$Cr_6Te_8(PEt_3)_6$ and a Molecule-Based Synthesis of Cr_3Te_4

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The molecular cluster compound $Cr_6Te_8(PEt_3)_6$ (**1**) is formed by the reaction of $TePEt_3$ with either $(Et_3P)_2Cr(allyl)_2$ or Cr(2,4-dimethylpentadienyl)$_2$. This compound can be converted to the extended inorganic solid state compound Cr_3Te_4 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, $\beta = 105.21(5)°$, $V = 6276(10)$ Å^3, $Z = 4$). The molecule is formed by a Cr_6 octahedron, a Te_8 cube, and a $(PEt_3)_6$ 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.[1–7] 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 later transition metals owing to the availability of low-valent complexes of those metals. Inasmuch as the earlier transition metals are harder Lewis acids, we have been curious how far to the left in the transition series this simple molecules-to-solids prescription may be pushed. Herein we report the extension of these investigations to the case of chromium.

We find that low-valent chromium species react with triethylphosphine telluride to form the cluster compound $Cr_6Te_8(PEt_3)_6$ (**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 Cr_3Te_4.

Experimental Section

Unless noted to the contrary, all manipulations were conducted under inert atmosphere using conventional techniques. Triethylphosphine (Aldrich), allyl magnesium 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.[8] Bis(2,4-dimethylpentadienyl)chromium was prepared by the method of Ernst and co-workers.[9,10] Magnetic susceptibility measurements were made on a SQUID magnetometer using standard techniques.

Preparation of $Cr_6Te_8(PEt_3)_6$, 1. (A) A solution of $(Et_3P)_2CrCl_2$ was prepared from $CrCl_2$ (0.59 g, 4.8 mmol) and PEt_3 (1.13 g, 9.6 mmol) in THF (25 mL). This was cooled to −80 °C and treated with C_3H_5MgCl (4.8 mL of 2.0 M solution in THF). After approximately 15 min, a solution of $TePEt_3$ in THF (1.57 g in 15 mL) was added dropwise. The mixture was allowed 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 $TePEt_3$ (3.12 g, 12.7 mmol) and PEt_3 (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 Cr(DMPD)$_2$ 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(DMPD)$_2$ to $TePEt_3$ of 3:4 the same percent yield was realized.

Anal. Calcd for $C_{36}H_{90}Cr_6P_6Te_8$: 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 μ_B per cluster.

Solution-Phase Cothermolysis of $Cr(C_7H_{11})_2$ and $TePEt_3$. $Cr(C_7H_{11})_2$ (0.23 g, 0.95 mmol) dissolved in toluene (10 mL) was treated with $TePEt_3$ (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

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Table I. Crystallographic Data for $Cr_6Te_8(PEt_3)_6$ (Monoclinic Form)

empirical formula	$Cr_6Te_8P_6C_{36}H_{90}$	Z	4
fw	2041.73	T	23 °C
space group	$I2/a$	ρ_{calc}	2.162 g/cm^3
a	13.03(2) Å	μ	4.81 mm^{-1}
b	21.129(5) Å	γ	0.709 30 Å Mo Kα
c	23.618(8) Å	R^a	0.040
β	105.21(5)°	$R_w{}^b$	0.041
V	6276(10) Å^3		

^{a} $R = [\Sigma(F_o - F_c)]/[\Sigma F_o]$. ^{b} $R_w = [\Sigma w(F_o - F_c)^2]/[\Sigma(wF_o^2)]$.

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 Cr_3Te_4.[11]

Crystallographic Determination of the Structure of $Cr_6Te_8(PEt_3)_6$. A. Monoclinic Crystal. Crystals of **1** 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.[12] The collected data are summarized in Table I. Calculations were performed on an Alliant FX/80 computer using the NRCVAX program package.[13] 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 PEt_3 ligands exhibits orientational disorder of the ethyl substituents. This was modeled using 12 carbon atom positions with half-occupancy. The heavy atoms (Cr, Te, and P) were refined using anisotropic temperature factors.

B. Rhombohedral Crystal. A crystal of the same molecular material was mounted as above and found to have rhombohedral rather than monoclinic symmetry. Diffraction data were collected and analyzed as above. (Details of this crystallography are included in the supplementary material.) The molecular structure of this material is essentially identical to that of the monoclinic sample. The crystal structure differs only in how the $Cr_6Te_8(PEt_3)_6$ units pack. The rhombohedral crystals decayed quickly in the X-ray beam. This led to a large number of reflections being unobserved (approximately 50% observed) and, consequently, to poor R values.

