

mg of sodium carbonate was added, and the mixture was heated to reflux under dinitrogen atmosphere for 2 h. The reaction mixture was allowed to cool to room temperature. After evaporation of the solution to ~5 mL, red-violet crystals started depositing. It was then kept in the refrigerator for 12 h. The precipitate was collected by filtration and washed thoroughly with ice-cold water and finally with diethyl ether. The precipitates were dried under vacuum over P_4O_{10} . The yield was 50%.

tc -[Ru(Hto)(tap)₂](ClO₄)₂·H₂O was similarly prepared starting from tc -[Ru(OH₂)₂(tap)₂](ClO₄)₂·H₂O and HHto.

Registry No. 6⁺ClO₄⁻ (L = pap, R = OMe), 86646-05-1; 6⁺ClO₄⁻ (L = pap, R = Me), 86646-07-3; 6⁺ClO₄⁻ (L = pap, R = H),

86646-09-5; 6⁺ClO₄⁻ (L = pap, R = Cl), 86646-11-9; 6⁺ClO₄⁻ (L = pap, R = CO₂Et), 86646-13-1; 6⁺ClO₄⁻ (L = pap, R = NO₂), 86646-15-3; 6⁺ClO₄⁻ (L = tap, R = H), 86646-17-5; 6²⁺ (L = pap, R = Me), 86646-18-6; 6²⁺ (L = pap, R = CO₂Et), 86668-07-7; tc -[Ru(bpy)(pap)₂](ClO₄)₂, 86645-93-4; tc -[Ru(bpy)(tap)₂](ClO₄)₂, 86645-95-6; cc -[Ru(bpy)(tap)₂](ClO₄)₂, 86707-54-2; tc -[Ru(en)(tap)₂](ClO₄)₂, 86668-04-4; mer -[Ru(pap)₃](ClO₄)₂, 86645-97-8; mer -[Ru(tap)₃](ClO₄)₂, 86645-99-0; [Ru(tap)(pap)₂](ClO₄)₂, 86646-01-7; [Ru(pap)(tap)₂](ClO₄)₂, 86646-03-9; tc -[Ru(acac)(tap)₂](ClO₄)₂, 86668-06-6; fac -[Ru(tap)₃](ClO₄)₂, 86707-56-4; tc -[Ru(OH₂)₂(pap)₂](ClO₄)₂, 84027-70-3; tc -[Ru(OH₂)₂(tap)₂](ClO₄)₂, 84027-73-6; cc -[Ru(OH₂)₂(tap)₂](ClO₄)₂, 84049-25-2; [Ru(pap)(bpy)₂](ClO₄)₂, 77321-13-2; [Ru(tap)(bpy)₂](ClO₄)₂, 77321-15-4.

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Superexchange in Chromium(III) Complexes: A Survey of Magnetic Behavior

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The magnetic susceptibilities at low temperatures of a series of 11 polycrystalline bimetallic coordination compounds of Cr(III) are presented. Materials such as [Cr(H₂O)(NH₃)₅][Co(CN)₆] are found to behave as simple paramagnets, while [Cr(H₂O)(NH₃)₅](CuCl₅) appears to undergo magnetic ordering at 298 mK. A number of other Cr/Cr compounds, such as [Cr(urea)₆][Cr(NCS)₆]·3H₂O, remain paramagnetic to temperatures as low as 40 mK. Exchange interactions are found to be remarkably weak in most of the compounds investigated. The compound [Cr(C₃H₅NO)₆](ClO₄)₃ also exhibits very weak exchange interactions.

