perpendicular to the electric dipole moment or little magnetic moment is induced by the stretching of the ligands in the ferric high-spin state and CO in the ferrous low-spin state. The relative orientation of the electric and magnetic dipole moments induced by the stretching of a ligand is approximately parallel for the cyanide but antiparallel for the azide in the ferric low-spin state. The orientation of the electric dipole moment depends on the coordination geometry of the ligand. Therefore, VCD is promising as to new insights into the electronic states as well as the coordination geometry of hemeproteins. Further studies on the VCD enhancement mechanism of porphyrin ligands are currently in progress.

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High-T_c Molecular-Based Magnets: A Ferromagnetic Bimetallic Chromium(III)–Nickel(II) Cyanide with T_c = 90 K

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$CsNi[Cr(CN)_6]\cdot 2H_2O$ obtained by slow addition of a dilute aqueous solution of a Ni^{II} salt to a concentrated aqueous solution of freshly prepared $Cs_2K[Cr(CN)_6]$ (1/1 molar ratio) exhibits a spontaneous magnetization at T_c = 90 K, due to a genuine short-range *ferromagnetic exchange interaction*. The elemental analysis fits with the proposed formula. The powder diffraction data display patterns of a face centered cubic cell with a unit cell parameter a = 10.57 Å. X-ray absorption data show octahedral Cr^{III} and Ni^{II} ions surrounded respectively by six carbon atoms at 2.06 Å and six nitrogen atoms at 2.10 Å. The $Cr(CN)_6$ group appears unchanged in the solid. The heavy atom peak in the Fourier transform, at $a/2$, at both edges confirms the presence of a three-dimensional (3D) bimetallic network with CN^- as a bridging ligand.

In the last few years, different groups have obtained encouraging results in the field of molecular-based ferromagnets, either with organic (i.e., fullerene),[2] metal–organic,[3,4a] metal–radical,[4b] or bimetallic[4c] systems. Among the data with an available crystal structure, the true molecular systems present the lowest T_c. One way to enhance the T_c value is to deal with bimetallic one-dimensional (1D) systems,[4b,c] with a strong and controlled interaction along one direction. However, the problem of inducing 1D–3D crossover in order to obtain the wanted magnets remains. Our approach is to build directly 3D frameworks through mild chemistry methods using *molecular* precursors specially chosen to achieve a 3D covalent bonding network between spin-bearing species. One of the simplest and most convenient molecular building blocks can be found in the hexacyanometalate family $[B(CN)_6]^{n-}$.

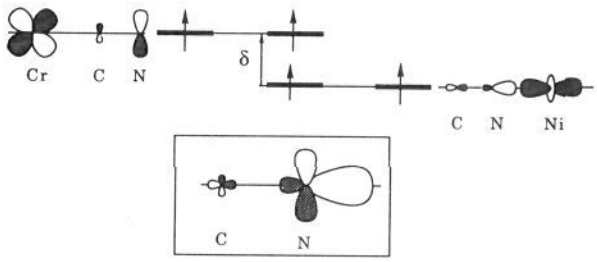

Figure 1. Orthogonality between t_{2g} (xy) Cr^{III} and e_g (z^2) Ni^{II} magnetic orbitals in $Cs^{I}Ni^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$.

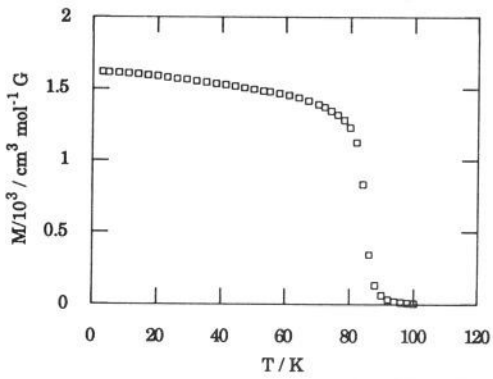

Figure 2. Field cooled magnetization curve $M = f(T)$ at H = 10 G.

The old but evergreen family of Prussian blue like bimetallic complexes leads to various k/l stoichiometries, $A_k[B(CN)_6]_l\cdot mH_2O$.[5] When $k/l > 1$, the structure presents $B(CN)_6$ vacancies and high water content. Ten years ago, among a series of uncoupled paramagnetic systems, Babel et al.[6] reported on the *ferrimagnetic* system $Cs^{I}Mn^{II}[Cr^{III}(CN)_6]\cdot 1H_2O$, with T_c *value* = 90 K. Using $[Fe^{III}(CN)_6]^{3-}$ (d^5, $(t_{2g})^5$, low-spin $S = {}^1/_2$) as a precursor, we obtained *ferrimagnetic* (with A^{II} = Mn^{II} and Co^{II}) and *ferromagnetic* (with A^{II} = Cu^{II} and Ni^{II}) systems and a $k/l = {}^3/_2$ stoichiometry, with T_c ranging from 9 to 23 K.[7] However, using chromicyanide instead of ferricyanide, we obtain a spectacular enhancement of T_c[8] (in the 55–65 K range), still with the ${}^3/_2$ stoichiometry. The presence of $B(CN)_6$ vacancies probably hinders a full interaction through the whole compound. To avoid such vacancies, a cesium cation Cs^{I} was used to stabilize ${}^1/_1$ stoichiometric compounds. We report here the magnetic properties of $Cs^{I}Ni^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$, which orders ferromagnetically at 90 K.

