Electrons at Work in Prussian Blue Analogues

by M. Verdaguer, N. Galvez, R. Garde, and C. Desplanches

Molecular magnetism is an evolving discipline relying on quantum chemistry, orbitals and Hamiltonians, organic and coordination chemistries, physics, and devices. Among the exciting molecule-based magnetic systems, Prussian blue analogues occupy a peculiar position. Prussian blue itself was described for the first time in 1704. Since this time, the history of Prussian blue analogues has been marked by electron transfer processes. It appears appropriate to present some of them in this article. After a brief introduction to their chemistry and structures, we comment on the identity between Prussian and Turnbull blue, the low temperature ferromagnetism of Prussian blue, the sensitivity of physical properties (magnetic, optical, electrochromism) to metal oxidation states, the recent discovery of photomagnetism of iron-cobalt analogues, and the design of thermodynamical machines.

Molecular magnetism is a new field in science dealing with the conception, design, study, and the use of molecular magnetic materials with new but predictable properties.[1] In this way, it follows and goes beyond magnetochemistry, which simply dealt with the magnetic properties of chemical systems. It is multidisciplinary in nature, relying on quantum mechanical principles to explain the properties, synthetic molecular chemistry, physical measurements, devices, biology (looking at biological magnetic models), and the like.

Molecular magnetism covers various topics (low spin/high spin crossover systems, exchange coupled oligonuclear compounds, organic magnets, transition metal magnets, mixed organic-inorganic magnets, etc.). We focus on some examples taken from our own work, where electron transfer and oxidation states, familiar to readers of this magazine, play a peculiar role. Prussian blue analogues have a long history in chemistry since the 18th century; they renew unexpectedly the chemistry of cyanides in the last ten years. The magnetic part of this story is of interest in that it can throw light on the steps followed in molecular magnetism in a rational approach to secure a wanted physical property. In other words, we attempt to answer to the question: Is it possible to assemble molecules in mild conditions and in a rational way to get magnetic materials whose properties can be used to ensure some useful functions in a molecule-based device?

Synthesis and Structure of Prussian Blue Analogues

The preparation of Prussian blue from aqueous solutions of potassium ferrocyanide and ferric salts is a routine college chemistry exercise. Precipitating Prussian blue is a common way to characterize iron(III) in solution[2]

$$3\,[\mathrm{Fe^{II}(CN)_6}]^{4-}\,(aq) + 4\,\mathrm{Fe}^{3+}\,(aq) + 14\,\mathrm{H_2O} \rightarrow \mathrm{Fe^{III}_4[Fe^{II}(CN)_6]_3}\,❑_1 \bullet 14\,\mathrm{H_2O}$$

where ❑ represents the vacancies of $[\mathrm{Fe^{II}(CN)_6}]$ due to the 4:3 stoichiometry. The substitution of $\mathrm{Fe^{III}}$ and $\mathrm{Fe^{II}}$ by other ions, A and B, leads to a large family of face-centred cubic systems $\mathrm{C_nA_p[B(CN)_6]q.xH_2O}$, where $[\mathrm{B(CN)_6}]$ occupies all the summits and all the centers of the faces, and A is located at the octahedral sites. C is a monovalent cation, which can be inserted in part of the tetrahedral sites of the cubic structure. The general reaction leading to a neutral solid is a simple Lewis acid-base reaction

$$q\ [\mathrm{B(CN)_6}]^{p-}_{aq}\ (\text{Lewis base}) + p\ \mathrm{A}^{q+}_{aq}\ (\text{Lewis acid}) \rightarrow \{\mathrm{A_p[B(CN)_6]_q}\}^0.\ x\ \mathrm{H_2O}\ (s)$$

Three kinds of structures appear in Fig. 1. The first two present an A/B 1:1 stoichiometry; in this case, the coordination sphere of A and B are $\{\mathrm{A(NC)_6}\}$ and $\{\mathrm{B(CN)_6}\}$; A(B) has 6 B(A) neighbors; the third structure displays an A/B 3:2 stoichiometry, with one third of $[\mathrm{B^{III}(CN)_6}]$ vacancies filled by water molecules; the B coordination sphere is left unchanged but the mean coordination sphere of A becomes $\{\mathrm{A(NC)_4(H_2O)_2}\}$. The mean number of B neighbors around A is now 4.

