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Cr₆Te₈(PEt₃)₉ and a Molecule-Based Synthesis of Cr₆Te₄

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The molecular cluster compound Cr₆Te₈(PEt₃)₉ (1) is formed by the reaction of TePET₃ with either (Et₃P)₂Cr(allyl)₂ or Cr(2,4-dimethylpentadienyl)₂. This compound can be converted to the extended inorganic solid state compound Cr₆Te₄ by simple thermolysis. We have determined the structure of the title compound crystallographically (monoclinic; a = 13.076(5) Å, b = 21.194(7) Å, c = 23.694(7) Å, β = 105.21(5)°, V = 6276(10) Å³, Z = 4). The molecule is formed by a Cr₆ octahedron, a Te₈ cube, and a (PEt₃)₉ octahedron, all of which are concentric. We compare and contrast the structure and properties of the cluster with those of related solid-state compounds.

Introduction

In the effort to elucidate and understand the pathways by which molecular reagents come together to form extended solids, we have found that a number of complexes of low-valent transition metals react with phosphine chalcogenides to give solid state metal chalcogenides.1-3 In each case, we have been able to isolate and characterize molecular compounds which occur in the molecules-to-solids process and have found that polynuclear metal chalcogenide clusters so isolated can be appreciated as distorted (reconstructed) fragments of associated solid-state compounds. Our studies to date have dealt primarily with the metals react with phosphine chalcogenides to give solid state molecular reagents come together to form extended solids, we find that low-valent chromium species react with triethylphosphine telluride to form the cluster compound Cr₆Te₈(PEt₃)₉ (1). We report the structure of this molecular cluster, as determined crystallographically. We also report that this paramagnetic material can be pyrolyzed in the solid state to form the ferromagnetic solid Cr₆Te₄.

Experimental Section

Unless noted to the contrary, all manipulations were conducted under inert atmosphere using conventional techniques. Triethylphosphine (Aldrich), allylmagnesium chloride (Aldrich), chromium dichloride (Strem), and tellurium (Aldrich) were used as received. Solvents were anhydrous and were used as received from Aldrich. Triethylphosphine telluride was prepared using literature methods.4 Bis(2,4-dimethylpentadienyl)chromium was prepared by the method of Ernst and co-workers.5 Magnetic susceptibility measurements were made on a SQUID magnetometer using standard techniques.

Preparation of Cr₆Te₈(PEt₃)₉. 1. (A) A solution of (Et₃P)₂CrCl₂ was prepared from CrCl₃ (0.59 g, 4.8 mmol) and PEt₃ (1.13 g, 9.6 mmol) in THF (25 mL). This was cooled to -80 °C and treated with C₂H₅MgCl (4.8 mL of 2.0 M solution in THF). After approximately 15 min, a solution of TePET₃ in THF (1.57 g in 15 mL) was added dropwise. The mixture was warmed to warm slowly to room temperature and was stirred overnight. The volatile components were removed in vacuo, and residual THF was removed by adding toluene (15 mL), agitating the mixture, and then removing the volatile material in vacuo. The solid was treated with pentane (20 mL), the mixture agitated again, and the volatile material again removed in vacuo. The resulting solid was extracted twice with toluene. The combined extracts were concentrated and cooled to -20 °C to yield 1 as dark brown crystals.

(B) Bis(2,4-dimethylpentadienyl)chromium (3.07 g, 12.7 mmol) dissolved in toluene (50 mL) was treated with a solution of TePET₃ (3.12 g, 12.7 mmol) and PEt₃ (1.50 g, 12.7 mmol) in toluene (40 mL). This solution was heated to reflux under argon. Upon heating, the original deep green color of CrDMPD₂ gave way to the deep brown color of 1. The mixture was cooled to room temperature after 18 h at reflux and filtered through a medium porosity glass frit. The solution was condensed in vacuo to approximately one-third of its original volume and then cooled to -20 °C to initiate crystallization. The resulting solid was isolated, washed with pentane (2 × 20 mL), and dried to give 1 (1.22 g, 0.60 mmol, 38%). There is latitude in the starting ratio of Cr and Te reagents. With a molar ratio of Cr(2DMPD)₂ to TePET₃ of 3:4 the same percent yield was realized.

