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Why Are $[Cu_8Te_{12}]^{4-}$ Cage Clusters and Metallocarbohedrenes M_8C_{12} Topologically Different? An ab Initio SCF Study

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Introduction

Kanatzidis and colleagues have reported the structure of the ternary copper−polytelluride compounds $K_4Cu_8Te_{11}$,[1] $A_3Cu_8Te_{10}$ (A = Rb, Cs), $AA'_2Cu_8Te_{10}$ (A, A′ = K, Rb, Cs), and $A_2BaCu_8Te_{10}$ (A = K, Rb, Cs).[2] The building blocks of those two- or three-dimensional structures are pentagonal dodecahedral $Cu_8(Te_2)_6$ clusters sharing Te−Te edges and encapsulating an alkali metal or a Ba^{2+} ion. Those inclusion clusters represent the first characterized examples of pentagonal dodecahedral M_8X_{12} cage clusters with a cubic framework of transition metal atoms. It is however strongly reminiscent of the new class of metallocarbohedrene or met−car cage clusters M_8C_{12} (M = Ti, Zr, Hf, V, Nb, Cr, Fe, Mo).[3,4] None of those clusters detected at the mass spectrometer has been structurally characterized yet, but there is now little doubt that their remarkable stability is due to a hollow cage structure.[5] A controversy has developed about the nature of this cage. On the one hand, a structure of pentagonal dodecahedron quite similar to that of the condensed Cu_8Te_{12} clusters had been proposed first by Castleman's group[3] and tentatively corroborated by the existence of a continuous series of mixed Ti/Zr clusters[6] and by arguments taken from the observed reactivity of met−cars.[7] On the other hand, theoretical models based upon ab initio DFT or Hartree−Fock calculations consistently predict met−cars to exist as tetracapped tetrahedra of metal atoms with 36 M−C bonds and two distinct metal sites (Figure 1).[8]

As noticed by Kanatzidis, the electronic structures of M_8C_{12} and Cu_8Te_{12} are different, and the characterization of a pentagonal dodecahedral structure for the latter cannot be taken *a priori* as an argument in favor of the same topology for met−cars.[2] However, the characterization of this new cage cluster provides an opportunity to test the validity of ab initio optimized geometries, to point out the differences between the electronic structures of met−car and Cu_8Te_{12} clusters, and to investigate the influence of the encapsulated cation, either singly or doubly charged, on the shape of the cluster.

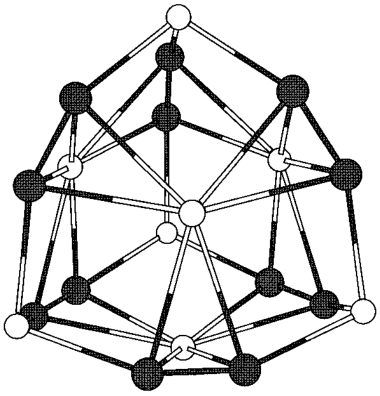


Figure 1. Structure of tetracapped tetrahedron of metal atoms (T_d symmetry) preferred for M_8C_{12} clusters from ab initio calculations.

Computational Details

Hartree−Fock calculations and geometry optimizations have been carried out on the isolated model clusters $[Cu_8Te_{12}]^{4-}$, $K^+@[Cu_8Te_{12}]^{4-}$, and $Ca^{2+}@[Cu_8Te_{12}]^{4-}$, by means of the TURBOMOLE program.[9] The basis sets used for the calculations are defined as follows.

Cu: All electron basis is due to Wachters[10] and made of 13s, 9p, 5d primitive Gaussian functions contracted into double-ζ (8s, 5p, 3d).

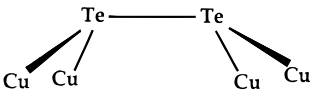
Te: An effective core potential due to Hay and Wadt[11] models the potential due to the 46 inner electrons. The 6 valence electrons are described by a 3s, 3p basis set also contracted into double-ζ.

K, Ca: All electron bases are due to Wachters[10] and contracted into double-ζ.

Geometry optimizations have been carried out assuming either the T_h or the T_d symmetry point group.

