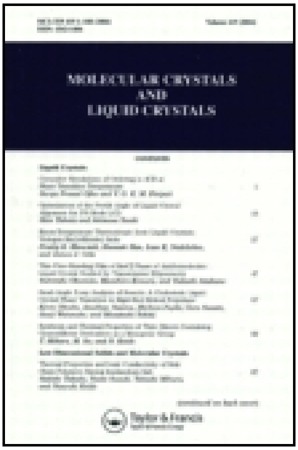

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New Molecule-Based Magnets: From Hexacyano to Octacyanometalates

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New Molecule-Based Magnets : from Hexacyano to Octacyanometalates

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Prussian blue molecule-based magnets can be designed to exhibit various magnetic properties. One of them based on chromicyanide and vanadium is a magnet at room temperature. Its properties are very sensitive to the synthetic reaction conditions, solvent effects and counterions which can be used to tune the T_C. To study the interaction between nearest metallic neighbours we explore also the influence of diffuse and high energy magnetic orbitals, i.e. 4d or 5d metallic orbitals. Two derivatives of $[W^V(CN)_8]^{3-}$ are presented.

Keywords: Prussian Blue analogs; molecular magnetism; hexacyanometalates; octacyanometalates; molecule-based magnets

INTRODUCTION

Prussian Blue molecule-based magnets with tunable Curie temperatures can be obtained through mild chemistry in aqueous media by mixing at room-temperature molecular building blocks $[M(CN)_6]^{q-}$ acting as Lewis bases with an assembling cation $[M'(H_2O)_6]^{p+}$ acting as a Lewis acid (M and M'= transition metal ions)[1]. The choice of M = Cr and M'= V allowed us to obtain the second room-temperature organometallic magnet (the first one is derived from vanadium and tetracyanoethylene)[2], $V[Cr(CN)_6]_{0.86}{\cdot}2{,}8H_2O$[3] whose T_C= 315K.
We studied the synthetic conditions (solvents, counterions,...) which not only play an important role in the obtention of the complex but also have large effects on the Curie temperature and on the magnetisation at saturation[4].

In a ferrimagnet, one of the key point to increase the short range antiferromagnetic interaction between nearest metallic neighbours is the use of metallic cations with diffuse and high energy magnetic orbitals such as V, at the left of the periodic classification. An increased overlap between magnetic orbitals provides an enhanced exchange interaction and a higher Curie temperature[3-5]. The use of molecular precursors built from metallic ions belonging to the second and third rows of the transition metals (4d or 5d orbitals) is another obvious choice. We undertook therefore the study of polycyanometalates of the 2nd and 3rd transition rows and we report hereunder preliminary studies.

VANADIUM-CHROMIUM DERIVATIVES

The room-temperature organometallic magnet, $V_3[Cr(CN)_6]_2.xH_2O$ is obtained by the general synthesis (eq. 1):

$$3[V(H_2O)_6]A_2 + 2C_3[Cr(CN)_6] \xrightarrow{\text{solvent}} V_3[Cr(CN)_6]_2.xH_2O$$

$A = SO_4^{2-}, I^-, \ldots$

$C = K^+, NH_4^+, NBu_4^+, \ldots$

Solvents = H_2O, MeOH, THF, DMSO, ...

The synthesis presents two important problems. The first one is the oxidation of V^{II} to V^{III} and V^{IV}. Several factors can take part in the oxidation: atmosphere, solvents, speed of addition and precipitation, temperature, pH, ... The second and related problem is the non-stoichiometry of the material. Different preparations using the same synthetic conditions lead to different stoichiometric ratios $\rho[V/[Cr(CN)_6]]$, Curie temperatures and magnetic properties. The size and coordination ability of the counterions, solvent, solubility and stability of starting materials, pH, ... are the important factors to control.

We studied the influence of two factors: the nature of the counteranion and the nature of the solvent.

