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Articles

Electronic Structure of $[Ta_5(NH)_4Cl_{17}]^{6-}$: A Cluster with a Distorted Square Pyramidal Ta_5 Core

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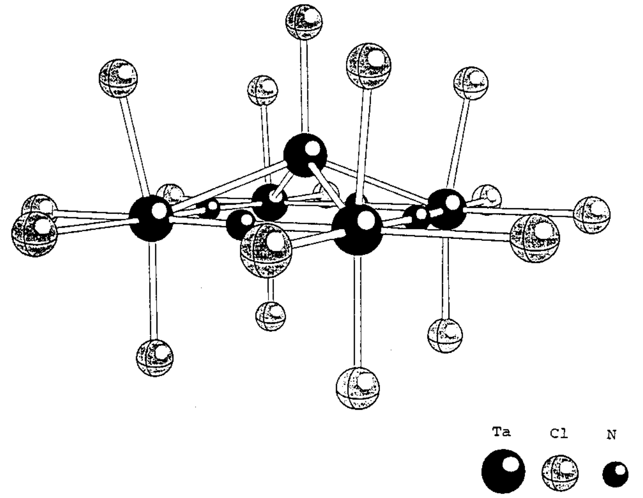
We report approximate molecular orbital calculations on the $[Ta_5(NH)_4Cl_{17}]^{6-}$ cluster synthesized by Simon and Meyer. The cluster is based on a "flattened" square pyramid of tantalum atoms, basal bridging imides, and terminal chlorides. This cluster was of interest to us due to the unusual presence of imide ligands, the distorted nature of the metal core, and the possible resemblance to B_5H_9. Our calculations indicate that metal−metal bonding is limited to $Ta_{apical}-Ta_{basal}$ bonding, with no significant bonding between the basal metal atoms. The imide ligands, which bridge the base of the pyramid, were found to have a significant amount of capping character. The metal−metal bonding orbitals have some unusual features due to the pyramid's distortion. Additionally, the flattened nature of the pyramid leads to an interesting energy ordering of the metal−metal bonding orbitals.

Simon and Meyer found that when ammonium chloride and tantalum metal were heated together, dark green crystals appeared. These were subsequently assigned the formula $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$ based on a crystal structure and IR data.[1] The crystal structure determination indicated that the compound is composed of isolated $[Ta_5(NH)_4Cl_{17}]^{6-}$ anions and ammonium ions.

This compound is interesting for a number of reasons. The first is that the presence of imide and amide ligands in transition metal clusters is relatively rare. Some clusters and cluster compounds containing NH and NH_2 groups are known, including $H_2Ru_3(NH)(CO)_9$, $Ni_6(NH_2)_{12}$, and $(ZrOC^tBu_3)_5N(NH)_4(NH_2)_4$.[2−4] Another interesting feature is the potential for metal-metal bonding in this system, as the Ta atoms are not fully oxidized. The observed structure of the $[Ta_5(NH)_4Cl_{17}]^{6-}$ anion, a distorted square pyramid, is curious as well.

The anion, shown in **1**, is based on a flattened square pyramid of Ta atoms. The imide hydrogens were not detected. For clarity, they are not shown in **1**. The basal Ta atoms have four terminal chlorides each and the apical Ta has one terminal chloride. Bridging each of the four basal edges of the pyramid is a μ_2 imide. The square pyramid is rather distorted, the apical atom lying only 1.04 Å above the basal plane. The fact that the pyramid is "squashed" leads to interesting questions about the effect this deformation has on the electronic structure and the relative stability of a distorted verses an ideal square pyramid.



1

Using the closed shell formalism for electron counting, the chloride and imide ligands may be considered −1 and −2 respectively. With the −6 charge on the cluster, we have 19 positive charges to distribute over five Ta atoms. This leads to an average oxidation state of +3.8 for each Ta and a total of six Ta d electrons. We would expect these electrons to be involved in Ta−Ta bonding in the cluster. The $Ta_{apical}-Ta_{basal}$ distance is 2.94 Å, which is similar to the nearest neighbor distance in Ta metal (2.86 Å). The basal Ta atoms are 3.88 Å apart and the imide ligands are situated almost directly between them (the $Ta_{basal}-N-Ta_{basal}$ angle is 168.9°). $Ta_{basal}-Ta_{basal}$ bonding is not expected to be significant, and the framework bonding in the base of the pyramid is likely to be through strong Ta−N interactions.

