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The effect of molecular packing on the occurrence of spin crossover phenomena in one-dimensional Fe(II)-bis-Schiff base complexes

Atsuhiro Nabei, Takayoshi Kuroda-Sowa *, Takashi Okubo, Masahiko Maekawa, Megumu Munakata

Department of Chemistry, Faculty of Science and Engineering, Kinki University, Higashi-Osaka, Osaka, Japan

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A B S T R A C T

Two new one-dimensional Fe(II)-bis-Schiff base complexes, $[Fe(L1)(pyz)]\cdot CH_2Cl_2$ (**1**) and $[Fe(L2)(pyz)]\cdot 2CH_2Cl_2$ (**2**) (H_2L1 = bis(*O*-vanillin)-*O*-phenylenediimine, H_2L2 = bis(*O*-vanillin)-2,3-naphthalenediimine, pyz = pyrazine) are reported with their crystal structures and magnetic property. Compound **1** shows a two-step SCO behavior while **2** shows HS at all the temperature range measured. Although the extension of aromatic moiety from benzene (L1) to naphthalene (L2) was introduced for the purpose of strengthening the cooperativity, it leads to the absence of SCO, due to the unanticipated π–π interaction, which leads to the longer Fe–N bond lengths and a weak ligand field around Fe(II) ion.

1. Introduction

Spin crossover (SCO) phenomenon is one of the most fascinating characteristics of metal complexes to show drastic change in magnetism by outer stimuli, which is the interconversion of the low-spin (LS) and the high-spin (HS) states in 3d transition metal complexes with d^4–d^7 electronic configuration. Due to not only scientific interests but also the potential applications including multivalued memory or switching devices, many studies have been reported so far concerning SCO compounds [1–3]. An abruptness of the transition and a wide hysteresis are both important factors to realize SCO compounds as such devices, and these factors are strongly related to the cooperativity of each SCO center [3]. Interconnection through coordination bonds [4], π–π stacking [5], hydrogen-bonds [6] is thought to enhance cooperativity. Among Fe(II) or Fe(III) SCO systems, an FeN_6 coordination sphere is commonly seen and FeN_4O_2 coordination or other is rare [6,7]. Bis-Schiff base ligands, as represented by salen or salophen,[1] are famous N_2O_2 donors and their metal complexes are known to show various catalytic activity by using vacant or labile axial sites, especially in solution [8]. By using a bis-Schiff base ligand as a planar tetradentate N_2O_2 donor together with two axial nitrogen donors from bridging ligands to complete N_4O_2 coordination around an Fe(II) ion, we intended to create a cooperativity-enhanced Fe(II) SCO system. The merit of using bis-Schiff base ligands is their easy chemical modification by changing combinations of corresponding amine and aldehyde. The ligands used in this work, L1 and L2, are shown in Chart 1. Although similar works appeared recently [9], our work has been conducted independently of them.

2. Experimental

All chemical and solvents used during the synthesis were of reagent grade. The ligand H_2L1 was synthesized by mixing *o*-phenylenediamine with *o*-vanilline in a 1:2 molar ratio in methanol. The same preparation was used for H_2L2 using 2,3-diaminonaphthalene instead of *o*-phenylenediamine.

2.1. Preparation of $[Fe(L1)(pyz)]\cdot CH_2Cl_2$ (**1**)

A 5 ml CH_2Cl_2 solution containing H_2L1 (37.1 mg, 0.1 mmol) and pyrazine (80.1 mg, 1.0 mmol) was placed in the bottom of a glass tube. Then, a 5 ml MeOH solution containing $Fe(BF_4)_2\cdot 6H_2O$ (33.7 mg, 0.1 mmol) and L-(+)-ascorbic acid (17.6 mg, 0.1 mmol) was added slowly. After standing for 2 weeks at −5 °C, black brick crystals of **1** were obtained. Complex **1** is insoluble in common solvents, indicating its polymeric structure. *Anal.* Calc. for $C_{27}H_{24}Cl_2FeN_4O_4$: C, 54.48; H, 4.06; N, 9.41. Found: C, 54.65; H, 3.88; N, 9.15%. IR (KBr pellet, cm^{-1}): 2954(w), 1608(s), 1570(s), 1468(s), 1256(s), 1208(s), 1078(m), 933(s), 737(s).