Introduction

There are relatively few known superexchange-coupled antiferromagnets of chromium(III), so we have begun a search for new ones. The major reason for doing so is that chromium is one of the few examples of an $S = 3/2$ ion, which means that zero-field splitting effects can be important for its magnetochemistry. So much of the subject of magnetism has been restricted to copper(II) ($S = 1/2$ and therefore a quantum ion), manganese(II) ($S = 5/2$ and therefore nearly a classical spin ion), and cobalt(II) (effective $S = 1/2$ in all cases studied to date at low temperatures, whether octahedral or tetrahedral in geometry). Nickel(II) is of course intermediate, with $S = 1$, but most of the experimental studies to date on $S = 3/2$ systems have centered around the unusual molecule FeCl(S₂CNEt₂)₂.^{1,2} Such systems as CrCl₃ ($T_c \sim 16.8$ K), CrBr₃ ($T_c \sim 32$ K), and Cr₂O₃ ($T_c \sim 308$ K) order at temperatures too high for the zero-field splitting of the ⁴A₂ ground state to affect in any way the magnetic character of the systems. The Cr alums order at very low temperatures, principally by dipolar interactions. So, it appeared reasonable to us to search for new (superexchange) antiferromagnets of chromium(III) whose magnetic interactions became important at intermediate temperatures, especially in the temperature range accessible to us (40 mK–20 K). A great deal of theory for $S = 3/2$ has already been done, but little of it includes crystal-field splitting terms. These become evident in some of our measurements even though the zero-field splitting with chromium is almost always smaller than 1 K.

Studies of [Cr(NH₃)₆](ClO₄)₂·Br·CsBr, for example, showed that magnetic exchange is particularly weak in this material. Susceptibilities measured down to 40 mK allowed us³ to evaluate the zero-field splitting parameter $2D/k$ as 0.53 K,

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Table I. Heterobimetallic Chromium(III) Compounds^a

	(g)	Θ ± 0.05, K
[Co(NH ₃) ₆][Cr(CN) ₆]	1.97	0
[Cr(H ₂ O)(NH ₃) ₅][Co(CN) ₆]	1.93	-0.08
[Co(H ₂ O)(NH ₃) ₅][Cr(CN) ₆]	1.92	0.02
<i>cis</i> -[Cr(H ₂ O) ₂ (NH ₃) ₄][Co(CN) ₆]	1.83	0
[Cr(H ₂ O)(NH ₃) ₅](CuCl ₅)	1.97	-0.15

^a From data taken over the temperature interval 1.2–4.2 K.

but magnetic ordering was not found.

The compound Cs₂CrCl₅·4H₂O is more interesting because it does undergo magnetic ordering at 180 mK.⁴ Magnetic exchange and the zero-field splitting appear to be comparable in magnitude; we found $D/k = -0.16$ K, $E/k = -0.05$ K, and $zJ/k = -0.09$ K. The compound exhibits lower dimensional behavior.

An early study⁵ observed that exchange interactions were very weak in the common compound [Cr(NH₃)₆]Cl₃, for the magnitude of the Weiss constant was less than 0.01 K. The compound [Cr(NH₃)₅Cl]Cl₂ was found to obey the Curie-Weiss law down to 1.5 K with $\Theta = -0.8$ K; magnetic ordering has not yet been reported for either compound. One may compare these results with those on [Ni(NH₃)₆]Cl₂⁶ and [Ni(NH₃)₆](NO₃)₂,⁷ for example, which have respective ordering temperatures of 1.02 and 1.35 K.

We recently reported⁸ that superexchange interaction in some chromium(III) salts can be enhanced by the presence

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Table II. Bimetallic Chromium Compounds^a

	(g)	$\Theta \pm 0.05, \text{K}$
$[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{NCS})_6]$	1.943	-1.44
$[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{CN})_6]$	1.958	+0.34
$[\text{Cr}(\text{urea})_6][\text{Cr}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$	1.98	-0.44
$[\text{Cr}(\text{urea})_6][\text{Cr}(\text{NCS})_6] \cdot 3\text{H}_2\text{O}$	2.01	-0.70
$[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$	2.02	-0.78
$[\text{Cr}(\text{Me}_2\text{SO})_6][\text{Cr}(\text{CN})_6]$	1.89	-0.20

^a From data taken over the temperature interval 1.2–4.2 K.

of a paramagnetic metal ion in both the cation and the anion of a compound. We refer to such systems as bimetallic and present here data on a number of new systems. What is fascinating about several of them is the observation that, contrary to our expectations, magnetic exchange remains so weak that magnetic ordering does not take place at temperatures as low as 40 mK. This is reminiscent of, but somewhat different from, the situation found⁹ with bimetallic $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6](\text{CoCl}_4)$ in which the $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6]^{2+}$ sublattice orders antiferromagnetically but does so without interacting with the $(\text{CoCl}_4)^{2-}$ sublattice, which remains paramagnetic down to 40 mK.

