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A new \{Fe\textsubscript{4}Co\textsubscript{4}\} soluble switchable nanomagnet encapsulating Cs\textsuperscript{+}: enhancing the stability, the redox flexibility and tuning the photomagnetic effect.

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We report a new cyanide-bridged Cs\textsubscript{4}\{Fe\textsubscript{4}Co\textsubscript{4}\} box, a soluble model of photomagnetic Prussian blue analogues (PBAs). The Cs\textsuperscript{+} ion has a high affinity for the box and can replace the K\textsuperscript{+} ion in the preformed K-cube. The exchange is kinetically impeded at room temperature but is accelerated by heating and using the 18-crown-6 ether. The inserted Cs\textsuperscript{+} confers a high robustness to the cube, which resists boiling as shown by variable-temperature NMR studies. The stability of this model complex in solution allows the probing of the electronic interaction between the alkali ion and the cyanide cage by using various techniques. These interactions are known to play a role in the photomagnetic behaviour of PBAs. Firstly, the \textsuperscript{133}Cs NMR spectroscopy proves that there is an electronic communication between the encapsulated alkali ion and the cyanide cage. The measured up-field signal, observed at \textit{ca}. -200 ppm at 300 K, reveals that a certain amount of spin density is transferred through the bonds from the paramagnetic Co(II) ion to the encapsulated cation. Secondly, the cyclovoltammetric studies show that the nature of the inserted ions affect the redox properties of the cage and influence the electronic communication between the metal ions. However, the differences in the electrochemical properties of the K-cube and the Cs one remain moderate. As the switching properties are influenced by the redox potential of the Fe and Co centers, similar photomagnetic behaviour are observed, both of them being highly photomagnetic. This result strikingly contrasts with previous studies on the 3D polymeric PBAs where the PBAs with a high Cs\textsuperscript{+} amount show poor photomagnetic behaviour. In that case cooperative behaviour likely influences the switching properties. Finally the EPR spectroscopy shows that the K-cube is more anisotropic than the Cs one. This difference is reflected in the changes occurring in the slow magnetic relaxation (Single Molecule Magnet behaviour) observed in the two cubes.

