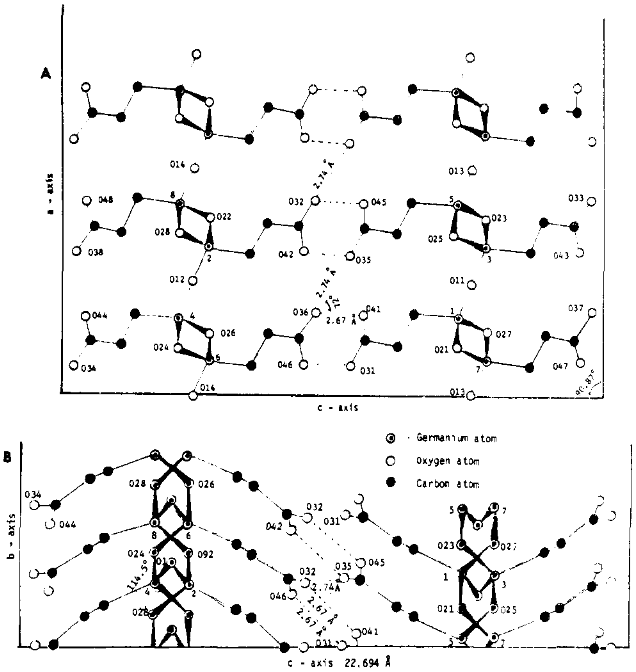

Figure 2. (A) Projection of unit-cell onto *a–c* plane of $O_3(GeCH_2CH_2CO_2H)_2$ array. (B) Projection of unit-cell onto b-c plane of $O_3(GeCH_2CH_2CO_2H)_2$ array.

$< 2(\text{Mo K}\alpha) \leq 45°$.

One heavy atom was determined by direct methods and the structure was then solved by the heavy atom method. Using the 180 reflections with E greater than 1.25 and 1000 phase relationship 16 phase sets were produced. Using an E-map prepared from the phase set showing the best probability statistics (absolute figure of merit = 0.985, residual = 31.65) one atom was located. This atom was assigned a Ge scattering factor and refined in least-squares, resulting in agreement factors of $R_1 = 0.27$ and $R_2 = 0.34$. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses.

In full-matrix least-squares refinement the function minimized was $\Sigma w(|F_0| - |F_c|)^2$ where the weight w is defined as $4F_0^2/\sigma^2(F_0^2)$. Only the 533 reflections having $F_0^2 > 3\sigma(F_0^2)$ were used in the refinement.

I has an infinite sheet structure which can be seen in Figures 1 and 2. Pertinent bond distances and angles for Ge, O, and C atoms are shown in Table I. (See paragraph at end of paper regarding supplementary material.) The basic unit of the infinite sheet network is a 12-membered ring made up of six Ge tetrahedra bridged by oxygen atoms. The carboxylate chains are arranged alternately above and below the Ge-O network around the ring. The sheets are bound together vertically by hydrogen bonds between the carboxyl groups attached to each sheet. The hydrogen-bonded O-O distance between nearest carbonyl groups is 2.67 Å. There also appears to be another hydrogen bond between the next nearest carbonyl groups (e.g., between O_{36}–O_{35}, Figure 2) in which the O-O distance is 2.74 Å. Although definite conclusions concerning such bifurcated hydrogen bonds must be postponed until neutron diffraction data are available. IR data do provide some evidence. The powder IR spectrum of I shows weak bands at 3400 and 2300-2500 cm^{-1} which may be attributed to such hydrogen bonding. Another feature of this crystal is the fact that the dihedral angle between the O_1-Ge-C_1 and Ge-C_1-C_2 planes is 164° rather than the normal value of 180°, and that between the Ge-C_1-C_2 plane and C_1-C_2-C_3 plane is 165°. The main reason for this conformation seems to be an accommodation to permit the observed hydrogen bond formation.

