Effect of Diverse Ligands on the Course of a Molecules-to-Solids Process and Properties of Its Intermediates
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Effect of Diverse Ligands on the Course of a Molecules-to-Solids Process and Properties of Its Intermediates


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We have been studying chemical processes that use discrete molecular reagents to form extended solid inorganic materials. The goals of this program have been to determine how best to design and implement these molecular precursor reactions and to discover what chemical intermediates lie on the molecules-to-solids paths. In this manuscript we report studies of the reactions of the low-valent iron complex Fe(C₅H₄)₂ with low-valent tellurium compounds of the form TePR₃ (R = various hydrocarbon groups) that lead ultimately to the exclusively inorganic extended solid compounds Fe₆Te₆. We have found four Fe₆Te₆ cluster types that are chemical intermediates in this process: Fe₆Te₆(PMe₃)₄, 1; Fe₆Te₆(PPr₃)₄, 2; Fe₆Te₆(PEt₃)₄, 3; (dmpe)₂Fe₆Te₆, 4; (depe)₂Fe₆Te₆, 5; Fe₆Te₆(dmpe)₂, 6.

(Here 'Pr' = CH₃C(CH₂)₂M; dmpe = Me₂PCH₂CH₂PMe₂, and depe = Et₂PCH₂CH₂PMe₂.) The different clusters form when different supporting phosphine ligands are employed. We report the syntheses, structures, and properties of these intermediates and the comparisons and contrasts between these molecular intermediates and the extended solid products. We note that when larger ligands are used smaller clusters are formed. We also note what features of the molecular structures lead to ferromagnetic versus antiferromagnetic coupling of the distinct Fe centers. We have determined the structures of the materials crystallographically: 2 (C₃H₅H₂FeTe₆P₃; tetragonal, P4/21c; a = 14.0469(7) Å; c = 13.5418(9) Å; Z = 2); 3 (C₁₂H₁₀Fe₆Te₆P₃; trigonal, R3, a = 11.859(2) Å; c = 26.994(5) Å; Z = 3); dmpe-2Te (C₅H₅H₂Fe₆Te₆P₃; monoclinic, P2₁/c, a = 6.0890(4) Å, b = 10.7934(7) Å, c = 9.8200(5) Å; β = 104.63(7); Z = 2); 5 (C₃H₅H₂Fe₆Te₆P₃; orthorhombic. Pbnn; a = 10.997(3) Å, b = 14.157(3) Å, c = 18.345(4) Å; Z = 4); 6 (C₃H₅H₂Fe₆Te₆P₃; orthorhombic. Aaura; a = 12.056(3) Å, b = 17.725(5) Å, c = 21.403(8) Å; Z = 4).

Introduction

The study of chemical processes that lead from molecular reagents to extended solid products has several goals. Among these is the determination of methods by which the otherwise runaway reactions can be controlled in a purposeful way. Were the appropriate methods of control available, one could envision the construction of very complex solids via strictly chemical means. At present such a level of fine control is not generally available.

In the present manuscript we describe our efforts to control the processes that lead from the initial combination of bis(cyclooctatetraene)iron, Fe(COT)₂, and triethylphosphine telluride, TeP₃, to the ultimate products, solid-state tellurides of iron, Fe₆Te₆. We find that the addition of different phosphine ligands to the reaction mixture results in the formation of different Fe₆Te₆-containing molecular compounds. We describe the syntheses of these materials, their molecular structures and properties, and their physical and chemical relationships among one another and to the associated extended solids.

Experimental Section

Unless noted to the contrary all manipulations were conducted under inert atmosphere using conventional techniques. Triethylphosphine (P₂Et₃, Aldrich), trimethylphosphine (P₂Me₃, 1 M solution in toluene, Aldrich), triisopropylphosphine (P₂Pr₃, Strem), bis(dimethylphosphino)ethane (depe, Strem), and tellurium (Al- drich) were used as received. Solvents were anhydrous and used as received from Aldrich. Simple trialkylphosphine tellurides¹ and bis(cyclooctatetraene)iron² were prepared using literature methods. Magnetic susceptibility measurements were made on a SQUID magnetometer using standard techniques.

