Communications

Structures of Molybdenum(V) Tetramers: A Solid-State Fragment with a Zigzag Chain and Reformulation of a Mixed-Valence Tetramer

Sir:

Solid-state transition-metal oxides and sulfides have many interesting structural, electronic, and technologically important properties.[1-6] We are investigating the chemistry of molecular fragments of these solid-state structures, particularly those with extended metal-metal bonding. We report on the structures of two such fragments, both tetrameric cluster complexes of molybdenum.

$Mo_4(HB(pz)_3)_2O_4(\mu\text{-}O)_4(\mu\text{-}OMe)_2(MeOH)_2$[7] (**1**) is prepared by methanol treatment of the yellow precipitate that results from the reaction of $KHB(pz)_3$ with an aqueous HCl solution of molybdenum(V) chloride.[8] The orange-red crystalline compound has been characterized by X-ray crystallography.[9] The basic structure of **1** (Figure 1) can be envisioned as an oligomer of four MX_6 octahedra linked together by edge sharing. It is a fragment of the zigzag chain structure found in many MX_4 solid-state structures such as $ZrCl_4$ and $MoOCl_3$ (monoclinic).[10] The centrosymmetric compound can best be described as a dimer of dimers. The structure of the two Mo1-Mo2 "dimers" is typical of the $Mo^{V}{}_2O_4{}^{2+}$ type.[11,12]

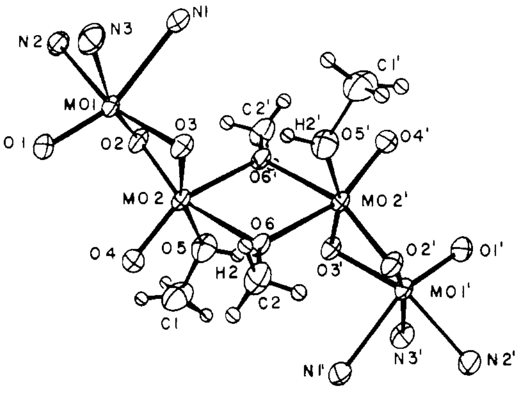

Figure 1. ORTEP drawing of **1**. For clarity, the pyrazoylborate ligands have been left out and the hydrogens have been assigned a temperature factor of 1.0. Selected distances (Å) and angles (deg): Mo1-Mo2, 2.553 (1); Mo2-Mo2′, 3.454 (1); Mo2-O6, 2.082 (3); Mo-O6′, 2.156 (3); Mo2-O5, 2.264 (3); O3-O5′, 2.896 (5); O5-H2, 0.86; O3′-H2, 2.2 Mo1-Mo2-Mo2′, 126.55 (2); Mo2′-Mo2-O3, 89.82 (9); Mo2′-Mo2-O5, 75.48 (9); Mo2-O5-Cl, 129.4 (4); Mo2-O5-O3′, 98.84 (1); Cl-O5-O3′, 119.7 (3); Cl-O5-H2, 95.5; Mo2-O5-H2, 128.9; O5-H2-O3′, 138.4.

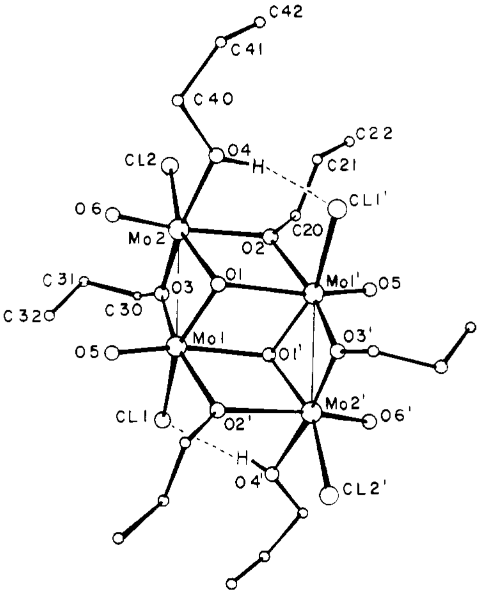

Figure 2. ORTEP diagram of **3** using the original coordinates. The propanolic hydrogens have been drawn in the positions where they should occur on the basis of close structural analogy to **1**. Selected distances (Å) and angles (deg): Mo1-Mo2, 2.669 (2); Mo(2)-Mo1′, 3.43; Mo2-O4, 2.13 (1); Mo1-O2′, 2.05 (1); Mo2-O3, 1.98 (1); Mo1-O3, 1.98 (1); O4-Cl1′, 3.00; Mo2-Mo1′-Cl1′, 86.5; Mo1′-Mo2-O4, 81.5; Mo2-O4-C40, 126; C40-O4-Cl1′, 123.2; Mo2-O4-Cl1′, 103.4.

