Structures and Structural Principles for Copper Carbohedrene Clusters [Cu13C12]+ to [Cu25C24]+

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Yamada and Castleman have reported experiments in which copper clusters in the gas phase are allowed to react with heated acetylene, cooled, and then laser ionized to generate a collection of positive metallocarbohedrene ions $[Cu_xC_y]^+$, detected mass spectrometrically.[1] This is the first report of carbohedrene clusters of the late transition metals, following the initial work on the formation[2,3] and theoretical structures[4] of $[Ti_8C_{12}]$ and other early transition metal carbohedrenes.

Particularly prominent in the copper carbohedrene mass spectra is the series $[Cu_{2n+1}C_{2n}]^+$, $n = 1$–10. In a previous paper[5] I have shown the significance of a *centro-Cu-cuboctahedro-Cu12-octahedro*-$(C_2)_6$ structure **1312D** for $[Cu_{13}C_{12}]^+$, as the copper topolog of $[Ti_8C_{12}]^+$. For these metals at opposite ends of the first transition series there is a substantial geometrical difference which arises in the Cu–Cu bonding at distances of ca 2.5–2.6 Å, substantially shorter than the computed Ti–Ti distances of ca. 3.0 Å in $[Ti_8C_{12}]^+$. In the structures of both $[Cu_{13}C_{12}]^+$ and $[Ti_8C_{12}]^+$ there can be isomerism due to different orientations of the C_2 groups, which may be aligned with the edges (label **E**) or with the diagonals (**D**) of the Cu_4 squares on the surface. A favorable surface feature involving diagonal C_2 occurs with folding of the Cu_4 quadrilateral into a butterfly conformation, allowing it to nestle the C_2 group; all C_2 groups in the optimized structure of isomer **1312D** have this geometry.

In the mass region above $[Cu_{13}C_{12}]^+$ the observed clusters are $[Cu_{15}C_{14}]^+$, $[Cu_{17}C_{16}]^+$, $[Cu_{19}C_{18}]^+$, and $[Cu_{21}C_{20}]^+$ in the $[Cu_{2n+1}C_{2n}]^+$ series, and two Cu_{even} clusters $[Cu_{16}C_{16}]^+$ and $[Cu_{20}C_{18}]^+$. I describe in this communication the structural principle which generates energetically favorable structures for the $[Cu_{2n+1}C_{2n}]^+$ series up to $[Cu_{25}C_{24}]^+$ and also accounts for $[Cu_{20}C_{18}]^+$. A favorable structure for $[Cu_{16}C_{16}]^+$ is also presented, thereby accounting for all of the ions in the high-mass region of the Castleman spectra. Local density functional methods are used to calculate the energy-minimized structures.[6] The first objective in understanding these copper carbohedrenes is to identify the energy minima and the broad structural principles that apply, before undertaking more detailed theoretical calcu-
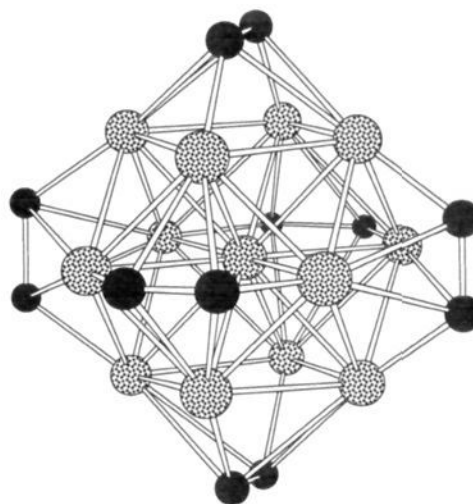
1312D

lations of electronic structure. The results developed here indicate that the principle which extends the $[Cu_{2n+1}C_{2n}]^+$ series from $[Cu_{13}C_{12}]^+$ is one of addition to the structure **1312D** rather than expansion of the centered cuboctahedron. Since C_{even} compositions prevail, I assume that these clusters contain C_2 groups rather than C atoms: this is supported also by calculations on the smaller copper carbohedrenes.[7]

