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Tridentate N^NN iron(II) and cobalt(II) complexes of ion-paired structures: Synthesis, characterization and magnetism

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1. Introduction

As the key part of coordination chemistry, rational design and synthesis of novel ligand always receive much attention. In recent years, rapid progress of ethylene reactivity was made in tridentate N^NN complexes, which are of considerable current interest and could be reflected by the recent articles [1]. It was found out that, while complexes bearing ligands containing bulky substituents are generally of trigonal bipyramid geometry and performed good catalytic activities for polymerization or oligomerization of ethylene [2], there is a tendency of the formation of ion-paired complexes for steric unhindered ligand [3]. In such ion-paired complex, there are two ligands coordinated with one metal core. It would be interesting to research the various properties derived from different structures, which were formed from same ligand framework along with varying steric effect.

In devising late-transition metal complexes as catalysts for ethylene polymerization and oligomerization, our group recently developed series of tridentate $N^N N$ complexes containing ligands such as 2-imino-1,10-phenanthrolines [4],2-(benzoimidazol-yl)-6-iminopyridines [5], 2-quinoxalinyl-6-iminopyridines [6], 2-(benzimidazol-2-yl)-1,10-phenanthrolines [7], 2-methyl-2,4-bis(6-iminopyridin-2-yl)- 1*H*-1,5-benzodiazepines [8] and *N*-((pyri-

ABSTRACT

Two kinds of ion-paired iron and cobalt complexes ligated by 2-(benzimidazolyl)-6-(1-(arylimino)ethyl)pyridyl [iron (**1a**) and cobalt (**1b**)] or *N*-(pyridin-2-yl)methylene)-quinolin-8-amine (iron, **2a**) were synthesized and well characterized by IR, EA and X-ray diffraction analysis. They were confirmed to be in the form of $[ML_2]^{2+}[MCl_4]^{2-}$ or $[ML_2]^{2+}2[MCl_4]^{1-}$ and the cations took octahedral coordinated geometry. Structure research indicated that complex **1a** was in low-spin state while complex **1b** was in high-spin state. Furthermore, their magnetic susceptibility measurements were performed and the complexes showed interesting magnetic properties.

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din-2-yl)methylene)-quinolin-8-amine [9]. In general, the trigonal bipyramid geometry was observed for those complexes with equal molar ligand to metal core, and those complexes performed good to high catalytic activities. However, the metal (iron and cobalt) complexes bearing 6-difluoro-*N*-(1-(6-(1-methyl-1*H*-benzo-imida-zol-2-yl)pyridin-2-yl)ethylidene)benzenamine (**1**, Scheme 1) and iron complex ligated by *N*-((pyridin-2-yl)methylene)-quinolin-8-amine (**2**, Scheme 1) did not show any activity toward ethylene. Single X-ray diffraction analysis was performed and the formation of the ion-paired complexes was confirmed. The ion-paired iron complexes have been wanted in magnetic materials [10], which have been widely investigated and indeed attracted much attention [11]. Herein, we report the synthesis, characterization of the titled ion-paired complexes and the study of their unique magnetic properties.

2. Experimental

2.1. General considerations

All manipulations of air and/or moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were refluxed over an appropriate drying agent, distilled and degassed before using. 1-(6-(1-Methyl-1H-benzo[d]imidazol-2-yl)pyridin-2-yl)ethanone was prepared by literature method [5]. Other reagents were purchased from Aldrich, Acros or local supplier. Elemental analyses were

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Scheme 1. Ligands 1 and 2.

performed on a Flash EA 1112 microanalyzer. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer using KBr disc in the range of 4000–400 cm⁻¹. The ¹H and ¹³C NMR spectra were recorded on a Bruker DMX-300 instrument with TMS as the internal standard. Variable-temperature magnetic susceptibilities (in the temperature range of 5–300 K) were measured on a Quantum Design MPMS-7 SQUID magnetometer in a field of 1 T. Diamagnetic corrections were made with Pascal's constants for all constituent atoms.

2.2. Synthesis of ligand and complexes

2.2.1. Synthesis of ligand 6-difluoro-N-(1-(6-(1-methyl-1H-benzo[d] imidazol-2-yl) pyridin-2-yl)ethylidene)benzenamine (**1**)

A solution of 2,6-difluoroaniline (106 mg, 0.875 mmol), 1-(6-(1methyl-1*H*-benzo [*d*] imidazol-2-yl) pyridin-2-yl) ethanone (200 mg, 0.796 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (25 mL) were refluxed for 24 h. After solvent evaporation, the crude product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) as eluent to afford the product as a white powder in 65.9% yield (Scheme 2). Mp 177.0-178.0 °C. ¹HNMR (300 MHz, CDCl₃, TMS): 8.56-8.54 (d, 1H, J = 7.5 Hz, -Py), 8.43-8.41 (d, 1H, J = 7.5 Hz, -Pv), 8.00–7.95 (t, 1H, / = 7.8 Hz, -Pv), 7.87–7.85 (d, 1H, / = 6.6 Hz, -Ph), 7.47-7.45 (d, 1H, J = 7.8 Hz, -Ph), 7.37 (m, 2H, -Ph), 7.10-6.96 (m 3H, -Ph), 4.35 (s, 3H, -CH3), 2.47 (s, 3H, -CH3). ¹³CNMR (75.45 MHz, CDCl₃, TMS): 172.07, 154.73, 151.38, 149.9, 149.57, 142.63, 137.66, 137.39, 126.36, 124.25, 123.60, 122.84, 122.08, 120.23, 111.91, 111.60, 109.99, 33.10, 18.06. ESI-MS: 363.1 (M⁺H⁺), 385.0 (M⁺Na⁺). IR (KBr; cm⁻¹): 3430; 1647 (C=N); 1582; 1470; 1434; 1388; 1364; 1329; 1276; 1238; 1215; 1153; 1116; 1071; 774; 743. Anal. Calcd for C₂₁H₁₆N₄F₂: C, 69.60; H, 4.45; N, 15.46. Found: C, 69.23; H, 4.55; N, 14.90.

