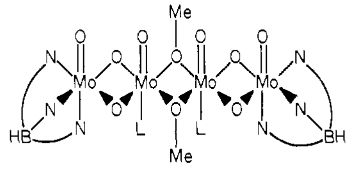
simple bonding considerations for this molybdenum(V) tetramer. The singly occupied d_{xy} orbitals on Mo1 and Mo2 (also Mo1′, Mo2′) overlap to give Mo–Mo single bonds. The conjugation is interrupted since the d_{xy} orbitals on Mo2 and Mo2′ are nearly parallel. This would not be the case in **4** (a possible structural isomer of **1**), which would possess a linear chain of metals.



4

A retrosynthetic analysis of **1** reveals that it most likely formed through dimerization of two $HB(pz)_3Mo^V{}_2O_4L_3$ (L = MeOH or MeO^-) units. The dimerization occurs through displacement of the ligand trans to the terminal oxo's, giving **1** rather than **4**. Attempts to isomerize **1** into **4** are in progress. The tridentate polypyrazolylborate ligands serve two structural roles. The ligands cap off the ends of the oligomer, preventing a more extended structure. The ligands also prevent the Mo_4 structure from collapsing to the more compact $Ti_4(OR)_{16}$[22] structure found in **2** and **3** (Figure 2).

The identification of the terminal ligand on Mo2 (Mo2′) as a methanol rather than a methoxide is crucial since it determines that **1** is a Mo(V) tetramer rather than a mixed-valence (2Mo(V), 2Mo(VI)) complex. The chemical[23] and structural evidence clearly indicates that the ligand is methanol. The Mo2–O5 distance 2.264 (3) Å is far outside the range for a $Mo-(OR)_t$[7] distance of 1.81–1.98 Å.[13,14,16] There is also ample structural evidence that in the presence of comparable trans ligands, $Mo-(OR)_t$ distances should be shorter than $Mo-(OR)_b$ distances.[13-19] This would not be the case in **1** if the ligand in question was methoxide. Finally, we were able to locate the methanolic hydrogen which is engaged in a hydrogen bond with O3. Quite analogous hydrogen bonding exists in $Ti_2(OPh)_8(HOPh)_2$[24] and $W_2Cl_4(OMe)_4(HOMe)_2$.[17]

During our structural analysis of **1** we realized that the structure reported for **3**[21] (Figure 2) contains a structural anomaly that leads us to conclude that **3** has been misformulated. The $Mo2-(O(4)Pr)_t$ distance (2.13 (1) Å) is outside the range for terminal alkoxides. It is longer than some $Mo-(OPr)_b$ distances in the same molecule. The result is particularly suspect since the structurally similar $Mo-(O\text{-}i\text{-}Pr)_t$ distance in **2** is 1.945 (3) Å.[20] The anomaly is removed if the two terminal propoxides in **3** are really propanols. Reformulating **3** as $Mo_4Cl_4O_6(O\text{-}n\text{-}Pr)_4(HO\text{-}n\text{-}Pr)_2$ makes it a Mo(V) tetramer like **1** and **2** rather than its original mixed-valence formulation. The rest of the structural parameters are quite consistent with the new formula.[25] For example, the Mo1–Mo2 distance (2.67 Å) in **3** with its mixed oxide–alkoxide bridges is, as might be expected, midway between the distances found in *Mo(V) dimers* with two oxide bridges (2.54–2.61 Å)[10,11,26] and those with two alkoxide bridges (2.73–2.80 Å).[14,18] We are attempting to synthesize **3** in a more direct manner in order to chemically and structurally confirm the new formulation.

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Registry No. **1**, 81610-96-0; **3**, reformulated, 81602-77-9; **3**, 42844-79-1.

Supplementary Material Available: Listings of final positional and thermal parameters and distances and angles for **1** (5 pages). Ordering information is given on any current masthead page.

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[22] Ibers, J. A. *Nature (London)* **1963**, *197*, 686–687.

