Inorganic Chemistry
Communication
pubs.acs.org/IC

A Hydrogen Bond Motif Giving a Variety of Supramolecular Assembly Structures and Spin-Crossover Behaviors

Koshiro Nishi,[†] Naohide Matsumoto,*[,†] Seiichiro Iijima,[‡] Malcolm A. Halcrow,[§] Yukinari Sunatsuki,[¶] and Masaaki Kojima[¶]

[†]Department of Chemistry, Faculty of Science, Kumamoto University, Kumamoto 860-8555, Japan
[‡]National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8566, Japan
[§]School of Chemistry, University of Leeds, Woodhouse Lane, Leeds LS2 9JT, U.K.
[¶]Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan

S *Supporting Information*

ABSTRACT: A series of spin-crossover (SCO) iron(II) compounds, *fac*-$[Fe^{II}(HL^R)_3]Cl\cdot PF_6$ [R = methyl (Me, **1**), ethyl (Et, **2**), *n*-propyl (*n*-Pr, **3**), *n*-butyl (*n*-Bu, **4**), and *n*-pentyl (*n*-Pen, **5**)], were synthesized, where HL^R denotes a series of [(2-methylimidazol-4-yl)methylidene]-monoalkylamines. The cations *fac*-$[Fe^{II}(HL^R)_3]^{2+}$ and chloride anions associate through 3:3 imidazole···chloride hydrogen bonding. This hydrogen-bonding motif gives rise to a variety of assembly structures consisting of a one-dimensional ladder for **3** and **4**, two kinds of two-dimensional networks for **1** and **2**, and a cubane-like structure for **5**. The compounds exhibit various types of SCO transitions between high-spin ($S = 2$) and low-spin ($S = 0$) states as a result of their intermolecular interactions.

Self-organization of a simple molecule into a supramolecular assembly has allowed the structural versatility and rational design of functional materials, in which the preorganized molecule has the programmed information to lead the supramolecular structure and specific function. A metal complex consisting of an inorganic metal ion and organic ligands can be a useful preorganized molecule for supramolecular assembly.[1,2] A spin-crossover (SCO) iron(II) complex exhibits a molecular bistability in which the electronic configuration changes between high-spin (HS; $S = 2$) and low-spin (LS; $S = 0$) states by external perturbations, such as temperature, light, pressure, and so on.[3−7] While the SCO phenomenon is essentially described as the phenomenon of a single molecule, SCO properties such as steep, multistep SCO, hysteresis, and light-induced excited spin state trapping (LIESST), which are useful for practical application, are brought about from the cooperative effect among the SCO molecules.[8−10] It is also well-known that the SCO properties are complicatedly and predominantly influenced by many subfactors such as the crystal solvent and counteranion. Because the SCO molecule changes its molecular volume and geometry during spin transition, intermolecular interaction is important for the SCO behavior. Therefore, a SCO compound with a supramolecular network structure is helpful in obtaining the precise and straightforward information of the cooperative effect. Here is the main reason that the approach from the field of supramolecular chemistry must be applied to the synthesis of novel SCO complexes. The perspectives on the SCO complexes so far reported demonstrate that a strong linkage in the bond strength between the SCO sites is not always necessary but rather a weak interaction such as hydrogen bonding and π−π stacking often provides "effective cooperativity" to achieve valuable SCO properties.[11,12] Here we report a supramolecular SCO system with the formula *fac*-$[Fe^{II}(HL^R)_3]Cl\cdot PF_6$ [R = methyl (Me, **1**), ethyl (Et, **2**), *n*-propyl (*n*-Pr, **3**), *n*-butyl (*n*-Bu, **4**), and *n*-pentyl (*n*-Pen, **5**)], where HL^R = [(2-methylimidazol-4-yl)methylidene]-monoalkylamine, a bidentate chelate with two N-donor atoms. This molecular system produces a variety of assembly structures constructed of an imidazole···chloride hydrogen bond as the common motif, including one- (1D) and two-dimensional (2D) networks and a cluster, and has pronounced cooperative effects in the SCO properties.

