

tainly experience more unfavorable intramolecular contacts with the COD ligands than the diphenylacetylene moiety.

Although dinuclear complex **1** is coordinately unsaturated, its chemistry did not include facile donor-ligand addition unless the donor had cylindrical form, so that it could penetrate the relatively congested region around the nickel atoms (Figure 1). Illustrative of this donor-acceptor chemistry was the observation that alkyl phosphites did not react with **1** up to 90 °C, whereas *tert*-butylisocyanide reacted instantly at 18 °C to give Ni(CNR)₄. Spectroscopic studies gave no evidence of dissociation of **1** in solution nor of complex formation with diphenylacetylene, although **1** slowly catalyzed cyclotrimerization of the acetylene to hexaphenylbenzene.

Hydrogen reacted with **1** with selective transfer of hydrogen atoms (presumably from nickel) to the acetylene to give *cis*-C₆H₅CH=CHC₆H₅;¹¹ no reduction of the cyclooctadiene ligand could be detected by GC analysis. Complex **1** served as a selective catalyst for the hydrogenation of acetylenes to cis-olefins at 18–20 °C. This facile reduction is completely consistent with the cluster thesis for activation of triple bonds toward hydrogen reduction.^{12–14} However, the bond order reduction that can be realized in such π² structures is not a sufficient condition. We have found that analogous acetylene cluster complexes in which the C≡C triple bond has been substantially lengthened show no evidence of dihydrogen reduction nor of catalysis of acetylene reduction by dihydrogen up to 80–100 °C. All these inactive clusters are formally coordinately saturated; complexes demonstrated to be inactive included Co₂(CO)₆(RC≡CR),⁵ Co₄(CO)₁₀(RC≡CR),¹⁵ and (C₅H₅)₂Ni₂(RC≡CR),² where R is phenyl. Clearly the effective coordination unsaturation in **1** plays a key role in this selective catalytic chemistry. We are now attempting a mechanistic definition of this reduction chemistry.

Through calculations, synthesis of analogues of **1** with ligands alternative to cyclooctadiene, and a thorough chemical exploration we are attempting a definitive characterization of the factor(s) that lead to the long metal-metal bond in this complex and the structure-chemistry relationship.

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Supplementary Material Available: Tables of fractional atomic coordinates (Table I) and anisotropic thermal parameters (Table II) for nonhydrogen atoms and fractional atomic coordinates and isotropic thermal parameters (Table III) for hydrogen atoms in crystalline (diphenylacetylene)bis(cyclooctadienenickel) (3 pages). Ordering information is given on any current masthead page.

References and Notes

- M. G. Thomas, W. R. Pretzer, B. F. Beier, F. J. Hirsekorn, and E. L. Muetterties, *J. Am. Chem. Soc.*, in press.
- O. S. Mills and B. W. Shaw, *J. Organomet. Chem.*, **11**, 595 (1968).
- (a) W. B. Pearson, "Lattice Spacings and Structures of Metals and Alloys", Pergamon Press, London, 1957; (b) C. Kruger, *Angew. Chem.*, **81**, 709 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 678 (1969).
- See paragraph at end of paper regarding supplementary material.
- W. G. Sly, *J. Am. Chem. Soc.*, **81**, 18 (1959).
- A. N. Nesmeyanov, A. I. Gusev, A. A. Pasyanski, K. N. Anisimov, N. E. Kolobova, and Y. T. Struchkov, *Chem. Commun.*, 1365 (1968); A. I. Gusev and Y. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 107 (1969).
- The first number in parentheses is the root mean square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively.
- L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.
- (a) K. Nicholas, L. S. Bray, R. E. Davis, and R. Pettit, *Chem. Commun.*, 608