We have undertaken approximate molecular orbital calculations of the extended Hückel type in order to understand the electronic features of the $[Ta_5(NH)_4Cl_{17}]^{6-}$ anion. Specifically, we will address the distortion of the pyramid and the nature of

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[‡] This work is dedicated to the memory of Haibin Deng (1962−1994), a gifted colleague and friend.

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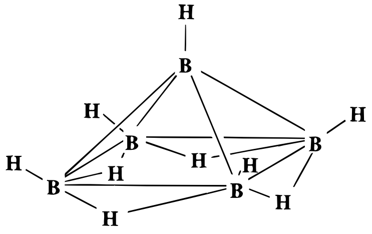
the cluster bonding in $[Ta_5(NH)_4Cl_{17}]^{6-}$. Details of the calculations are provided in the Appendix.[5]

A Related Main Group Molecule: Pentaborane (B_5H_9)

The structure and electron count of $[Ta_5(NH)_4Cl_{17}]^{6-}$ lead one to think of pentaborane, B_5H_9, shown in **2**. Pentaborane is a *nido* cluster, containing $n + 2 = 7$ pairs of framework bonding electrons.[6] Of the fourteen framework bonding electrons in B_5H_9, eight can be considered to be involved in three-center two-electron B−H−B bonds, leaving six electrons for primarily B−B bonding. We briefly discuss here the frontier molecular orbitals and electronic structure of B_5H_9 in preparation for our discussion of $[Ta_5(NH)_4Cl_{17}]^{6-}$.[7]



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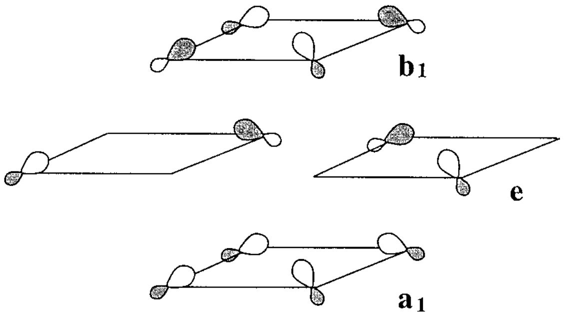
One may consider pentaborane as composed of a basal fragment, B_4H_8, and an apical fragment, BH. Looking first at the B_4H_8 fragment, we notice that each of the basal boron atoms is bonded to three hydrogens, occupying three tetrahedral sites around the borons. These hydrogens may be thought of as utilizing three of the four sp^3-like hybrids on the boron atoms. The remaining sp^3-like hybrid on each basal boron points into the center of the cluster. From the four hybrid orbitals on the basal borons, we can make four symmetry-adapted linear combinations. These combinations are shown in **3** and transform as a_1, e, and b_1 in C_{4v}.



3

The fragment molecular orbitals (FMO's) of the apical BH fragment consist of the pure p_x and p_y orbitals of the boron atom and an s−p_x hybrid pointing down toward the base of the pyramid. The p_x and p_y orbitals transform as e in C_{4v} and the s−p hybrid transforms as a_1. Much lower in energy lies the a_1 FMO which is primarily B−H bonding.

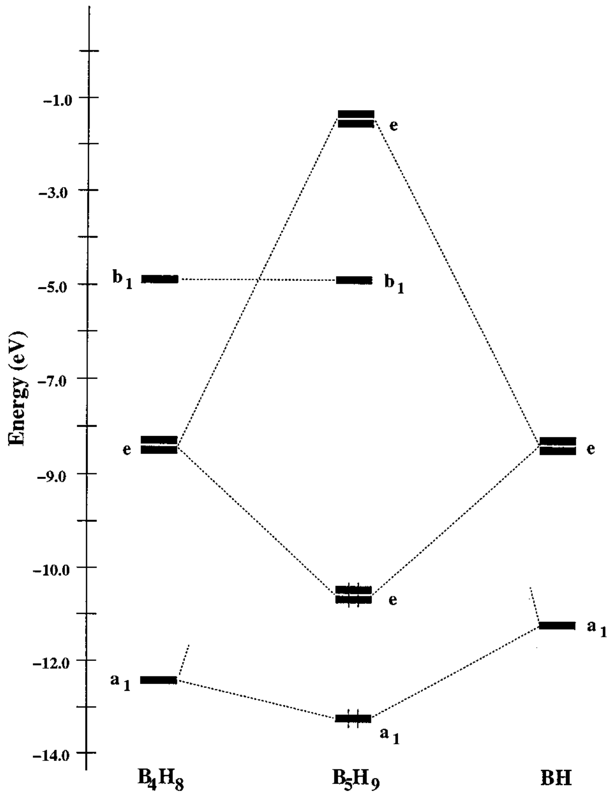
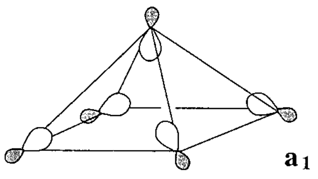


Figure 1. Interaction diagram for B_4H_8 with BH.

