originally proposed becomes an intermediate, (b) a dissociative mechanism in which CO is lost from **1** to form the intermediate $Rh_2(CO)_2(dppm)_2$, and then recoordinates on the opposite face of this metal–metal-bonded species, (c) an associative process in which a tetracarbonyl species acts as an intermediate, and (d) a process involving dppm dissociation/recombination.

Further studies using ^{13}C NMR spectroscopy are being undertaken to address this question and to determine conclusively whether all carbonyl ligands are involved in the exchange process. What does seem clear, however, is that the dppm ligands in their bridging mode appear relatively flexible and are not locked into simple trans positions at the metal centers of the binuclear complex.

Acknowledgment. We thank the National Science Foundation (Grant CHE83-08064) for partial support of this research and Johnson Matthey and Co. for a generous loan of precious metal salts. We also acknowledge helpful discussions with Professor J. Mague, Professor W. D. Jones, Dr. C. Johnson, and Dr. D. Berry.

Registry No. 1, 74507-92-9.

Supplementary Material Available: Listings of refined positional and anisotropic thermal parameters, observed and calculated structure factor amplitudes, and bond distances and angles (65 pages). Ordering information is given on any current masthead page.

Department of Chemistry
University of Rochester
Rochester, New York 14627

Carrie Woodcock
Richard Eisenberg*

Received November 8, 1984

Synthesis and Characterization of a Tetranuclear Oxomolybdate Containing Coordinatively Bound Diazenido Units. $[Mo_4O_8(OCH_3)_2(NNC_6H_5)_4]^{2-}$: A Versatile Precursor for the Synthesis of Complexes with the $[Mo(NNC_6H_5)_2]^{2+}$ Unit

Sir:

The recent interest in the coordination chemistry of polymolybdates with species such as CH_3O^-,[1] HCO^-,[2] and pyridine[3] is a consequence of the importance of these species in developing an understanding of the modes of interaction of small organic molecules with catalytic oxide surfaces.[4,5] In each of the examples cited above, each molybdenum atom is octahedrally coordinated either exclusively to oxygen donors or to five oxygen donors and a single nitrogen donor.

Since these studies establish the ability of polymolybdates to coordinate to nitrogen donors, we sought to extend this chemistry to the organodiazenido group, –NNR, a ligand known to form robust complexes with molybdenum, indeed often displacing oxo groups to give the *cis*-$[Mo(NNR)_2]^{2+}$ structural unit.[6] Furthermore, the organodiazenido group is of some intrinsic interest as a model for understanding the chemistry of metal-bound dinitrogen and NO.[7] The parallel between organodiazenido complexes and those of the diazenide ion, $HN{=}N^-$, a potential but inaccessible reduction product of dinitrogen, has also been noted.[8]

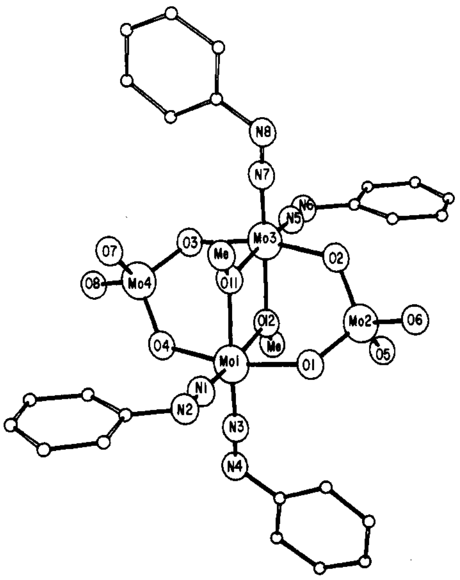

Figure 1. ORTEP view of the tetranuclear anion, $[Mo_4O_8(OCH_3)_2(NNC_6H_5)_4]^{2-}$, showing the atom-labeling scheme.