- (1971); (b) H. J. Schmitt and M. L. Ziegler, *Z. Naturforsch. B.*, **28**, 508 (1973); (c) J. L. Calderon, S. Fontana, E. Frauendorf, V. W. Day, and S. D. A. Iske, *J. Organomet. Chem.*, **64**, C16 (1974); (d) T. Aoki, A. Furusaki, Y. Tomiie, K. Ono, and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **42**, 545 (1969); (e) F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Organomet. Chem.*, **94**, C53 (1975); F. A. Cotton, J. D. Jamerson, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 1774 (1976).
- Values for the bond angles at C(4) (average value 109.4°) and the C(4)–H(42) bond length of 1.05 (7) Å are those expected for an sp³-hybridized carbon atom. Although not required by symmetry, the C(4)–H(42) and C(4)′–H(42)′ bonds are nearly collinear; the H(42)–C(4)–H(42)′ angle is 21°.
- The other products were nickel metal and 1,5-cyclooctadiene.
- M. G. Thomas, E. L. Muetterties, R. O. Day, and V. W. Day, *J. Am. Chem. Soc.*, **98**, 4645 (1976).
- E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **85**, 0000 (1976).
- E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975).
- L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **84**, 2450 (1962).
- Camille and Henry Dreyfus Teacher-Scholar.

V. W. Day,*¹⁶ S. S. Abdel-Meguid, S. Dabestani
Department of Chemistry, University of Nebraska
Lincoln, Nebraska 68588

M. G. Thomas, W. R. Pretzer, E. L. Muetterties*
Cornell Materials Science Center
and Spencer T. Olin Chemistry Laboratory
Cornell University
Ithaca, New York 14853
Received July 20, 1976

Synthesis and Interconversion of the Isomeric α- and β-Mo₈O₂₆⁴⁻ Ions

Sir:

Although Mo₈O₂₆⁴⁻ isomers have been suspected for some time,¹ their structural differences have only recently been clarified^{2,3} (see Figure 1a). In an effort to determine the precise conditions which favor selective synthesis of a single isomer, we have prepared several alkylammonium salts of the Mo₈O₂₆⁴⁻ ion and discovered a facile isomerization process which rapidly interconverts these structurally disparate isomers.

When R_nNX (R = CH₃, C₂H₅, *n*-C₃H₇, *n*-C₄H₉; X = Cl or Br) is added to an acidified aqueous sodium molybdate solution (pH 3–4), the compounds β-[(CH₃)₄N]₂Na₂Mo₈O₂₆·2H₂O,⁴ β-[(C₂H₅)₄N]₃NaMo₈O₂₆,⁵ β-[(*n*-C₃H₇)₄N]₃-NaMo₈O₂₆·2H₂O,⁵ and α-[(*n*-C₄H₉)₄N]₄Mo₈O₂₆⁶ are precipitated.⁷ When (*n*-C₄H₉)₄NX addition is preceded by addition of a large excess of KCl, however, the compound β-[(*n*-C₄H₉)₄N]₃KMo₈O₂₆·2H₂O is obtained.⁷ In order to determine whether this cation dependent α-β selectivity might reflect different solution equilibria instead of selective precipitation, the compounds [(*n*-C₄H₉)₄N]₃KMo₈O₂₆·2H₂O (**1**) and [(*n*-C₄H₉)₄N]₄Mo₈O₂₆ (**2**) were subjected to an infrared study in acetonitrile. Remarkably, this study revealed that **1** and **2**, although pure β and α isomers, respectively, in the solid state, consist of α-β mixtures in acetonitrile, with the solid state structure predominating (see Figure 1b–e). This equilibrium is most easily followed by comparing the strong 808-cm⁻¹ absorption characteristic of the α isomer with the weak 965- and strong 717-cm⁻¹ absorptions characteristic of the β isomer. The equilibrium may be shifted toward the α isomer by adding [(*n*-C₄H₉)₄N]Cl to acetonitrile solutions of **1** or **2** (see Figure 1e and f).⁸ This cation dependent equilibrium can be exploited to synthesize a wide variety of compounds by mixing solutions of **2** in acetonitrile with various aqueous halide solutions. These compounds⁷ include the families β-M₄Mo₈O₂₆·*n*H₂O (M =

