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Tadashi Matsubara, Carol Creutz*

Chemistry Department, Brookhaven National Laboratory
*Upton, New York 11973*

Figure 1. Structure of the $Mo_4I_{11}^{2-}$ anion with numbering scheme for the molybdenum atoms. Atoms are represented by thermal ellipsoids scaled to enclose 50% of the electron density.

The Molybdenum Iodide Cluster Anion $Mo_4I_{11}^{2-}$. A New Cluster Type Structurally Related to the $Mo_6I_8^{4+}$ Octahedral Cluster

Sir:

Recently interest in metal cluster compounds has been stimulated by their potential participation in important catalytic processes where discrete cluster species may to some degree serve as models for reactions which take place at surfaces of metals.[1,2] The progress of work in this area will depend heavily on the success of synthetic methods which must be developed in order to efficiently construct cluster species having the desired structural and chemical properties.

We earlier reported[3] the preparation of a new compound $[(C_4H_9)_4N]_2Mo_4I_{10}Cl$ whose formulation was based on composition and magnetic susceptibility information, but whose structure was not determined because of lack of success in obtaining suitable single crystals. This compound, however, was obtained in good yields as a result of our efforts to develop the approach shown below as a useful method for preparing metal cluster compounds:

$$M(CO)_4X_3^- \xrightarrow[\Delta]{solvent} [MX_3^-] + 4CO \qquad (1)$$

$$MX_3^- \longrightarrow M_nX_{3n}^{n-} \qquad (2)$$
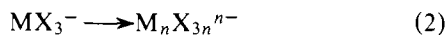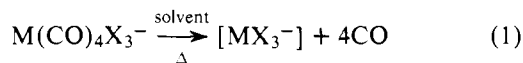
When applied to the thermal decomposition of $[(n\text{-}Bu)_4N]Mo(CO)_4I_3$ in refluxing chlorobenzene, a product of uncertain composition near $[(n\text{-}Bu)_4N]_2Mo_4I_{10}$ was obtained, which provided the salt of $Mo_4I_{10}Cl^{2-}$ after crystallization from 1,2-dichloroethane.

Based upon this observation that the initial product easily abstracted chlorine from 1,2-dichloroethane, subsequent work demonstrated that addition of iodine sufficient for the required oxidation, according to

$$4[(n\text{-}Bu)_4N]Mo(CO)_4I_3 + \tfrac{1}{2}I_2$$
$$= [(n\text{-}Bu)_4N]_2Mo_4I_{11} + 16CO + 2(n\text{-}Bu)_4N^+I^- \qquad (3)$$
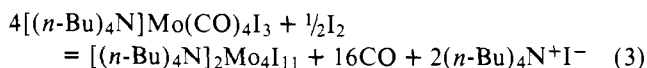
provided crystalline $[(n\text{-}Bu)_4N]_2Mo_4I_{11}$ in high yield.[4] After slow recrystallization from acetonitrile, crystals suitable for structure determination were obtained.[5] Full details of the
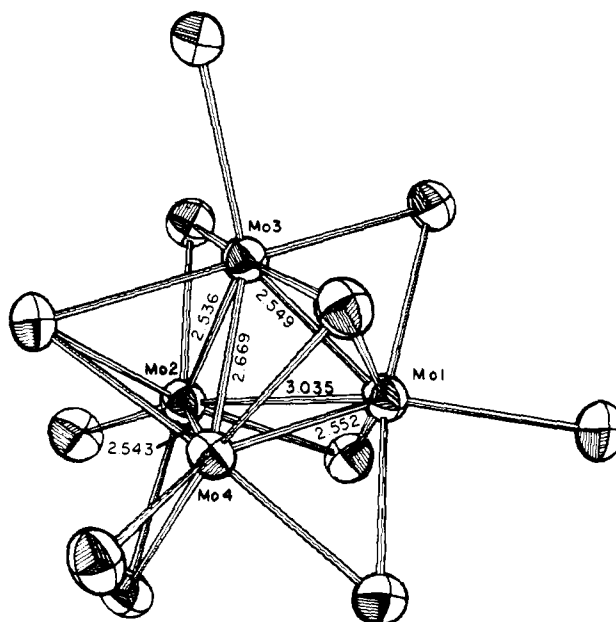
structure determination, which presented some unusual problems, will be reported at a later date.

From data taken at −75 °C with Mo Kα radiation (λ = 0.70954 Å) the cell parameters are a = 19.99 (3), b = 12.49 (3), c = 23.67 (2) Å; α = 89.89 (6), β = 105.80 (5), and γ = 90.27 (8)°; z = 4, $P\bar{1}$. Using 6791 reflections with $I > 3\sigma_I$, the structure has been refined with anisotropic thermal parameters for all nonhydrogen atoms to the final conventional discrepancy factors R = 0.090 and R_w = 0.122. The novel structure of the $Mo_4I_{11}^{2-}$ anion thus revealed is shown in Figure 1.

