A Mixed-Valence Mixed-Spin Prussian-Blue-Like Heptanuclear Complex[**]

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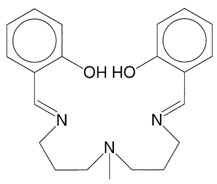
Cyanide-bridged systems have been at the forefront in the field of molecular magnetism during the last eight years.[1] Room-temperature molecule-based magnets as well as electro- and photo-induced magnetization in Prussian blue analogues have been reported.[2–4] In addition, high-spin molecules were prepared by using $[M^{III}(CN)_6]^{3-}$ (M = Cr, Fe) as building blocks to assemble heptanuclear and pentanuclear complexes with ground spin states up to 27/2.[5, 6]

Prussian blue, a three-dimensional network with a cubic structure and the formula $Fe_4^{III}[Fe^{II}(CN)_6]_3 \cdot 15\,H_2O$, has been known for almost three hundred years.[7, 8] It is well established that the Fe^{II} ions surrounded by the carbon ends of the cyanide bridges are in the low-spin $S = 0$ state while Fe^{III} ions surrounded by the nitrogen atoms of the cyanide groups and by water molecules are in the high-spin $S = 5/2$ state. This compound is famous because of its intense blue color, which arises from an intervalence band centered at 14080 cm^{-1} associated with a charge transfer from the diamagnetic low-spin Fe^{II} ion to the high-spin Fe^{III} ion.[9] Another, maybe less well known, property of Prussian blue is the occurrence of ferromagnetic ordering below the Curie temperature (T_C) of 5.6 K.[10] Mayoh and Day proposed a model for the ferromagnetic exchange interaction based on a partial delocalization of the electrons occupying the Fe^{II} t_{2g} orbitals on to the neighboring high-spin Fe^{III} sites.[11]

In order to gain more insights into the mechanism responsible for the ferromagnetic interaction we decided to use a molecular approach and prepare a discrete species that may reproduce the optical and the magnetic properties of Prussian blue. Thus, a new mixed-valence mixed-spin heptanuclear complex **1** containing a central low-spin $S = 0$ Fe^{II} ion linked to six high-spin $S = 5/2$ $Fe^{III}(L)$ species through cyanide bridges was prepared.

$[Fe^{II}\{CNFe^{III}(L)\}_6]Cl_2 \cdot 6\,H_2O$ **1**

H_2L is the pentadentate ligand bis(3-salicylideneaminopropyl)methylamine. The magnetic and the optical properties of **1** are compared to those of the tetranuclear compound **2** having the diamagnetic low-spin $S = 0$ Co^{III} as a central ion surrounded by three $[Fe^{III}(L)]$ complexes.



$[(NC)_3Co^{III}\{CNFe^{III}(L)\}_3] \cdot 6\,H_2O$ **2**

The Mössbauer spectrum of **1** at $T = 77$ K shows two absorption peaks with an isomer shift ν of −0.159 and 0.797 mm s^{-1} (Figure 1). The experimental spectrum can be fitted by two absorptions, one at $\nu = -0.195$ mm s^{-1}, attributed to low-spin $Fe^{II}(CN)_6$, and the other centered at $\nu = 0.337$ mm s^{-1} with a quadrupole splitting ΔQ of 0.923 mm s^{-1}, as expected for high-spin Fe^{III} ions in a distorted environment. The analysis of the band intensities leads to a $_{HS}Fe^{III}/_{LS}Fe^{II}$ ratio of 5.5 which is compatible with the expected value of 6.

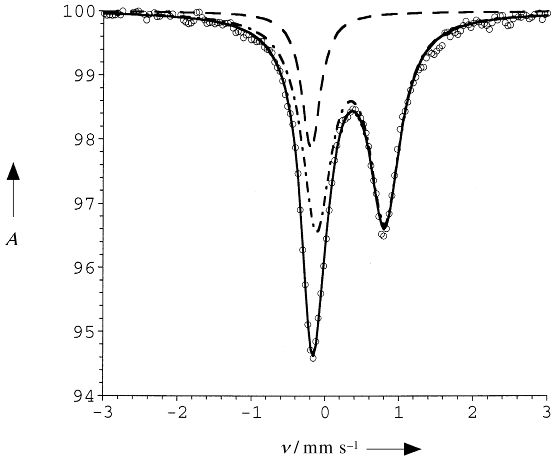


Figure 1. Absorption versus isomeric shift Mössbauer spectrum of **1**, experimental(○), best fit(——), calculated absorption for Fe^{II}(- - - -), calculated absorption for Fe^{III}(— - — -).

