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Communications to the Editor

Structure and Bonding in M_8C_{12} Clusters

Zhenyang Lin and Michael B. Hall*

Department of Chemistry
Texas A&M University
College Station, Texas 77843

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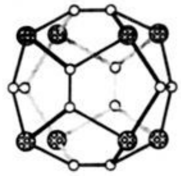
Recently, a new class of highly stable, 20-atom, molecular clusters with eight transition-metal atoms and 12 carbon atoms was discovered, when titanium, vanadium, zirconium, or hafnium was laser-vaporized in the presence of small hydrocarbon species, such as methane, acetylene, ethylene, and benzene.[1] The proposed structure, a pentagonal dodecahedron with T_h symmetry, is remarkable[2] since the all-carbon analog, dodecahedral C_{20}, is unstable because the severe strain in its structure leads to ineffective C–C π bonding. In this communication, we attempt to provide an explanation for the high stability of these M_8C_{12} clusters.

In the proposed M_8C_{12} structure (see **1**), each pentagonal face has two nonadjacent transition metals. In one view, this structure consists of eight metals in a cubic arrangement with six C–C units capping its square faces. This view emphasizes the C═C π interactions that are completely preserved, if the eight transition-metal atoms interact with sp^2-hybridized C atoms in a σ-only fashion and metal–carbon π interactions are weak (and negligible). The maximum C═C π-bonding interaction would be achieved if the six C═C units were in the six square faces of the cube. In such an arrangement, however, the C═C···C═C separations are too small, e.g., the distance between two nonadjacent C atoms is only 2.5 Å when M—C is 2.4 Å. Because the formal charge of each C═C unit is 4–, the C═C units move off the square faces to reasonable C═C···C═C separations (≥3.35 Å, the separation of two adjacent layers in graphite) to avoid strong electrostatic and van der Waals repulsions. Even though the C═C units are not on the M_4 square-face planes, each carbon in M_8C_{12} cluster can retain sp^2 hybridization, but at the cost of geometric strain. Compared to carbon atoms, transition metals can reduce such strain because they can use d orbitals in hybridization schemes which allow small ligand–metal–ligand angles. This view, M—C single bond, C═C double bond, explains why the transition metal in M_8C_{12} cluster can be either Ti, Zr, Hf, or V, and perhaps others with different numbers of valence electrons.



C-C	1.36Å
Y-C	2.38Å
Y-C-C	120.1°
Y-C-Y	103.9°
C-Y-C	93.8°

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For a dodecahedral C_{20} molecule, the 20 π orbitals transform as $a_{1g} + 2t_{1u} + h_g + g_u + g_g$ irreducible representations. An energy ordering of $a_{1g} < t_{1u} < h_g < g_u < g_g \sim t_{1u}$ can be roughly deduced on the basis of the number of nodal planes of these 20 π molecular orbitals. A partial occupation of g_u orbitals in a C_{20} cluster would make the cluster subject to a Jahn–Teller distortion. Therefore, the instability of the C_{20} cluster is, at least, partially due to the extensive delocalization of the 20 π electrons across the nonplanar framework. Replacement of eight carbons by eight transition metals in the structure of the M_8C_{12} cluster provides an opportunity to localize those π electrons on carbon atoms because of weaker M–C d_π–p_π bonding. In the M_8C_{12} cluster, if one metal is replaced by a carbon, the replacing carbon will behave like the carbons in the three adjacent C═C units and compete for π bonding with other carbons. The competition for π bonding leads to delocalization of carbon π electrons like that in the unstable C_{20} molecule mentioned above. Alternatively, replacement of a carbon by a metal in M_8C_{12} again results in delocalization in the π electrons because two transition-metal atoms are bonded to each other. Therefore, alternative combinations of metal and carbon atoms seem not as stable as the M_8C_{12} clusters.

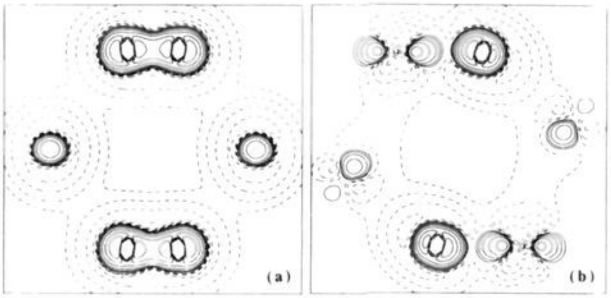

Figure 1. The plots of $-\nabla^2\rho$ in the Y_8C_{12} cluster: (a) on a plane containing two parallel C═C units and bisecting another two parallel C═C units, and (b) on a plane containing two Y—C bonds, which are related by a center of inversion, and crossing another two Y—C bonds.