On one hand this structure may be viewed as a severely distorted tetrahedral cluster of Mo atoms bridged on two faces by triply bridging I atoms and on five edges by doubly bridging I atoms. The coordination sphere of each Mo atom is completed by one bond to a terminal I atom such that each metal atom attains coordination number 8, viz., by bonding to five I atoms and three Mo atoms. The anion has approximate C_{2v} symmetry with the C_2 axis passing through the unique atom I(1) and the midpoint of the bonds Mo(1)–Mo(2) and Mo(3)–Mo(4) of length 3.035 (5) and 2.669 (5) Å, respectively. All other atoms and bonds related by the C_2 axis have average distances as follows: d(Mo–Mo) = 2.542 (5), d(Mo–I$_t$) = 2.848 (5), d(Mo–I$_{db}$) = 2.758 (5), and d(Mo–I$_{tb}$) = 2.826 (5) Å (where t = terminal, db = doubly bridging, tb = triply bridging). The very acute Mo–I$_{db}$–Mo and Mo–I$_{tb}$–Mo bond angles, which average 57.3 (1) and 54.5 (1)°, respectively, testify to strong Mo–Mo bonding between all Mo–Mo pairs; even in the case of the "long bond" between Mo(1)–Mo(2), the Mo(1)–I(1)–Mo(2) angle is very acute, 66.8 (1)°. The average of all six Mo–Mo bond distances of 2.645 Å may be compared with the Mo–Mo distance in the metal, 2.73 Å.[6]

On the other hand this structure is more fruitfully viewed as a fragment of the well-known octahedral clusters $Mo_6X_8^{4+}$. As shown in Figure 2 the structure of $Mo_4I_7^{2+}$ (terminal I atoms omitted) can be derived from that of $Mo_6I_8^{4+}$ by removing two adjacent Mo atoms from the Mo_6 octahedron and one I atom from the I_8 cube. The I atom remaining on the cube edge adjacent to the positions of the two removed Mo atoms then is shifted to the midpoint of that edge and becomes the unique atom I(1) which bridges the long bond Mo(1)–Mo(2). From the standpoint of Mo–I bonding and net charge on the cluster, the fragment $Mo_4I_8^+$ also would seem quite reason-
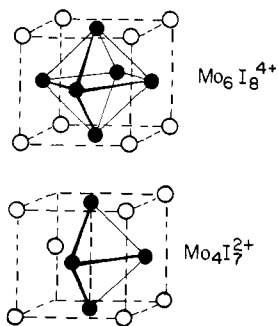
Figure 2. Representation of the structures for the $Mo_6I_8^{4+}$ and $Mo_4I_7^{2+}$ cluster cores showing the close relation between the two units.

able. However, we may surmise that loss of one I atom from the I_8 cube is necessary to permit close approach and bonding between Mo(1) and Mo(2). In $Mo_6X_8^{4+}$ clusters the distance between trans Mo atoms is ca. $\sqrt{2}(2.60) = 3.67$ Å.[7] With all eight I atoms retained in the cube, this distance cannot contract without large translation of the trans Mo atoms toward the interior of the cube, i.e., out of the plane of the surrounding I atoms. Thus, better Mo–Mo bonding resulting from this translation would be opposed by unfavorable electrostatic interactions. Loss of one I atom from the I_8 cube overcomes the latter problem and permits much stronger bonding between Mo(1)–Mo(2).

Thus $Mo_4I_{11}^{2-}$ becomes the second example of a cluster which is best viewed as a fragment of the $Mo_6X_8^{4+}$ unit; the ion $Mo_5Cl_{13}^{2-}$ represents the first.[8] In the latter case formation of the $Mo_5Cl_8^{3+}$ core formally requires only removal of one Mo^+ atom from the $Mo_6Cl_8^{4+}$ unit. The Mo–Mo distances of 2.602 (3) and 2.563 (3) Å reported for $Mo_5Cl_{13}^{2-}$ are quite comparable with the distances for the five short bonds of $Mo_4I_{11}^{2-}$. By comparison with $Mo_6X_8^{4+}$ clusters the ready removal of one electron per cluster, as dictated for the net oxidation states of 2.20 and 2.25 per Mo for $Mo_5Cl_{13}^{2-}$ and $Mo_4I_{11}^{2-}$, respectively, appears to be a result of abundant nonbonding electrons localized on the basal Mo atoms of $Mo_5Cl_{13}^{2-}$ and on Mo(1) and Mo(2) of $Mo_4I_{11}^{2-}$. These in turn may be ascribed to the "unsatisfied" orbitals created by the removal of either one or two metal atoms from the Mo_6X_8 unit.[9,10]