The Prussian blue analogues have a unit cell dimension ranging from 10.0 to 10.9 Å.[3] This value corresponds to the A-A (B-B) distances between two identical metallic ions in the network. In Prussian blue itself, the $\mathrm{Fe^{III}}$-$\mathrm{Fe^{III}}$ distance is 10.18 Å, separated by the $[\mathrm{Fe^{II}(CN)_6}]^{4-}$

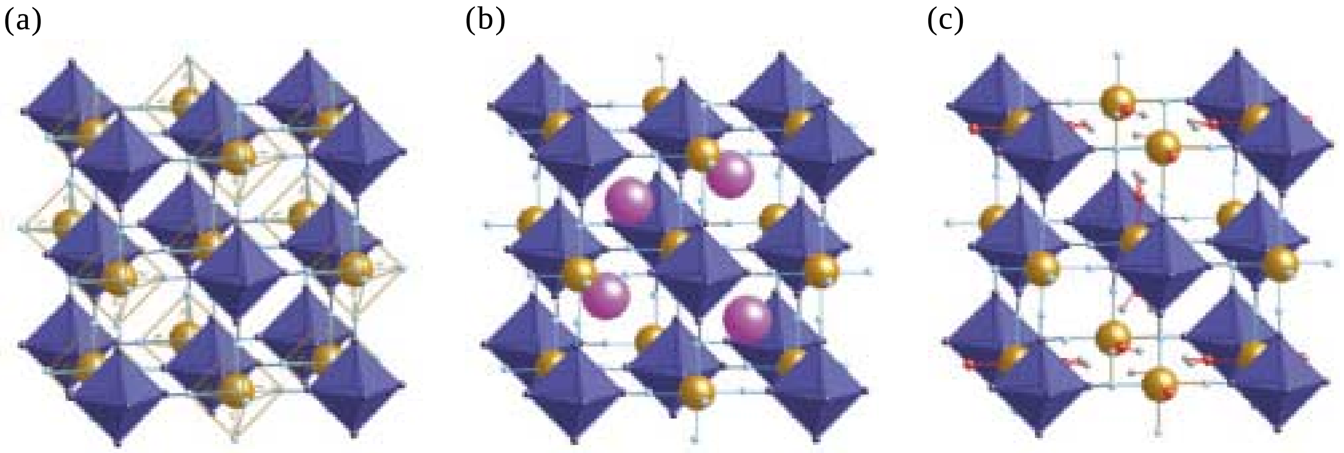
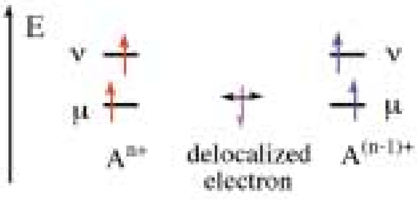


FIG. 1. Cubic structures of Prussian blue analogues: (a) $\mathrm{A^{III}[B^{III}(CN)_6]}$, or $\mathrm{A_4B_4}$; (b) $\mathrm{C^IA^{II}[B^{III}(CN)_6]}$, or $\mathrm{C_4A_4B_4}$; (c) $\mathrm{A^{II}_3[B^{III}\ (CN)_6]_2 \bullet xH_2O}$, or $\mathrm{A_4B_{8/3}}$. $[\mathrm{B(CN)_6}]$ are the blue solid octahedrons surrounded by CN (very small spheres); A are the orange spheres; C are the pink spheres; $\mathrm{H_2O}$ are the light grey spheres.

entities[2] and explains why the material behaves magnetically as a paramagnet with very weak interactions between two neighboring magnetic Fe^{III} centers, which are high spin d^5, $(t_{2g})^3(e_g)^2$, (S = 5/2).[4] As for the Fe^{II} centers, d^6, $(t_{2g})^6$, they are low spin and diamagnetic. Prussian blue is a typical example of a mixed valence system, class II in the classification of Robin and Day.[5]

For a long time, it was believed that this species was different from Turnbull blue, obtained when reacting hexacyanoferrate(III) and iron(II). But it was realized in the eighties that very fast electron transfer occurs during the precipitation and that Prussian and Turnbull Blues are a unique compound, *i.e.* $Fe^{III}_4[Fe^{II}(CN)_6]_3\,\square_1{\bullet}nH_2O$.