A series of iron(II) compounds were synthesized as follows: The HL^R ligands were prepared by mixing 2-methyl-4-formylimidazole and the appropriate primary alkylamine in a 1:1 molar ratio in methanol. The iron(II) compounds were obtained as well-grown red (**1**) or yellow (**2**−**5**) crystals by mixing the corresponding ligand, $Fe^{II}Cl_2\cdot 4H_2O$, and KPF_6 in a 3:1:1 molar ratio in methanol. The compounds were thermochromic between yellow at the higher temperature and red at the lower temperature in the solid state, as observed for similar SCO complexes.[13]

The crystal structures of **1**−**5** were all determined by single-crystal X-ray diffraction analyses at 296 K (**1**−**3**, **5**) and 250 K (**4**). All of the structures contain the cation $[Fe^{II}(HL^R)_3]^{2+}$, one Cl^- ion, and one PF_6^- anion. The Fe^{II} ion in all of the compounds is octahedrally coordinated by six N-donor atoms from three bidentate ligands, and the cation adopts the *facial* (*fac*) configuration of the two possible *fac* and *mer*-isomers. The cation is a chiral species with either Δ or Λ configurations due to clockwise or anticlockwise arrangements of the three bidentate ligands in *fac*-$[Fe^{II}(HL^R)_3]^{2+}$ (Figure 1a).

As shown in Figure 1b, the three imidazole groups of *fac*-$[Fe^{II}(HL^R)_3]^{2+}$ are hydrogen-bonded to three Cl^- ions, while

Received: September 13, 2011
Published: October 25, 2011

dx.doi.org/10.1021/ic201993z | *Inorg. Chem.* 2011, 50, 11303−11305

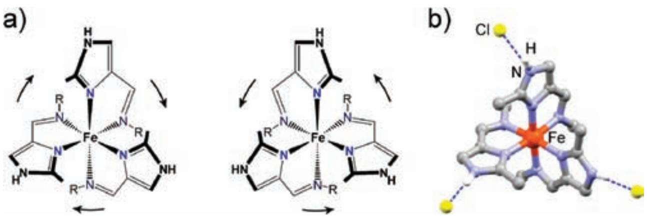

Figure 1. (a) Molecular structures of Δ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$ (left) and Λ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$ (right). (b) Structure of Δ-*fac*-$[Fe^{II}(HL^{Me})_3]^{2+}$ and the three hydrogen-bonded Cl^- (yellow ball) ions in **1** (R = methyl). Three imidazole NH groups of Δ-*fac*-$[Fe^{II}(HL^{Me})_3]^{2+}$ are hydrogen-bonded to three Cl^- anions, and the Cl^- ions are further hydrogen-bonded to two other complex cations.

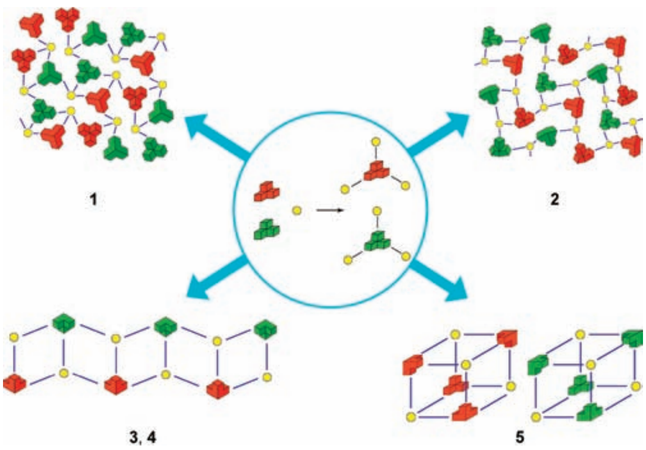

Figure 3. Schematic drawing of various assembly structures of **1**−**5** generated by the assembly reaction of Δ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$ or Λ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$ and Cl^- ions through the common motif of the 3:3 imidazole⋯chloride (NH⋯Cl^-) hydrogen bond. The two enantimorphs, Δ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$ and Λ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$, are represented by red and green blocks, respectively. The NH⋯Cl^- hydrogen bonds are represented by blue lines, and the Cl^- ions are yellow balls.

