the quantum yield for this step is very high as compared with that of the first step (2).

The absorption peak of Ir at ca. 356 nm and that of 2 at ca. 300 nm are due to the charge transfer from the bridging peroxide to cobalt(III). Such a charge-transfer excited state should be involved in the photodegoygenation. The d-d excited state does not seem to lead to deoxygoygen.

The quantum yield of Ir on irradiation at 356 nm is relatively low as compared with those reported for the redox decomposition of some mononuclear cobalt(III) complexes upon irradiation of the ligand-to-metal charge-transfer band. It is 1 or 2 orders of magnitude lower than those for the decomposition of \((\mu\text{-superrox})\text{dicobalt(III)}\) complexes.5,7

Despite the low quantum yield, the photoinduced deoxygoygenation is interesting, since it indicates the photocontrolled reversible oxygen uptake. The reversibility is unfortunately not maintained in the present systems due to the slow irreversible photodecomposition of the binuclear species to mononuclear cobalt(III) complexes.

2. Irreversible Decomposition of Ir to Mononuclear Cobalt(III) Complexes. Ir undergoes irreversible decomposition both ther- mally and photochemically, the thermal reaction being much slower and observed appreciably only at >50°C. The mechanism of the thermal reaction is discussed first, since some relevant studies1,2,5,6 permit more detailed discussion.

(a) The Thermal Reaction. A mononuclear (hydroperoxo)co- balt(III) complex was confirmed as an intermediate of the decom- position of \([(\text{CN})\text{Co}^{III}(\mu\text{-O}_{2})\text{Co}^{III}(\text{CN})]^{-}\) in neutral solution2 and of \([\text{NO}_{3}\text{O}](\text{en})\text{Co}^{III}(\mu\text{-O}_{2})\text{Co}^{III}(\text{en})(\text{NO}_{3})]^{-}\) in acid solution.28 Thus reaction 4 is likely to be the initial step of the decomposition of Ir.

\[
[\text{en}]\text{Co}^{III}(\mu\text{-OH})\text{O}_{2}^{-}](\text{en})\text{Co}^{III}[\text{en}] \rightarrow \text{[Co}^{III}[\text{en}]\text{(H}_{2}\text{O})]^{2+} + \text{[Co}^{III}[\text{en}]\text{(H}_{2}\text{O})]^{2+}
\]

In the absence of other ingredients, initially produced \([\text{Co}^{III}[\text{en}]\text{H}_{2}\text{O})]^{2+}\) would slowly react with coordinated ligand or ion-exchange resin during product analysis to give “orange species”. Free ethylenediamine added to the solution of Ir would be oxidized by \([\text{Co}^{III}(\text{en})\text{(H}_{2}\text{O})])^{2+}\). The decrease in decomposition rate in the presence of free ethylenediamine is not clearly accounted for.34

(b) The Photochemical Decomposition. The reaction products contain various unidentified species. The reaction may be initiated by homolytic cleavage of the \([\text{Co}^{III}(\text{en})\text{(H}_{2}\text{O})])^{2+}\) bond as is the thermal reaction. The reactive intermediate, \([\text{Co}^{III}(\text{en})\text{(H}_{2}\text{O})])^{2+}\), would undergo further complicated reactions. It is also plausible that the photo- decomposition may be initiated by the reaction of 1 with \([\text{Co}^{II}]\) species, which is produced by the initial photoequilibration. Addition of free ethylenediamine considerably decreases the amount of \([\text{Co}^{II}]\) species by shifting the equilibrium to the dimer side, and it would retard the photodecomposition.28

Finally, it should be pointed out that previous studies on \((\mu\text{-peroxo})\text{dicobalt(III)}\) complexes with amines might have been affected by possible photochemical reactions and mght require reexamination.

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Hypervalent Tellurium in One-Dimensional Extended Structures Containing \(\text{Te}^{5+}\) Units

JOEL BERNSTEIN and ROALD HOFFMANN

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The electronic structure of three one-dimensional chains containing square-planar \(\text{Te}^{5+}\) units is presented, with employment of both molecular and band calculations. Two chains containing only \(\text{Te}^{5+}\) in different conformations and one in which they are modulated by Sn are treated. The \(\text{Rb}_{2}\text{Te}_{2}\) or \(\text{Cs}_{2}\text{Te}_{2}\) and \(\text{K}_{2}\text{SnTe}_{2}\) structures are thus modeled. A three-center, four-electron model can be used to understand the elongation of the Te-Te bonds within the Te unit, whose inherent instability is overcome by the formation of the chains. It is suggested how oxidation of the chain, for instance, by suitable choice of synthetic conditions, would alter the geometric physical properties of these polymers.

