2(NNPh_2)_2]$ [9] with excess phenylhydrazine in methanol yields violet crystals, analyzing for $[Bu^n_4N]_2[Mo_4O_{10}(OCH_3)_2(NNPh)_2]$, in *ca.* 20% yield. Infrared bands at 1590 cm^{-1} and 1565 cm^{-1}, assigned to ν_a(N=N) and ν_s(N=N) of the *cis*-bisdiazenidomolybdenum unit, confirmed that ligand substitution had occurred. The medium intensity transition at 525 nm ($\epsilon = 8.8 \times 10^3$ M^{-1} cm^{-1}) in the electronic spectrum is characteristic of the *cis*-bisdiazenidomolybdenum unit.

Crystal Data: $C_{46}H_{88}Mo_4O_{12}N_6$, monoclinic space group $C2/c$, $a = 15.472(2)$, $b = 20.516(3)$, $c = 19.077(3)$ Å, $\beta = 91.23(1)°$, $V = 6054.1(11)$ Å^3, $D_c = 1.43$ g cm^{-3} for $Z = 4$. Structure solution and refinement based on 1670 reflections with $I_o \geqslant 3\sigma(I_o)$ converged at R (R_w) = 0.063 (0.065).

As illustrated in Fig. 1, the structure of dianion consists of discrete tetranuclear molecular units. The crystallographic two-fold axis along the Mo2–Mo3 vector relates the two halves of the molecule and

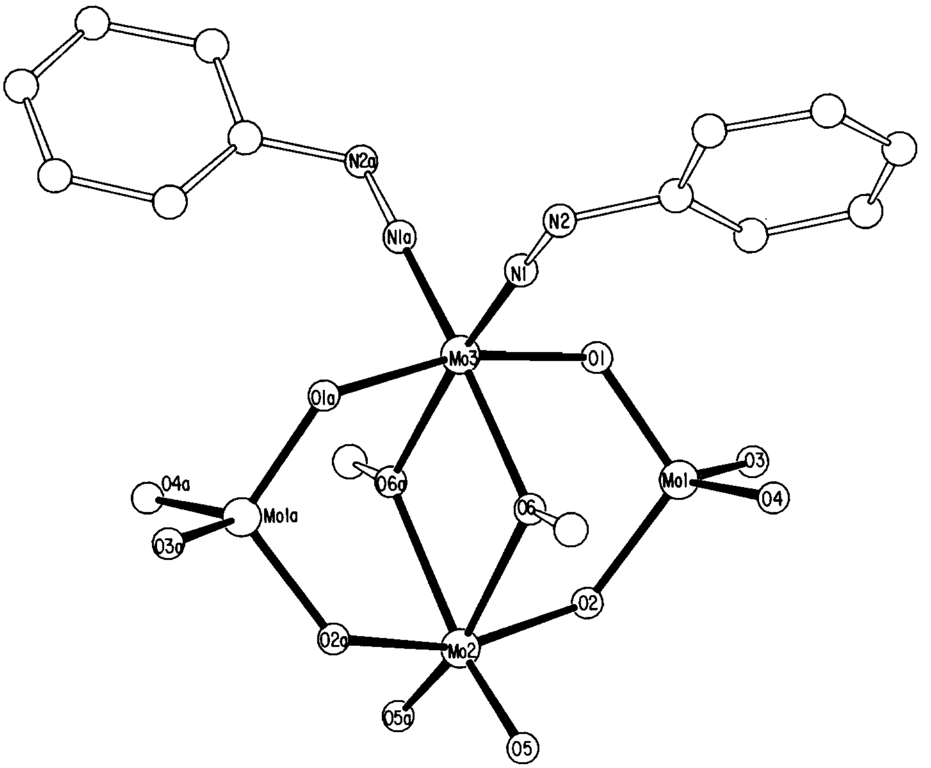

Fig. 1. ORTEP view of the structure of $[Mo_4O_{10}(OCH_3)_2(NNC_6H_5)_2]^{2-}$, showing the atom-labelling scheme. Relevant bond lengths (Å) and angles (°): Mo1–O1, 1.80(1); Mo1–O2, 1.87(1); Mo1–O3, 1.69(1); Mo1–O4, 1.69(1); Mo2–O2, 1.94(1); Mo2–O5, 1.70(1); Mo2–O6, 2.25(1); Mo3–O1, 2.07(1); Mo3–O6, 2.13(1); Mo3–N1, 1.85(1); N1–N2, 1.23(1); O–Mo1–O, 109.1(10); O5–Mo2–O6, 161.5(5); O2–Mo2–O2′, 159.9(7); O6–Mo3–N1, 166.9(5); O1–Mo3–O1′, 164.9(6); Mo3–N1–N2, 173.6(11).