Figure 1 shows the interaction diagram for B_4H_8 with BH, forming pentaborane. Note the stabilization of the a_1 and e levels. The bonding combinations which are formed are illustrated schematically in **4** and **5**. The B_{apical}−B_{basal} overlap population is 0.603, which arises primarily from these three orbitals. The B_{basal}−B_{basal} overlap population is 0.299. Some of the bonding between the basal borons comes from the a_1 orbital in



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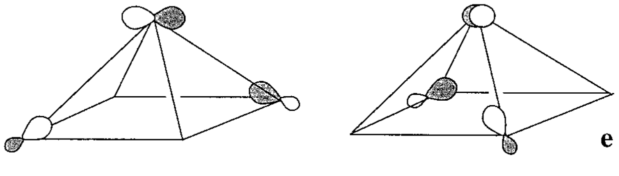

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(5) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

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(7) Electron counting rules for boranes and related compounds can be found in: Wade, K. *Chem. Commun.* **1971**, 792−793. Mingos, D. M. P. *Nature*: *Phys. Sci.* **1972**, *236*, 99−102. Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1−66. *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum Press: New York, 1982.

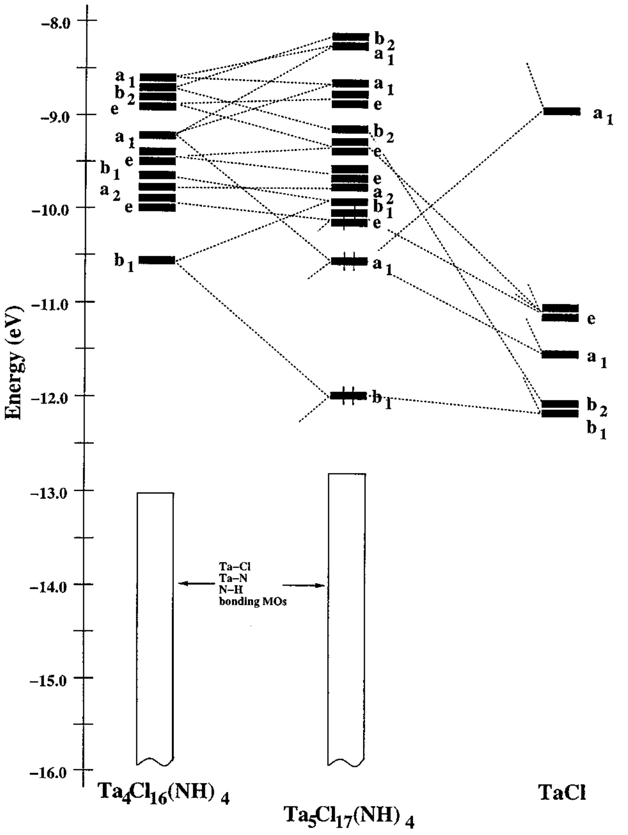


Figure 2. Interaction diagram for $Ta_4(NH)_4Cl_{16}$ with TaCl.

5; the remainder is through the B_{basal}–H bonding levels. Note that the b_1 B_4H_8 FMO does not interact with the BH fragment; in C_{4v} this would require d orbitals on the apical atom.

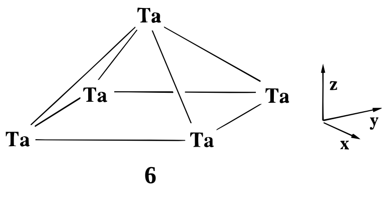
Electronic Structure of $[Ta_5(NH)_4Cl_{17}]^{6-}$

We move on to the electronic structure of the $[Ta_5(NH)_4Cl_{17}]^{6-}$ anion, first detailing the relationship of this anion to B_5H_9.

Following our treatment of pentaborane, let us view $[Ta_5(NH)_4Cl_{17}]^{6-}$ as built up from a basal and apical fragments. If we first consider the $Ta_4Cl_{16}(NH)_4$ basal fragment, we note that each of the basal Ta atoms is surrounded by four chlorides and two imides in a near octahedral arrangement. The d orbitals of each basal Ta should be split in the typical octahedral "three below two" pattern. This should give rise to a low-lying block of $3 \times 4 = 12$ Ta d orbitals, the remnants of the t_{2g} set.