Synthesis of Fe₆Te₆(PPh₃)₄, 2. Fe(COT)₂ (1.00 g, 3.79 mmol) dissolved in toluene (15 ml) was treated with a mixture of TeP₃ (1.09 g, 3.79 mmol) and P₂Pr₃ (1.82 g, 11.4 mmol) in toluene (15 ml). The resulting solution was heated to reflux 4.5 h, after which the deep brown mixture was cooled to room temperature and filtered through a medium-porosity glass frit. The solution was concentrated in vacuo to roughly half its original volume. Cooling this latter solution to -20 °C overnight gave crystallization of Fe₆Te₆(P₃Ph₂), that was isolated, washed with pentane (2 × 5 ml), and dried (0.293 g, 8.53 × 10⁻³ mol, 23%). Anal. Calcd for C₃H₅H₂Fe₆Te₆P₃: C, 31.57; H, 6.12; Fe, 16.50; P, 8.83; Te, 37.05.

Synthesis of dmpe-2Te, 3. A solution of Fe(COT)₂ (1.00 g, 3.79 mmol) in toluene was distributed equally in three vials. Additional toluene (13 g of a stock 1 M toluene solution of P₂Me₃) was added to each vial. A solution of dmpe (0.15 g, 1.0 mmol) in toluene (15 mL) was treated with a mixture of TeP₃ (1.00 g, 3.79 mmol) and P₂Pr₃ (1.82 g, 11.4 mmol) in toluene (15 mL). The resulting solution was heated to reflux 4.5 h, after which the brown deep mixture was cooled to room temperature and filtered through a medium-porosity glass frit. The solution was concentrated in vacuo to roughly half its original volume. Cooling this latter solution to -20 °C overnight gave crystallization of Fe₆Te₆(P₃Ph₂), that was isolated, washed with pentane (2 × 5 ml), and dried (0.12 g, 6.6 × 10⁻³ mol, 23%). Anal. Calcd for C₃H₅H₂Fe₆Te₆P₃: C, 31.45; H, 6.16; Fe, 16.25; P, 9.01; Te, 37.13. Found: C, 31.57; H, 6.12; Fe, 16.50; P, 8.83; Te, 37.05.

Synthesis of dmpe-2Te, 3. A solution of Fe(COT)₂ (1.00 g, 3.79 mmol) in toluene was distributed equally in three vials. Additional toluene (3 × 10 ml) was carefully layered onto each. In a separate vessel elemental Te (0.065 g, 5.1 mmol) was dissolved in a solution of PMe₂ in toluene/pentane (13 g of a 1 M toluene solution of PMe₂ plus an additional 10 mL of toluene and 15 mL of pentane). The phosphine telluride solution was filtered and then layered evenly onto each of the three Fe(COT)₂ solutions. After 3 days at room temperature the layers had interdiffused and crystals of Fe₆Te₆(P₃Ph₂), had formed. This solid was isolated, washed (2 × 5 ml of pentane), and dried (0.12 g, 6.6 × 10⁻³ mol, 10%). Anal. Calcd for C₃H₅H₂Fe₆Te₆P₃: C, 31.92; H, 6.58; Fe, 18.49; P, 9.26; Te, 36.13. Found: C, 31.20; H, 2.91; Fe, 18.55; P, 10.15; Te, 56.40.

Pyrolysis of Fe₆Te₆(P₃Ph₂). A Pyrex ampule was charged with Fe₆Te₆(P₃Ph₂) (0.044 g, 0.024 mmol), connected through a liquid-nitrogen trap to a vacuum pump, and heated to 170 °C for 5 min. During this time the trimethylphosphine evolved as evidenced by the increase and subsequent decrease in the observed pressure. The residual solid (0.033 g, corresponding to 100% PMe₂ loss) was sealed in an evacuated Pyrex tube and annealed for 2 h at 350 °C. The residual solid was collected, washed with pentane, and dried in vacuo (0.030 g). Powder X-ray diffraction showed this to be a mixture of β- and ε-Fe₆Te₆.³ (N.B., during the annealing process a small amount of Te was transported to the cool end of the tube. This accounts for the small mass loss.)

