Mixed valency and magnetism in cyanometallates and Prussian blue analogues

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Prussian blue (PB) is a well-known archetype of mixed valency systems. In magnetic PB analogues \( \text{C}_x\text{A}_y\text{[B(CN)\_6]}_z \cdot n\text{H}_2\text{O} \) (C alkali cation, A and B transition metal ions) and other metallic cyanometallates \( \text{C}_x\text{(AL)}_y\text{[B(CN)\_8]}_z \cdot n\text{H}_2\text{O} \) (L ligand), the presence of two valency states in the solid (either A–B, or A–A‘ or B–B‘) is crucial to get original magnetic properties: tunable high Curie temperature magnets; photomagnetic magnets; or photomagnetic high-spin molecules. We focus on a few mixed valency pairs: V(II)/V(III)/V(IV); Cr(II)/Cr(III); Fe(II)–Fe(III); Co(II)–Co(III); Cu(I)–Cu(II); and Mo(IV)/Mo(V), and discuss: (i) the control of the degree of mixed valency during the synthesis, (ii) the importance of mixed valency on the local and long-range structure and on the local and macroscopic magnetization, and (iii) the crucial role of the cyanide ligand to get these original systems and properties.

Keywords: cyanometallates; Prussian blue analogues; mixed valency; high \( T_C \) molecule-based magnets; photomagnetism; photomagnetic high-spin molecules

1. Introduction

When the draper Diesbach discovered in 1704 in Berlin a new blue pigment instead of the red one he was looking for, he evidently did not immediately realize the possible impact of his discovery not only for the chemistry of blue pigments but also for the chemistry of materials. He did not imagine that the blue colour would become an archetype of metal-to-metal, intervalence electronic transition in mixed valency complexes, and an outstanding example of class II in the Robin & Day (1967) classification of mixed valency systems. Nowadays, we are accustomed to prepare Prussian blue (PB) and its analogues as shown below rather than by following the old recipe of Diesbach:

\[
4\text{Fe}^\text{III}\text{Cl}_3 + 3\text{K}_4\text{[Fe}^\text{II}\text{(CN)\_6]} + n\text{H}_2\text{O} \rightarrow \text{Fe}_4^\text{III}\text{[Fe}^\text{II}\text{(CN)\_6]}_3 \cdot n\text{H}_2\text{O} + 12\text{KCl.}
\]

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One contribution of 15 to a Discussion Meeting Issue ‘Mixed valency’.

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A wide family of PB analogues (PBA) has followed, using the amazingly flexible structure of the molecule-based perovskite, often cubic (figure 1) (Ludi & Güdel 1973):

\[ y(A^{p+}X^-) + z(C_{(6-q)}^+(B(CN)_6)^{(6-q)-)} + nH_2O \rightarrow \{C_xA_y[B(CN)_6]_x \cdot nH_2O\}^0 \]

+ py(C^+X^-)

(C is an alkali cation, A and B are transition metal ions).

Figure 1. Perspective view of the face-centred cubic structure of PB analogue \( \{A_1[B(CN)_6]^z \cdot nH_2O\}^0 \). Dark filled octahedra, B sites surrounded by (CN) units (C, small light grey spheres; N, small dark grey); large light grey spheres, A sites; medium grey spheres, O (water molecules).

Figure 2. (a) Linear B–CN–A unit and the systems reviewed (above, hexacyanometallate derivatives; below, octacyanomolybdate ones). (b) Bent B–CN–A unit. The bent angle \( \theta \) can strongly depart from 180°.
We review the magnetic properties of a few systems where the mixed valency of transition metal ions A or B is crucial (figure 2).