If one realizes that in Prussian blue, the $[Fe^{II}(CN)_6]$ core is diamagnetic and only the Fe^{III} ions are magnetic, it is difficult to understand why the paramagnetic solid transforms to a ferromagnet at T_c = 5.6K.[6,7] Indeed, some delocalization of the electrons "polarizes" the unpaired electrons on the Fe(III) sites in a ferromagnetic manner through a mechanism called "double exchange" as shown in the scheme below (the delocalized electron allows to reach a S = 3/2 ground state in a mixed valence $A^{n+}/A^{(n-1)+}$ complex). Extended to the whole network, the phenomenon leads to a ferromagnetic coupling and three-dimensional order.[4]



Room Temperature Vanadium-Chromium Magnets

Magnetic exchange interaction in Prussian blue[8]—The coupling constant J between two spins, S_1 and S_2, is given by the Hamiltonian $H = -J\,S_1\,S_2$. The high symmetry of Prussian blue and the linear bridging unit [B-CN-A] allow us to foresee the nature of the exchange interaction between A and B through the cyanide bridge. In a $(NC)_5$-B-CN-$A(NC)_5$ binuclear unit, when the orbitals containing the unpaired electrons are of the same symmetry (t_{2g}), they overlap and combine as shown in Fig. 2a. The energy between the magnetic orbitals is initially δ; after interaction, the energy gap between φ_2 and φ_1 is Δ. The interaction is antiferromagnetic (the larger Δ, the larger the antiferromagnetic coupling). On the contrary, interaction between orthogonal t_{2g}(B) and e_g(A) orbitals is shown in Fig. 2b. In the insert (Fig. 2c), we emphasize the spin density borne by the nitrogen in the two orthogonal p_y and p_z orbitals. The overlap density $[\rho = t_{2g}(B)\,e_g(A)]$ is strong on the nitrogen and we expect a strong ferromagnetism interaction since the exchange integral is related to ρ^2.[9] (Figure 2 displays the triplet configuration.) In general both interactions J_F and J_{AF} are present and compete and one has to sum the different $J_{\mu\nu}$ over all the exchange pathways: $J = \sum_{i,j} J_{i,j} = J_F + J_{AF}$.[1] Néel proposed that in ferrimagnets, the ordering temperature T_c is proportional to |J| and to z the number of magnetic neighbors.

Synthesis of VCr and sensitivity of magnetism to oxidation state—In order to obtain a molecule-based magnet with a T_c as high as possible we used the above orbital model to increase |J| and to chose the best A-B pair of transition metal ions. In the V^{II}-Cr^{III} pair, d^3-d^3, there is no ferromagnetic interaction and nine antiferromagnetic pathways $J_{i,j}$ the antiferromagnetic interaction J is maximum. Mixing aqueous solutions of $[Cr^{III}(CN)_6]^{3-}$ and V^{II} lead to $V_4Cr_{8/3}$ Prussian blue analogues, which are room-temperature magnets.[10] We observed that the Curie temperature is sensitive to the oxidation state of vanadium, so that different synthetic conditions lead to different magnetic properties due to different concentrations in V^{II}, V^{III}, and V^{IV} in the compounds. When we synthesized, for instance, $V^{II}_{0.42}V^{III}_{0.58}[Cr^{III}(CN)_6]_{0.86}{\bullet}2.8H_2O$[10] and $(V^{IV}O)[Cr^{III}(CN)_6]_{2/3}{\bullet}10/3H_2O$[11], T_c = 315K and 115K respectively arose. V^{III}, d^2, and VO^{IV}, d^1, are less efficient than V^{II}, because they provide less antiferromagnetic pathways with Cr(III).