In fact, this is what we observe in the calculations. The interaction diagram for the two fragments is shown in Figure 2. The energies of the FMO's for the basal fragment are shown on the left side of Figure 2. Note the 12 t_{2g} orbitals, which lie approximately 2 eV higher than the pure Ta d orbitals (Ta $H_{ii} = -12.10$ eV), due to π donation from the chloride and imide ligands. The e_g set and the basal tantalum s and p orbitals lie much higher in energy, and are not in the energy region shown.

The basal tantalum orbitals which are likely to be involved in Ta_{apical}–Ta_{basal} bonding are the t_{2g} orbitals. We have set up our coordinate system such that the basal Ta atoms lie on the x,y coordinate axes, as shown in **6**. For this choice of coordinates the t_{2g} set is composed of the Ta_{basal} $d_{x^2-y^2}$, d_{xz} and d_{yz} orbitals. The t_{2g} orbitals for one basal Ta are shown in **7**.



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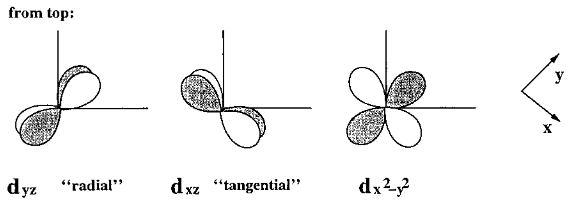

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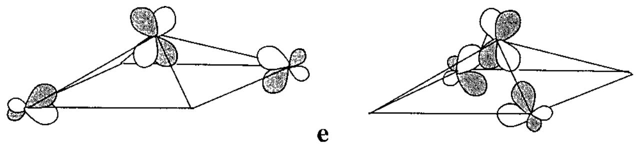
For each basal Ta, either the d_{xz} or the d_{yz} orbital lies in the plane which passes through the center of the pyramid, the other lies tangential to the corners of the base. We do not expect the tangential orbitals to interact much, but the others are important, because they have lobes which point into the center of the pyramid. Four combinations can be formed from these radial orbitals; they transform as $a_1 + e + b_1$. The $d_{x^2-y^2}$ orbitals are located in the basal plane and have lobes pointing into the center of the base of the pyramid. For each combination of the radial d_{xz} or d_{xy} orbitals, there is a $d_{x^2-y^2}$ combination of the same symmetry. Thus the radial orbitals can mix with the $d_{x^2-y^2}$ orbitals. As we will see, this mixing becomes very important because of the distortion of the pyramid.

The apical Ta–Cl fragment consists of two pure Ta d orbitals (the b_1 $d_{x^2-y^2}$ and b_2 d_{xy}) at -12.10 eV (right side of Figure 2). The a_1 d_{z^2} hybrid which points down toward the base of the pyramid lies at -11.48 eV. The degenerate Ta d_{xz} and d_{yz}, which have been destabilized by interaction with the Cl lone pairs, lie at -11.02 eV. In a perfect square pyramid we would expect the apical orbitals primarily responsible for Ta_{apical}–Ta_{basal} bonding to be the d_{z^2} hybrid and the d_{xz}, d_{yz} pair. We would not expect the Ta_{apical} $d_{x^2-y^2}$ orbital to be involved in Ta_{apical}–Ta_{basal} bonding, since it lies parallel to the basal plane, and its overlap with basal tantalum orbitals would be poor.

Next, we bring the apical and basal fragments together to form the $[Ta_5(NH)_4Cl_{17}]^{6-}$ anion; its molecular orbital energies are shown at the center of Figure 2. We find two low-lying Ta_{apical}–Ta_{basal} bonding orbitals of a_1 and b_1 symmetry. The HOMO lies at the bottom of the remainder of the Ta_{basal} t_{2g} block. Since so many orbitals are very close in energy to the "Fermi level", it is not possible to unambiguously assign which of these is likely to be the HOMO. In our calculation, we find that the HOMO is a half-filled e set, composed of the Ta_{apical} d_{xz} and d_{yz} orbitals and the e combination of the Ta_{basal} d_{xz} or d_{yz} orbitals. These orbitals are analogous to the orbitals of the doubly degenerate HOMO in B_5H_9, except for one important difference. Because of the distortion of the pyramid (its flatness), the apical Ta d_{xz} and d_{yz} orbitals are set up to interact with the basal d_{xz} (or d_{yz}) orbitals in more π- than σ-type fashion. They are shown in **8**. In **9** on the left we show one of these