Finally, the series of molecules $[\text{M}^{\text{II}}(\text{C}_5\text{H}_5\text{NO})_6]\text{X}_2$, where M is divalent manganese,¹⁰ iron,¹¹ cobalt,¹² nickel,¹³ or copper,¹⁴ $\text{C}_5\text{H}_5\text{NO}$ is pyridine *N*-oxide, and X is perchlorate, fluoborate, or nitrate, has been extensively studied recently and provided a number of rewarding results. We therefore decided to investigate $[\text{Cr}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_3$ as well. The results to date, which are reported below, are not encouraging for the continued study of the pyridine *N*-oxide compounds of the series of trivalent ions.

Experimental Section

The bimetallic compounds reported here are listed in Tables I and II. The starting materials, $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{ClO}_4)_3$,¹⁵ $\text{K}_3\text{Cr}(\text{CN})_6$,¹⁶ $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$,¹⁷ $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{NO}_3)_3$,¹⁸ $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{ClO}_4)_3$,¹⁹ $\text{K}_3[\text{Co}(\text{CN})_6]$,²⁰ *cis*- $[\text{Cr}(\text{H}_2\text{O})_2(\text{NH}_3)_4](\text{ClO}_4)_3$,²¹ $[\text{Cr}(\text{urea})_6]\text{Cl}_3$,^{22,23} $[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$,²⁴ and $[\text{Cr}(\text{Me}_2\text{SO})_6](\text{ClO}_4)_3$,²⁵ were prepared according to the literature methods. The compounds $[\text{Co}(\text{NH}_3)_3][\text{Cr}(\text{CN})_6]$, $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Co}(\text{CN})_6]$, $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{SCN})_6]$, $[\text{Cr}(\text{urea})_6][\text{Cr}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, and $[\text{Cr}(\text{urea})_6][\text{Cr}(\text{SCN})_6] \cdot 3\text{H}_2\text{O}$ were prepared by mixing concentrated equimolar solutions of the corresponding compounds. The materials $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{CN})_6]$, *cis*- $[\text{Cr}(\text{H}_2\text{O})_2(\text{NH}_3)_4][\text{Co}(\text{CN})_6]$, $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{CN})_6]$, and $[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ were prepared by mixing equimolar solutions of the corresponding compounds, and then CH_3COOH was added for precipitation. When

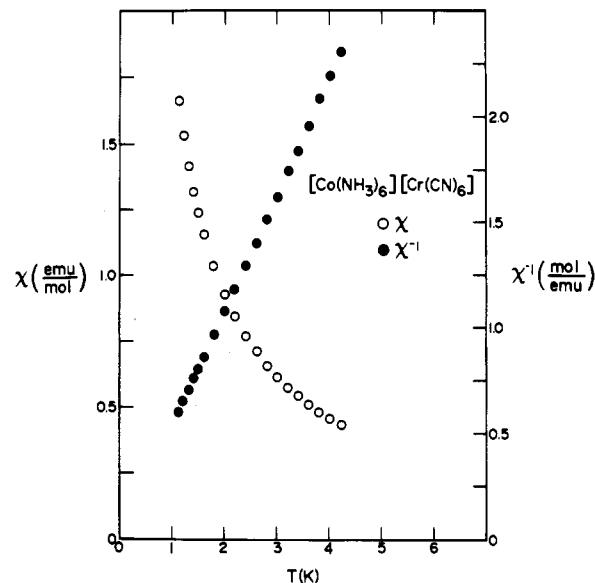


Figure 1. Magnetic susceptibility of $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ plotted as χ (O) and χ^{-1} (●) vs. T .

necessary, $\text{K}_3\text{Co}(\text{CN})_6$ and $\text{K}_3\text{Cr}(\text{CN})_6$ were transformed into the sodium salts on a cation-exchange resin. The sample of $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{CuCl}_5]$ was prepared by adding the stoichiometric quantity of CuCl_2 to a hydrochloric acid solution of $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{ClO}_4)_3$. Finally, $[\text{Cr}(\text{Me}_2\text{SO})_6][\text{Cr}(\text{CN})_6]$ was prepared as follows. To a cold solution of $[\text{Cr}(\text{Me}_2\text{SO})_6](\text{ClO}_4)_3$ (1 g) in a 1:1 mixture of $\text{H}_2\text{O}/\text{Me}_2\text{SO}$ (10 mL) was added the stoichiometric quantity of $\text{K}_3\text{Cr}(\text{CN})_6$. The perchlorate precipitate was filtered, and then CH_3OH was added for precipitation, while $[\text{Cr}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_3$ was prepared as described previously.²⁶ All compounds gave satisfactory elemental analyses.

