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Direct two-step spin-crossover through [HS–HS]···[LS–LS] at the plateau in dinuclear diiron(II) complex $[\{Fe(NCBH_3)(4phpy)\}_2(\mu\text{-}bpypz)_2]$†

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The variable temperature magnetic susceptibility, X-ray crystallography, and IR and Raman spectra of a new dinuclear complex $[\{Fe^{II}(NCBH_3)(4\text{-}phpy)\}_2(\mu\text{-}bpypz)_2]$ demonstrated the first two-step spin-crossover associated with a 1 : 1 mixture of high-spin pair [HS–HS] and low-spin pair [LS–LS] at the plateau.

Spin-crossover (SCO) metal complexes exhibit intriguing molecular bistability driven by external stimuli. Among them, SCO in Fe(II) complexes with a d^6 electron configuration are expected to lead to promising functional molecular devices such as molecular memory or switches.[1] Integration of an intramolecular magnetic interaction and SCO in polynuclear Fe(II) complexes could provide auxiliary functionality, whereas much attention has been paid to two-step SCO in mono- or dinuclear Fe(II) complexes where cooperativity is associated with inter- and intramolecular (short- and long-range) interactions.[2,3] However, only a limited number of two-step SCO dinuclear complexes are known. There have been extensive studies of a family of bpym (2,2′-bipyrimidine) bridged complexes,[4–6] following the latest report on the phdia (4,7-phenanthroline-5,6-diamine) bridged complex.[7] These complexes exhibit two-step SCO through the mixed spin intermediate [HS–LS] in the plateau which was directly monitored unambiguously by Mössbauer spectroscopy.[5c,7] However, there were no X-ray analyses for both two-step SCO complexes, until the first X-ray structure of the SCO dinuclear diiron(II) complex was very recently reported for $[\{Fe(NCSe)(\mu\text{-}pzpy)(pzpyH)\}_2]$ (pzpyH = 2-pyrazolylpyridine) by Murray *et al.*[8] Shortly afterwards, we studied the X-ray structure of $[\{Fe^{II}(NCBH_3)(py)\}_2(\mu\text{-}bpypz)_2]$ (Hbpypz = 3,5-bis(2-pyridyl)-pyrazole),[9] which was followed by the direct light induced SCO in terms of Raman spectra.[10] The bpypz bridged dinuclear complex with a replaceable axial pyridine is expected to lead to two-step SCO processes by controlling the intermolecular interactions.

$[\{Fe^{II}(NCBH_3)(4phpy)\}_2(\mu\text{-}bpypz)_2]$ (4phpy = 4-phenylpyridine) (complex **1**) was prepared by a similar method to the corresponding pyridine complex.‡ The variable temperature behavior of a product of magnetic susceptibility χ_m and T shows the overall SCO from the quintet ($\chi_m \cdot T$ = *ca.* 3.3 emu mol^{-1} K) fully high spin [HS–HS] to the singlet (0.2–0.1 emu mol^{-1} K) fully low spin [LS–LS] state, associated with the plateau of *ca.* 1.5 emu mol^{-1} K at 200 K (Fig. 1), showing the two-step SCO.

The differential scanning calorimetry gives two exo- and endothermic peaks, respectively, in the cooling and warming modes (Fig. 1(inset)). The temperatures at the maxima are fairly close to those estimated from the magnetic susceptibility measurements, supporting the two-step SCO. The Mössbauer spectra confirm that the sample consists of a single phase structure exhibiting the two-step SCO, because only two pairs of the doublets corresponding to the HS and LS species are observed at the halfway point of the SCO.

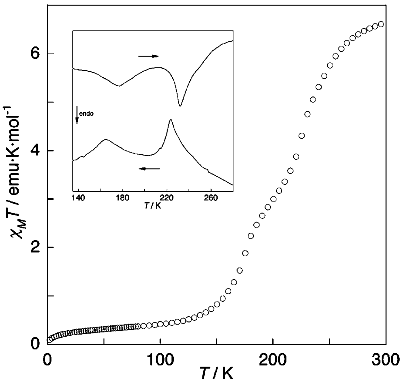

Fig. 1 $\chi_m T$ *vs.* T for complex **1**; inset: DSC in the cooling and heating modes.