A core structure type for $[Cu_{15}C_{14}]^+$ can be derived from **1312D** by removal of one C_2 and addition of a Cu_2 group in its place, thereby creating two new Cu_4 quadrilateral faces, each of which can accommodate C_2, a net addition of Cu_2C_2. The surface framework of the 14 Cu atoms can be regarded as a cuboctahedron and a trigonal prism sharing a square face. There are again many connectivity isomers arising from the edge and diagonal alignment of each C_2 group within its Cu_4 quadrilateral. In the edge configuration each C atom is bonded to two Cu, while in the diagonal configuration each C has one strong C–Cu bond almost axial to the C–C bond, and two slightly longer C–Cu bonds transverse to the C–C bond. The two most symmetrical isomers have the C_2 groups all-edge, **1514E**, or all-diagonal, **1514D**. In each structure the bond distances are normal: Cu–Cu ranges 2.4–2.8 Å depending on coordination, Cu–C ranges 1.9–1.95 Å in **1514E**, Cu–C^{axial} and Cu–C^{transverse} respectively range 1.85–1.9 and 2.05–2.15 Å in **1514D**, C–C = 1.29 Å. The diagonal isomer **1514D** where all of the C_2 groups can nestle into their Cu_4 environments has a slight energy advantage. In order to compare binding energies for different cluster compositions in the copper carbohedrene series, binding energies reported in this paper are expressed per atom, by dividing by the number of atoms in the cluster. Thus the binding energies per atom of **1514D** and **1514E** are −115 and −111 kcal mol⁻¹ atom⁻¹ respectively,[8] slightly better than the values for the corresponding high-symmetry isomers **1312D** and **1312E**.

The structures of the remaining members of the $[Cu_{2n+1}C_{2n}]^+$ series can be generated by further capping of the core cuboctahedron, adding Cu_2C_2 at each stage, up to $n = 12$, $[Cu_{25}C_{24}]^+$. For $[Cu_{17}C_{16}]^+$ to $[Cu_{21}C_{20}]^+$, with two to four caps on the cuboctahedron, there are additional opportunities for isomerism

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(6) All of the theoretical results in this paper are obtained by local density functional calculations, using the program DMol (Biosym Technologies, Inc.). Double numerical basis sets with *d* polarization functions are used, with frozen core orbitals (C, 1s; Cu 1s, 2s, 2p) and restricted spin. Symmetry C_2 or D_2 is imposed according to the structure. Details of the calculations will be presented separately.

(7) Dance, I. G. To be published.

(8) Fine details of the optimization of the energy and geometry of some structures are still in progress. Comparative binding energies as used in this paper are more reliable than absolute energies.
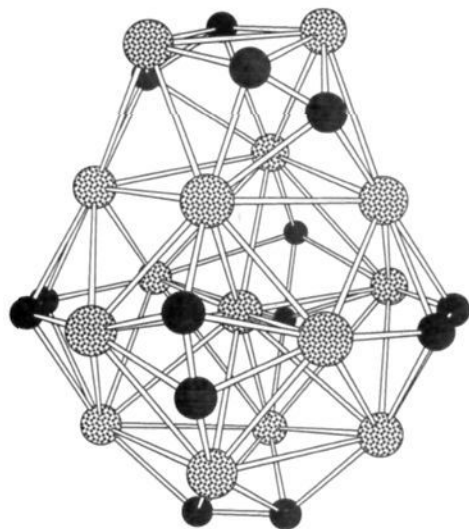
1514D

2018D

arising in the placements of the caps, but there are no interferences between contiguous caps. The binding energies for the trans bicapped cuboctahedron structures **1716D** and **1716E**, with all-diagonal and all-edge C_2 configurations, are -114 and -109 kcal mol^{-1} atom^{-1}, respectively.[8] The fully capped structure, $[Cu_{25}C_{24}]^+$, is illustrated as the more favorable diagonal isomer **2524D** with symmetry T and a binding energy of -110 kcal mol^{-1} atom^{-1}. Note that this and all **D** isomers are chiral.
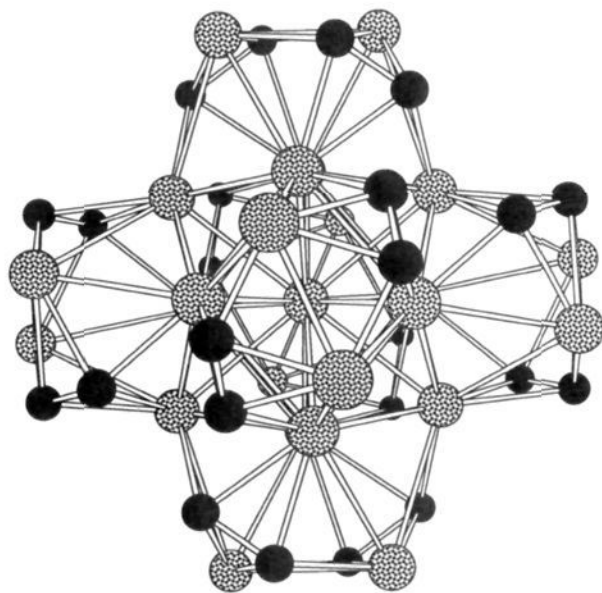
2524D

