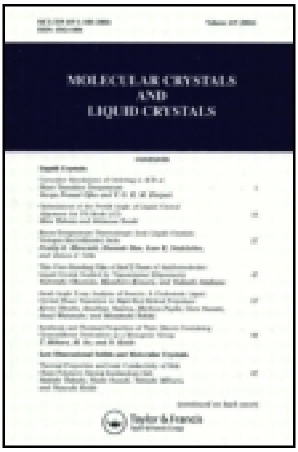

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Hexacyanometalates: Molecular Precursors for High-Spin Molecules and High-T_C Molecule-Based Magnets

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HEXACYANOMETALATES : MOLECULAR PRECURSORS FOR HIGH-SPIN MOLECULES AND HIGH-T_C MOLECULE-BASED MAGNETS

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Abstract Hexacyanometalates $[B^{III}(CN)_6)]^{3-}$ react with Lewis acids $[AL]^{2+}$ or A^{2+} to give either oligonuclear complexes with high-spin ground states $[B^{III}(CN\text{-}A^{II}L)_6)]^{9+}$ or three-dimensional (3D) networks with variable Curie temperature T_C. We report the magnetic properties of (i) an heptanuclear complex $[Cr(CN\text{-}Ni(tetren)_6](ClO_4)_9$ (tetren is tetraethylenepentamine) exhibiting a S = 15/2 ground state and (ii) a series of hexacyanometalates-based magnets, with T_C ranging from 9K to room temperature. We present the magnetic dichroic properties of some of the 3D materials, in the visible and in the X-ray range.

INTRODUCTION

Hexacyanometallates $[B^{III}(CN)_6)]^{3-}$ behave as Lewis bases since the six cyanide ions can bind to Lewis acids through the nitrogen lone-pairs and build three-dimensional (3D) systems exhibiting many useful properties[1-4]. When the Lewis acid A^{II} is chelated by a suitable polydentate ligand L, the reaction can be stopped at its first step and may in principle lead to oligonuclear bimetallic clusters $[B^{III}(CN\text{-}A^{II}L)_6]^{9+}$.

Our group is engaged in the design and characterization of molecular and molecule-based magnetic materials with unusual but predictible properties. Hexacyanometalates appeared to us some years ago as useful precursors in order to obtain systems with expected magnetic, optical and magneto-optical properties [6-8]. The stable and inert character of most of the molecular precursors and the large choice of available A and B transition metal ions offer the oppotunity to build many different materials. The high symmetry of the systems, the control of the electronic structure of A (d^{nA}) and B (d^{nB}) allow to foresee the nature of the short-range interaction between A and B through the cyanide ion and to control some of the physical (magnetic, optical) properties of the materials. Bimetallic and mixedvalence cyanides are therefore particularly attractive for new achievements in the field of (i) molecule-based magnets with tunable and high Curie temperatures (for use in magnetic devices at room temperature) along with magneto-optical properties related to their transparency (for use in magneto-optical devices) ; (ii) high-spin anisotropic molecules, whose peculiar magnetization and relaxation properties were recently demonstrated[9].

We give here a brief account of our results about a low-lying high-spin ground state molecule $[Cr^{III}(CN\text{-}Ni^{II}(tetren)_6](ClO_4)_9$, (compound **1**) and about some of the 3D materials.

LARGE SPIN CLUSTERS : A S = 15/2 GROUND STATE MOLECULE[5]