Introduction

In 1996, Sato \textit{et al.} discovered that the Curie temperature in a FeCo Prussian Blue Analogue (PBA) of the formula K\textsubscript{1.2}Co\textsubscript{4}[Fe(CN)\textsubscript{6}]\textsubscript{3.1}·15.4H\textsubscript{2}O could be increased by a light irradiation.\textsuperscript{4} This photomagnetic effect was ascribed to an Electron Transfer Coupled to a Spin Transition (ETCST), which converts [Fe\textsubscript{II}\textsubscript{15}-CN-Co\textsubscript{II}\textsubscript{15}] paramagnetic pairs into [Fe\textsubscript{II}\textsubscript{15}-CN-Co\textsubscript{II}\textsubscript{15}] paramagnetic ones. The paramagnetic metastable state can then relax optically or thermally. The ETCST phenomenon can also be induced by other stimuli such as a temperature change. However, it has been shown that the switchable properties of these FeCo PBAs strongly depends on their chemical composition, in particular, on the amount and nature of the intercalated alkali ion, which itself is correlated to their (microscopic) structure.\textsuperscript{2,3} For example, the Cs\textsubscript{4}Co\textsubscript{4}[Fe(CN)\textsubscript{6}]\textsubscript{4} which contains Cs\textsuperscript{+} ions in each 8g tetrahedral site of the cubic structure, does not show any photomagnetic effect. In contrast, its analogue of the formula Cs\textsubscript{4}Co\textsubscript{4}[Fe(CN)\textsubscript{6}]\textsubscript{4}·11H\textsubscript{2}O (where \square represents [Fe(CN)\textsubscript{6}]\textsuperscript{4} vacancies) shows a very efficient photomagnetic effect.\textsuperscript{5} This striking difference has been associated with the presence of vacancies in the second example, which confers some flexibility to the PBA network. Indeed, the ETCST is accompanied by important structural changes in the cobalt coordination sphere where metal-ligand distances vary by ca. 0.18 Å. In the diamagnetic compound Cs\textsubscript{4}Co\textsubscript{4}[Fe(CN)\textsubscript{6}]\textsubscript{4}, the framework is believed to be stiff because of the absence of vacancies and the presence of Cs\textsuperscript{+} ion in all the cubic unit cells. The ETCST phenomenon is also highly dependent on the nature of the alkali ion. In order to clarify this aspect, Bleuzen \textit{et al.} studied a family of A\textsubscript{2}Co\textsubscript{4}[Fe(CN)\textsubscript{6}]\textsubscript{4}·11H\textsubscript{2}O (A = Na\textsuperscript{+}, Rb\textsuperscript{+}, Cs\textsuperscript{+}) PBAs. They showed that the photomagnetic effect is more efficient when the polarizing character of the alkali cation increases. Thus, the strongest photomagnetic effect was observed for the Na\textsuperscript{+} analogue. The observed trend was correlated to the interaction between the alkali ion and the \pi cloud of the cyanides that tends to stabilize the metastable photo-induced state.\textsuperscript{6} Many questions remain open. What is the nature of the intermediate excited states involved in the photoconversion? How can the photo-conversion rate be improved? How can the relaxation temperature be increased? Overall, the rationalizing
of the magnetic properties in PBA systems remains difficult because of their complex local structure. For example, various metal sites such as \{M(NC)₃(H₂O)₂\}, \{M(NC)₆(H₂O)₃\}, \{M(NC)₃(H₂O)₁\}, and \{M(NC)₆(H₂O)₃\} coexist in PBA systems, even in stoichiometric phases.\(^6\) Thus, their physical properties, such as the photomagnetism, result from the interaction of different metal sites. In the last decade, there has been a strong interest in the design of low dimensional systems, which could be used as molecular models to help understanding the ETCST phenomenon. The self-assembly strategy, based on the reaction of iron building blocks having a reduced number of cyanide ligands, \{Fe⁺⁹(L)CN\}³⁻, and Co building blocks with a reduced number of labile site \(S\), \(\{Co⁻¹(L')(S)\}^{m⁺}\), has allowed the design of a wide range of low dimensional Fe-Co based materials.\(^1\)\(^-\)\(^6\) A first \(\{Fe₂Co₄\}^{⁴⁺}\) cyanide-bridged photomagnetic cube was investigated by Holmes, Mathonière and Clérac in 2008.\(^\text{13}\) In this cationic complex, the metastable state exhibits a long lifetime and a high relaxation temperature, which is measured in magnetometry (ca. 200 K). The phenomenon was also observed in FeCo square complexes in 2010,\(^\text{14,15}\) or in FeCo bimetallic complexes more recently.\(^\text{16}\) Interestingly, beside the occurrence of the ETCST phenomenon, other interesting features can be obtained in low-dimensional cyanide-bridged systems, including a multi-redox stability,\(^\text{17,18}\) the occurrence of slow magnetic relaxation,\(^\text{19-21}\) and dielectric bistability associated with electron transfer.\(^\text{22}\) An appealing feature of some of these low-dimensional systems is also their solubility. On one hand, the solubility facilitates the insertion of the functional units into hybrid systems in the perspective of designing advanced materials of molecular devices. On the other hand, it allows the execution of interesting solution studies to enlighten the electronic properties of the individual molecules. In this context, we recently reported a neutral \(\{Fe₂Co₄\}\) cage encapsulating an alkali K⁺ cation (K-cube)\(^\text{23}\), which shows a photomagnetic effect similarly to the original K₂Co₄[Fe(CN)₆]₁·15.4H₂O PBA. We showed that the cage is highly soluble and stable in CH₂Cl₂. In this contribution, we show that the encapsulated K⁺ can be fully replaced by Cs⁺ ions in solutions containing a caesium salt. We also describe the impact of the cation substitution on the chemical and physical properties of the \(\{Fe₂Co₄\}\) molecular cube. Interestingly, the presence of the inserted Cs⁺ ion confers a better stability in solution to the cube even at high temperatures. The insertion of the Cs⁺ also leads to an improved redox flexibility of the Cs-box, which exhibits up to eight accessible redox states (instead of 6 for K-cube). Furthermore, the Cs⁺ encapsulation does not lead to a disappearance of the photomagnetic effect, in contrast with what was observed in the three dimensional PBA phases containing high amount of intercalated caesium.

Results and discussion

Solid-state structure

The mixed-valence cube of the formula Cs⁺[(Fe⁺³(Tp)(CN)₆]₁{Co⁻¹(Tp)(S)₃·Fe⁺³(Tp)}]·12CH₂CN (Cs-cube) was prepared by first reacting \[PPh₃][Fe⁺³(Tp)(CN)₆]\, \[Co⁻¹(Tp)(S)₃\] with \[Co⁺(ClO₃)₃·6H₂O\] and \[Na⁺(Tp)\] in the presence of CsClO₃ and then by recrystallizing the product from an acetonitrile solution (see details in ESI). Deep blue prismatic single crystals suitable for X-ray diffraction were obtained by slow evaporation of the acetonitrile solution.