When the reaction was carried out with the Tutton salt $C_2V^{II}(SO_4)_2.6H_2O$ ($C= K^+, NH_4^+$)[6], as a starting material, with SO_4^{2-} as counteranion, we obtained compound **1**[1]. The infrared spectrum of **1** (Figure 1) shows two wide bands centered at 2110 cm^{-1} assigned to the ν(CN) stretching in Cr^{III}-CN-V^{II}- and at 2169 cm^{-1} assigned to -Cr^{III}-CN-(V^{II}-V^{III})- or -Cr^{III}-CN-(V^{II}-V^{IV}=O)- sequences. When the reaction is performed in H_2O with

---

[1] Elemental Analyses for the proposed compound **1** $\{V^{II}_{0.78}V^{III}_{0.22}[Cr(CN)_6]_{0.56}\ (SO_4^{2-})_{0.28}\ (K^+)_{0.11}\}.4H_2O$: % Calc.; V, 18.8; Cr, 10.76; C, 14.91; N, 17.38; H, 2.95; K, 1.6; S, 3.3. % Found; V 18.3; Cr, 10.5; C, 20.6; N, 16.07; H, 3.32; K, 2.00; S, 3.10.

$[V(MeOH)_6]I_2$[7] as starting reactants we obtained compound **2**[2]. The IR spectrum of **2** is very similar to the one of **1** and therefore the bonding mode of the cyanide in both complexes can be considered as the same[8].

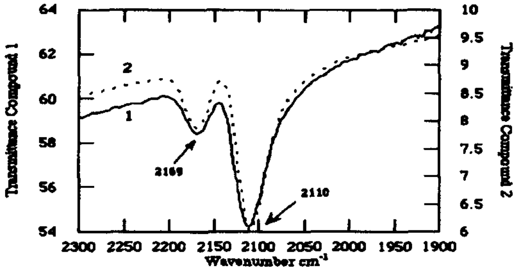

FIGURE 1 Infrared spectra of Compounds **1** and **2**

Moreover, we found non negligible amounts of SO_4^{2-} in **1** according to the elemental analyses. This fact can be explained by means of the stronger coordination ability of SO_4^{2-} compared to I^-. The presence of SO_4^{2-}, induces a purity of **1** smaller than the one of **2** and contributes to decrease the Curie temperature (T_C= 295K); in **2**, T_C= 330K, the highest obtained until now in our hands[9] (Figure 2). The magnetisation at saturation is different too, since $M/N_A\beta = 1\mu_B$ for **1** and $0.26\mu_B$ for **2**. The behaviour of magnetisation at saturation as a function of stoichiometry and vanadium oxidation states is described in detail in reference [4].

On the other hand, when the reaction is carried out in organic solvents in absence of water, we obtained systems such as compound **3** [3] which displays an infrared spectrum different from the one of compound **1** and **2** (Figure 3). The elemental analyses [1-3] are not so different but the two bands centered on 2117 cm⁻¹ and 2159 cm⁻¹ in the IR spectrum of **3** demonstrate a different bonding mode of the cyanide in **2** and **3**.

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[2] Elemental Analyses for the proposed compound **2** $\{V^{II}_{0.58}V^{III}_{0.42}[Cr(CN)_6]_{0.77}(I^-)_{0.2}(NBu_4^+)_{0.1}\}.5H_2O$: % Calc.; V, 14.52; Cr, 11.41; C, 21.29; N, 18.84; H, 3.87; I, 7.23. % Found; V 14.17; Cr, 11.23; C, 22.06; N, 18.14; H, 2.76; I, 7.52.

[3] Elemental Analyses for $\{V[Cr(CN)_6]_{0.69}(I^-)_{0.03}\}.1.5MeOH$: % Calc.; V, 19.52; Cr, 13.75; C, 25.94; N, 22.22; H, 2.29. % Found; V 20.40; Cr, 14.35; C, 26.50; N, 17.88; H, 3.85.

