Prussian blue derivatives

The Co Ligand Field: A Key Parameter in Photomagnetic CoFe Prussian Blue Derivatives[**]

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Various interesting electrochemical,[1] magnetic,[2] or photomagnetic[3] properties have been revealed in Prussian blue and its analogues. In the face-centered-cubic structure of the CoFe Prussian blue analogues of chemical formula $C_xCo_4[Fe(CN)_6]_{(8+x)/3}\square_{(4-x)/3}\cdot n\,H_2O$, where C^+ is an alkali-metal cation and □ represents the intrinsic $[Fe(CN)_6]$ vacancies, both of which are randomly distributed throughout the solid,[4] the Wyckoff positions 4a (0,0,0) are occupied by Fe ions or □ and the 4b positions (1/2,1/2,1/2) are occupied by Co ions.[5] The alkali-metal cations are distributed over the tetrahedral sites.[5] Such compounds may display unusual photomagnetic effects due to a light-induced Co^{III}(low spin, $S=0$)–Fe^{II}(S=0)→(Co^{II}(high spin, $S=3/2$)–Fe^{III}(S=1/2))* electron transfer accompanied by a spin change of Co and a lengthening of the Co–ligand bonds from 1.91 Å for Co^{III}(LS) to 2.08 Å for Co^{II}(HS).[3,6,7]

It has been proposed that the stabilization of the Co^{III}(LS)–Fe^{II} switchable pairs is correlated with the average number of cyanide ligands in the Co coordination sphere. The average chemical composition of the Co coordination polyhedron is given by $Co(NC)_{(8+x)/2}(OH_2)_{(4-x)/2}$. When x increases,

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weak-field H_2O ligands are replaced by stronger ones (CN^-) in the Co coordination sphere. An increase of the number of cyanide ligands in the Co coordination sphere should then lead to an increase of the Co ligand field and of the reducing power of Co, and therefore stabilize the Co^{III}(LS)–Fe^{II} photoactive diamagnetic pairs.[4,8,9] As the $[Fe(CN)_6]$ entity is stable and rigid,[10–12] the Co ligand field appears to be a key parameter for understanding the switchable properties of CoFe Prussian blue analogues.

Since a quantitative UV-vis spectroscopic investigation is impossible due to the existence of large charge-transfer bands in the visible range (the compounds are all dark violet or dark brown),[9] we used X-ray absorption spectroscopy (XAS) to determine the Co crystal-field parameter ($10\,Dq$) in two well-crystallized compounds for which the Co coordination sphere is expected to be different. For $Co^{II}_4[Fe^{III}(CN)_6]_{2.7}\square_{1.3}\cdot 18\,H_2O$[6] (**1**) and for $Rb_{1.8}Co^{III}_{3.3}Co^{II}_{0.7}[Fe^{II}(CN)_6]_{3.3}\square_{0.7}\cdot 13\,H_2O$[6] (**2**), which has photomagnetic properties, the average Co coordination spheres and cell parameters are $Co(NC)_4(OH_2)_2$ ((10.32 ± 0.05) Å) and $Co(NC)_5(OH_2)$ ((9.96 ± 0.05) Å), respectively.[12] This study allowed us to measure unexpected $10\,Dq$ values and to propose a structural model that explains the Co crystal-field parameter and the oxidation- and spin-states of Co in these compounds.

The L_3 edge can be used to directly probe the 3d levels of the metallic ion ($2p^63d^n \rightarrow 2p^53d^{n+1}$ transitions) as it is sensitive to the crystal-field parameter. X-ray absorption spectra of **1** and **2** were therefore recorded at the Co L_3 edge and compared to the spectrum of $[Co^{II}(OH_2)_6](NO_3)_2$ (Figure 1).

Peaks A to D are the signature of Co^{II}(HS) in an octahedrally symmetric environment,[7,13] and peaks E to G, at higher energy, the signature of Co^{III}(LS) also for octahedral symmetry.[7] Given the spectral shapes of compounds **1** and **2**, any Co coordination number other than six can be excluded.[14]

Simulation of the spectra using the ligand-field multiplet model[13,15] reproduces very well the experimental data (Figure 1). The Co^{II} signature is different from one spectrum to the other. These differences in the energy positions of the multiplet features are significant. Multiplet calculations show that an increase of the energy gap between the peaks A and D of Co^{II} species corresponds to an increase of $10\,Dq(Co^{II})$.[14] Attempts to reproduce any of the Co^{II} experimental contributions with more than one $10\,Dq(Co^{II})$ value, that is, different Co environments, failed. This surprisingly shows that $10\,Dq$(Co) is the same (within the experimental error) for all Co^{II} atoms in a single compound. In the same way, $10\,Dq(Co^{III})$ is, within the experimental error, the same for all Co^{III} atoms in **2**.