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* Corresponding author.
E-mail address: kuroda@chem.kindai.ac.jp (T. Kuroda-Sowa).

[1] salen = bis(salicylaldehyde)ethylenediiamine, salophen = bis(salicylaldehyde)-*O*-phenylenediimine.

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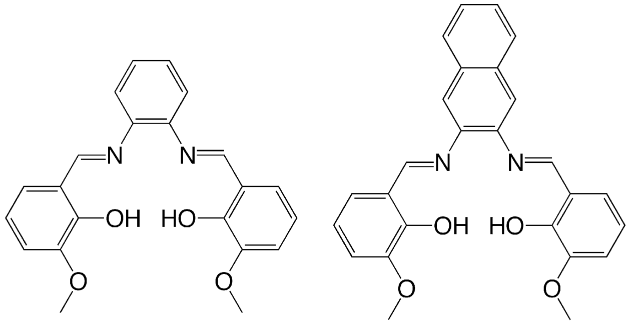

H_2L1 **H_2L2**

Chart 1.

2.2. Preparation of [Fe(L2)(pyz)] · $2CH_2Cl_2$ (**2**)

The same preparation as that presented for **1** was used for **2** replacing H_2L2 instead of H_2L1. Complex **2** is also insoluble in common solvents, indicating its polymeric structure. *Anal.* Calc. for $C_{32}H_{28}Cl_4FeN_4O_4$: C, 52.63; H, 3.86; N, 7.67. Found: C, 52.84; H, 4.10; N, 7.43%. IR (KBr pellet, cm^{-1}): 2934(w), 1607(s), 1574(m), 1465(s), 1254(s), 1095(m), 972(m), 739(s).

2.3. X-ray crystal structure determination

A suitable crystal of **1** or **2** was mounted on a glass fiber. The X-ray measurements were made on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The diffraction data were collected at 120 K (LS) and 280 K (HS) for complex **1** and 150 K for complex **2** by the *w* scan mode. Of the 30083, 39791 and 18712 reflections which were collected for complexes **1**(LS), **1**(HS), and **2**, respectively, data were collected and processed using the CRYSTALCLEAR program (Rigaku). The structures were solved by direct methods (SIR-88 for **1**(LS) and **2**, SIR-92 for **1**(HS)) [10] and expanded using Fourier techniques [11]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement [12] was based on 7263, 6001 and 6261 reflections ($I > 2\sigma(I)$) and 685, 685 and 406 variable parameters, respectively. The unweighted and weighted agreement factors of $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$ are used. The R_1 and R_w values were {0.119 and 0.257}, {0.181 and 0.358}, and {0.073 and 0.134} for complexes **1**(LS), **1**(HS), and **2**, respectively. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation [13]. Crystal data and details of the structure determination are summarized in Table 1.