The recent literature contains a number of examples of a square-planar tellurium structural unit which may formally be defined as \(\text{Te}^{5+}\). In some cases such as \(\text{Rb}_{2}\text{Te}_{2}\) and \(\text{Cs}_{2}\text{Te}_{2}\), the stoichiometry clearly defines the charge on the unit as \(2-\). In these instances the unit is the basic building block of a one-di-
1D Extended Structures Containing Te$_5^{6-}$ Units

In Cs$_2$Te$_5$ the Te$_5^{6-}$ units are screw axis related (2) while in Rb$_2$Te$_5$ the Te$_5^{6-}$ units are related by translation (3).

For most of the other cases in which the Te$_5^{6-}$ unit appears, the attribution of a particular charge to the unit is more ambiguous. For instance, on K$_2$SnTeS$_3$, the unit again appears embedded in a one-dimensional chain (4) but the Te$_5^{6-}$ units alternate with tetrahedral Sn in making up the chain. Formally, at least, the square-planar units could still be considered TeS$_2^-$ if the tin is Sn(0), but the Te-Sn bond length of 2.74 Å is almost identical with the sum of the tetrahedral covalent radii (2.72 Å) given by Pauling. This suggests a formal oxidation state of 4+ for the Sn and a net charge of 6- on the Te$_5^{6-}$ unit.

A similar ambiguity arises in the case of Ga$_2$Te$_5$, although this is no longer a linear-chain structure but a three-dimensional one, as depicted in 5 in a view down the c axis of the tetragonal cell.

The Te$_5$ units are clearly present, with Te(1) as the central atom and four Te(2) atoms in the square-planar arrangement. The gallium is tetrahedrally surrounded by four Te(2) atoms. A choice of the "normal" valence state of Ga(II) leads to a formal charge of 6- on the Te$_5^{6-}$ unit.

The structures of NdTe$_5$ and NdTe$_7$ also contain identifiable units of Te$_5^{6-}$ where assignment of a formal charge is virtually ruled out by the complexity of the structures. Part of the NdTe$_5$ structure is shown in 7.

Finally, the fascinating structure of Re$_2$Te$_5$ has been reported by Klaiber, Petter, and Hulliger. The structure is composed of [Re$_6$Te$_8$]$^{2+}$ clusters linked by butterfly-like units formally written as [][Te$_6$]Te$_2$, where the last-noted Te is the central one of the unit (8). The Te$_5^{6-}$ unit is easily recognized here, however,

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Table I. Geometric Features of the Te$_5^{6-}$ Unit

<table>
<thead>
<tr>
<th></th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, deg</th>
<th>d, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$Te$_5$</td>
<td>3.046 (1)</td>
<td>...</td>
<td>90.5</td>
<td>89.5</td>
</tr>
<tr>
<td>Rb$_2$Te$_5$</td>
<td>3.039 (1)</td>
<td>...</td>
<td>92.0</td>
<td>88.0</td>
</tr>
<tr>
<td>K$_2$SnTeS$_3$</td>
<td>3.015 (5)</td>
<td>3.052 (5)</td>
<td>95.0</td>
<td>88.2, 88.8</td>
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<tr>
<td>Ga$_2$Te$_5$</td>
<td>3.027 (2)</td>
<td>...</td>
<td>90.0</td>
<td>...</td>
</tr>
<tr>
<td>AgTe$_3$</td>
<td>3.052 (5)</td>
<td>...</td>
<td>89.8</td>
<td>89.8, 90.5</td>
</tr>
<tr>
<td>NdTe$_5$</td>
<td>3.076 (5)</td>
<td>...</td>
<td>90.0</td>
<td>...</td>
</tr>
<tr>
<td>Re$_2$Te$_5$</td>
<td>2.983 (3)</td>
<td>3.022 (3)</td>
<td>91.2</td>
<td>88.8</td>
</tr>
</tbody>
</table>

The structures of NdTe$_5$ and NdTe$_7$ also contain identifiable units of Te$_5^{6-}$ where assignment of a formal charge is virtually ruled out by the complexity of the structures. Part of the NdTe$_5$ structure is shown in 7.

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and exhibits geometric features characteristic of other units we have already noted.