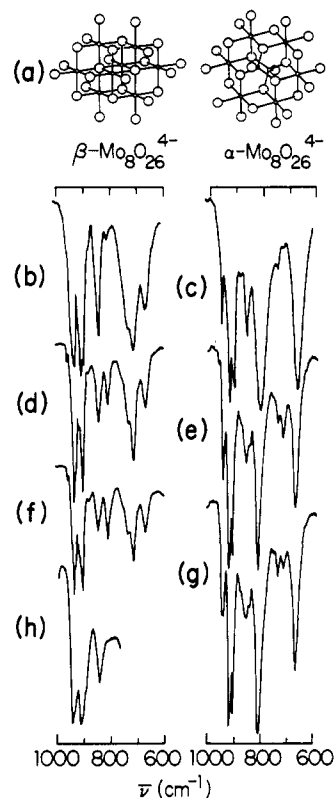


Figure 1. Idealized structures of the β - and α - $\text{Mo}_8\text{O}_{26}^{4-}$ isomers are shown in (a). Small circles represent molybdenums and large circles represent oxygens. Below are IR spectra of (b) $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{KMo}_8\text{O}_{26}\cdot 2\text{H}_2\text{O}$ (**1**) in KBr pellet, (c) $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{Mo}_8\text{O}_{26}$ (**2**) in KBr pellet, (d) **1** in CH_3CH , (e) **2** in CH_3CN , (f) **1** plus $(n\text{-C}_4\text{H}_9)_4\text{NCl}$ in CH_3CN , (g) **2** plus $(n\text{-C}_4\text{H}_9)_4\text{NCl}$ in CH_3CN , (h) $(\text{ND}_4)_4\text{Mo}_8\text{O}_{26}\cdot 4\text{D}_2\text{O}$ in D_2O .

Rb, K) and β - $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{MMo}_8\text{O}_{26}\cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Rb}, \text{K}, \text{NH}_4$). Heating, however, should be avoided since **2** in acetonitrile is quite hygroscopic, and such hydrated solutions react

(reversibly) to form $\text{Mo}_6\text{O}_{19}^{2-}$ when heated.

The rapid isomerization of α - $\text{Mo}_8\text{O}_{26}^{4-}$ under anhydrous conditions⁹ is difficult to reconcile with current mechanistic theories of polyoxoanion transformations.¹⁰ We propose therefore a mechanism based on the intramolecular process shown in Figure 2. For clarity of presentation, all coordination polyhedra have been idealized. In fact, all five- and six-coordinate molybdenums are strongly displaced toward polyhedral edges. Such off-center displacements lead to distortion of the coordination polyhedra. In the γ - Mo_8O_{26} structure, the coordination at Mo(a) (and Mo(a')) leads to instability in that Mo(a)-O(1) and Mo(a)-O(2) bond orders of about two and an Mo(a)-O(7) bond order of about one imply a total Mo(a)-O(11) plus Mo(a)-O(8) bond order of about one to achieve hexavalency at Mo(a). This is unlikely since these last two bonds are trans to double bonds. It is quite possible, therefore, that the isomerization is catalyzed by traces of water⁹ such that the vacant coordination positions at Mo(a) (and Mo(a')) are occupied by hydroxyl ions (vide infra).