In most cases, the B–CN–A unit is linear or considered as such (figure 2a) but its bending (figure 2b) is often observed. A recent general review on magnetic PBA is available (Verdaguer & Girolami 2005). In most of the cases reported here, the systems are class I where the valencies on A and B are localized. In two of them, the valency is switching by photoinduced electron transfer, giving rise to typical photomagnetic materials. All the systems have in common the presence of the cyanide ion bonding two transition metal ions. It is wise to remember that the cyanide ligand is at the same time a very friendly ligand, since it gives rise to so many interesting magnetic systems, and also a very dangerous one (see Sharpe 1976; Dunbar & Heintz 1997): (i) cyanide is friendly with the synthetic chemist since it is small and dissymmetric; it is able to give molecular precursors with strong metal–carbon bonds, stable and inert such as \([B^{q+}(CN)_{6}]^{(6-q)-}\) and \([B^{q+}(CN)_{8}]^{(8-q)-}\); these complexes can be used in turn as Lewis bases to give ordered bimetallic systems based on the B–CN–A units; the electronic structure of cyanide allows to transmit ferro- or antiferromagnetic (AFM) interactions depending on the electronic structures of the coordinated metallic ions A and B, and (ii) cyanide is also a very dangerous ligand, even a lethal one; when placed in an acidic medium it transforms into hydrogen cyanide, a very toxic gas. Every effort must be undertaken to avoid such situations, to work in well-ventilated places and to eliminate unreacted cyanide as cyanate in basic hypochlorite baths (as it was done in the present work).

The magnetic properties are governed first by the electronic structure of the transition metal ions B and A. In PBA, the electrons are distributed in \(t_{2g}\), \(\pi\) symmetry, and \(e_g\), \(\sigma\) symmetry, orbitals (figure 3a). The electron distribution obeys the ligand field rules (always \(t_{2g}\) low spin (LS) on the B site, and high spin (HS; often) or LS on the A site) and varies with valency. For localized electrons, the nature of the interaction between A and B (ferromagnetic (FM) or AFM) depends on the overlap between orbitals on neighbouring sites and agrees pretty well with the Kahn & Briat model (Kahn 1993), where the coupling constant \(J\) between A and B, using the Hamiltonian \(\mathbf{H} = -J\mathbf{S}_A\mathbf{S}_B\), is \(J = 2k + 4\beta S\) (\(k\), exchange integral; \(\beta\), resonance integral; \(S\), overlap integral). As shown by PB itself, electrons are not always strictly delocalized and other models are useful. Moreover, the exchange properties are also influenced by the energies.
of the orbitals. Even if many theoretical endeavours were already made to understand bonding and exchange in PBA, the four orbitals interaction scheme shown in figure 4 still has many features to reveal to allow to understand and predict bonding, exchange, electron (de)localization, electron transfer in the B–CN–A unit, linear or bent (figure 2; S. Alvarez et al. 2005, unpublished work; B. Siberchicot & M. Verdaguer 2007, unpublished work). Another important point for the magnetic properties is the presence of $[\text{B(CN)}_6]$ vacancies in the structure, when the stoichiometry coefficient $z$ is less than 1. In figure 1, the vacancies are visible above and below the central atom. They are filled with water molecules, some coordinated to the A centres, others (not shown for clarity) bonded by hydrogen bonds. Vacancies, statistically distributed, are intrinsic to non-stoichiometric PBA, and they are not defects. The B centres are always connected to six A centres through cyanide bridges, whereas the number of B centres connected to the A ones depends on the stoichiometry $(\text{A(CN)}_4(\text{H}_2\text{O})_2)$ of the A site at the centre in figure 1. A useful tool to evaluate the Curie temperature is a simple relation derived from Néel, suggesting that $T_C$ should be proportional to the number of magnetic neighbours $Z$ ($T_C \propto Z|J|$), which depends on the number of vacancies.