What are these features? They are summarized in Table I. The variation in geometry among these units is not large, considering the differences in crystalline environment in which they are found. The average Te–Te bond length is 3.039 Å, and except for the one large angle in K2SnTe5, they are all essentially square planar in geometry. This characteristic bond length is significantly longer by 0.25–0.30 Å than twice the covalent radius* of 1.37 Å, since normal covalent Te–Te bonds fall in the range 2.69–2.80 Å.11

The essential questions we wish to address here, then, are as follows: how can the formation of the chain compounds be visualized, and why are the Te(central)–Te(peripheral) bond lengths longer than normal Te–Te bond lengths by ~0.25 Å? We note that the same questions have been recently examined in a paper by Bullett.12

We turn to the second question first, by recalling an observation we made earlier regarding the [SnTe^3^-] anionic chain. Considering the building blocks of this polymeric chain as Te6^- and Sn(IV) may at first glance lack chemical aesthetic appeal. However, by analogy with some other well-known species such an approach can lead to an understanding of the bonding in this system.

The square-planar unit is reminiscent of mixed-halogen anions BrF4^- and ICl^- and of XeF4, an observation already made by others.2,10 Let us initially examine the first two members of this group. Both are well-documented square-planar structures,13-15 in which the Br–F bond length is 1.89 (2) Å while I–Cl ranges from 2.42 (1) to 2.60 (1) Å and averages 2.51 (2) Å.16 These distances are again significantly longer than the respective single-bond distances of Br–F (1.756 Å) and I–Cl (2.321 Å) in the diatomic molecules. They are just below the σ level. In the 32-electron count the C1 geometry is more stable by about 0.45 eV. Filling the a2σ level for a 34-electron count raises the energy of the C1s above the D4h geometry. For the 34-electron systems, e.g. SF6, there is a delicate balance in the calculations between planar and C2v structures.19 However, the 36-electron count raises the energy of the C1 geometry by an additional 1.43 eV, so the latter geometry is clearly preferred.

Let us now carry the analogy directly over to the Te6^- unit. First, we must take care of the electron count, which again will be 36 if n = 6. The formal oxidation state on the central Te is II, considering each of the peripheral Te's as 2-.

When the Te–Te distance is increased from 2.84 to 3.04 Å, the a2σ level drops by 2.95 eV and the a2u level drops by 0.4 eV while other levels remain essentially constant. Thus the antibonding character is significantly decreased with almost no loss in bonding character. So why does the Te6^- unit not exist as an independent entity like ICl^- and its analogues? The reason is the difference in electronegativity in the two atom types for ICl^- and the lack

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**Figure 1.** Energy level diagram for ICl^- at two different geometries.

**Figure 2.** Walsh diagram for the D2h–C2v transformation of the Te6^- unit.

The energy level diagram for ICl^- in D2h symmetry is given in Figure 1. The two highest occupied MO's in this 36-electron system are both antibonding (a2g and a2u) and are clearly destabilizing at a normal I–Cl bond length of 2.32 Å. Their influence, especially that of the a2g, is significantly decreased by extending the bond length to 2.505 Å. Formation of the anion from I^- and four Cl atoms leads to a net decrease in energy of 49.8 kcal/mol per I–Cl bond formed, a value that compares favorably with the literature value of 49.7 kcal/mol.20 It would appear that lengthening of the I–Cl bonds is required to reduce the antibonding character of the HOMO. An analogy could, in principle, be made with SF6, which has the C2v trigonal-bipyramidal structure with one lone pair of electrons in an equatorial orbital; it is a 34-electron system. The Walsh diagram for the D4h → C2v transformation for a Te6^- unit with Te–Te bond lengths of 2.91 Å is given in Figure 2. For a 32-electron count for D2h Te6^- the e2g level is the HOMO, while for the 36-electron count the a1u level is the HOMO. The filled a2u and a1u orbitals of Figure 1 are not shown in Figure 2. We are finding that the e2g level. In the 32-electron case the C1 geometry is more stable by about 0.45 eV. Filling the a2u level for a 34-electron count raises the total energy of the C2v structure by 0.54 eV, barely favoring the D4h geometry. For the 34-electron systems, e.g. SF6, there is a delicate balance in the calculations between planar and C2v structures.19 However, the 36-electron count raises the energy of the C1 geometry by an additional 1.43 eV, so the latter geometry is clearly preferred.

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**References:**

whereas, as expected, there is much less polarization in the Te$_5^{6-}$ case. Thus, in spite of the bond lengthening there is still sufficient antibonding character between central and peripheral Te's to destabilize an individual unit.

