Geometric and Electronic Structures of [Ti₈C₁₂]: Analogies with C₆₀

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Local density functional calculations for [Ti$_8$C$_{12}$], observed as a positive ion by Castleman *et al.*, yield distances Ti–C 1.99, C–C 1.40, Ti–Ti 3.02 Å for the pentagonal dodecahedral (T_h) structure in which C$_2$ units cap the faces of the Ti$_8$ cube, but indicate a much more stable isomer in which six C$_2$ units occupy the butterflies of a Ti$_8$ tetracapped tetrahedron, and point to significant reactivity patterns.

Castleman *et al.* have recently reported that the ion [Ti$_8$C$_{12}$]$^+$ and homologues [M$_8$C$_{12}$]$^+$ (M = V, Zr, Hf) are generated by reactions of gaseous metal ions and clusters with gaseous hydrocarbons.[1–4] Other ions [M$_x$C$_y$]$^+$ are generated in these mass spectrometric experiments, but there is evidence for the predominance of [M$_8$C$_{12}$]$^+$, implying special stability. This ion contains 20 atoms, and with knowledge of dodecahedrane C$_{20}$H$_{20}$[5] and of the structures of the fullerene clusters based on the truncated icosahedron and special significance for five membered rings, it is entirely reasonable to propose, as Castleman has done, that the [M$_8$C$_{12}$] possess a pentagonal dodecahedral cage structure. Accordingly they have been named metallo-carbohedrenes.

Each of the pentagonal faces in pentagonal dodecahedral Ti$_8$C$_{12}$ would contain three C atoms and two Ti atoms, with each Ti connected to three C and each C connected to one C and two Ti. The geometry and isomerism of this structure deserves evaluation. Certainly the pentagonal dodecahedron cannot be regular because the Ti–C and C–C bond distances

are unequal. Further, the Ti$_8$ atoms constitute a cube, the edge length of which is 1.618 [the golden ratio, $\tau = (1 + \sqrt{5})/2$] times the edge length of a regular pentagonal dodecahedron. Any reasonable values for the Ti–C, C–C distances lead to a Ti–Ti distance indicative of some Ti–Ti bonding, and Ti$_8$C$_{12}$ is therefore reinterpreted as a Ti$_8$ cube, with C$_2$ units over the six faces, structure **1**.

While retaining T_h symmetry, the Ti–Ti, Ti–C and C–C distances in **1** can independently adopt acceptable values. I have used the local density functional method,[6] as embodied in the program DMOL,[7,8] to optimise the geometry of **1** by minimisation of the electronic energy. D_{2h} symmetry was imposed. The calculations use the double numerical basis with polarisation functions up to 4p on Ti and 3d on C, in closed shell configuration. The accuracy of structures calculated this way has been demonstrated for transition metal compounds and clusters.[9] The calculated distances for **1** are Ti–Ti 3.02, Ti–C 1.99, C–C 1.40 Å, with T_h symmetry retained. These Ti–C distances are shorter than those in conventional organo-

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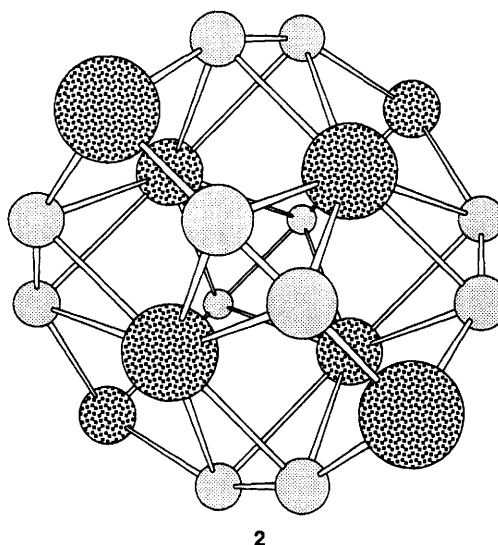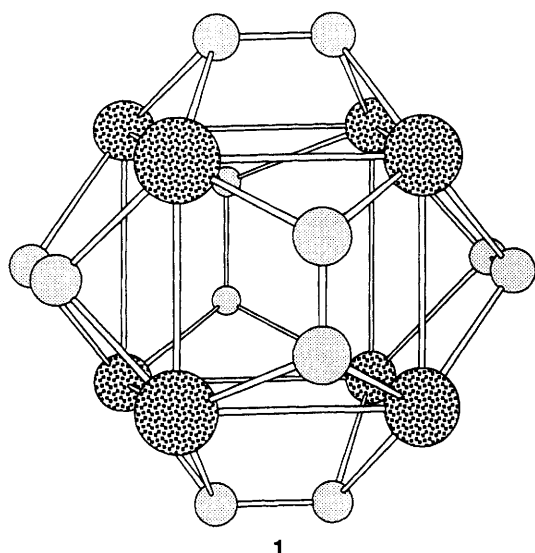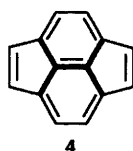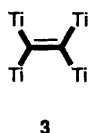
Ti clusters, as is usual for the bonds in a metal cluster devoid of terminal ligands. The contiguous C atoms are double bonded. Although the pentagonal faces of **1** are irregular, they retain virtual planarity.†