Susceptibility measurements were made as described previously^{3,9} by an ac method. This yields $\chi = \chi' - i\chi''$, where χ' is the isothermal susceptibility when the frequency is low enough.²⁷ This is the quantity reported here. The out-of-phase component, χ'' , is zero in this limit and becomes nonzero only when relaxation effects become important. Under the experimental conditions used here, a nonzero χ'' would be indicative of a ferromagnetic contribution to the susceptibility.

Results and Discussion

The magnetochemistry of paramagnetic chromium(III) is relatively straightforward. The $3d^3$ system has a 4A_2 ground state in an octahedral crystalline field; virtually every chromium compound known is six-coordinate and essentially octahedral. The applicable spin Hamiltonian is

$$\mathcal{H} = g\mu_B\vec{H} \cdot \vec{S} + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2)$$

where g is usually isotropic with a value of about 1.98. The axial zero-field splitting term is usually less than 1 K. The rhombic E term is smaller than D and expected to be of lesser importance for most analyses of magnetic ordering phenomena. Expressions have been given earlier for the susceptibility of chromium(III) in both axial³ and rhombic⁴ crystalline fields.

Exchange interaction between the chromium ions may be represented by the term $\mathcal{H}' = -2J\sum_{ij}\vec{S}_i \cdot \vec{S}_j$. The isotropic nature of the free ions suggests that the magnetic exchange will be isotropic, i.e., that the Heisenberg magnetic model will be followed. This is true of course only when $z|J| \gg 2D$, and while D is usually small, J is apparently also small for many Cr(III) complexes.

For comparison purposes, several bimetallic compounds of the Co/Cr type have also been investigated. With octahedral

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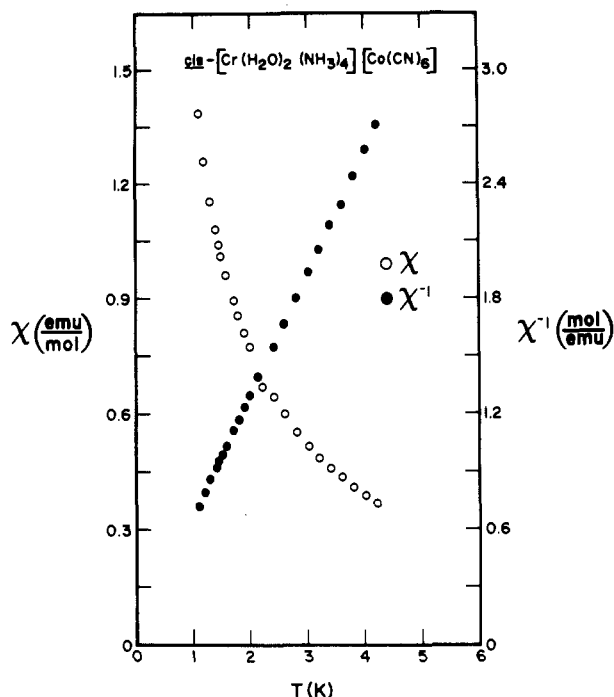


Figure 2. Magnetic susceptibility of *cis*-[Cr(H₂O)₂(NH₃)₄][Co(CN)₆] plotted as χ (○) and χ^{-1} (●) vs. T .

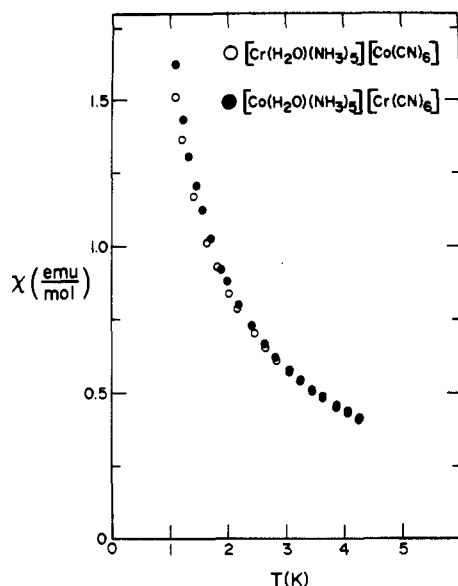


Figure 3. Susceptibilities of [Cr(H₂O)(NH₃)₅][Co(CN)₆] (○) and [Co(H₂O)(NH₃)₅][Cr(CN)₆] (●).

