

Structural Principles for Copper Carbohedrene Clusters $[\text{Cu}_x\text{C}_y]^+$

Ian Dance

School of Chemistry, University of New South Wales, Kensington, NSW 2033, Australia

Probable structure types and isomerism for the new clusters $[\text{Cu}_{2n+1}\text{C}_{2n}]^+$ (g) are developed, with local density functional methods used to define energy minima for $[\text{Cu}_{13}\text{C}_{12}]^+$, for which a *centro*-Cu-cuboctahedro-Cu₁₂ core capped with six C₂ moieties is the copper analogue of $[\text{Ti}_8\text{C}_{12}]^+$.

Yamada and Castleman¹ have very recently described experiments in which copper clusters in the gas phase react with heated acetylene to form a new class of metallocarbohedrene clusters of the general type $[\text{Cu}_x\text{C}_y]^+$, in which y is invariably even and x is predominantly odd. The most prominent ions formed using relatively high concentrations of heated acetylene occur in the series $[\text{Cu}_{2n+1}\text{C}_{2n}]^+$, up to $n = 10$. There are additional ions such as $[\text{Cu}_7\text{C}_8]^+$, $[\text{Cu}_9\text{C}_{10}]^+$ and $[\text{Cu}_{12}\text{C}_{12}]^+$, for which Yamada and Castleman conceived structures as fragments of the solid state structure of copper acetylide. However, there are substantial geometrical problems with these structures: for example, for Cu₇C₈ the proposed Cu-centred Cu₆ octahedron with C₂ groups capping four of the triangular faces cannot have normal Cu–Cu and Cu–C bond distances.

I communicate here some key structural principles for ions $[\text{Cu}_{2n+1}\text{C}_{2n}]^+$. In theoretical analyses for new classes of metal cluster such as the metallocarbohedrenes it is important to establish initially the geometries of the energy minima, and to seek the global minimum for each composition. Most of the theoretical reports^{2–6} on $[\text{Ti}_8\text{C}_{12}]^+$ have adopted the *hexa-*

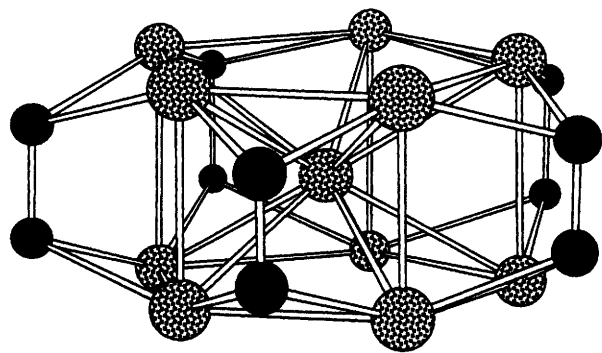
hedro-Ti₈-octahedro-(C₂)₆ structure, which is approximately 1450 kJ mol⁻¹ higher in energy than an alternative with a tetracapped-tetrahedro-Ti₈ array.^{7,8} The relative energy of a suggested trigonal alternative structure containing two Ti₄ moieties in the dodecahedron is not known.⁹

The composition $[\text{Cu}_{2n+1}\text{C}_{2n}]^+$ prompts consideration of a general structural type which might appear to be applicable to all ions with $n \geq 3$. The structure type is the Cu-centred Cu_{2n} n -gonal prism, which has n quadrilateral faces, each of which is capped by a C₂ group. Calculations on $[\text{Ti}_8\text{C}_{12}]^+$ have explored the two common modes for C₂ capping of M₄ quadrilateral faces, namely aligned with the edges or with the diagonal of the quadrilateral, with the general conclusion that the latter provides more bonding interactions and greater stability.^{7,8} The Cu-centred Cu_{2n} n -gonal prism structures have multiple possibilities for isomerism. For instance, each C₂ group may be aligned approximately parallel (*lel*) or obverse (*ob*) to the n -fold axis of the prism, or diagonal (*diag*) to the face, and many distinct combinations of these local C₂ isomers may constitute the full molecule. On twisting around the principal axis, the Cu_{2n} prism becomes antiprismatic, and