Synthesis of dmpe-2Te. A solution of dmpe (0.15 g, 1.0 mmol) in toluene (5 mL) was treated with a solution of TeP₃ (0.5 g, 2 mmol) in toluene (5 mL) was treated with a solution of TeP₃ (0.5 g, 2 mmol).
in toluene (5 mL). The precipitation of dmpe-2Te began immediately. The mixture was left undisturbed several hours. The pale yellow microcrystalline solid was isolated by filtration, washed with pentane (3 × 5 mL), and dried (0.23 g, 0.51 mol%, 51%). Anal. Calcld for CH₃₅P₇. TeC₆: C, 17.78; H, 3.98; P, 15.28; Te, 62.96. Found: C, 17.80; H, 3.94; P, 15.08; Te, 62.70. This compound is quite insoluble in toluene and pentane but is soluble in toluene to which several equivalents of PE₈ have been added. Crystals suitable for diffraction were prepared by allowing the same two solutions to interdiffuse slowly at room temperature.

### Synthesis of (dmpe)Fe²⁺Te₄.

A Schlenk tube was charged with a solution of dmpe·2Te (44 mg, 0.19 mmol) in toluene (10 mL) and a solution of Fe(COT)₂ (264 mg, 1.0 mmol) in toluene (10 mL). The resulting mixture was agitated to ensure complete mixing and then was left at room temperature overnight. At this point the volatile components of the mixture were removed in vacuo and the resulting dark, sticky solid was washed with pentane (15 mL), dried, and subsequently extracted with toluene (10 mL). The extract was condensed to approximately half its original volume and then cooled to -20 °C, at which point crystallization of (dmpe)Fe²⁺Te₄ occurred. The solid was isolated, washed (2 × 5 mL of pentane), and dried (0.14 g, 0.23 mmol, 23%). Anal. Calcld for CH₃₅P₇. TeC₆: C, 41.65; H, 3.98; P, 15.28; Te, 62.96. Found: C, 41.65; H, 3.94; P, 15.08; Te, 62.70. This compound is original volume and then cooled to -20 °C. The densely colored product formed as a crystalline solid (0.22 g, 30%). Anal. Calcd for CH₃₅P₇. TeC₆: C, 41.65; H, 3.98; P, 15.28; Te, 62.96. Found: C, 41.65; H, 3.94; P, 15.08; Te, 62.70. This compound is

### Results

We have previously reported[1] that the reaction of Fe(COT)₂ with TePe₃ in the presence of additional Pe₈ yields the cluster compound Fe₁₀Te₄(P₆Te₄)₃. The structure of this compound is a tetrahedron of four Fe atoms in which each tetrahedral face is capped with a triply-bridging Te atom. The structure is completed by four phosphine ligands, one coordinated to each Fe. We sought the answer to the question of how strongly the nature of the cluster product resulting from the combination of Fe(COT)₂ with phosphinetellurides depends on the supporting ligand by conducting a series of similar reactions in which we simply varied the phosphine.

When we used P₆Te₃ in place of Pe₈, the first observation was that the FeTe reaction required more forcing conditions. While Fe(COT)₂ and TePe₃ react upon combination at room temperature, the same iron compound reacts with TePP₃ only on heating to reflux in toluene. After this reaction mixture had been at reflux for 4.5 h, it was cooled, filtered, and condensed. The cluster product Fe₁₀Te₄(P₆Te₄)₃, 2, formed as a crystalline solid (eq 1). We determined the structure of this compound by X-ray crystallography (Tables 1 and 2, and Figure 1) and found that it is essentially that of 1, i.e., formed by concentric Fe₄Te₄ and P₆ tetrahedra. Compound 2 is thus the latest member of the large family of Fe₄E₄ cubane cluster compounds[12–15] and of the

**Reference**

much smaller family of Fe$_4$Te$_6$ compounds.\textsuperscript{16-19} The data in Table 2 show that the bond distances in 2 are generally longer than the corresponding distances in 1. This is best explained by the greater steric bulk of PPr$_5$. While 1 is crystallographically cubic, 2 is distorted from this ideal. This is ultimately due to the structural asymmetry of PPr$_5$. The cluster 2 differs from 1 in solubility; while 1 is only slightly soluble in toluene, 2 is exceedingly so. Both the sluggish reactivity of TePPr$_3$ and the increased solubility of 2 can be rationalized by the bulk of the tris(propyolphosphine)ligands.