Catalytic role of V(III)—The oxidation state of vanadium is clearly important for the magnetic properties. Working in strictly anaerobic conditions to obtain $V^{II}Cr^{III}$ derivatives, we observed that the compounds obtained were not room-temperature magnets, in contrast with the results obtained by the

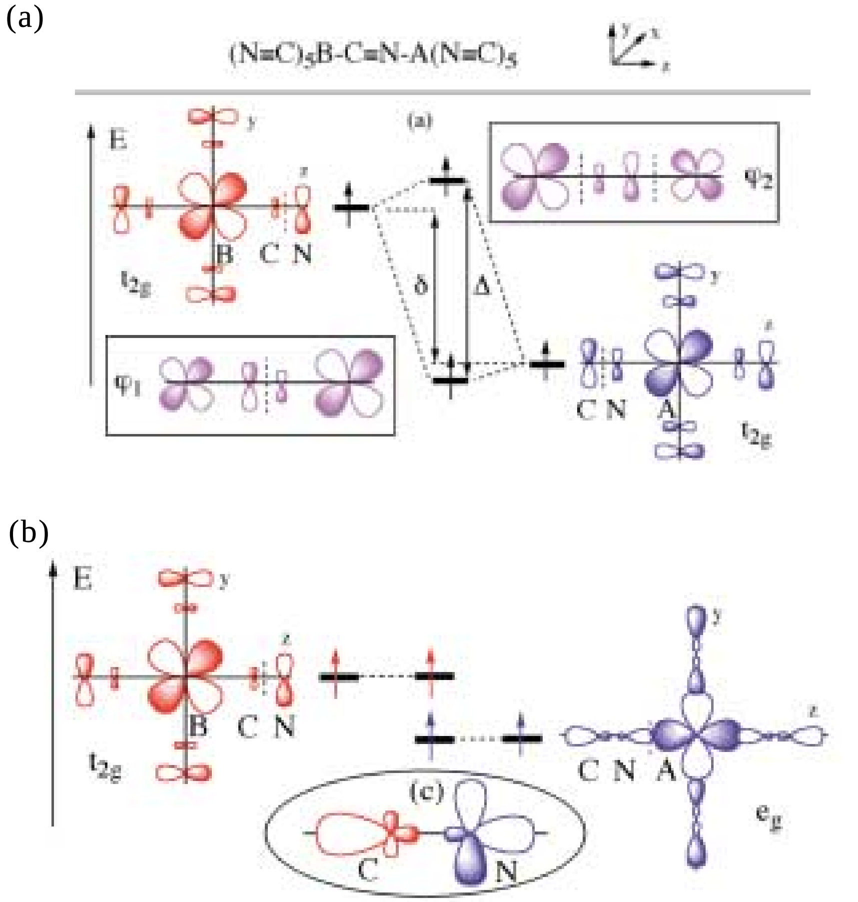


FIG. 2. *(a) Overlap and antiferromagnetic interaction in a $(NC)_5$-B-CN-$A(NC)_5$ binuclear unit. (b) Orthogonality and ferromagnetism in a $(NC)_5$-B-CN-$A(NC)_5$ binuclear unit. Orthogonal t_{2g}(B) and e_g(A) orbitals left unchanged in the binuclear unit. (c) Inset: spin density in two orthogonal p orbitals of nitrogen (p_y and p_z).*

Schlenk technique when some oxidation of vanadium(II) may arise. Therefore, we studied the influence of V^{III} ion during the synthesis.[12] We varied the amounts of V^{III} in solution and we characterized the compounds obtained. Without V^{III} in solution during the reaction $V[Cr(CN)_6]_{0.65}(I)_{0.05}$ $4H_2O$, compound 1 displayed a Curie temperature $T_c = 260K$ and a weak magnetization at saturation value $M/N_A\mu_B = 0.3$. The compounds obtained with small amounts of V^{III} in solution during the synthesis ($V[Cr(CN)_6]_{0.67}$ $(TBAI)_{0.012}$ $5H_2O$ $1.44EtOH$, compound 2, TBA = tetrabutylammonium) display a $T_c = 310K$ and a magnetization at saturation $M/N_A\mu_B = 0.98$ very close to the expected value ($M/N_A\mu_B = 1$) for a V/Cr=3/2 stoichiometry (Fig. 3). At least 1% of V^{III} was necessary to obtain room-temperature magnets. The solids do not contain V^{III}, the magnetic properties do not change with the amount of V^{III} used during the synthesis: Indeed, V^{III} plays a catalytic role in getting improved materials (Fig. 4).