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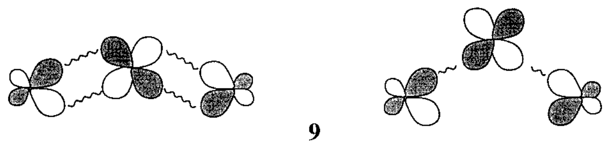

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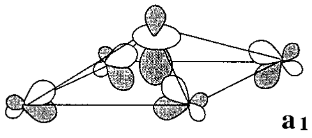
orbitals from the side. In **9**, on the right, is the analogous bonding orbital we would expect if the cluster were a perfect square pyramid. Note the π-like nature of the orbital on the left, compared to the σ-type on the right.

The HOMO-1 lies at −10.48 eV and has a_1 symmetry. It is composed of the d_{z^2} hybrid on the apical Ta and basal d_{xz} (or d_{yz}) and $d_{x^2-y^2}$ orbitals. The basal Ta $d_{x^2-y^2}$ orbitals combine with the basal d_{xz} (or d_{yz}) orbitals in such a way as to enhance the lobes of the d_{xz} (or d_{yz}) orbitals pointing "down" or away from the center of the cluster. Though this may seem strange,this actually enhances the $Ta_{apical}-Ta_{basal}$ bonding. Due to the distortion of the pyramid, the apical d_{z^2} lobe pointing down actually overlaps more effectively with the basal lobe that lies below the basal plane. The upper lobe of the basal d_{xz} (or d_{yz}) falls close to the nodal surface of the apical d_{z^2} orbital. This molecular orbital is somewhat analogous to the a_1 B−B bonding orbital in B_5H_9. It is shown in **10**.



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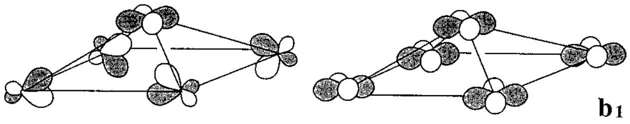
The HOMO-2 lies at −11.96 eV and has b_1 symmetry. This orbital is composed of the $d_{x^2-y^2}$ Ta_{apical} orbital, mixed with the b_1 combinations of the basal $d_{x^2-y^2}$ and d_{xz} (or d_{yz}) orbitals. The HOMO-2 can be thought of as a hybrid of the two orbitals depicted in **11**. The radial d_{xz} and d_{yz} orbitals mix into the $d_{x^2-y^2}$, effectively rotating the $d_{x^2-y^2}$ orbital such that the inner lobe tilts up, toward the lobes of the apical $d_{x^2-y^2}$. There is no comparable $B_{apical}-B_{basal}$ bonding orbital in pentaborane; the apical atom has no d orbitals, thus no orbitals of b_1 symmetry. Additionally, the b_1 combination of the basal sp^3 hybrids is strongly $B_{basal}-B_{basal}$ antibonding and lies high in energy. In $[Ta_5(NH)_4Cl_{17}]^{6-}$, apical−basal interaction though the basal b_1 orbitals becomes possible because of the presence of apical d orbitals. There are also low-lying FMO's of b_1 symmetry in the $Ta_4Cl_{16}(NH)_4$ fragment. The fact that the pyramid is severely distorted plays a big role in determining the magnitude of this interaction.



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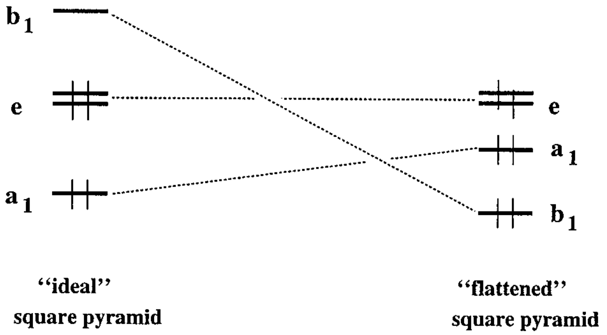
The only Ta_{apical} orbital of b_1 symmetry is the $d_{x^2-y^2}$, and it lies parallel to the basal plane. In an ideal square pyramid, we might not expect the interaction of this orbital with the basal fragment to be significant. However, in the distorted $[Ta_5(NH)_4Cl_{17}]^{6-}$ cluster this interaction becomes very important. As in B_5H_9, the basal b_1 combinations are basal−basal antibonding. In $[Ta_5(NH)_4Cl_{17}]^{6-}$, however, the basal Ta atoms are separated by the imide ligands and are too far away to interact with each other directly. The apical atom lies only about 1 Å above the basal plane. Because of this, the lobes of the Ta_{apical} $d_{x^2-y^2}$ orbital are in a position to overlap much more effectively with the basal orbitals then they would be in an ideal pyramid. The distorted square pyramid leads to the interesting cluster bonding orbital ordering of b_1 below a_1 below e, the implications of which we discuss next.