An infinite sheet structure similar to that of I is observed in the silicate anion ($Si_2O_5^{2-}$)[7] and in organosilicon polymers derived from the silicate anion by grafting trimethylsilyl groups on both sides of the silicate sheet.[8] While the silicate sheets are bound by ionic attractions, I is the first reported organogermanium oxide having an infinite sheet structure bound together by hydrogen bonds.

An intriguing aspect of the crystal structure of I is that the cyclic structure of the infinite sheet's basic unit is similar to the crown ethers[9] which demonstrate novel metal ion and amino acid complexation. This unique feature of the structure may well be related to its reported biological activity.[5] It is noteworthy that I is sensitive to the phenylfluorene[10] coloring test for germanium oxide. It seems likely that in aqueous solution I dissociates into carboxyethylgermanetriol, $HOOCCH_2CH_2Ge(OH)_3$, II, resulting in an equilibrium between I and II. This could facilitate metal ion and amino acid complexation by I. Research on this subject is in progress.

Acknowledgment. This research was supported by a grant from the Asai Germanium Institute.[11]

Supplementary Material Available: A listing of bond distances, bond angles, and structure factor amplitudes (6 pages). Ordering information is available on any current masthead page.

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(11) This research was supported by the Asai Germanium Research Institute. The x-ray diffraction analysis was performed by the Molecular Structure Corporation, College Station, Texas 77840.
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Metal Clusters in Catalysis. 7.[1] Molecular Structure and Chemical Properties of a Novel Metal–Metal Bonded Nickel Complex

Sir:

In this communication we describe the synthesis, structure, and chemistry of a novel dinuclear complex which is formally "electron deficient" and possesses unusual chemical properties. The reaction of diphenylacetylene with bis(1,5-cyclooctadiene)nickel(0) at 20 °C yielded the dinuclear complex, (diphenylacetylene)bis(cyclooctadienenickel) (**1**). If one assumes that the 1,5-cyclooctadiene (COD) and diphenylacetylene ligands bind as four-electron donating groups in **1**, the two nickel atoms can both attain an 18-electron configuration only if a four-electron double bond exists between them. The precise x-ray structural analysis of **1** reported below, however, reveals a 2.617 (2)-Å Ni-Ni separation which is much more consistent with a formal two-electron bond between the metals. A value of 2.329 (4)-Å has been reported[2] for the formal two-electron Ni-Ni single bond in the closely related and *electron-precise* dinuclear complex, (diphenylacetylene)bis(cyclopentadienylnickel) (**2**); a value of 2.36 Å was reported[2] for a similar single bond in $[(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}CO)]_2$. The Ni-Ni separation of 2.492 Å in metallic nickel[3a] and 2.590 Å in bis(pentadienyl)dinickel[3b] are closer to the value found in **1.** Complex **1** is therefore either formally "electron deficient" or it contains a considerably "stretched" (and weakened) Ni-Ni double bond, either of which would be consistent with the observed chemical properties. The structural data for **1** indicate that steric factors may be responsible for the Ni–Ni bond elongation and its effect on the chemical properties.

Single crystals of **1,** obtained from the reaction of equimolar amounts of diphenylacetylene and bis(1,5-cyclooctadiene) nickel in pentane at 20 °C (~5 h), are tetragonal, space group $P4_12_12$-D_4^4 (No. 92) with a = 11.595 (2), c = 18.083 (2) Å, and Z = 4. Three-dimensional diffraction data were collected on a computer-controlled four-circle Syntex $P\bar{1}$ autodiffractometer using graphite-monochromated Mo $K\bar{\alpha}$ radiation and full (1° width) ω scans. The structure was solved using the "heavy-atom" technique. The resulting structural parameters have been refined to convergence [$R = 0.024$ for 748 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$] using unit-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The largest peak in a difference Fourier synthesis calculated at this point revealed no peaks with a density greater than 0.17 $e/Å^3$. Refinement is continuing with those reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 55°$.