The susceptibility and magnetization measurements were performed using a SQUID magnetometer. Upon cooling down from room temperature to 90 K, $\chi_M T$ increases continuously, expressing a short-range *ferromagnetic exchange interaction* between nearest metallic ions. Such a short-range interaction, expected from the strict orthogonality of the t_{2g} orbitals of Cr^{III} and the e_g orbitals of Ni^{II} (Figure 1), had already been predicted by Ginsberg[9] and experimentally demonstrated by Pei et al.[10] At 90 K, $\chi_M T$ diverges, suggesting a long-range *ferromagnetic order*. The field-cooled magnetization vs temperature plot at H = 10 G in the 3–100 K range (Figure 2) presents a break at T_c = 90 K confirming the onset of a 3D long-range *ferromagnetic order* within the compound. The value is well above that observed for the ${}^3/_2Ni_3[Cr(CN)_6]_2\cdot 12H_2O$ compound (T_c = 60 K),[8] showing the importance of a lack of $[Cr(CN)_6]^{3-}$ vacancies in these com-

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(2) Allemand, P. M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Grüner, G.; Thompson, J. D. *Science* **1991**, *253*, 301.
(3) Manriquez, J. M.; Yee, G. T.; McLean, R. S.; Epstein, A. J.; Miller, J. S. *Science* **1991**, *252*, 1415.
(4) *Molecular magnetic materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; NATO ASI Series, Series E, Vol. 198; Kluwer: Dordrecht, 1991; (a) Miller, J. S., pp 151–158; (b) Rey, P., pp 203–214; Caneshi, A., pp 215–232; (c) Kahn, O., pp 35–52.
(5) Lüdi, A.; Güdel, H. *Struct. Bonding (Berlin)* **1973**, *14*, 1.
(6) Griebler, W. D.; Babel, D. *Z. Naturforsch.* **1982**, *87b*, 832.
(7) Gadet, V., et al., pp 281–296 in ref 4.
(8) Gadet, V.; Mallah, T.; Verdaguer, M. Work in progress.
(9) Ginsberg, A. P. *Inorg. Chim. Acta, Rev.* **1971**, *5*, 45.
(10) Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1989**, *28*, 100.

0002-7863/92/1514-9213$03.00/0

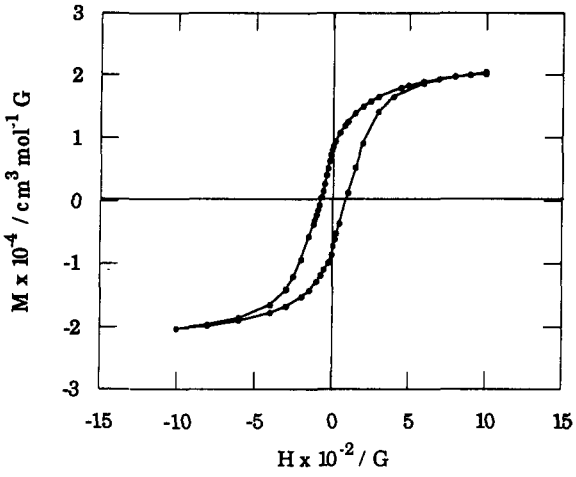

Figure 3. Hysteresis loop $M = f(H)$ at 3 K.

pounds. The magnetization vs field curve of our sample at 3 K shows a hysteresis loop with a coercitive field $H_C = 71$ G and a remnant magnetization M_R of 7.6×10^3 cm^3 mol^{-1} G (Figure 3).[11] The magnetization at high field ($H = 4000$ G) corresponds to the expected value for parallel spins $S_{Ni} = 1$ and $S_{Cr} = {}^3/_2$.

All these features are consistent with the behavior of a ferromagnet synthesized from molecules (i.e., molecular-based). The value of T_c is sensitive to the stoichiometry, correlated to the water content.[12] Neutron diffraction, X-ray absorption experiments, and chemical conditioning of the compound, with fewer or no water molecules, are in progress to elucidate the effect of water molecules upon T_c.

(11) The H_C and M_R values are not an intrinsic property of the material, since they depend upon (i) the value when the applied field is reversed (here, $H = 1000$ G) and (ii) the grain size of the sample. Increasing the grain size is underway.

(12) From our own experience and from a private communication from Prof. D. Babel.

