Molecular structure of Ti_8C_{12} and related complexes

(M_8C_{12}, M = V, Zr, and Hf/metal–carbon double bonds/resonance of double bonds/complexes of ethylene)

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ABSTRACT Application of valence-bond theory leads to the assignment to the molecule Ti_8C_{12} of a cubic structure, point group $O_hm\bar{3}m$, with 8 Ti at the cube corners, $\pm(x\ x\ x, x\ \bar{x}\ \bar{x}, \circlearrowleft)$ where $x = 1.78$ Å, and with 12 C in pairs in the cube faces, $\pm(0\ y\ z, \circlearrowleft, 0\ \bar{y}\ \bar{z}, \circlearrowleft)$ where $y = 1.78$ Å and $z = 0.71$ Å. The Ti—C and C—C bonds have bond number 4/3, corresponding to resonance of single and double bonds in 2:1 ratio.

Guo, Kerns, and Castleman (1) recently reported their discovery by mass spectroscopy of the stable ion $Ti_8C_{12}^+$ while they were investigating the dehydration effects of metal atoms and ions on hydrocarbons. They assumed that the parent molecule Ti_8C_{12} is also stable and suggested that the 20 atoms are at the corners of a nearly regular pentagonal dodecahedron, as shown in Fig. 1. Guo *et al.* (2) then reported that they had observed the formation of similar stable ions $M_8C_{12}^+$ with M = V, Zr, and Hf. In both ref. 1 and ref. 2 the electronic structure is discussed. It is suggested that σ bonds C—C and M—C are formed and that the remaining valence forms delocalized π bonds.

A great deal is known about bond lengths, bond angles, change in valence by formal transfer of electrons between atoms, resonance of molecules among alternative valence-bond structures, and other aspects of molecular structure. Much of this knowledge is contained in my book *The Nature of the Chemical Bond* (3). I have applied some of it to the problem of the structure of the M_8C_{12} complexes and have concluded that they have a somewhat different structure from that shown in Fig. 1.

Valences of Ti and C

The number of outer electrons per atom is four for both Ti and C. The difference in electronegativity indicates that the Ti—C bonds have 22% ionic character, giving $Ti_8^{+0.9}C_{12}^{-0.6}$ if there are four Ti—C bonds per Ti and suggesting formal transfer of electrons to Ti to achieve a closer approach to electroneutrality for the atoms; the bond energy of C bonds is so much greater than that of Ti bonds, however, as to resist this electron transfer, and Ti and C are expected to remain quadrivalent.

Nature of the Bonds

It will be shown later that the Ti atoms are so far from one another that there is no' significant Ti—Ti bonding. The complex Ti_8C_{12} is so stable as to justify that all of the outer electrons are involved in Ti—C and C—C bonds. With quadrivalent Ti and C the atomic ratio 8/12 requires that there be some C—C bonds; accordingly, the simplest structure contains pairs of carbon atoms, and the molecule can be considered to be a compound of Ti and ethane or ethylene, as suggested in refs. 1 and 2 (Fig. 1). The quadrivalence of Ti and C then requires that each Ti atom form two Ti—C single
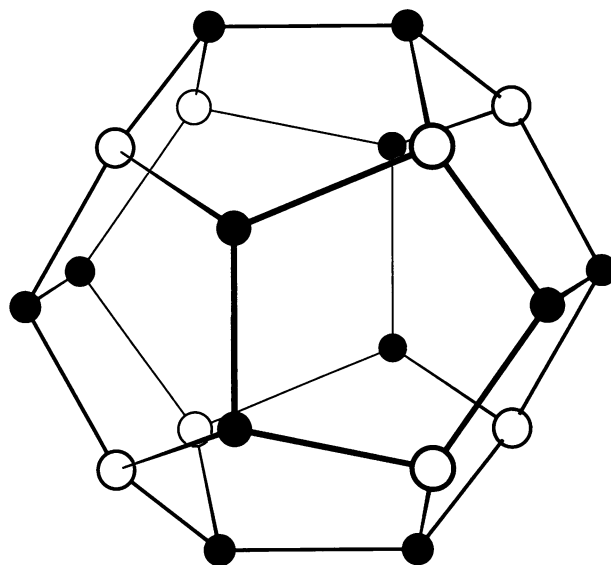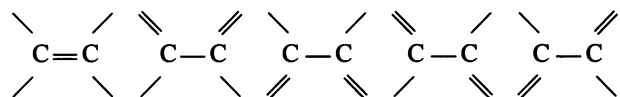
FIG. 1. The structure of Ti_8C_{12} and related molecules and ions (the pentagonal dodecahedron) suggested in refs. 1 and 2.

bonds and one double bond and that each C atom form two single bonds and one double bond with its three neighbors (2 Ti and 1 C).

Structure of the Molecule

In this first-approximation treatment, with the valence 4 for each atom, the following structures about each C_2 group are allowed:

$$\begin{array}{ccccc} \diagup \diagdown & \diagup \diagdown & \diagup \diagdown & \diagup \diagdown & \diagup \diagdown \\ C=C & C—C & C—C & C—C & C—C \\ \diagup \diagdown & \diagup \diagdown & \diagup \diagdown & \diagup \diagdown & \diagup \diagdown \end{array}$$

There is, of course, resonance among these structures, giving each bond the bond number 4/3. In each structure each carbon atom forms two single bonds and one double bond. There is ample evidence that the tetrahedral arrangement of four single bonds about a carbon atom [sp^3 hybrid bond orbitals, with the double bond consisting of two bent single bonds (p. 237 of ref. 3)] can be accepted, leading to the planarity of the group of the two C atoms and the four surrounding Ti atoms. Thus, we are led to the conclusion that Ti_8C_{12} has the structure shown in Fig. 2, a cube with 8 Ti at its corners and 12 C lying in pairs in the six cube faces. The point group is $O_hm\bar{3}m$ (not T_h, as given in refs. 1 and 2). The structure is topologically the same as that shown in Fig. 1, but from the standpoint of the structural chemist it is much different.