Electrochromism and magneto-optics of thin layers of VCr—An appealing property of most of the molecular materials, when compared to metal or oxide magnets, is their optical transparency. Combined with high Curie temperatures, the transparency makes the VCr Prussian blue analogues suitable candidates for magneto-optical recording. A prerequisite is the deposition of the compound as a transparent thin layer. Prussian blue itself has been deposited as a thin film in 1978, using electrochemistry[13] and has been extensively studied since. More recently, thin films of high Curie temperature Prussian blue analogues have been obtained by electrochemistry: $Cr^{II}_3[Cr^{III}(CN)_6].nH_2O$[14] and VCr.[15] However in the last case, the films were prepared using a potentiostatic method, with starting materials V^{3+} and chromicyanide $[Cr(CN)_6]^{3-}$. We used instead vanadyle VO^{2+} and chromicyanide as starting materials and cyclic voltammetry, which allows at the same time to form the film and to study its electrochemical behavior. A typical cyclic voltammogram, conducted in the presence of KCl as supporting electrolyte, is presented in Fig. 5a.

Several cycles were recorded. The edge at low potential (E < -0.6 V / SCE) do not change in intensity with time. It is attributed to the reduction of the VO^{2+} ion in solution into V^{2+} and/or V^{3+}. The reduced vanadium species will thus react with $[Cr(CN)_6]^{3-}$ and form the V-Cr thin film, adherent to the electrode. The waves of reduction and oxidation in the range +0.1 and -0.6 V / SCE are attributed to the subsequent reduction and oxidation of the thin layer itself. These waves increase in intensity with time, as the film grows. The electrochromism of the film is clearly evident: The film is colorless when oxidized and transparent blue when reduced.

If CsCl is used instead of KCl as the supporting electrolyte, the electrochemical peak in oxidation disappears, and the film cannot be oxidized when formed. In order to understand the processes, which are at work, the oxidation states of vanadium were studied using K edge spectroscopy. Indeed, the very small quantity of deposited compound precluded classical (wet) chemical analysis. The reduced form of the thin layer prepared in the presence of Cs^+ was studied by magneto-optics. The measurements were recorded at different temperatures, in the transmission mode (Faraday effect) (Fig. 5b).

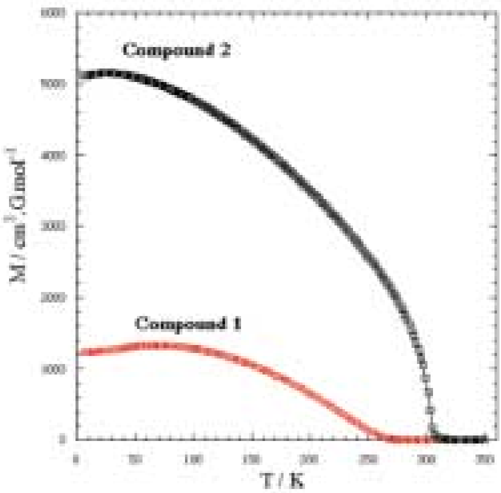


Fig. 3a. Thermal dependence of the magnetization of compound 1 (—o—) and compound 2 (—□—).