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TABLE I. Comparison of Bonding Parameters for Organonitrogen Derivatized Tetranuclear Polymolybdates of the Class $[Mo_4O_{10-n}(OCH_3)_2(NN-)_{2+n}]^{2-}$

	Mo–O_t[a]		Mo–O_b		Mo–O(CH_3)	Mo–N	Reference
	Mo(tet)	Mo(oct)	Mo(tet)	Mo(oct)			
$[MoO_{10}(OCH_3)_2(NNMePh)_2]^{2-}$	1.707(5)[b]	1.715(7)	1.824(6)	2.040(5)	2.158(6) 2.204(5)	1.780(7)	9
$[Mo_4O_8(OCH_3)_2(NNPh)_4]^{2-}$	1.71(1)	–	1.80(1)	2.06(1)	2.14(1)	1.81(1)	6
$[Mo_4O_{10}(OCH_3)_2(NNPh)_2]^{2-}$	1.69(1)	1.70(1)	1.80(1) 1.87(1)	2.07(1) 1.94(1)	2.13(1) 2.25(1)	1.85(1)	this work

[a]Abbreviations: O_t ≡ terminal oxo-group; O_b ≡ bridging oxo-group; O(CH_3) ≡ bridging methoxy group; Mo(tet) ≡ tetrahedral Mo-site; Mo(oct) ≡ octahedral Mo-site. [b]Distances in Å.

imposes planarity on the Mo2–06–Mo3–06a rhombus. The overall geometry may be described as a *cis*-dioxomolybdenum unit, $[MoO_2]^{2+}$ and a *cis*-bisdiazenidomolybdenum unit, $[Mo(NNPh)_2]^{2+}$, bridged by two methoxy groups and two $[MoO_4]^{2+}$, units functioning as bidentate bridging ligands. The resulting Mo_4O_4 heterocycle is puckered and crown-shaped, while the $[Mo_2O_2(OCH_3)_2(NN-)_2]^{2+}$ core is essentially planar. There are three chemically and crystallographically unique molybdenum centers: Mo1, Mo2 and Mo3. The bridging $[MoO_4]^{2-}$ units display tetrahedral geometry about the molybdenum atoms with unexceptional bonding parameters. The Mo2 center is pseudo-octahedral with ligation to two bridging oxo-groups, two bridging methoxy-groups and two terminal oxo-groups. The organonitrogen derivatized center Mo3 displays distorted octahedral geometry through coordination to the oxygen donors of the bridging methoxy-groups, to the bridging oxo-groups of the $[MoO_4]^{2-}$ units and to the α-nitrogen of the diazenido-groups. The short Mo3–N1 and N1–N2 bond distance, together with the linearity of the Mo3–N1–N2 moiety, suggest extensive delocalization and significant multiple bond character throughout the unit. The significantly different Mo2–O6 and Mo3–O6 bond distances, 2.25(1) Å *vs.* 2.13(1) Å, are indicative of the more pronounced *trans* influence of the oxo-group relative to the organodiazenido-ligand. The Mo–O(bridging) distances are also inequivalent, suggesting that while Mo2 is best described as a Mo(VI) center, the Mo3 center may be more appropriately described as Mo(O). Table I compares relevant bonding parameters for $[Mo_4O_{10}(OCH_3)_2(NNPh)_2]^{2-}$ with those for related structural types.

Synthetic studies suggest that the $[Mo_2O_2(OCH_2)_2(NNPh)_2]^{2+}$ core is chemically robust and that a variety of species of the general type $[Mo_2O_2(OCH_3)_2(NNPh)_2L_2L'_2]^n$ may be prepared by displacing the relatively weakly bound $[MoO_4]^{2-}$ units with common donor groups. Details of these studies will be presented in forthcoming publications.

Supplementary Material

Tables giving data on atomic positional parameters, bond lengths, bond angles and temperature factors can be obtained from the authors.

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