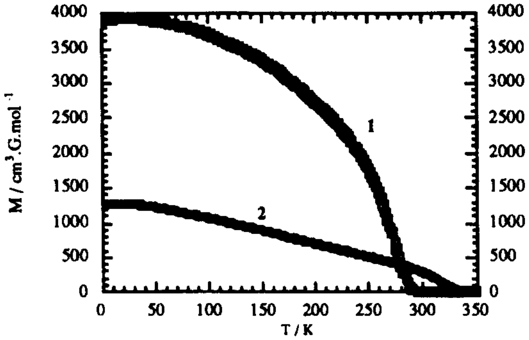

FIGURE 2 Magnetisation *vs* Temperature of Compounds **1** and **2**

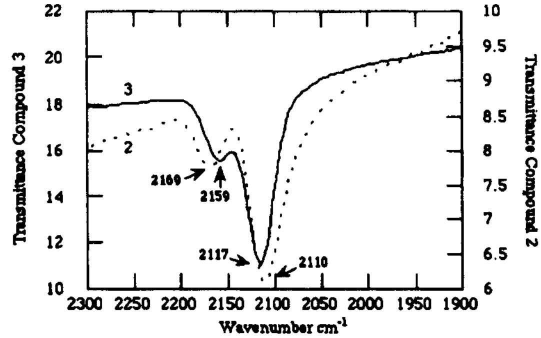

FIGURE 3 Infrared spectra of Compounds **2** and **3**

Moreover, the Curie temperature of compound **3** (T_C= 200K) is much lower than the one of **2** (T_C= 330K) (Figure 4) and the magnetisation at saturation is evanescent. Our hypothesis is that these differences are related to the kinetics of solvent exchange in the coordination sphere of V^{II}. The solvent exchange in $[V(solvent)_6]^{2+}$ is faster with water than with organic solvents. The substitution of a coordinated solvent molecule by CN^- around the V^{II} cation is more effective with water than with organic solvents that leads to a larger number of magnetic neighbours, a more compact structure, a different V^{II}/V^{III} ratio and to improved magnetic properties in **2** compared to **3**.

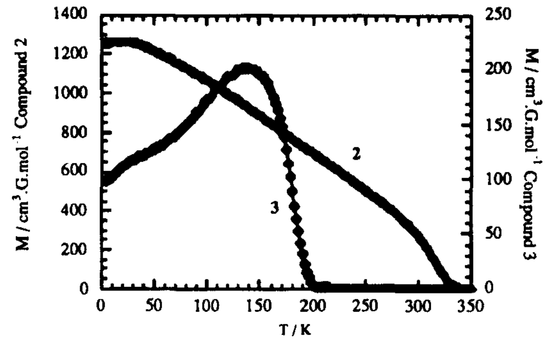

FIGURE 4 Magnetisation *vs* Temperature of Compounds 2 and 3

DERIVATIVES WITH THIRD ROW OCTACYANOMETALATES.

Another attempt to increase the interaction between nearest magnetic neighbours uses diffuse and high energy magnetic orbitals, not only with 3d metals at the left of the periodic table but also with 4d or 5d metals. An increased overlap may lead to an enhanced isotropic interaction and to higher Curie temperatures.

The magnetic precursors having the general formula $[\mathrm{M(CN)_m}]^{q-}$, (M = second or third row transition metal) which were well caracterised have all a spin S = 1/2 ground state. They are $[\mathrm{Mo^{III}(CN)_7}]^{4-}$[10], $[\mathrm{Ru^{III}(CN)_6}]^{3-}$[11], $[\mathrm{Os^{III}(CN)_6}]^{3-}$[12], $[\mathrm{Nb^{IV}(CN)_8}]^{4-}$[13], $[\mathrm{Mo^{V}(CN)_8}]^{3-}$[14], $[\mathrm{W^{V}(CN)_8}]^{3-}$[14].

