A Theoretical Study of Te_6^{4+} and $Te_4S_4^{2+}$

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Geometry optimizations and molecular orbital calculations were performed on Te_6^{4+} and $Te_4S_4^{2+}$ ions based on approximate density functional theory within the local-density approximation. The Te_6^{4+} ion was found to have an elongated trigonal-prismatic geometry (D_{3h}) as its ground-state structure, in agreement with experimental results. A molecular orbital analysis of this non-classical structure in comparison to an alternative C_{2v} boat structure for the Te_6^{4+} ion was performed and an explanation is offered for their relative stabilities. Experimentally, the $Te_4S_4^{2+}$ ion is reported to adopt a geometry isostructural to As_4S_4. The present calculations on $Te_4S_4^{2+}$ with the experimental geometry indicate that the ion has a half-filled doubly degenerate highest occupied molecular orbital which is strongly antibonding between the tellurium atoms. The geometries of $Te_4S_4^{2+}$ with triplet and singlet electronic structures have been optimized. These geometries differed from the experimental geometry, with a considerable lengthening of the Te–Te bonds for the triplet species, and cleavage of a Te–Te bond for the singlet species to produce a C_{2v} structure similar to that of the isoelectronic Se_8^{2+} ion.

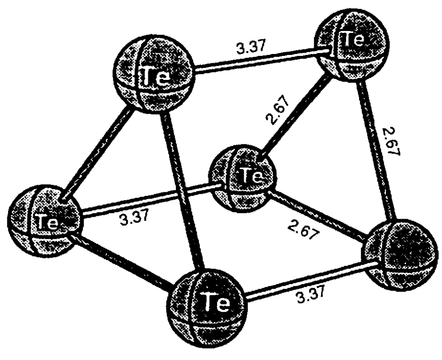
Polyhedral skeletal electron pair theory, developed primarily by Williams,[1] Wade,[2] Mingos[3] and Rudolph,[4] has proved extraordinarily useful for predicting the polyhedral geometries adopted by main-group and transition-metal clusters. It relates the cluster geometry to the total number of valence electrons associated with the cluster (the polyhedral skeletal electron count). In particular different classes of polyhedra, *e.g.* three-connected and deltahedral, are associated with characteristic numbers of valence electrons. Mingos[3] initially proposed that electron pairs in excess of the optimum count for a three-connected polyhedron result in cleavage of a skeletal bond for each electron pair in excess of the polyhedral electron count. As the nuclearity of clusters increases, the number of possibilities for bond cleavage increases. Similarly, when dealing with electron-rich clusters, questions arise about site preferences in the structure. Recently, Lyne and Mingos[5] have addressed the factors influencing bond cleavage and site preferences in these electron-rich clusters.

While the majority of clusters do conform to this generalization, there are two clusters which do not behave in the predicted manner. The first, Te_6^{4+}, has a polyhedral skeletal electron count of 32, two more than that in the related electron-precise prismane molecule.[6] Therefore, Te_6^{4+} would be expected to adopt a structure based on a prism, but with one of the skeletal bonds broken. There are two possibilities for cleavage of a bond in a prism. First, a bond in the triangular faces of the prism may be cleaved, or a bond parallel to the C_3 axis may be cleaved. The latter process has been predicted to be more favourable using semiempirical molecular orbital calculations, producing a C_{2v} boat structure.[5] This ion may also be described as a *hypho* cluster derived from $B_9H_9^{2+}$ by the loss of three capping equatorial groups[2] and retaining a trigonal-prismatic structure.

The structure reported for Te_6^{4+} is the latter and based on an elongated (along the intertriangular bonds) prism of D_{3h} symmetry. The extra pair of electrons has caused the three bonds parallel to the C_3 axis to lengthen simultaneously, producing three long Te–Te bonds. Extended-Hückel and Fenske–Hall calculations on the Te_6^{4+} ion as the D_{3h} prism and as the C_{2v} boat give the wrong ground-state geometries. For both structures, bond lengthening results in a large stabilization of a high-lying a_2'' orbital, which is strongly antibonding along the bonds being lengthened.[5] The calculations demonstrated that greater stability is conferred on this orbital by lengthening three bonds simultaneously as opposed to cleaving one bond. However, the total energies for the two structures predicted the incorrect, ground-state structure; the boat structure was calculated to be more stable. In view of the deficiencies associated with these calculations this problem was reinvestigated using density functional calculations to ascertain the optimum geometry for Te_6^{4+} and perhaps to offer an explanation for the elongated-prismatic structure being preferred over the boat structure.