2. Room-temperature magnets: vanadium–chromium analogues

We begin with mixed valency vanadium in the systems $\{\text{C}_x\text{V}_y[\text{Cr}^{\text{III}}(\text{CN})_6]_z\} \cdot n\text{H}_2\text{O}$, which provide the highest Curie temperature within the PBA family (see Verdaguer et al. 1999a, b). Well-defined systems with only one oxidation state of vanadium have been described: with vanadium(II) by Holmes & Girolami (1999) $\{\text{KV}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_z\} \cdot 2\text{H}_2\text{O}$; the PBA with the highest Curie temperature so far, $T_C = 376$ K and by Garde et al. (2002); $\{\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{8/3}\} \cdot n\text{H}_2\text{O}$ ($T_C \approx 315$ K) and also with vanadyl V(IV) by Ferlay et al. (1999); and $\{\text{V}^{\text{IV}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{8/3}\} \cdot n\text{H}_2\text{O}$ ($T_C \approx 115$ K). Two observations can be made: first, for a given oxidation state, the Curie temperature depends on the stoichiometry, even if it does not exactly follow the indication of Néel that $T_C$ should be proportional to the number of magnetic neighbours ($T_C \propto Z|J|$): if one takes Garde’s compound as the reference for $T_C$, then Girolami’s one should be approximately 472 K. Second observation, for different oxidation states on the A site, the higher $T_C$ corresponds to the less oxidized state, i.e. the one where the energies of the d orbitals are closer to those of the $\pi^*$ orbitals of the cyanide (figure 4). This is also true for the cyanovanadate of manganese (II) with $T_c = 250$ K (Entley & Girolami 1995).

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Nevertheless, in many syntheses, the vanadium is in different oxidation states V(II)–V(III) or V(IV). The first PBA published with a \( T_C \) above ambient was obtained by adding the Tutton salt \((\text{NH}_4)_2\text{V(SO}_4)_2\cdot6\text{H}_2\text{O}\) to \( K_3\text{Cr(CN)}_6 \). A midnight blue solid precipitates from a solution that has a stoichiometry of \( \text{V[Cr}^{\text{III}}(\text{CN})_6]_{0.86}\cdot2.8\text{H}_2\text{O} \) and a magnetic ordering temperature of 315 K. It is indeed a mixed valency system, \( \text{V}^{\text{III}}-\text{V}^{\text{VIII}}-\text{Cr}^{\text{III}}(\text{CN})_6 \) with \( \alpha=0.42 \). The A sites contain \( \text{V}^{\text{II}} \) and \( \text{V}^{\text{III}} \). The weak magnetization at saturation (0.15 \( \mu_B \)) fits with the formula. The coercive field corresponds to a very soft magnet (25 Oe at 10 K). The compound is very sensitive to dioxygen, since the vanadium species are slowly oxidized to the vanadyl derivative. Dujardin et al. (1998); Miller (2000); Ohkoshi & Hashimoto (2001) were able, by varying the synthetic conditions, to improve the magnetic properties of the systems by changing the stoichiometry \( z \) and the \( \text{V}^{\text{II}}/\text{V}^{\text{III}} \) ratio \( \alpha \). We are touching here on one of the key point of using mixed valency PBAs for tuning the magnetic properties: the A sites can accommodate metallic cations with different oxidation states and spins. Besides the number of vacancies and the \( J \) values, this opportunity changes the total magnetization \( M_T \). In our VCr ferrimagnets, the antiparallel alignment of the neighbouring spins in the magnetically ordered phase leads to a resulting total magnetization \( M_T \), which is the difference between that arising from the subset of chromium ions \( M_Cr \) and that from the subset of vanadium ions, \( M_V \), \( M_T=|M_{Cr}-M_V| \). The larger magnetic moments can be borne either by the chromium ions and they aligned parallel to the external applied field (\( M_{Cr}>M_V \)) or by the vanadium ions when \( M_V>M_{Cr} \). Then the magnetic moments of vanadium ions lie parallel to the field. In between, the magnetization can be zero. More precisely, in the analogues \( \text{C}^y_\alpha \text{V}^{\text{III}}_{2/3} \text{V}^{\text{II}}_{1-\alpha}[\text{Cr}^{\text{III}}(\text{CN})_6]_z\cdot n\text{H}_2\text{O}, M_T=-(3z-\alpha-2) \). The corresponding spin \( S=M_T/2 \) is represented in figure 5 when \( \alpha \) varies from 0 to 1 and \( z \) varies from 2/3 to 1.