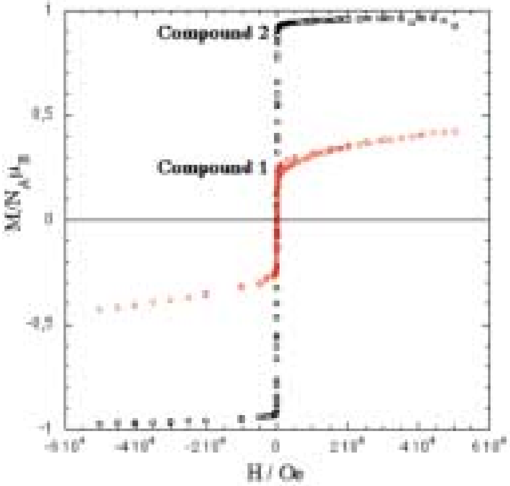


Fig. 3b. Field dependence of the magnetization of compound 1 (—o—) and compound 2 (—□—) at 5K.

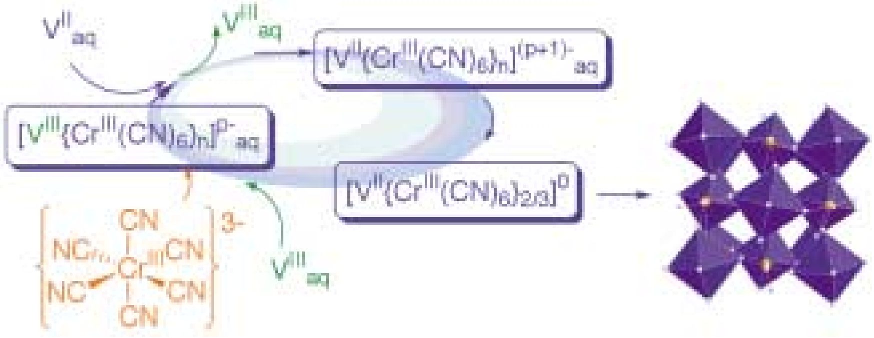


Fig. 4. Catalytic role of V(III) in the synthesis of VCr.

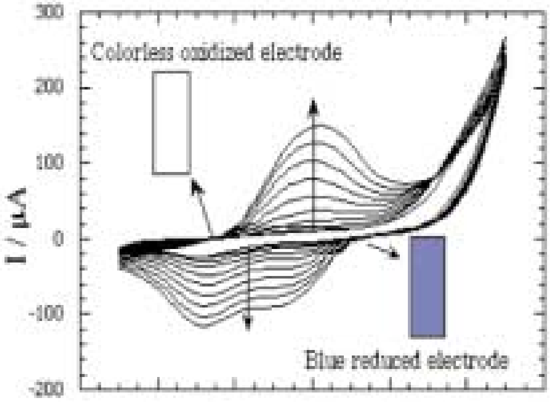


FIG. 5a. Cyclic voltammogram of a thin layer of V-Cr formed in the presence of K^+ cations.

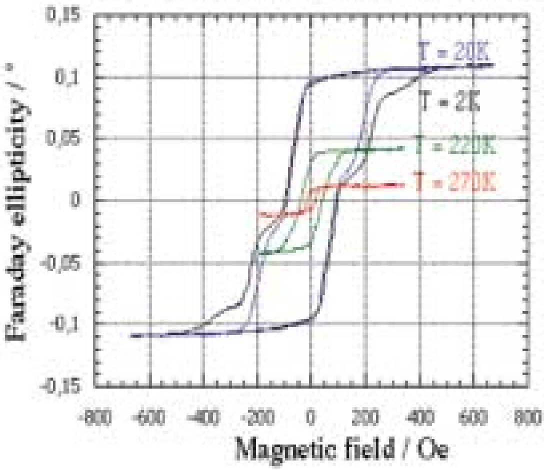


FIG. 5b. Magneto-optical Faraday ellipticity of a blue reduced VCr thin film synthetized in the presence of Cs^+.