There are other geometrical isomers for Ti_8C_{12}. In structure **2** (also T_h) the Ti_8 array occurs as a tetracapped tetrahedron, containing six Ti_4 faces in butterfly topology; each Ti_4 face can accommodate a C_2 unit. The Ti in **2** are in two sets: the four outer, Ti^o, are within potential bonding distance of three other Ti, while the four inner, Ti^i, can bond to three Ti^i and three Ti^o all at the same distance. Each C can bond to three Ti as well as one C, so the net bonding capacity of **2** is greater than that of **1**. The Ti–Ti, Ti–C (two types) and C–C distances are less independent in **2** than they are in **1**. Geometry optimisation using the same density functional method as above yields the dimensions Ti^i–Ti^i 2.86, Ti^i–Ti^o 2.90, C–C 1.34, Ti^i–C 2.19, Ti^o–C 1.93 Å. Further, the total electronic binding energy of **2** is more favourable than that of **1**, by 1470 kJ mol^{-1}, and at this stage **2** is proposed as the most probable structure for $[Ti_8C_{12}]$. Experimental evidence in favour of **2** might be found in the details of the association energies of the eight ND_3 molecules that bind to $[Ti_8C_{12}]^+$:[1,2] for **2** they should differentiate as 4 + 4, while for **1** there would be no discontinuity in the association energies.

Structure **1** has significant analogies with the structure of C_{60}:[10,11] both are composed of an 'octahedral' (T_h) array of functional moities each having at their centre a C–C multiple bond, namely **3** for Ti_8C_{12} and the pyracylene unit **4** for C_{60}. The C_2 units of Ti_8C_{12} are very similar to this electron-deficient double bond (length $ca.$ 1.38 Å[12]) in C_{60}, the demonstrated site of reactivity.[13] This readily leads to conjecture that the reactivities of Ti_8C_{12} may be similar to the additions of C_{60}.

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† *Note added in proof:* After submission of this communication similar calculations of the structure of **1** were reported: R. W. Grimes and J. D. Gale, *J. Chem. Soc., Chem. Commun.,* 1992, 1222.

Extension of the calculations to other ions in the $[M_xC_y]^+$ series is in progress.

References

1 B. C. Guo, K. P. Kerns and A. W. Castleman, Jr., *Science*, 1992, **255**, 1411.

2 B. C. Guo, S. Wei, J. Purnell, S. Buzza and A. W. Castleman, Jr., *Science*, 1992, **256**, 515.

3 S. Wei, B. C. Guo, J. Purnell, S. Buzza and A. W. Castleman, Jr., *Science*, 1992, **256**, 818.

4 S. Wei, B. C. Guo, J. Purnell, S. Buzza and A. W. Castleman, Jr., *J. Phys. Chem.,* 1992, **96**, 4166.

5 R. J. Ternansky, D. W. Balogh and L. A. Paquette, *J. Am. Chem. Soc.*, 1982, **104**, 4503; J. C. Gallucci, C. W. Doecke and L. A. Paquette, *J. Am. Chem. Soc.*, 1986, **108**, 1343.

6 R. O. Jones and O. Gunnarsson, *Rev. Mod. Phys.*, 1989, **61**, 689; *Density Functional Methods in Chemistry*, ed. J. Labanowski and J. Andzelm, Springer–Verlag, Heidelberg, 1991.

7 B. Delley, *J. Chem. Phys.*, 1990, **92**, 508.

8 Dmol, v2.2 1992, Biosym Technologies, San Diego, USA.

9 J. Andzelm, E. Wimmer and D. R. Salahub, in *The Challenge of d and f Electrons*, ed. D. R. Salahub and M. C. Zerner, ACS Symposium Series, **394**, 1989, ch. 16; C. Sosa, J. Andzelm, B. C. Elkin, E. Wimmer, K. D. Dobbs and D. A. Dixon, *J. Phys. Chem.*, 1992, **96**, 6630; D. A. Dixon and J. L. Gole, *Chem. Phys. Lett.*, 1992, **189**, 390.

10 *Fullerenes*, ed. G.S. Hammond and V. J. Kuck, *ACS Symposium Series*, 1992, **481**.

11 *Acc. Chem. Res.*, 1992, **25**, issue number 3.

12 W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor and D. R. M. Walton, *Nature*, 1991, **353**, 147; S. Liu, Y.-J. Lu, M. M. Kappes and J. A. Ibers, *Science*, 1991, **254**, 408; K. Hedberg, L. Hedberg, D. S. Bethune, C. A. Brown, H. C. Dorn, R. D. Johnson and M. de Vries, *Science*, 1991, **254**, 410.

13 F. Wudl, A. Hirsch, K. C. Khemani, T. Suzuki, P.-M. Allemand, A. Koch, H. Eckert, G. Srdanov and H. M. Webb, in ref. 10, ch. 11; P. J. Fagan, J. C. Calabrese and B. Malone, *J. Am. Chem. Soc.*, 1991, **113**, 9408; F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157; P. J. Fagan, J. C. Calabrese and B. Malone, *Acc. Chem. Res.*, 1992, **25**, 134; B. Chase and P. J. Fagan, *J. Am. Chem. Soc.*, 1992, **114**, 2252.