

solids were handled under an atmosphere of nitrogen gas. Samples of $B_4H_8 \cdot PH_3$ were prepared in reaction tubes, as needed, by the published method.⁴ A commercial sample of $NaBH_4$ (Alfa Products) was purified by extracting with ammonia. Tetrahydrofuran and diethyl ether were refluxed and distilled over $LiAlH_4$ and stored over molecular sieves. A Varian XL-300 NMR spectrometer was used for the ^{11}B (96.2 MHz) and ^{31}P (121.4 MHz) spectral acquisitions. The ^{11}B chemical shift values for $B_4H_8 \cdot PH_3$,⁴ $BH_3 \cdot PH_3$,^{10c} $B_2H_7^-$,¹¹ $BH_3 \cdot THF$,^{10b} and BH_4^- ^{10c} are found in the respective references cited, and these were used to identify the components in the reaction mixtures.

Reaction of $B_4H_8 \cdot PH_3$ with $NaBH_4$. A 1.12-mmol sample of $B_4H_8 \cdot PH_3$ was treated with a 4.88-mmol sample of PH_3 in a 22 mm o.d. Pyrex reaction tube, which was equipped with a Teflon valve, to prepare a sample of $B_4H_8 \cdot PH_3$. Then, a 3-mL sample of tetrahydrofuran was condensed into the tube to dissolve the $B_4H_8 \cdot PH_3$ at $-80^\circ C$. The solution was frozen at $-197^\circ C$, nitrogen gas was admitted into the tube, and a 4.63-mmol sample of $NaBH_4$ was introduced into the reaction tube through a side arm that had been provided at the upper end of the tube. The side arm was then sealed, and the tube was reevacuated and allowed to warm. At $-80^\circ C$, slow bubbling of a gas (H_2) was seen. At $-45^\circ C$, the bubbling was rapid. When the bubbling stopped (total 30 min), a total of 0.52 mmol of H_2 gas was collected. Volatile components in the tube were then distilled out, first at $-45^\circ C$ and finally at $0^\circ C$, to leave a white solid residue. To the volatile components that were collected was added a sample of $N(CH_3)_3$ (in a large excess). The mixture was warmed to $0^\circ C$ to convert any BH_3 adduct in the mixture to $BH_3 \cdot N(CH_3)_3$. Phosphine and $BH_3 \cdot N(CH_3)_3$ were separated from this mixture, and their quantities were measured to be 0.53 and 0.58 mmol, respectively. The solid residue in the original reaction tube was leached with diethyl ether. From the leachate, 85.9 mg of a white solid [0.54 mmol as $Na[PH_2 \cdot 2B_4H_8]$] was obtained by pumping out the solvent ether. The diethyl ether insoluble component was $NaBH_4$.

The NMR spectra of the reaction mixtures at various stages of the reaction process were obtained by preparing the reaction mixtures in 12-14 mm o.d. Pyrex tubes. These tubes were placed in the cold probe of the spectrometer for spectrum recording. The amounts of $B_4H_8 \cdot PH_3$ used for these experiments were 0.3-0.5 mmol. The diethyl ether solution of $Na[PH_2 \cdot 2B_4H_8]$ for the NMR study was prepared by leaching the initial product residue with diethyl ether directly into a 12 mm o.d. Pyrex tube.

Acknowledgment. This work was supported by the U.S. Army Research Office through Grants DAAG 29-81-K-0101 and 29-85-K-0034.

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Magnetic Properties of Linear Chromium(III) Trimeric Clusters: $[(C_6H_5)_4P]_3[Cr_3Te_{24}]$ and $[(C_6H_5)_4P]_3[Cr_3Se_{24}]$

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The chemistry of binary metal polyselenides and polytellurides is considerably less well-known than that of the metal polysulfides.² However, recent work has shown that reaction of metal salts with polychalcogen sources under anhydrous conditions can generate a wide variety of soluble binary metal polyselenides and polytellurides.³⁻⁷

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Following the recent report of the preparation and characterization of salts of two novel clusters having the formulas $[Cr_3Se_{24}]^{3-}$ and $[Cr_3Te_{24}]^{3-}$,⁸ we have undertaken the magnetic characterization of these compounds. Both compounds have three chromium(III) ions linked in a linear fashion by bridging tetra-chalcogenide chelates. These compounds are structurally similar to another linear cluster containing three chromium(III) ions and bridging chelate ligands.⁹ Clusters such as these are under scrutiny as potential precursors to metal chalcogenide polymers.¹⁰

Given the current interest in systems with several magnetically active metal centers bridged by chalcogen atoms,^{11,12} as well as the lack of data on selenide and telluride bridging groups, we have undertaken magnetochemical measurements of these systems. In this paper, we report the results of low-temperature magnetic measurements of these systems using a SQUID susceptometer, as well as analysis of this data using the linear trimer Heisenberg exchange model.