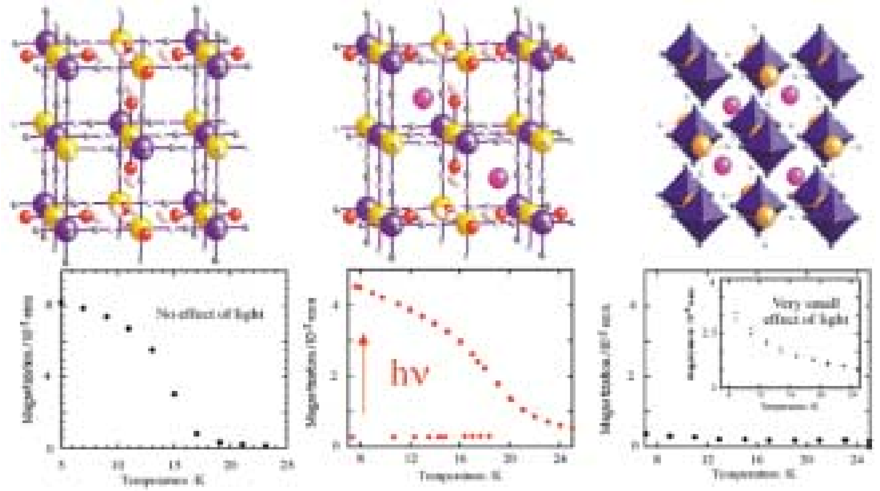


FIG. 6. Photo-induced magnetization in cobalt-iron Prussian blue analogues, controlled by alkali cation insertion (from Anne Bleuzen, Ref. 18b).

At low temperatures, the signal consists of the superposition of different hysteresis curves, showing the complexity of the material. The important fact to point out is that some hysteresis remains at temperatures as high as 270 K: It demonstrates the possibility of preparing room T_c VCr thin film, opening the way for magneto-optical data storage.

We characterized the reduced (blue) state of the thin layer, deposited in the presence of KCl and CsCl by X-ray absorption at the vanadium K edge. Three compounds were used as references, namely VCr powders where vanadium was identified as being at the oxidation degrees II ($V^{II}Cr$), III ($V^{III}Cr$) and IV ($V^{IV}OCr$) respectively. In the case of the reduced layer obtained in the presence of K^+, we determined, by means of the references, the presence of V essentially at the oxidation degree III. Contrarily, in the layer obtained in presence of Cs^+ the vanadium is present as oxidation degree II. Alkaline cations have thus an important influence in the electrosynthesis of the film.

Photo-induced electron transfer in photomagnetic Prussian blue—Another efficient way to modify the magnetic properties of Prussian blue analogues is the use of photons. The phenomenon was discovered by Hashimoto and coworkers,[16] commented on by Verdaguer,[17] and developed further by the two teams[18] and the one of Miller.[19] The mechanism of the creation of diamagnetic pairs in the solid was proposed as follows. The insertion of x alkali cations in the octants of the structure induces the insertion of x/3 $[Fe^{III}(CN)_6]^{3-}$ to ensure electroneutrality. So that the mean coordination sphere of cobalt(II), which is $[Co^{II}(NC)_4(OH)_2]$ in $Co^{II}_4[Fe^{III}(CN)_6]_{8/3}\,\square_{4/3}\bullet nH_2O$ becomes $[Co^{III}(NC)_6]$ in $Rb_4Co^{III}_4[Fe^{II}(CN)_6]_4\,\square_0$, since the ligand field induced around the cobalt by the N-bonded cyanides increases and so does the reducing power of cobalt, hence an electron transfer from cobalt^{II} to iron^{III} and the formation of the diamagnetic Co^{III}-Fe^{II}.

When irradiated (Fig. 6), the samples show no sign of photo-activity in the absence of Co^{III}-Fe^{II} pairs, as in case (a); or when the network is too constrained, as in case (c). The photoactivity is maximum in case (b) when both Co^{III}-Fe^{II} pairs and vacancies are present, which act as relaxation points in the network. Case (b) is remarkable, and is the first example of a phase transition between a diamagnetic phase to a ferrimagnetic one by photo-excitation. At 110-140 K, the metastable state comes back to the diamagnetic fundamental state. This example opens the way to photo-excitable rewritable memories.

Devices: How to Transform Light into Mechanical Energy for Free

Once room temperature is reached, it becomes possible to think about the applications and design of devices. A molecule-based magnet such as the vanadium-chromium system (T_c = 42°C), can be a useful tool to illustrate easily, near room temperature, what is a Curie temperature. Figure 7 displays a demonstrator designed for this purpose.