The idealized mechanism shown in Figure 2 can be analyzed from two points of view. From a global point of view, the α , γ , and β structures consist of cubic closed packed (ccp) oxygens with molybdenums occupying tetrahedral and octahedral holes. The α - γ and β - γ structures consist of close packed oxygens with molybdenums occupying trigonal bipyramidal and octahedral holes. Here, however, the oxygen close packing is based on interpenetrating hexagonally close packed (hcp) layers similar to those found in the α -Keggin structure.¹¹ By following the packing of the oxygens bonded to Mo(b), Mo(c), Mo(b'), and Mo(c') as the isomerization proceeds, a shear plane becomes apparent, arising from the repeated ccp-hcp transformations. Note also that the proposed mechanism preserves overall inversion symmetry. From a local point of view, each molybdenum atom alters its coordination polytope in a precedented fashion. Polytopal expansion proceeds via facial attack on tetrahedra yielding trigonal bipyramids or edge attack on trigonal bipyramids yielding octahedra. Polytopal isomerization of Mo(a) and Mo(a') in the course of the α - γ

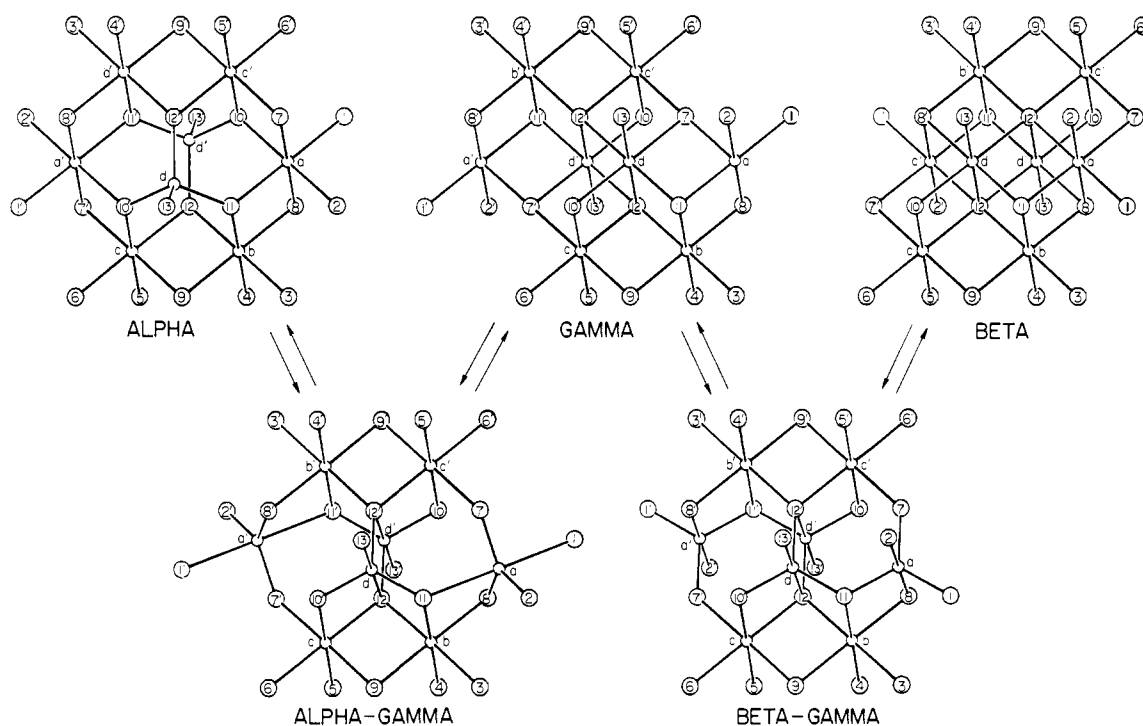


Figure 2. Proposed mechanism for the α - β $\text{Mo}_8\text{O}_{26}^{4-}$ isomerization, represented by three structures along the reaction pathway. All structures are idealized. Small circles represent molybdenums, large circles represent oxygens. Nuclei with primed labels are related to nuclei with same label, unprimed, by inversion symmetry.

to β - γ transformation rigorously follows the Berry mechanism with O(7) and O(7') acting as "pivots".