The X-ray analysis of **1** demonstrates that the space group at 296 K is identical to that at 200 K and 100 K.§ The geometrical configurations around the iron ions (Fig. 2) at 296 and 100 K are fundamentally the same as those of the corresponding py complex:[9] the iron atoms coordinated to two bpypz to form the centrosymmetric dimer with only one kind of Fe(II) and the ligands in a distorted octahedral environment belonging to a pseudo C_{2h} point group. At 200 K, the X-ray analysis shows the existence of each one

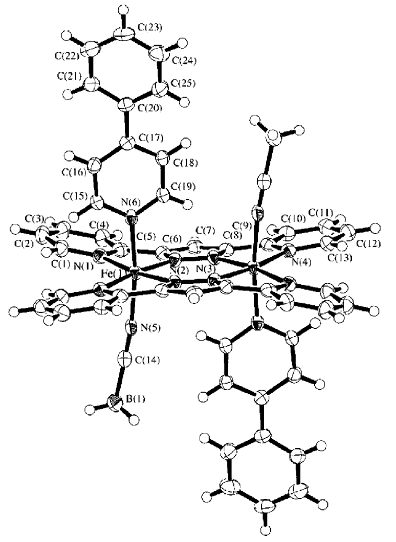

Fig. 2 ORTEP drawing for **1** at 100 K.

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† Electronic supplementary information (ESI) available: Fig. S1: Mössbauer spectra, Fig. S2: ORTEP drawing at 296 K, Fig. S3: ORTEP drawing at 200 K, Fig. S4: Far IR and Raman spectra. See http://www.rsc.org/suppdata/cc/b4/b411190g/

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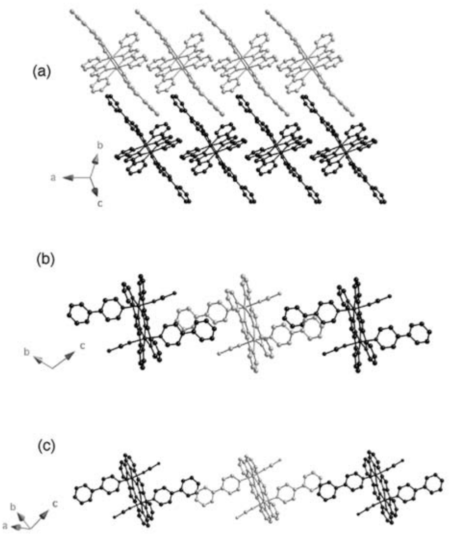

Fig. 3 Perspective views of complex **1** at 200 K: views (a) nearly along the *c* axis or parallel to the *ac* plane, (b) and (c) nearly from the negative and positive side of the *a* axis, respectively (see text).

of the high-spin [HS–HS] and low-spin [LS–LS] dinuclear complexes in the asymmetric unit doubled in size from 296 and 100 K. That is, the bond lengths around the Fe(1) and Fe(2) at 200 K correspond to those around Fe(1) at 296 and 100 K, respectively; average Fe–N = 2.116 Å (Fe(2)) and 2.0005 Å (Fe(1)) at 200 K; 2.1667 Å (Fe(1)) at 296 K and 1.9795 Å (Fe(1)) at 100 K; Fe(2)–Fe(2)* = 4.2000(8) Å and Fe(1)–Fe(1)* = 4.0605(8) Å at 200 K; Fe(1)–Fe(1)* = 4.2147 (8) Å at 296 K and 4.0434(6) Å at 100 K. There are π–π stacking interactions between the adjacent bpypz, by which a layer and a chain are formed as found for the py complex.[9] At 200 K, the [HS–HS] and [LS–LS] complexes are arranged in alternate chains through the π–π stackings not only between the 4-phpy, but also between the pyridyls of the bpypz. The π–π stackings between the bpypz exist for the pz···py between [HS–HS] and [HS–HS] as well as [LS–LS] and [LS–LS] and for the pyridyl (HS)···pyridyl(LS) (Fig. 3(a)) as the py complex. For a given 4-phpy in [HS–HS] or [LS–LS] at 200 K, strong π–π stackings of the pyridyl and phenyl on one side are made, respectively, with the phenyl and pyridyl for the 4-phpy in the adjacent [LS–LS] or [HS–HS] (Fig. 3(b)), and on the other back side weak phenyl···phenyl π–π stackings with the other neighboring 4-phpy in the [LS–LS] or [HS–HS] (Fig. 3(c)). There are significant voids in the crystals, but no electron density is found. All these crystallographic characteristics support the occurrence of a direct two-step spin transition from [HS–HS] to [LS–LS] through a mixture of [HS–HS]···[LS–LS] intermediates.