The second compound[7] which has an anomalous structure is $Te_4S_4^{2+}$, which has a polyhedral skeletal electron count of 46. Thus, it would be predicted to have a structure related to that of cuneane (pentacyclo[3.3.0.0^{2,4}.0^{3,7}.0^{6,8}]octane, C_8H_8) but with three skeletal bonds cleaved. The cluster is reported as being isostructural with As_4S_4 which has only two bonds broken relative to cuneane. Extended-Hückel calculations on $Te_4S_4^{2+}$ have shown it to have a half-occupied doubly degenerate highest occupied molecular orbital. This is clearly not a stable electronic configuration. The cluster would be expected to undergo a Jahn–Teller type geometrical distortion,[8] in order to remove the degeneracy of the highest occupied molecular orbital (HOMO). There is no evidence from the crystal structure that a geometrical distortion has occurred, since the cluster has an idealized D_{2d} geometry. Furthermore the molecule is expected to be paramagnetic. Unfortunately, there is no reference to magnetic properties in the original paper, but the general absence of paramagnetic ions in clusters of this type suggests that the molecule is probably diamagnetic. The anomalous geometry of the cluster, together with the highly unstable electronic configuration obtained from extended-Hückel calculations, prompted us to perform a density functional calculation on $Te_4S_4^{2+}$ to determine the optimum geometry and ground-state electronic configuration.

In the past decade an increasing number of density functional theory calculations have been reported and used for accurately defining molecular energetics and dynamics. The method is now applied to many problems previously covered exclusively by *ab initio* Hartree–Fock and post-Hartree–Fock calculations. Approximate density functional calculations have proven themselves to be very reliable in estimating a wide range of molecular properties. We refer the reader to two recent reviews[9] outlining the use of density functional theory for chemical problems. Main-group polyhedral molecules appeared to be excellent



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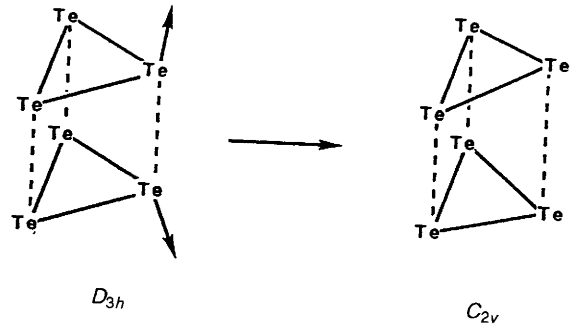

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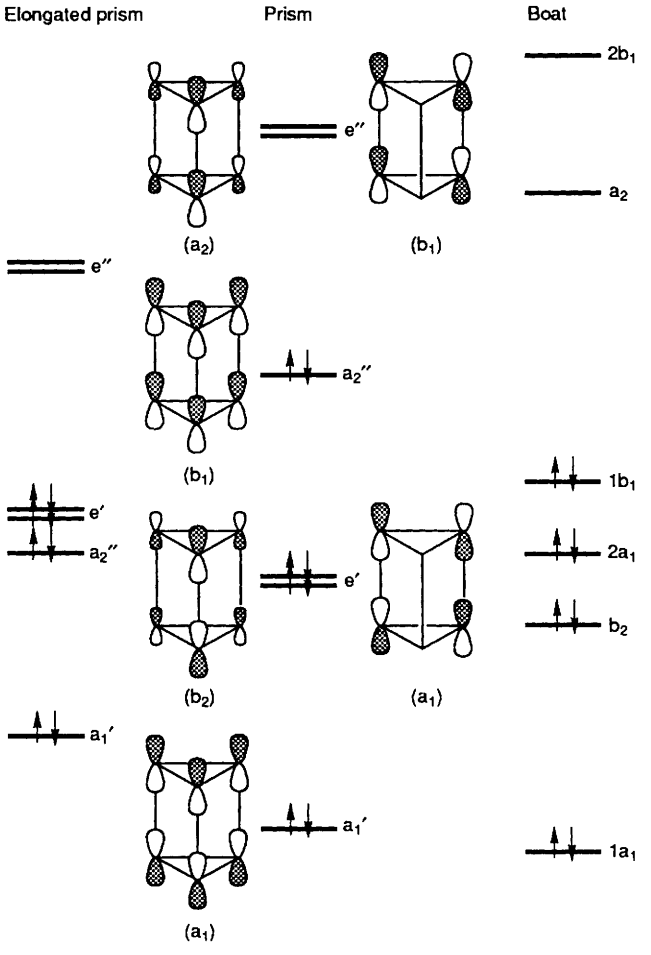


Fig. 1 Intertriangular bonding and antibonding orbitals for the prism, elongated prism and boat. The C_{2v} symmetry labels of the orbitals of the prism are shown in parentheses

candidates for this type of analysis since they are relatively small and conventional semiempirical and Fenske–Hall calculations have proved to be unreliable.