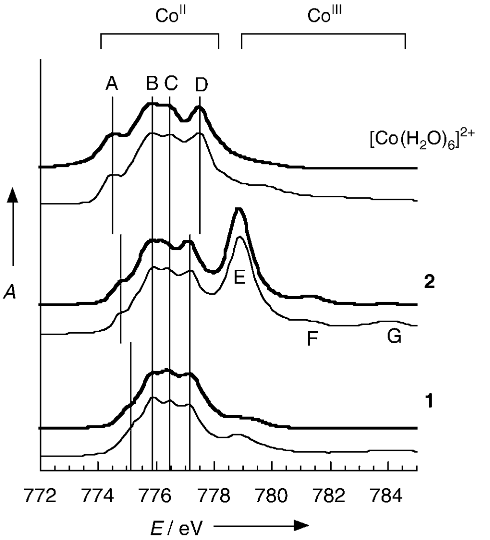

Figure 1. Experimental Co L_3-edge spectra (——) and best simulations (——) obtained from the ligand-field multiplet model for $[Co^{II}(OH_2)_6](NO_3)_2$, **1**, and **2**.

To characterize the influence of the ligands on $10\,Dq$, the model developed by Jorgensen[16] to formulate the spectrochemical series for octahedral complexes was used. In this model, the crystal-field parameter is treated as the product of two independent factors f and g ($10\,Dq = fg$), where f describes the strength of a ligand relative to water, which is assigned a value of 1, and g is characteristic of the metal ion. The $10\,Dq$ values given by multiplet calculations, and the corresponding f values, are gathered in Table 1.

Table 1: $10\,Dq$ parameters, obtained by multiplet calculations, and the corresponding f values.

	$10\,Dq$ [eV]	f
Co^{II} in $[Co(OH_2)_6]^{2+}$	1	1
Co^{II} in **1**	0.55	0.55
Co^{II} in **2**	0.7	0.7
Co^{III} in **2**	2.4	1.2[a]

[a] This value was calculated from the ratio $g(Co^{III})/g(Co^{II}) = (18\,600/9300) = 2$.[17]

The $10\,Dq$ values of Co^{II} in $[Co(OH_2)_6](NO_3)_2$ and of Co^{III} in **2** are in the expected spectral range for Co^{II}(HS) and Co^{III}(LS) molecular species, respectively.[18] The f factor corresponding to the environment of Co^{III} in **2** is the expected one for a metal ion surrounded by an average of five CN^- and one H_2O ligands, in the range of the f factors of most N-ligating ligands (NH_3 ($f = 1.25$), $NH_2CH_2CH_2NH_2$ (1.28), CH_3CN (1.22)).[17]

Surprisingly, the f factors corresponding to the environment of Co^{II} in **1** and **2** are, to the best of our knowledge, much weaker than any f value reported for octahedral Co^{II}(HS) molecular coordination compounds ($f = 0.7$ for the weak-field bromide ion and almost always > 1 for N-ligating ligands[17]). Such weak crystal fields, which have never been found in molecular compounds, are probably associated with three-dimensional network strains. The replacement of H_2O in the Co^{II} coordination sphere by CN^- does not strengthen the Co crystal field and does not explain the stabilization of the Co^{III}–Fe^{II} photoactive pairs in CoFe Prussian blue analogues. The stabilization of the Co^{II}(HS)–Fe^{III} or of the Co^{III}(LS)–Fe^{II} state is not simply due to a local chemical effect but to a cooperative structural one associated with the three-dimensional character of the compounds.

To explain these values, we have proposed a hypothesis based on structural considerations. In a molecular compound without steric hindrance, linear most-stable Co^{II}–NC bonds are expected with an f value close to 1.2.[17] In **1**, we propose that the geometry of the Co^{II}–NC–Fe entities deviates from the linear one: as a consequence of 3D network strains they are bent,[10] as shown for the (100) plane of one unit cell of **1** in Figure 2a. This bending leads to a weaker orbital interaction between Co and CN$^-$ and a weaker ligand field than for a linear geometry. The geometry of the Co–OH$_2$ entities also deviates from the most stable one,[19] leading again to a decrease of the ligand field exerted by H$_2$O. These deviations can be explained by the formation of hydrogen bonds between H$_2$O bonded to Co and the electronic density on the CN$^-$ ligand, as shown, with sensible structural parameters,[20] in Figure 2b. As a consequence of these interactions, the H$_2$O ligands rotate around the O position so that the orbital interaction between Co and H$_2$O is also weakened. Such interactions may also explain the bending of the Co–NC–Fe entities in **1**. A bent Co-N-C geometry, probably stabilized by an H bond, stabilizes the Co^{II}(HS) state in **1**.

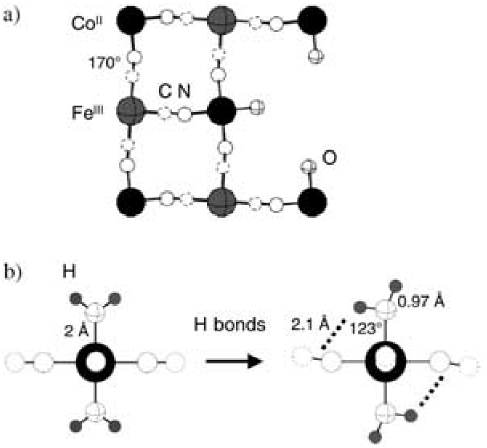

Figure 2. Proposed scheme for the (100) plane of one unit cell (a) and the Co^{II} coordination polyhedron with sensible structural parameters (b) for compound **1**.