The bonding between Mo2-Mo2′ is not as familiar, with each of the bridging methoxides trans to a single terminal oxo giving a slightly unsymmetric bridging arrangement. The large number of dialkoxide-bridged dimers which have been reported in the past several years[13-19] provides some precedents. This structural unit is also present as part of the structures of $Mo_4O_8(py)_4(O\text{-}i\text{-}Pr)_4$ (**2**)[20] and $Mo_4Cl_4O_6(O\text{-}n\text{-}Pr)_6$ (**3**).[21] The alternating short (2.553 (1) Å), long (3.454 (1) Å), and short (2.553 (1) Å) metal-metal distances is quite consistent with

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(7) $HB(pz)_3$ = hydrotris(1-pyrazolyl)borate; t = terminal, b = bridging.

(8) Several other compounds are also obtained from this reaction: Millar, M.; Lincoln, S.; Koch, S. A. *J. Am. Chem. Soc.* **1982**, *104*, 228-289. Koch, S. A.; Lincoln, S., to be submitted for publication.

(9) An X-ray diffraction study of **1**, $Mo_4O_{12}N_{12}C_{22}B_2H_{34}$, has revealed that it crystallizes in the space group $P2_1/c$ with $a = 14.763$ (6) Å, $b = 8.965$ (3) Å, $c = 14.076$ (4) Å, $\beta = 104.25$ (3)°, $V = 1806$ (2) Å^3, $\rho_{calcd} = 1.96$ g cm^{-3}, $\rho_{obsd} = 1.90$ g cm^{-3}, and $Z = 2$. X-ray diffraction data ($0 < 2\theta < 56°$) were collected at room temperature with use of Mo Kα radiation on an Enraf-Nonius CAD4A diffractometer. The structure was solved by Patterson and difference Fourier methods using the computer programs of the Enraf-Nonius Structure Determination Package. Final least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms and isotropic parameters for the hydrogens gave $R = 0.038$ and $R_w = 0.048$ using 3151 reflections $I > 3\sigma(I)$.

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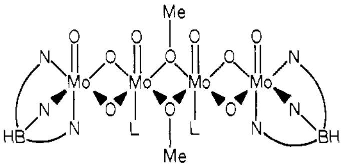
simple bonding considerations for this molybdenum(V) tetramer. The singly occupied d_{xy} orbitals on Mo1 and Mo2 (also Mo1′, Mo2′) overlap to give Mo–Mo single bonds. The conjugation is interrupted since the d_{xy} orbitals on Mo2 and Mo2′ are nearly parallel. This would not be the case in **4** (a possible structural isomer of **1**), which would possess a linear chain of metals.



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A retrosynthetic analysis of **1** reveals that it most likely formed through dimerization of two $HB(pz)_3Mo^V{}_2O_4L_3$ (L = MeOH or MeO^-) units. The dimerization occurs through displacement of the ligand trans to the terminal oxo's, giving **1** rather than **4**. Attempts to isomerize **1** into **4** are in progress. The tridentate polypyrazolylborate ligands serve two structural roles. The ligands cap off the ends of the oligomer, preventing a more extended structure. The ligands also prevent the Mo_4 structure from collapsing to the more compact $Ti_4(OR)_{16}$[22] structure found in **2** and **3** (Figure 2).

The identification of the terminal ligand on Mo2 (Mo2′) as a methanol rather than a methoxide is crucial since it determines that **1** is a Mo(V) tetramer rather than a mixed-valence (2Mo(V), 2Mo(VI)) complex. The chemical[23] and structural evidence clearly indicates that the ligand is methanol. The Mo2–O5 distance 2.264 (3) Å is far outside the range for a $Mo–(OR)_t$[7] distance of 1.81–1.98 Å.[13,14,16] There is also ample structural evidence that in the presence of comparable trans ligands, $Mo–(OR)_t$ distances should be shorter than $Mo–(OR)_b$ distances.[13–19] This would not be the case in **1** if the ligand in question was methoxide. Finally, we were able to locate the methanolic hydrogen which is engaged in a hydrogen bond with O3. Quite analogous hydrogen bonding exists in $Ti_2(OPh)_8(HOPh)_2$[24] and $W_2Cl_4(OMe)_4(HOMe)_2$.[17]