The Cu_{even} odd-electron ion $[Cu_{20}C_{18}]^+$ appears not to fit this pattern, but it can be accounted for in the same way. The first member of the $[Cu_{2n+1}C_{2n}]^+$ series able to have three mutually cis caps on the cuboctahedron is $[Cu_{19}C_{18}]^+$. These three mutually cis Cu_2C_2 caps can be configured such that three C atoms are within bonding distance of an additional Cu atom on the 3-fold axis. The resulting structure of $[Cu_{20}C_{18}]$, **2018D**, has acceptable geometry throughout.

The other Cu_{even} ion observed by Castleman is $[Cu_{16}C_{16}]^+$. A reasonable hypothesis for this cluster is based on the Frank–Kasper 15-hedron,[9] which comprises 26 triangular faces and is akin to a prolate icosahedron. Placement of a Cu atom at the

(9) Frank, F. C.; Kasper, J. S. *Acta Crystallogr.* **1958**, *11*, 184.
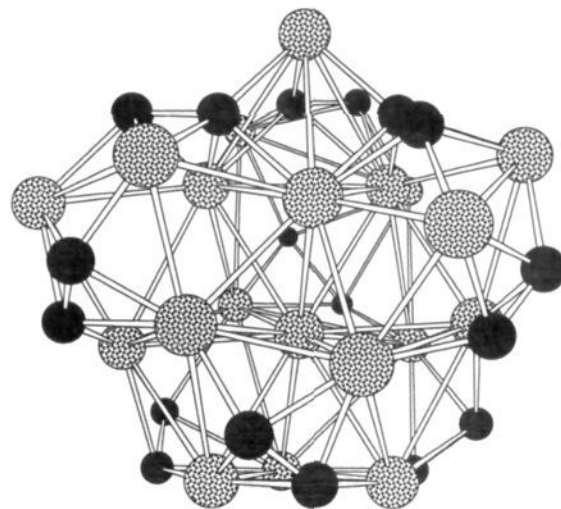
center of this Cu_{15} polyhedron, and the breaking of eight selected Cu–Cu connections on the surface to create Cu_4 butterflies to accommodate the eight C_2 groups, yields structure **1616D** (symmetry C_3). This has been optimized as the closed-shell neutral species $Cu_{16}C_{16}$, which has very favorable binding energy of at least -118 kcal mol^{-1} atom^{-1}. Other arrangements of the C_2 groups over the surface of the Cu-centered Cu_{15} Frank–Kasper polyhedron yield less favorable bonding.

Consistent postulates have been provided which are favorable geometrically and energetically for each of the ions observed by Castleman, but some further questions remain. Are there other similarly favorable postulates? How deep are the energy wells for the structures postulated? Why are other Cu_xC_y ions not observed? On the last question, the reported mass spectra represent a low abundance of copper carbohedrene clusters in the first experiments, and other compositions may appear in higher yielding preparations. Nevertheless, I have drawn attention to a direct structural principle that accounts for the series of most intense clusters. None of the other globular arrangements of Cu and C_2 conceived so far has the degree of bonding with appropriate bond distances, and the binding energies, of the proposed structure series. On the question of the depth of the energy well, it can be stated that the optimization procedures worked well starting from geometries with bond distances within 0.1 Å of the optimized values, at energies ca. 100 kcal mol^{-1} cluster^{-1} higher. These investigations are continuing.

Finally I recognize a relationship between the $[Cu_{2n+1}C_{2n}]^+$ series of clusters and the $[Cu_{2n-1}S_n]^-$ series of clusters.[10] Both are electron precise and can be regarded as containing Cu$^+$ with C_2^{2-} or S^{2-}, respectively. Quadruple bridging by S (or more commonly by Se) of four copper or other metal atoms is very well established in metal chalcogenide cluster chemistry[11,12] and frequently occurs in a Cu_4 butterfly. This provides credence for the structures proposed in this communication.

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