The structural analysis reveals that the crystal is composed of discrete neutral dinuclear $(\mu_2(\eta^2)\text{-}C_6H_5C{\equiv}CC_6H_5)$ $(NiCOD)_2$ molecules (Figure 1) which possess rigorous crystallographic C_2 symmetry.[4] Each nickel atom is π-bonded to the two double bonds of a single COD ligand and bonded to the bridging diphenylacetylene ligand through a μ-type bond similar to that observed for this ligand in **2**,[2] (diphenylacetylene)bis(tricarbonylcobalt),[5] and bis(η^5-cyclopentadienyl-$\mu_2(\eta^2)$-diphenylacetylenecarbonylniobium).[6] The average lengths of 2.105 (7, 17, 32) and 1.927 (6, 35, 35) Å[7] for the four crystallographically independent complexing COD Ni–C and two independent acetylenic Ni–C bonds, respectively, are in agreement with previously reported values for similar bonds in related molecules. The average distances to the midpoints of the acetylenic bond (C_a) and the two COD double bonds (C(1,2) and C(5,6)) are 1.799 and 1.999 (–, 3, 3) Å,[7] respectively. The midpoints of these three bonds (C_a, C(1,2), and C(5,6)) and the nickel atom are all coplanar to within 0.07 Å; the C_a–Ni–C(1,2), C_a–Ni–C(5,6) and C(1,2)–Ni–C(5,6) bond angles are 134.1, 133.8, and 91.2°, respectively. The four complexing COD carbon atoms (C(1), C(2), C(5), and C(6)) are coplanar to within 0.05 Å; the nickel atom and C_a are displaced by 1.39 and 3.16 Å, respectively, from this four-atom least-squares mean plane. The acetylene C(9)–C(9)′ bond is within 4.3° of being oriented normal to the Ni–Ni′ bond. The C(9)–C(9)′ bond length of 1.386 (11) Å and C(9)′–C(9)–C(10) bond angle of 140.6 (4)° are in agreement with (and more precise than) values reported for this ligand in similar compounds.[2,5,6] Average lengths for other bonds include: C(9)–C(10), 1.446 (7); phenyl C–C, 1.388 (10, 13, 19); C=C(COD), 1.367 (12, 2, 2); C–C(COD), 1.509 (12, 13, 31); and C–H, 1.00 (7, 8, 21) Å. The Ni–C(9)–Ni′, Ni–C_a–Ni′, and Ni′–Ni–C_a bond angles have values of 85.5 (2), 93.3, and 43.3°, respectively.

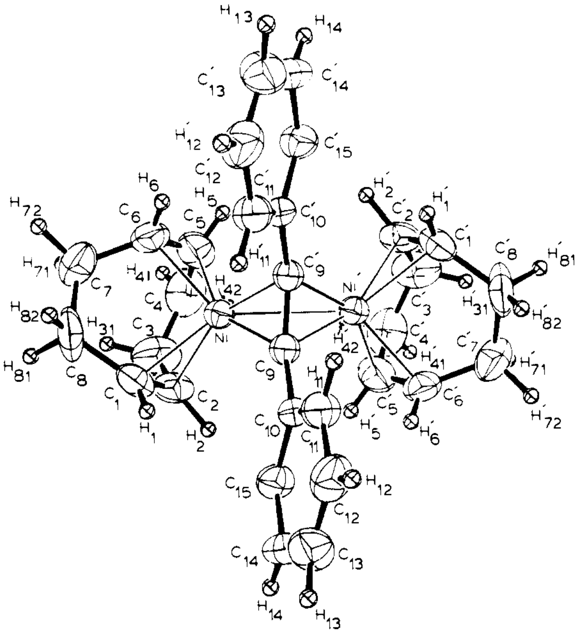

Figure 1. Perspective ORTEP drawing of the $(\mu_2(\eta^2)\text{-}C_6H_5C{\equiv}CC_6H_5)$ $[Ni(1,5\text{-}C_8H_{12})]_2$ molecule viewed along the crystallographic twofold axis which passes through the midpoints of the acetylenic C(9)–C(9)′ and Ni–Ni′ bonds. All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion. Atoms labeled with primes (′) are related to those without primes by the crystallographic twofold axis. Hydrogen atoms H(15), H(15)′, H(32), and H(32)′ are hidden from view by their respective carbon atoms.