Anal. Calcd for C₃₇H₃₀Cr₆P₉Te₈: C, 21.18; H, 4.44; Cr, 15.28; P, 9.10; Te, 50.00. Found: C, 21.13; H, 4.38; Cr, 15.10; P, 9.07; Te, 49.75. The compound is soluble in toluene and THF. In solution (toluene) 1 shows intense but featureless absorption across the UV-visible region. The material is paramagnetic with an effective magnetic moment of 2.8 μB per cluster.

Solution-Phase Cothermolysis of Cr(C(H₃)₁₂)₂ and TePET₃. Cr(C(H₃)₁₂)₂ (0.23 g, 0.95 mmol) dissolved in toluene (10 mL) was treated with TePET₃ (0.31 g, 1.26 mmol). The resulting solution was heated at reflux for 20 h. At the end of this time, the mixture was cooled to room temperature and filtered. The solid was washed (pentane, 2 × 5 mL) and dried to give a dark gray powder (0.19 g). This powder was amorphous as judged by powder X-ray diffraction.

A portion of this amorphous solid (0.18 g) was sealed in an evacuated Pyrex tube and heated at 400 °C for 3 h. The solid...
was washed (pentane, 2 × 5 mL) and dried to give a dark gray solid (0.15 g). Powder X-ray diffraction from this material shows only Cr₆Te₉.

Crystallographic Determination of the Structure of Cr₆Te₉(PE₃)₆

A. Monoclinic Crystal. Crystals of I were obtained by slowly cooling a THF solution to -25 °C. A crystal fragment suitable for X-ray diffraction (approximately 0.2 × 0.2 × 0.2 mm) was mounted into a Lindemann capillary in a He-filled drybox, and the capillary was subsequently sealed. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation and the NRCCAD program package. The collected data are summarized in Table I. Calculations were performed on an Alliant FX/80 computer using the NRCAVX program package. Spherical absorption corrections were applied. Lattice parameters were determined from absolute 2θ values of 24 reflections with 36.9° < 2θ < 44.0°.

The structure was solved using direct methods. One of the independent PE₃ ligands exhibits orientational disorder of the ethyl substituents. This was modeled using 12 carbon atom sites, each with a cube of eight Te atoms, with the structure being completed by representing P atoms. The carbon and hydrogen atoms have been omitted for clarity.

Pyrolysis of Cr₆Te₉(PE₃)₆

We examined the thermal behavior of solid samples of Cr₆Te₉(PE₃)₆ with differential scanning calorimetry (DSC). This showed a broad endotherm between 210 and 250 °C. To determine the products of the thermal reaction, we thermolyzed the cluster on a larger scale; Cr₆Te₉(PE₃)₆ (90 mg, 0.044 mmol) was sealed in an evacuated Pyrex tube and heated at 315 °C for 19 h. The tube was cooled and opened, and the solid was collected, washed (2 × 5 mL pentane), and dried in vacuo to give 55 mg (complete removal of PE₃; would give 59 mg) of a dark gray solid. Powder X-ray diffraction (Cu Kα) showed only Cr₆Te₉.

Results

We sought convenient sources of reactive, low-valent chromium and two candidates emerged: (1) Jolly and co-workers reported recently that (Et₃P)₃CrCl₄ reacts with 2 equiv of CH₃MgCl to give (Et₃P)₃Cr(C₂H₅Cl), which decomposes at low temperature (15) in vacuo to give 55 mg (complete removal of PE₃; would give 59 mg) of a dark gray solid. Powder X-ray diffraction (Cu Kα) showed only Cr₆Te₉.

![Figure 1](image)

Figure 1. Molecular structure of Cr₆Te₉(PE₃)₆. (1). The unlabelled circles represent P atoms. The carbon and hydrogen atoms have been omitted for clarity.

(>70 °C), presumably to give a low-valent chromium species. (2) Ernst and co-workers have reported that bis(2,4-dimethylpentadienyl)chromium (Cr(DMPD)₂) reacts like “naked” chromium in the sense that the “open chromocene” gives Cr(Me₂PC₆H₄PMc₆)₂ and Cr(CN(t-C₅H₃)₃) when it is treated with Me₂PC₆H₄PMc₆ and CN(t-C₅H₃), respectively. We find that each of these candidates provides a functional equivalent of Cr(0) on reaction with triethylphosphine telluride and have found that each can be used in a molecule-based synthesis of solid-state chromium telluride. (One might imagine that Cr(CO₆) would be a good alternative source of Cr(0). We find Cr(CO₆) to be reluctant to react with the phosphine chalcogenides to give the corresponding extended solids. For a related study, see ref 18.)