each Cl^- ion is, in turn, hydrogen-bonded to three imidazole groups of three different *fac*-$[Fe^{II}(HL^R)_3]^{2+}$ cations. One Cl^- ion with $[Ne]3s^23p^6$ electronic configuration has four paired electrons distributed tetrahedrally. Three of the four paired electrons are used for the formation of Cl^-⋯HN hydrogen bonds, and one remaining paired electron exists as a lone paired electron, giving different assemblies. The 3:3 imidazole⋯chloride (NH⋯Cl^-) hydrogen bond is the common motif for **1**−**5** governing the assemblies, affording a variety of supramolecular structures when combined with different arrangements of Δ- or Λ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$ centers. The PF_6^- anions are not involved in the network structures but simply occupy voids made by the network structures in the crystal lattices.

The different assembly structures exhibited by **1**−**5** are shown in Figures 2 and 3. Compounds **1** and **2** adopt two different types of 2D network structures, consisting of alternating cyclic binuclear and cyclic tetranuclear net units of *fac*-$[Fe^{II}(HL^R)_3]^{2+}$ (R = Me or Et) species. The cyclic binuclear unit of $\{\cdots fac\text{-}[Fe^{II}(HL^R)_3]^{2+}\cdots Cl^-\cdots\}_2\supset$ contains one Δ complex and one Λ complex, whereas the tetranuclear unit of $\{\cdots fac\text{-}[Fe^{II}(HL^R)_3]^{2+}\cdots Cl^-\cdots\}_4\supset$ contains four complexes with combined ΔΔΛΛ chirality. Compounds **3** and **4** exhibit 1D structures with a stepped-ladder topology, consisting of Δ- and Λ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$ (R = *n*-Pr or *n*-Bu) species. Each side of the ladder is homochiral, but the two sides are of opposite chirality. The PF_6^- anions of **1**−**4** are not involved in the formation of the 1D and 2D network structures but accommodate in the space among the network structures. Finally, **5** forms a discrete cubane-like tetranuclear assembly, consisting of four *fac*-$[Fe^{II}(HL^{n\text{-Pen}})_3]^{2+}$ cations and four Cl^- ions, with the sides of the cube being formed by 12 NH⋯Cl^- hydrogen bonds. There are two crystallographic PF_6^- sites: one anion is encapsulated within the cubane assembly, while the