Very recently was published the synthesis of $\mathrm{Mn_2(H_2O)_5[Mo(CN)_7].n\ H_2O}$[15] which has been characterised by single crystal X-ray diffraction, which exhibits a complex magnetic behavior. The last three precursors are all octacyanometalates, d^1. They form a family of interest to check the influence of magnetic orbitals, within a row (Nb, Mo) or within a column (Mo, W).

The first precursor that we have studied was $[\mathrm{W^{V}(CN)_8}]^{3-}$. The compound was synthesized as described in reference[14]. Three-dimensional magnets were obtained by preparing aqueous solution of 0.5 mmol $\mathrm{K_3W(CN)_8}$ 2 $\mathrm{H_2O}$ and 0.75 mmol $\mathrm{M(NO_3)_2}$ n $\mathrm{H_2O}$ (M = Cu, Ni) in 5 ml of distilled water and by adding the $\mathrm{Cu^{II}}$ or $\mathrm{Ni^{II}}$ solutions dropwise in the $[\mathrm{W^{V}(CN)_8}]^{3-}$ solution. A precipitate occured (grey green for Cu, orange for Ni) which was centrifugated, washed twice with 10 ml of water and dried over vacuum. The precursor $\mathrm{K_3W(CN)_8}$ 2 $\mathrm{H_2O}$ and its derivatives are light sensitive and must be handled in the dark. The analysis[4] of the copper compound is consistent with the formula $Cu_3[W(CN)_8]_2$ .3.4 H_2O, **4**. Powder X-ray diffraction, shows a non-cubic structure, unlike Prussian blue analogs, due to the non-octahedral symmetry of the molecular precursor. Extraction of more information from the powder diffraction data is underway.

The infrared spectrum shows the presence of coordinated water (at ≈ 3500 cm^{-1}). The C≡N stretching band of the cyanide stays at 2162 cm^{-1}, and a weaker one is observed at 2198 cm^{-1}, shifted to higher energy if compared to the molecular precursor (broad band near 2150 cm^{-1}) (Fig. 5). This increase, already observed in Prussian Blue analogs, is attributed to the presence of bridging cyanide.

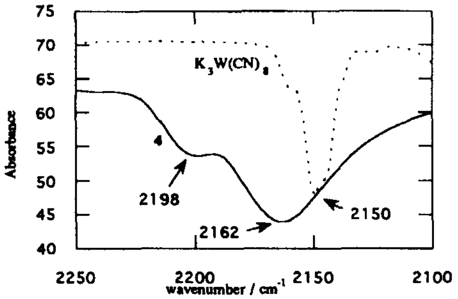

FIGURE 5 Infrared spectra of $K_3W(CN)_8$ and **4**

The solid state EXAFS spectra of $K_3[(CN)_8]$ and of **4** were recorded at the tungsten L_{III} edge, at LURE the french synchrotron facility. The Fourier transforms of the EXAFS signals are presented in figure 6. The first two peaks are identical and due to the first two shells of neighbours of the tungsten, C and N, from the cyanides. Hence, the molecular precursor remains unchanged in the final structure. The third peak, appears only in compound **4** and is a clear signature of the W-C≡N-Cu sequence.

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[4] Elemental Analyses for $Cu_3[W(CN)_8]_2$ 3.4 H_2O: % Calc.; Cu, 18.40; W, 35.50; C, 18.54; N, 21.63; H, 0.7. % Found; Cu 18.35; W, 35.5; C, 18.99; N, 20.92; H, 0.6.