The structure of $Mo_4I_{11}^{2-}$ also may be compared with those of $CsNb_4X_{11}$ (X = Cl or Br)[11] and $Mo_4S_4Br_4$.[12] In each of the latter cases the formal M–M bond order may be assigned a value of 1.0. Yet in both cases the average M–M bond distances are much longer than in $Mo_4I_{11}^{2-}$, viz., 2.86 Å for $CsNb_4Cl_{11}$, 2.98 Å for $CsNb_4Br_{11}$, and 2.80 Å for $Mo_4S_4Br_4$. Neither of the $CsNb_4X_{11}$ or $Mo_4S_4Br_4$ structures is capable of housing all 15 of the metal electrons found in $Mo_4I_{11}^{2-}$ without occupation of antibonding orbitals.[13,14] A rough MO analysis of the Mo–Mo bonding in $Mo_4I_{11}^{2-}$ indicates that there are six bonding and two nonbonding orbitals available to accommodate the 15 electrons.[10] The formal Mo–Mo bond order is thus 1.0 (12 electrons, six bonds) and 3 electrons reside in nonbonding orbitals localized mainly on Mo(1) and Mo(2). Since in C_{2v} symmetry these orbitals are nondegenerate, the cluster ion should have a magnetic moment corresponding to one unpaired electron. The observed moment $\mu = 1.87$ μ_B is temperature independent and in agreement with this requirement.

The presence of the formally nonbonding MO's with 3 electrons indicates that $Mo_4I_{11}^{2-}$ should exhibit interesting redox chemistry. Also the electron-rich character of this cluster suggests that it should be unusually susceptible to attack by electrophillic reagents and addition of metal atoms to expand the cluster. These aspects of the chemistry are presently under investigation.

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(5) Anal. Calcd for Mo, 16.95; I, 61.64; C, 16.97; H, 3.20; N, 1.24. Found: Mo, 16.85; I, 61.58; C, 17.06; H, 3.22; N, 1.44.
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(10) In C_{2v} symmetry the M–M bonding in $Mo_4I_{11}^{2-}$ can be described as $(3a_1 + a_2 + b_1 + b_2)^{12}_b(a_2 + b_1)^3_{nb}$. The latter a_2 and b_1 orbitals involve mainly interactions at the distance 3.035 Å between d orbitals lying in planes perpendicular to the Mo(1)–Mo(2) axis. These orbitals thus should have neither strong bonding or antibonding character.
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(13) In the planar Nb_4 cluster of $CsNb_4X_{11}$ two of the Nb atoms have coordination number 9 (6Nb–X + 3Nb–Nb) and two have coordination number 8 (6Nb–X + 2Nb–Nb). The two Nb atoms with coordination number 8 each have an unoccupied nonbonding orbital which could accommodate a total of 4 more electrons. Thus a total of 14 metal–metal electrons might be housed in either bonding or nonbonding MO's. In these compounds the nonbonding orbitals are vacant; addition of electrons to these orbitals would require a large difference in formal oxidation number of the two nonequivalent pairs of Nb atoms.
(14) The formula of $Mo_4S_4Br_4$ is better written as $Mo_4S_4Br_{12/3}$ which reflects the fact that the cluster units are interconnected by bridging Br atoms. Each Mo thus attains a coordination number 9 (3Mo–S + 3Mo–Br + 3Mo–Mo) and it is readily seen that this leads to a closed configuration for the cluster where all bonding MO's are filled and all antibonding orbitals are vacant. In this cluster unit there are no nonbonding orbitals centered on the metal atoms. The Mo–Mo bonding can be described as $(a_1 + e + t_2)$.[12]

Steven Stensvad, Barbara J. Helland, M. W. Babich
Robert A. Jacobson, Robert E. McCarley*
Ames Laboratory, USDOE, and Department of Chemistry
Iowa State University, Ames, Iowa 50011
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A Novel Mode of Carbonate Binding. Structure of Spin-Paired μ-Carbonato-bis(2,4,4,7-tetramethyl-1,5,9-triazacyclododec-1-ene)dicopper(II) Perchlorate

Sir:

Partial spin pairing by antiferromagnetic coupling is relatively common for dinuclear Cu(II) compounds,[1] but few examples have been well characterized where complete spin pairing results in diamagnetism.[2-4]

The twelve-membered triaza macrocycles L_1 and L_2 form a number of dinuclear compounds with five-coordinate Cu(II), or Ni(II), with di-μ-chloro, di-μ-hydroxo, μ-oxalato, etc.,