Our belief that unfavorable steric interactions between ligands in **1** are responsible for the observed 2.617 (2)-Å Ni–Ni′ bond is based on: (1) the presence of several intramolecular C···C and H···H contacts in **1** which are shorter than or equal to the >3.40- and 2.40-Å van der Waals diameters[8] of carbon and hydrogen, respectively; and (2) structural comparisons with other dinuclear compounds reported to have multiple-order bonds between first transition series metals.[9] The (critical) intramolecular contacts include: C(9)···C(1), 3.22; C(9)···C(6)′, 3.32; C(9)···C(2), 3.41; C(9)···C(5)′, 3.42; H(11)···H(11)′, 2.37; H(15)···H(2), 2.31; and H(42)···H(42)′, 2.48 Å.[10] Interestingly, three of the compounds[9a,b,e] reported to have formal metal-metal double bonds contain ($\mu_2(\eta^2)$-acetylene)-bridged iron atoms with internuclear separations of 2.215–2.316 Å. The remaining coordination sites in these dinuclear complexes are, however, occupied by smaller and sterically less hindered (relative to COD) carbonyl groups. The possibility of having a ~2.30-Å Ni–Ni bond which is $\mu_2(\eta^2)$-bridged by a substituted acetylene ligand is clearly indicated by the structure of **2**,[2] which contains a formal two-electron *single* bond between the two nickel atoms (Ni–Ni separation: 2.329 (4) Å). Decreasing the Ni–Ni′ separation in **1** by >0.317 Å to a more acceptable double bond value of <2.30 Å, while maintaining the geometries of the Ni(COD) units would undoubtedly reduce the already short intramolecular C···C and H···H contacts to unacceptable values. This would be especially true for the H(42)···H(42)′ contact[10] if **1** maintains (rigorous or) approximate C_2 molecular symmetry in solution. Shortening the Ni–Ni′ bond to <2.30 Å would shrink H(42)···H(42)′ by >0.317 Å, since it is directly below and nearly parallel to the Ni–Ni′ bond. Our observation that alkyl-substituted acetylenes tend not to give isolable products similar to **1** also may be structure related. These ligands would certainly 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*-butylisonitrile 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*-$C_6H_5CH{=}CHC_6H_5$;[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 π^2 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 $Co_2(CO)_6(RC{\equiv}CR)$,[5] $Co_4(CO)_{10}(RC{\equiv}CR)$,[15] and $(C_5H_5)_2Ni_2(RC{\equiv}CR)$,[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.

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(10) 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 sp^3-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°.
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Synthesis and Interconversion of the Isomeric α- and β-$Mo_8O_{26}{}^{4-}$ Ions

Sir:

Although $Mo_8O_{26}{}^{4-}$ 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 $Mo_8O_{26}{}^{4-}$ ion and discovered a facile isomerization process which rapidly interconverts these structurally disparate isomers.

When R_4NX (R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9; X = Cl or Br) is added to an acidified aqueous sodium molybdate solution (pH 3–4), the compounds β-$[(CH_3)_4N]_2Na_2Mo_8O_{26}\cdot 2H_2O$,[4] β-$[(C_2H_5)_4N]_3NaMo_8O_{26}$,[5] β-$[(n\text{-}C_3H_7)_4N]_3NaMo_8O_{26}\cdot 2H_2O$,[5] and α-$[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$[6] are precipitated.[7] When $(n\text{-}C_4H_9)_4NX$ addition is preceded by addition of a large excess of KCl, however, the compound β-$[(n\text{-}C_4H_9)_4N]_3KMo_8O_{26}\cdot 2H_2O$ 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 $[(n\text{-}C_4H_9)_4N]_3KMo_8O_{26}\cdot 2H_2O$ (**1**) and $[(n\text{-}C_4H_9)_4N]_4Mo_8O_{26}$ (**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 $[(n\text{-}C_4H_9)_4N]Cl$ 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 compounds[7] include the families β-$M_4Mo_8O_{26}\cdot nH_2O$ (M =