A solution containing (Et₃P)₃Cr(C₅H₅)₂ in THF was prepared at low temperature by following a procedure similar to that described by Jolly and co-workers. A cooled solution of Et₃PMe in THF was added, and the mixture was allowed to warm to room temperature. Evaporation, extraction, and crystallization gave a compound which we subsequently identified as Cr₆Te₉(PE₃)₆(I; eq 1).

The same compound, I, can be prepared from the “open chromocene” Cr(DMPD)₂. When Cr(DMPD)₂, TePE₃, and PE₃ are combined in equimolar amounts in toluene, there is no apparent reaction at room temperature, but on being heated at reflux the initially deep green solution becomes dark brown and the hexanuclear cluster I can be isolated as a dark crystalline solid (eq 2). The product of eq 2 is identical in all respects to that formed in eq 1.

6Cr(C₅H₅)₂ + 8TePE₃ → Cr₆Te₉(PE₃)₆

We have determined the structure of I crystallographically, and a drawing of its structure is shown in Figure 1, with selected intramolecular bond distances and angles given in Table II. The cluster can be idealized as an octahedron of six Cr atoms concentric with a cube of eight Te atoms, with the structure being completed...
by a set of six PEt₃ ligands, one phosphine coordinated to each Cr. The edge Cr-Cr distance in the Cr₆ octahedron is 2.94 Å, and the edge Te-Te distance in the Te₈ cube is 3.74 Å. The Cr-P distance is in the normal range, 14 but the Cr-Cr distance, 2.652 Å, is shorter than those reported for other Cr-Te molecular compounds: 2.807 Å in [Cp(CO)₂Cr₄Te₈] and 2.726 Å in [CO₃(Cr₂Te₆)₅]2. The cluster compound also occasionally formed crystals that showed rhombohedral symmetry, and we solved the structure of this crystal modification as well. The molecular connectivity of Cr₆TE₆(PEt₃)₃ in this form is the same as that in the monoclinic modification. The interatomic distances and angles differ very slightly. (See Table II for the differences in average values and the supplementary material for the complete crystallographic information concerning the rhombohedral form of this compound.) We observed the rhombohedral material only rarely, and this made both the complete study of the rhombohedral compound (a) possible. In our study of molecules-to-solids processes, we are observing a general pattern: first, that the combination of low-valent complexes of various transition metals with TePEt₃ gives extended solid state metal tellurides, and, second, that polynuclear metal telluride molecular clusters form when the reaction conditions are appropriately tempered. In the present case, we also find the additional feature that the identical cluster, Cr₂Te₆(PEt₃)₉, results from the reaction of two different chromium reagents with TePEt₃, even though the reactions are conducted under different conditions. This emphasizes that there is particular stability, either kinetic or thermodynamic, connected with the cluster compound. When viewed in toto, these results suggest that there are significant correspondences to be found (and exploited) between the molecular clusters and associated extended solids. In this sense, the obvious solid-state relatives of Cr₆Te₆(PEt₃)₉ are Cr₂Te₆, the compound which results from the thermolysis of the cluster, and the family of solid metal chalcogenides known as Chevrel phases.

**Discussion**

In our study of molecules-to-solids processes, we are observing a general pattern: first, that the combination of low-valent complexes of various transition metals with TePEt₃ gives extended solid state metal tellurides, and, second, that polynuclear metal telluride molecular clusters form when the reaction conditions are appropriately tempered. In the present case, we also find the additional feature that the identical cluster, Cr₂Te₆(PEt₃)₉, results from the reaction of two different chromium reagents with TePEt₃, even though the reactions are conducted under different conditions. This emphasizes that there is particular stability, either kinetic or thermodynamic, connected with the cluster compound.