There is another factor operating to make XY$_4$ hypervalent molecules kinetically unstable. Orbitals such as 9 or 10 have substantial electron density on the external Y ligands and are X-Y antibonding. The less electronegative Y is relative to X, the more will such orbitals be localized on the external atoms; these in turn will be activated with respect to electrophiles. The general prescription for kinetic stability for XY$_4$ molecules of this type is to make the external Y groups as electronegative as possible. In lieu of a large difference in electronegativity electron "pileup" on terminal atoms can be alleviated by forming interfragment bonds.

For Te$_5^{6-}$ stabilization can be achieved by the formation of bonds between units, as in the chain compounds 2 and 3, or between Te$_5^{6-}$ units and a suitable "mediator" such as Sn. Let us demonstrate how this happens, by first building model molecules from these Te$_5^{6-}$ units, and then extending them to the infinite chains observed.

Let us make the bonding in Te$_5^{6-}$ explicit by structure 11, which shows the electron pairs as bars. The central Te has four electrons in this extreme resonance structure and uses two formally empty p orbitals to engage in electron-rich three-center bonding with the external tellurium atoms. Please do not consider the crude assignment of electrons in 11 as anything but an extreme formalism.

Where are the frontier orbitals 9 and 10, $a_{1g}$ and $a_{2g}$, in this picture? They are to be identified with the two lone pairs at the central atom in 11, as approximate as these identifications perforce must be.

The rough formalism illustrated in structure 11 does indicate how a Te$_5^{6-}$ fragment can bond to other entities. If it retains all of its electrons, it can only act effectively as a Lewis base, through either the terminal or central atom lone pairs. This is what it does in 4, the formal Sn(IV) complex of Te$_5^{6-}$.

If we allow oxidation of the Te$_5^{6-}$ unit, further bonds may be formed. For instance, one view of the Te$_5^{2-}$ system obtained by removal of four electrons from Te$_5^{6-}$ is shown in 12. We have chosen to oxidize the terminal tellurium atoms. 12 is a tetraradical, set up to polymerize with itself to form Te-Te bonds and extended structures of type 2 and 3.

We now return to another approach to the electronic structure of the polymeric (Te$_5^{6-}$)$_n$ chains by examining the bonding in two model compounds, 13 and 14. We have termed them cisoid and transoid, in view of their topological similarity to cis- and trans-polyacetylene. In the Rb$_2$Te$_5$ structure Te-Te bonds within a square-planar unit are 3.04 Å, while those between units are 2.76 Å. An intermediate value of 2.91 Å was chosen for all. All bond angles were chosen as 90° around a central Te atom, while 102.5° was used for the angle around the peripheral atoms.

The entire unit is assigned a charge of 2-. One way to reach this 72-electron count is to begin with a 96-electron trimer (Te$_5^{6-}$)$_3$ which is terminated by four H-groups instead of Te$_2^-$. The 24 lost electrons are essentially the lone pairs on the replaced Te atoms. In an analysis of the bonding in 13 or 14 let us first consider a fragmentation scheme wherein the central Te$_5$ unit is one fragment and the two peripheral units comprise the second fragment. Again, all Te-Te bond lengths were given an intermediate value of 2.91 Å. Te-H was taken as 1.72 Å.

The interaction diagram is shown in Figure 3. The interaction of the two terminal TeH$_2$ groups with the central Te$_5$ results in the formation of four Te-Te σ bonds, from the interaction of essentially p$_z$ orbitals. The antibonding combinations are pushed above the $a_1$ orbital derived from the $a_{2g}$ level of the Te$_5$ unit, which now becomes the HOMO for the system. This and the second highest filled orbital, also $a_1$, are both antibonding within the Te$_5$ unit. The interfragment bonding combinations are not stabilized to the same extent as the destabilization of the intrafragment
antibonding combinations. The HOMO's for the fragments are at approximately -10.6 eV while the HOMO for the full molecule is at -6.9 eV. As a result of this large difference, the net effect of forming the molecule is a destabilization of the structure with respect to the two fragments by 1.66 eV. The overall situation may be described as the formation of four σ bonds between units at the expense of filling antibonding orbitals within a unit.

The net positive energy for this process still leaves us with no rationalization for the formation of the compound. Recall that we chose an intermediate value of 2.91 Å for all the Te(peripheral)-Te(peripheral) bond lengths. If we now increase the Te(peripheral)-Te(clear) bond length to that observed in the crystal (3.034 Å) and likewise reduce the Te-Te bond length between square-planar units to 2.84 Å, we obtain a net stabilization of 2.2 eV, or about 1.26 kcal per Te-Te bond. The stabilization is due principally to a lowering of the HOMO (by 1.3 eV). This rather dramatic change with geometry demonstrates the strong competition between the antibonding character of the Te(central) unit discussed earlier and the stabilization obtained by forming chains of these units.