The foregoing discussion of single bonds and double bonds, with resonance, is similar to the discussion in refs. 1 and 2 of a framework of 30 Ti—C and C—C single bonds supporting 10 π bonds that resonate among the 30 positions. An advantage

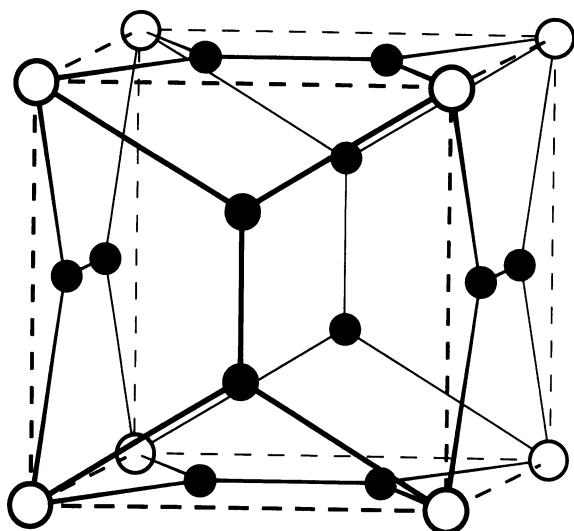FIG. 2. The structure found by application of valence-bond theory, a Ti_8 cube with C_2 groups in the cube faces, point group $O_hm\bar{3}m$.

of the valence-bond treatment is that it shows that Fig. 1 does not represent the structure of the molecule so well as Fig. 2.

The pentagonal rings of Fig. 2 are not the rings defining the pentagonal faces of the pentagonal dodecahedron because each pentagon is bent into two orthogonal planes. The structure can be best described as cubic, with a C_2 group lying in each of the cube faces.

Although with this structure each Ti atom is described as forming two single bonds and one double bond, it is not required (as it is for the C atom) that the Ti atom and its three C neighbors be coplanar. The stereochemistry of C is determined by its $2s$ and $2p$ orbitals and their hybrids, whereas the outer orbitals of Ti have $4s$, $4p$, and $3d$ available (p. 50 of ref. 3). The best spd hybrid orbitals make the angle $73.15°$ with one another (p. 152 of ref. 3), and the single-bond:double-bond angles can be similarly small, not requiring planarity.

Bond Lengths and Bond Angles

The single-bond radius of C is 0.772 Å (p. 224 of ref. 3) and that of Ti is 1.384 Å (4). A treatment of single-bond:double-bond resonance (p. 237 of ref. 3) leads to 1.422 Å and 2.074 Å for C—C and Ti—C bonds with bond number 4/3. With a suitable value of the Ti—C—Ti bond angle, the two ways of calculating the edge of the Ti_8 cube give the same answer, 3.56 Å. This value is so much larger than the expected Ti—Ti single-bond value, 2.78 Å, as to permit neglect of Ti—Ti bonding (application of the equation on p. 255 of ref. 3 gives Ti—C bond number 0.05, probably not significant). The value of the Ti—C—Ti bond angle is calculated to be $118.4°$; the expected value, with the assumption that Ti—C and C—C bonds with bond number 4/3 can be considered to be equivalent, is $120°$.

Summary

The application of valence-bond theory has led to what seems to be a reasonable structure, different from the pentagonal dodecahedral structure described in refs. 1 and 2. The structure has point-group symmetry $O_hm\bar{3}m$, with 8 Ti at the cube corners, $\pm(x\,x\,x,\,x\,\bar{x}\,\bar{x},\,\circlearrowleft)$ where $x = 1.78$ Å, and with 12 C in pairs at the cube faces, $\pm(0\,y\,z,\,\circlearrowleft,\,0\,\bar{y}\,z,\,\circlearrowleft)$ where $y = 1.78$ Å and $z = 0.71$ Å. The Ti—C and C—C bonds are assigned bond number 4/3 (resonance of single and double bonds) and lengths 2.08 Å and 1.42 Å, respectively. The compound $Ti_8C_{12}8N^2H_3$, reported in ref. 2, involves Ti—N bonds, as suggested in ref. 2. The expected bond length is about 1.96 Å, and the electronegativity difference corresponds to transfer of 0.57 electrons from Ti to N, leaving Ti with a resultant charge $+0.31$. The decrease from $+0.88$ (better agreement with the electroneutrality principle, p. 172 of ref. 2) contributes to the stability of the complex.

The same structure, with appropriate changes in the bond lengths, is expected also for the compounds of V, Zr, and Hf (2). Many larger complexes of Zr and Ta have also been reported (5); their structures are not known.

1. Guo, B. C., Kerns, K. P. & Castleman, A. W., Jr. (1992) *Science* 255, 1411–1413.
2. Guo, B. C., Wei, S., Purnell, J., Buzza, S. & Castleman, A. W., Jr. (1992) *Science* 256, 515–516.
3. Pauling, L. (1960) *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, NY), 3rd Ed.
4. Pauling, L. & Kamb, B. (1986) *Proc. Natl. Acad. Sci. USA* 83, 3569–3571.
5. Wei, S., Guo, B. C., Purnell, J., Buzza, S. & Castleman, A. W., Jr. (1992) *Science* 256, 818–820.