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The structure of Cr₂Te₆ is a distortion of the metal-deficient NiAs structure type 22 in which each Cr atom is central to a distorted octahedron of six Te atoms. In this solid, the average Cr-Te distance is 2.76 Å, significantly longer than the average Te-Te bonding distance in I (2.65 Å). Direct Te-Te bonding is important neither in the solid nor in the cluster: the shortest Te-Te distances in Cr₂Te₆ and I are 3.81 and 3.74 Å, respectively. The question of Cr-Cr bonding is not as clear-cut. The short

### Table II. Selected Interatomic Distances (Å) and Angles (deg) in Cr₆Te₆(PET₃)₉

<table>
<thead>
<tr>
<th></th>
<th>Cr₁-Te₁</th>
<th>Cr₁-Cr₁</th>
<th>Cr₁-P₁</th>
<th>Cr₁-Te₁-Te₂</th>
<th>Cr₁-Te₁-Te₄</th>
<th>Cr₁-Te₁-Te₃</th>
<th>Cr₁-Te₁-P₁</th>
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<tr>
<td><strong>Average values</strong></td>
<td>90.7</td>
<td>171.4</td>
<td>169.0(2)</td>
<td>60.0(2)</td>
<td>60.0(3)</td>
<td>60.0(2)</td>
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### Table II. Continued

<table>
<thead>
<tr>
<th></th>
<th>cr₁-cr₁</th>
<th>cr₁-te₁</th>
<th>cr₁-te₃</th>
<th>cr₁-te₄</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Average values</strong></td>
<td>90.0(2)</td>
<td>60.0(2)</td>
<td>60.0(2)</td>
<td>60.0(2)</td>
</tr>
</tbody>
</table>

### Notes

Cr-Cr distance is 3.09 Å in Cr₄Te₈ and 2.94 Å in 1. Both of these values are long compared to the nearest neighbor distance of 2.48 Å in elemental Cr; however, the extremes of Cr-Cr bonding distances are typified by [Cr(CO)₅]²⁺ and (COT)Cr₂. In the former case, interligand repulsion accounts for the very long (3.281 Å) single bond, and in the latter case, the short Cr-Cr distance (2.214 Å) is cited as evidence for a quadruple bond. The Cr-Cr distances of 3.09 Å in Cr₄Te₈ and 2.94 Å in Cr₄Te₆ are within this very generous range, and therefore direct Cr-Cr bonding is possible in each case.

In addition to bond length comparisons, other structural relationships can be found between Cr₄Te₈(PEt₃)₆ and Cr₄Te₆. These more complex relationships are very similar to those between elemental Cr. The Cr-Cr distances of 3.09 Å in Cr₄Te₈ and 2.94 Å in Cr₄Te₆ are within this very generous range, and therefore direct Cr-Cr bonding is possible in each case.

### Table III. Structural Comparison of M₄Te₈(PET₃)₆ (Å)²

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(M-Te)₀</td>
<td>2.65</td>
<td>2.52</td>
</tr>
<tr>
<td>d(M-Te)ᵡ</td>
<td>2.94</td>
<td>3.23</td>
</tr>
<tr>
<td>d(M-Te)‴</td>
<td>3.74</td>
<td>3.48</td>
</tr>
<tr>
<td>d(M-PET₃)</td>
<td>2.43</td>
<td>2.13</td>
</tr>
<tr>
<td>f₀ctahedron</td>
<td>2.08</td>
<td>2.28</td>
</tr>
<tr>
<td>f₀C₀ₖ</td>
<td>3.24</td>
<td>3.02</td>
</tr>
<tr>
<td>δ = displacement of M above Te plane</td>
<td>0.21</td>
<td>0.54</td>
</tr>
</tbody>
</table>

² From refs 5 and 6.

### Figure 2. Behavior of I in a magnetic field as a function of temperature.

The magnetization of the sample is represented by the small squares and the scale at the left. The effective magnetic moment derived from the magnetization data is given by the small triangles and the scale at the right. A constant diamagnetic background value has been subtracted to give Curie-Weiss law behavior at high temperature. The anomaly at approximately 60 K is due to a small amount of oxygen trapped in the magnetometer. The apparent decrease in μ eff at low temperature is under investigation.

The compounds are extended solid-state compounds built from Mo₆E₈ (E = S, Se, Te) units where the shape of each Mo₆E₈ unit is generally the same as the Mo₆E₈ cores of 1 and 2. The majority of Chevrel-type materials have Mo as the metallic element. Several examples involving other metals have been reported, although no Chevrel-type solids based on either Cr or W have appeared.