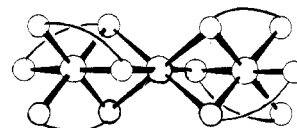
Experimental Section

Magnetic susceptibility data were recorded with an SHE Corp. VTS superconducting SQUID susceptometer. The sample bucket was fabricated from an Al-Si alloy obtained from the SHE Corp. The magnetic susceptibility of the sample bucket was measured independently over the temperature range 8-300 K, and the magnetic data for all samples were then corrected for the bucket contribution. Magnetic data were recorded on polycrystalline samples weighing 50 mg or so, which were packed into the buckets with tightly sealed caps in an argon-filled glovebox containing less than 1 ppm of oxygen. The samples were measured at 5 kOe. Measurement and calibration procedures are reported elsewhere.¹³

The magnetic susceptibility corrected for diamagnetism by using Pascal's constants is plotted as trimer susceptibility (i.e., three Cr^{III} ions per molecule) as a function of temperature. The diamagnetic corrections for the selenide and telluride complexes are 0.001 239 and 0.001 582 emu/mol, respectively.

Results and Discussion

The preliminary crystal structure data published previously⁸ has shown the selenide and telluride analogues ($[Cr_3X_{24}]^{3-}$) have the same molecular structure. A ball and stick diagram that shows the molecular geometry as well as the coordination of the six Te_4^{2-} chelates is shown in 1. The selenide and telluride analogues are



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similar, although they crystallize in distinctly different unit cells. Each structure contains a linear arrangement of three chromium(III) ions. The terminal metals are octahedrally chelated by three E_4^{2-} groups while a coordinated atom from each E_4^{2-} chain

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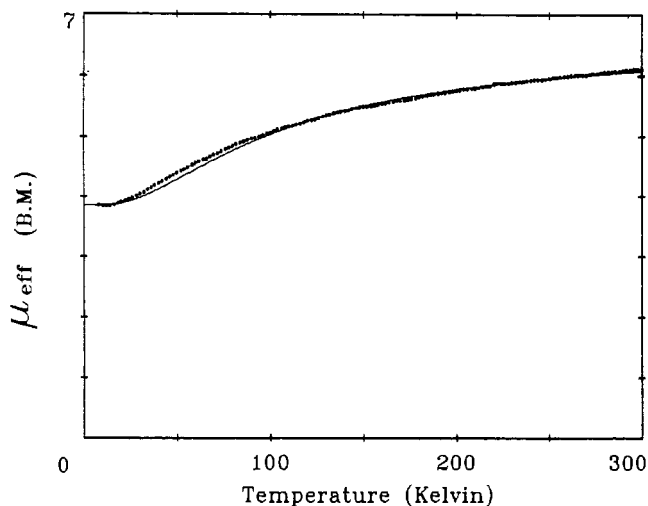


Figure 1. Effective magnetic moment ($\mu_{\text{eff}} = (8\chi T)^{1/2}$) plotted as a function of temperature for $[(\text{C}_6\text{H}_5)_4\text{P}]_3[\text{Cr}_3\text{Te}_{24}]$. The smooth curve drawn through the points is the least-squares fit of the data using eq 3 as described in the text.

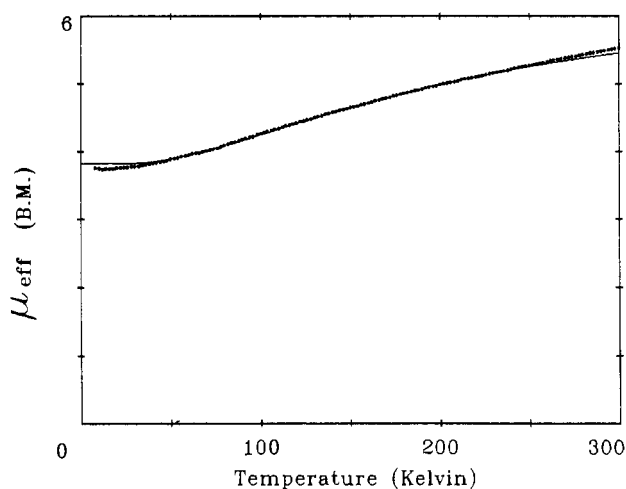


Figure 2. Effective magnetic moment ($\mu_{\text{eff}} = (8\chi T)^{1/2}$) plotted as a function of temperature for $[(\text{C}_6\text{H}_5)_4\text{P}]_3[\text{Cr}_3\text{Se}_{24}]$. The smooth curve drawn through the points is the least-squares fit of the data using eq 3 as described in the text.