We report herein the synthesis and structural characterization of an unusual tetranuclear dianion $[Mo_4O_8(OCH_3)_2(NNC_6H_5)_4]^{2-}$, a species containing $[Mo(NNC_6H_5)_2]^{2+}$ units bridged by two methoxy groups and by two MoO_4^{2-} units.

Reaction of $[MoO_2(butane\text{-}2,3\text{-}diolate)_2]\cdot 2\text{-}butane\text{-}2,3\text{-}diol$[9] with excess phenylhydrazine and $N(C_2H_5)_3$ in acidified methanol yields lustrous black crystals, analyzing as $(HNEt_3)[Mo_2O_4(OMe)(NNC_6H_5)_2]$.[10] Conductivity in acetonitrile revealed that the complex behaved as a 2:1 electrolyte. The infrared spectrum showed bands at 1631, 1616, 1574, and 1522 cm^{-1} that are characteristic of ν(N–N) for cis coordination of the diazenido groups in $[Mo(NNR)_2]^{2+}$ units.

An X-ray diffraction study[11] of this complex reveals the tetranuclear structure of the anion (Figure 1). The location of a center of symmetry on the midpoint of the Mo1–Mo3 vector imposes planarity on the Mo1–Mo3–O11–O12 rhombus; in fact, the entire $[Mo_2(OCH_3)_2(NN-)_4]$ unit is nearly planar, with maximum deviations of ca. 0.05 Å from the least-squares plane through all atoms. The overall geometry may be viewed as two $[Mo(NNC_6H_5)_2]^{2+}$ units bridged by two methoxy groups and two MoO_4^{2-} units, functioning as bidentate bridging ligands. The Mo_4O_4 heterocycle is slightly puckered, with Mo2 below the Mo1–Mo3–O1–O2–O3–O4 plane and with Mo4 somewhat above this plane. The bridging MoO_4^{2-} units display tetrahedral geometry about the molybdenum atoms with valence angles in the range 106.3 (3)–113.0 (3)° and average Mo–terminal oxo distances and Mo–bridging oxo distances of 1.716 (9) and 1.798 (9) Å, respectively. The diazenido-coordinated molybdenum atoms

---

(1) McCarron, E. M., III; Harlow, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 6179.

(2) Adams, R. D.; Klemperer, W. G.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1979**, 256.

(3) McCarron, E. M., III; Whitney, J. F.; Chase, D. B., *Inorg. Chem.* **1984**, *23*, 3275.

(4) Day, V. W.; Fredrick, M. F.; Klemperer, W. G.; Liu, R.-S. *J. Am. Chem. Soc.* **1979**, *101*, 491.

(5) McCarron, E. M., III; Staley, R. H.; Sleight, A. W. *Inorg. Chem.* **1984**, *23*, 1043.

(6) Dahlstrom, P. L.; Dilworth, J. R.; Shulman, P.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 933.

(7) Sutton, D. *Chem. Soc. Rev.* **1975**, *4*, 443.

(8) Bishop, M. W.; Butler, G.; Chatt, J.; Dilworth, J. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1843.

(9) Butcher, R. J.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1976**, *6*, 1.

(10) Synthesis of $(NHEt_3)_2[Mo_4O_8(OMe)_2(NNC_6H_5)_4]$: A mixture of phenylhydrazine (4.32 g) and triethylamine (8.08 g) in 50 mL of methanol was added to a refluxing solution of $[MoO_2(C_4H_9O_2)_2]\cdot 2C_4H_{10}O_2$ (2.43 g) in methanol/trimethylsilyl chloride (200 mL/1 mL). A deep purple color developed immediately. After refluxing for 0.5 h, the solution was allowed to cool to room temperature whereupon ethyl ether was added until a perceptible turbidity formed. After the mixture was allowed to stand for 1 week, lustrous black crystals were observed. No special precautions were required as the reaction appears to be neither air nor moisture sensitive. Anal. Calcd for $C_{38}H_{58}Mo_4N_{10}O_{10}$: C, 38.1; H, 4.84; N, 11.7. Found: C, 37.7, H, 4.79; N, 11.8. Yield: 20–30%.