Even though the α - γ and β - γ structures are constitutionally identical, differing only in configuration at Mo(a) and Mo(a'), we have included the γ structure in Figure 2 since it is a fragment of the $\text{Mo}_{10}\text{O}_{34}^{8-}$ and $(\text{Mo}_8\text{O}_{27}^{6-})_\infty$ structures found in the compounds $(\text{NH}_4)_8\text{Mo}_{10}\text{O}_{34}^{12}$ and $(\text{NH}_4)_6\text{Mo}_8\text{O}_{27} \cdot 4\text{H}_2\text{O}$,¹³ respectively. The formation of these compounds, which occurs in acidified aqueous molybdate solutions, can readily be accounted for by the present mechanistic scheme. If MoO_4^{2-} ions attack the Mo(a) and Mo(a') centered trigonal bipyramids on the O(2)-O(8) and O(2')-O(8') edges in the α - γ structure or the O(1)-O(11) and O(1')-O(11') edges in the β - γ structure, the $\text{Mo}_{10}\text{O}_{34}^{8-}$ structure is generated. Either analogous attack by hydroxyl ions followed by proton transfer and polycondensation or hydroxyl attack on the O(2)-O(7) and O(2')-O(7') edges in the α - γ structure followed by polycondensation leads to the $(\text{Mo}_8\text{O}_{27}^{6-})_\infty$ structure.

These speculations, however, can be rendered meaningful only by experimental data regarding aqueous solution structures. Preliminary infrared spectroscopic data of concentrated aqueous sodium and ammonium molybdate solutions thus far rule out the α - $\text{Mo}_8\text{O}_{26}^{4-}$ structure as a major component at pH 3-4 (see Figure 1h). We are currently measuring infrared, Raman, and ^{17}O NMR spectra of aqueous molybdate species as a function of pH, counterion, temperature, and concentration, and hope to be able to better define their structural and dynamic characteristics.

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References and Notes

- (1) The earliest evidence for $\text{Mo}_8\text{O}_{26}^{4-}$ isomerism was presented in an infrared study by M. J. Schwing-Weill and F. Arnaud-Neu, *Bull. Soc. Chim. Fr.*, 853 (1970).
- (2) For the structure of α - $\text{Mo}_8\text{O}_{26}^{4-}$ see (a) J. Fuchs and H. Hartl, *Angew. Chem., Int. Ed. Engl.*, **15**, 375 (1976), (b) M. F. Fredrich, V. W. Day, W. Shum, and W. G. Klemperer, American Crystallographic Association, Summer Meeting, 1976, paper M5.
- (3) For the structure of β - $\text{Mo}_8\text{O}_{26}^{4-}$ see (a) L. O. Atovmyan and O. N. Krasochka, *J. Struct. Chem.*, **13**, 319 (1972); (b) I. Lindqvist, *Ark. Kemi*, **2**, 349 (1950).
- (4) This compound has been incorrectly reported as $[(\text{CH}_3)_4\text{N}]_2\text{Mo}_8\text{O}_{25} \cdot 5\text{H}_2\text{O}$ by J. Fuchs, I. Knopnadel, and I. Brüdgam, *Z. Naturforsch. B*, **29**, 473 (1974).
- (5) We have been unable to reproduce preparations of the anhydrous compounds $[\text{R}_4\text{N}]_4\text{Mo}_8\text{O}_{26}$, R = C_2H_5 and C_3H_7 , reported by Fuchs et al., in ref 4.
- (6) The identical compound was reported by Fuchs et al., in ref 2a and 4.
- (7) Satisfactory elemental analyses were obtained for all compounds reported here. Structures were assigned by Raman and infrared spectroscopy.
- (8) We do not understand the reasons for this shift in the equilibrium. Selective ion pairing is a possibility, and conductivity measurements in acetonitrile show that **1** behaves as a 3:1 electrolyte and **2** behaves as a 4:1 electrolyte.
- (9) Although we have observed the isomerization of **2** in acetonitrile solutions prepared from dried solvent and compound, it is of course impossible to rule out the presence of traces of water. We are currently performing ^{18}O labeling experiments which may rule out a hydrolytic mechanism.
- (10) See K. H. Tylko, *Z. Naturforsch. B*, **31**, 737 (1976), and references therein.
- (11) J. W. Linnett, *J. Chem. Soc.*, 3796 (1961).
- (12) J. Fuchs, H. Hartl, W. D. Hunnius, and S. Mahjour, *Angew. Chem., Int. Ed. Engl.*, **14**, 644 (1975).
- (13) I. Böschen, B. Buss, and B. Krebs, *Acta Crystallogr., Sec. B*, **30**, 48 (1974).