Figure 1. (top) View of the X-ray structure of Cs-cube (recorded at 200 K). Thermal ellipsoids are drawn at the 50 % level (C: black; N: blue; B: orange). Lattice solvents and hydrogen atoms have been omitted for clarity. (Bottom) View of the octametallic core encapsulating Cs⁺ (Fe⁺³: yellow; Co⁺³: violet; Co⁻¹: blue). The Cs-cube crystallizes in a triclinic phase (P̅T, Z = 2).\(^\text{23}\) Its structure was obtained at 200 K. It is made of Cs=FeCo₄ cubic motifs and acetonitrile lattice molecules (instead of CH₂Cl₂ molecules in the recently reported K-cube). No chemical interactions were detected between the lattice acetonitrile and the terminal organic ligands surrounding the octametallic core. The shortest intermolecular metal-metal distance (ca. 9.0 Å) is found between the Co ions. In each cube, four iron and four cobalt atoms alternatively occupy the vertices to form a heterocubane structure. The metal ions are linked to each other by bridging cyanides along the cube edges, the carbon atoms being always linked to the iron side. The Fe-CN-Co edge lengths are similar in both K-cube\(^\text{23}\) and Cs-cube, with an average distance of 4.99 Å. However, the overall deviations from linearity of the Fe-C-N and Co-N-C links are smaller in the Cs-cube as compared to the K-cube. The Fe-C-N angle are almost linear here (ca. 178 ± 1°) whereas they show bigger deviations, ranging from 174.1(3)° to 178.4(3)°, in the K-cube. The Co-N-C angles also show less deviation in the Cs-cube (ranging from 174.1(3)° to 178.79(3)°) than in the K-cube (from 171.1(3)° to 178.8(3)°). These differences are coherent with the distortions observed in the Co⁺³⁶ coordination sphere (see below). Overall, Cs-cube is less distorted than K-cube. This is also reflected in the location of the alkali ion inside the (Fe-Co₄) box. Because of its smaller size, the K⁺ tends to be displaced toward a (Co(NC)₃) corner of the cube, which is occupied by the Co(II) ions. The K⁺ and K⁺-N distances of ca. 3.2-3.4 Å account for the small interactions with the three cyanide π systems. In the present Cs-cube, the alkali ion is located approximately at the centre of the cage. In fact, it is slightly closer to one of the faces. The Cs⁻/N distances vary between 3.43-3.58 Å (with the closer face) and 3.50-3.66 Å.
(with the opposite one). In addition, the Fe-CN-Co distances in the Cs⁺ preferential face average 5.02 Å, while in the opposite one, the distances are slightly shorter, averaging 4.94 Å. This larger distance is caused by the presence of the Cs⁺ ion in one of the faces (ΔCo₁⁻₃=N is 0.2 Å larger than ΔCo₁⁻₄=N). Overall the interaction between the caesium ions and the twelve cyanide bridges likely contributes to the increased stability of the cage in solution at high temperatures (vide infra).

All the metal ions show a slightly distorted octahedral coordination sphere. They are coordinated in a facial mode to a scorpionate ligand (Tp or µ²-Tp) whereas the three other positions are occupied by the C atoms (for Fe) or the N atoms (for Co) of the cyanide bridges. Thus all coordination spheres exhibit a pseudo C₃ axis along the boron-metal axis. The Fe-C bond lengths fall in the range of 1.866(4)-1.900(4) Å and are similar to those previously reported for other [Fe₃(Tp)(CN)₅] motifs. The Co-N distances show less deviation than those observed in the K-cube. In contrast with the K-cube where one site was preferentially assigned to the Co(II) ions (with an occupancy of ½), two different pairs of cobalt sites can be distinguished from the XRD data of the Cs-cube. One site exhibits an average Co-N bond length of 1.91 Å, which is typical of low-spin Co(II). The other site exhibits an average Co-N bond length of 1.98 Å, which corresponds to an average value between those expected for a HS Co(II) and a LS Co(II) ion. Thus, the unique HS Co(II) ion seems equally shared between two Co sites of the same face. The distortion of the Co(II) coordination spheres of the Cs-cube can be compared to that obtained in the K-cube (comparing the sites with a ½ occupancy). A significantly less distorted octahedral environment is found in Cs-cube (Σ = 18° compared to Σ = 28° for the K-cube). It is worth noticing that the displacement of the Cs⁺ ion toward this face probably reduces the local negative charge. The presence of a unique paramagnetic Co(II) ion is unambiguously revealed by other physical and chemical characterization. For example, the EPR spectrum of Cs-cube in frozen solution is typical of a magnetically isolated high-spin Co(II) ion (with I = 7/2) exhibiting an effective spin, S_eff = 7/, at low temperature with an axial symmetry. The g values remain close to those found in the K-cube (g_eff = 1.85 g_eff = 7.71) but the tensor shows a lower anisotropy (g_eff = 2.02 g_eff = 7.54). The remarkable variation of the g_eff values is linked to the conformation of the complex. The Cs⁺ ion, which is more centred than the K⁺ in the cage, causes a weaker local distortion of the “in-plane” cobalt coordination environment, which decreases the anisotropy of g_eff (see ESI).

