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ARTICLE TYPE

Photo- and thermo-induced spin crossover in a cyanide-bridged $\{\text{Mo}^{\text{V}}_2\text{Fe}^{\text{II}}_2\}$ rhombus molecule†Abhishake Mondal,^a Yanling Li,^a Lise-Marie Chamoreau,^a Mannan Seuleiman,^a Lionel Rechinat,^b Azzedine Bousseksou,^b Marie-Laure Boillot^c and Rodrigue Lescouëzec.^{*a}⁵ Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

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The self-assembly of $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$ and $[\text{Fe}^{\text{II}}(\text{bik})_2(\text{S})_2]^{2+}$ affords a cyanide-bridged $\{\text{Mo}^{\text{V}}_2\text{Fe}^{\text{II}}_2\}$ 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.¹ 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.² 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 $[\text{Fe}^{\text{II}}(\text{L})_x(\text{S})_y]^{2+}$ complexes with diamagnetic metalloligands ($L =$ monodentate ligand, $S =$ solvent).³ 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.³ 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.⁴ Following this approach, Okhoshi *et al.* have recently obtained several two and three dimensional SCO systems using $[\text{M}(\text{CN})_8]^{n-}$ metalloligands ($M = \text{Nb}, \text{Mo}$).⁵ This strategy allowed the observation of original photo-induced magnets.^{5a} Until now, there are however fewer examples of related cyanide-based discrete SCO systems. $\{\text{Fe}_2\text{Fe}_2\}$ squares have been reported, some include diamagnetic cyanoferrate connectors⁶ whereas only one exhibits a paramagnetic iron(III) linker.⁷ 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 $\{\text{Mo}^{\text{V}}_2\text{Fe}^{\text{II}}_2\}$ complex, which exhibit thermo-induced spin crossover near room temperature and

photomagnetic effect at low temperatures.

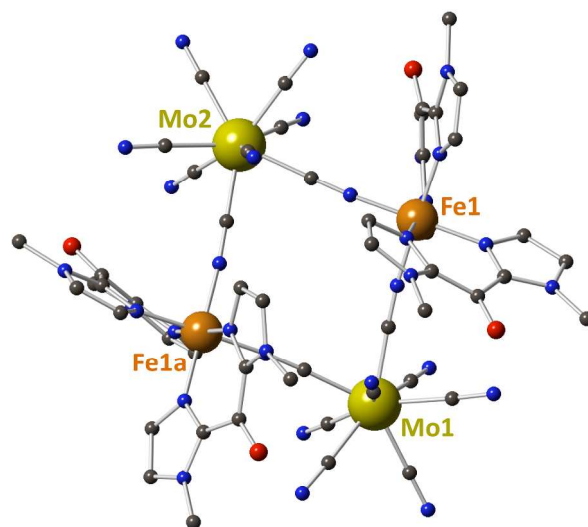


Fig. 1 View of the cyanide-bridged $\{\text{Mo}^{\text{V}}_2\text{Fe}^{\text{II}}_2\}$ rhombus unit. The hydrogen atoms are omitted for clarity. C-gray, N-blue, O-red, Mo^{V} -olive, Fe^{II} -orange.

Compound **1** of formula $\{[\text{Mo}(\text{CN})_8]_2[\text{Fe}(\text{bik})_2]_2\}(\text{H}^{\text{Me}}\text{Im})_2 \cdot 5\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ ($\text{bik} =$ bis(1-methylimidazol-2-yl)ketone, $\text{MeImH}^+ =$ N-methyl-imidazolium cation) is obtained as red plate-like crystals by the reaction in acetonitrile of mononuclear complexes, $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$ and $[\text{Fe}^{\text{II}}(\text{bik})_2(\text{S})_2]^{2+}$, in presence of MeImH^+ (see ESI† for experimental details). It crystallizes in the $P2_1/m$ space group and its structure, collected at 200 K, is made of tetranuclear anionic $\{\text{Mo}_2\text{Fe}_2\}^{2-}$ units, protonated N-methylimidazole molecules, and water and acetonitrile molecules. The $\{\text{Mo}_2\text{Fe}_2\}^{2-}$ unit exhibits a rhombus-like shape in which two $[\text{Mo}^{\text{V}}(\text{CN})_8]^{3-}$ complexes at opposite corners act as bis-monodentate ligands toward two $\{\text{Fe}^{\text{II}}(\text{bik})_2\}$ units in a cisoid mode (Figure 1). The $\text{Mo}^{\text{V}}\text{-CN-Fe}^{\text{II}}$ edges are quasi-identical [*ca.* 5.2 Å] and the corners angles significantly depart from orthogonality: those at the Mo atom are acute [$\text{Fe-Mo-Fe} = 77.703(8)\text{-}78.094(8)^\circ$] whereas those at the Fe atom are obtuse [$\text{Mo1-Fe-Mo2} = 99.046(9)^\circ$]. The Mo^{V} ions adopt square antiprismatic coordination spheres and their C4 symmetry axes are almost orthogonal to each other (Fig. S1, S2 ESI†). The Mo-C bond lengths are equal to 2.140(4) Å for the bridging cyanides and range between 2.148(6) and 2.171(6) Å for