Moreover, the far IR and Raman spectra confirm the direct two-step SCO through [HS–HS]···[LS–LS]. Since the IR and Raman spectra of complex **1** are different from each other, the mutual exclusion selection rules in the C_{2h} point group for the vibrational spectra hold. At 200 K, the IR and Raman bands give the additive pattern of those at 296 and 100 K, maintaining the selection rule for IR and Raman spectra. This fact suggests that the molecular symmetry remains pseudo C_{2h} point group for each unit of [HS–HS] and [LS–LS], but does not convert to the C_s point group of mixed spin state [HS–LS] at 200 K. In fact, there is no extra band at 200 K except the IR and Raman bands observed at 296 and 100 K. Each IR active band at 366.5 and 357 cm^{-1} exhibits only single occupancy at 296 and 100 K, respectively. The corresponding bands at 200 K are observed at 364.6 and 357 cm^{-1}. On the other hand, the intensities of the Raman active bands at 380 and 250 cm^{-1} increase on decreasing the temperature. Therefore, these spectral behaviors demonstrate the coexistence of [HS–HS] and [LS–LS].

In conclusion, the two-step SCO of complex **1** is found to proceed through a mixture of [HS–HS] and [LS–LS] at the plateau which behaves like a mononuclear type in contrast to the step-wise two-step SCO through a mixed spin state [HS–LS] for the bpym and phdia complexes.[4–7] Such a two-step SCO process may result from the difference in intra- and intermolecular interactions. The intramolecular interactions in complex **1** are characteristic of the rigid bridging site comprising two tetradentate bpypz ligands as compared with the flexible bidentate bridging moiety in the μ-bpym and μ-phdia Fe(II) complexes. As for the intermolecular interactions in complex **1**, there are additional π–π stackings between the pyridyl and phenyl of the 4-phpy other than those between the bpypz ligands as for the pyridine complex.[9] Since the synergy between the inter- and intramolecular interactions is considered to be responsible for two-step SCO, the strong intermolecular interactions in complex **1** are likely to favor the like-spin pair ([HS–HS]···[LS–LS]) rather than the mixed spin one ([HS–LS]). The two-step SCO occurrence for the present 4-pypy complex along with the preliminary observation for the corresponding isoquinoline complex could give a clue to deeper understanding of two-step SCO phenomena in dinuclear complexes.

Notes and references

‡ The complex was prepared from *trans*-[Fe(NCBH$_3$)$_2$(py)$_4$] and excess amounts of 4-phenylpyridine in methanol solutions under an N$_2$ stream. Yield 36%. Anal. Calcd. for $C_{50}H_{42}N_{12}B_2Fe_2$ = (**1**): C, 63.60; H, 4.48; N, 17.80%. Found: C, 63.06; H, 4.31; N, 17.28%.

§ Crystal data for $C_{50}H_{42}N_{12}B_2Fe_2$(**1**). For T = 296 K, a red block crystal, M = 944.28, triclinic, space group $P\bar{1}$, Z = 1, a = 9.4567(2), b = 10.7576(6), c = 13.1355(5) Å, α = 92.519(6), β = 108.793(9), γ = 105.710(5)°, V = 1205.1(1) Å^3, D_c = 1.301 g cm^{-3}, μ(MoKα) = 6.50 cm^{-1}, R/wR_2: 0.056/0.1638, F_{000} = 488.00, total reflections: 8427, unique (R_{int}): 5236 (0.036). For T = 200 K, a red block crystal, M = 944.28, triclinic, space group $P\bar{1}$, Z = 2, a = 9.3509(2), b = 14.9124(1), c = 17.1648(4)Å, α = 99.612(1), β = 94.551(1), γ = 98.174(1)°, V = 2322.89(8) Å^3, D_c = 1.350 g cm^{-3}, μ(MoKα) = 6.74 cm^{-1}, R/wR_2: 0.0739/0.1755, F_{000} = 976, total reflections: 14676, unique (R_{int}): 10011 (0.073). For T = 100 K, a black block crystal, M = 944.28, triclinic, space group $P\bar{1}$, Z = 1, a = 9.0589(3), b = 10.682(1), c = 12.6458(8)Å, α = 93.521(8), β = 109.12(1), γ = 104.560(8)°, V = 1105.2(2) Å^3, D_c = 1.419 g cm^{-3}, μ(MoKα) = 7.08 cm^{-1}, R/wR_2: 0.0574/0.1745, F_{000} = 488.00, total reflections: 5896, unique (R_{int}): 4314 (0.039). CCDC 241137–241139. See http://www.rsc.org/suppdata/cc/b4/b411190g/ for crystallographic data in .cif or other electronic format.

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