Figure 5. Variation of the total magnetization (or spin \( S \)) for mixed valency compounds with formula \( \text{C}^y_\alpha \text{V}^{\text{III}}_{2/3} \text{V}^{\text{II}}_{1-\alpha}[\text{Cr}^{\text{III}}(\text{CN})_6]_z\cdot n\text{H}_2\text{O} \) (A\(^{-1}\) represent an anionic species with charge 1).
The maximum spin $S=1$ corresponds to stoichiometries $V^{III}_1Cr^{III}_1$ (majority spin on Cr) or $V^{II}_1Cr^{III}_{2/3}$ (majority spin on V). The minimum spin is zero, when the spins of vanadium and chromium, antiferromagnetically coupled, exactly compensate (bold diagonal line between $V^{II}_1Cr^{III}_{2/3}$ and $V^{IV}_1Cr^{III}_1$ in figure 5). In between, mixed valency allows to tune the total spin. Compound 1 is $\{V^{III}_{0.43}V^{III}_{0.53}(V^{IV}O)_{0.02}[Cr(CN)_{6}]_{0.69}(SO_4^{2-})_{0.23}(K_{2}SO_4)_{0.02}\} \cdot 3H_2O$, with an experimental magnetization at saturation $M_S=0.36 N_A \beta$ and a positive calculated $M_T$ value, $M_T=+0.36 N_A \beta$. Another plane (not shown) represents the $V^{II}/V^{IV}$ systems. Compound 2 is $\{Cs^{I}_{0.82}V^{III}_{0.60}(V^{IV}O)_{0.34}[Cr(CN)_{6}]_{0.92}(SO_4^{2-})_{0.20}\} \cdot 3.6H_2O$, presents an experimental $M_S=0.42 N_A \beta$ and a negative calculated $M_T$ value ($M_T=-0.36 N_A \beta$). The crucial difference between the two compounds is the sign of $M_T$, influenced by the balance between the values of $z$ (Cr$^{III}$/V ratio) and the mixed valency ratio $V^{II}/V$. It is amazing that, contrary to conventional magnetization measurements, which give the absolute value of the macroscopic magnetization, X-ray magnetic circular dichroism (XMCD) can demonstrate the local magnetization of the chromium and vanadium (see Sainctavit et al. 2001). XMCD of compounds 1 and 2 was studied by Dujardin et al. (1998). At the chromium or vanadium edges, the XMCD signals have the characteristic shape shown in figure 6. The signal is either $+/-$ or $-/+$. This shape can easily be related to the orientation of the magnetic moments in the applied magnetic field (table 1).

Table 1. Schematic description of the K-edge XMCD signals of chromium and vanadium; orientation of the magnetic moments in the applied magnetic field; nature of interaction between Cr(III) and its magnetic neighbours.

<table>
<thead>
<tr>
<th>part A</th>
<th>interaction</th>
<th>chromium XMCD</th>
<th>magnetization Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>compound CsNiCr</td>
<td>FM</td>
<td>$-/+\uparrow$</td>
<td>$+/$</td>
</tr>
<tr>
<td>compound CsMnCr</td>
<td>AFM</td>
<td>$+/-\uparrow$</td>
<td>$-/$</td>
</tr>
</tbody>
</table>

Table 1.