also bridges to the central metal atom. Thus the central chromium is also octahedrally coordinated but by six bridging chalcogenide atoms. The chromium(III) ions are too far apart to be considered to have any significant metal-metal interaction. The chromium-chromium distances are 3.207 (1) and 3.41 (1) Å for the selenide and telluride respectively.⁸ The propagation of magnetic exchange occurs via the bridging chalcogenide ligand. The bridging angles average 77.8 (4) and 77.3 (2)° for the selenide and telluride, respectively.⁸

The magnetic susceptibility data for the two complexes are shown in Figures 1 and 2 as the effective magnetic moment (μ_{eff}) plotted as a function of temperature.

The general feature of the magnetic data for both complexes is approximate for a trimer with dominant antiferromagnetic exchange within the chromium(III) trimeric unit. Thus the temperature dependence of the reciprocal susceptibility follows the Curie-Weiss Law at high temperatures ($T > 160$ K for the telluride and $T > 200$ K for the selenide), exhibits non-Curie-Weiss behavior at intermediate temperatures, and again exhibits Curie-Weiss behavior at the lowest temperatures, but with a reduced effective spin value. The magnetic susceptibility data in the high- and low-temperature limits were fit with the Curie-Weiss expression

$$\chi = \frac{C}{T - \theta} = \frac{Ng^2\mu_B^2S(S+1)}{3k(T - \theta)} \quad (1)$$

Table I. Magnetic Parameters for $[(\text{C}_6\text{H}_5)_4\text{P}]_3[\text{Cr}_3\text{Te}_{24}]$ and $[(\text{C}_6\text{H}_5)_4\text{P}]_3[\text{Cr}_3\text{Se}_{24}]$

Curie-Weiss Parameters				
compd	T , K	θ , K	C , (emu K)/mol	g
$[\text{Cr}_3\text{Te}_{24}]^{3-}$	180-300	-93.47	2.03	2.08
	8-20	-0.24	1.91	2.02
$[\text{Cr}_3\text{Se}_{24}]^{3-}$	200-300	-167.34	1.93	2.03
	8-20	0.00	1.76	1.94
Trimer Parameters				
compd	T , K	J/k , K	J'/k , K	g
$[\text{Cr}_3\text{Te}_{24}]^{3-}$	8-300	-5.3	1.44	1.99
$[\text{Cr}_3\text{Se}_{24}]^{3-}$	8-300	-10.8	3.5	1.98

where $S = 3/2$ for chromium(III) and all of the other parameters have their usual meaning. The least-squares-fitted parameters are listed in Table I. The high-temperature Curie constant and g values are averages for the three chromium(III) ions of the trimeric unit, while the low-temperature values are for the trimer as a whole.

From the Curie-Weiss relationship with $S = 3/2$ for each of the three Cr^{III} ions, an average of the three g values of 2.08 is obtained for the telluride analogue. At 300 K, the magnetic moment is $6.18 \mu_B$ per trimer or $3.57 \mu_B$ per chromium(III) ion, which is only slightly less than the value $3.87 \mu_B$ observed for Cr^{III} systems without magnetic coupling. This indicates that the magnetic coupling in the telluride complex is not strong enough to significantly depopulate the higher energy magnetic energy levels at high temperatures. The magnetic moments decrease slowly as temperatures decrease to 16 K. Below 16 K, the magnetic moment varies little with the temperature and is $3.85 \mu_B$ per trimer, which is appropriate for a system with a spin $3/2$ ground state. That is, the three spins $S = 3/2$ of the chromium(III) ions have coupled together to yield a single spin $S = 3/2$ for the trimer molecule as a whole in the strong antiferromagnetic exchange interaction limit. At low temperatures ($T < 20$ K), the temperature dependence of the reciprocal susceptibility is linear and the data extrapolate to a Weiss constant θ of -0.27 K. The source of this Weiss constant is probably a zero-field splitting of the $S = 3/2$ trimer ground state. The depopulation of high-spin paramagnetic states to low-spin paramagnetic states for a linear trimeric material is observed in some other linear trimer systems of the transition metals, for example, $\text{Cr}_3(\text{C}_{17}\text{H}_{12}\text{O}_3)_2(\text{H}_2\text{O})_3(\text{O}-\text{H})_5^{14}$ and $(\text{C}_5\text{N}_5\text{H}_6)_2\text{Cu}_3\text{Cl}_8 \cdot 4\text{H}_2\text{O}^{15}$.

