J. Am. Chem. Soc. **1996,** *118,* 3315−3316 3315

Hypothetical Three-Dimensional Metallic Compounds of C_{60} with Transition Metal Clusters

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Received November 17, 1995
Revised Manuscript Received February 2, 1996

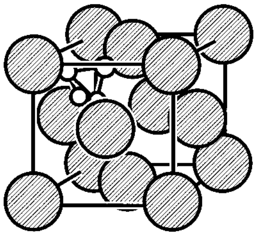
Solid C_{60} crystallizes at room temperature in a face-centered cubic (fcc) lattice, $a = 14.11$ Å, with a shortest C−C contact of 3.10 Å.[1] The fcc lattice has tetrahedral and octahedral interstices, into which alkali and alkaline earth metal atoms enter, in the remarkable superconducting M_3C_{60} species, M = Na, K, Rb, Cs.[2,3] The parent C_{60} fcc lattice expands just a little ($a = 14.24$ Å for K_3C_{60}) in the process.[4]

The holes in the fcc C_{60} lattice are in fact quite large. And π-bonded substructures of the fullerene surround the holes—so 8 of the 20 C_6 rings of C_{60} face the 8 tetrahedral holes around. The octahedral holes all face a C−C bond connecting two 5-membered rings, or a 6,6-ring junction.

We suggest these interstices might be filled with transition metal clusters, not just donating electrons to the C_{60}, but bonded to the fullerenes.[5]

If we wanted real chemical bonding, which clusters might we choose? The tetrahedral holes have fronting arene rings, so a metal which forms a stable M_4(arene)$_4$ cluster is what is needed. While these are unknown, it is clear that 18-electron considerations and a desire to have at least single M−M bonds leads to M = Co, Rh, Ir. The known $M_4(CO)_{12}$ clusters[6] are a convenient model for the metrics of the metal cluster.

The geometrical fit is snug. We insert (in the computer!)[7,8] the M_4 tetrahedra into all the tetrahedral interstices of C_{60}, each vertex facing the center of a fronting arene. The structure is shown schematically in **1**; the resulting stoichiometry is $C_{60}(M_4)_2$. If the metal tetrahedra adopt geometries similar to those in the carbonyl clusters ($d_{Co-Co} = 2.54$ Å and $d_{Rh-Rh} = 2.72$ Å),[9] we arrive at metal−carbon distances of 1.92 and 1.85 Å for Co and Rh, respectively. These are slightly shorter separations than those in η^6-arene compounds of these metals, where $d_{Co-C} \approx 2.1$ Å and $d_{Rh-C} \approx 2.3$ Å.[10] Indeed our extended Hückel calculations (not too reliable for energetics) indicate that the C_{60} lattice will expand somewhat when we introduce these metal clusters in the tetrahedral holes.[11] The total energy of the solids minimizes at a lattice constant of 14.37 Å for the $C_{60}(Co_4)_2$ phase and 15.41 Å for the $C_{60}(Rh_4)_2$ phase. This leads to Co−C and Rh−C bond distances of 1.99 and 2.14 Å, respectively, and to shortest $C_{60}-C_{60}$ contacts of 3.22 and 3.96 Å. The dilation in the Rh case is worrisome because the resulting inter-fullerene contact, presumably important for the conducting properties, now is outside the van der Waals π contact of around 3.3 Å.



In Figure 1 (left) we show a density of states (DOS) diagram[12] for the $C_{60}(Co_4)_2$ phase. The Fermi level of this compound is found to lie in a region of high DOS at −11 eV intersecting several bands in the bandstructure (not shown).[13] $C_{60}(Co_4)_2$ is therefore likely to be metallic.[14] The contributions of the metal d-orbitals (filled region in Figure 1) and of the C_{60} frontier orbitals (not shown, but roughly the remainder of the DOS) demonstrate that the levels around the Fermi energy are comprised of the C_{60} HOMO (h_u) as well as the metal d-orbitals. The average net charge per metal atom is −0.49. Approximately 4 electrons are transferred from C_{60} to the Co clusters. The levels near the Fermi energy turn out to be metal−carbon antibonding; however, there is an overall bonding interaction between the metal and the fullerene, as indicated by a positive value of 0.05 for the average overlap population of a metal−carbon (C_6 ring) bond.

In $C_{60}(Rh_4)_2$ (right side in Figure 1) the Fermi level lies in a region of a large DOS as well, so this material should also be

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[5] To our knowledge there are no reports in the literature on the characterization of such fullerene compounds. In fact, we are only aware of one study on the incorporation of a transition metal into the host lattice of C_{60}; however, the exact structure of the obtained $C_{60}Fe_x$ material was not resolved: Werner, H.; Wohlers, M.; Belz, T.; Schlögl, R. *Mol. Cryst. Liq. Cryst.* **1994**, *245*, 295. For earlier calculations on C_{60} η^6 bonded to M(arene) fragments, see: Gal'pern, E. G.; Gambaryan, N. P.; Stankevich, I. V.; Chistyakov, A. L. *Russ. Chem. Bull.* **1994**, *43*, 547. Rogers, J. R.; Marynick, D. S. *Chem. Phys. Lett.* **1993**, *205*, 197. The bonding of C_{60} to M(cyclopentadienyl) fragments has been discussed: López, J. A.; Mealli, C. *J. Organomet. Chem.* **1994**, *478*, 161.