Since an increase in the size of the phosphine gave the same effect, it has a Fe$_4$Te$_6$ core and not the Fe$_8$Te$_8$ core of 1 and 2. The crystallographic data collection is reviewed in Table 1, and the structure of the cluster is summarized in Table 3 and Figure 2.

### Table 2. Structural Comparison of Fe$_4$Te$_6$(PPr$_5$)$_4$ and Fe$_4$Te$_6$(PEt$_3$)$_4$\textsuperscript{a}

<table>
<thead>
<tr>
<th>ligand</th>
<th>Fe-Fe</th>
<th>Fe-Te</th>
<th>Fe-P</th>
</tr>
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<tr>
<td>PPr$_5$</td>
<td>2.687(5)</td>
<td>2.623(3)</td>
<td>2.447(6)</td>
</tr>
<tr>
<td>2.675(5)</td>
<td>2.620(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.687(5)</td>
<td>2.614(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEt$_3$</td>
<td>2.623(4)</td>
<td>2.609(1)</td>
<td>2.390(6)</td>
</tr>
</tbody>
</table>

### Table 3. Selected Interatomic Distances (Å) and Angles (deg) in Fe$_4$Te$_6$(PMe)$_4$\textsuperscript{a}

<table>
<thead>
<tr>
<th>Distances</th>
<th>Angles (deg)</th>
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<tbody>
<tr>
<td>Fe-Te$_{1a}$</td>
<td>2.541(1)</td>
</tr>
<tr>
<td>Te$<em>{1a}$-Te$</em>{1c}$</td>
<td>3.684(1)</td>
</tr>
<tr>
<td>Fe-Te$_{1b}$</td>
<td>2.544(1)</td>
</tr>
<tr>
<td>Te$<em>{1b}$-Te$</em>{2}$</td>
<td>3.485(1)</td>
</tr>
<tr>
<td>Fe-Te$_{1c}$</td>
<td>2.542(2)</td>
</tr>
<tr>
<td>Fe-Te$_2$</td>
<td>2.566(1)</td>
</tr>
<tr>
<td>Fe-Te$_{1*}$</td>
<td>3.518(1)</td>
</tr>
<tr>
<td>Te$<em>{1*}$-Te$</em>{2*}$</td>
<td>3.684(1)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Data concerning Fe$_4$Te$_6$(PEt)$_4$ were taken from ref 6.

### Figure 1. Structure of Fe$_4$Te$_6$(PPr$_5$)$_4$, 2. The largest circles represent Te atoms, the smallest circles represent Fe atoms, and the medium circles represent the P atoms of the PPr$_5$ ligands. Selected distances and angles are given in Table 2.

### Compound 3, Fe$_4$Te$_6$(PMe)$_4$, is a member of the M$_8$E$_6$ family of “Chevrel-type” clusters\textsuperscript{20,29}

\[ 6\text{Fe(COT)$_2$} + 8\text{TePMe$_3$} \rightarrow \text{Fe$_4$Te$_6$(PMe)$_4$} \]  
(2)

In this system smaller monodentate phosphines yield larger clusters than do larger phosphines. The next issue is the effect of "Chevrel-type" clusters.\textsuperscript{25,29,30,31}
of multidentate phosphines on the Fe(0)/Te(0) reaction. The most direct experiment in the series would be to allow Fe(COT)$_2$ to react with dmpe·2Te; however, this is hampered by the virtually complete insolubility of dmpe·2Te in toluene. In order to understand this phosphine telluride and its behavior, we prepared it and examined its structure. As distinct from the usual synthesis (direct combination of elemental Te with the phosphine), the most convenient method of preparation of dmpe·2Te is to deliver Te to dmpe in the form of TePEt$_2$ (eq 3). As the dmpe telluride forms, it precipitates from toluene as a microcrystalline solid. (In order to form crystals that are suitable for crystallography, the slow interdiffusion of solutions of the two reagents is required.) The crystallographic description of dmpe·2Te is summarized in Tables 1 and 4 and in Figure 3. The molecular structure is that of a typical phosphine telluride; however, the source of the insolubility of dmpe·2Te is apparent from the crystal packing diagram (Figure 3b); the molecules pack together very tightly in a zipper-like arrangement, aligning the Te atoms from adjacent layers.

\[
dmpe + 2\text{TePEt}_2 \rightarrow \text{dmpe·2Te} + 2\text{PEt}_3
\]  