Co(III) in either the cation or the anion, this is of course a diamagnetic ion, and the only magnetic contribution is from the paramagnetic Cr(III) moiety. Thus, these compounds were expected to behave as simple paramagnets, and that has indeed been found (Table I). The Curie behavior of two of these salts is illustrated in Figures 1 and 2. The compounds [Cr(H₂O)(NH₃)₅][Co(CN)₆] and [Co(H₂O)(NH₃)₅][Cr(CN)₆] are expected to be structural isomorphs. Their magnetic susceptibilities are virtually identical over the temperature interval 1.2–4.2 K, as illustrated in Figure 3. It was decided that it was not worth the effort to measure these compounds to lower temperatures, for neither significant zero-field splitting effects would be expected nor was it anticipated that magnetic ordering would be observed. The measured g value of *cis*-[Cr(H₂O)₂(NH₃)₄][Co(CN)₆] is inexplicably smaller than that of the other compounds and must be ascribed to some systematic error. This is of little consequence to this work, for

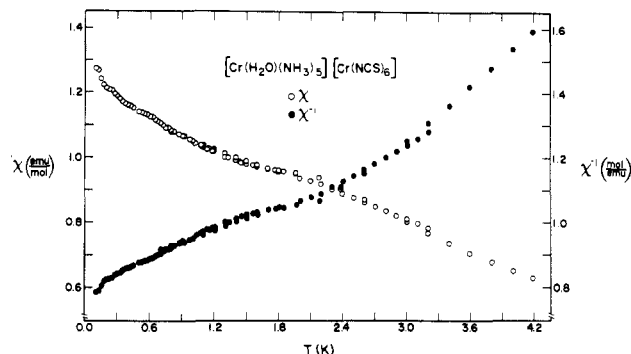


Figure 4. Magnetic data on [Cr(H₂O)(NH₃)₅][Cr(NCS)₆] plotted as χ (○) and χ^{-1} (●) vs. T . Note that the two ordinates differ and are offset differently from zero.

the material is a simple paramagnet down to 1.2 K.

We have previously reported⁸ susceptibility data for [Cr(H₂O)(NH₃)₅][Cr(CN)₆] and [Cr(urea)₆][Cr(CN)₆] \cdot 3H₂O. The measured Weiss constants are 0.34 and -0.44 K, respectively, and the compounds were found to order at 0.38 and 0.30 K. Thus, the size of the Weiss constant appeared to be a reliable guide for the determination of the strength of the exchange interaction. Each of these compounds orders with an important ferromagnetic interaction. The transition temperatures are rather low for such magnetically concentrated materials. Of the other Cr/Cr compounds reported here, only one gives as clear an indication of undergoing magnetic ordering to temperatures as low as 40 mK, yet some rather unusual behavior has nevertheless been observed for several of the compounds. No out-of-phase signals indicative of ferromagnetic absorption have been observed with any of the other compounds.

For example, the susceptibility of [Cr(H₂O)(NH₃)₅][Cr(NCS)₆] rises slightly as the temperature is lowered (Figure 4), but the increase is much smaller than that predicted by the Curie–Weiss law. There is a break in the χ vs. T curve at about 2.2 K, but the behavior is not typical of that commonly observed when ordering occurs. The Curie–Weiss plot (Figure 4) is rather unusual because there is no linear portion but only an S-shaped behavior. This behavior is not that expected from zero-field splitting effects alone.