(11) Crystal data for $C_{38}H_{58}Mo_4N_{10}O_{10}$: space group triclinic $P\bar{1}$, $a = 12.326$ (3) Å, $b = 12.799$ (3) Å, $c = 16.190$ (3) Å, $\alpha = 86.56$ (1)°, $\beta = 83.94$ (1)°, $\gamma = 83.67$ (1)°, $V = 2521$ (1) Å^3, $Z = 2$. The X-ray data were collected in a Nicolet R3m diffractometer, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å. The structure was solved by using Patterson and difference Fourier methods using local versions of the SHELXTL program package. Final anisotropic refinement for all non-carbon and non-hydrogen atoms, based on 4243 independent reflections with $I_o \geq 3\sigma(I_o)$, converged at residual of 0.050, with a goodness of fit of 1.48.

0020-1669/85/1324-1287$01.50/0

enjoy distorted octahedral geometry through ligation to the bridging oxygen atoms of the methoxy groups, to the terminal nitrogen donors of the diazenido units, and to the bridging oxo groups of the molybdate units that span the $Mo_2(OCH_3)_2$ rhombus; the average bond distances are 2.140 (8), 1.823 (9), and 2.063 (8) Å, respectively. The Mo1–Mo3 distance of 3.465 Å is indicative of the absence of a significant metal–metal interaction within the $[Mo_2(OCH_3)_2(NNC_6H_5)_4]^{2+}$ moiety. Molybdenum–molybdenum distances for oxo-bridged units average 3.413 Å.

The short average Mo–N distance of 1.823 (9) Å, together with the average N–N distance of 1.227 (12) Å and the linearity of the Mo–N–N unit, is common to the molybdenum–diazenido grouping, indicating extensive delocalization throughout the unit and significant multiple-bond character to the Mo–N and N–N bonds. The electron count for this anion is consistent with the diazenido ligand behaving as a three-electron donor and consequently with the absence of a metal–metal bond, a feature consistent with the observed Mo1–Mo3 bond distance.

The structure is not related to the isopolymolybdate structures mentioned earlier where the molybdenum atoms are pseudooctahedrally coordinated Mo(VI) units. In the present case, the tetrahedral molybdate unit MoO_4^{2-} shares a vertex with each of the Mo1 and Mo3 octahedra, which in turn share an edge defined by the O11–O12 vector. The $[Mo(NNC_6H_5)_2]^{2+}$ unit appears to be a robust chemical unit that persists in the structural chemistry of molybdenum. The oxidation state of the molybdenum in this unit is somewhat ambiguous, as assignment of an average oxidation state of +3 to the molybdenum atoms of the diamagnetic anion is not particularly instructive. However, comparison of the metrical parameters for the metal–diazenido moiety of this structure with those of other examples of organodiazo complexes[12] confirms that the phenyldiazo grouping is best described as the three-electron-donating $-N_2R^+$ structure. Hence, the molybdenum oxidation state may be assigned, in a formal sense, as Mo(0).[13]

The complex anion is reactive toward both oxidation–reduction reactions and substitution reactions at the oxo centers, providing a useful synthetic precursor for a variety of complexes incorporating the $[Mo(NNC_6H_5)_2]^{2+}$ core. Reaction with arenethiolate ligands yields binuclear species $[Mo_2(NNAr)_4(SR)_5]^-$,[14] whereas reactions with sterically demanding thiolates such as 2,4,6-triisopropylthiophenol, TIPT, give monomeric species, $[Mo(NNC_6H_5)L(TIPT)_3]$ ($L = CH_3CN$).[15] With alcohols a variety of products may be isolated, the most remarkable of which is $[Mo_2Cl_2(OC_2H_5)_4(NNC_6H_5)_4]$, an ethoxy-bridged binuclear complex formed by C–C bond cleavage of butane-2,3-diol in CH_2Cl_2 solution[16]

Synthetic studies are in progress to exploit the synthetic potential of the tetranuclear precursor and to test the persistence of the *cis*-$[Mo(NNC_6H_5)_2]^{2+}$ unit, a moiety that appears to exhibit structural and chemical characteristics similar to those of the well-known *cis*-$[MoO_2]^{2+}$ unit, a characteristic feature of Mo(VI) chemistry.