Figure 2. X-band EPR spectra of K-cube (red) and Cs-cube (black) in CH₂Cl₂ frozen solution at 4 K.

NMR and UV-vis studies

The ¹H-NMR spectrum of the Cs-cube has been recorded in CD₃CN. It shows strongly shifted signals, which appear at high field and low field, from 86.7 to +90.5 ppm at 300 K, and well-defined features located in the diamagnetic range (see ESI). Some of the signals are quite broad even though the resolution is improved in CD₂Cl₂ (present work) as compared to CD₂Cl₂ (our previous work). Thus more features are observed at room temperature. Moreover, unlike for the K-cube measured in CD₂Cl₂, we were able to detect the broad B-H protons (more details in ESI). The presence of a paramagnetic HS Co(II) in one of the vertices of the {Fe₃Co₄} box leads to a C₃v molecular point-group. Considering the C₃ axis situated along the B-Co₁⁻₃-Cs direction, a set of 26 proton signals with an overall intensity corresponding to 88 protons (belonging to the pyrazolyl rings and the B-H of the Tp and µ²-Tp capping ligands) is expected. The peak assignment was done by considering the relative intensities of the signals and their chemical shifts: the closer the proton to the paramagnetic source is, the bigger the chemical shift appears. The half-width of the peaks can also be considered for the assignment, as the signals of protons close to the paramagnetic centre tend to broaden because of the fast magnetic relaxation due to the through-space dipolar interaction between the unpaired electron and the probed nucleus. Overall, the ¹H NMR spectrum of the Cs-cube resembles that of the K-cube, although the signals are slightly less shifted. This trend is more visible on the most shifted proton signals and is likely correlated to the larger magnetic anisotropy observed in the K-cube as compared to that measured in the Cs-cube (see EPR spectra). Indeed, in paramagnetic species, the observed paramagnetic shift contains a pseudo-contact contribution (also called “dipolar shift”), δ_p, which is directly correlated to the magnetic anisotropy (see below, equation 1). The bigger the anisotropy is, the bigger the pseudo-contact term is. As a consequence, the differences in the chemical shift values allow distinguishing both cubes in solution studies (vide infra). It is also worth underlying that the absence of other paramagnetic or diamagnetic signals (apart from those of solvent traces) accounts for the purity of the samples and the stability of the cubes at ambient temperature.

Solution studies
The $^1$H NMR has also been used to probe the stability of the cage and the cation exchange in solution at different temperatures. No decomposition was observed in the case of the Cs-cube in the explored temperature range. In fact, upon slow heating (2 K/min) up to 350 K and further cooling to room temperature, the $^1$H NMR signals of the Cs-cube show a perfectly reversible temperature dependence (see ESI). Furthermore, the boiling of CD$_3$CN solution during 30 minutes does not affect the NMR spectrum. This behaviour contrasts with that of the K-cube, which shows some decomposition upon heating up to 80°C (see ESI). Overall, these NMR experiments demonstrate that the inserted Cs$^+$ ion confers a higher stability to the (Fe$_6$Co$_4$) cage.

The Cs-cube can be directly prepared by using a caesium salt in the reaction medium (following the synthetic procedure mentioned above) but it can also be obtained from the K-cube by replacing the K$^+$ by Cs$^+$. However, the $^1$H NMR experiments realized on solution containing K-cube and Cs salts show that the cation exchange is kinetically unfavourable. At room temperature, and even at 50°C, only traces of the Cs-cube were observed after several days (see ESI). In contrast, the experiments carried out at 65°C show a significant exchange in approximately 32 hours (about 60% of Cs-cube). The insertion of 18-crown-6-ether (18-C-6), under the same experimental conditions, allows an acceleration of the cation exchange. A full exchange between K$^+$ and Cs$^+$ is thus observed after 32 hours. This points out the fact that the limiting step for the cation exchange involves the K$^+$ loss. The slow K$^+$-by-Cs$^+$ exchange observed here contrasts with the rapid exchange observed by Rauchfuss et al., within similar cyanide-bridged Co$_4$ and Rh$_2$Co$_4$ organometallic cages. The difference is correlated to a higher inertia of our neutral Cs-cube, which contains only one labile Co(II) ion (versus four labile ions in the Rauchfuss cubes). Moreover, in order to confirm the better template effect of the Cs$^+$ ion, the synthesis of the cube was conducted in the presence of equimolar amounts of Cs$^+$ and K$^+$. The resulting products were isolated 3 minutes after the addition of the mixture of alkali salts and only the Cs-cube was identified by NMR spectroscopy.