Hexacyanometallates can be suitable precursors for the synthesis of heptanuclear bimetallic complexes. The synthetic approach is based on the reaction between aqueous $K_3[Cr^{III}(CN)_6]$ and $[A^{II}L]^{2+}(ClO_4)_2$ where L is a suitable pentadentate ligand for the transition metal ion A^{II}. We report here the preliminary structure determination and the magnetic properties of $[Cr(CN\text{-}Ni(tetren)_6](ClO_4)_9$, **1**. **1** crystallizes in the $P2_1/n$ space group with cell parameters a = 16.14 Å, b = 24.38 Å, c = 15.38 Å, ß = 115.65°, V = 5455.5 Å^3. Due to structural disorder on the perchlorate anions, no reliable refinement is available up to now. It is nevertheless possible to locate heavy atoms and their neighbors, as shown qualitatively in Figure 1.The experimental measured density is 1.76, which corresponds to Z = 2 : the unit cell contains 2 heptanuclear units and 18 perchlorate ions, in line with the elemental analysis. The infra-red spectrum in the 2000-2200 cm^{-1} region is consistent with the presence of the $Cr^{III}\text{-}C{\equiv}N\text{-}Ni^{II}$ sequence (ν = 2150 cm^{-1}). With such a linear alignment, we have already shown that the t_{2g} orbitals describing the d^3 unpaired electrons of Cr(III) ion are orthogonal to the e_g orbitals describing the d^8 unpaired electrons of Ni(II) ion, leading to a ferromagnetic short-range interaction[2,3].The $\chi_M T$ values increase from T = 250K down to 6K. The room temperature $(\chi_M T)_{RT}$ is slightly higher than the one expected for isolated Cr^{III} and Ni^{II} ions. These data are consistent with a short-range ferromagnetic interaction between Cr^{III} and Ni^{II} through the cyanide bridge. The best fit of the experimental $\chi_M T$ to the analytical expression derived from the spin Hamiltonian (1) :

$$H = - J_{Cr\text{-}Ni}\, S_{Cr^{III}} \bullet [\Sigma_{i=1,6} (S_{Ni^{II}})_i] + g\text{ß}\, H \bullet (S_{Cr^{III}} + \Sigma_{i=1,6} (S_{Ni^{II}})_i \qquad (1)$$

neglecting the Ni-Ni interactions and the nickel zero-field splitting, gives $J = +16.8$ cm^{-1} and $g = 2.00$. The magnetization of the sample at $T = 6K$, in an applied field up to 7.5 Teslas, can be fitted,with $g_{15/2} = 1.97$, by a Brillouin function corresponding to a $S = 15/2$ ground state, as shown in Figure 2.

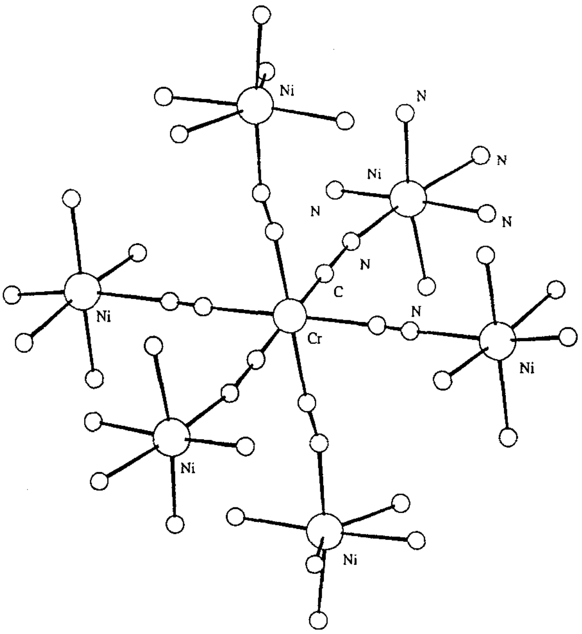

FIGURE 1 View of compound **1** where only heavy atoms and their neighbors are shown.

No hysteresis is observed in **1** at $T = 2K$ in the 0-2 Teslas range, contrarily to the case of the very anisotropic Mn_{12} cluster reported recently [9]. Indeed, Cr^{III} and Ni^{II} ions in **1** are expected to present isotropic behavior. One important information given by our study is the value of the ferromagnetic interaction constant between Cr^{III} and Ni^{II}, $J \approx +17$ cm^{-1}, which is to the best of our knowledge a record for a ferromagnetic interaction in a Cr-Ni pair at a distance larger than 5Å and allows to understand the high T_C value (90K) in the parent 3D material $CsNi[Cr(CN)_6]\cdot 2H_2O$, (compound **2**).

Work is in progress in order to synthesize along the same lines similar molecules with higher spin ground states and with significant molecular anisotropy.