Ideal vs Distorted Square Pyramid

The distortion from a ideal square pyramid to a "squashed" square pyramid clearly has an effect on the ordering of the molecular orbitals. We expect an ideal square pyramid (all Ta−Ta contacts of equal length) to have the ordering a_1 below e, with the degenerate e set the HOMO for a six electron system. As previously mentioned, the $d_{x^2-y^2}$ orbital on the apical atom is not very important, as its lobes lie parallel to the basal plane.

The effect of the distortion of an M_5 pyramid can be summed up schematically in **12**. As the pyramid is flattened, basal−basal distances are lengthened; thus these interactions become less important. One effect of this is the destabilization of the a_1 orbital, which loses its basal−basal bonding character. Though at first it appears that apical−basal bonding should be enhanced by the distortion, this is not necessarily the case. In this particular distortion, as the apical d_{z^2} orbital moves closer to the basal plane, the basal atoms move away from the center of the base. Additionally, the interaction between the apical d_{z^2} hybrid and the basal orbitals in the a_1 level changes as the pyramid is flattened. In an ideal pyramid, we expect the upper lobes of the radial basal orbitals (d_{xz} or d_{yz}) to have bonding-type overlap with the apical d_{z^2} orbital. However, in a very flat pyramid, the lowest-lying a_1 orbital looks like **10**, where the d_{z^2} orbital overlaps with the lower lobes of the basal radial orbitals. The net result of is that the a_1 orbital is not *significantly* stabilized or destabilized.



12

The basal−basal antibonding character of the b_1 orbital diminishes and this orbital is stabilized. The apical $d_{x^2-y^2}$ orbital begins to overlap more effectively with the basal orbitals, thus stabilizing the b_1 orbital further. The e orbitals change in character somewhat, with the apical-basal interaction becoming more π-like in nature. In a perfect square pyramid, this orbital has some antibonding character between the basal Ta atoms diagonally across from one another. This is diminished in the "squashed" pyramid. Thus, we might expect the e set to remain at relatively the same energy. The net result is the level ordering we find in $[Ta_5(NH)_4Cl_{17}]^{6-}$, b_1 below a_1 below e.

In a six-electron system, this raises the question of whether a "squashed" pyramid would distort further to try to gain overall stabilization. One possibility is a stretching of the pyramid, back toward an ideal square pyramid. Stretching the pyramid is unfavorable due to destabilization of the b_1 orbital and unfavorable ClN interactions. In $[Ta_5(NH)_4Cl_{17}]^{6-}$ further flattening of the cluster leads to unacceptably long Ta−N distances and destabilizing Cl−Cl interactions.

Another possibility is a Jahn−Teller distortion of the pyramid, reducing the symmetry to C_{2v} and splitting the e set. As previously mentioned, the nature of the HOMO in the $[Ta_5(NH)_4Cl_{17}]^{6-}$ anion is ambiguous. In our calculation, the degenerate set of orbitals at −10.04 eV is indeed the HOMO. However, a mere 0.04 eV higher in energy lies another b_1 orbital, composed of basal $d_{x^2-y^2}$ and radial d_{xz} and d_{yz} components, which is apical-basal non-bonding. (From the basal b_1 $d_{x^2-y^2}$ combination, the basal b_1 d_{xy}, d_{yz} combination, and the apical $d_{x^2-y^2}$ orbital, we expect three orbitals, one apical−basal bonding, one essentially nonbonding, and one antibonding.) Not much higher in energy, at −9.84 eV, is an $a_2$nonbonding combination of tangential d_{xz} and d_{yz} orbitals. These are followed by several more unoccupied orbitals reasonably close in energy. Since there are so many orbitals in a small energy region, it is impossible to assign the e set as the HOMO, but the pyramid might still distort, lifting the degeneracy of the e set and pushing one component lower in energy. We tried distorting the pyramid from C_{4v} to C_{2v}. Though this led to stabilization of one component of the e set, it considerably destabilized the a_1 and b_1 cluster bonding levels, leading to overall destabilization.