The first striking difference between **1** and **2** is their color. Complex **2** has the same color as the mononuclear complex [Fe(L)Cl] (dark red) while **1** is dark blue. The electronic spectrum of **2** and that of the mononuclear complex [Fe(L)Cl] in the 10000–32000 cm^{-1} region (Figure 2) are almost identical. This is not surprising as the substitution of Cl^- ligands by the nitrogen end of $[Co(CN)_6]^{3-}$ in the coordination sphere of the Fe^{III} ion should not have a dramatic influence on the spectrum. The band centered at 18700 cm^{-1} (ε(per Fe^{III}) = 2000 L mol^{-1} cm^{-1}) is actually a result of the phenolate →Fe^{III} charge transfer.[12] In contrast the spectrum of **1** shows the presence of an additional band in the 10000–20000 cm^{-1}

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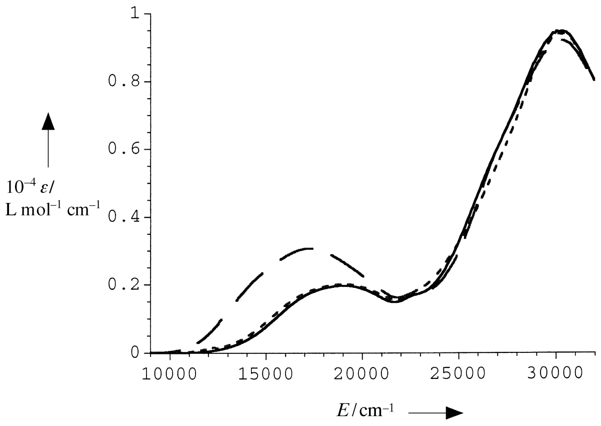

Figure 2. Absorption per Fe^{III} center versus energy in solution (CH_2Cl_2) electronic spectra for [Fe(L)Cl](——), **2** (- - - -), and **1** (– – –).

region (Figure 2). The deconvolution of the spectrum shows that the new band is centered at 14950 cm^{-1}(ε = 7800 L mol^{-1} cm^{-1}). This new optical transition can be assigned as the intervalence band associated with the mixed-valence compound **1**.

The investigation of the magnetic properties of compound **2** shows a Curie-law behavior between room temperature and 80 K with a $\chi_M T$ value (13.62 emu mol^{-1} K; 1 emu = 10^{-6} m^3) corresponding to that expected for three uncoupled high-spin Fe^{III} ions. A decrease of $\chi_M T$ is observed below $T = 80$ K (Figure 3), which indicates a weak antiferromagnetic exchange coupling between the localized $S = 5/2$ Fe^{III} ions through the diamagnetic Co^{III} central ion.[13] The magnetic behavior of **1** should be similar to that of **2** because the central Co^{III} and Fe^{II} ions have the same electronic configurations. The experimental magnetic data of **1** again show a Curie behavior between room temperature ($\chi_M T$ = 26.1 emu mol^{-1} K) and 50 K. However, below $T = 50$ K, $\chi_M T$ increases up to 35 emu mol^{-1} K at $T = 2$ K indicating the occurrence of a weak ferromagnetic interaction instead of the antiferromagnetic one observed in **2** (Figure 3).[14] Thus, the spin ground state can be evaluated as being larger or equal to 8, if an average g value of 2 is asumed. This behavior can be rationalized by an antiferromagnetic contribution similar to that of **2**, and of an additional ferromagnetic contribution with larger magnitude. That $\chi_M T$ at low temperature does not reach the expected value for $S = 15$ (120 emu K mol^{-1}) may result from competition between the two contributions that leads to an intermediate spin state.

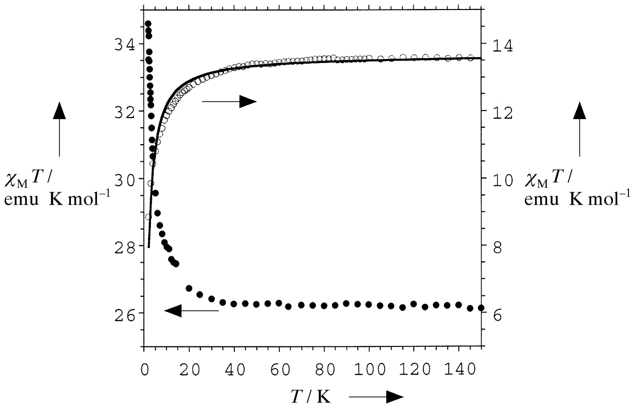

Figure 3. $\chi_M T$ = f(T) curves for **1** (●) and **2** (experimental (○), and best fit (——)).