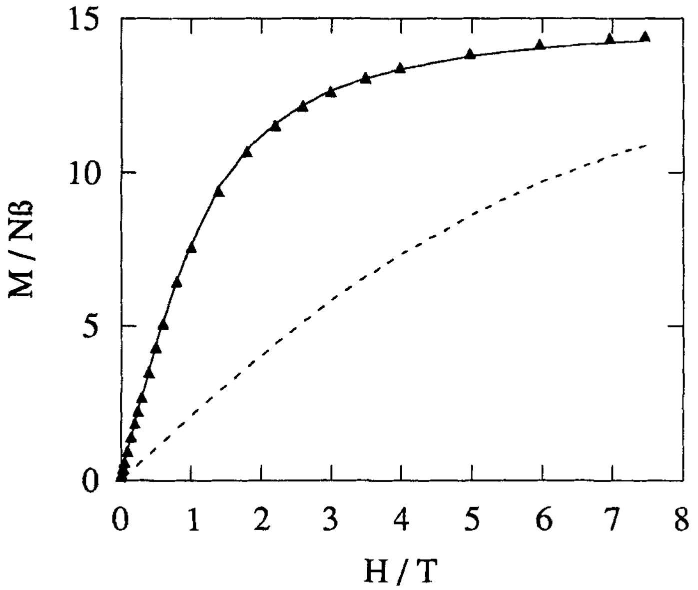

FIGURE 2 Plot of M = f(H) at T = 6 K; (Δ) experimental data, (——) best fit, (-----) Brillouin function corresponding to magnetically isolated one Cr^{III} (S = 3/2) and six Ni^{II} (S= 1).

THREE-DIMENSIONAL SYSTEMS

Synthesis and Structure

When an aqueous solution of the molecular precursor $[B^{III}(CN)_6]^{3-}$ is mixed with an aqueous solution of the aqua complex of the Lewis acid A^{II}, a neutral precipitate appears, where the $[B(CN)_6]$ entities embedded in a 3D network and is shown to be practically unchanged by EXAFS studies [10]. Lüdi and Güdel gave the key to understand the structure of the 3D systems [11] : The network is most often a face-centred-cubic (fcc) arrangement of metal ions A^{II}, saying that the octahedral holes being occupied either by the $[B^{III}(CN)_6]^{3-}$ entities, or, in case of vacancies, filled by water molecules. Depending on the charges of the ions and on the presence of other counter-cations such as Cs^I, able to fit in the tetrahedral sites of the fcc structure, different A/B stoichiometries arise : 3/2 as in $A^{II}_3[B^{III}(CN)_6]_2$. nH_2O or 1/1 as in $Cs^IA^{II}[B^{III}(CN)_6]$. $n'H_2O$, etc .... The color of the compounds changes from very light (forbidden d-d transitions) to very deep (charge transfer between the metallic ions and the cyanide or between the two metallic ions) [2].

Compounds $A^{II}_3B^{III}_2$ a	T_C / K	Short-range interaction^b	Color
Ni_3Fe_2	23	F (1x 2f)^c	deep green
Co_3Fe_2	14	AF (1x [2f + 1af])	black
Mn_3Fe_2	9	AF (1x [2f + 3af])	brown
Ni_3Mn_2	20	F (2 x 2f)	brown
Co_3Mn_2	16	F (2 x [2f + af])	brown
Mn_3Mn_2	33	AF (2x [2f + 3af])	brown
Ni_3Cr_2	53	F (3 x 2f)	light green
Co_3Cr_2	23	F (3 x [2f + 1af])	light pink
Fe_3Cr_2	16	F(3 x [2f + 2af])	deep red
Mn_3Cr_2	60	AF (3 x[2f + 3af])	yellow
Cr_3Cr_2	240	AF (3 x [f + 3af])	grey
"X_3Cr_2"^{d}	≈ 300	AF (3 x 3af) ?	deep blue

TABLE I Magnetic properties and colors of selected A_3B_2 cyanides. (a) The complete formula is written as $A^{II}_3[B^{III}(CN)_6]_2.15\text{-}18\ H_2O$; (b) AF : antiferromagnetic ($J_{AB} < 0$) ; F = ferromagnetic ($J_{AB} > 0$) ; short-range AF leads to ferrimagnetic magnets and short-range F leads to ferromagnets ; (c) in parenthesis are shown the nature and the numbers of orbital exchange pathways (f = t_{2g}-e_g ; af = t_{2g}-t_{2g}) ; (d) we give a possible formula for a recently synthesized room temperature magnet, whose full characterization is underway.