Cluster Bonding and the Role of the Imido Ligands

The Ta_{apical}−Ta_{basal} overlap population is 0.271, indicating a significant degree of metal−metal bonding. In order to have some way of gauging the magnitude of this interaction, we have sought out a few comparison structures. One such structure is $[Ta(OSi^tBu_3)_2H_2]_2$, which contains a formal Ta−Ta single bond.[8] We have modeled this as $[Ta(OSiH_3)_2H_2]_2$, which gives an overlap population of 0.703 for a Ta−Ta single bond. Another comparison is Ta_6Cl_{15}; this structure contains Ta_6Cl_{12} units linked together via chloride linkages at the vertices of the Ta_6 octahedra.[9] We can model this compound as the isolated cluster $[Ta_6(\mu_2\text{-}Cl)_{12}Cl_6]^{3-}$, which contains the same number of cluster bonding electrons as the solid.

The classic edge-bridge octahedral system here is $[M_6X_{18}]^{q-}$ with its magic electron count of 14 or 16 electrons.[10] Our case, $[Ta_6(\mu_2\text{-}Cl)_{12}Cl_6]^{3-}$, has 15 cluster bonding electrons to share over 12 short Ta−Ta contacts. A calculation on $[Ta_6Cl_{18}]^{3-}$ yields a Ta−Ta overlap population of 0.424 for a partial single bond. Though the $[Ta_5(NH)_4Cl_{17}]^{6-}$ anion has six electrons to share over four bonds, the overlap population is significantly lower. The distortion of the pyramid causes many changes in the bonding orbitals, but there is another important difference. The Ta atoms in $[Ta_6Cl_{18}]^{3-}$ are surrounded by only five ligands, leaving one octahedral site open. Thus, the we do not expect the bonding exhibited by $[Ta_6Cl_{18}]^{3-}$ to be directly analogous to that in $[Ta_5(NH)_4Cl_{17}]^{6-}$. As an example, in the M_6X_{12}-type clusters there is a low-lying a_{1g} cluster bonding orbital. This orbital is composed of in-phase d_{z^2} hybrids pointing into the center of the octahedron and is responsible for a good deal of Ta−Ta bonding. In the case of $[Ta_5(NH)_4Cl_{17}]^{6-}$, each of the basal Ta atoms is already six-coordinate, thus there is no comparable low-lying orbital. We conclude that there is a significant amount of metal−metal bonding in the cluster, but that bonding is somewhat limited due to the presence of six ligands around the basal atoms. As stated previously, this metal−metal bonding is limited to Ta_{apical}−Ta_{basal} bonding. The assignment of the four highest-lying electrons does not change these qualitative conclusions.

The bridging imides play a very important role in cluster framework bonding. As there is no direct Ta_{basal}−Ta_{basal} bonding (in fact the Ta_{basal}−Ta_{basal} overlap population is slightly negative), bonding in the base of the pyramid is limited to strong Ta−N interactions. Due to the distorted nature of the pyramid, the imido nitrogens lie only 2.37 Å away from the apical Ta atom. This is not much longer than the Ta_{basal}−N distance: 1.95 Å. This led us to wonder whether or not there was bonding between the apical tantalum and the imides as well. The calculated Ta_{apical}−N overlap population is actually 0.225. In comparison, the Ta_{basal}−N overlap population in 0.625. Thus, the nominally μ_2-bridging imido ligand has quite a bit of μ_3-capping character as well! Optimization of the imido H positions (see Appendix) supports this conclusion. The Ta_{apical}−N interaction is very significant in terms of cluster framework bonding and is one of the forces leading to the creation of a such a flattened pyramidal cluster. Basal bridging ligands in a more regular pyramidal cluster would be unable to contribute in this way, and the creation of symmetrically capping μ_3 ligands is probably precluded by the presence of the near-octahedral chloride ligands on the basal tantalum atoms.

It should be noted that Simon and Meyer point out that the assignment of the base bridging atoms as imido ligands is somewhat ambiguous; there is the possibility that these positions are actually filled by oxide ligands.[1] This does not change our analysis of the important bonding interactions in the cluster.