The solubility of dmpe·2Te is greatly enhanced by including a monodentate phosphine such as PEt$_3$ in the solvent mixture. One can imagine that the dynamic exchange of Te between dmpe and PEt$_3$ (the transition state for which process contains the R$_3$P·Te·PR$_3$ array that is, in the limit of triphenylphosphine, a stable molecule$^{30,31}$) interferes with the formation of the densely packed dmpe·2Te crystal. This feature accounts for the low isolated yield of dmpe·2Te when the latter is prepared from dmpe and TePEt$_3$ and also allows the study of the reactions of Fe(COT)$_2$ with the reaction-equivalent of dmpe·2Te.

When Fe(COT)$_2$ is treated with dmpe and TePEt$_3$ in toluene (dmpe)$_2$FeTe$_2$, 4, forms at room temperature (eq 4). The stoichiometry used in this reaction is not critical as 4 forms readily. This compound appears to form good crystals, and we attempted to determine its molecular structure; however, there is disorder in the system and the structure did not refine well. The disorder is with respect to a crystallographic mirror plane that passes approximately through the Fe atom and one of the Te atoms. We hoped that the replacement of dmpe with a closely related bidentate phosphine would give the same inorganic molecular core but one which would pack into regular crystalline order. With this in mind we combined Fe(COT)$_2$ with TePEt$_3$ in the presence of depe. The reaction with depe follows the same path, and (depe)$_2$FeTe$_2$, 5, is formed as a crystalline solid (eq 5). We were able to determine the structure of this material crystallographically, and those results are summarized in Tables 1 and 5 and Figure 4. The iron atom in 5 is coordinated by four phosphorus and two tellurium atoms that form a very distorted octahedron. The Fe-Te and Te-Te distances within the FeTe$_2$ triangle are within the ranges considered normal, although the Fe-Te distance is on the short side and the Te-Te distance is on the short side (see below).

\[
\begin{align*}
\text{Fe(COT)}_2 + 2\text{TePEt}_3 + 2\text{dmpe} & \rightarrow (\text{dmpe})_2\text{FeTe}_2 \\
\text{Fe(COT)}_2 + 2\text{TePEt}_3 + 2\text{depe} & \rightarrow (\text{depe})_2\text{FeTe}_2
\end{align*}
\]

The room-temperature absorption spectrum of 5 in the visible region shows three distinct features, all of which are quite intense. There is a strong similarity between this spectrum and that of 4. On the basis of this, and on the elemental analysis of 4, and the information to be gleaned from the incomplete X-ray structural refinement, we conclude that 4 is isostuctural with 5.

When the compounds that are formed by dmpe and depe are compared with those based on monodentate phosphines, it is tempting to suggest that cluster growth is very effectively curtailed by the bidentate ligands. This deduction must be modified in view of the formation of Fe$_3$Te$_6$(dmpe)$_4$, 6. Compound 6 is also formed by the reaction of Fe(COT)$_2$, dmpe, and TePEt$_3$; however, in this case a minimum amount of dmpe is used, and the iron reagent and the tellurium reagent are allowed to combine only very slowly (eq 6). The synthesis of 6 is frustratingly unreliable;
Molecules-to-Solids Processes

\[ 4\text{Fe(COT)}_2 + 6\text{TePES} + 4\text{dmpe} \rightarrow \text{Fe}_2\text{Te}_6(\text{dmpe})_4 \] (6)

however it is repeatable, and we have been able to prepare enough of the material to both determine its structure and measure its magnetization. The crystallographic structure determination is summarized in Tables 1 and 6 and in Figure 5. The structure of 6 is best appreciated as a dimer of \((\text{dmpe})_2\text{FeTe}_3\) in which the two subunits are connected by four equivalent Te-to-Fe donor/acceptor bonds. Discounting the potential Fe-Fe interaction (see below), each Fe atom is coordinated by six atoms, the six describing a distorted octahedron. Within each \(\text{Fe}_2\text{Te}_6\) subunit the three crystallographically distinct Fe-Te bonds are practically identical, and the Fe-Te internuclear distance of 2.586 Å as well within the normal range for covalent bonding.\(^{19,32}\) The Te-Te internuclear distances are all well over 3 Å; therefore, no Te-Te bonding is evident. Given this, the Fe atoms are conveniently viewed as being in oxidation state III, again ignoring Fe-Fe bonding.