Results and Discussion

Extended Hückel calculations carried out on $[Cu_8Te_{12}]^{4-}$ with T_h and with T_d symmetry, and on the fragments $(Te_2)^{2-}$ and $[Cu_4Te_2]^{2+}$ explain the origin of the stabilizing interactions. Those interactions involving the fully occupied, doubly degenerate set of π^* orbitals in $(Te_2)^{2-}$ with the proper combination of unoccupied sp hybrids centered on the Cu^+ atoms (T_h symmetry) have been discussed by Kanatzidis et al.[2] It should be noticed however that not only the π^* frontier orbitals, but also the underlying π orbitals, and even the σ bonding orbital of $(Te_2)^{2-}$, are stabilized by the valence, essentially s-type orbitals of copper. This clearly appears from the interaction diagram between one $(Te_2)^{2-}$ fragment and 4 copper atoms in a square arrangement (Figure 2, right-hand side). The bonding scheme of $(Te_2)^{2-}$ can then be schematized as follows:



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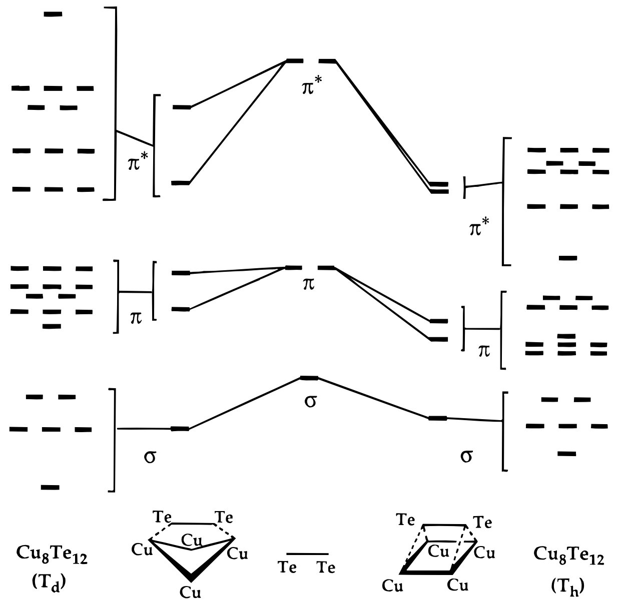
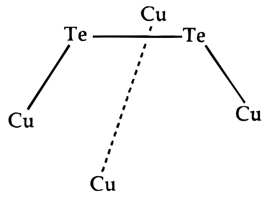


Figure 2. Diagram of the ditellurium valence orbitals (from extended Hückel calculations) resulting from the interactions between $(Te_2)^{2-}$ and Cu^+ which yield the $(Cu_4Te_2)^{2+}$ fragment and the $[Cu_8Te_{12}]^{4-}$ cluster: (a) left-hand side, T_d symmetry; (b) right-hand side, T_h symmetry. All represented orbitals are doubly occupied.

The reason why the structure of tetracapped tetrahedron is not competitive in this case is also evidenced by the interaction diagram (Figure 2, left-hand side). The degeneracy of the π and of the π^* levels of $(Te_2)^{2-}$ is split due to donation interactions specifically oriented toward the two metal atoms that form a plane with the ditellurium fragment:



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Since $(Te_2)^{2-}$ cannot act as an acceptor, the two other underlying metal atoms have little influence on the ligand orbitals, except for destabilizing 4-electron interactions involving the d shell of copper. The coalescence of the Cu_4Te_2 fragments leading to the Cu_8Te_{12} cage clusters, either T_h or T_d, yields relatively broad, but nonoverlapping band systems associated with the σ, π, and π^* electrons of the $(Te_2)^{2-}$ fragments. The center of gravity of those bands is not significantly modified with respect to the average energy of the corresponding fragment orbitals, except for a slight upward shift of the π^* bands (0.11eV for T_d, 0.07eV for T_h, Figure 2).

The result of ab initio calculations provides a quantitative assessment to the orbital interaction reasoning. The free ion $[Cu_8Te_{12}]^{4-}$ is found most stable with the structure of pentagonal dodecahedron, the energy difference being 181 $kcal{\cdot}mol^{-1}$ with respect to the tetracapped tetrahedron. This energy gap increases when a cation is encapsulated: 231 $kcal{\cdot}mol^{-1}$ for $K^+@[Cu_8Te_{12}]^{4-}$ and 280 $kcal{\cdot}mol^{-1}$ for $Ca^{2+}@[Cu_8Te_{12}]^{4-}$. The structure of the isolated cage seems to be relatively flexible and sensitive to the electrostatic field induced by an encapsulated cation. The positively charged Cu atoms (Mulliken net charge +0.61 e) are repelled from the center O of the cavity by 0.28 Å due to a single charge and by 0.49 Å when a dication is encapsulated (Figure 3). The opposite trend is noticed for the negatively charged Te atoms (−0.74 e): the O−Te distance decreases from 4.24 Å in the empty cluster to 4.16 Å with K^+ and 4.04 Å with Ca^{2+} inside. The 12 $\overline{\text{Cu−Te−Cu−Te−Te}}$ pentagons forming the cluster are close to planarity in $Ca^{2+}@[Cu_8Te_{12}]^{4-}$, but they are visibly distorted in $K^+@[Cu_8Te_{12}]^{4-}$ and they strongly deviate from planarity in the empty cluster. This flexibility of the isolated cluster is not observed in the recently characterized solids. No significant geometry change is observed as a function of the charge of the encapsulated ion, except for a slight increase of the O−Cu distance (∼0.04 Å) when Ba^{2+} replaces an alkali metal cation inside the cluster.