To examine the arguments presented above, we performed an ab initio geometry optimization on the model cluster Y_8C_{12} at the Hartree–Fock level with effective core potentials.[3] Double-ζ basis sets were used for C atoms while a double-ζ representation of 4d orbitals and a single-ζ representation of 5s/5p orbitals were employed for Y atoms. The optimized structural parameters are shown with the representation of **1**. Calculations on the experimentally realized cluster Zr_8C_{12} are under way, and results together with its magnetic properties will be discussed in a subsequent paper. At the same level of accuracy, we also optimized the geometries of C_2H_6 and C_2H_4, and we obtained a C–C single bond length of 1.56 Å and a C–C double bond length of 1.36 Å. Although each C═C unit in Y_8C_{12} is off the square-face plane by 0.85 Å, the C–C bond distance is almost equal to that predicted for ethylene (C–C double bond). In each pentagon (CM_2C_2), the plane formed by the carbon bonded to two metals is at a 30° angle with respect to the M_2C_2 plane. This distortion away from a planar CM_2C_2 pentagon decreases significantly the M—C d_π–p_π delocalizations in the cluster and results in strong, localized C═C π interactions. The separation between two adjacent C═C units is 3.87 Å, which is slightly larger (0.52 Å) than the layer separation in graphite.

In Figure 1, we show plots of the Laplacian of the valence electron density, i.e., $-\nabla^2\rho$,[4] from the ab initio calculation. Figure 1a is a plot on a plane containing two parallel C═C units and bisecting another two parallel C═C units, while Figure 1b shows a plot on a plane containing two Y—C bonds, which are related by a center of inversion, and crossing another two Y—C bonds. The elliptical shape of electronic charge concentration in the bisection of the C–C bonds (see Figure 1a) gives strong evidence

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of C–C double bond character. In Figure 1b, one can see that the largest electronic charge concentration around a carbon atom is significantly off the Y–C bonding direction. This result shows a significantly bent Y–C bond which results from the C atoms' use of sp^2 hybrids to maximize C–C π bonding.

In summary, the high stability of the M_8C_{12} cluster is due to the weak metal–carbon d_π–p_π interaction. This weak π interaction allows maximum C–C π bonding. The role of the transition metal in this class of clusters is simply linking the six C=C double bonding units through σ bonding. Each metal atom in the M_8C_{12} cluster has local C_{3v} symmetry and contributes three orbitals to form σ bonds with carbon atoms. On each metal, there are six unused orbitals with $2a_1 + 2e$ symmetry. We expect that only one set of $a_1 + e$ orbitals is energetically favorable enough to be occupied by additional d electrons. Therefore, in addition to group 4 and 5 transition metals, other transition-metal atoms with three to nine valence electrons are possible for M_8C_{12} clusters. However, with an increase in the number of valence electrons in the transition-metal atoms, the repulsive interactions between metal d electrons and C–C π-bonding electron pairs increase, and the stabilities of M_8C_{12} clusters decrease. Therefore, M_8C_{12} clusters are expected to be less stable for transition-metal atoms with more than five valence electrons. Our model with weak M–C π bonding predicts that the Ti and V clusters would be paramagnetic, while a model with strong M–C π bonding could lead to diamagnetic clusters.

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Quantitative Evaluation of TOCSY Data. Application to Sugar Ring Conformational Analysis

J. P. M. van Duynhoven,[†] J. Goudriaan,[‡] C. W. Hilbers, and S. S. Wijmenga[*]

Nijmegen SON Research Centre for
Molecular Design, Structure and Synthesis
Laboratory of Biophysical Chemistry
National HF-NMR Facility, Toernooiveld
6525 ED Nijmegen, The Netherlands

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For the structure determination of (bio)molecules by NMR, extraction of J-coupling constants from NMR spectra is of vital importance, since from this information torsion angle values can be derived via Karplus equations.[1] J-Coupling constants are usually obtained from the fine structure of the cross peaks in COSY spectra.[1-3] For large molecules this becomes difficult due to cancellation of the components of the cross peaks and/or overlap. An alternative is then to use TOCSY,[4,5] which has become very popular as an assignment tool for crowded spectra, but not as a tool to extract J-couplings or related structural parameters. We show that quantitative structure information can be obtained directly from TOCSY spectra, via the method of iterative back-calculation of the cross peak intensities. We demonstrate this approach through the quantitative analysis of the conformation of the sugar rings in the cyclic dinucleotide cd(CpGp).