Complex **2** contains a majority of Co^{III}(LS), with an f(Co^{III}) value corresponding to linear Co^{III}–NC–Fe entities.[10] These globally impose the short cell parameters and the structure of the compound. The relatively high X-ray crystallinity of a sample containing a mixture of Co^{III}(LS) and Co^{II}(HS), which have very different Co-to-ligand bond lengths,[6] implies that the remaining 20% of the Co^{II}(HS) ions are situated in particular positions and fit into the structure as proposed in Figure 3. They are close to the [Fe(CN)$_6$] vacancies (□), and are displaced slightly from the crystallographic site toward the vacancy. Along the Co^{II}–□ fourfold axis, the Co–NC entity prefers the most stable geometry due to the presence of the vacancy on the opposite site of this Co–NC bond. In the equatorial plane, the four Co–NC entities are bent (due to network strains), with an angle fixed by the Co^{II}–N bond lengths along the fourfold axis. The f(Co^{II}) value in **2** (0.73), which is close to the experimental value (0.7), can be estimated by assuming an average f value for bent Co–NC entities deduced from **1** (0.55), an approximate f value for linear Co–NC entities deduced from **2** (1.2), and the f value for the Co–OH$_2$ entity in the most stable geometry (1).[21]

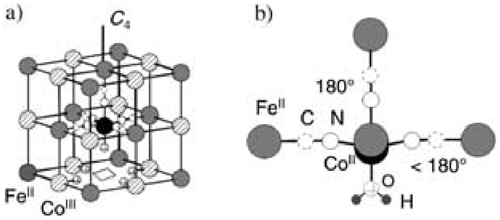

Figure 3. Co^{II} coordination polyhedron in a) a conventional unit cell, in which the alkali-metal cations have been omitted for clarity, and b) extracted from the unit cell of compound **2**.

In **2**, 80% of the Co ions are low-spin with an oxidation state of +3. These oxidation- and spin-states of Co are probably due to the linearity of the Co–NC–Fe entities associated with a stronger orbital interaction between Co and CN$^-$ and a stronger Co ligand field. We can propose three ways to explain this linear geometry: 1) the stoichiometry (x) implies a reduced amount of H$_2$O in the Co coordination sphere, which means that it is no longer able to form enough hydrogen bonds to impose the bent Co–NC geometry; 2) Rb in the tetrahedral sites interacts with the CN bridges,[10] and this interaction imposes the linear geometry; 3) the interactions between Rb and the CN bridges reduce the number of CN bridges available to form hydrogen bonds with Co-linked water molecules.

This is the first experimental determination of Co crystal-field parameters in photomagnetic CoFe Prussian blue analogues by XAS. We have shown that, contrary to expectation, the Co^{II} crystal-field parameter is, to the best of our knowledge, smaller than for any other octahedral Co^{II}(HS) molecular entities.[18] The $10\,Dq$ value is essentially determined by the geometry of the Co coordination polyhedron, which is imposed by weak and strong cooperative interactions within the three-dimensional structure rather than by the chemical nature of the ligands.

It is noticeable that the Co crystal-field parameter values are all far from HS–LS frontier values. In the switch from one state to the other, the Co spin-state change is therefore probably not the driving effect. Work is in progress to determine $10\,Dq$(Co) in the photo-induced metastable state of **2**.

Experimental Section

The syntheses of compounds **1** and **2** have been described elsewhere.[6]

The Co L_3-edge spectra were collected at the Beamline for Advanced diCHroism (BACH)[22] at the ELETTRA Synchrotron Radiation Source in Trieste, Italy.

XAS data parameters of the calculated spectra, a brief description of the simulation method, and determination of the f parameters are available as Supporting Information.

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[19] If only the geometry of the Co–NC entities were responsible for the small $10\,Dq(\mathrm{Co^{II}})$ values in **1** and **2**, with the Co−OH$_2$ bonds being similar to those in $[\mathrm{Co^{II}(OH_2)_6}]^{2+}$, one would expect a smaller $10\,Dq(\mathrm{Co^{II}})$ for **2** than for **1**, firstly because the number of CN$^-$ ligands involved in bent Co–NC entities in the Co coordination sphere would be higher in **2** than in **1** (due to the stoichiometry), and secondly because the cell parameters, which are smaller in **2** than in **1**, imply a shorter Co^{II}–Fe distance (fixed by the Co^{III}–Fe distance) in **2** and therefore a narrower Co-N-C angle and weaker orbital interaction between Co and NC. However, the reverse is observed experimentally. The geometry of the Co–NC entities is therefore probably not the only effect responsible for the small $10\,Dq(\mathrm{Co^{II}})$ values.

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[21] $f = 1/6 + 4 \times 0.55/6 + 1.2/6 = 0.73$.

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