Pyrolysis of $Cr_6Te_8(PEt_3)_6$. We examined the thermal behavior of solid samples of $Cr_6Te_8(PEt_3)_6$ 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: $Cr_6Te_8(PEt_3)_6$ (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 PEt_3 would give 59 mg) of a dark gray solid. Powder X-ray diffraction (Cu Kα) showed only Cr_3Te_4.[11]

Results

We sought convenient sources of reactive, low-valent chromium and two candidates emerged: (1) Jolly and co-workers reported recently[14] that $(Et_3P)_2CrCl_2$ reacts with 2 equiv of C_3H_5MgCl to give $(Et_3P)_2Cr(C_3H_5)_2$, which decomposes at low temperature (>−70 °C), presumably to give a low-valent chromium species. (2) Ernst and co-workers have reported[15-17] that bis(2,4-dimethylpentadienyl)chromium ($Cr(DMPD)_2$) reacts like "naked" chromium in the sense that the "open chromocene" gives $Cr(Me_2PC_2H_4PMe_2)_3$ and $Cr(CN(t\text{-}C_4H_9))_6$ when it is treated with $Me_2PC_2H_4PMe_2$ and $CN(t\text{-}C_4H_9)$, 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 $Cr(CO)_6$ would be a good alternative source of Cr(0). We find $Cr(CO)_6$ to be reluctant to react with the phosphine chalcogenides to give the corresponding extended solids. For a related study, see ref 18.)

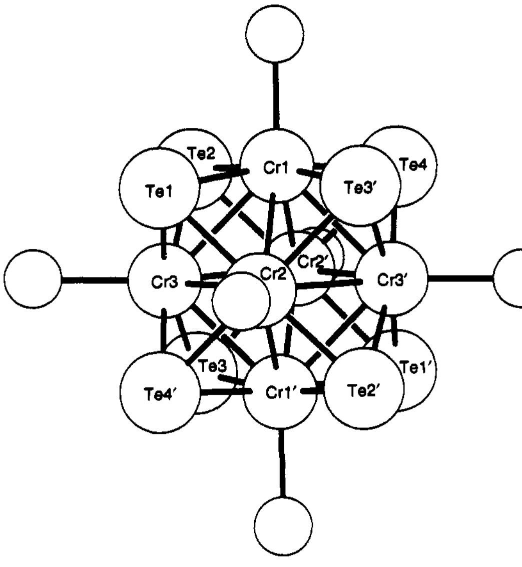

Figure 1. Molecular structure of $Cr_6Te_8(PEt_3)_6$ (**1**). The unlabeled circles represent P atoms. The carbon and hydrogen atoms have been omitted for clarity.

A solution containing $(Et_3P)_2Cr(C_3H_5)_2$ in THF was prepared at low temperature by following a procedure similar to that described by Jolly and co-workers.[14] A cooled solution of Et_3PTe 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 $Cr_6Te_8(PEt_3)_6$ (**1**; eq 1).

$$6(Et_3P)_2Cr(C_3H_5)_2 + 8TePEt_3 \rightarrow Cr_6Te_8(PEt_3)_6 \quad (1)$$

The same compound, **1**, can be prepared from the "open chromocene" $Cr(DMPD)_2$. When $Cr(DMPD)_2$, $TePEt_3$, and PEt_3 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 **1** 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.

$$6Cr(C_7H_{11})_2 + 8TePEt_3 + PEt_3(\text{excess}) \rightarrow Cr_6Te_8(PEt_3)_6 \quad (2)$$

We have determined the structure of **1** 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

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Table II. Selected Interatomic Distances (Å) and Angles (deg) in $Cr_6Te_8(PEt_3)_6$[a]

Cr1–Te1	2.653(3)	Cr2–Te1	2.647(3)	Cr3–Te1	2.655(5)
Cr1–Te2	2.662(4)	Cr2–Te2′	2.639(3)	Cr3–Te2	2.655(3)
Cr1–Te3′	2.648(3)	Cr2–Te3′	2.649(4)	Cr3–Te3	2.657(4)
Cr1–Te4	2.651(3)	Cr2–Te4′	2.653(4)	Cr3–Te4′	2.652(3)
Cr1–Cr2	2.945(5)	Cr2–Cr1	2.945(5)	Cr3–Cr1	2.896(5)
Cr1–Cr2′	2.939(4)	Cr2–Cr1′	2.939(4)	Cr3–Cr1′	2.943(4)
Cr1–Cr3	2.896(5)	Cr2–Cr3	2.953(4)	Cr3–Cr2	2.953(4)
Cr1–Cr3′	2.943(3)	Cr2–Cr3′	2.935(4)	Cr3–Cr2′	2.935(4)
Cr1–P1	2.428(6)	Cr2–P2	2.436(5)	Cr3–P3	2.435(5)

	av values			av values			av values	
	monoclinic	rhombohedral		monoclinic	rhombohedral		monoclinic	rhombohedral
d(Cr–Te)	2.652	2.668	*d*(Cr–Cr)	2.935	2.979	*d*(Cr–P)	2.433	2.435

