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Photo- and thermo-induced spin crossover in a cyanide-bridged \{Mo^{V}_{2}Fe^{II}_{2}\} rhombus molecule†

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The self-assembly of [Mo^{V}(CN)_{6}]^{3-} and [Fe^{II}(bik)_{2}(S)_{2}]^{2+} affords a cyanide-bridged \{Mo^{V}_{2}Fe^{II}_{2}\} rhombus molecule that shows photomagnetic effect under laser light irradiation at low temperature and exhibits thermo-induced spin crossover near ambient temperature.

Switchable magnetic molecules are currently attracting massive attention for their potential applications in molecular electronics. One of the challenging goals is to reproduce at the molecular scale classical electronic functional units such as memories or switches. In this context, spin-crossover (SCO) complexes are of particular interest since their spin state, and consequently both magnetic and optical properties, can be switched upon an external stimulus such as heat or light. Among the SCO complexes, those involving octahedral iron(II) ions are especially relevant as they show reversible conversion from a diamagnetic state (S = 0, low spin, LS) to a paramagnetic one (S = 2, high spin, HS). Recently, a strong interest has been devoted to the synthesis of cyanide-based iron(II) SCO systems. More specifically, numerous coordination polymers, including porous ones, have been obtained by reacting partially-blocked [Fe^{III}(L)_{x}(S)_{y}]^{2+} complexes with diamagnetic metalloligands (L = monodentate ligand, S = solvent). These compounds can show interesting cooperative effects, thermo-, photo- and also chemically-driven SCO. The variety of cyanide-based metalloligands, whose geometries and electronic properties can be tuned, has given access to a great variety of structures and properties. Interestingly, when the connector is paramagnetic the exchange interaction between the metal centres is switched on and off as the spin state of iron(II) ion changes. Following this approach, Okhoshi et al. have recently obtained several two and three dimensional SCO systems using [M(CN)_{6}]^{3-} metalloligands (M = Nb, Mo). This strategy allowed the observation of original photo-induced magnets. Until now, there are however fewer examples of related cyanide-based discrete SCO systems. \{Fe_{2}Fe\} squares have been reported, some include diamagnetic cyanoferate connectors whereas only one exhibits a paramagnetic iron(III) linker. To the best of our knowledge, there is no SCO molecule involving 3d-4d ions to date. Here, we present the synthesis, structural and spectroscopic characterisations and the magnetic study of an unprecedented cyanide-bridged \{Mo^{V}_{2}Fe^{II}_{2}\} complex, which exhibit thermo-induced spin crossover near room temperature and photomagnetic effect at low temperatures.

Fig. 1 View of the cyanide-bridged \{Mo^{V}_{2}Fe^{II}_{2}\} rhombus unit. The hydrogen atoms are omitted for clarity. C-gray, N-blue, O-red, Fe-orange.

