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Ligand Field Tuned Spin Crossover for an Iron (II)-di(diamine) System

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Abstract: Investigation of spin-crossover in iron (II)-di(diamine) system, based on ligands L_1 , 4, 5-dimethy-2-(pyridine-2-yl)imidazole, has been presented in this paper. The methyl group at the adjacent sites of the donor atoms in ligand L_1 can generate the crossover situation for the iron (II) tris(diimine) system. While for the iron (II)-di(diamine) system with L_1 , the results are complicated: complex 1 {Fe(L_1)₂(SCN)₂} displays paramagnetic behaviour while 2 {Fe(L_1)₂(SeCN)₂} is in crossover situation. The difference was attributed to the various ligand field strength of SCN⁻ and SeCN⁻, which also resulted to the blue-shift of IR and Raman spectra, as well as red-shift and decrease in molar absorptivity of UV-vis absorption spectrum.

1. Introduction

As is one of the most impressive examples of molecular bi-stability and potential application in memory, molecular switch, sensor devices and intelligent contrast agents, the design and synthesis of molecular architectures displaying spin crossover (SCO) properties has attracted great attention over the past decade. ¹ The spin transition of a SCO system between high-spin (HS, ${}^{5}T_{2}$) and low-spin (LS, ${}^{1}A_{1}$) electronic states of an octahedral $3d^{4}$ - $3d^{7}$ transition metal complexes scan be induced under such external perturbations as light irradiation, variation in temperature/pressure, or magnetic/electric fields,² and the resulted SCO behaviours are varied as complete, incomplete,

abrupt, gradual, one-step, multi-step transitions, or hysteretic.³ To date over 200 SCO systems, many of them are interesting mononuclear Fe^{II} complexes with N-heterocyclic ligands ⁴ or polymeric Fe^{II} complexes with triazole or pyrazine ligands,⁵ as well as some Fe^{III, 6} Co^{II 7}, Mn^{III 2b} and Cr^{II 8} complexes, have been reported. Most of these reported SCO studies were centred on detailed structural analysis along with magnetic studies duo to the key relationship between solid state structural features (intra- and intermolecular interactions) and lattice cooperativity (the extent to which spin-state changes are propagated in the solid-state). For instance, the intermolecular interactions promoting effective cooperativity, ^{9a} the existence or absence of solvent molecules turning the spin transition behaviour of the metal centre,^{9b} and the counter anions triggering SCO transition through supramolecular host-guest binding.^{9c}



Scheme 1. Molecular structures of complexes 1 and 2.

The iron (II) tri(diimine) system, which act as one of the most common models for spin crossover behavior due to their important feature that they can be modified readily to tune the ligand-field strength, have attracted much attention in the past years. ¹⁰ While among the diimine system, 2-(pyridin-2-yl) imidazole-related ligands has occupied a special position as ideal candidate for probing and understanding the fundamental science of spin crossover. ¹¹ The $[FeN_6]^{2+}$ derivative of 2-(pyridin-2-yl)imidazole was shown continuous above room temperature spin transition both in solid state and in solution,¹² which was relatively early on to be a crossover system,¹³ thus, an appropriate variation in either their σ -donor and/or π -acceptor character of this ligand may result in crossover situation in this $[FeN_6]^{2+}$ systems. In our other

work,¹⁴ we introduced methyl group at the adjacent sites of the donor atoms ligand 2-(pyridin-2-yl)imidazole, which generated ligand L_1 (4, 5-dimethy-2 -(pyridine-2-yl)imidazole) and we have made a complete complexes formation of ligand L_1 with different Fe (II) salts (Fe(ClO₄)₂, Fe(BF₄)₂, Fe(PF₄)₂ and Fe(SbF₄)₂). PPMS results revealed that these [FeN₆]²⁺ systems with L_1 were all shown crossover situation, which display counter-anions-dependent transition temperatures due to interactions between counter-anions and L_1 . Hence in this work, we investigated the iron (II) di(diimine) system with L_1 by introduce of ligands field of SCN⁻ and SeCN⁻, and we have obtained two new complexes {Fe(L_1)₂(SCN)₂} (1) and {Fe(L_1)₂(SeCN)₂} (2) (Scheme 1). PPMS results revealed that the 1 displays paramagnetic behaviour while 2 is in complete crossover situation. Single-crystal X-ray diffraction, PXRD, TGA, Raman and IR spectra as well as UV-vis absorption measurements (Supporting Information) were performed.



Figure 1. Crystal structures and connecting motif of complex 1, hydrogen atoms are omitted for clarity: (a) The ASU of complex 1; (b) The "di-Fe^{II}" sites packed by C-H... π and π ... π contacts; (c) The 1D connecting motif of complex 1.