Compounds $Cs^IA^{II}B^{III}$ a	T_C / K	Short-range interaction^b	Color
CsNiCr, **2**	90 [3]	F (1x(2f + 3af)	light blue
CsMnCr, **3**	90 [12]	AF (1x(2f + 3af)	light beige

TABLE II Magnetic properties and colors of selected AB cyanides
(a) The complete formula is written as $Cs^IA^{II}[B^{III}(CN)_6]$. 0-2 H_2O
(b) AF : antiferromagnetic ($J_{AB} < 0$) ; F = ferromagnetic ($J_{AB} > 0$).;
(c) in parenthesis are shown the nature and the numbers of orbital exchange pathways (f = t_{2g}-e_g ; af = t_{2g}-t_{2g})

Magnetic Properties

The magnetic properties offer a wide range of ordering temperatures from a paramagnetic phase to a magnetically ordered state at low temperature [2-8, 12], as shown in Tables I and II and illustrated in Figure 3.

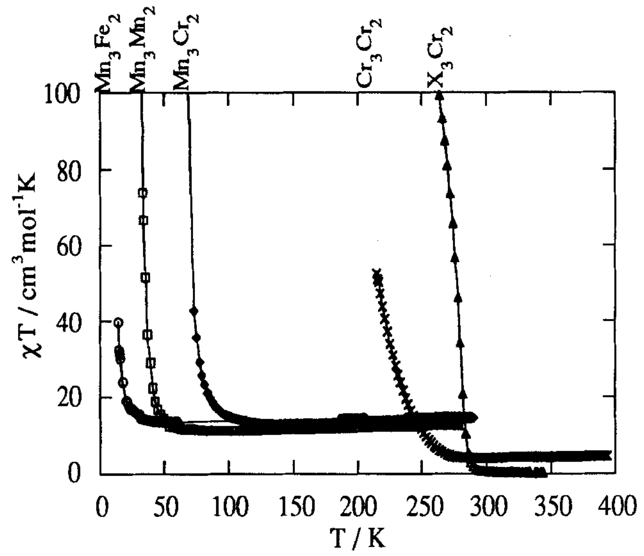

FIGURE 3 $\chi_M T = f(T)$ plots for selected A_3B_2 magnets

The Curie temperature varies with different parameters.

1) Electronic configurations of the transition metal ions A and B

a) To obtain magnetic ordering at non negligible T_C temperatures, both transition metal ions A and B must be paramagnetic. In a series of systems with an A/B stoichiometry, Babel has shown[12] that a Curie law behavior results when one of the ions is diamagnetic : (i) A (Zn^{II}, d^{10}) diamagnetic and B (Cr^{III}, d^3) paramagnetic; (ii) A (Ni^{II}, Co^{II}, Fe^{II} and Mn^{II}) paramagnetic and B (Co^{III}, low spin d^6) diamagnetic. Prussian Blue (with B = low-spin d^6 Fe^{II} and A = high-spin d^5 Fe^{III}) becomes a magnet only below $T_C \approx 5.5K$.

b) When the number of unpaired electrons on the B site increases, everything being equal, the T_C value increases : for A_3B_2 stoichiometry and antiferromagnetic interaction, this statement is perfectly illustrated by the series $Mn^{II}{}_3B^{III}{}_2$, with B = Fe, low spin d^5, $S = 1/2$ (T_C = 9K), = Mn, low spin d^4, $S = 1$ (T_C = 33K), and = Cr, d^3, $S = 3/2$ (T_C = 60K). The increase of the number of exchange pathways in the three directions of space enhances the interaction.