Following the assumption of Day and Mayoh about the origin of the ferromagnetic interaction in Prussian blue[11] a comparison of the properties of **1** and **2** implies that the mixed-valence nature of compound **1**, and hence the presence of an intervalence band (absent in **2**), is the origin of this additional ferromagnetic contribution. A simple mechanism based on the interaction of the ground configuration with the excited configuration, generated by electron transfer from the low-spin Fe^{II} ion to one of the high-spin Fe^{III} ions, may account for this additional ferromagnetic contribution, but only if the exchange coupling within the excited configuration is ferromagnetic.

The six degenerate excited configurations resulting from charge transfer $(_{LS}Fe^{III})_c((_{HS}Fe^{II})(_{HS}Fe^{III})_5)_p$ (c and p refer to central and peripheral, respectively), which correspond to the transfer of an electron from the central low-spin Fe^{II} ion to one of the peripheral high-spin Fe^{III} ions through the t_{2g} orbitals, can mix with the ground configuration $(_{LS}Fe^{II})_c$-$((_{HS}Fe^{III})_6)_p$. The electron transfer between the central low-spin Fe^{II} center and one of the peripheral high-spin Fe^{III} ions insures a parallel spin alignment between these two ions because the cost in energy is less when the moving electron retains its spin during the transfer process. In the excited configuration $(_{LS}Fe^{III})_c((_{HS}Fe^{II})(_{HS}Fe^{III})_5)_p$ the magnetic interaction between the central $_{LS}Fe^{III}$ and the peripheral $_{HS}Fe^{III}$ ions may be ferro- or antiferromagnetic. If this interaction is ferromagnetic, through mixing with the ground manifold a ferromagnetic state will be stabilized. If the same interaction is antiferromagnetic, an antiferromagnetic spin ground state will appear. Thus, in order to explain the ferromagnetic interaction observed in **1**, the magnetic coupling in the excited charge-transfer configuration between a low-spin Fe^{III} and a high-spin Fe^{III} ion must be ferromagnetic. Floriani et al. have reported that in the two-dimensional compound $[(NEt_4)$-$\{Fe^{III}(salen)\}_2\{Fe^{III}(CN)_6\}_n]$ (salen = *N*,*N'*-bis(salicylidene)-ethylenediamine anion) the interaction between low-spin and high-spin Fe^{III} ions is indeed ferromagnetic.[15] Another example from our own work shows the same result in a tetranuclear compound containing a central low-spin Fe^{III} center and three peripheral high-spin Fe^{III} ions.[16] Thus, the ferromagnetic exchange interaction observed in **1** is the result of the sum of two contributions: one antiferromagnetic arising from the pure ground-state configuration and the other ferromagnetic arising from the charge-transfer configuration that mixes with the ground-state configuration. The ferromagnetic contribution cannot be present in **2** because the charge transfer configuration $(_{LS}Co^{IV})_c((_{HS}Fe^{II})(_{HS}Fe^{III})_2)_p$ is very high in energy and no band associated with such a transfer was observed in the electronic spectrum of **2** below 50000 cm^{-1}.

The mechanism we present suggests that the magnitude of the ferromagnetic contribution is directly linked 1) to the magnitude of the ferromagnetic coupling within the charge transfer configuration, and 2) to the degree of mixing between the charge-transfer and the ground-state configurations. The degree of mixing depends on the energy and the intensity of the intervalence band. The lower the energy of this band, the smaller the energy gap between the ground-state and the charge-transfer configurations is and thus the better the mixing is. The energy of the intervalence band depends on several parameters, including the stability of the Fe^{II} ion when complexed to the pentadentate ligand. Thus, by changing the nature of the pentadentate ligand we should be able to influence the electron transfer to favor an increase in the degree of mixing between the ground-state and the charge-transfer configurations. This would shift the intervalence band to lower energy. The result should be an enhancement in the magnitude of the ferromagnetic contribution. Recently two Fe^{III} complexes with different pentadentate ligands and the corresponding Prussian blue complexes have been prepared by us. The optical spectra of these compounds confirm our prediction concerning the shifting of the intervalence band (see Supporting Information).

Experimental Section

H_2L was prepared by mixing salicylaldehyde (0.1 mol) with bis(3-aminopropyl)methylamine (0.05 mol) in ethanol (100 mL). Evaporation of the solvent led to a yellow oil, yield 100%. ^1H NMR (200 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 1.83$ (q, $J = 6.96$ Hz, 4H), 2.20 (s, 3H), 2.41 (t, $J = 7.08$ Hz, 4H), 3.6 (t, $^1J = 6.84$ Hz, 4H), 6.85 (m, 4H), 7.24 (m, 4H), 8.31 (s, 2H).