Supplementary Material Available: Listings of atomic positional parameters, bond lengths, bond angles, anisotropic temperature factors, and hydrogen atom positions (8 pages). Ordering information is given on any current masthead page.

---

(12) Cowie, M.; Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, 14, 2617. Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, 14, 1369. Hillhouse, G. L.; Haymore, B. L.; Hermann, W. A. *Inorg. Chem.* **1979**, 18, 2423. Gaughan, A. P.; Haymore, B. L.; Ibers, J. A.; Myers, W. H. Nappier, T. E.; Meek, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 6859 and references therein.

(13) Reference 6 describes the structure of the complex $[Mo(NNC_6H_4OCH_3)_2L]$, previously assigned as a Mo(VI) species. Although the structure is somewhat poorly resolved, the parameters associated with the $[MoN_2R]$ unit are in fact more similar to those observed for hydrazido(2−) complexes, $[MoN_2HR]$, than to those associated with the molybdenum–diazenido moiety, $[MoN_2R]$. This raises some question as to the true identity of this complex and suggests that more accurate crystallographic data be obtained, in conjunction with spectroscopic studies of the molybdenum–nitrogen unit.

(14) Hsieh, T.-C.; Zubieta, J. *Inorg. Chim. Acta*, in press.

(15) Dilworth, J. R.; Hsieh, T.-C.; Zubieta, J., unpublished results.

(16) Hsieh, T.-C.; Zubieta, J. Fifth International Conference on the Chemistry and Uses of Molybdenum, University of Newcastle, England, 1985.

Department of Chemistry
State University of New York at Albany
Albany, New York 12222

Tze-Chen Hsieh
Jon Zubieta*

Received December 11, 1984

Articles

Contribution from the Anorganisch-Chemisches Institut
and Institut für Physikalische Chemie, Universität Münster, 4400 Münster, West Germany

Solid-State ^{11}B NMR Studies on Boron–Chalcogenide Systems

HANS-ULRICH HÜRTER,[1a] BERNT KREBS,*[1a] HELLMUT ECKERT,[1b] and WERNER MÜLLER-WARMUTH*[1b]

Received August 8, 1984

Solid-state ^{11}B NMR techniques are used to study the structural nature of various phases obtained in the systems boron–sulfur, boron–selenium, boron–sulfur–selenium, and boron–tellurium. It is demonstrated that the method can be used efficiently for the structural characterization of these hydrolytically sensitive and glass-forming systems. In the system B–S the novel compound BS_2 is observed at higher S:B ratios besides B_2S_3 at lower ones. In the system B–Se, BSe_2 rather than the expected B_2Se_3 is observed as the only product besides a subselenide with B–B bonds. All phases except the subselenide contain trigonally coordinated boron. No binary boron–tellurium compounds are detected. Quadrupole coupling constants of B_2S_3 (2.46 MHz), BS_2 (2.16 MHz), and BSe_2 (2.07 MHz) are determined and interpreted in terms of the bond properties.

Introduction

Investigation of non-oxide boron–chalcogenide chemistry in the solid state is hampered by severe experimental difficulties. High-temperature synthetic conditions are required that may involve considerable chemical attack of the different container materials by the reaction products. Moreover, the inherent tendency toward vitrification makes an X-ray characterization of these systems very difficult. Finally, the physicochemical investigation is severely restricted by the extreme sensitivity of the non-oxide boron chalcogenides toward hydrolysis. Owing to these unfavorable properties, the present state of the art appears rather diffuse. Although several studies have been undertaken, neither is there a clear picture of the existing compounds in the solid state nor are many of those published in the literature[2-15]

---

(1) (a) Anorganisch-Chemisches Institut. (b) Institut für Physikalische Chemie.

0020-1669/85/1324-1288$01.50/0