<table>
<thead>
<tr>
<th>part B</th>
<th>chromium XMCD</th>
<th>vanadium XMCD</th>
<th>interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>compound 1 VCr</td>
<td>$+/-(-\downarrow)$</td>
<td>$-/+(\uparrow)$</td>
<td>AFM</td>
</tr>
<tr>
<td>compound 2 CsVCr</td>
<td>$-/+(\uparrow)$</td>
<td>$+/-(-\downarrow)$</td>
<td>AFM</td>
</tr>
</tbody>
</table>

Figure 6. K-edge XMCD signals typical for transition metal with a d shell less than half filled (Cr(III), V(II)) and direction of the magnetic moment (black arrow) compared with the applied magnetic field H: (a) magnetic moment of the transition metal parallel to the applied magnetic field; (b) magnetic moment of the metal antiparallel to the field.
In part A of the table, the interactions in model compounds are known: (i) FM in CsNi[Cr(CN)₆], all the magnetic moments, hence the ones of chromium(III) are aligned parallel to the magnetic field (↑) and the signal is −/+ , (ii) AFM in CsMn[Cr(CN)₆], the magnetic moments of chromium(III) (S=3/2), opposite to the majority ones of manganese(II) (S=5/2), are aligned antiparallel to the magnetic field (↓) and the signal is +/−. In part B, the preceding identifications are used to determine the alignment of the magnetic moments and the AFM nature of the AFM interaction between chromium and vanadium ions.

3. Mixed valency and synthesis of improved high $T_C$ PBAs

Mixed valency is also important to get pure V(II)₁Cr(III)₂/₃ derivatives as demonstrated by Garde et al. (2002). During the synthesis, a catalytic amount of V(III) is added (1–4% of total vanadium in solution). The materials obtained display a stoichiometry close to the V₁Cr₂/₃ ideal one. They are better organized, and present reproducible and stable Curie temperatures and magnetization at saturation in agreement with the observed V/Cr stoichiometry. Their structure, obtained from EXAFS, is made of [Cr(III)(CN)₆] units linked to octahedral vanadium(II) ions by bent C–N–V units ($\alpha=168^\circ$; figure 2b). The proposed mechanism is

$$V^{3+}(aq) + n[Cr(CN)_6]^{3-}(aq) \rightarrow [V^{3+}(-NC-Cr)_n]^{3(n-1)-}(aq),$$

$$[V^{3+}(-NC-Cr)_n]^{3(n-1)-}(aq) + V^{2+}(aq) \rightarrow [V^{2+}(-NC-Cr)_n]^{3(n-2)-}(aq) + V^{3+}(aq)$$

and

$$[V^{2+}(-NC-Cr)_n]^{3(n-2)-}(aq) \rightarrow [V(-NC-Cr)_{2/3}]^0 ↓ \text{ (precipitate when } n \approx 2/3).$$

4. The mixed valency chromium(II)–chromium(III) derivatives

The synthesis of two PBA prepared by adding [Cr(H₂O)₆]³⁺ to [Cr(III)(CN)₆]³⁻ was described by Mallah et al. (1993). In the absence of caesium cations, the light grey Cr⁺ᴵ[Ir(III)(CN)₆]₂/₃·10H₂O precipitates (ferrimagnetic ordering at 240 K). The magnetization at saturation is below the expected value, if one assumes that all the Cr⁺ᴵ centres are HS. It suggests that some Cr⁺ᴵ centres on A sites are LS. The same reaction carried out in the presence of Cs⁺ gives a green compound Cs₀.₆₇Cr⁺ᴵ[Ir(III)(CN)₆]₀.₉·4.₅H₂O (ferrimagnetic ordering at 190 K and weak magnetization at saturation). Unpublished X-ray diffraction powder and EXAFS data (decrease in the cell parameter and short chromium-neighbours distances) demonstrate not only that chromium has mixed valency but also that some of the chromium(II) ions are LS. When pressure is applied on Cr⁺ᴵ[Ir(III)(CN)₆]₂/₃·10H₂O (J. Bonjour & M. Verdagon 1994, unpublished work) to try to enhance orbital overlaps, to increase the AFM interaction, and thus to increase the ordering temperature, a magnetic disaster happens. At a pressure of 4 kbar, all the Cr⁺ᴵ centres become LS, and the Cr⁺ᴵ–Cr⁺ᴵ AFM coupling causes a transition to an AFM ordered state because the spins of the low-spin Cr⁺ᴵ centres exactly cancel those of the Cr⁺ᴵ centres,

