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COMPOUND FULLERENES

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Sir,

Almost immediately after the first report[1] of the possible truncated icosahedron structure of C_{60} and other fullerenres, there were efforts to dope them with metal atoms[2]. In particular LaC_{60} was found to be particularly abundent and it was believed that La was trapped inside the fullerene cage. Recently the truncated icosahedron structure of C_{60} has been confirmed[3] and it has been even possible to prepare $La@C_{60}$ and higher metallofullerenes and to trap Y, K etc. inside the fullerene cage[4]. Besides this it is possible to replace a carbon atom by B and form substitutionally doped fullerenes[5]. In a significant new development Guo et at[6] have recently observed a super magic cluster of Ti_8C_{12} and suggested a pentagonal dodecahedron structure for this. Interestingly this is the smallest fullerene possible for carbon. There is some supporting evidence for this structure as only 8 ammonia molecules could be accomodated, one for each Ti atom when the clusters were exposed to ammonia in a reaction cell, suggesting that all the Ti atoms lie on the surface of the cluster. In the suggested structure of this 20 atom cluster all the 8 Ti atoms have equivalent environment. Each Ti atom has three carbon atoms as nearest neighbours and each carbon atom has two Ti and one carbon as nearest neighbours. This we trust is very important for the stability of this molecule. One can think the growth of these clusters from dimers of carbon and Ti-C. As Ti-C[7] and C-C and $C\text{-}C^-$ dimers are much more strongly bonded than Ti-Ti it is expected that there will be a tendency to maximize such bonds.

In the pentagonal dodecahedron structure of C_{20} the carbon bonds are considerably strained and this cluster is also not so abundant[8] as compared to C_{60} and other higher fullerenes. However, in the suggested structure of Ti_8C_{12} there are only carbon dimers and the Ti-C-Ti bonds are likely to be less rigid because of the s-p-d hybridization. Two Ti atoms lie on each pentagon and all the 8 Ti atoms form approximately a cube. In the idealized pentagonal dodecahedron structure all the bond lengths are equal. However, we expect two bond lengths which can be associated with the C-C ($\approx 1.4Å$) and C-Ti ($\approx 2.0Å$) bonds. From the fact that small carbon clusters form either chain, ring or fullerene type open structures, the suggested structure of Ti_8C_{12} is very likely to be true. Ti has four valence electrons in the $3d^24s^2$ configuration and therefore in this structure the Ti-C bonding is covalent as for the C-C bond. Both C-C and Ti-C bonds can be single or double. In one model , also suggested by Guo et al, the six pairs of carbon atoms can be double bonded. A small excess of charge in such dimers is also favorable[7]. The remaining electrons on Ti atoms participate in the metal-metal interaction and reactions and could also give rise to interesting magnetic properties. Since the Ti-Ti distance is large this interaction is, however, expected to be weak. In another model, the bonding is envisioned to be similar to C_{20} where in addition to three σ - bonds on each site, the remaining electron participate in the π - bonding. While the reality is to be seen from detailed electronic structure calculations, Guo et al also mention about the existence of higher clusters but do not provide any details. It would be very interesting and would broaden the scope of fullerene structures for *compound clusters* if the higher clusters could have similar structures as for carbon.