The UV-Vis absorption studies in acetonitrile solution (10$^{-4}$ M) confirm the relative robustness of the Cs-cube compared to the K-cube. A broad absorption band centred at ca. 630 nm is observed in both species (see ESI). This absorption is assigned to the Fe$^{III}$Co$^{III}$ charge transfer band as previously observed in other molecular FeCo charge transfer systems. Upon heating the K-cube solution, this band disappears and the blue solution turns yellow (see ESI). The colour change is irreversible and accounts for a decomposition of the K-cube. In contrast, the Fe$^{III}$Co$^{III}$ charge transfer band persists in the Cs-cube solution, although its intensity slightly decreases upon heating. The same result was obtained in butyronitrile solution, by heating up to ca. 110°C. In conclusion, the $^1$H NMR and UV-vis spectroscopic results demonstrate that: (i) the K$^+$ ion can be efficiently replaced by the Cs$^+$ ion upon heating, (ii) the Cs$^+$ has a better template effect as compared to K$^+$ one, (iii) the Cs:Fe$_6$Co$_4$ cage is remarkably robust in organic solvents.

![Figure 3. K$^+$-by-Cs$^+$ exchange followed by $^1$H-NMR (400 MHz) in CD$_3$CN at 65°C and at different times (0, 1, 4, 24 and 32h) in absence (left) and in presence (Right) of 18-C-6. The full exchange is obtained after 6 days in absence of 18-C-6, while it is observed after 32 h in presence of 18-C-6.](image-url)
The unique signal is remarkably shifted and it appears at −236 ppm at 300 K, out of the $^{133}$Cs diamagnetic range (vs. CsNO$_3$; $\delta = 0$ ppm in D$_2$O). This high field signal confirms that the Cs$^+$ is encapsulated in the cage and senses the HS Co(II) ion. The measured chemical shift thus contains an important paramagnetic contribution, $\delta^{\text{param}}$, which arises from two effects (inset, figure 4): (i) the electron-nucleus dipolar interaction, which is a through-space interaction, leading to the pseudo contact shift, $\delta^{\text{pc}}$; (ii) the Fermi contact term, which arises from the propagation of the unpaired electrons from the paramagnetic source to the probed nucleus, through the bonds. This interaction leads to a contact term, $\delta^{\text{con}}$. In summary, the $^{133}$Cs NMR signal brings an experimental proof of the occurrence of a through-bond communication between the paramagnetic source and the Cs$^+$ ion. This communication occurs either directly through the valence orbital of the Cs$^+$ and the Co(II) ions, as suggested by Köhler et al., or indirectly through the $\pi$ orbital of the cyanide where the unpaired electron is delocalized.