During our structural analysis of **1** we realized that the structure reported for **3**[21] (Figure 2) contains a structural anomaly that leads us to conclude that **3** has been misformulated. The $Mo2–(O(4)Pr)_t$ distance (2.13 (1) Å) is outside the range for terminal alkoxides. It is longer than some $Mo–(OPr)_b$ distances in the same molecule. The result is particularly suspect since the structurally similar $Mo–(O\text{-}i\text{-}Pr)_t$ distance in **2** is 1.945 (3) Å.[20] The anomaly is removed if the two terminal propoxides in **3** are really propanols. Reformulating **3** as $Mo_4Cl_4O_6(O\text{-}n\text{-}Pr)_4(HO\text{-}n\text{-}Pr)_2$ makes it a Mo(V) tetramer like **1** and **2** rather than its original mixed-valence formulation. The rest of the structural parameters are quite consistent with the new formula.[25] For example, the Mo1–Mo2 distance (2.67 Å) in **3** with its mixed oxide–alkoxide bridges is, as might be expected, midway between the distances found in *Mo(V) dimers* with two oxide bridges (2.54–2.61 Å)[10,11,26] and those with two alkoxide bridges (2.73–2.80 Å).[14,18] We are attempting to synthesize **3** in a more direct manner in order to chemically and structurally confirm the new formulation.

Acknowledgment. Financial support was provided by a Dow Chemical U.S.A. Grant of the Research Corp.

Registry No. **1**, 81610-96-0; **3**, reformulated, 81602-77-9; **3**, 42844-79-1.

Supplementary Material Available: Listings of final positional and thermal parameters and distances and angles for **1** (5 pages). Ordering information is given on any current masthead page.

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[23] **1** is diamagnetic. Its mass spectrum shows a continuous emission of methanol at room temperature. A resonance for the methanolic proton is found in the proton NMR spectrum. However, no hydroxyl band could be detected in the IR spectrum. Similar IR results have been reported for another metal complex with a methanol ligand: Bandoli, G.; Clemente, D. A.; Croatto, U.; Vidali, M.; Vigato, P. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2331–2335.

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[25] The difference in the $Mo–(OHR)_t$ distances in **1** and **3** reflects their different trans-effecting ligands; the propanolic hydrogen in **3** will be hydrogen bonded with Cl1 in a completely analogous manner to that seen in **1**.

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Ordered Bimetallic Magnets: Ferromagnetism in $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ and $[Cr(urea)_6][Cr(CN)_6]\cdot3H_2O$

Sir:

Numerous studies have been reported on the magnetic ordering phenomena that occur in transition-metal complexes.[1] By and large, the compounds studied have only one system of metal ions such as is found in $CuCl_2\cdot2H_2O$, $MnCl_2\cdot4H_2O$, and a host of similar materials. Aside from possible inequivalence of crystallographic position, the metal ions in these systems are in chemically similar environments. In addition, pairwise interactions between equivalent metal ions are also well-known in copper acetate and many related molecules.[2]

Recently there have been reports on the pairwise magnetic interactions in several heterobimetallic dimers such as $CuCo(fsa)_2en\cdot6H_2O$[3] and $[Fe^{II}(C_{18}H_{18}N_6)(bipym)Cu^{II}(acac)_2](ClO_4)_2$.[4] Few studies of bimetallic compounds in which there are extended magnetic interactions have been reported, one new example being $[Co(C_5H_5NO)_6](CoCl_4)$.[5] It has been found that there are two independent magnetic subsystems present in this compound, one being the set of octahedral ions and the other the set of tetrahedral ions.

We report here preliminary susceptibility measurements as a function of temperature on two bimetallic coordination compounds of chromium(III). They are $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ (A) and $[Cr(urea)_6][Cr(CN)_6]\cdot3H_2O$ (B). The latter compound is of interest because luminescence measurements have shown that excitation energy transfer occurs from chromium in the cation to chromium in the anion.[6] Compound A was prepared from $[Cr(H_2O)(NH_5)_5](NO_3)_3$[7] and $K_3Cr(CN)_6$,[8] while compound B was prepared as previ-

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