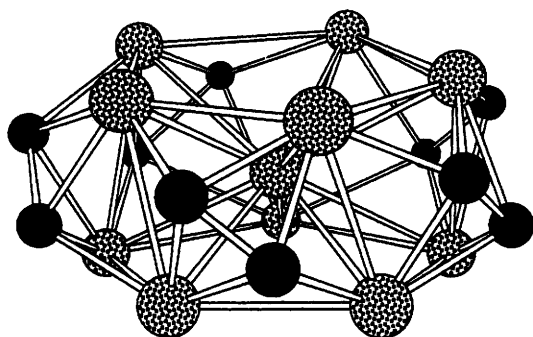
Table 1 Calculated^a structures for the Cu-centred Cu_{2n} n -gonal prism model of $[\text{Cu}_{2n+1}\text{C}_{2n}]^+$

Ion	Symmetry		Binding energy/ kJ mol ⁻¹ (per Cu)	$d/\text{Å}$				
	Actual	For calc.		Cu ^c –Cu	Cu–Cu (<i>lel</i>)	Cu–Cu (<i>ob</i>)	Cu–C	C–C
$[\text{Cu}_9\text{C}_8]^+$	D_4	D_2	–810	2.43	2.67	2.89	1.87, 2.00	1.29
$[\text{Cu}_{11}\text{C}_{10}]^+$	D_5	C_2	–844	2.62–2.63	2.54–2.56	2.69–2.72	1.86–1.96	1.29
$[\text{Cu}_{13}\text{C}_{11}]^+$	D_6	D_2	–854	2.82	2.51	2.62	1.87, 1.94	1.29

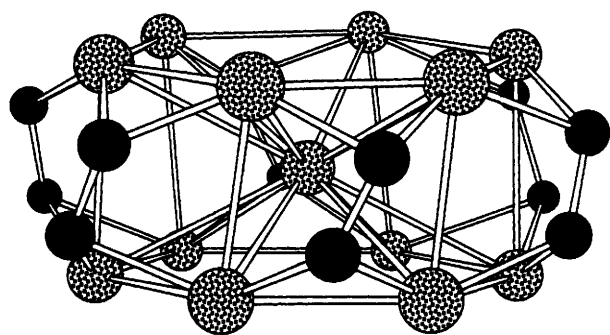
^a See text. Calculations are continuing with higher precision, and with analysis of the electronic state.