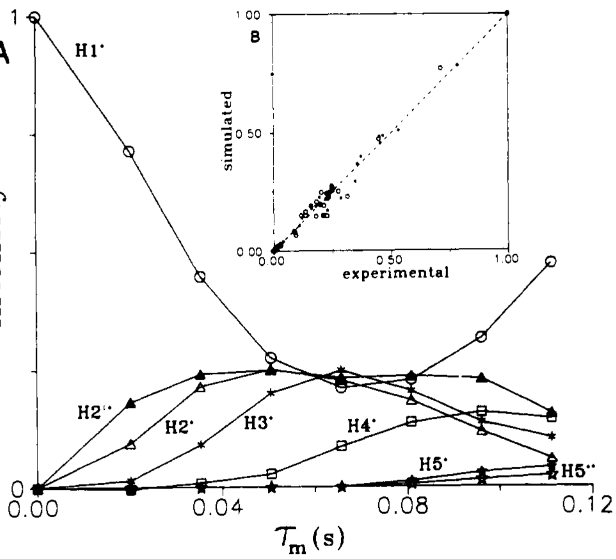

Figure 1. (A) Experimental buildup curves for coherence transfer in TOCSY (MLEV17) from the H1′ resonance of the dG moiety in cd(CpGp), recorded at 400 MHz and 298 K, with the carrier at 4.75 ppm and a radio-frequency field strength of 10 kHz. The TOCSY intensities were scaled in a manner that preserved the total magnetization. The inset (B) shows a plot of the experimental H1′ TOCSY ladder connectivities of the cytidine (*) and guanosine (O) sugar ring spin system in cd(CpGp) versus the values of the simulation which employed experimental J-couplings in hertz [$J_{1'2'} = 3.8$ (2.9), $J_{1'2''} = 7.5$ (7.7), $J_{2'2''} = -14.3$ (−14.2), $J_{2'3'} = 7.5$ (7.7), $J_{2''3'} = 7.5$ (8.4), $J_{3'4'} = 6.5$ (7.5), $J_{4'5'} = 3.5$ (2.5), $J_{4'5''} = 2.5$ (1.9), $J_{5'5''} = -11.8$ (−11.6)] and chemical shift data in ppm [H1′, 6.27 (6.20); H2′, 2.92 (2.57); H2″, 2.72 (2.63); H3′, 5.00 (4.85); H4′, 4.23 (4.16); H5′, 4.12 (4.20); H5″, 4.02 (4.05)]; the data for cytidine are given in parentheses.

The correct back-calculation of the TOCSY spectra requires numerical evaluation of the evolution of the density matrix under the influence of the mixing Hamiltonian.[4-6] The computer program written to perform this evaluation allows for a variety of different types of mixing Hamiltonians (e.g., WALTZ,[7] MLEV,[4,8] and DIPSY[9]). In addition, the program is provided with the J-couplings and the determinants of the off-resonance effects, namely, chemical shifts and the strength of the applied radio-frequency field. With this approach the experimental coherence transfer can indeed by correctly reproduced, as shown in Figure 1. Figure 1A presents the experimentally determined evolution of the TOCSY (MLEV17[4]) intensities of the cross peaks between H1′ of dG and the other members of the scalar coupled network, while Figure 1B shows the neat correspondence between the experimental TOCSY and the numerically simulated intensities. Thus, the inclusion of off-resonance effects in the calculation is sufficient to correctly reproduce the experimental TOCSY intensities.

It it well-known that deoxyribose sugars may rapidly interconvert between two puckered states, the N- and S-conformers, which can be characterized by the phase angle of pseudorotation, P, and the puckering amplitude, Φ, with their pseudorotation angles in the ranges $-20° < P_N < 20°$ and $117° < P_S < 189°$,

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[*] Corresponding author.

[†] Present address: Department of Chemical Analysis, Faculty of Chemical Technology, Technical University of Twente, 7500 AE Enschede, The Netherlands.

[‡] Present address: Department of Organic Chemistry, Faculty of Chemical Technology, Technical University of Twente, 7500 AE Enschede, The Netherlands.

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