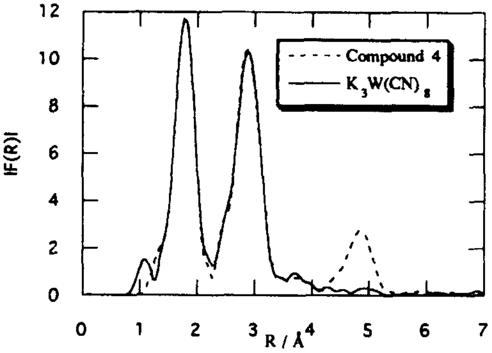

FIGURE 6 Fourier transform of EXAFS data for $K_3W(CN)_8$ and 4

The thermal dependence of the magnetisation of 4 is shown in figure 7. The transition temperature is observed at T_C = 50K. This is a non negligible value for two electrons centered on two sites far apart by more than 5Å. The observed T_C corresponds to a significant increase if compared with the first row analog $Cu_3[Fe(CN)_6]_2$ ($T_C \approx 20K$)[16]. The plot of $\chi_M.T$ *vs* T shows a continuous increase when T decreases which indicates a short range ferromagnetic interaction between W^V and Cu^{II}. Hysteresis loop (not shown) shows the compound to be a soft magnet.

The nickel compound 5 was studied more recently. No chemical analysis is still available but is likely $Ni_3[W(CN)_8]_2\ .nH_2O$. The powder diffracts X-ray with very broad diffraction lines. As in 4, IR spectrum of 5, shows the presence of coordinated water and C≡N stretching band at 2155 and 2189 cm^{-1}. The energy increase of the band compared to the one in the free precursor is attributed to bridging cyanide. The transition temperature is observed at $T_C \approx 40K$ (Fig. 8). As with the Cu-W system, the T_C is much higher than with the corresponding first row analog $Ni_3[Fe(CN)_6]_2$ ($T_C \approx$ 23K)[16]. The interaction between nearest neighbours is ferromagnetic. 5 behaves also as a soft magnet.

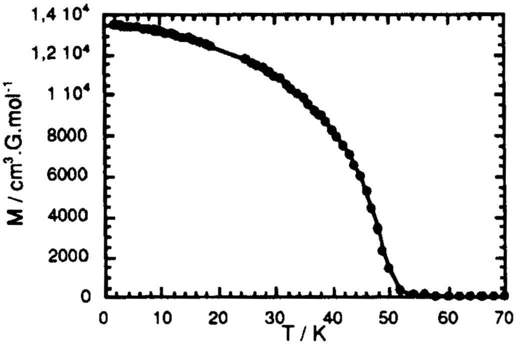

FIGURE 7 Magnetisation *vs* Temperature of compound **4**.

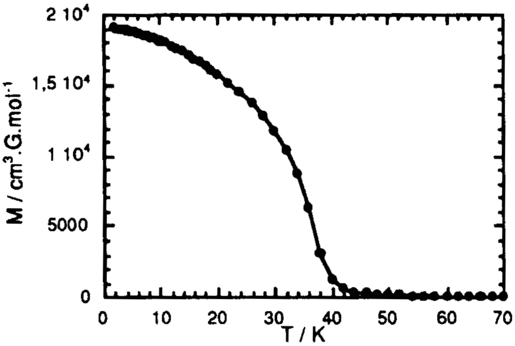

FIGURE 8 Magnetisation *vs* Temperature of compound **5**.

Conclusions

The synthetic conditions in general and more precisely, the counteranions and the solvents have large effects on the Curie temperatures and magnetisation at saturation in the VCr Prussian blues series. When the anions do not induce disorder in the structures the magnetic properties are improved. In particular the Curie temperature increases with the number of magnetic neighbours according to Néel[17]. On the other hand, in $[V(solvent)_6]^{2+}$ the solvent exchange is faster with water than with methanol or with other organic solvents, the substitution of the solvent

molecules by CN^- around V^{2+} is more effective and the number of interactions between Cr and V increases. The best synthetic conditions require (i) a large size and a weak coordination ability of the counterions and (ii) water as solvent, in spite of the oxidation of V^{II}.

We have shown also that it is possible to build three dimensional magnets from molecular precursors containing W, a third row transition metal. The first two compounds prepared exhibit non negligible Curie temperatures and encourage us to preparate new octacyanometalates $M'_3[M(CN)_8]_2$ derivatives, varying both M' (V^{II} to Co^{II}) and M (Nb, Mo) together with other teams[18].

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