The general feature of the magnetic data for $[(\text{C}_6\text{H}_5)_4\text{P}]_3[\text{Cr}_3\text{Se}_{24}]$ is essentially the same as that for the telluride analogue, except that the magnetic coupling is stronger. At 300 K, the magnetic moment for the selenide complex is $3.20 \mu_B$, which is significantly lower than that found for the telluride complex, indicating stronger antiferromagnetic exchange interaction between neighbors and a much greater depopulation of excited magnetic energy levels. Thus, the reciprocal susceptibility versus temperature becomes linear only above 200 K. Similarly to the telluride, the selenide has a value of the magnetic moment, $3.76 \mu_B$ per trimer at low temperatures, corresponding to a spin $3/2$ ground state.

We have fit the magnetic susceptibility data over the entire temperature range to a theoretical model using the trimeric spin Hamiltonian

$$\mathcal{H} = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3) - 2J' \mathbf{S}_1 \cdot \mathbf{S}_3 \quad (2)$$

By use of the spin product basis set of wave functions ($\Psi = |m_{S1}, m_{S2}, m_{S3}\rangle$), a total of 64 wave functions are obtained. The action of the spin Hamiltonian (eq 2) on these wave functions yields 12 energy levels distributed with coupled spin quantum numbers as follows: $S_T = 9/2$ (1), $7/2$ (2), $5/2$ (3), $3/2$ (4), $1/2$ (2), where the numbers in parentheses represent the degeneracies of

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the S_T states with the corresponding quantum number. The energy levels were determined by diagonalizing the H_{ij} matrix ($H_{ij} = \langle \Psi_i | \mathcal{H} | \Psi_j \rangle$). The diagonalization was simplified by block-factoring the matrix into M_{ST} submatrices, where $M_{ST} = m_{S1} + m_{S2} + m_{S3}$. The magnetic susceptibilities of the trimer were calculated from the spin-coupled wave functions by using a simplified form of the Van Vleck equation¹⁶

$$\chi = N \frac{\sum_{i=1,n} \frac{|\langle \Psi_i | \hat{\mu} | \Psi_i \rangle|^2}{kT} e^{-E_i/kT}}{\sum_{i=1,n} e^{-E_i/kT}} \quad (3)$$

where E_i is the energy of the energy level with wave function Ψ_i and $\hat{\mu}$ is the moment operator ($\hat{\mu} = g\mu_B \hat{S}_z$).

The results of a least-squares fit of the magnetic data are illustrated in Figures 1 and 2 as plots of the effective magnetic moment ($\mu_{\text{eff}} = (8\chi T)^{1/2}$) for the selenide and telluride complexes, respectively. The smooth curves drawn through the points represent the best fit of the trimer model using the fitted parameters listed in Table I.

It is concluded that the nearest-neighbor chromium centers are antiferromagnetically coupled following the symmetric linear trimer model with a quartet ground state for both complexes. The magnetic coupling is sufficiently strong that the highest energy

levels are not fully populated in the accessible temperature range and the high-temperature moment is less than the normal value associated with chromium(III). The lowest temperature data however are consistent with the coupled total spin of $S = 3/2$ for the trimer as a whole. The selenide complex has a significantly stronger antiferromagnetic exchange when compared with the tellurium analogue, but this could be attributed to the closer bonding proximity of the chromium(III) ions in the selenide complex (Cr1–Cr2 distance of 3.207 Å for the selenide and 3.41 Å for the telluride). Attempts to fit the magnetic data to a model that neglected the J' coupling term (i.e., coupling between the two outer Cr^{III} ions) gave inferior results. Other authors have often used a biquadratic term to analyze chromium(III) dimer systems.¹⁷ This term was not needed for our analysis, since we obtained acceptable fits with the unmodified spin Hamiltonian given (eq 2). Any improvement of the fit that would occur upon the addition of more terms to the spin Hamiltonian could be attributed to overparameterization.

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Additions and Corrections

1989, Volume 28

Robert L. Blackburn and Joseph T. Hupp*: Electron-Transfer Reactions in Mixed Solvents. An Electrochemical Probe of Unsymmetrical Selective Solvation.

Page 3788. The caption to Figure 3 is incorrect. The correct caption is as follows: E_f vs solvent composition ($\text{CH}_3\text{CN} + \text{DMSO}$ mixtures) for reduction of (a) $\text{Ru}(\text{bpy})_3^{3+}$, (b) $(\text{NH}_3)_2\text{Ru}(\text{bpy})_2^{3+}$, (c) $(\text{NH}_3)_4\text{Ru}(\text{bpy})^{3+}$, (d) $(\text{NH}_3)_5\text{Ru}(\text{py})^{3+}$, and (e) $\text{Ru}(\text{NH}_3)_6^{3+}$.—Joseph T. Hupp