The difference in the nature of the Te-Te bonds in this model, with all Te-Te distances equal. The overlap would be the four ditelluride (Te-Te) units that make up the links the geometry with all Te-Te bonds of

in which the fragmentation is chosen to examine the effect of that the bonds to the square-planar coordinated Te elongate. It is no wonder that the bonds to the square-planar coordinated Te elongate.

Further evidence for this driving force for Te(clear)-Te(peripheral) bond elongation may be derived from a calculation in which the fragmentation is chosen to examine the effect of bonding within these square-planar units, rather than between them, in the stabilization of the chain structure. One fragment would be the four ditelluride (Te-Te) units that make up the links between square-planar units, while the remainder of the molecule (two TeH2 units plus Te) comprises the second fragment. For the geometry with all Te-Te bonds of 2.91 Å, the bringing together of these fragments (formation of bonds within square-planar Te5 units) is unstable with respect to the fragments by 3.52 eV. Recall that relaxation of the geometry to that found in the crystal for the square-planar fragmentation did result in a net stabilization of 2.2 eV. The same process for this fragmentation still does not suggest a net bonding situation—the energy of the whole is 1.24 eV higher than the sum of the fragments.

In summary, the square-planar Te5- system can find a way of overcoming a delicately balanced but essentially antibonding situation by losing four electrons and by forming bonds between neighboring units. Now that we have seen the basis for the formation of bonds between square-planar units, we wish to ask if the geometry also plays an important role in this process, for we have already seen that even a homoatomic chain can adopt at least two different geometries, 13 and 14. For the transoid model compound, 14, the interaction diagram is virtually identical with that for the cisoid, 13, already discussed. This is not unreasonable: the structure is stabilized by the formation of σ bonds between essentially D4h units, and the propagation of these bonds “above” or “below” the plane would seem to be equally possible on an energetic basis. The only real difference in interatomic interactions between the two molecules is a possible through-space Te-Te interaction indicated in 15. But the distance is nearly 6 Å, so this may be ignored.

We are now in a position to look at the SnTe52- chain, 4, and again we choose a model compound, 16, to get some idea of the bonding in this system. We suggested earlier two possible ways

of thinking about the electron count: either as a combination of Sn2+ and Te52- units or as Sn(V) and Te5+. In light of what has been said above, clearly there is a preference for the second choice. Calculations were carried out for two geometries, 17a and 17b. The restrictions of 90° bond angles around the central Te and Te-Sn bond lengths of 2.78 Å determine the Te-Te-Sn and Te-Sn-Te bond angles. In the experimental structure the Te-

Te-Te angles within a Te5Sn ring are 88.5 and 95.0° while exocyclic ones are 88.5°. The angles about the Sn are 102.1, 103.9, and 112.8° (4X) so strict square-planar geometry is not obtained in the former case and ideal tetrahedral geometry is not obtained in the latter case.

The interaction diagram for a fragmentation into planar Te5 (and two planar Te5H2 units) in one fragment and two Sn in the second fragment for geometry 17a is given in Figure 4. A pattern similar to that which we encountered earlier for 13 is observed here as well. Eight bonding orbitals are only slightly lowered with respect to their energy in the Te5 and Te5H2 fragments, but the antibonding orbitals are pushed way above the by now familiar antibonding a1 orbital within the central Te5 unit, which becomes the HOMO. The lowest antibonding combination can be found at +0.59 eV. Note that the HOMO is lowered by ~0.25 eV upon formation of the molecule due to a small contribution from the p orbital of the Sn, which leads to some Te(peripheral)-Te(peripheral) bonding character. When the geometry is altered to 17b, increasing the bonded Te-Te distance and decreasing the inter-
action between peripheral Te's through the Sn in the HOMO, the HOMO is lowered by 1.25 eV, indicating again the importance of the antibonding character within this unit. However, the block of bonding orbitals at $\sim 11.5$ eV does not contain any contribution to bonding within Te$_5$ units.

The formation of the molecule from these two fragments with geometry 17a yields a net binding energy of 15.3 eV or 44 kcal per Sn-Te bond formed. Relaxation to the geometry of 18 yields 18.5 eV or 53 kcal per Sn-Te bond. The molecule may also be fragmented as in 18 to examine the effect of the formation of Te(central)--Te(peripheral) bonds. With a charge of 2-- on the central Te, the net binding energy (for the formation of eight Te-Te bonds) is 0.56 eV, for the geometry in 17a. Clearly the first fragmentation scheme with the geometry in 17a is preferable in accounting for the bonding in this model compound.