the non-bridging ones. The Fe^{II} ions are in FeN₆ distorted octahedral coordination spheres built by four bik nitrogen atoms and two cyanide nitrogen atoms. The Fe-N_{bik} [from 1.961(3) to 1.978(3) Å] and Fe-N_{cyanide} [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^{II} ion in a N₆ surrounding.⁸ The bite angles subtended by the bik ligands at the Fe^{II} ions are close to orthogonality [88.87(14)°, 89.75(14)°]. The cyanide bridges are slightly bent on both the Fe^{II} ions [172.7(3)-175.7(3)°] and the Mo^V sides [176.1(3)-178.4(3)°]. The occurrence of low-spin {Mo^V-CN-Fe^{II}_{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.

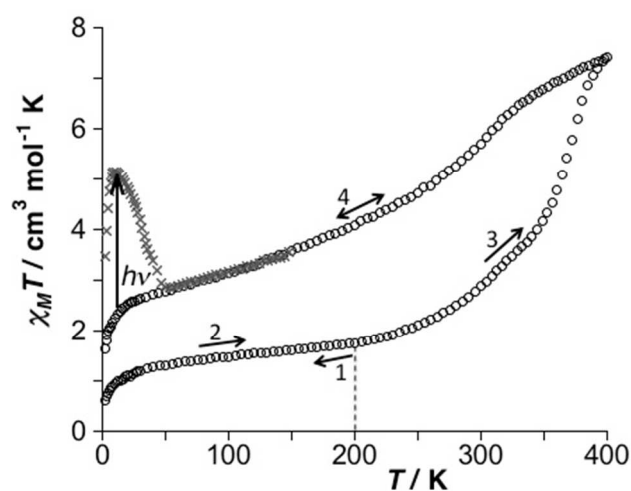


Fig. 2 Graph of the $\chi_M T$ versus T plot of **1**: (i) measurement on the bulk (circles); (ii) dehydrated sample irradiated at 405 nm (5 mW/cm²) at 20 K (crosses). The arrows' numbers refer to the measurement sequence.

The magnetic properties of **1** were investigated in the 2.0–400 K range by measuring the thermal dependence of the $\chi_M T$ product per {Mo₂Fe₂} unit (χ_M is the molar magnetic susceptibility). The magnetic behaviour of the compound is very dependent on its solvation state and thus on the measurement procedure. In a typical experiment, a fresh sample of **1** 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 $\chi_M T$ 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 $\chi_M T$ curve of the fresh sample exhibits a pseudo plateau below 200 K, with $\chi_M T = 1.74$ cm³ mol⁻¹ K at 200 K. This value is higher than the expected one for a set of non-interacting ions made of two Mo^V ($S = 1/2$) and two LS Fe^{II} ($S = 0$), and it suggests the presence of residual HS Fe^{II} ions (ca. 7% from Mössbauer data). The $\chi_M T$ curve shows a S-shape above this temperature: the $\chi_M T$ value first increases smoothly from 200 to 340 K and then more abruptly until 400 K, reaching almost a plateau, with $\chi_M T = 7.44$ cm³ mol⁻¹ K. This overall increase of 5.7 cm³ mol⁻¹ K can be ascribed to a partial spin crossover of the Fe^{II} ions that would correspond to 78% LS \rightarrow HS conversion. The transition is not complete at 400 K, the expected $\chi_M T$ value being 8.06 cm³ mol⁻¹ K (for a set of non-interacting ions made of two Mo^V ions and two high-spin Fe^{II} ions: $\chi_M T = 2 \times 0.375 + 2 \times 3.63$