Computational Details

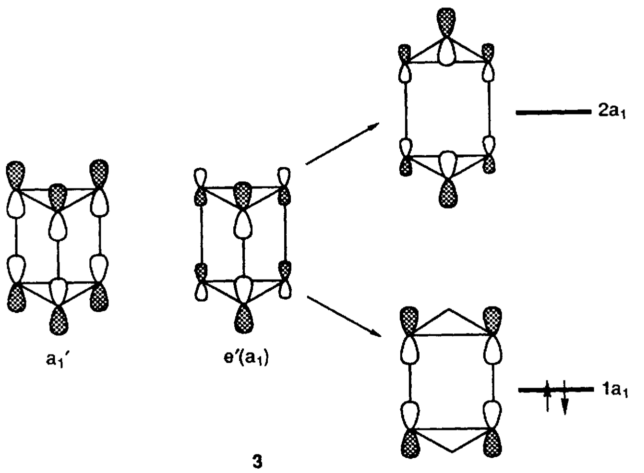
All calculations were based on approximate density functional theory (DFT) within the local density approximation,[10] LDA. The exchange factor, α_{ex}, was taken as 2/3 and the correlation potential was that of Stoll *et al.*[11] in the parametrization by Vosko *et al.*[12] The reported calculations were performed utilizing the vectorized version of the HFS-LCAO program system developed by Baerends *et al.*[13] and vectorized by Ravenek.[14] The numerical integration procedure applied for the calculations was developed by Becke.[15] All molecular structures were optimized on the singlet energy surface within the C_{2v} symmetry group. The geometry optimization procedure was based on the method developed by Versluis and Ziegler.[16] The electronic configurations of the molecular systems were described by an uncontracted triple-ζ Slater Type Orbitals (STO) basis set,[17] s, p, d, f and g STO functions, centred on all nuclei, were used in order to fit the molecular density[18] and present coulomb and exchange potentials accurately in each self consistent field (SCF) cycle. All calculations were spin restricted.

Results and Discussion

Initially, to demonstrate the reliability of density functional calculations, benchmark calculations on related molecules whose structures are undisputed were performed. Full optimizations were carried out for Se_4^{2+} and Te_4^{2+}. The optimized geometries were found to be in excellent agreement with the experimental structures. Both ions optimized at a square-planar geometry with bond distances of 2.31 and 2.68 Å respectively (*cf.* experimental values of 2.28[19] and 2.66 Å[20] respectively.

A calculation was performed on the Te_6^{4+} ion using density functional theory within the local density approximation. The optimized structure for Te_6^{4+} at the LDA level of theory is shown in **1**. The compound is seen to adopt the experimentally observed D_{3h} elongated prism as its optimum structure. The short Te–Te distances of 2.67 Å are in agreement with the experimentally observed values. However, the long Te–Te distances are 3.37 Å in **1** as compared to the experimental value of 3.13 Å. The energy of the Te_6^{4+} system, using the experimental geometry, was calculated to be 92 kJ mol^{-1} higher in energy than the optimized structure. A possible explanation for the deviation between the optimized and experimental geometries is that the optimized geometry refers to the gas phase whereas the experimental geometry refers to the solid state in which Te_6^{4+} is surrounded by negatively charged counter ions. An elongation of one of the long bonds in **1** results in a structure of C_{2v} symmetry (see **2**). Such an elongation is facile. Thus, stretching the bond by 0.5 Å only results in an increase in energy by 25 kJ mol^{-1}. However, an equilibrium structure of C_{2v} symmetry was not found despite an extensive search. Optimizations starting from various C_{2v} structures converged in all cases to the trigonal-prismatic structure **1**.