2. Results and discussion

2.1 Crystal structure of 1 and 2

Complex 1 was crystallized from methanol solution as yellow block crystals, complex 2 was crystallized as yellowish-brown micro-crystals. The crystal structures of complexes 1 was characterized by single-crystal X-ray diffraction, and the phase purity of complex 2 was confirmed by powder X-ray diffraction. The crystal data and structure refinement for complex 1 was listed in

Table S1. Complex **1** crystallizes in triclinic *P-1* space group, the Fe^{II} ion adopts a distorted octahedral geometry formed by four N atoms of the ligands L_1 and two N atoms of SCN⁻, and it displays a "batterfly-like" motif (Figure 1a). Every two "batterfly" motif form "di-Fe^{II}" sites through C-H... π (C...C distance 3.312 Å) and π ... π (centre...centre distance 3.854 Å) contacts between adjacent L_1 ligands (Figure 1b). The "di-Fe^{II}" sites further packed into 1D chains through C-H... π and π ... π contacts (Figure 1c), and the 1D chains then stacked into3D motif (Figure S1). For the "batterfly-like" unit, the average Fe-N distance is 2.18 Å (Table 1), and the distortion parameters \sum^{15} is 88.05° (Table 2), typical values for a HS Fe^{II} atom.

Table 1. The bond length (Å) of the distorted octahedral geometry for 1

Fe1-N1	Fe1-N2	Fe1-N3	Fe1-N4	Fe1-N5	Fe1-N6	Mean	
2.197	2.229	2.129	2.202	2.113	2.212	2.18033333	

Table 2. The bond angles (°) and distortion parameter $(\sum)^{\circ}$ of the distorted octahedral geometry for 1



Figure 2. PXRD profiles of complexes 1 and 2.

Shown in Figure 2 were the PXRD profiles of complex **1** and **2** in 5-40° range, which revealed that these two complexes shown almost identical crystal lattice, demonstrating that the different magnetic properties between **1** and **2** may attribute to various ligand field of SCN⁻ and SeCN⁻ rather than the crystal lattice or intermolecular interactions.



Figure 3. The $\chi_m T$ versus T plots of the direct-current (dc) magnetic measurement for complexes 1 and 2 over the temperature range 400-5 K.

2.2 Magnetic properties

The variable-temperature direct-current (dc) magnetic-susceptibility measurements for crystalline samples of complexes **1** and **2** were performed on a PPMS under 2000Oe in temperature range 400-5 K. Shown in Figure 3 were the $\chi_m T$ versus T plots of them. Complex **1** shows $\chi_m T = 3.11$ cm³mol⁻¹K at the room temperature, typical value for a HS Fe^{II} atom. Upon cooling, this value kept constant until 50 K, then it undergo a gradual decrease to $\chi_m T = 2.92$ cm³mol⁻¹K at 25 K, followed by a drop to 1.82 cm³mol⁻¹K at 3 K owing to the combined effect of spin-orbit coupling and zero-field splitting of the HS Fe^{II} ion. The $\chi_m T$ versus T plots of complex **2** shows a significant different behaviour with **1** when the SCN⁻ was changed to SeCN⁻, the latter possess a larger ligand field strength than the former one. Complex **2** shows $\chi_m T = 3.05$ cm³mol⁻¹K at the upper

temperature limit, typical value for a HS Fe^{II} atom. Upon cooling, the $\chi_m T$ versus T curve displays a complete one-step spin transition. The $\chi_m T$ values undergo a gradual decline to reach a plateau close to 0cm³mol⁻¹K at around 120 K, indicating a complete LS Fe^{II} sites. The spin transition temperature $T_{1/2}$ for complex **2** is 214 K. Thus, the combination of ligand L_1 with SeCN⁻ can provided appropriate ligand-field strength for a SCO mononuclear Fe^{II} site.

3. Conclusions

In conclusion, the combination of ligand L_1 (4, 5-dimethy-2-(pyridine-2-yl)imidazole) with ligand SeCN⁻ can generated the crossover situation for iron (II)-di(diamine) complex 2 {Fe(L_1)₂(SeCN)₂}, while the combination of ligand L_1 with ligand SCN⁻ cant' provide appropriate ligand-field strength for a SCO mononuclear Fe^{II} site thus resulted paramagnetic behaviour for complex 1{Fe(L_1)₂(SCN)₂}. The stronger ligand field strength of SeCN⁻ than SCN⁻ shown pronounced effect on the spin transition, blue-shift of Raman spectra as well as the red-shift and decrease in molar absorptivity of UV-vis absorption spectrum for complexes 1 and 2.