2) Stoichiometry

When the stoichiometry varies, for a given AB pair, the T_C varies as well. In ferrimagnets, if we summarize the Néel's results[13] by equation (3), T_C is proportional to z the mean number of paramagnetic neighbors in the lattice

$$T_C = z\,[C_A\,C_B]^{1/2}\,|J|\,/\,Ng^2\beta^2 \qquad (2)$$

C_A and C_B are Curie constants, N, g and ß have their usual meanings, z = 4 for A_3B_2 and z = 6 for AB stoichiometries. Using the data of Table I, the relation fits quite perfectly for the ferrimagnetic Mn-Cr pair ($J_{Mn3Cr2}\,/\,J_{MnCr} = 2/3$) and not too bad for the ferromagnetic Ni-Cr one ($J_{Ni3Cr2}\,/\,J_{NiCr} = 0.59$).

3) Electronic configuration of the transition metal ion A, with B = Cr

The 3D framework contains the linear B-C≡N-A fragment, which allows to foresee the nature of the short-range exchange interaction between A and B when A and B are both paramagnetic. In a first approach, the unpaired electrons can be described using the localized electron model of Kahn and Briat [14, 15] : in this model, the total interaction is the sum of orbital exchange pathways $J_{\mu\nu}$ between μ and ν symmetry orbitals :

$$J = (1/n_A n_B) \bullet \Sigma_{\mu,\nu}\, J_{\mu\nu} \qquad (3)$$

Each orbital exchange pathway can be either antiferromagnetic when the orbitals are of the same symmetry and overlap ($J_{\mu\mu} < 0$) or ferromagnetic when the orbitals are orthogonal ($J_{\mu\nu} > 0$) :

In most cases, when ferromagnetic and antiferromagnetic pathways are competing, the nature of the overall interaction can be predicted considering that when the antiferromagnetic contributions are present, they are larger than the ferromagnetic ones. Table I demonstrates both the validity of the assumption and its limits. In fact, in the cases of $Co^{II}{}_3Mn^{III}{}_2$, $Co^{II}{}_3Cr^{III}{}_2$, $Fe^{II}{}_3Cr^{III}{}_2$, a ferromagnetic coupling is observed[16]. One of the plausible explanation is the presence of low-lying charge-transfer states (such as Fe^{III}-Cr^{II}) able to stabilize the highest spin multiplicity of the ground state[16] (another explanation lies in the importance of orbital contribution).

We would like to point out one of the striking results reported in Table I; the X_2Cr_3 compound presents a room temperature T_C[17]. It was obtained through a simple approach where the decrease of the number of ferromagnetic pathways leads to an enhancement of the absolute value of the overall antiferromagnetic coupling constant and therefore the T_C. Furthermore, two other trends enhance the efficiency of the preceeding effect : when starting from Mn and proceeding leftward in the periodic table, both the energy[18] and the spread of the magnetic orbitals increase and favor a larger t_{2g}-t_{2g} overlap and thus a larger |J| value.

We did not report the magnetization *vs* field studies : they present systematically hysteresis loops and properties of soft magnets. The remnant magnetization and the coercitive fields (some tens to some hundreds of gauss) are rather low . Since T_C can rise up to room temperature, we are now engaged in new endeavors to control the coercitivity of the materials in order to favor their use in devices. Other very useful properties of the hexacyanometalates family are the optical ones : as shown in Table I, the samples are often light-colored, practically transparent in the visible range and useful for optical purposes, and in some cases deeply-colored, giving rise to possible pigments applications.

Magneto-Optical Properties

1) Visible range [19]

We performed magneto-optical experiments in the visible range with one of the transparent compounds, $CsNiCr(CN)_6 . 2H_2O$, compound **2**. Using a 0.5 mm thick compressed pellet of the polycristalline material, we were able to record magnetic dichroism at l = nm (laser). We measured a rotating power of 0.2 degrees per mm [19].