The compound is sealed in a glass vessel under vacuum and suspended at the bottom of a pendulum (equilibrium position in absence of permanent magnet). It is then cycled between its two magnetic states: the 3D-ordered ferrimagnetic one, when T < 42°C and the paramagnetic one, when T > 42°C. The three steps are: (1) the room temperature magnet is cold ($T < T_c$, ferrimagnetic state). It is attracted by the permanent magnet and deviated from the vertical direction (position 2). Its temperature increases because it is heated by a light beam focused above the permanent magnet; (2) the room temperature magnet is hot ($T > T_c$ paramagnetic state). It is no longer attracted and is moving away from the magnet (position 1). Its temperature decreases since it is air-cooled. (3) The room temperature magnet is now cold ($T < T_c$). It is attracted again by the permanent magnet and the process is ready for a new oscillation. The demonstrator has been operating for a long time in our laboratory and millions of cycles have been accomplished without any fatigue. The device is an example of a thermodynamical machine working between two energy reservoirs with close temperatures (sun and shadow), allowing the conversion of light into mechanical energy.

Conclusion

We hope to have shown, even if too briefly, that molecular magnetism is a multi-disciplinary area, which allows the molecular chemist, with the help of quantum chemistry, to obtain molecular materials with targeted magnetic properties, to study them in close collaboration with physicists, and to use their functions in useful devices such as rewritable memories and storage of solar energy,. ■

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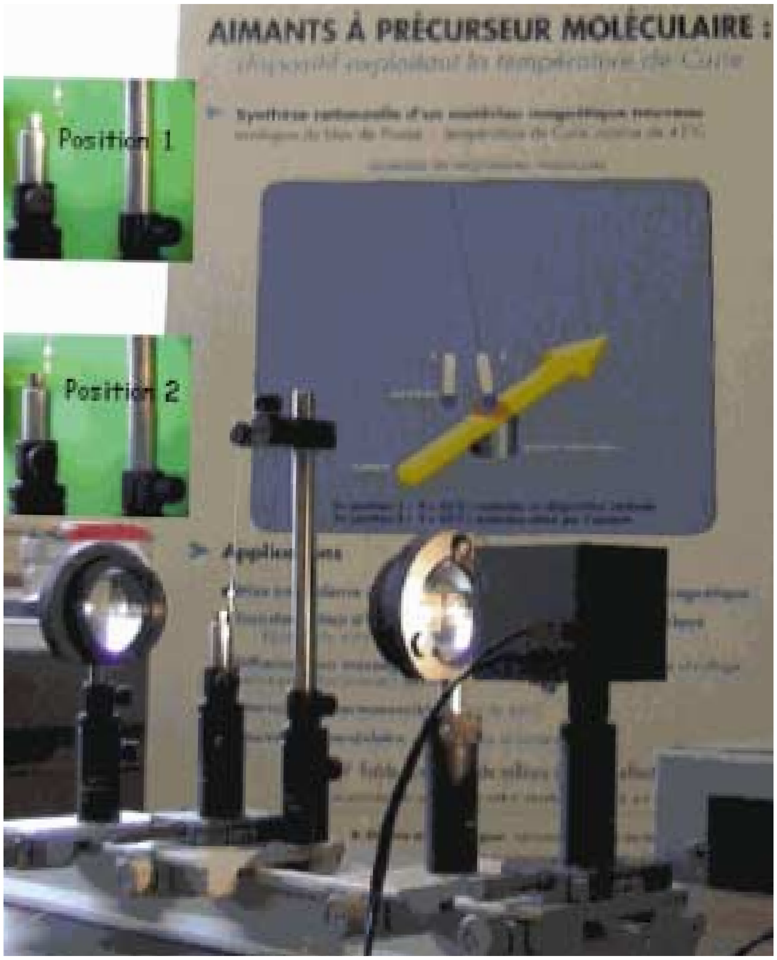

FIG. 7. *The device, a thermodynamical machine, transforming light into mechanical energy for free.*

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