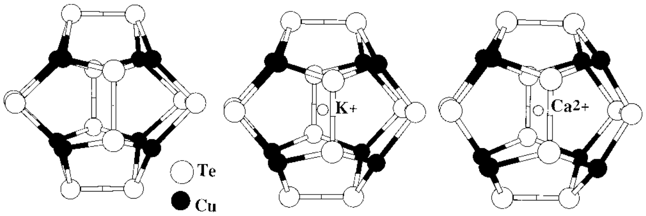
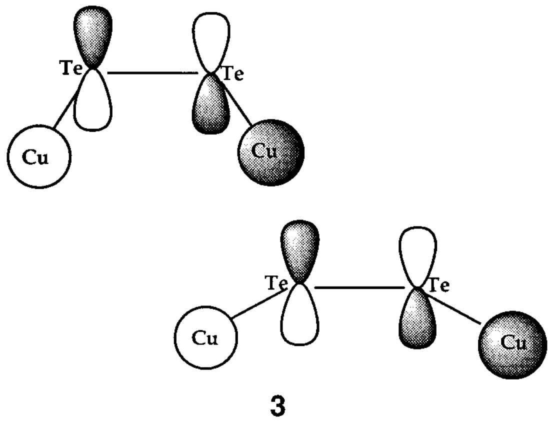


Figure 3. Optimized geometries (T_h symmetry) (a) left-hand side, $[Cu_8Te_{12}]^{4-}$; (b) center, $K^+@[Cu_8Te_{12}]^{4-}$ (c) right-hand side, $Ca^{2+}@[Cu_8Te_{12}]^{4-}$. Key: white circles, Te atoms; gray circles, Cu atoms.

The computed bond lengths, Te−Te and Cu−Te, are much less sensitive to the influence of the inserted ion. The Te−Te distance is computed to be 2.89 Å (observed: 2.765−2.856 Å with an average of 2.80−2.81 Å). The computed Cu−Te distances vary from 2.825 to 2.864 Å, which is larger by ∼0.25 Å than the observed distances involving the unshared ditellurides.

Extended Hückel calculations show that the changes in the shape of the cage induced by the presence and the nature of the encapsulated ion have little influence on the electronic effects stabilizing the pentagonal dodecahedron. However, if similar changes, i.e. increase of the O−Cu and Cu−Cu distances and decrease of the O−Te distances, are considered in the structure of tetracapped tetrahedron, the stabilizing interactions will be severely weakened by the presence of a positive charge at the center of the cluster. The overlap between the π_z/π^*_z orbitals of $(Te_2)^{2-}$ and the proper combination of the metal 4s acceptor orbitals rapidly vanishes with the expansion of the metal framework, which yields an opening of the Cu−Te−Te angle. The influence of the angle opening on the Te→Cu donation can be appreciated from the two following diagrams of the π^* orbital of $(Te_2)^{2-}$:



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The variation of the computed energy gap between the T_h and the T_d forms as a function of the encapsulated charge appears consistent with the dependence of the Cu−Te interactions on the extension in space of the tetrahedral metal framework.

Chalcogenide and Carbide Clusters: A Comparison

In their recent article introducing the new class of solid state copper tellurides, Kanatzidis and colleagues[2] suggest the possibility for the $Cu_8(Te_2)_6$ dodecahedral cluster to be stable enough to exist in discrete form. To our knowledge, the only gas phase copper telluride clusters reported to date have been obtained by laser ablation from solid samples of Cu_2Te and analyzed through mass spectrometry.[12] The dominant series of ions identified using this technique corresponds to the stoichiometry $[Cu_{2n-1}Te_n]^-$. The same pattern of composition was observed with other chalcogens[12] and is largely independant of the composition of the sample ablated by the laser pulse. Cu/Se and Ag/Se cationic species assigned as $[M_2Se]_n^+$ and $M[M_2Se]_n^+$ were also produced by a gas aggregation source.[13] The combination of those observations suggests that the $(M_2X)_n$ stoichiometry corresponds to a peak in the internal stability of ions.[12] The kinetically controlled stability of copper chalcogenide clusters with different stoichiometries cannot be excluded so far. The recent interest for metal carbide clusters has led to the characterization of two completely unrelated structural types, the met−car cage clusters and the fcc crystallites[14] depending on the experimental conditions[15] and, possibly, on the relative concentrations of metal and carbon atoms.[16] A similar behavior cannot be excluded for metal chalcogenides.