**Cyclic voltammetry studies**

In order to investigate the impact of the encapsulated Cs$^+$ ion on the electronic properties of the [Fe$_4$Co$_4$] box, we have investigated the cyclic-voltammetry (CV) of the Cs-cube and and compared the results with the CV of the K-cube. The cyclic-voltammogram of the Cs-cube measured in dichloromethane solution shows 7 oxidation waves (figure 5). The first oxidation wave located at -0.2 V (versus ferrocene) corresponds to the oxidation of the HS Co$^+$ ion. The system looks irreversible as the corresponding reduction wave is shifted to lower potential, at -0.6V, and is broadened (see ESI). This behaviour is typical of slow redox systems where the electron transfer is associated with a spin transition on the metal complex. In the present case, the HS Co(II) center is oxidized in LS Co(II). This induces a strong structural rearrangement in the cobalt coordination sphere ($\Delta$Co-N $\approx 0.18$ Å) and a strong shift in the oxidation/reduction wave (the electron transfer can be fast on the electrochemical time scale but the structural rearrangement is slow). Such features have been observed for example in other slow redox systems such as the mononuclear Co(II) complexes containing scorpionate ligands similar to the Tp and $^{18}$Tp and also in the K-cube. The four waves located at higher potential correspond to the quasi-reversible oxidation of the Fe$^{\text{III}}$ ions: Fe$^{\text{II}}$Fe$^{\text{III}}$Co$_4$ E$_{1/2} = 0.36$ V; Fe$^{\text{II}}$Fe$^{\text{III}}$Co$_4$ E$_{1/2} = 0.47$ V; Fe$^{\text{II}}$Fe$^{\text{III}}$Co$_4$ E$_{1/2} = 0.65$ V; Fe$^{\text{III}}$Co$_4$ E$_{1/2} = 0.86$ V (versus ferrocene). These redox potentials are centred at the same average potential, 0.575 V, in the K-cube and in the Cs-cube, however they appear in a slightly broader range for the Cs-cube. This difference can be quantified by comparing the comproportionation constants, $K_\nu$, which reflect the relative stability of the mixed valence states with respect to its (monovalent) reduced and oxidation forms. The comproportionation constant is calculated through the expression $K_\nu = \exp(\Delta E/RT)$, where $\Delta E$ is the difference between successive oxidation waves. $\Delta E$ values of 0.13, 0.15 and 0.17 C lead to $K_\nu$ values of 157, 343 and 750 for (Fe$^{\text{II}}$Fe$^{\text{III}}$Co$_4$), (Fe$^{\text{II}}$Fe$^{\text{III}}$Co$_4$)$_2$ and (Fe$^{\text{II}}$Fe$^{\text{III}}$Co$_4$)$_5$ in the Cs-cube, meanwhile, higher values, of 307, 1030 and 3566 are found for the K-cube. This measurement highlights the small but noticeable influence of the nature of the alkali cation on the electronic communication between the metal ion through the cyanide bridges. The weaker separation between the successive redox waves of the iron ions and the lower $K_\nu$ values measured in the Cs-cube account for a weaker electronic communication between the metal ions when the K$^+$ ion is replaced by the Cs$^+$ one.
of the $\chi_M T$ value observed above 350 K is the onset of a thermally-induced ETCST (see ESI). Its gradual aspect is coherent with the absence of remarkable intermolecular interactions between the cubes in the crystal lattice. The photomagnetic properties were probed using an 808 nm laser diode of moderate power (5mW/cm$^2$). The Cs-cube shows a significant photomagnetic effect at 20 K. Indeed, upon irradiation, the paramagnetic signal quickly increases and reaches a saturation value of $ca. \chi_M T = 12.8$ cm$^3$ mol$^{-1}$ K after 20 minutes (figure 6). This value is higher than that observed for the K-cube ($ca. 10$ cm$^3$ mol$^{-1}$ K) and could indicate a better conversion rate of the diamagnetic pairs into the paramagnetic ones. However, the magnetic exchange interaction through the cyanide bridge (and the spin-orbit coupling) may be different in the metastable states of the K-cube and the Cs-cube (because of structural differences) and thus impact their $\chi_M T$ values. It is thus difficult to make a conclusion about the relative efficiency of the photomagnetic effect. The increase of the $\chi_M T$ value before and after irradiation can also be compared to that measured in the related $\{Fe_2Co\}^{4+}_{\text{III}}$ cationic cube ($ca. 12$ cm$^3$ mol$^{-1}$ K) where a full conversion was reported. The increase in the Cs-cube is inferior ($ca. 10$ cm$^3$ mol$^{-1}$ K) but only three $\{Fe^{II}_{\text{LS}}-CN-Co^{III}_{\text{LS}}\}$ vertices can be converted into three $\{Fe^{III}_{\text{LS}}-CN-Co^{II}_{\text{HS}}\}$ paramagnetic pairs, because of the presence of the paramagnetic Co(II) ion in the ground state. Overall, the increase in both cubes are comparable. Although advanced physical measurements are needed to precisely measure the efficiency of the photo-induced electron transfer, these comparisons point to the occurrence of an efficient photo-induced ETCST effect. This strikingly contrasts with the absence of photomagnetic effect observed in the FeCo PBAs containing high amount of intercalated Cs$^+$. This difference is likely related to the structure of the materials. In the Cs$_4$Co$_2$(CN)$_6$$_{\text{PBA}}$, there are no vacancies and the stiffness of the network likely impedes the structural reorganisation accompanying the ETCST. Here, the molecular cubes are well isolated from each other (see above) and there is likely no such structural constraint. It is also worth noticing that the photo-induced metastable state in the Cs-cube persists up to $T_{\text{relax}} \approx 70$ K, a value slightly inferior to that measured in the K-cube ($T_{\text{relax}} \approx 80$ K, in the same experimental conditions). This observation is consistent with the results previously obtained in FeCo PBAs. Indeed Bleuzen et coll. showed that small alkali ions tend to stabilize the photo-induced paramagnetic pairs. In summary, the Cs$^+$ ion leads to a reduced metastable time life (a reduce $T_{\text{relax}}$) as for the PBA, but it does not alter the photoconversion, in contrast with the situation observed in FeCo photomagnetic PBAs.