K with $g_{Mo} = 2$ and $g_{Fe} = 2.2$). The $\chi_M T$ value obtained at 400 K corresponds to 91.2 % Fe^{II} ions in the HS state. This $\chi_M T$ 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 $\chi_M T$ curve is then reproducible upon cycling in the 2.0–400 K range (arrow 4). At this stage, the $\chi_M T$ value measured at 80 K, ca. 3.0 cm³ mol⁻¹ K, suggest the presence of an important amount of residual high-spin Fe^{II} ions (ca. 31 % in absence of any magnetic interaction). The presence of these residual paramagnetic HS Fe^{II} ions may also contribute to the small but significant decrease of $\chi_M T$ occurring upon cooling as antiferromagnetic exchange interactions could be expected between the paramagnetic Mo^V and Fe^{II} ions.⁹ The discrepancies observed in the $\chi_M T$ 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.¹⁰ In the present case, the crystals of **1** quickly lose their crystallinity when removed from the mother solution. Besides TGA analysis showed that **1** 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^{II} up to 32 % (Fig. S4 ESI†).

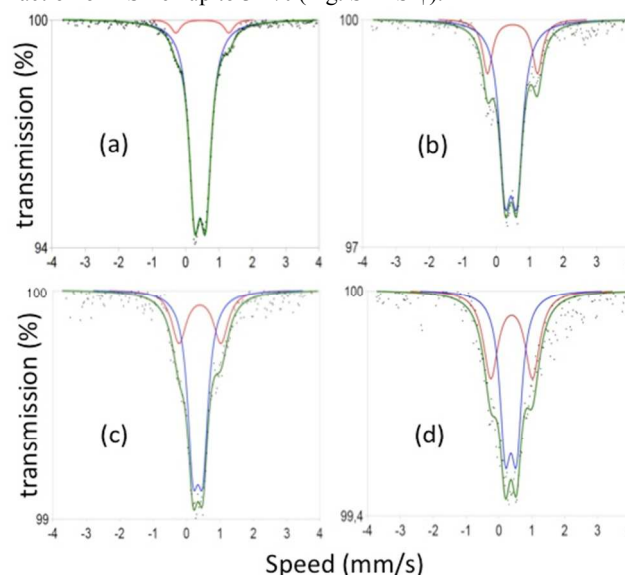


Fig. 3 Mössbauer spectra recorded at 80 (a, c) and 300 K (b, d), for a fresh sample of **1** (a, b) and after heating this very sample up to 400 K for 1 hour (c, d). The red and green lines represent the quadrupole doublets of the high-spin and low-spin Fe^{II} ions, respectively (the speed is relative to the iron metal).

⁵⁷Fe Mössbauer spectroscopy measurements were carried out in order to check the electronic states of the iron ions in **1**. The spectra have been recorded at 80 and 300 K on fresh and dehydrated sample (Fig. 3). For the fresh sample, two quadrupole doublets with parameters typical for HS-Fe^{II} ($\delta = 0.50$ mm s⁻¹, $\Delta E_Q = 1.59$ mm s⁻¹) and LS-Fe^{II} ($\delta = 0.43$ mm s⁻¹, $\Delta E_Q = 0.33$ mm s⁻¹) were observed at 80 K.^{7,11} Upon heating the intensity of the HS-Fe^{II} ($\delta = 0.49$ mm s⁻¹, $\Delta E_Q = 1.50$ mm s⁻¹) peak increases and the LS-Fe^{II} one ($\delta = 0.44$ mm s⁻¹, $\Delta E_Q = 0.35$ mm s⁻¹) decreases. The relative amounts of HS/LS ions obtained from the Mössbauer

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^{II} ions notably increases (Fig. 3, Table S1 ESI†).