2) X-rays magnetic circular dichroism (XMCD) [20-23]

For a better understanding of the exchange interaction in our high T_C molecule-based magnets, we recorded X-ray magnetic circular dichroism at the K and L edges of the transition metals (Cr, Mn, Ni) in the magnetically ordered phase of $Cs^IA^{II}[Cr^{III}(CN)_6]$ (A = Ni, compound **2** and A = Mn, compound **3**) and at the nitrogen K edge in **2** [20, 21].

The experiments were performed at LURE, Orsay, at the dispersive EXAFS station D11 for metallic K edges, at the SU22 SuperACO station for the L edges of the metal and at the Brookhaven Dragon beam line for the nitrogen K edge. Experimental details can be found in references [20, 21]. We present, in Figure 4, only one example of the normalized isotropic spectra, recorded without applied field and the magnetic circular dichroic signal (XMCD), difference between the left (+) and right (-) polarized spectra, normalized to the isotropic signal (Chromium K edge in **2**). The energy scale is relative to the metallic K edge.

The isotropic edge spectrum displays the main features expected from metallic K edge in nearly octahedral surroundings : weak preedge signal (forbidden 1s-3d levels transitions), very intense white line (allowed 1s-4p levels transitions), multiple-scattering structures close to the white line, due to the colinearity of Cr-C-N-A units, followed by the EXAFS oscillations at higher energies. In the rising edge, the shoulder is assigned to a forbidden transition to mixed 3d-π*(CN) levels.

An intense dichroic signal is detected in the energy range corresponding to the allowed transition (white line) to the p-symmetry levels of the metal (abbreviated as 4p). The intensity is strong, compared to the one exhibited by metals and oxides. This due (i) to the localized p states in these molecule-based materials ; (ii) to the spin-orbit coupling in the excited 4p levels (since there is no spin-orbit coupling at the 1s level) and (iii) to a spin polarization of the 4p orbitals of the absorbing metallic ion by the surroundings. No X-ray dichroic signal is detected in the transitions to 3d-containing levels (t_{2g}, e_g, d-π*(CN)) for the octahedral metallic sites. The dichroic signal shown by arrows is assigned to a multi-electronic excitation [23]. Such dichroic signals are detected at all the edges. One of the striking results of such a study is the following : the sign of the dichroic signal at the Cr K edge does not change from the ferrimagnetic CsMnCr, to the ferromagnetic CsNiCr, contrarily to the change of the magnetic moment beared by the d orbitals of Cr^{III} : in both cases, the vacant 4p Cr orbitals appear to be spin-polarized in the direction of the field. This kind of phenomenon is observed for the first time. It demonstrates that the lowest unoccupied MO levels are implied in the exchange mechanism and allows to foresee a better description of the exchange mechanism, beyond the localized "magnetic orbital" model.

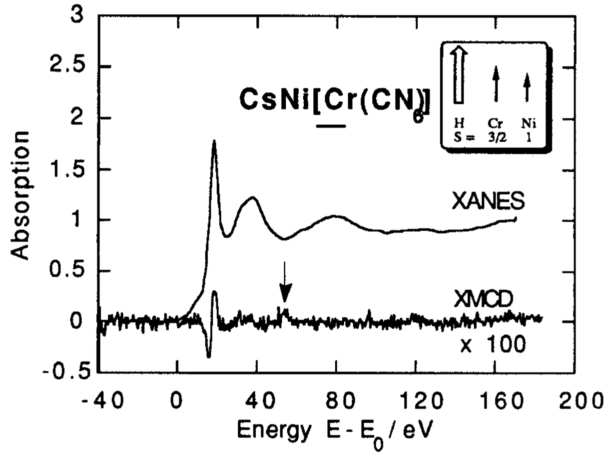

FIGURE 4 X-ray absorption spectrum and XMCD signal at the chromium K edge in **2**. In insert : ferromagnetic alignment of the spins of Cr^{III} and Ni^{II} in the applied field.

Quantitative data at the K edges can be found in reference 20 and numerical computations of the nickel L edge XMCD in compound **2**, in reference 22.

Another important result is the presence of a nitrogen K edge XMCD signal at the vacant σ* and π* levels of the cyanide bridge in **2**, which clearly shows the spin delocalization from Ni and Cr to the σ* and π* orbitals of the bridge [20].

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