		Angles around Cr1[b]			
Te1–Cr1–Te2	91.18(7)	Te1–Cr1–Te4	171.7(1)	Te1–Cr1–P1	93.0(2)
Te1–Cr1–Te3′	89.40(7)	Te2–Cr1–Te3′	171.1(1)	Te2–Cr1–P1	96.2(2)
Te2–Cr1–Te4	89.20(8)			Te3–Cr1–P1	92.7(2)
Te3′–Cr1–Te4	88.96(8)			Te4–Cr1–P1	95.1(2)
averages	89.7		171.4		94.3
(av_{rhomb}	87.9(2)		169.0(2)		88.1(2))
Cr2–Cr1–Cr2′	91.0(1)	Cr2–Cr1–Cr3	60.7(1)		
Cr3–Cr1–Cr3′	90.1(1)	Cr2–Cr1–Cr3′	59.8(1)		
		Cr2′–Cr1–C3	60.4(1)		
		Cr2′–Cr1–Cr3′	60.3(1)		
(av_{rhomb}	90.0(2)		60.0(3))		
		Angles around Te1[c]			
Cr1–Te1–Cr2	67.4(1)	Cr2–Te1–Cr3	67.2(1)	(av_{rhomb}	67.9(1.3))
Cr1–Te1–Cr3	66.1(1)				

[a] Values are for the monoclinic modification unless noted otherwise. [b] The angles around Cr2 and Cr3 are similar. [c] The angles around Te2, Te3, and Te4 are similar.

by a set of six PEt_3 ligands, one phosphine coordinated to each Cr. The edge Cr-Cr distance in the Cr_6 octahedron is 2.94 Å, and the edge Te–Te distance in the Te_8 cube is 3.74 Å. The Cr–P distance is in the normal range;[14] however, the Cr–Te distance, 2.652 Å, is shorter than those reported for other Cr–Te molecular compounds: 2.807 Å in $[Cp(CO)_3Cr]_2Te$,[19] 2.726 Å in $[(CO)_4CrTe_4]^{3-}$,[20] and 2.719 Å in $[Cr_3Te_{24}]^{3-}$.[21]

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 $Cr_6Te_8(PEt_3)_6$ 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 modification and a complete comparison of the two forms of $Cr_6Te_8(PEt_3)_6$ difficult. It is interesting to note in passing that the calculated volume per cluster for the rhombohedral form of **1** is approximately 10% larger than that for the monoclinic form. We saw no evidence to suggest that the voids implied by the larger calculated volume per cluster were filled with solvent; however, we cannot exclude that possibility. Whether the voids were filled or empty, we believe that the decay of the diffraction from the rhombohedral crystals is due to the metastable crystals crumbling in the attempt to pack the clusters more closely.

When $Cr(DMPD)_2$ and $TePEt_3$ were combined in a 3:4 molar ratio in the absence of additional PEt_3 and heated at reflux in toluene for an extended period, a dark, insoluble material formed. We have not analyzed this material *per se*, but the subsequent annealing of this amorphous solid yielded polycrystalline Cr_3Te_4. The same solid-state compound is the result of the direct thermolysis of $Cr_6Te_8(PEt_3)_4$. These results establish that $TePEt_3$ can be used in conjunction with either $Cr(PEt_3)_2(C_3H_5)_2$ or $Cr(DMPD)_2$ to yield solid-state tellurides of chromium.

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[1-7] with $TePEt_3$ 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, $Cr_6Te_8(PEt_3)_6$, results from the reaction of two different chromium reagents with $TePEt_3$, 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 $Cr_6Te_8(PEt_3)_6$ are Cr_3Te_4, the compound which results from the thermolysis of the cluster, and the family of solid metal chalcogenides known as Chevrel phases.

The structure of Cr_3Te_4 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,[11] significantly longer than the average Cr–Te bonding distance in **1** (2.65 Å). Direct Te–Te bonding is important neither in the solid nor in the cluster: the shortest Te-Te distances in Cr_3Te_4 and **1** are 3.81 and 3.74 Å, respectively. The question of Cr–Cr bonding is not as clear-cut. The short

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Table III. Structural Comparison of $M_6Te_8(PEt_3)_6$ (Å)[a]

	Cr	Co
d(M–Te)$_{av}$	2.65	2.52
d(M–M)$_{av}$	2.94	3.23
d(Te–Te)$_{av}$	3.74	3.48
d(M–P)$_{av}$	2.43	2.13
$r_{octahedron}$	2.08	2.28
r_{cube}	3.24	3.02
δ = displacement of M above Te_4 plane	0.21	0.54

[a] From refs 5 and 6.