We are now ready to examine the extended systems containing Te$_5$ units. The band structure for the transoid Te$_5$-- chain is shown in Figure 5. The Fermi level is at $-6.95$ eV ($k = 0$) corresponding to the energy of the HOMO in the trimer 14. There is very little dispersion in this band due to the near-orthogonality of the now familiar orbitals on the peripheral Te's at both edges of the Brillouin zone.

Two bonds are formed per unit cell (or more correctly between unit cells as defined here), so by analogy with the molecular unit we expect two essentially antibonding levels above the Fermi level; these appear at $-5.71$ and $-5.33$ eV, respectively. The material is thus expected to be a semiconductor with band gap $1.24$ eV at $k = 0$.

Figure 5. Density of states for the transoid Te$_5$-- chain.

Then, we expect two bonding bands, again corresponding to the A and S combinations in 20. In fact, four bands may be associated with the bonding due to rather extensive mixing between bands at the edges of the Brillouin zone. The highest S antibonding band at $k = 0$ (7) correlates with the highest bonding band at $k = 0.5$ (4'). The latter is, in turn, antibonding with respect to its origin at $k = 0$ due to the presence of antibonding interactions within the Te$_5$ unit. The symmetric antibonding band at $k = 0$ (6) also correlates with the lower S bonding band at $-12.1$ eV (2).

As one starts from $k = 0.5$ for the S antibonding band (6') there is a correlation with the lower S bonding band at $-12.1$ eV (2). These correlations from antibonding to bonding bands lead to avoided crossings which account for the change in topology of the band orbitals in moving across, e.g., a bonding band.

A similar correlation may be made for the antisymmetric bands. The antibonding one at $k = 0$ (6) correlates with the higher bonding one at $k = 0.5$ (3') while the lower A band at $k = 0$ (1) correlates with A antibonding at $k = 0.5$ (7').

Associated with the band structure of the transoid chain is the density of states (DOS) in the polymer. This is plotted in Figure 5, along with a partitioning that shows the contribution of the four peripheral telluriums. The remaining in the DOS curve is the contribution of the single central Te. The total charge on a peripheral Te atom is $-0.587$, and that on the central Te is $+0.348$. 
This is the same trend as in the Te$_5$ model. The total overlap populations in the polymer are 0.155 for Te$_c$-Te$_c$ and 0.429 for Te$_p$-Te$_p$, where the subscripts c and p stand for central and peripheral, respectively. A more detailed decomposition of the bonding is obtained through COOP curves. These are overlaps of population-weighted densities of states, i.e., DOS curves in which the relative number of states in a given interval is weighted by the contribution that those states make to bonding or antibonding for a specified bond. We have found these COOP curves most useful for analyzing bonding trends. A COOP curve for the Te$_3$- polymer is shown in Figure 7. Note that the highest occupied band in the polymer is both Te$_c$-Te$_c$ and Te$_p$-Te$_p$ antibonding, especially so in the latter bond. The antibonding nature of the model and the polymer has been discussed earlier. It is interesting to speculate here that a material with stronger Te-Te bonding could be made if one could oxidize the TeS$_2$- chain.

Figure 7. Crystal orbital overlap population (COOP) curves for the two different Te-Te bonds in the Te$_3$- chain.


Figure 8. Band structure of the cisoid Te$_5$- chain. Only bands contributing to Te$_p$-Te$_p$ interaction are included. The two-letter symmetry classifications refer to the mirror plane parallel to the chain propagation direction and the 2$_z$ screw axis. E refers to a degenerate pair of bands.

Figure 9. Band structure for the SnTe$_5$- chain. The two-letter symmetry classifications refer to the mirror plane parallel to the chain propagation direction and the 4$_z$ screw axis. E refers to a degenerate pair of bands.

Figure 10. Total density of states and contributions from the three different atom types in the SnTe$_5$- chain.

The similarity between the model cisoid and transoid molecules 13 and 14 is expected to be maintained in the extended structures as well. The major difference is the presence of the additional screw-axis element in the cisoid chain, causing the repeat distance to double. The symmetry of the chain is thus nonsymmorphic, resulting in a “folding back” of the bands, as seen in Figure 8. Again, only those bands that contribute to bonding between Te, units have been included. The topology of the orbitals is the same for both structures. Indeed, if we could “unfold” the bands for the cisoid polymer, the two band structures would be essentially superimposable.