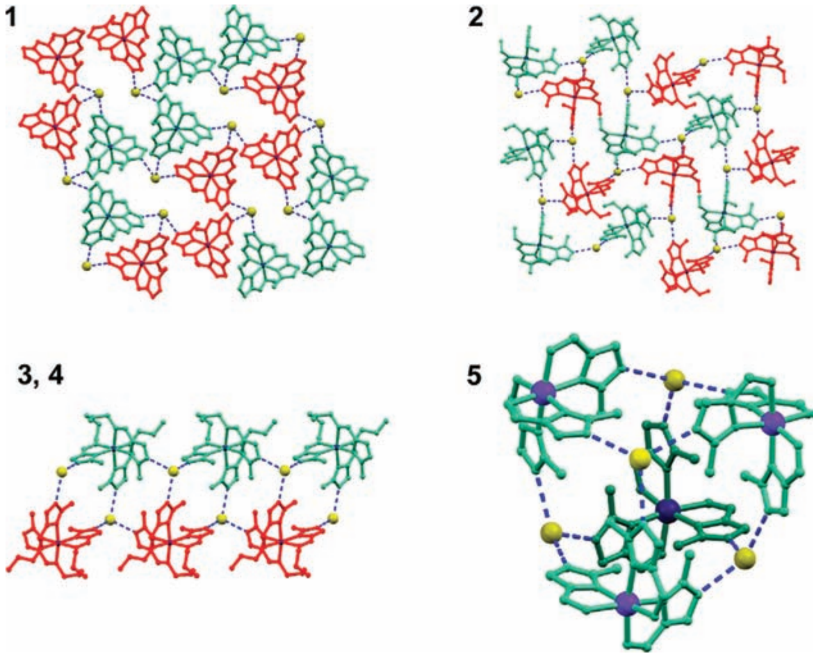

Figure 2. Variety of assembly structures drawn on the basis of the X-ray structural analyses of **1**−**5**. The two enantiomorphs, Δ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$ and Λ-*fac*-$[Fe^{II}(HL^R)_3]^{2+}$, are represented by red and green colors, respectively. The NH⋯Cl^- hydrogen bonds are represented by blue broken lines, and the Cl^- ions are drawn by yellow balls. The anions PF_6^- and alkyl chains of **5** are omitted for clarity.

other anion is accommodated in the space between the cubanes. Each cubane is a chiral species because the cubane contains four Δ- or Λ-$[Fe^{II}(HL^{R})_3]^{2+}$ species with the same chirality. In the crystal lattice, cubanes with opposite chiralities are alternately arrayed.

The SCO properties of **1**−**5** were investigated using magnetic susceptibility measurements. The $\chi_M T$ vs T plots in the temperature range of 5−300 K are shown in Figure 4, where χ_M and T represent the magnetic susceptibility per Fe atom and the absolute temperature, respectively. The compounds exhibit a variety of SCO behavior. Compound **1** is fully LS at 5−200 K but undergoes a gradual SCO upon further heating. Compound **2** behaves similarly but with a lower $T_{1/2}$ of 208 K. Compound **3** exhibits an abrupt and complete one-step SCO with thermal hysteresis. The midpoint temperatures in cooling and heating modes calculated by $\delta(\chi_M T)/\delta T$ are $T_{1/2}(\downarrow) = 135.5$ K and $T_{1/2}(\uparrow) = 152.5$ K, giving a hysteresis loop of 17.0 K. Although **4** is isostructural with **3**, it undergoes a more complicated multistep SCO process. Compound **5** exhibits an abrupt one-step SCO at $T_{1/2} = 174.1$ K without thermal hysteresis. Compounds **1**−**5** show a variety of SCO properties between the HS and LS states as a result of their intermolecular network interactions.

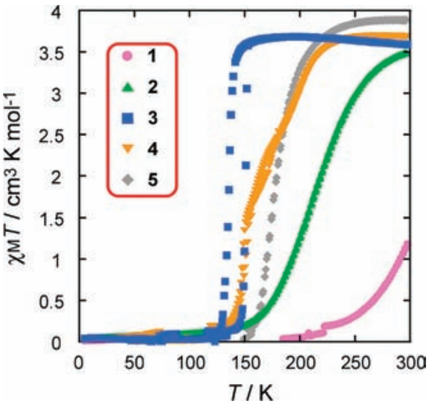

Figure 4. Variety of SCO properties of **1**−**5** in the form of $\chi_M T$ vs T plots.

The present assembly structures can be classified by the dimensionality. 2D compounds **1** and **2** have a gradual SCO, 1D ladder compounds **3** and **4** show abrupt SCO with hysteresis and multistep, and zero-dimensional cluster compound **5** shows an abrupt SCO.

In summary, a series of iron(II) complexes with the general chemical formula *fac*-$[Fe^{II}(HL^{R})_3]Cl\cdot PF_6$ were synthesized, where HL^{R} is a bidentate chelate ligand of the 1:1 condensation reaction of 2-methyl-4-formylimidazole and monoalkylamine. The Fe^{II} ion in all of the compounds is octahedrally coordinated by six N-donor atoms from three bidentate ligands, and the cation adopts the *facial* (*fac*) configuration. Further, the cation is a chiral species with either Δ or Λ configurations due to clockwise or anticlockwise arrangements of the three bidentate ligands. In these complexes, a common motif of the 3:3 imidazole···chloride hydrogen bonds produces a variety of assembly structures, including a 1D structure, two kinds of 2D structures, and a cubane-like cluster structure. These complexes show a variety of SCO properties, consisting of one-step gradual and steep SCO without hysteresis and one-step steep and multistep unusual SCO with hysteresis, demonstrating that the intermolecular interaction through the hydrogen bonds affects the SCO properties effectively. The present result demonstrates that supramolecular assembly due to hydrogen bonding can produce the useful SCO properties. The small modification of the components in *fac*-$[Fe^{II}(HL^{R})_3]Cl\cdot PF_6$ can generate new valuable SCO properties. The study along this line is now in progress in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for **1**−**5** in CIF format and syntheses and characterizations (elemental analyses and thermogravimetric analyses). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: naohide@aster.sci.kumamoto-u.ac.jp.