$$M_T = M_{Cr}^{I} - M_{Cr}^{II} = 0((2/3)·3/2 - 1·1) \text{ with Cr}^{III}, d^3, S=3/2 \text{ and low-spin Cr}^{II}, d^4, S=1,$$

instead of 2 with high-spin Cr⁺ᴵ. Mixed valency does not have always happy
influences... Nevertheless, the mixed valency flexibility of this system was further exploited by Buschmann et al. (1998); Ohkoshi et al. (1998) to get electrochemically versatile thin layer derivatives.

5. The photomagnetic mixed valency cobalt–iron PBAs

The last example deals with an electronically labile system under external constraint (temperature, pressure, irradiation, ...). Indeed, a new field opened in the magnetic PBs story and in molecular magnetism, when Hashimoto and his team (Sato et al. 1996) reported the existence of an exciting photomagnetic effect in a PB analogue formulated K$_{0.4}$Co$_{1.3}$[Fe(CN)$_6$]$_1$·5H$_2$O (or K$_{0.3}$Co$_1$[Fe(CN)$_6$]$_{0.77}$·3.8H$_2$O), close to Co$^{II}$Fe$^{III}$_2, known for a long time. Verdaguer (1996) considered that the work represents a significant step towards molecular electronics in molecular magnetism. Sato’s compound is indeed a mixed valency system containing HS Co(II) and LS Co(III) in the A sites and LS Fe(II) and Fe(III) in the B sites. Since 1996, many studies have been devoted to the Co–Fe PB analogue family, which is very electronically labile. Several reviews are available (Ohkoshi & Hashimoto 2001; Varret et al. 2001; Escax et al. 2003; Sato 2003; Sato et al. 2007). Basically, the phenomenon implies diamagnetic Co(III)–Fe(II) pairs, which are photoexcited to metastable paramagnetic Co(II)–Fe(III) pairs with a related enhancement of the magnetization and the Curie temperature due to the increase in the number of magnetic pairs in the photoinduced state. But the system is very complex and it is necessary to define the conditions of the appearance of the metastable state and its properties: the role of the ligand field around cobalt; the role of the vacancies; the importance of the structural modifications around the cobalt from HS Co(II) to LS Co(III); the very specific role of the alkali cations; the presence of one or several phases; the AFM coupling of the photoinduced Co(II)–Fe(III) pairs, etc. There is not room to give an exhaustive survey, but four features should be underlined: the possibility to switch some metastable systems at room temperature by a one-shot laser pulse (Shimamoto et al. 2002); the electrical changes accompanying the phenomenon (Sato et al. 2004); the movement of the inserted cations in the lattice (Bleuzen et al. 2004); and the influence of pressure to provoke the electron transfer (Ksenofontov et al. 2003). Figure 7 shows a new trend in our own endeavours, trying to combine the complex (photoswitchable magnetic material) with the tiny (nanoparticles) to try to get nanosize ‘memory’ elements. Figure 7 shows how we are going, through controlled precipitation, to nanosize particles with narrow-size distribution, how we characterize them by electronic microscopy and microSQUID measurements after in situ controlled irradiation (Bachschmidt & Bleuzen in preparation).