We have measured the magnetization of 1, 2, and 6. Both 1 and 2 are paramagnetic. Above 100 K, each has a temperature-independent effective magnetic moment (8.3 and 8.49 \(\mu_B\), respectively) that corresponds roughly to 8 parallel spins. Compound 6 is diamagnetic.

We have shown previously\(^7\) that complexes of the form \(\text{Fe}_2\text{Te}(\text{PR}_3)_2\) undergo pyrolytic condensation to give solid-state tellurides of iron. Here we report that in the same way \(\text{Fe}_2\text{Te}_4(\text{PMe}_3)_6\) can be converted to \(\text{FeTe}_{12}\), and \((\text{dmpe})_2\text{FeTe}_3\) can be converted to \(\text{FeTe}_2\); thus, all of these FeTe molecular and cluster compounds are chemically related to FeTe extended compounds.

**Discussion**

From the results described above it is clear that a variety of clusters result from the interaction of Fe(COT)_2, with prevalent tellurium in the form of TeP=, and that which of that variety one is able to isolate depends critically on which supporting phosphine is used. This suggests a level of reaction control that is available for moderating molecules-to-solids processes and raises the question of why a given phosphine results in a particular cluster. One explanation is crystallization: perhaps all of the cluster types we have observed in this system are present to some extent, and that the question of why a given phosphine results in a particular Inorganic cluster core that we observe only because that phosphine-cluster superstructure crystallizes most promptly.

A second explanation is essentially kinetic. When the supporting ligands effectively hide the growing Fe/Te core from the reaction environment, the cluster so-hidden will be kinetically trapped since the ligands must be moved out of the way for further cluster growth to occur. It is reasonable that phosphines that are larger (all else being equal) will cover smaller clusters more effectively than will smaller phosphines. This reasoning predicts that the use of larger phosphines (all else being equal) will result in the isolation of smaller Fe/Te clusters. This rationalization is consistent with what we find.

In the limit of bidentate phosphines one might conjecture that this steric effect would shut down cluster growth entirely and that for this reason the FeTe_2 compounds, 4 and 5, result. The simple explanation based on steric protection is alone not sufficient to rationalize the formation of the FeTe_2 compounds, however, since the Te_2 unit in each is still quite exposed to the reaction environment. One might expect that the Te-Te bond would be reactive toward the (essentially) zerolvalent iron remaining in the reaction mixture, but in fact neither 4 nor 5 reacts even with added Fe(COT)_2. The resolution of this puzzle lies in the electronic structure of the complex. The Te-Te bond in 5 is short for a Te-Te single bond; the bond in 5 is 2.674 Å, while the


\[ \text{Fe-Te bond length is 2.763 Å in L}_\text{2MnTe2-TeMnL}_2, \] (38) Huang, S.-P.; Kanazadis, M. Inorg. Chem. 1993, 32, 821.

\[ \text{Fe-Te bond length is 2.763 Å in L}_\text{2MnTe2-TeMnL}_2, \] (39) Brostigen, G.; Kjekshus, A. Acta Chem. Scand. 1970, 24, 1925.


\[ \text{Distances} \]

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\[ \text{Angles around Fe} \]

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\[ \text{Angle around Te} \]

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</tr>
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<td>FeTe2-FeTe3</td>
<td>98.99(6)</td>
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</tbody>
</table>

\[ \text{Selected Interatomic Distances (Å) and Angles (deg) in FeTe}_6(\text{dmpe})_4 \]

Figure 5. Structure of and labeling for FeTe_{6}(dmpe)$_{4}$. 6. Selected distances and angles are given in Table 6.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) in FeTe_{6}(dmpe)$_{4}$.
The low-temperature magnetic behavior of these materials will be
more accessible the closer the metal and the anion are in
electronegativity. Since Fe and Te are closer in electronegativity
than Fe and S, the ferromagnetic coupling is expected to
be stronger in FeTe clusters than in FeSe clusters. If the reverse
charge transfer is energetically inaccessible, then antiferromag-
etic coupling is expected to dominate via conventional through-
bond coupling (albeit in this case "through-lone pair" coupling).