### Solid state magnetic properties

#### Magnetic and photomagnetic properties

The temperature variation of the $\chi_M T$ is similar to those observed in the K-cube and is coherent with the presence of only one high-spin Co(II) paramagnetic ion per molecule. The magnetic data between 2 and 300 K can be simulated (using the PHI software), and the best fit leads to a set of values which is similar to that obtained for the K-cube with a good agreement factor: $\lambda = -143$ cm$^{-1}$, $\alpha = 0.77$, $\Delta = -922$ cm$^{-1}$ (where $\lambda$ is the spin-orbit coupling, $\alpha$ is the reduction factor, $\Delta$ is the axial distorsion). Interestingly, the slight and gradual increase

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**Table 1. Redox potential, $E_{1/2}$, for the successive Fe$^\text{II}$/Fe$^\text{III}$ oxidation waves in the K-cube and Cs-Cube**

<table>
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<th>$E_{1/2}$ (Fe$^\text{II}$/Fe$^\text{III}$)</th>
<th>$E_{1/2}$ (3Fe$^\text{II}$/Fe$^\text{III}$)</th>
<th>$E_{1/2}$ (4Fe$^\text{II}$/Fe$^\text{III}$)</th>
</tr>
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<td>K-cube</td>
<td>0.32 V</td>
<td>0.47 V</td>
<td>0.65 V</td>
</tr>
<tr>
<td>Cs-cube</td>
<td>0.36 V</td>
<td>0.49 V</td>
<td>0.64 V</td>
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Figure 5. Cyclic voltammogram of the Cs-cube in CH$_2$Cl$_2$ (vs. FC/Fc$^+$). [Bu$_4$N][PF$_6$] 0.1 M, scan rate 100 mV s$^{-1}$ WE: C, CE: Pt, Ref.E: ECS.
In order to probe the dynamics of the magnetization, AC magnetic susceptibility was recorded as a function of temperature, field and frequency. At first the field dependent multifrequency AC measurements were performed at a very low temperature (3 K) to find the optimum static magnetic field giving the highest relaxation time. Then thermal variations of the AC magnetization were measured at different frequencies under the optimized static field. The frequency-dependence for both in-phase and out-of-phase of the ac susceptibility was observed only in the presence of a static magnetic field. The ac out-of-phase susceptibility signal exhibits a frequency-dependent maximum. The Cs-cube thus shows typical field-induced single-ion magnet (SIM) behaviour below 10 K (see details in ESI). The Cole-Cole plots (figure 7) at the optimal field of 1800 Oe show semi-circular shapes and can be fitted using a generalized Debye model in order to obtain the temperature dependence of the relaxation time $\tau$. The $\ln(\tau)$ vs $(1/T)$ curve shows strong deviation from linearity at high temperatures, which is correlated with the coexistence of Raman and Orbach relaxation pathways. The simplified Arrhenius law $\tau = \tau_0 \exp(U_{eff}/kT)$, which is often used to estimate the energy barrier ($U_{eff}$) and the relaxation rate in the high temperatures range, leads to erroneous values of $U_{eff}$ (underestimated) and $\tau$ (overestimated). Due to the presence of multiple relaxation mechanisms, it is more adequate to model the data following the equation:

$$\tau^{-1} = AH^mT + B_1/(1 + B_2H^2) + CT^n + \tau_0^{-1}\exp(-U_{eff}/kT)$$

where the first and second terms correspond to direct and QTM (quantum tunnelling) relaxation mechanisms, the third and fourth represent the Orbach and Raman processes. Here we decided to adopt this approach to study the relaxation process and compare it to our previous results (see details in ESI). The obtained values, summarized in table 2, are similar to those reported for other Co(II) SIMs with a distorted octahedral coordination environment. The higher anisotropy of the cobalt(II) in the K-cube shows a remarkable agreement with the observed $U_{eff}$ values. While the cobalt in the Cs-cube presents an energy barrier of 49.7 cm$^{-1}$, the slightly more distorted cobalt in K-cube shows an enhancement of $U_{eff}$, reaching a value of 90.7 cm$^{-1}$.

![Figure 6. $\chi_MT$ vs $T$ curve of the Cs-cube obtained after irradiation at 808 nm at 20 K during 2 h. Inset: time dependence of $\chi_MT$ of the Cs-cube at 20 K under irradiation at 808 nm (5mW/cm$^2$).](image)

![Figure 7. Cole-Cole plot of the Cs-cube between 2 and 10 K under a 1800 Oe magnetic field (top). Plot of the $\ln(\tau)$ vs $1/T$ for the Cs-cube. (bottom). The solid lines represent the least square fitting of the data (see details in text and ESI).](image)

<table>
<thead>
<tr>
<th>Direct</th>
<th>Tunnel</th>
<th>Raman</th>
<th>Orbach</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A T$^{-1}$K$^{-2}$</td>
<td>B1/B2</td>
<td>m</td>
<td>n</td>
</tr>
<tr>
<td>Cs-cube</td>
<td>39.3</td>
<td>209</td>
<td>1.64</td>
</tr>
<tr>
<td>K-cube</td>
<td>70.3</td>
<td>292</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Table 2. Values deduced from the fit of the relaxation processes and (see details in text and ESI).