As far as a comparison can be carried out between copper tellurides Cu_8Te_{12} and metallocarbohedrenes M_8C_{12}, it appears that the key difference found from theoretical investigation on the electronic and geometric structures of those clusters lies in the metal to ligand back-donation interactions. Such interactions are clearly impossible with dichalcogen $[X_2]^{2-}$ ligands. The optimal stability will therefore be obtained by maximizing the number of σ donation interactions, as in the structure of pentagonal dodecahedron (24 σ donations).

In met−cars M_8C_{12} involving metals of groups IV and V, the 24 σ donation interactions are still present if a dodecahedral structure is assumed, but no advantage is taken of the six empty π^* orbitals available on the $[C_2]^{4-}$ ligands. As shown by Hay[17] the 8 (for group IV) or 16 (for group V) d metal electrons are accommodated in d_{z^2}-like orbital combinations with no interaction with the ligand orbitals. As a consequence, the optimized C−C distance remains approximately constant for the hypothetic scandium met−car Sc_8C_{12} (no d electron, $d_{C-C} = 1.330$ Å), for Ti_8C_{12} (8 d electrons, $d_{C-C} = 1.346$ Å), and for V_8C_{12} (16 d electrons, $d_{C-C} = 1.336$ Å).[17]

In the structure of tetracapped tetrahedron first proposed by Dance,[8a] the dicarbon ligands display an acetylenic coordination and should be formally described as $[C_2]^{2-}$. Twelve ligand π^* levels are formally unoccupied, but those levels are now engaged in strong back donation interactions with 16 d metal electrons. The remaining metal electrons, 4 for group IV metals, 12 for group V metals are accommodated in nonbonding d_{z^2}-like orbital combinations.[8e−g] Those back-donation interactions offset the loss of 12 σ donations and provide with respect to the dodecahedral structure the additional stability of 190−300 kcal·mol^{-1} computed by means of Hartree−Fock or DFT calculations.[8]

Let us finally mention that copper carbide cluster ions have been formed by means of the gas aggregation technique.[18] The most prominent ions formed using relatively high concentration of heated acetylene occur in the series $[Cu_{2n+1}C_{2n}]^+$ up to $n = 10$. DFT calculations carried out by Dance on $[Cu_{13}C_{12}]^+$ [19] and on larger copper carbide ions[20] suggest for those clusters carbohedrene-like structures derived from the *centro*-Cu-*cuboctahedro*-Cu_{12} framework surrounded with acetylene-like $[C_2]^{2-}$ ligands nested each in a Cu_4 butterfly and stabilized through π back donation. Once again, the replacement of the dicarbon by dichalcogen ligands, should it be possible, can be expected to modify the orientation of the $[X_2]^{2-}$ ligands in order to maximize the number of σ donation interactions. If the *centro*-Cu-*cuboctahedro*-Cu_{12} metal core is considered, each capping X_2 ligand would then adopt a conformation parallel to two edges of the underlying Cu_4 face, resulting in the cluster shape with T_d symmetry also considered by Dance in his investigations on copper carbohedrenes.[19]

Conclusion

Ab initio Hartree−Fock calculations carried out on $[Cu_8Te_{12}]^{4-}$ suggest that the isolated cluster, should it be stable enough to be found in discrete molecular form, would display the same topology as characterized in the two- and three-dimensional frameworks. The structure of pentagonal dodecahedron is preferred for the telluride ion to the framework of tetracapped tetrahedron of metal atoms consistently computed to be more stable for metallocarbohedrenes M_8C_{12}. The differences in the computed structures are to be related to the distinct electronic characters of the X−X ligands (X = C, Te). The ditellurium fragment $[Te_2]^{2-}$ is an electron-saturated species with no acceptor potentiality. In the case of $[Cu_8Te_{12}]^{4-}$, the structure of pentagonal dodecahedron maximizes the number of donation interactions (24) toward all symmetry-adapted combinations of the copper 4s orbitals.

For met−cars, the two possible structures of the M_8C_{12} cage are associated with distinct electron distributions in both the C−C fragments and the metal framework. The structure of pentagonal dodecahedron corresponds to an ethylenic hybridization for the dicarbon units with a formal electron count $[C_2]^{4-}$. All metal atoms are in the oxidation state III, which corresponds for M = Ti to a high-spin configuration with 8 d electrons and no possibility for back-donation.[17] The alternative structure of tetracapped tetrahedron requires formally acetylenic dicarbons, i.e. $[C_2]^{2-}$ ligands and 12 electrons more in the metal framework. Tetrahedral met−cars are then mixed-valence clusters with d electrons available for large back-donation effects. The latter description is largely favored by ab initio calculations. The present work suggests that the acceptor potentialities of the X−X fragment could condition the topology of a hypothetic M_8X_{12}—or larger—cage cluster.

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