The band structure for the SnTe$_5$- chain (Figure 9) shows even less dispersion than the pure Te$_5$ chains. The band gap in this case is 2.66 eV, again indicating a semiconductor. Following the model molecule 16, the conduction band (~5.5 eV) is composed of nonbonding orbitals on the tellurium atoms. The band structure has been simplified here by eliminating all nonbonding orbitals except those in the conduction band. A discussion similar to that given for the pure Te$_5$ chains relating to the avoided crossings could
The Te-K distance is 4.24 Å, the central Te. Thus there is a concentration of electron density along this axis and, not unexpectedly, the two cations for each chain may be understood on the basis of the symmetry of Sn in a band -7 eV below the Fermi level.

The COOP curves for the two bond types in the SnTeS2- chain is shown in Figure 11. COOP curves for the two bond types in the SnTeS2- chain be given here; however, the bonding in the chain can be understood on the basis of the model compound 16 discussed above.

The total density of states of SnTeS2- is shown in Figure 10. The fact that the topmost filled bands are strongly antibonding in the cisoid and transoid all-Te chains suggests that oxidation of the chain would lead to shorter Te-Te bond lengths within that unit. With the Fermi level at ~7 eV oxidation is not excessively difficult and all three chains with a formal building unit of Te5-2 might be attainable with proper choice of synthetic conditions. All three known compounds were obtained by heating stoichiometric quantities of the elements involved;1-3 compounds such as Rb2Te5 and K2SnTeS with the lower electron count on the Te5 unit might result from starting materials in the proper stoichiometric ratios.

The symmetry properties of the chains aid in understanding the location of the cations with respect to the central Te of a Te5 unit. In the cisoid and transoid all-Te chains 2 and 3 the cations (Cs and Rb, respectively) are located on axes perpendicular to the Te5 unit. In 2 the Cs-Te distances are 3.92 and 3.96 Å, while in 3 the Rb-Te distance is 3.88 Å.

In the K2SnTe5 structure the K+ cations lie on an axis that runs through the central Te but in preservation of the symmetry of the tetragonal space group I4cm is at a 45° angle to the Te5 plane. The Te-K distance is 4.24 Å. In fact, the cation is closer to the Te5 unit. In the cisoid and transoid all-Te chains 2 and 3 the cations (Cs and Rb, respectively) are located on axes perpendicular to the Te5 unit. In 2 the Cs-Te distances are 3.92 and 3.96 Å, while in 3 the Rb-Te distance is 3.88 Å.

The presence of an inversion center at Te in the transoid chain prevents s, p2 mixing; however, it does require equal Te-Cs bond distances above and below the plane. Similarly, there is no physical basis for mixing as in 21 since the Te5 units lie on a mirror plane. There is less of a concentration of electron density on Te5, and the alternate location of the cation is preferred.

Another interesting feature of the structures is the short Te--Te interchain distance of 3.47 Å found in the transoid structure. Short distances such as this are found in many tellurium and selenium structures where steric factors do not prevent the close approach of these atoms. For instance, in α-tellurium, the helical chains have Te--Te bond lengths of 2.83 Å, but each tellurium has four neighbors at distances of 3.494 Å.22

The geometric nature of the interaction between transoid chains is shown in 22 and 23. 22 indicates in a side view the short contact. In 23 the same structure is shown in projection onto the plane of a Te5 unit. One atom has been darkened and another shaded to aid in identifying the interaction. 23 in particular strongly suggests an interaction between p2-type orbitals.

Calculations were carried out on a “dimer” composed of two molecules of 14. For the geometry as shown in 22 the dimer is not bound with respect to the two monomers by 0.47 eV. Shifting the molecules closer to 3.27 Å leads to a worse situation where the difference is ~1 eV. A lateral shift of the chains to bring the two interacting atoms into an eclipsed orientation does not