Valence Contrast by Synchrotron Resonance Scattering: Application to a Mixed-Valence Manganese Compound

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The tunability of synchrotron radiation makes it possible to vary the scattering power of atoms of specific elements in the vicinity of the atomic absorption edges. The effect is due to the contribution of low-lying electronically excited states to the X-ray scattering process, which is accounted for in the second Born approximation of X-ray scattering theory. The variation of the anomalous components of the atomic scattering, f' and f'', may be used to create a contrast between multiwavelength results that can be applied in the determination of atomic site occupancy.[1] In addition, the variation shows a chemical shift which is about 2.5 eV for each increase in unit of formal valency of vanadium,[2]

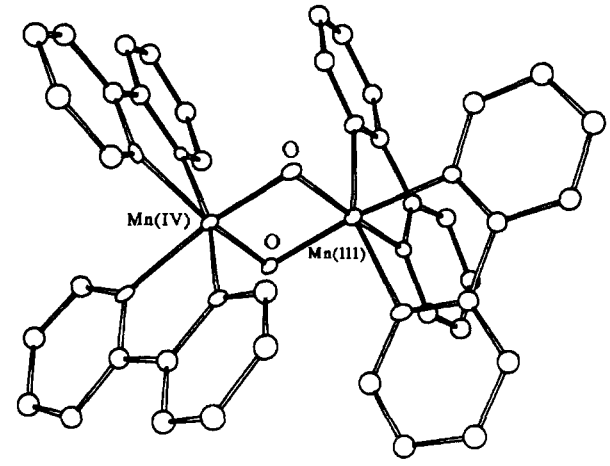

Figure 1. Diagram of the cation.

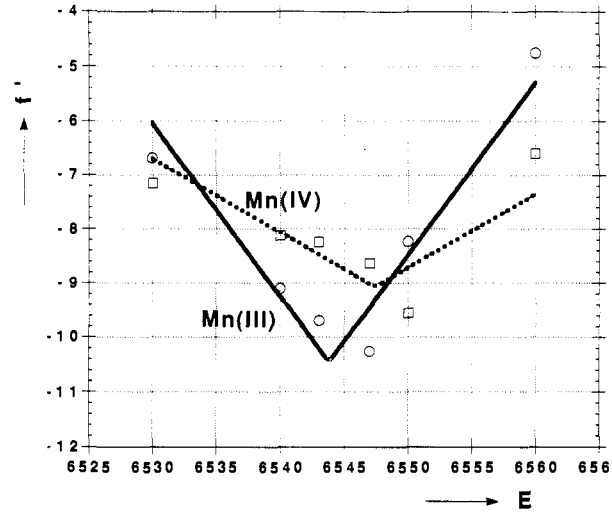

Figure 2. Triangle fit to f' values: solid line, Mn(III); broken line, Mn(IV).

and about 5 eV for Fe in $Fe^{II}(NH_4)_2(SO_4)_2 \cdot 6H_2O$ relative to $Fe^{III}(NO_3)_3$.[3] This difference can be used to obtain direct information on the electronic environment of specific atoms, as shown in powder diffraction studies of mixed-valence solids by Attfield[4] (Eu_3O_4), by Wilkinson, Cheetham, and Cox[5] ($GaCl_2$), and in our work on $NbSe_3$.[6] We report here on a first application to a mixed-valence molecular crystal, in which f' is determined from the refinement of a set of selected reflection data collected at eight wavelengths on both sides of the absorption edge.

The enzyme-photosystem model compound (μ-dioxo)Mn-(2,2′-bipyridyl)$_2$)$_2$ $(BF_4)_3 \cdot 3H_2O$ (Figure 1) was synthesized as described elsewhere.[7] It is centrosymmetric and isomorphous to the previously reported perchlorate salt.[8] A nearly cube-shaped crystal of volume 0.0135 mm^3 was used for data collection at the SUNY X3 beamline at Brookhaven National Laboratory.

The intensities of a selected set of 24 reflections were collected at eight different energies around the Mn K edge at 6540 eV, using a Si(111) double-crystal monochromator. Structure factors obtained after absorption correction were refined in terms of the

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(1) Coppens, P.; Lee, P.; Gao, Y.; Sheu, H.-S. *J. Phys. Chem. Solids* **1991**, *52*, 1267-1272.
(2) Wong, J.; Lytle, F. W.; Mesmer, R. P.; Maylotte, D. H. *Phys. Rev.* **1984**, *B30*, 5596.
(3) Coppens, P. *Synchrotron Radiation Crystallography*; Academic Press: London, 1992; p 125.
(4) Attfield, J. P. *Nature* **1990**, *343*, 46.
(5) Wilkinson, A. P.; Cheetham, A. K.; Cox, D. E. *Acta Crystallogr.* **1991**, *B47*, 155.
(6) Gao, Y.; Darovsky, A.; Pressprich, M. R.; Coppens, P. Site Specific Anomalous Scattering Study of the Valence Difference between the Nb Atoms in $NbSe_3$. 1992 NSLS User Meeting.
(7) Cooper, S. R.; Calvin, M. *J. Am. Chem. Soc.* **1977**, *99*, 6623-6630.
(8) Plaksin, P. M.; Stoufer, R. C.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 2121-2122.

0002-7863/92/1514-9214$03.00/0