Cr–Cr distance is 3.09 Å in Cr_3Te_4[11] 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 $[Cp(CO)_3Cr]_2$[23] and $(COT)_3Cr_2$.[24] 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 Cr_3Te_4 and 2.94 Å in **1** 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 $Cr_6Te_8(PEt_3)_6$ and Cr_3Te_4. These more complex relationships are very similar to those between the analogous compounds $Co_6Te_8(PEt_3)_6$ and Co_3Te_4. We have described the latter in detail in earlier publications[5,6] and will not repeat those discussions here.

$Cr_6Te_8(PEt_3)_6$ is the most recent member of the $M_6E_8L_6$ (M = transition metal, E = chalcogen, L = donor ligand) family of cluster compounds.[25–32] In order to appreciate the structure and bonding in **1**, it is instructive to it compare to other members of the M_6E_8 series. Arguably, the closest relative of **1** is $Co_6Te_8(PEt_3)_6$ (**2**), the only other reported example of a molecular M_6Te_8 cluster. The two clusters are compared in Table III. The most apparent feature is that the effective size of the Cr atoms is larger than that of the Co atoms. This is shown by both the M–P distances and the M–Te distances and is expected on the basis of normal atomic radii.

Since the Cr–Te bonds in **1** are more than 0.1 Å longer than the Co–Te bonds in **2**, one might expect that the M_6Te_8 core of **1** would be simply an expanded version of the core of **2**, but this is not the case. Although the Te_8 cube in **1** is larger than that in **2**, the Cr_6 octahedron is significantly smaller than the Co_6 octahedron. (It is an equivalent statement that the $CrTe_4$ segments in **1** are closer to being planar than are the $CoTe_4$ segments in **2**. The deviations from planarity are quantified by "δ" in Table III.) The contraction of the M_6 octahedron in **1** relative to **2** must be due to the presence of Cr–Cr bonding in **1** and the absence of Co–Co bonding in **2**.

The presence or absence of Cr–Cr bonding bears on a comparison of **1** to the Chevrel phases.[33–35] The Chevrel phase compounds are extended solid-state compounds built from Mo_6E_8 (E = S, Se, Te) units where the shape of each Mo_6E_8 unit is generally the same as the M_6E_8 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[36–38] although no Chevrel-type solids based on either Cr or W have appeared.

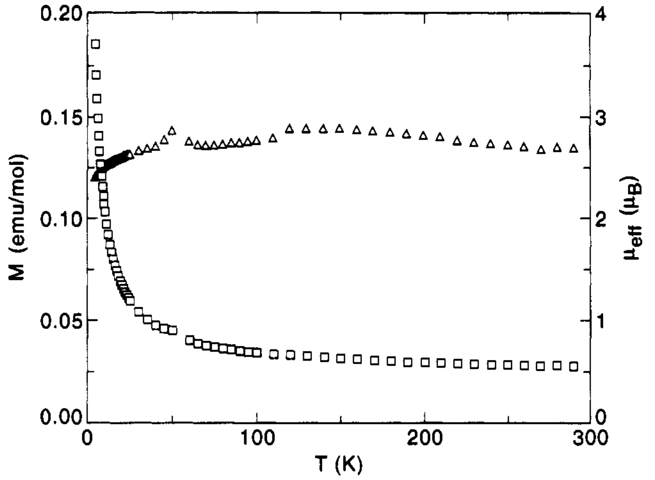

Figure 2. Behavior of **1** in a magnetic field as a function of temperature. The magnetization of the sample is represented by the small squares and the scale at the left. The effective magnetic moment derived from the magnetization data is given by the small triangles and the scale at the right. A 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.

Structural studies of the Mo_6E_8 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.[34,35,39,40] 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 Cr_3Te_4 would convert to the known NiAs-type on heating. As a consequence preparative routes to a Chevrel-type Cr_3Te_4 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 $Co_6E_8(PEt_3)_6$ (E = Te, Se, S)[41] all show three distinct and pronounced peaks in the visible region. The compounds $Mo_6E_8(PEt_3)_6$ 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

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note that, with 84 valence electrons (6 from each Cr and 6 from each Te), the Cr_6Te_8 core of **1** is predicted to have a triplet ground state according to the very simple "quasi-atomic" prescription of Bacci.[42] The clusters $Mo_6E_8(PEt_3)_6$ (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_3Te_4 that is made *via* traditional solid state synthesis is ferromagnetic.[11,43] The Cr_3Te_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: $Cr_6Te_8(PEt_3)_6$ (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, varyingly 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.

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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.

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