[23] **1** is diamagnetic. Its mass spectrum shows a continuous emission of methanol at room temperature. A resonance for the methanolic proton is found in the proton NMR spectrum. However, no hydroxyl band could be detected in the IR spectrum. Similar IR results have been reported for another metal complex with a methanol ligand: Bandoli, G.; Clemente, D. A.; Croatto, U.; Vidali, M.; Vigato, P. A. *J. Chem. Soc., Dalton Trans.* **1973**, 2331–2335.

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[25] The difference in the $Mo-(OHR)_t$ distances in **1** and **3** reflects their different trans-effecting ligands; the propanolic hydrogen in **3** will be hydrogen bonded with Cl1 in a completely analogous manner to that seen in **1**.

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Ordered Bimetallic Magnets: Ferromagnetism in $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ and $[Cr(urea)_6][Cr(CN)_6]\cdot 3H_2O$

Sir:

Numerous studies have been reported on the magnetic ordering phenomena that occur in transition-metal complexes.[1] By and large, the compounds studied have only one system of metal ions such as is found in $CuCl_2\cdot 2H_2O$, $MnCl_2\cdot 4H_2O$, and a host of similar materials. Aside from possible inequivalence of crystallographic position, the metal ions in these systems are in chemically similar environments. In addition, pairwise interactions between equivalent metal ions are also well-known in copper acetate and many related molecules.[2]

Recently there have been reports on the pairwise magnetic interactions in several heterobimetallic dimers such as $CuCo(fsa)_2en\cdot 6H_2O$[3] and $[Fe^{II}(C_{18}H_{18}N_6)(bipym)Cu^{II}(acac)_2](ClO_4)_2$.[4] Few studies of bimetallic compounds in which there are extended magnetic interactions have been reported, one new example being $[Co(C_5H_5NO)_6](CoCl_4)$.[5] It has been found that there are two independent magnetic subsystems present in this compound, one being the set of octahedral ions and the other the set of tetrahedral ions.

We report here preliminary susceptibility measurements as a function of temperature on two bimetallic coordination compounds of chromium(III). They are $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ (A) and $[Cr(urea)_6][Cr(CN)_6]\cdot 3H_2O$ (B). The latter compound is of interest because luminescence measurements have shown that excitation energy transfer occurs from chromium in the cation to chromium in the anion.[6] Compound A was prepared from $[Cr(H_2O)(NH_5)_5](NO_3)_3$[7] and $K_3Cr(CN)_6$,[8] while compound B was prepared as previ-

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[1] For example: Carlin, R. L.; van Duyneveldt, A. J. "Magnetic Properties of Transition Metal Compounds"; Springer Verlag: New York, 1977.

[2] For example: Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209.

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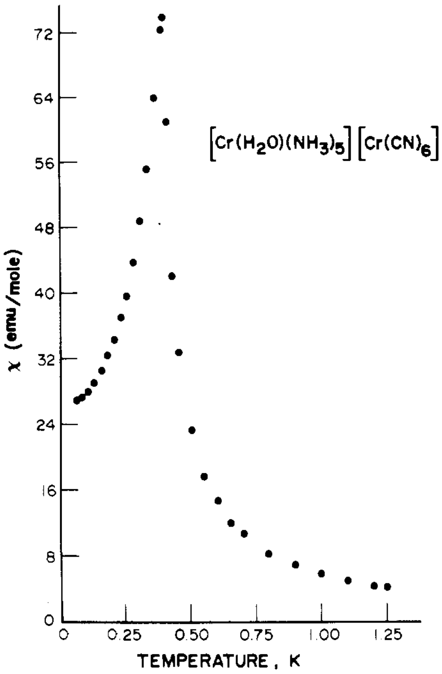

Figure 1. Zero-field magnetic susceptibility of $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$.

ously described.[6] Neither compound appears to have yet been studied crystallographically.