[Fe(L)Cl] was obtained by adding a solution of $FeCl_3 \cdot 6H_2O$ (0.02 mol) in ethanol (50 mL) to a solution of H_2L (0.022 mol) in ethanol (30 mL). Triethylamine (0.044 mol) was added and the solution heated at 60 °C for 20 min. The black precipitate obtained was recrystallized from acetonitrile to give black needles, yield 60%. Elemental analysis calcd (%) for $C_{21}H_{25}N_3O_2ClFe$: C 56.96, H 5.65, N 9.49, Cl 8.06, Fe 12.51; found: C 56.79, H 5.68, N 9.41, Cl 8.01, Fe 12.60.

Compound **1** was obtained by adding a solution of $K_4[Fe(CN)_6] \cdot 3H_2O$ (5×10^{-4} mol) in methanol/water (4/1, 40 mL) dropwise to a solution of [Fe(L)Cl] (3×10^{-3} mol) in methanol (50 mL). The microcrystalline powder formed was filtered, washed with cold methanol then water, and then dried under vacuum. Elemental analysis calcd (%) for $C_{132}H_{162}N_{24}O_{18}Cl_2Fe_7$: C 55.92, H 5.76, N 11.86, Cl 2.50, Fe 13.79; found: C 55.89, H 5.79, N 11.93, Cl 2.50, Fe 13.65. The IR spectrum contains all the bands expected from [Fe(L)Cl] as well as an additional band at 2079 cm^{-1}, which is assigned to the asymmetric elongation of the cyanide bridge. Thermogravimetric analysis confirms a mass loss between 20 and 150 °C corresponding to six water molecules per heptanuclear complex. Decomposition is observed above 190 °C and was confirmed by thermodifferential studies. The same synthetic procedure was used with $K_3[Co(CN)_6]$ and led to the formation of the neutral tetranuclear complex **2**. IR spectroscopy shows two bands in the cyanide region at 2160 and 2131 cm^{-1} which are assigned to bridging and nonbridging cyanide groups. Elemental analysis calcd (%) for $C_{69}H_{87}N_{15}O_{12}Fe_3Co$: C 53.62, H 5.68, N 13.60, Fe 10.87, Co 3.82; found: C 53.65, H 5.59, N 13.26, Fe 10.80, Co 3.69.

The Mössbauer samples were thin (~ 15 mg cm^{-2}); the source was 25 mCi ^{57}Co:Rh. The typical instrumental line width is ≈ 0.215 mm s^{-1}. The spectrum were least-square fitted by lorentzian lines (single line + symmetrical doublet) with independent line widths, isomer shift data refer to metallic iron at 295 K. The electronic spectra were measured in CH_2Cl_2 using a Cary 5E spectrophotometer. The concentration of the solutions were [Fe(L)Cl] $c = 3 \times 10^{-4}$ mol L^{-1}, for **2** $c = 10^{-4}$ mol L^{-1}, and for **1** $c = 5 \times 10^{-5}$ mol L^{-1}.

The magnetic measurements were carried out using a SQUID susceptometer. The susceptibility was performed in the 300–20 K temperature range with an applied field of 5 kOe (1 Oe = 10^3 Am^{-1}) and below 20 K with $\mathbf{H} = 30$ Oe in order to avoid saturation effects in compound **1** that are observed down to 500 Oe. Magnetization measurements with a different applied field at a given temperature confirm the absence of ferromagnetic impurities that can be present in iron compounds.

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[13] The $\chi_M T = f(T)$ data of **2** can be fitted using the following spin Hamiltonian: $\mathcal{H} = -J_{Fe,Fe}(S_{Fe1}S_{Fe2} + S_{Fe2}S_{Fe3} + S_{Fe3}S_{Fe1}) + g\beta \boldsymbol{HS}$. The fit leads to the following values : $J_{Fe,Fe} = -0.15$ cm^{-1}, $g = 1.99$ and an agreement factor $R = 1.2 \times 10^{-4}$.

[14] Fitting the $1/\chi = f(T)$ curve of **1** with the Curie–Weiss equation $1/\chi = C/(T-\theta)$ (not shown here) leads to a Curie constant value C of 26.07 emu mol^{-1} K and a positive Weiss constant θ of 0.58 K. The magnetization versus field measurements show that saturation (29.2 Bohr Magnetons) is reached for an applied field of 5.5 Tesla, thus confirming the presence of six Fe^{III} ions per formula unit.

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