6. The photomagnetic mixed valency copper–molybdenum systems

Leaving the PBA and the three-dimensional network area, we would like finally to quote one of our recent results in the field of molecular photomagnetic mixed valency octacyanometalate derivatives (see Herrera et al. 2004). The heptanuclear complex [Mo$^{IV}$(CN)$_2$(CNCu(II)L)$_6$]$^{8+}$ (L = tris(2-amino)ethylamine) (Mo$^{IV}$Cu(II)$_6$) as a perchlorate or triflate derivative behaves as a paramagnetic species, where the six Cu(II) ions ($S$=1/2) are practically isolated. Upon light
irradiation, an intramolecular electron transfer occurs resulting in the high-spin molecule containing \([\text{Mo}^{V}(\text{CN})_2(\text{CNCu}{}^{(II)}L)_5[\text{CNCu}{}^{(I)}L]}_1^{8+} (S = 3) (\text{Mo}^{V})\text{Cu}{}^{(II)}_5\text{Cu}{}^{(I)}_1\) (figure 8). In figure 8, the sample is irradiated at low temperature. The measurements are then done without continuous irradiation. The photoinduced state is metastable up to 280 K, which means a very high activation energy barrier to come back to the groundstate. The photomagnetic effect is thermally reversible. Figure 9 demonstrates that the irradiation at low temperature creates a hole in the d orbitals of Mo(IV) and the process is reversible. Such a molecular photoswitch is rich in possible applications. Several other molecular systems are now under study (V. Marvaud 2004–2007, unpublished work) and theoretical analyses of the phenomenon are in progress (E. Ruiz & S. Alvarez 2006–2007, personal communication).

Figure 7. Photomagnetic Co–Fe PBA: (a) self-organized nanoparticles, (b) deposit of nanoparticles on a microSQUID array and (c) photoinduced magnetization on a few nanoparticles (Bachsmit et al. work in progress).
Figure 8. Photomagnetic high-spin Mo–Cu₆ molecules: (a) photoinduced change in the \(\chi_M T\) product (in a 2 T applied field), (b) structure of Mo(IV)–Cu(II)₆, (c) scheme of the photoinduced electron transfer and (d) mixed valency Mo(V)–Cu(II)₅Cu(I).1

Figure 9. Molybdenum L₃ edge spectra: 1, Mo(IV)–Cu(II)₆ molecule (10 K); 2, a Mo(V)–[Cu(II)L]₁ model (10 K); 3, Mo(V)–Cu(II)₅Cu(I)₁ molecule, after irradiation (10 K); and 4, Mo(IV)–Cu(II)₆ molecule (relaxed state at room temperature after irradiation at 10 K). The open square points out the presence of an electronic vacancy in the d orbitals of the Mo(V) model and in the photoinduced metastable state (A. Bachschmidt, V. Marvaud & F. Villain 2006, unpublished work). The spectra have been arbitrarily shifted vertically for clarity.

*Phil. Trans. R. Soc. A* (2008)
7. Conclusion

Many of cyanometallate derivatives, combined with mixed valency of transition metal ions, present a wealth of new and important magnetic properties. This is due to their electronic lability, either in their groundstate (PB itself) or under constraint (pressure and irradiation). We gave only a few examples chosen from the systems that we are studying, but new mixed valency pairs are now appearing, combining electron transfer, spin cross-over switching and other phenomena. New exciting stories and knowledge can be expected in this field in the near future.

We would like to acknowledge many colleagues for common works, appearing in the references, and their helpful discussions, V. Gadet, S. Ferlay, V. Escax, C. Helary, A. Scuiller and F. Tuyères for chemistry, S. Alvarez, J. Cano, E. Ruiz, J. Tercero and B. Siberchicot for theory, M.-A. Arrio, P. Saintavit and C. Cartier dit Moulin for XMCD results, J. P. Itié and P. Münch for synchrotron diffraction experiments, J. Vaissermann and Y. Dromée for crystallography, P. Gütlich and V. Ksenofontov for Mössbauer spectroscopy, and J. Bonjour for magnetic measurements under pressure and funding support from UPMC, CNRS, LURE, DFG, ESF and EU in the 4th, 5th and 6th programmes.

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