The intertriangular σ-bonding and antibonding orbitals of the Te_6^{4+} prism are shown in the centre of Fig. 1 (the C_{2v} symmetry labels of the orbitals are included in parentheses to facilitate a comparison with the orbitals of the C_{2v} boat structure). An electron-precise trigonal-prismatic structure is associated with the 30 valence electrons occupying the orbitals up to e′. Introduction of an extra pair of electrons into the Te_6^{4+} molecule has resulted in the occupation of the a_2'' orbital of the prism. This orbital may be stabilized either by cleavage of a bond parallel to the C_3 axis, or the simultaneous lengthening of the three bonds parallel to the C_3 axis, as found experimentally. The effect of these geometric distortions on the energies of the intertriangular σ-bonding and antibonding orbitals of the prism are illustrated in Fig. 1.



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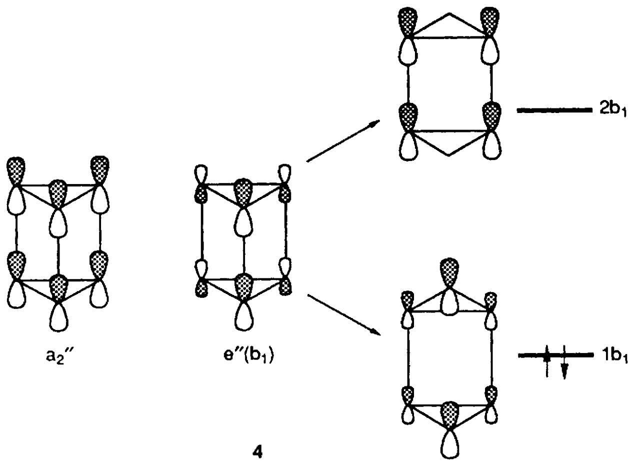

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Lengthening three bonds simultaneously destabilizes the energies of the bonding orbitals and stabilizes the energies of the antibonding orbitals. Indeed, the a_2'' orbital is stabilized to such an extent that it is no longer the HOMO of the Te_6^{4+} molecule. The net result of this geometric distortion is to weaken the three intertriangular bonds of the prism. The alternative geometric distortion is to cleave one of the intertriangular bonds of the prism to produce a C_{2v} boat structure. The consequent effects on the intertriangular bonding and antibonding orbitals are shown on the right-hand side of Fig. 1. The b_2 component of the e′ set does not have any contribution across the bond being broken and thus will not undergo a major change in energy. However, the a_1' and the a_1 component of e′ do have contributions across the bond being cleaved and their energies change significantly. The reduction in symmetry that has accompanied the bond cleavage now allows the a_1' and the a_1 component of e′ to combine to produce the $1a_1$ and $2a_1$ orbitals of the boat structure shown in **3**.

Similarly, for the antibonding orbitals the a_2 component of the e″ set does not have a contribution across the bond being broken and so the geometric distortion from prism to boat will have little effect on the energy of this orbital. However, the a_2'' orbital and the b_1 component of e″ do have contributions across the bond being cleaved and so will change in energy. These orbitals have the same symmetry in C_{2v} and can mix to produce the $1b_1$ and $2b_1$ orbitals of the boat **4**.

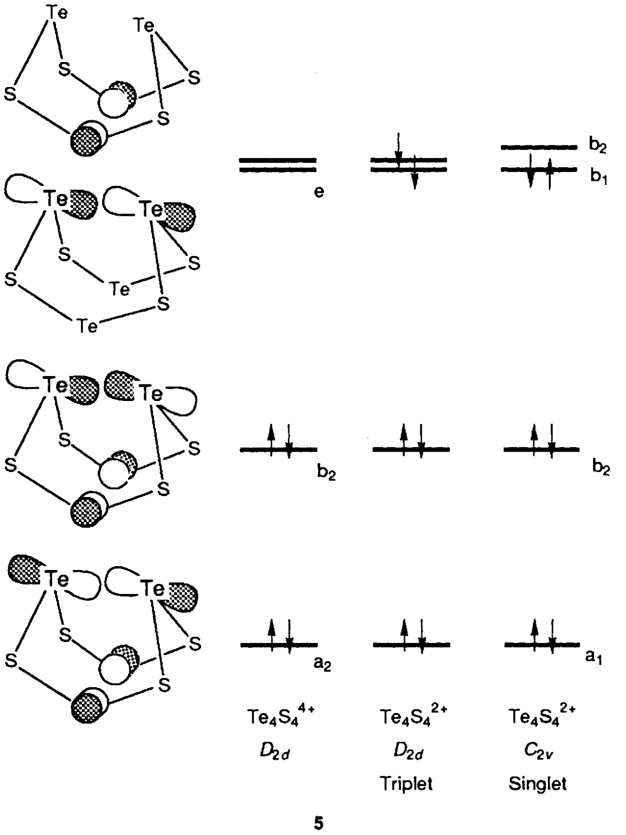
The effects of the two possible geometric distortions considered on the intertriangular σ bonding and antibonding orbitals of the prism may now be summarized. A symmetric distortion of the prism to produce an elongated prism has resulted in a structure with three weak intertriangular bonds. The distortion has had no effect on the intratriangular π bonding/antibonding of these orbitals. The occupied orbitals of the elongated prism in Fig. 1 may be described as intratriangular π bonding (a_1', a_2''), weakly π antibonding (a_1 component of e′) and π antibonding (b_2 component of e′). An asymmetric distortion from a prism to a boat results in a structure with two intertriangular σ bonds and the development of orbitals which resemble linear combinations of localized lone pairs on the tellurium atoms which have been separated. The nature of the intratriangular π interactions has altered. The occupied orbitals of the boat are seen to be intratriangular π bonding ($1a_1$), weakly π bonding ($1b_1$ and $2a_1$) and π antibonding (b_2).