Another reason for the ferromagnetic coupling in 1 and 2 is the
high local spin state ($S = 1$) on each Fe. The coupling between the
Fe-centered Fe-Te bonding electrons and the nonbonding (yet
magnetically active) d electrons on the same Fe atom is stronger
the larger the number of high-spin coupled d electrons there are.
Since this spin-polarization is one of the components of
superexchange, the ferromagnetic coupling is expected to
weaken as electrons are removed from the Fe centers. This is a
plausible explanation for the increased importance of anti-
ferromagnetic coupling in FeTe$_2$(EPh)$_4$.

The diamagnetism of 6 implies the antiferromagnetic coupling of
the Fe(III) centers. The antiferromagnetic coupling can be due
either to the formation of direct Fe-Fe bonds or to
superexchange, the shorter Fe-Fe intranuclear distance in 6
(2.795 Å) is long for a direct Fe-Fe covalent bond, but it is within
the reported range. For example, the Fe-Fe bond in [(T$_1$C$_3$H$_7$)$_2-
Fe(CO)$_3$]$_2$ is 3.138 Å. As mentioned above, the conventional
description of superexchange would predict ferromagnetic cou-
pling of the Fe centers in 6 since the Fe-Te-Fe angle is less than
90°, therefore direct Fe-Fe bonding seems the more plausible
reason for the observed antiferromagnetic ground state.

Note that even though the Fe-Fe intranuclear distances are
shorter in 1 and 2 than in 6, our data indicate that covalent bonds
exist between the Fe centers in the latter but not in the former.

We have shown that complexes of the form FeTe$_x$(PR$_3$)$_3$,
Fe$_2$Te$_x$(PR$_3$)$_3$$_x$, and Fe$_3$Te$_x$(PR$_3$)$_3$ can all be converted to cor-
responding FeTe$_x$ solid-state compounds. We have not been able
to isolate 6 in sufficient quantity to test its conversion to FeTe;
however, we are confident that that molecules-to-solids process
will occur. Since these chemical relationships exist between the
clusters and the solids, we sought other comparisons and
contrasts between the molecular materials and their extended-
solid relatives. The most striking structural relationship between
any of the clusters we report here and the corresponding extended
solid occurs in the case of 6. The Fe$_2$Te$_3$ subunit that
constitutes the core of 6 can be found directly in the NiAs-type
FeTe solid. Crystaline Fe$_1$Te$_3$(NiAs structure type) can be
viewed as being constructed by Fe-centered Te$_6$ octahedra.
The Fe$_2$Te$_3$ unit is found in the FeTe structure, the Te$_6$ triangle being
a single face of a Te$_6$ octahedron that is shared between the two
Fe centers. The Fe-Te intranuclear distance in the Fe$_2$Te$_3$ unit
corresponds to the $c$-direction in the NiAs-type solid. The two
Fe$_2$Te$_3$ fragments (one from FeTe(dmpe)$_4$, the other from
FeTe$_2$(dmpe)$_4$) are compared in Table 7. The numerical comparison
shows that the two structures are quite similar.

Table 7. Comparison of Fe$_2$Te$_3$ Fragments in FeTe and
FeTe$_2$(dmpe)$_4$

<table>
<thead>
<tr>
<th></th>
<th>Fe$_2$Te$_3$</th>
<th>Fe$_2$Te$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(FeTe)</td>
<td>(dmpe)$_4$</td>
</tr>
<tr>
<td>$r$(Fe-Te) (Å)</td>
<td>2.609</td>
<td>2.586</td>
</tr>
<tr>
<td>$\theta$(Te-Fe) (deg)</td>
<td>93.5</td>
<td>93.4</td>
</tr>
<tr>
<td>$\theta$(Te-Fe) (deg)</td>
<td>65.3</td>
<td>65.6</td>
</tr>
<tr>
<td>$\theta$(Fe-Fe) (deg)</td>
<td>2.83</td>
<td>2.80</td>
</tr>
</tbody>
</table>

* Values based on data from refs 3 and 45.