Structural studies of the Mo₆E₈ compounds imply not only Mo-E skeletal bonding but also substantial Mo-Mo bonding. In fact, discussions of the electronic structure of the Chevrel phases often are based on direct metal-metal covalent bonding. The length of the Cr-Cr bonds in 1 may indicate why Chevrel-type phases are not seen for chromium chalcogenides. The Cr-Cr bonding is certainly not strong in the cluster, and one can infer that it would not be strong in the Chevrel-type solid. This suggests that a Chevrel-type Cr₄Te₈ would convert to the known Ni₆As₆-type on heating. As a consequence preparative routes to a Chevrel-type Cr₄Te₈ must be mild to be successful.

The physical properties of 1 lead to some noteworthy comparisons. At room temperature, 1 absorbs light all across the visible region, giving a brown solution. The optical absorption spectrum does not show peaks; i.e., the optical density monotonically decreases from 300 to 800 nm. By contrast, the absorption spectra of Co₆E₈(PET₃)₆ (E = Te, Se) all show three distinct and pronounced peaks in the visible region. The compounds Mo₆E₈(PET₃)₆ show absorption peaks in the visible region and have more well-defined colors than does 1. We suggest that the featureless absorption shown by 1 is due to the long Cr-Cr bonds.

Static magnetic susceptibility measurements (Figure 2) show that 1 is paramagnetic, having μ eff = 2.8 μ B (corresponding to two parallel electronic spins if the paramagnetism is due to spin alone) from 100 to 300 K. Although a detailed description of the electronic structure which leads to this moment is wanting, we

### References


(38) In the Chevrel phases, the solid frame actually distorts each Mo₆E₈ cluster to D₅h symmetry, thereby leading to two intraclad Mo-Mo bond lengths. In Mo₆Se₈, the two intraclad Mo-Se lengths are 2.836 and 2.684 Å. We cite only the shorter.
note that, with 84 valence electrons (6 from each Cr and 6 from each Te), the Cr$_6$Te$_8$ core of 1 is predicted to have a triplet ground state according to the very simple “quasi-atomic” prescription of Bacci. The clusters Mo$_6$E$_8$(PET$_3$)$_6$ (E = S (3), Se, (4)) are reported to be diamagnetic, and since 3 and 4 have the same number of valence electrons as 1, the magnetic susceptibilities of 3 and 4 do not conform to the model proposed by Bacci. We presume that this difference also is based on weaker and less localized M-M bonding in 1 than in 3 and 4.

The solid-state compound Cr$_3$Te$_4$ that is made vía traditional solid state synthesis is ferromagnetic. The Cr$_3$Te$_4$ we prepare from 1 is also ferromagnetic. It is valuable to determine if the paramagnetism of 1 is related to the ferromagnetism of the pyrolysate, and work on this topic is in progress.

We continue to investigate the chemical reactivity of 1. One feature of note is its thermal stability. The compound does not appear to change at all even after prolonged heating in solution and can be recovered essentially quantitatively after 18 h in refluxing toluene. The thermal stability of 1 was assayed as follows: Cr$_6$Te$_8$(PET$_3$)$_6$ (51 mg, 0.025 mmol) was dissolved in toluene (5 mL), and the solution was heated at reflux for 18 h.

The mixture appeared homogeneous, and filtration through a medium-porosity glass frit removed no solid. The solution was evaporated to dryness, and the resulting solid was washed with pentane and dried to give 48 mg of a polycrystalline solid whose X-ray powder diffraction pattern was that of 1.

When Cr(DMPD)$_2$, TePET$_3$, and PET$_3$ are combined under similar conditions, varying large amounts of insoluble solid are formed (see above). It is important to determine whether the insoluble solid so formed is an unrelated side product or a solid to which 1 can be converted by the action of an appropriately chosen coreagent. If the latter is the case, it suggests an alternative way to make extended solids out of molecular clusters.

**Acknowledgment.** We gratefully acknowledge Paula Trevor for the collection and interpretation of X-ray fluorescence data.

**Supplementary Material Available:** Tables S1-S4, giving crystallographic data collection information, final positional parameters, thermal parameters, and complete interatomic distances and angles for the monoclinic form of 1, Tables S5-S7, giving crystallographic data collection information, positional and thermal parameters, and complete interatomic distances and angles for the rhombohedral form of 1, and ORTEP diagrams of the molecular structure of 1 in the monoclinic crystal and in the rhombohedral crystal (20 pages). Ordering information is given on any current masthead page.