A second magnetically concentrated compound is [Cr(H₂O)(NH₃)₅](CuCl₅), which is isostructural with the well-known [Cr(NH₃)₆](CuCl₅).²⁸ The average g value for the compound measured over the temperature interval 1.2–4.2 K is 1.97; if the reasonable value of $g \approx 2.1$ is assigned to the CuCl₅²⁻ ion, then one calculates a g of 1.83 for the chromium complex ion. This appears to be a bit low when compared with the measured g value of 1.93 for [Cr(H₂O)(NH₃)₅][Co(CN)₆], in which the only magnetic ion is the same as that in the bimetallic Cr/Cu compound, but is within acceptable error limits. The Curie–Weiss $\theta = -0.15 \pm 0.05$ K may be assigned to exchange interaction within the compound. Since this θ appears to be significantly different from 0 (while that of [Cr(H₂O)(NH₃)₅][Co(CN)₆] is not), we felt it would be worthwhile to examine the compound at lower temperatures. The susceptibility goes through a peak (Figure 5) at about 298 mK and then falls in a rather dilatory fashion. Ferromagnetic ordering may be indicated, but the behavior is unlike that observed for the other two ferromagnetic compounds. The out-of-phase component is zero. Demagnetization effects may obscure the situation, but the data do not go through the broad maximum anticipated for antiferromagnetic ordering. The Curie–Weiss plot is linear down to nearly 300 mK. We therefore assume that this polycrystalline material is indeed undergoing magnetic

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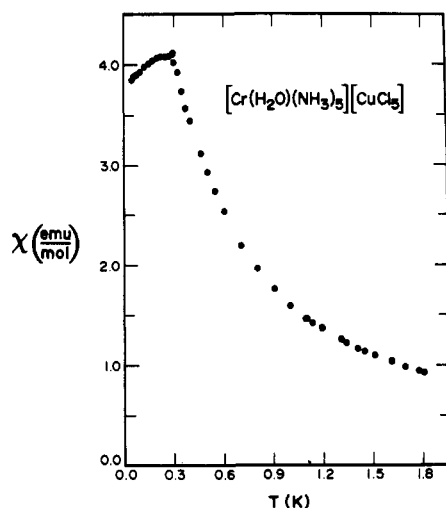


Figure 5. Magnetic susceptibility of $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{CuCl}_5]$.

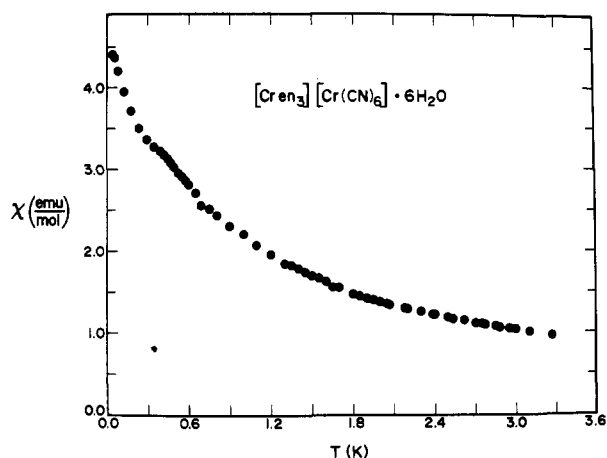


Figure 6. Magnetic susceptibility of $[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$.

order at 298 mK, but further information is needed in order to characterize the ordering better. Complicated low-temperature behavior for this material is not unexpected, for the substance is cubic at room temperature with 32 formula weights per unit cell. As with all the materials described here, both specific heat data and single-crystal susceptibilities are still needed.

The susceptibility of polycrystalline $[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$ presents another type of behavior (Figure 6). It rises Curie-Weiss-like with decreasing temperature, goes through an inflection point at about 350 mK, and then continues to increase to the lowest temperatures measured. The susceptibility reaches about 4.5 emu/mol at 45 mK, which is quite a large value. But then one must recognize that the temperature is quite low, and that there are two magnetic ions per mol. Magnetic ordering is not evident in the data, yet the interpretation of the inflection point is also not definitive. Perhaps one type of chromium remains paramagnetic to the lowest temperatures, while the other type orders at around 400 mK. This is what happens with $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6](\text{CoCl}_4)$. The fact that there are two different magnetic ions present, each with its own zero-field splitting, makes an unequivocal analysis from these data impossible. Further studies, such as on single crystals or in an applied field, are required here.