Compound 1 of formula \{[Mo(CN)_{6}]_{2}[Fe(bik)_{2}](\text{Im}^{+}\text{Im}^{-})\}_{2} \cdot 3\text{H}_{2}\text{O} \cdot \text{CH}_{3}\text{CN} (\text{bik} = \text{bis}(1\text{-methylimidazol-2-yl})\text{ketone}, \text{ImH}^{+} = \text{N-methylimidazolium cation}) is obtained as red plate-like crystals by the reaction in acetonitrile of mononuclear complexes, \{Mo^{V}(CN)_{6}\}^{3-} and [Fe^{III}(bik)_{2}(S)_{2}]^{2+}, in presence of \text{ImH}^{+} (see ES1† for experimental details). It crystallizes in the \text{P}_{2}_{1}/m\text{ space group and its structure, collected at 200 K, is made of tetranuclear anionic \{Mo^{V}_{2}Fe^{III}_{2}\}^{2-} units, protonated N-methylimidazole molecules, and water and acetoni­trile molecules. The \{Mo_{2}Fe_{2}\}^{2-} unit exhibits a rhombus-like shape in which two [Mo^{V}(CN)_{6}]^{3-} complexes at opposite corners act as bis-monodentate ligands toward two \{Fe^{III}(bik)_{2}\} units in a cisoid mode (Figure 1). The \text{Mo}^{V}-\text{CN-Fe}^{III} edges are quasi-­identical [ca. 5.2 \text{ Å}] and the corners angles significantly depart from orthogonality: those at the \text{Mo} atom are acute [Fe-Mo-Fe = 77.703(8)-78.094(8)°] whereas those at the \text{Fe} atom are obtuse [Mo1-Fe-Mo2 = 99.046(9)°]. The \text{Mo}^{V} ions adopt square antiprismatic coordination spheres and their \text{C4} symmetry axes are almost orthogonal to each other (Fig. S1, S2 ES1†). The \text{Mo}-\text{C} bond lengths are equal to 2.140(4) \text{ Å} for the bridging cyanides and range between 2.148(6) and 2.171(6) \text{ Å} for...
the non-bridging ones. The Fe\textsuperscript{II} ions are in FeN\textsubscript{6} distorted octahedral coordination spheres built by four bidentate CN ligands and two ammine nitrogen atoms. The Fe-N(amine) [from 1.961(3) to 1.978(3) Å] and Fe-N(CN) [from 1.912(3) to 1.914(3) Å] bond lengths are similar to those observed in related complexes and they are in agreement with a low-spin Fe\textsuperscript{II} ion in a N\textsubscript{6} surrounding.\textsuperscript{8} The bite angles subtended by the bidentate ligands at the Fe\textsuperscript{II} ions are close to orthogonality [88.87(14), 89.75(14)].\textsuperscript{8} The cyanide bridges are slightly bent on both the Fe\textsuperscript{II} ions [172.7(3)-175.7(3)]° and the Mo\textsuperscript{V} ions [176.1(3)-178.4(3)]°.\textsuperscript{9} The occurrence of low-spin {Mo\textsuperscript{V}-CN-Fe\textsuperscript{LS}} pair below 200 K is also supported by spectroscopic and magnetic data (vide infra). The molecular rhombi are well isolated from each other, the shorter intermolecular metal-metal distances being 8.4372(7) Å.