chains is ML_{4/2} or ML_2. The magnificent world of structural lead to any significant improvement. Interestingly, the reduced overlap populations for atoms that might be involved in this interaction show that indeed there is a small bonding interaction (+0.0039) but there is an antibonding one of similar magnitude (−0.0037) between the darkened Te and the central Te in the Te_5 unit containing the shaded Te. These two interactions are of similar magnitude in all the other geometries. As we move the two trimers toward each other, past the equilibrium separation of the Teerver the central Te bond length by ~0.25 Å over a normal bond, and the unit is shown to be an unstable species, compared with, e.g., ICl^−. However, the formation of infinite one-dimensional chains due to covalent or dative bonding between units (Te,^2_5) or with another modulating atom (SnTe,^2_5) is energetically sufficient to stabilize the overall structure. In spite of the significant topological difference between the Cs_2Te_5 (cisoid) and Rb_2Te_5 (transoid) chains their electronic structures are virtually identical. These have been interpreted for all three compounds by employing model molecules, which provided a basis for understanding the band structure of the infinite chains. The HOMO in the model compounds is an antibonding orbital within the square-planar unit, leading to the suggestion that modification of the synthesis of these compounds could lead to an oxidized form of the chain with modified properties and greater inherent stability of the Te_{5/2}^− units. The electronic basis for the short interchain Te−Te distance of 3.47 Å, reminiscent of a similar contact in elemental tellurium, was investigated but apparently is beyond the capability of the extended Hückel method.

Acknowledgment. J.B. wishes to thank S. Alvarez and J. Silvestre for many helpful discussions. We are grateful to Eleanor R. Stagg for typing the manuscript and to Jane Jorgensen for the figures. Our work was supported by NSF Grant CHE8406119. We have benefited greatly from the comments of a careful and conscientious reviewer. Many of his or her suggestions have been included in the final version of the manuscript.

Appendix

Table II. Extended Hückel Parameters

<table>
<thead>
<tr>
<th>orbital</th>
<th>H_o, eV</th>
<th>exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te</td>
<td>−20.78</td>
<td>2.51</td>
</tr>
<tr>
<td>Sn</td>
<td>−11.04</td>
<td>2.16</td>
</tr>
<tr>
<td>H</td>
<td>−8.32</td>
<td>1.82</td>
</tr>
<tr>
<td>l</td>
<td>−13.60</td>
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Tetrahedral and Square-Planar One-Dimensional Chains: The Interplay of Crystal Field and Bandwidth in MS_2 Compounds

JÉRÔME SILVESTRE and ROALD HOFFMANN

Received March 29, 1985

One-dimensional ML_2 chains with edge-sharing tetrahedral or square-planar coordination at the transition metal are the subject of this theoretical analysis. The band structures of these systems are examined in substantial detail. The local ligand field at the metal is a good starting point for an understanding of the band ordering in these extended structures, but inter unit cell interactions, both through the bridges and directly between the metals, are important for setting the energy order and dispersion of the bands and especially for determining unexpected electron counts for semiconducting behavior; one such case is d^6 for the tetrahedral chain. Pairing distortions, chain folding, and uniform contractions and elongations are also studied in some detail for these materials.

The two most frequently encountered geometrical arrangements of four ligands L around a metal atom are tetrahedral (1) or square planar (2); the complex stoichiometry in both cases in ML_4. If the ligand L has the ability to function as a bridge between two metal centers, it is in principle possible to generate from 1 and 2 the polymers 3 and 4, respectively. The stoichiometry of these chains is ML_{4/2} or ML_2.

Table I. Some Known ML_2 Structures

<table>
<thead>
<tr>
<th>compd</th>
<th>chain</th>
<th>type</th>
<th>θ, deg</th>
<th>M−M, Å</th>
<th>d^o</th>
<th>ref</th>
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<tr>
<td>KFeS_2</td>
<td>FeS_2^-</td>
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<td>106.0</td>
<td>2.70</td>
<td>d_6^a</td>
<td>2a</td>
</tr>
<tr>
<td>RbFeS_2</td>
<td>FeS_2^-</td>
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<td>105.0</td>
<td>2.71</td>
<td>d_6^b</td>
<td>2b</td>
</tr>
<tr>
<td>CsFeS_2</td>
<td>FeS_2^-</td>
<td>3</td>
<td>105.0^a</td>
<td>2.71^b</td>
<td>d_6^c</td>
<td>2b, 3</td>
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<td>106.0</td>
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<td>3.11</td>
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<td>82.5</td>
<td>3.54</td>
<td>d_6^f</td>
<td>6</td>
</tr>
<tr>
<td>Na_2PtS_2</td>
<td>PtS_2^-</td>
<td>4</td>
<td>82.5</td>
<td>3.55</td>
<td>d_6^g</td>
<td>6</td>
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<td>87.0</td>
<td>3.34</td>
<td>d_6^j</td>
<td>8</td>
</tr>
</tbody>
</table>

^a Average value.

solid-state chemistry shows us that infinite systems such as 3 and 4 are not just the fruit of our imagination: they do occur in reality.1