W. G. Klemperer,* W. Shum

Department of Chemistry, Columbia University
New York, New York 10027

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Formation of Ethylenebenzenium and Protonated Benzocyclobutene, but Not α -Phenylethyl, Cations from the Ionization of Gaseous β -Phenylethyl Halides^{1,2}

Sir:

Solution ionization and solvolysis studies of a wide variety of β -arylethyl systems have indicated the intermediacy of both ethylenarenium and α -arylethyl ions. The recent definitive study by Olah and Porter³ of the ionization of β -phenylethyl chloride (**1-Cl**) in superacid medium gives detailed NMR evidence for the formation of the ethylenebenzenium (**2**) and α -phenylethyl (**3**) cations in proportions ranging from 1:2 to 10:1, with the β -ethylphenyl ion (**4**) as the proposed intermediate^{3,4} (see Scheme I). Although this medium should minimize solvent effects, we find that the unimolecular decomposition of gaseous **1-Cl** (and *n*-propylbenzene, **1-CH₃**) ions produces negligible amounts of either **2** or **3** as stable (lifetimes $>10^{-5}$ s) ionic products, yielding instead a protonated benzocyclobutene ion (**5**)^{6,7} and an unknown ion (X); X appears to be formed by the isomerization of **2** or **5**. In contrast, ionization of β -phenylethyl bromide and iodide (**1-Br**, **1-I**) yields **2** and X.

These conclusions are based on collisional activation (CA) mass spectra⁸ of the product ions. A preliminary communication⁵ on **1-Br** reported the formation of **2** at low electron energies, but erroneously interpreted the high energy results as evidence for the formation of **3** and **4**. Our present conclusions are based on data obtained from improved CA instrumentation⁹ of substantially higher resolution, sensitivity, and precision. The new CA data show no evidence at any ionizing energy for greater loss of C^βH_2 than $\text{C}^\alpha\text{H}_2$, which would be expected for **4**.¹⁰ Also the better-resolved CA spectrum of **3** generated from α -phenylethyl bromide shows substantial quantitative differences in comparison to any of the CA spectra of any other of the C_8H_9^+ isomers studied.^{11,12}

Variation of the CA peak abundances (Figure 1) with change of the electron energy used in forming the C_8H_9^+ ions gives strong evidence that only binary mixtures of C_8H_9^+ isomers are formed from ionization of **1** with 70 eV electrons; **1-Cl** and **1-CH₃** give 20:80 and 40:60 mixtures of **5**:X, respectively, and **1-Br** and **1-I** give 25:75 and 30:70 of (presumably) **2**:X, respectively. The CA spectra of the C_8H_9^+ ions formed at low energies indicate a single isomer, those from **1-Cl** and **1-CH₃** matching closely that from C_8H_9^+ ions formed by ion source protonation of benzocyclobutene, **5**.⁶ No compound could be obtained for the unequivocal generation of **2**, but this appears to be the most logical structure for the C_8H_9^+ ions formed from **1-Br** and **1-I** at low energies. The equivalence of the α - and β -carbons⁸ is consistent with structure **2**, and the value of $[-\text{CH}_2]/[-\text{CH}_3]$ is far greater than that in the CA spectrum of any other C_8H_9^+ isomer studied. In fact, the spectra of none of these isomers (*o*-, *m*-, and *p*-methylbenzyl,

Scheme I