The magnetic properties of I were investigated in the 2.0-400 K range by measuring the thermal dependence of the $\chi_M$ product per {Mo\textsubscript{2}Fe\textsubscript{2}} unit ($\chi_M$ is the molar magnetic susceptibility). The magnetic behaviour of the compound is very dependent on its solvatisation state and thus on the measurement procedure. In a typical experiment, a fresh sample of I is wrapped in a polyethylene film and introduced in the SQUID at 200 K to avoid the loss of crystallization molecules prior to the experiment. The $\chi_M$ product was first measured upon cooling down to 2.0 K, then upon heating up to 400 K, and finally upon cooling down to 2.0 K again. The $\chi_M$ curve of the fresh sample exhibits a pseudo plateau below 200 K, with $\chi_M = 1.74$ cm\textsuperscript{3} mol\textsuperscript{-1} K at 200 K. This value is higher than the expected one for a set of non-interacting ions made of two Mo\textsuperscript{V} ($S = 1/2$) and two LS Fe\textsuperscript{II} ions ($S = 0$), and it suggests the presence of residual HS Fe\textsuperscript{II} ions (ca. 7% from Mössbauer data). The $\chi_M$ curve shows a S-shape above this temperature: the $\chi_M$ value first increases smoothly from 200 to 340 K and then more abruptly until 400 K, reaching almost a plateau, with $\chi_M = 7.44$ cm\textsuperscript{3} mol\textsuperscript{-1} K. This overall increase of 5.7 cm\textsuperscript{3} mol\textsuperscript{-1} K can be ascribed to a partial spin crossover of the Fe\textsuperscript{II} ions that would correspond to 78% LS → HS conversion. The transition is not complete at 400 K, the expected $\chi_M$ value being 8.06 cm\textsuperscript{3} mol\textsuperscript{-1} K (for a set of non-interacting ions made of two Mo\textsuperscript{V} ions and two high-spin Fe\textsuperscript{II} ions: $\chi_M = 2 \times 0.375 + 2 \times 3.63$ K with $g_{Mo} = 2$ and $g_{Fe} = 2.2$). The $\chi_M$ value obtained at 400 K corresponds to 91.2% Fe\textsuperscript{II} ions in the HS state. This $\chi_M$ increase is irreversible as after the 400 K annealing the sample exhibits a smoother spin-crossover curve that is shifted toward lower temperatures. This second $\chi_M$ curve is then reproducible upon cycling in the 2.0-400 K range (arrow 4). At this stage, the $\chi_M$ value measured at 80 K, ca. 3.0 cm\textsuperscript{3} mol\textsuperscript{-1} K, suggest the presence of an important amount of residual high-spin Fe\textsuperscript{II} ions (ca. 31% in absence of any magnetic interaction). The presence of these residual paramagnetic HS Fe\textsuperscript{II} ions may also contribute to the small but significant decrease of $\chi_M$ occurring upon cooling as antiferromagnetic exchange interactions could be expected between the paramagnetic Mo\textsuperscript{V} and Fe\textsuperscript{II} ions.\textsuperscript{9} The discrepancies observed in the $\chi_M$ curves before and after heating up to 400 K result from the partial loss of crystallization solvent molecules upon heating and under reduced pressure in the SQUID magnetometer. Indeed, the removal of solvent molecules is expected to modulate the spin-crossover process.\textsuperscript{10} In the present case, the crystals of I quickly lose their crystallinity when removed from the mother solution. Besides TGA analysis showed that I exhibits a weight loss (ca. 10%) above room temperature (Fig. S3 ESI†). The magnetic study of previously desolvated samples confirmed that the thermal treatment (and the concomitant alteration of crystallinity) lead to an increased fraction of HS Fe\textsuperscript{II} up to 32% (Fig. S4 ESI†).

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data (7% / 93% at 80 K and 32% / 68% at 300 K) reasonably match with those derived from magnetometry (9% / 91% at 80 K and 29% / 71% at 300 K). After heating the sample at 400 K, the amount of HS Fe\textsuperscript{II} ions notably increases (Fig. 3, Table S1 ESI\textsuperscript{†}). Overall these measurements also confirm that the amount of the residual HS-Fe\textsuperscript{II} increases after the thermal treatment.

Spectroscopic measurements have also been performed to probe the vibrational and electronic states of the metal ions in 1 at different temperatures. The FT-IR spectrum of 1 was recorded between 100 and 400 K on KBr pellet (Fig. S5 ESI\textsuperscript{†}). The cyanide stretching vibrations observed in the 2138-2057 cm\textsuperscript{-1} range do not allow to unambiguously identify the Mo oxidation state as both Mo\textsuperscript{IV}-CN and Mo\textsuperscript{III}-CN cyanide stretching vibration ranges overlap.\textsuperscript{15} Upon heating, apart from the intensity decrease of the peaks at 2065 and 2057 cm\textsuperscript{-1}, only small shifts (ca. < 3 cm\textsuperscript{-1}) are observed in the spectrum. Overall it seems here that the Fe\textsuperscript{II} spin crossover has small influence on the IR spectrum as previously observed in some other cyanide-based complexes.\textsuperscript{7,12c}

The solid-state UV-vis absorption spectrum of 1 shows a clear temperature dependence with a strong decrease of the Fe\textsuperscript{II} spin crossover has small influence on the IR spectrum as previously observed in some other cyanide-based complexes.\textsuperscript{7,12c}

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Notes and references


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