Conclusions

A new multifunctional CsCsFe$_n$Co$_{1-n}$ cube has been obtained and its electronic, optical, magnetic and photomagnetic properties have been investigated. The complex can be obtained by direct reaction of the starting materials using the template effect of the cation. It can also be obtained by post-synthesis, replacing K$^+$ by Cs$^+$ within a preformed K-cube,
taking profit of the high affinity of the cage for the caesium ion. The exchange is kinetically blocked at room temperature but a full conversion is observed by heating. This study shows that these boxes are not “inert object” but can be opened and closed. The solution studies also showed that the Cs\(^+\) ion confers a remarkable stability to the \(\{\text{Fe}_4\text{Co}_4\}\) box, which stays stable even in boiling acetonitrile.

The robustness of the Cs\((\text{Fe}_4\text{Co}_4)\) cube in organic solvents allows us to probe its electronic properties by using different solution studies. The interaction between the inserted cation and the molecular cyanide box is of particular interest as previous studies on PBAs materials tend to show that this interaction has an impact on the photomagnetic properties. First of all, the strongly shifted \(^{133}\text{Cs}\) chemical shift reveals the occurrence of an efficient spin transfer from the Co(II) paramagnetic ion of the \(\{\text{Fe}_4\text{Co}_4\}\) box to the inserted caesium ion. The spin transfer can occur directly through the interaction of the Co(II) and Cs\(^+\) valence orbitals as suggested previously by Köhler et al. It could also occur indirectly through the interaction of the Cs\(^+\) ion with the \(\pi\) cloud of the cyanide ligands, which bear some unpaired electrons. In any case, the occurrence of one paramagnetic source in this model compound reveals this electronic interaction by tracking the spin transfer with NMR spectroscopy.

The interaction between the encapsulated alkali ion and the \(\{\text{Fe}_4\text{Co}_4\}\) box is also revealed by cyclovoltammetry. These experiments show that the electronic communication between the iron ions is affected by the nature of the cation (the communication being weaker for the Cs\(\text{-cube}\)). Moreover, the electrochemical studies showed that the encapsulated Cs\(^+\) ion not only confers a better stability to the \(\{\text{Fe}_4\text{Co}_4\}\) box but also a higher redox flexibility as eight redox states are accessible (instead of six in the K\(\text{-cube}\)). The \(\{\text{Fe}_4\text{Co}_4\}\) box thus becomes stable in almost the full dichloromethane electrochemical window when the caesium ion is inserted. These experimental results are consistent with each other. The interaction between the caesium ion and the cyanide ligand obviously confers a higher chemical stability to the box, and it is likely responsible of the reduced electronic communication observed between the metal ions through the cyanide bridges. It may also reduce the donor ability of the cyanide ligand on the nitrogen side, leading thus to a stabilization of the reduced forms of the box.

Magnetic structural correlation can also be drawn between EPR experiments and the field-induced slow magnetic relaxation of the Co(II) ion. The bigger the axial anisotropy is, the larger the effective barrier \(U_{\text{eff}}\) is.

Finally, the influence of the K\(^+\)/Cs\(^+\) substitution on the efficiency of the photo-induced electron-transfer appears to be less critical in the \(\{\text{Fe}_4\text{Co}_4\}\) molecular model as compared to the three-dimensional FeCo PBAs. Here, the cubes remain quite isolated from each other, and no intermolecular interactions are observed in the crystal lattice. The structural reorganisation, which accompanies the ETCT phenomenon is thus less critical than in the cooperative three dimensional PBA networks (where a high amount of inserted Cs\(^+\) ions confer a stiffness to the material). However, the nature of the cation impacts the relaxation temperature of the photo-induced metastable in a similar way as that observed for PBAs. In fact, the more polar cations, which may exhibit a stronger interaction with the \(\pi\)-cloud of some of the cyanide ligands, would stabilize the metastable states, leading thus to higher \(T_{\text{relax}}\).

Overall, the study of these cubic complexes made way for the opportunity to evaluate some of the outcomes that were obtained from previous studies on the FeCo PBAs. As accurate electronic and structural information can be obtained on these molecular models, in the future we hope to reach a better understanding of the photomagnetic effect, in particular, the impact of the cyanide-ion interaction on the electronic, chemical and physical properties of these fascinating functional molecules. We are now investigating functional cages containing other cations.

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Notes and references


25. $\Sigma$ is the sum of the deviation from 90° (in absolute values) of the twelve pseudo orthogonal N-Co-N angles of the octahedral coordination sphere (for comparison see ref. 24). Here, the Co$^{II}$ crystallographic sites have a ½ occupancy, so $\Sigma$ is underestimated. However the values can be compared as the occupancy is the same in both cubes.