It is not clear when one can expect that a compound containing the tris(ethylenediamine)metal cation will undergo magnetic ordering. The metal is well hidden in these chelates, and therefore one does not expect to find a very strong superexchange path. This view is justified by the results reported

here for $[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$, and yet the anticipatively more magnetically dilute $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ was found to order²⁹ at 1.25 K. This temperature was unexpectedly high, but the Cr/Cr bimetallic orders (if at all) at an unexpectedly low temperature. We note further that $[\text{Cu}(\text{en})_3]\text{SO}_4$ orders³⁰ at 109 mK; though this is a low temperature, it is clear that $[\text{M}(\text{en})_3]^{2+}$ ions are not so well shielded from superexchange paths that they cannot participate in magnetic ordering. Since $[\text{Cr}(\text{CN})_6]^{3-}$ also participates in the ordering of at least a few salts, we cannot explain at this time why the Cr/Cr compounds exhibit such weak exchange interaction.

The replacement of the $[\text{Cr}(\text{CN})_6]^{3-}$ anion by the $[\text{Cr}(\text{NCS})_6]^{3-}$ anion in $[\text{Cr}(\text{urea})_6][\text{Cr}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ is interesting because the stoichiometry of the substance remains the same even though the crystal structure undoubtedly changes. It is not known whether the thiocyanate is N bonded or S bonded, so one cannot compare very easily the magnetic behavior of the two compounds. Nevertheless, the cyano compound orders at 300 mK, but the thiocyanate does not order above 45 mK. In the 0.7–4.2 K temperature region, this compound exhibited a Weiss θ of -0.70 K, which led us to proceed with measurements to lower temperatures. The low-temperature data exhibit a curvature in the Curie-Weiss plot, suggesting that ordering may occur at some very low temperature. At 45 mK, the susceptibility has reached the very high value of some 22.3 emu/mol.

As would be expected, the insertion of chromium into a very large cation without providing a compensating superexchange path leads to a system that remains paramagnetic to the very lowest temperatures. This is observed with both $[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6] \cdot 6\text{H}_2\text{O}$, as pointed out above, and $[\text{Cr}(\text{Me}_2\text{SO})_6][\text{Cr}(\text{CN})_6]$. The latter compound exhibits a θ of -0.20 K in the ^4He temperature region, yet it does not undergo magnetic ordering down to 40 mK. Since Me_2SO is a tripodal-type ligand, it presumably does not permit a superexchange path of the kind Cr-O...O-Cr, analogously to the Co-O...O-Co path that is so important for the $[\text{Co}(\text{C}_5\text{H}_5\text{NO})_6]\text{X}_2$ series of molecules.¹² In any case, it is apparent from this work that a Weiss constant of reasonable magnitude (e.g., 0.2–0.8 K) is not a satisfactory indicator of whether or not a bimetallic Cr/Cr compound of the type reported here will achieve magnetic ordering above the temperature of 40 mK. Thus, the hypothesis asserted above has not been validated. Part of the problem is that zero-field splittings can also contribute to the Weiss constant.

The situation found with these compound is vastly different from that found in a number of hydroxo-bridged (Cr-OH-Cr) dimers of chromium(III). Relatively strong exchange is found in many such compounds.³¹ Furthermore, we note that $\text{CsMn}^{\text{II}}[\text{Cr}(\text{CN})_6]$ is a ferrimagnet with transition temperature of 90 K.³² In this compound, the manganese ions bridge the chromiums via superexchange paths as Cr-CN...Mn...NC-Cr. So it is clear that the lack of a suitable superexchange path in most of the compounds reported here is the reason that magnetic exchange is so weak. What is not so clear is why the exchange is so much stronger in the two compounds reported earlier, $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{urea})_6][\text{Cr}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, although a contributing factor to the superexchange path may be the extent of hydrogen bonding and its variation from compound to compound. Complete crystal structure analyses are required before we speculate further on this point. Unfortunately we have not succeeded

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in many attempts to grow large single crystals of any of the compounds described in this paper. Measurements on such crystals would provide more information on what is happening in these systems. Specific heat studies are also required.