Extended-Hückel calculations indicate that the boat structure is the more stable geometry for the Te_6^{4+} ion. A difference in the results of the molecular orbital calculations at the extended-Hückel and DFT levels is the extent of stabilization of the a_2'' orbital of the prism. The extended-Hückel calculations indicate a more dramatic stabilization of the a_2'' orbital for the geometric distortions to an elongated prism and a boat. Additionally, the a_2'' orbital is stabilized more for the distortion to a boat. The opposite is found with the DFT calculations, with the a_2'' orbital of the elongated prism being more stable than the analogous orbital of the boat.

When dealing with such a highly charged molecule as Te_6^{4+}, electrostatic interactions must also be taken into consideration when trying to rationalize the experimental structure. Electrostatically the problem may be viewed as determining which of the two geometries will maximize the interactions between the extra pair of electrons and the +6 charge distributed over the tellurium centres. From Fig. 1 it can be seen that the elongated prism delocalizes the electrons over the six tellurium centres, resulting in a homogeneous charge distribution (see **3** and **4**). The boat structure has localized two electron pairs on the two connected sites with a resultant inhomogeneous charge distribution. Ideally, the electron pair is stabilized more in a spherical distribution of positive charge. The vertices of the elongated prism approximate better to lying on the surface of a sphere than do the vertices of the boat structure. In addition the boat structure has larger electron–electron repulsion terms associated with the electron pairs localized on specific tellurium atoms rather than delocalized over the three lengthened edges of the elongated trigonal prism. The neglect of coulombic interactions in the calculation of the total energy in the extended-Hückel method may be a reason for the incorrect ordering of the total energies of the elongated prism and boat structure found previously.[5]

The frontier orbitals of $Te_4S_4^{n+}$ ($n = 2$ or 4) are shown in **5**. The left-hand side presents the orbitals for D_{2d} symmetry. We have optimized the geometry of $Te_4S_4^{4+}$ and found the most stable structure to have D_{2d} symmetry with an $a_2^2b_2^2$ electron configuration, and the e orbitals remaining unoccupied. The molecule has a structure analogous to As_4S_4 which has the same number of valence electrons. The structure optimized at the LDA level of theory is illustrated in **6**. The structure of $Te_4S_4^{4+}$ has a short bond of 2.32 Å which is close to the distance of 2.30 Å observed by Gillespie and co-workers.[7] The experimentally observed Te–Te distance of 2.70 Å corresponds to a normal Te–Te bond length. We find two long Te–Te bonds of 3.11 Å. This finding is similar to that in the case of the isoelectronic S_4N_4, where sulfur occupies a similar non-planar bridging position to tellurium in $Te_4S_4^{4+}$ and the S–S bond length of 2.58 Å is much longer than a single S–S bond length.

For $Te_4S_4^{2+}$ we have considered two possible electronic states. The first is a triplet with electron configuration $a_2^2b_2^2e^2$ and of D_{2d} symmetry. The optimized structure of the triplet is shown in **7**. We note that it has longer Te–Te bonds than does $Te_4S_4^{4+}$. This is understandable as two electrons have entered an antibonding orbital which is localized predominantly on the tellurium atoms. On the other hand, the Te–S bonds are seen to