■ REFERENCES

(1) Lehn, J. M. *Science* **2002**, *295*, 2400−2403.

(2) Sun, Q.-F.; Iwasa, J.; Ogawa, D.; Ishido, Y.; Sato, S.; Ozeki, T.; Sei, Y.; Yamaguchi, K.; Fujita, M. *Science* **2010**, *328*, 1144−1147.

(3) Gütlich, P.; Goodwin, H. A.Spin Crossover in Transition Metal Compounds I−III. *Topics in Current Chemistry*; Springer: New York, 2004; *233*−*235*.

(4) Gütlich, P.; Garcia, Y.; Goodwin, H. A. *Chem. Soc. Rev.* **2000**, *29*, 419−427.

(5) Real, J. A.; Gaspar, A. B.; Niel, V.; Muñoz, M. C. *Coord. Chem. Rev.* **2003**, *235*, 121−141.

(6) Létard, J. F.; Guionneau, P.; Nguyen, O.; Costa, J. S.; Marcen, S.; Chastanet, G.; Marchivie, M.; Capes, L. G. *Chem.—Eur. J.* **2005**, *11*, 4583−4589.

(7) Halcrow, M. A. *Polyhedron* **2007**, *26*, 3523−3576.

(8) Kahn, O.; Martinez, C. J. *Science* **1998**, *279*, 44−48.

(9) Real, J. A.; Andres, E.; Muñoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265−267.

(10) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762−1765.

(11) (a) Weber, B.; Bauer, W.; Obel, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 10098−10101. (b) Chernyshov, D.; Hostettler, M.; Törnroos, K. W.; Bürgi, H.-B. *Angew. Chem., Int. Ed.* **2003**, *42*, 3825−3830.

(12) (a) Yamada, M.; Hagiwara, H.; Torigoe, H.; Matsumoto, N.; Kojima, M.; Dahan, F.; Tuchagues, J. P.; Re, N.; Iijima, S. *Chem.—Eur. J.* **2006**, *12*, 4536−4549. (b) Sunatsuki, Y.; Ikuta, Y.; Matsumoto, N.; Ohta, H.; Kojima, M.; Iijima, S.; Hayami, S.; Maeda, Y.; Kaizaki, S.; Dahan, F.; Tuchagues, J. -P. *Angew. Chem., Int. Ed.* **2003**, *42*, 1614−1618. (c) Sato, T.; Nishi, K.; Iijima, S.; Kojima, M.; Matsumoto, N. *Inorg. Chem.* **2009**, *48*, 7211−7229.

(13) (a) Furusho, D.; Nishi, K.; Hashibe, T.; Fujinami, T.; Hagiwara, H.; Matsumoto, N.; Halcrow, M. A.; Iijima, S.; Sunatsuki, Y.; Kojima, M. *Chem. Lett.* **2011**, 72−74. (b) Hashibe, T.; Fujinami, T.; Furusho, D.; Matsumoto, N.; Sunatsuki, Y. *Inorg. Chim. Acta* **2011**, *375*, 338−342. (c) Fujinami, T.; Nishi, K.; Matsumoto, N.; Iijima, S.; Halcrow, M. A.; Sunatsuki, Y.; Kojima M. *Dalton Trans.* **2011**, DOI: 10.1039/C1DT11063B.