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[7] We use the extended Hückel method: Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

[8] The extended Hückel calculations were performed with the YAeHMOP package: Landrum, G. *YAeHMOP*—Yet Another extended Hückel Molecular Orbital Package, version 1.1, Ithaca, New York, 1995. This freeware package is available on the World Wide Web: http://overlap.chem.cornell.edu:8080/yaehmop.html. For the calculations a primitive unit cell was sampled over 10k points, see: Ramirez, R; Böhm, M. C. *Int. J. Quantum Chem.* **1988**, *34*, 571.

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[11] Note that this is not a true geometry optimization of the phases. All we do is vary the lattice constant of the crystal unit cell while keeping the local geometries of the carbon and metal clusters.

[12] For an introduction to the description of the chemical bond in the solid state, see: (a) Hoffmann, R. *Solids and Surfaces: a Chemist's View of Bonding in Extended Structures*; VCH: New York, 1988. (b) Burdett, J. K. *Chemical Bonding in Solids*; Oxford University Press: New York, 1995.

[13] For comparison, the Fermi level of undoped C_{60} (lattice constant 14.24 Å) is calculated by us to lie at −11.37 eV.

[14] It would take eight electrons per $C_{60}(Co_4)_2$ to reach the gap in the DOS.

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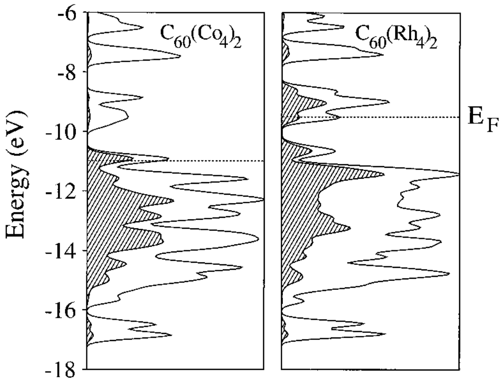

Figure 1. Density of states of $C_{60}(Co_4)_2$ (left) and $C_{60}(Rh_4)_2$ (right). The filled area corresponds to the projection of the metal d-orbitals. The dotted line indicates the Fermi level (E_F).

metallic. However, now the charge transfer is in the other direction from the Co case. Each Rh is positive (+0.18 in our calculations), so that 1.40 electrons are transfered to each C_{60}. Near the Fermi level states have both Rh d and C_{60} LUMO (t_{1u}) character; there is a distinct gap in the DOS for four fewer electrons per formula unit.[15]

These surprising differences between Co and Rh can be traced to the diffuseness of the d-orbitals of rhodium as compared to the first-row transition metals and the significantly larger energy difference between p- and d-levels in second-row transition metals. A detailed analysis of why these materials, which might have been expected to be semiconductors since they locally satisfy the 18-electron rule, are in fact metallic, the reasons for the difference in the direction of electron transfer between the Co and Rh cases, the weaker $C_{60}-Rh_4$ bonding, and the relationship of the latter to the relative scarcity of $Rh_4(arene)_x$ cluster compounds will be discussed in our full paper.

Further calculations also indicate that rotation of the C_{60} polyhedra (or the metal tetrahedra) from the ideal geometry described would be strongly hindered.

What about the bonding capabilities of the octahedral interstices? These holes are surrounded by 6,6-ring junctures (or fulvenoid double bonds). The distance between the center of such a CC bond and the center of the holes is 3.65 Å (for a lattice constant of 14.24 Å). The tetrahedral clusters (typical radius of one is 1.66 Å) are too small to fill these holes. We calculate weak bonding and unhindered rotation for tetrahedral metal clusters in the octahedral C_{60} interstices.

In principle, one can envision larger clusters, such as M_6 octahedral fragments, in these holes, binding at each M in an η^2-fashion to the fulvenoid double bonds. In known M_6 clusters of Co, Rh, and Ir the average M−M distance is around 2.50, 2.78, and 2.76 Å, respectively.[16] Thus we arrive at a quite realistic metal−carbon distance of 2.00, 1.82, and 1.83 Å for the compounds with octahedral M_6 clusters in the octahedral holes of the fcc lattice. The molecular compounds that are known have generally two to three ligands bound to each metal, as in $Rh_6(CO)_{12}(POPh_3)_4$.[17] η^2-Olefin complexes of the composition $M_6(olefin)_6$ are not known; they would be very electron deficient. Calculations to be reported elsewhere indicate that $C_{60}(M_6)$, M = Co, Rh, Ir, should be metallic as well.

What we see is that the bonding in these hypothetical solids is quite different from that of the well-studied alkali-metal fullerene systems. While the latter can be regarded as nearly pure ionic systems—the valence electrons of the metal are practically fully transferred to the empty C_{60} orbitals—the hypothetical transition-metal cluster fullerenes discussed by us display significant degrees of covalent metal−carbon bonding. Our calculations suggest that the two $C_{60}(M_4)_2$ phases will be conductors, but we cannot say if they will be superconducting.

We look forward to the synthesis of these theoretically reasonable, potentially conducting, three-dimensional organometallics, perhaps by co-condensation and treatment of preformed ligated clusters and C_{60}.

Acknowledgment. N.G. would like to thank Greg Landrum and Hugh Genin and the other members of the group for their assistance and helpful discussions. N.G. is grateful to the Deutsche Forschungsgemeinschaft (DFG) for the award of a research fellowship. We are indebted to the National Science Foundation for supporting our work through Research Grant CHE-9408455.

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(15) We also calculated $C_{60}(Ir_4)_2$ with results resembling the Rh case.

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