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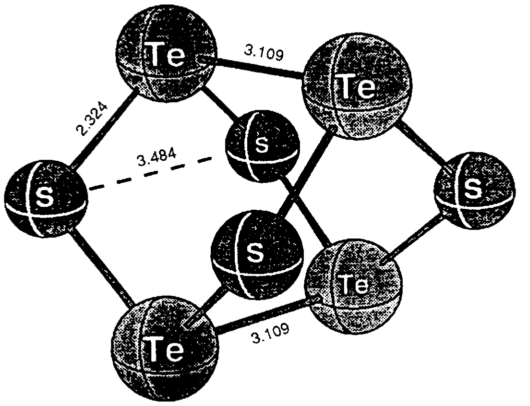

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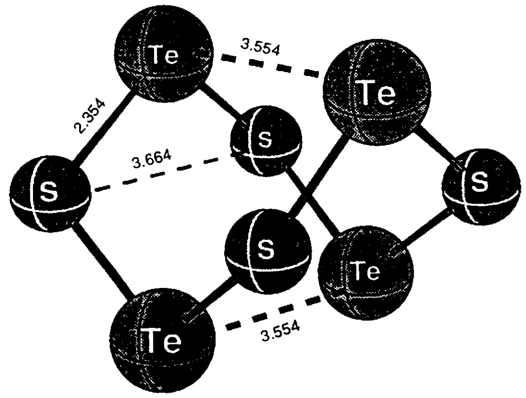

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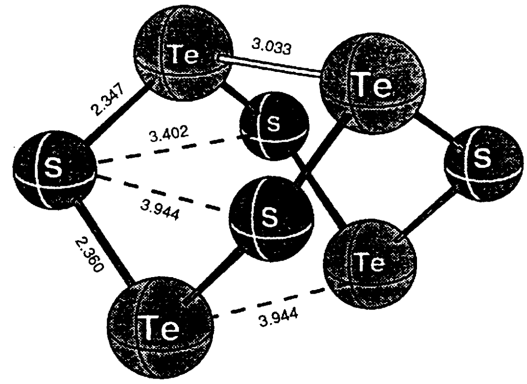

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remain short. This is in agreement with the structure that would be expected for a compound with three pairs of electrons in excess of the electron-precise cuneane, C_8H_8. We have also considered a singlet structure **8**. This has one Te–Te antibonding orbital occupied and one empty. It distorts as a consequence to a C_{2v} structure with one Te–Te bonding distance of 3.03 Å and one non-bonding Te $\cdots$ Te distance of 3.94 Å. The structure is in many ways similar to that reported for Se_8^{2+}, which is isoelectronic. The calculations therefore reinforce the simple concept derived from empirical models that $Te_4S_4^{2+}$ is likely to distort in such a way that one additional bond of the cuneane structure is cleaved. In conclusion, it seems highly unlikely that the addition of an electron pair into the lowest unoccupied molecular orbital of $Te_4S_4^{4+}$, which is strongly antibonding along the edges between the tellurium atoms, would not, at the very least, cause a lengthening of the Te–Te bonds away from the average bond distance of 2.70 Å. The results presented above lead us to suggest that the charge, or the molecular formula, reported for the cluster may be incorrect.

Conclusion

From the molecular orbital analyses of the Te_6^{4+} ion we may conclude that this ion may be regarded as adopting a non-classical structure. Density functional calculations indicate that the elongated-prismatic structure, found experimentally, is the most stable geometry. Classically the 32-electron Te_6^{4+} ion is predicted to have a boat structure, resulting from the cleavage of one of the intertriangular bonds of a prism. The preference for the elongated-prismatic over the boat structure may be rationalized by a consideration of the respective overlap changes in the intertriangular bonding and antibonding orbitals, and by a consideration of the charge distribution in this highly charged species. Our analysis of the $Te_4S_4^{2+}$ ion leads us to predict that this molecule should adopt the classical structure for a 46-electron main-group cluster. The electronic structure of the $Te_4S_4^{2+}$ ion with the experimental geometry has a half-occupied doubly degenerate level as the HOMO which is noded in an antibonding fashion along the Te–Te bonds. This results in cleavage of the Te–Te bond. We do not feel that it is possible for the structure to accommodate the antibonding electrons without some degree of structural distortion. The structure reported in the literature for $Te_4S_4^{2+}$ is the same as expected for $Te_4S_4^{4+}$. We conclude that the structure reported by Gillespie and coworkers[7] is not $Te_4S_4^{2+}$, but most likely $Te_4S_4^{4+}$.

The density functional theory calculations have been shown to be more reliable than the extended-Hückel and Fenske–Hall calculations in predicting the structures of these main-group clusters. Therefore, they provide an excellent method for confirming structures where the amount of unambiguous structural information is limited.

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