The possibility that the base bridging ligands are nitrides also exists. The electronic structure of the cluster of $[Ta_5Cl_{17}N_4]^{6-}$ lends some support to this possibility. Nitrides are formally N^{3-}, thus the number of electrons available for direct Ta−Ta bonding decreases to 2. Replacing the imido ligands with nitrides opens up a substantial HOMO−LUMO gap of 2 eV. The HOMO becomes the b_1 orbital show in **11**. Metal−metal bonding is still limited to Ta_{apical}−Ta_{basal} bonding; however the overlap population has decreased to 0.177. This is replaced by an increase in Ta_{basal}−N and Ta_{apical}−N bonding. The Ta_{basal}−$N_{nitride}$ and Ta_{apical}−$N_{nitride}$ overlap populations are 0.781 and 0.286 respectively, a 25% increase over Ta−N_{imide} overlap populations.

Conclusions

The cluster bonding in the $[Ta_5(NH)_4Cl_{17}]^{6-}$ anion is primarily a result of Ta_{apical}−Ta_{basal} bonding and Ta−N bonding. The six metal d electrons in $[Ta_5(NH)_4Cl_{17}]^{6-}$ are primarily involved in Ta_{apical}−Ta_{basal} bonding. Though this compound resembles B_5H_9 in terms of structure and electron count, the availability of apical d orbitals and the distortion of the pyramid lead to an electronic structure for $[Ta_5(NH)_4Cl_{17}]^{6-}$ which in the end is only partially analogous to that of B_5H_9. The distortion of the square pyramid leads to changes in the shapes of the cluster orbitals, as well as an unusual ordering of the Ta−Ta bonding orbitals. The in-plane apical $d_{x^2-y^2}$ and d_{xy} orbitals become important in apical−basal Ta−Ta and Ta−N interactions due to the distortion. The basal bridging imide ligands have a significant bonding interaction with the apical tantalum atom, indicating some degree of capping character. This Ta_{apical}−N interaction helps to stabilize the distorted square pyramid. Thus, the "flattened" nature of the pyramid is extremely important. It allows the cluster to maximize Ta_{apical}−Ta_{basal} bonding, particularly in the b_1 Ta_{apical}

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(10) For a discussion of bonding in such clusters and condensed cluster compounds see: Hughbanks, T. *Prog. Solid State Chem.* **1989**, *19*, 329−372.

$d_{x^2-y^2}$ orbital. It also allows the pyramid to gain additional cluster framework bonding due to the significant amount of $Ta_{apical}-N$ interaction.

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Appendix: Details of the Calculations

Extended Hückel parameters used in the calculations were taken from previous work.[12] Parameters used in the calculations are listed in Table 1.

Distances available from the X-ray crystal structure determination of $(NH_4)_6[Ta_5(NH)_4Cl_{17}]$ were averaged and used in all the calculations. Distances used are listed in Table 2. Angles which were not reported by Simon and Meyer[1] include the orientation of the chlorides around the basal Ta atoms and the location of hydrogens on the bridging imides. The chlorides in the basal plane and below were arranged in octahedral sites around the basal Ta's, preserving the C_{4v} symmetry. The placement of the basal chlorides which lie above the plane was optimized, as in an idealized position they were involved in unfavorable interaction with the apical chloride. The angle the H−N bond makes with the line between the nitrogen and the center of the base of the pyramid was also optimized. The hydrogens prefer to be rotated above the plane, much like the geometry we would expect the hydrogen of a μ_3-capping ligands to adopt. The N−H vector makes a 130° angle with the base of the pyramid when this variable is optimized. This value was used in the calculations.

Table 1. Extended Hückel Parameters Used in the Calculations

		H_{ii}	ξ_1	c_1	ξ_2	c_2
Ta	6s	−10.10	2.28			
	6p	−6.86	2.24			
	5d	−12.10	4.762	0.6815	1.938	0.6815
N	2s	−26.00	1.950			
	2p	−13.40	1.950			
B	2s	−15.20	1.300			
	2p	−8.50	1.300			
H	1s	−13.60	1.300			
Cl	3s	−26.30	2.183			
	3p	−14.20	1.733			

Table 2. Angles and Distances Used in the Calculations

Distances (Å)			
$Ta_{apical}-Ta_{basal}$	2.935	$Ta_{basal}-Cl_{out\ of\ plane}$	2.40
$Ta_{apical}-Cl$	2.34	$Ta_{basal}-N$	1.95
$Ta_{basal}-Cl_{inplane}$	2.61	N−H	1.00
Angles (deg)			
$Ta_{basal}-N-Ta_{basal}$	168.9	$Cl_{out\ of\ plane}-Ta_{basal}-Cl_{out\ of\ plane}$	168.0
$Cl_{in\ plane}-Ta_{basal}-Cl_{in\ plane}$	90.0	(Ta_4 base)−N−H	130.0

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