Table 1
Crystallographic data for complexes **1**(LS), **1**(HS), and **2**

	1(LS)	**1**(HS)	**2**
Formula	$C_{27}H_{24}Cl_2FeN_4O_4$	$C_{27}H_{24}Cl_2FeN_4O_4$	$C_{32}H_{28}N_4O_4FeCl_4$
M_w	595.26	595.26	730.26
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T (K)	120 ± 1	280 ± 1	150 ± 1
a (Å)	13.43(1)	14.31(1)	7.359(6)
b (Å)	13.71(1)	13.70(2)	13.74(1)
c (Å)	15.46(1)	15.18(2)	16.13(1)
α (°)	91.543(10)	91.91(3)	81.44(2)
β (°)	115.20(1)	114.56(2)	84.13(2)
γ (°)	91.12(1)	89.46(4)	86.24(2)
V (Å^3)	2572 (3)	2705(4)	1602(2)
Z	4	4	2
D_c (cm^{-1})	1.537	1.461	1.514
$F(000)$	1224.0	1224.0	748.0
μ (Mo Kα) (cm^{-1})	8.36	7.95	8.47
Measured reflections	30083 (total)	39791 (total)	18712 (total)
Observed reflections ($I > 2\sigma(I)$)	7263	6001	6261
Residual electron density (Å^{-3})	088 (max); −0.73 (min)	0.54 (max); −0.50 (min)	0.56 (max); −0.57 (min)
R_1	0.119	0.181	0.073
R_w	0.257	0.357	0.134
Goodness-of-fit	1.14	1.21	1.18

2.4. Physicochemical measurements

Magnetic susceptibility data were collected on fresh microcrystalline samples on a Quantum Design MPMS2 SQUID magnetometer equipped with a 1 T magnet and capable of achieving temperatures of 1.7–400 K. A diamagnetic correction to the observed susceptibilities was applied using Pascal's constants. Infrared spectra were recorded on KBr pellets using a JASCO FT/IR-430 spectrophotometer.

3. Results and discussion

3.1. Crystal structure of **1**

On the basis of the magnetic data of **1** (*vide infra*), X-ray structure determinations of **1** were performed at 120 and 280 K, which

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1**(LS), **1**(HS), and **2**

*Complex **1**(LS)*			
Fe1–O1	1.953(5)	Fe1–O2	1.952(5)
Fe1–N1	1.932(6)	Fe1–N2	1.912(6)
Fe1–N3	1.960(7)	Fe1–N4	1.960(7)
Fe2–O5	1.951(4)	Fe2–O6	1.952(5)
Fe2–N5	1.929(6)	Fe2–N6	1.916(6)
Fe2–N7	1.963(7)	Fe2–N8	1.971 (7)
O1–Fe1–O2	88.1(2)	O5–Fe2–O6	89.1(2)
*Complex **1**(HS)*			
Fe1–O1	1.947(7)	Fe1–O2	1.938(7)
Fe1–N1	2.076(9)	Fe1–N2	2.083(9)
Fe1–N3	2.17(3)	Fe1–N4	2.17(3)
Fe2–O5	1.974(6)	Fe2–O6	1.971(7)
Fe2–N5	2.116(8)	Fe2–N6	2.125(8)
Fe2–N7	2.27(1)	Fe2–N8	2.194(10)
O1–Fe1–O2	102.9(3)	O5–Fe2–O6	106.3(3)
*Complex **2***			
Fe1–O1	1.987(2)	Fe1–O2	1.983(2)
Fe1–N1	2.129(3)	Fe1–N2	2.124(3)
Fe1–N3	2.249(3)	Fe1–N4$^{(1)}$	2.306(3)
O1–Fe1–O2	109.0(10)		

Symmetry code: (1) $X - 1$, Y, Z.

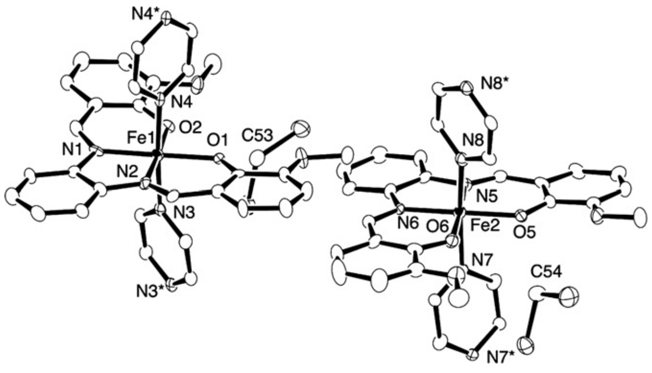

Fig. 1. ORTEP drawing of **1**(LS), showing the 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.