(42) The low-temperature magnetic behavior of these materials will be
reported separately.
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B. A.; Kirner, J. F.; Muetterties, E. L. J. Am. Chem. Soc. 1978, 100,
4107.
(46) Useful descriptions of the NiAs structure are included in the following
texts. (a) West, A. R. Solid State Chemistry and Its Applications; John
In this case the cluster-to-solid similarity is more than just structural. The ideal NiAs structure is described as an hexagonally close-packed array of anions in which the octahedral interstitial sites are occupied by the cations. Assuming hard sphere atoms, this predicts a crystallographic \( c/a \) ratio of 1.633. Few metal chalcogenides or pnictides show this ideal value of \( c/a \). Most show \( c/a \) ratios less than 1.633, and the departure from the ideal is rationalized by the presence of metal-metal bonding along the \( c \)-direction. This metal-metal bonding shrinks the \( c \)-axis and thereby leads to values of \( c/a \) less than the ideal. The Fe-Fe vector in the \( \text{Fe}_2\text{Te}_3 \) fragment of FeTe referred to in Table 7 is coincident with the \( c \)-direction, and therefore, the metal-metal bonding implied by \( c/a = 1.487 \) in FeTe corresponds to the Fe-Fe covalent bonding between these two Fe atoms. Thus, the diamagnetism of 6 (which implies Fe-Fe covalent bonding in 6) and the lattice contraction in FeTe (which implies Fe-Fe covalent bonding along the \( c \)-direction in FeTe) are distinctly related.

**Conclusion**

We have found that the reaction of \( \text{Fe} (\text{COT})_2 \) with \( \text{TePR}_3 \) leads to solid-state iron tellurides, and that when the reaction conditions are moderated, molecular compounds can be retrieved from the mixture. As a general rule, the use of larger phosphines leads to lower nuclearity molecular clusters. Bidentate phosphines also tend to yield small molecular compounds. The Fe(II)-based clusters \( \text{Fe}_4\text{Te}_6 (\text{PR}_3)_4 \) (\( R = \) ethyl, isopropyl) are high-spin compounds while the Fe(III)-based compound \( \text{Fe}_4\text{Te}_6 (\text{dmpe})_4 \) is diamagnetic, showing direct Fe-Fe bonding. The latter compound is clearly identifiable as a fragment of FeTe in the NiAs modification.

**Supplementary Material Available:** Table S-1, listing crystallographic data for \( \text{Fe}_6\text{Te}_6 (\text{PPr}_3)_6 \), \( \text{Fe}_6\text{Te}_6 (\text{PMe}_3)_6 \), \( \text{dmpe-2Te} \), \( \text{FeTe} (\text{depe})_2 \), and \( \text{FeTe} (\text{dmpe})_2 \), Table S-2, listing positional and thermal parameters for \( \text{Fe}_6\text{Te}_6 (\text{PPr}_3)_6 \), Table S-3, listing interatomic distances and angles in \( \text{Fe}_6\text{Te}_6 (\text{PPr}_3)_6 \), Figure S-1, showing an ORTEP diagram for \( \text{Fe}_6\text{Te}_6 (\text{PPr}_3)_6 \), Table S-4, listing positional and thermal parameters for \( \text{Fe}_6\text{Te}_6 (\text{PMe}_3)_6 \), Table S-5, listing interatomic distances and angles in \( \text{Fe}_6\text{Te}_6 (\text{PMe}_3)_6 \), Figure S-2, showing an ORTEP diagram for \( \text{Fe}_6\text{Te}_6 (\text{PMe}_3)_6 \), Table S-6, listing positional and thermal parameters for \( \text{dmpe-2Te} \), Table S-7, listing interatomic distances and angles in \( \text{dmpe-2Te} \), Figure S-3, showing an ORTEP diagram for \( \text{dmpe-2Te} \), Table S-8, listing positional and thermal parameters for \( \text{FeTe} (\text{depe})_2 \), Table S-9, listing interatomic distances and angles in \( \text{FeTe} (\text{depe})_2 \), Figure S-4, showing an ORTEP diagram for \( \text{FeTe} (\text{depe})_2 \), Table S-10, listing positional and thermal parameters for \( \text{FeTe} (\text{dmpe})_2 \), Table S-11 listing interatomic distances and angles in \( \text{FeTe} (\text{dmpe})_2 \), and Figure S-5, showing an ORTEP diagram for \( \text{FeTe} (\text{dmpe})_2 \). (28 pages). Ordering information is given on any current masthead page.

(47) Reference 45a, p 250.