Overall these measurements also confirm that the amount of the residual HS-Fe^{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†). The cyanide stretching vibrations observed in the 2138-2057 cm⁻¹ range do not allow to unambiguously identify the Mo oxidation state as both Mo^V-CN and Mo^{IV}-CN cyanide stretching vibration ranges overlap.¹² Upon heating, apart from the intensity decrease of the peaks at 2065 and 2057 cm⁻¹, only small shifts (*ca.* < 3 cm⁻¹) are observed in the spectrum. Overall it seems here that the Fe^{II} spin crossover has small influence on the IR spectrum as previously observed in some other cyanide-based complexes.^{7,12c} The solid-state UV-vis absorption spectrum of **1** shows also a clear temperature dependence with a strong decrease of the Fe^{II} MLCT band centered at 620 nm between 273-433 K. This change is coherent with a spin-crossover phenomenon (Fig. S6-S7 ESI†).

The photomagnetic properties of **1** were probed in the visible range using different laser-diodes ($\lambda = 808, 635, 532$ and 405 nm, with the respective powers: 6, 12, 10 and 5 mW/cm²; Fig. S8 ESI†). The experiments were carried out at 20 K in order to minimize the thermal effect due to laser light irradiation. Whereas a very small effect is detected for the hydrated sample, the dehydrated sample undergoes a significant increase of the magnetization upon irradiation: a paramagnetic signal appears which intensity increases with the irradiation time. The effect is maximized using the 405 nm laser light, the $\chi_M T$ value increasing from 2.50 to ~ 5.34 cm³ mol⁻¹ K, and the saturation being observed after *ca.* 60 minutes in the present experimental conditions (Fig. S8 ESI†). From the UV-vis absorption data, this observation could correspond to a favourable light penetration as the UV-vis absorption is reduced. The photomagnetic effect is likely due to a Light-Induced Excited Spin-State Trapping (LIESST) effect, the low-spin Fe^{II} ($S = 0$) ions being converted in metastable high-spin Fe^{II} ($S = 2$) ions by the laser light. After switching off the light, the light-induced metastable spin state persists up to $T_{LIESST} = 48$ K when heating the sample at 0.3 K/min (Fig. 2).¹³ This behaviour is reminiscent of that observed for the previously reported {Fe^{III}₂Fe^{II}₂} square complex in which the Fe^{II} centres exhibit the same coordination surrounding {Fe^{II}(bik)₂(NC-)₂} than that of **1**. Consistently with the respective optical properties of the two compounds, the most efficient photomagnetic effect is observed under UV excitation (at 405 nm) for the {Mo^V₂Fe^{II}₂} compound and NIR excitation (at 808 nm) for the iron mixed-valence square molecule.⁷

Conclusions

In conclusion, a new cyanide-based {Mo^V₂Fe^{II}₂} rhombus molecule has been obtained. This complex exhibits a thermally induced spin transition near ambient temperature, which is strongly dependent on the hydration rate of the sample. The dehydrated sample shows a significant photomagnetic effect at low temperatures, which is likely due to a LIESST effect. The

present {Mo^V₂Fe^{II}₂} molecule is reminiscent of the reported {Fe^{III}₂Fe^{II}₂} square complex which also shows spin-crossover photo-induced and thermally-induced phenomena. We are currently investigating the influence of the nature of the [M(L)(CN)_x]ⁿ⁻ metalloligands on the switching properties of the {Fe^{II}(bik)₂(NC-)₂} subunit.

Notes and references

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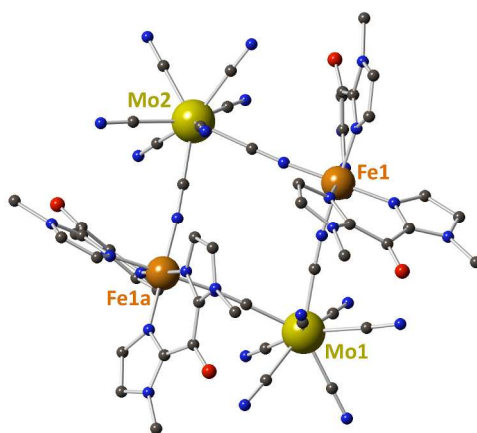
† Electronic Supplementary Information (ESI) available: Experimental section, Physical characterization data, additional Fig. S1-S8 and crystallographic refinement details for **1** CCDC: 970795.

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