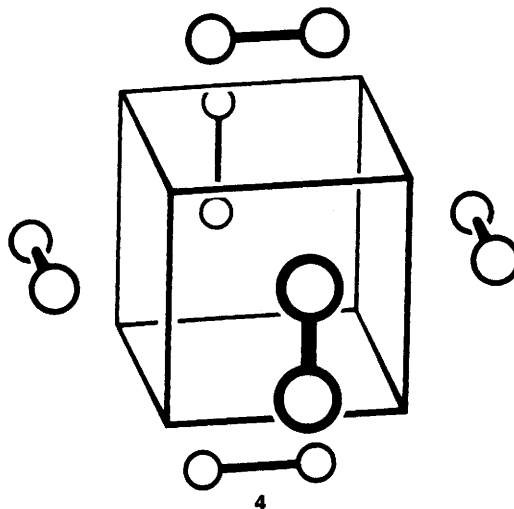
1



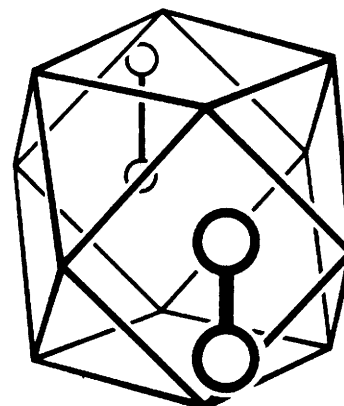
2



3



4



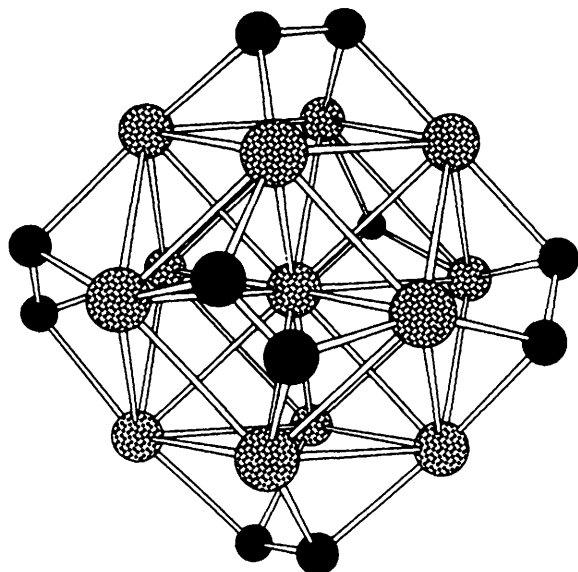
5

the C_2 groups favour the diagonal bonding mode. Illustrations 1 and 2 are the *centro-Cu-pentagonal-prismo-Cu₁₀-(*lel*-C₂)₅* and *centro-Cu-pentagonal-antiprismo-Cu₁₀-(*diag*-C₂)₅* isomers of $Cu_{11}C_{10}$. Further, the Cu-centred Cu_{2n} n -gonal prism is subject to geometrical restrictions due to the bonding requirements of the central atom Cu^c . Thus, this model cannot account satisfactorily for $[Cu_7C_6]^+$ because the Cu^c-Cu distances to the central Cu are too short, and there will be an upper limit to n beyond which the Cu^c-Cu distances are too long. Three distances are defined for the Cu_{2n+1} core, under D_n symmetry: Cu^c-Cu , $Cu-Cu$ (*lel*) for the bonds (approximately) parallel to the principal axis, and $Cu-Cu$ (*ob*) for those (approximately) obverse to the principal axis.

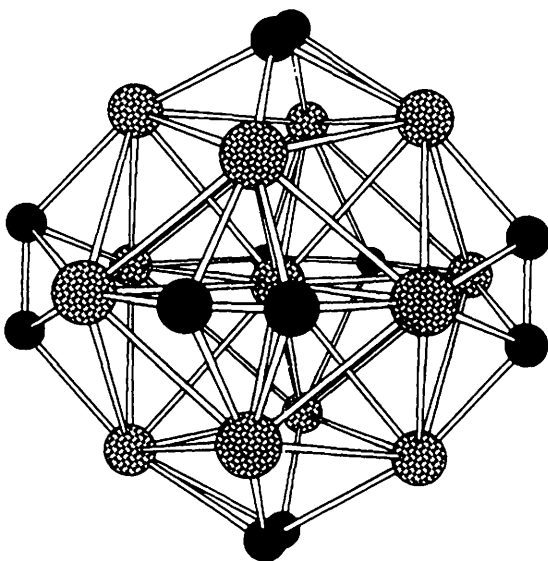
In order to demonstrate the geometrical constraints, the conformations for $[Cu_{2n+1}(lel-C_2)_n]^+$ with D_n symmetry for $n = 4, 5, 6$ have been optimised by local density functional calculations using DMol.^{7,10} Results, which are preliminary, but reliable for the present geometrical analysis, are contained in Table 1. The outcome about geometry is clear. The $[Cu-Cu_{2n}(lel-C_2)_n]$ structure for $[Cu_9C_8]^+$ is strained by compression in that the bonds to the central Cu atom are 0.2 to 0.4 Å shorter than the others and 0.13 Å less than the $Cu-Cu$ distance in copper metal (2.56 Å). The corresponding structure for $[Cu_{11}C_{10}]^+$ is favourable in that all $Cu-Cu$ distances are close to that of the metal, while for $[Cu_{13}C_{12}]^+$ the Cu^c-Cu distances are longer and the other $Cu-Cu$ distances shorter than in the metal, and despite the increased number of connections to Cu^c there is marginal advantage in

the binding energy. I conclude that the Cu-centred Cu_{2n} n -gonal prism model is most favourable for $n = 5$, at least for the (*lel*) _{n} isomer. It is significant that the $[Cu_{11}C_{10}]^+$ ion is more intense than its neighbours in Castleman's spectra. Calculations are continuing on the other isomers of the Cu-centred Cu_{2n} n -gonal prism hypothesis, and on the details of the electronic states.