4. Experimental

4.1 Materials and physical measurements

All syntheses were performed under ambient conditions. $Fe(ClO_4)_2 \cdot 6H_2O$, KSCN and KSeCN were all obtained commercially from Aldrich and used as received. All syntheses were performed under ambient conditions. Elemental analyses were performed by a Vario-EL III elemental analyzer for carbon, hydrogen, and nitrogen for complexes 1 and 2. Temperature-dependent magnetization (M-T) of the complexes 1 and 2 were measured in the temperature range 305-3 K and 305-50 K using a quantum design vibrating sample magnetometer in a physical property measurement system. Measurements were performed on ground polycrystalline samples of 15-20 mg. The magnetic data were corrected from the sample holder and the diamagnetic contributions.

4.2 Synthesis of *L*₁ (4, 5-dimethy-2-(pyridine-2-yl)imidazole)

The synthetic routes of the ligand L_1 are illustrated in Scheme S1.¹⁶ 1 ml oxalylchloride (10 mmol) was added drop-wise to a CH₂Cl₂ solution (100 ml) with 1.5 g N-methylacetamide (20 mmol) at 0 °C under heavy gas evolution. After stirred for about 30 min, 2-pyridine carboxamide (2.74 g, 10 mmol) was added. The obtained mixture was stirred for 3 h at rt, and the volatiles were removed under reduced pressure. The residue was dissolved in an aqueous solution of NaHCO₃ (60 ml) and refluxed for a further 2 h at 100 °C. The water phase was extracted three times with CHCl₃. The organic phase was concentrated and re-crystallized from MeOH gave the ligand L_1 . Yield: 1.14 g, ca. 78%, M.p. 116-118°C. Elemental analysis (%) for L (C₁₀H₁₁N₃): calcd: C 69.34, H 6.40, N 24.25, found: C69.27, H6.44, N 24.19. IR (KBr, cm⁻¹): 3048, 2980, 2180, 1750, 1560, 1562, 1533, 1482, 1340, 1269, 1235, 1120, 1040, 1015, 987, 960, 798, 747, 721. ¹H NMR δ : 2.67-2.75 (d, 6H), 7.36 (m, H), 7.85 (m, 1H), 8.38 (d, 1H), 8.59 (d, 1H), 13.00 (s, 1H). ¹³C NMR δ : 12.6, 43.5, 124.5, 125.6, 131.6, 137.2, 143.4, 149.2, 155.1, 165.9.

4.3 Synthesis of complexes 1 and 2

A methanol solution (10 mL) of ligand L_1 (0.8 mmol) were added dropwise to an methanol solution (5 mL) of Fe(ClO₄)₂·4H₂O (0.4 mmol), Potassium thiocyanate (Potassium Selenocyanate) (0.8 mmol) and a small amount of ascorbic acid (to avoid oxidation of Fe (II)). The resulting brown solution was filtered after stirred for about 30 minutes. Crystals suitable for X-ray single-crystal diffraction or PXRD were obtained within two weeks and collected by filtration. Yield: ca. 85%. Elemental analysis (%) for **1** (C₂₂H₂₀FeN₈S₂): calcd: C 51.17, H 3.90, N 21.69; found: C 51.43, H 3.78, N 21.52. **2** (C₂₂H₂₀FeN₈Se₂): calcd: C 43.30, H 3.30, N 18.36; found: C 43.51, H 3.46, N 18.44.

X-ray crystallographic study

The single-crystal X-ray diffraction data of complex **1** was collected with graphite-monochromated Mo Ka radiation ($\lambda = 0.071073$ nm). A Rigaku SCXmini diffractometer with the v-scan technique was used.¹⁷ The

lattice parameters were integrated using vector analysis and refined from the diffraction matrix, the absorption correction was carried out by using Bruker SADABS program with the multi-scan method. The structures were solved by full-matrix least-squares methods on all F2 data. The SHELXS-97 and SHELXL-97 programs ¹⁸ were used for structure solution and structure refinement, respectively. The molecular graphics were prepared by using the mercury program. ¹⁹

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Electronic Supplementary Information (ESI) available: [crystal data and structure refinement for compounds 1, TGA profiles, Raman and IR spectra as well as UV-vis absorption spectra for complexes 1 and 2]. See DOI: 10.1039/b000000x/.

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Investigation of spin-crossover in iron (II)-di(diamine) system, based on ligands L_1 , 4, 5-dimethy-2-(pyridine-2-yl)imidazole, has been presented. The methyl group at the adjacent sites of the donor atoms in ligand L_1 can generate the crossover situation for the iron (II) di(diimine) system. For complex 1 {Fe(L_1)₂(SCN)₂}, it displays paramagnetic behaviour, while for 2 {Fe(L_1)₂(SeCN)₂}, it is in complete crossover situation. The difference was attributed to the various ligand field strength of SCN⁻ and SeCN⁻.

Highlights

>> Two new complexes from 4, 5-dimethy-2-(pyridine-2-yl)imidazole and NCX have been presented.

>> Influences of NCX on spin-crossover have been investigated.

>> The vibrational and absorption spectra of these two complexes have been quantificationally visualized.

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