One of the most interesting structures in higher fullerenes is the truncated icosahedron for 60 atom cluster in which all the carbon atoms have the same environment. This has 12 pentagons and 20 hexagons. From the two environments corresponding to Ti and C atoms in Ti_8C_{12}, we have constructed a $Ti_{24}C_{36}$ molecule (Fig. 1) from a C_{60} structure in which each Ti has exactly the same environment, namely three carbon atoms as the nearest neighbours. Also each carbon atom has two Ti and one carbon as nearest neighbours similar to Ti_8C_{12}, but there are two such environments which differ from each other slightly in bond angles. The two Ti atoms can be on the same pentagon or on two neighbouring pentagons. As in Ti_8C_{12}, there are 12 pentagons in fullerenes and each pentagon has two Ti atoms. This accounts for 24 Ti atoms. Since this molecule will again be very symmetrical, we expect high stability for this as well and call this class of fullerenes as *compound fullerenes* since compounds like TiC etc exist in the bulk. Also from the point of view of valence, all the bonds joining two hexagons will be double bonds and all the bonds joining a pentagon and a hexagon a single bond as in the C_{60} molecule. There are 12 C-C and 18 Ti-C bouble bonds and 12 C-C and 48 Ti-C single bonds. The structure shown in Figure 1 has cubic symmetry. There are eight hexagons which have three Ti and 3 carbon atoms. Centres of these hexagons form a cube. There are 12 hexagons which have two Ti atoms each. The bonds joining these hexagons lie along the 3 coordinate axes.

It would be of interest to study how C-C and Ti-C dimers fuse together to form larger clusters. We therefore suggest a careful study of such small clusters which might also help to understand the growth of bigger compound fullerenes. There are nearly equally spaced peaks on either side of the Ti_8C_{12} peak in the mass spectrum given by Guo et al. These may correspond to removal or addition of one carbon atom successively in contrast to dimers seen in the case of the fullerenes.

Like the higher fullerenes, it may be possible to have $Ti_{24}C_{46}$ and other related molecules in which the number of pentagons remain 12. Though it is possible to substitute Ti in place of C in the remaining hexagons, we note that generally it is not possible to substitute Ti according to two neighbourhoods of Ti and C atoms. Therefore if the number of Ti atoms exceed 24, then different carbon atoms will have different environments. This suggests that $Ti_{24}C_{36}$ may be another unique cluster in these new materials.

If these structures become true, it will open a new way to produce a much wider class of materials and can have important implications in the study of reactions as carbon often poison reactions and also in the study of materials in which TiC particles are present. Also it should be possible to form such molecules with other metals and also with species other than carbon such as boron and nitrogen.

REFERENCES AND FOOTNOTES

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7. Dissociation energies for C_2, C_2^-, and Ti_2 are 6.21, 8.4, and 1.3 eV respectively. We could not find a value for Ti-C but from the fact that for Ti-O and Ti-N dimers it is 6.87 and 4.9 eV and the fact that TiC is a very strongly bonded material with high melting point, we expect a high value for it also.

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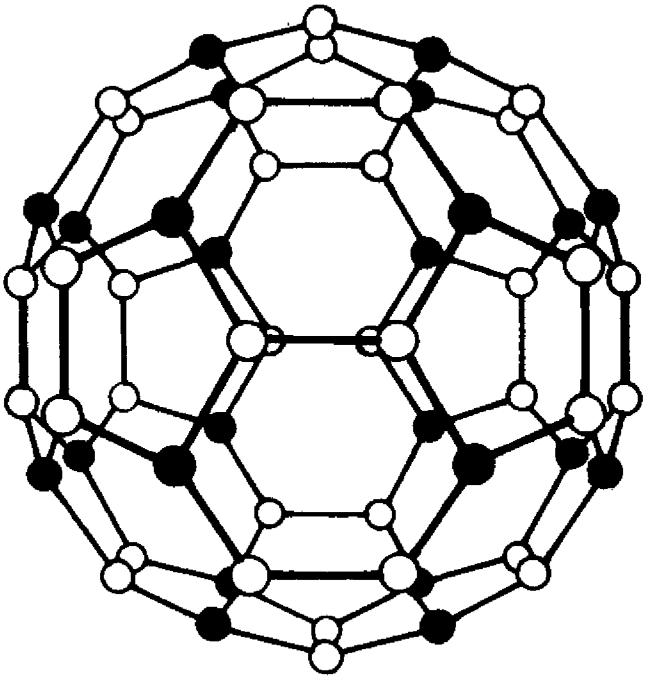

Fig. 1. A possible $Ti_{24}C_{36}$ molecule. Filled(empty) circles represent Ti(C) atoms.