There are more interesting structural possibilities for $[Cu_{13}C_{12}]^+$. The structure of copper metal is cubic close packed, for which a fundamental fragment is the centred cuboctahedron, Cu_{13} . This has six square faces, accommodating C_2 groups, and accounting for the observed composition, $[Cu_{13}(C_2)_6]$. Again the C_2 caps could be parallel to the edges or to the diagonals of the Cu_4 faces. The centred cuboctahedral basis for consideration of the structures for $[Cu_{13}C_{12}]^+$ is in fact analogous to the cubic basis for consideration of the structure of $[Ti_8C_{12}]^+$. Where there are Ti atoms in $[Ti_8C_{12}]^+$ 4 there are Cu_3 triangles in $[Cu_{13}C_{12}]^+$ 5. Many of the considerations of geometry, distortion and symmetry for the structure of $[Ti_8C_{12}]^+$ can in fact be transferred to this structural postulate for $[Cu_{13}C_{12}]^+$, but with the significant difference that C_2 groups parallel to the edges of the Ti_4 quadrilaterals correspond to C_2 groups diagonal to the Cu_4



6



7

quadrilaterals, and *vice versa*. There is a large range of structural isomers arising from different arrangements of the C_2 groups on the faces of *centro*-Cu-cuboctahedro-Cu₁₂.

I have optimised^{10†} the two highest symmetry *centro*-Cu-cuboctahedro-Cu₁₂ isomers, **6** (T_d) with parallel C_2 groups and **7** (T_h) with diagonal C_2 groups. The relative energies are $-11\,570\text{ kJ mol}^{-1}$ for **6** and $-11\,870\text{ kJ mol}^{-1}$ for **7**, to be compared with $-11\,110\text{ kJ mol}^{-1}$ for **3**. The distinctive energy advantage for **7** is associated with Cu_4 faces which become concave in order to nestle each C_2 group, in similar fashion to the deeper nesting of C_2 by the Ti_4 faces in the most stable isomer of Ti_8C_{12} . Notable bond distances (Å) for **6** and **7** are: Cu^c-Cu, 2.58 (**6**), 2.67 (**7**); Cu-Cu, 2.57, 2.60 (**6**), 2.68 (**7**); Cu-C, 1.92 (**6**), 1.87, 2.08 (**7**); C-C, 1.28 (**6**), 1.28 (**7**).

I propose these structures and their isomers as the basis for further calculations of the copper carbohedrenes. The geometries and energy minima for other ions observed by Castleman are under investigation. Details of the calculations, including description of the highest occupied molecular orbitals, the spin state, and the HOMO-LUMO gap, will be included in the full publication of this work.

This research is supported by the Australian Research Council. The generous provision of resources by Australian Supercomputing Technology is gratefully acknowledged.

Received, 28th May 1993; Com. 3/03052K

References

- 1 Y. Yamada and A. W. Jnr. Castleman, *Chem. Phys. Lett.*, 1993, **204**, 133.
- 2 R. W. Grimes and J. D. Gale, *J. Chem. Soc., Chem. Commun.*, 1992, 1222.
- 3 M.-M. Rohmer, P. de Vaal and M. Benard, *J. Am. Chem. Soc.*, 1992, **114**, 9696.
- 4 Z. Lin and M. B. Hall, *J. Am. Chem. Soc.*, 1992, **114**, 10054.
- 5 B. V. Reddy, S. N. Khanna and P. Jena, *Science*, 1992, **258**, 1640.
- 6 M. Methfessel, M. van Schilfgaarde and M. Scheffler, *Phys. Rev. Lett.*, 1993, **70**, 29.
- 7 I. G. Dance *J. Chem. Soc., Chem. Commun.*, 1992, 1779.
- 8 M. Benard, personal communication.
- 9 A. Ceulemans and P. W. Fowler, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2797.
- 10 DMol v2.2, Biosym Technologies Inc., San Diego, USA.: spin restricted; double numerical basis set with d polarisation functions; frozen core orbitals.

† D_2 symmetry imposed.