We have tried a number of methods but have never succeeded in growing single crystals of $[\text{Cr}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_3$. This stands in marked contrast to the great success we have had in preparing single crystals of the pyridine *N*-oxide complexes of the divalent iron series ions. Nevertheless we measured the susceptibility of a polycrystalline sample of this material and find that it obeys the Curie-Weiss law over the temperature interval 1.2-4.2 K with a *g* value of 1.965 and a θ of -0.03 ± 0.05 K. In view of the other results reported here, it was decided that this compound probably would not order at an accessible temperature, and so no further measurements were made. Again this behavior stands in stark contrast to that observed with the other pyridine *N*-oxide complexes, as well as with $[\text{Gd}(\text{C}_5\text{H}_5\text{NO})_8](\text{ClO}_4)_3$.³³

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Registry No. $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$, 38670-48-3; $[\text{Cr}(\text{H}_2\text{O})(\text{N}-\text{H}_3)_5][\text{Co}(\text{CN})_6]$, 62534-93-4; $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{CN})_6]$, 60897-44-1; *cis*- $[\text{Cr}(\text{H}_2\text{O})_2(\text{NH}_3)_4][\text{Co}(\text{CN})_6]$, 86668-08-8; $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5](\text{CuCl}_2)$, 86646-30-2; $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{NCS})_6]$, 86646-31-3; $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_5][\text{Cr}(\text{CN})_6]$, 75058-08-1; $[\text{Cr}(\text{urea})_6][\text{Cr}(\text{CN})_6]$, 23540-67-2; $[\text{Cr}(\text{urea})_6][\text{Cr}(\text{NCS})_6]$, 27933-99-9; $[\text{Cr}(\text{en})_3][\text{Cr}(\text{CN})_6]$, 23540-71-8; $[\text{Cr}(\text{Me}_2\text{SO})_6][\text{Cr}(\text{CN})_6]$, 86646-32-4.

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Metal-Nitroxyl Interactions. 31. Single-Crystal EPR Spectra of a Spin-Labeled Vanadyl Porphyrin

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Single-crystal EPR spectra have been obtained for a spin-labeled vanadyl porphyrin doped into zinc tetraphenylporphyrin. Four conformations of the molecule were observed. The dependence of the spin-spin splittings on the orientation of the crystal in the magnetic field was analyzed to obtain the isotropic exchange and anisotropic dipolar contributions to the spin-spin interaction. The interspin distance, *r*, ranged from 9.8 to 13.6 Å. The exchange interaction was found to be small, with values of the coupling constant, *J*, ranging from -3 to $+4 \times 10^{-4}$ cm⁻¹. The *g* and *A* values for the vanadyl electron in the spin-labeled complex agreed well with those obtained for vanadyl tetraphenylporphyrin doped into the same host.

Introduction

The understanding of spin-spin interaction between non-equivalent unpaired electrons is important to a variety of chemical and biochemical problems. Radical pairs have been observed in the EPR spectra of several photochemical systems.¹ Spin-spin interaction between a cobalt(II) center and a free radical has been detected in vitamin B₁₂ coenzyme systems.²⁻⁴ Nitroxyl spin labels attached to paramagnetic biomolecules⁵ can exhibit spin-spin interaction.⁶ In these and other similar cases, considerable insight into the structure of the system can be obtained by an analysis of the spin-spin interaction. In general, the interaction will consist of an anisotropic dipolar contribution and an isotropic exchange contribution. These two terms provide complementary information about the system. The magnitude of the dipolar interaction is determined by the distance between the two unpaired spins and the orientation of the interspin vector relative to the external magnetic field. When the EPR spectrum of the interacting spins includes resolved anisotropic nuclear hyperfine splitting, the orientation of the interspin vector relative to the nuclear hyperfine tensor can be obtained.⁷⁻⁹ Thus the dipolar interaction provides geometric information. The exchange interaction is dependent on the through-bond pathway between the two electrons and thus can provide information about the connectivity in the system. In addition, it is important to de-

termine the conditions under which it is reasonable to assume that either the exchange or dipolar contributions would be expected to dominate the spin-spin interaction in a complex system. Elucidation of the effect of the bonding pathway on exchange is also important to an understanding of electron transport and electron polarization.

Recent results from our laboratories have shown that for spin-labeled copper(II), silver(II), and vanadyl(IV) complexes that are tumbling rapidly in solution, exchange interactions in the range of $(3-2000) \times 10^{-4}$ cm⁻¹ can be determined by analysis of the EPR spectra.^{6,10,11} Since the dipolar interaction depends on the orientation of the interspin vector relative to the magnetic field, its contribution to the spin-spin splitting

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