The magnetic susceptibilities (χ'), measured[9] at 16 Hz, at zero applied field of polycrystalline samples of the two salts are presented in Figures 1 and 2. The compound $[Cr(H_2O)(NH_3)_5][Cr(CN)_6]$ obeys the Curie–Weiss law over the temperature interval 1–4 K with $\langle g \rangle = 1.96 \pm 0.01$ and $\Theta = 0.34 \pm 0.05$ K, with the presence of two $S = {}^3/_2$ ions assumed. At low temperatures, the susceptibility rises rapidly, reaching a maximum value of more than 70 emu/mol, and $T_c = 0.380 \pm 0.005$ K. The peak drops sharply at lower temperatures and approaches a value of about 26 emu/mol at 0 K. This is behavior typical of a powdered sample of a ferromagnetic material, in which demagnetization effects become important.

The susceptibility of $[Cr(urea)_6][Cr(CN)_6]\cdot 3H_2O$ is rather different. The Curie–Weiss law is obeyed above 1 K with $\langle g \rangle = 1.98 \pm 0.01$ and $\Theta = -0.44 \pm 0.05$ K. A sharp peak is observed at $T_c = 0.300 \pm 0.010$ K, with a maximum value of about 8 emu/mol. A broad maximum of as yet unknown origin is observed at 150 mK. The sharp peak at T_c, combined with the antiferromagnetic sign of the Weiss constant, suggests that this compound is probably a canted antiferromagnet.[10] Absorption (χ'') was observed over the temperature interval of the peaks for each compound.

That the superexchange interaction in these bimetallic systems is enhanced by the presence of two magnetic ions per formula unit may be illustrated by a comparison with such molecules as $[Cr(H_2O)(NH_3)_5][Co(CN)_6]$, which obeys the Curie–Weiss law above 1 K with a Θ of nearly zero value. The compound $[Co(H_2O)(NH_3)_5][Cr(CN)_6]$ similarly exhibits a Θ of 0.02 ± 0.02 K. These Co/Cr systems, which from X-ray powder diffraction measurements appear to be isostructural with the Cr/Cr system, exhibit superexchange interactions more than 20 times smaller.

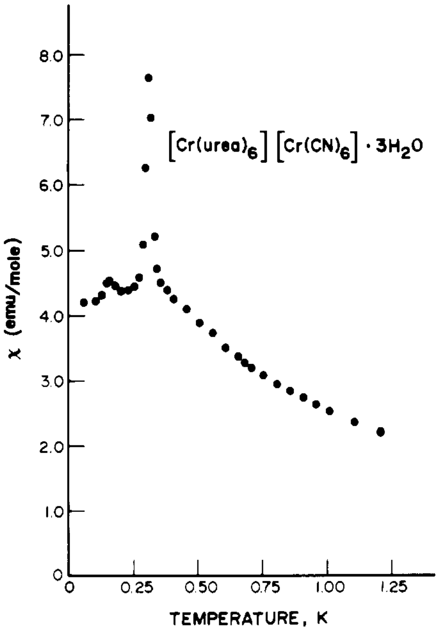

Figure 2. Zero-field magnetic susceptibility of $[Cr(urea)_6][Cr(CN)_6]\cdot 3H_2O$.

What has been demonstrated here is that superexchange interaction can be enhanced by the presence of a paramagnetic metal ion in both the cation and the anion of a compound. This is true even when the ligands present are as inefficient in providing a superexchange path as those in the present examples. It is clear that both cation and anion are interacting collectively as one magnetic system, as the susceptibilities do not exhibit any paramagnetic contributions below T_c. This was observed, however, with $[Co(C_5H_5NO)_6](CoCl_4)$, in which the tetrahedral ions do not take part in the ordering of the octahedral ions.[5]

Future work requires the preparation and measurement of single crystals of these materials, in order to determine the anisotropies and demagnetization effects. The details of the spin structures remain to be determined, especially in view of the apparent ferromagnetism observed with both compounds. Other bimetallic compounds are also being investigated.

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(10) See ref 1, p 184.