2.2.2. Synthesis of complexes

2.2.2.1. Synthesis of complexes complex 1a. The complex 1a were synthesized by the reaction of FeCl₂·4H₂O with the corresponding ligand 1 in ethanol. A typical synthetic procedure for 1a can be de-



Scheme 2. Synthesis of ligand 1 and complexes 1a and 1b.

scribed as follows (Scheme 2). Ligand **1** (152 mg, 0.42 mmol) and FeCl₂·4H₂O (79.5 mg, 0.4 mmol) were added to a Schlenk tube, followed by the addition of freshly distilled ethanol (2 mL) with rapid stirring at room temperature. The solution turned deep blue immediately, and after 1 min blue power was obtained. The reaction mixture was stirred for 10 h, and after the mixture stood for 30 min, the supernatant was removed. The precipitate was washed with diethyl ether twice and dried in vacuum to furnish the pure product as a blue powder in 79.5% yield. IR (KBr; cm⁻¹): 3395; 2362; 2342; 1591 (C=N); 1540; 1525; 1472; 1419; 1390; 1335; 1283; 1241; 1022; 1003; 782; 748. Anal. Calcd for $C_{42}H_{32}Cl_4F_4Fe_2N_8$: C, 51.57; H, 3.30; N, 11.45. Found: C, 52.05; H, 3.81; N, 11.53.

2.2.2.2. Synthesis of complexes complex **1b**. Complex **1b** was synthesized by the reaction of $CoCl_2$ with the corresponding ligand **1** in ethanol (Scheme 2). Ligand **1** (152 mg, 0.42 mmol) and $CoCl_2$ (51.6 mg, 0.4 mmol) were added to a Schlenk tube, followed by the addition of freshly distilled ethanol (2 mL) with rapid stirring at room temperature. The solution turned deep green immediately, and after 1 min green power was obtained. The reaction mixture was stirred for 10 h, and after the mixture stood for 30 min, the supernatant was removed. The precipitate was washed with diethyl ether twice and dried in vacuum to furnish the pure product as a green powder in 72.7% yield. IR (KBr; cm⁻¹): 3450; 3093; 3057; 1594 (C=N); 1486; 1471; 1422; 1401; 1370; 1330; 1280; 1256; 1002; 1003; 781; 748. Anal. Calcd for $C_{42}H_{32}Cl_4Co_2F_4N_8$: C, 51.24; H, 3.28; N, 11.38. Found: C, 51.24; H, 3.72; N, 10.85.

2.2.2.3. Synthesis of complexes complex **2a**. Complex **2a** was prepared by one-pot reaction as the reported procedure [9] (Scheme 3). A suspension of pyridine-2-aldehyde (2.00 mmol), 8-aminoquinoline (2.00 mmol), and FeCl₂·4H₂O (2.00 mmol) in glacial acetic acid (25 mL) was refluxed for 2 h. The precipitate was collected by filtration and washed with diethyl ether (3×5 mL). Then the collected solid was dissolved in methanol, concentrated and precipitated with diethyl ether. After washing with diethyl ether the collected solid was dried in vacuum. The desired complex **2a** was obtained as a green powder in 91.5% yield (0.56 g) IR (KBr): 3397, 3262, 1594 (C=N), 1532, 1503, 1460, 1428, 1390, 1296, 1252, 1214, 1069, 1028, 829, 766 cm⁻¹. Anal. Calcd for C₃₀H₂₂Cl₈Fe₃N₆·2MeOH: C, 39.15; H, 3.08; N, 8.56. Found: C, 38.97; H, 3.23; N, 8.09%.

2.3. X-ray crystallography measurements

Single-crystal X-ray study for complex **1b** was carried out on a Rigaku R-AXIS Rapid IP diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293(2) K. Intensity data for crystals of **1a** and **2a** were collected on a Bruker SMART 1000 CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities



Scheme 3. Synthesis of complexes 2a.

Table 1Summary of crystallographic data for 1a, 1b and 2a

	1a-5H ₂ 0	1 b ·H ₂ O	2a
CCDC No.	667620	667621	667622
Formula	$C_{42}H_{32}Cl_4F_4Fe_2N_8O_5$	C42H32Cl4Co2F4N8O	C30H22Cl8Fe3N6
Fw	1058.26	1000.42	917.69
Cryst. syst.	Triclinic	Triclinic	Monoclinic
Space group	ΡĪ	ΡĪ	P2(1)/c
a (Å)	11.3600(1)	10.752(2)	15.4132(4)
b (Å)	14.8427(2)	14.351(3)	13.3718(3)
c (Å)	15.5477(2)	17.534(4)	19.9764(5)
α (deg)	70.615(5)	108.67(3)	90
β (deg)	81.300(8)	107.71(3)	90
γ (deg)	78.660(8)	97.18(3)	90
V (Å ³)	2414.1(5)	2366.4(8)	4117.18(17)
Ζ	2	2	4
D_{calcd} (g cm ⁻³)	1.456	1.404	1.480
$\mu [mm^{-1}]$	0.888	0.983	1.590
F(000)	1072	1012	1832
θ Range [°]	1.39-25.01	1.55-25.01	1.32-28.35
No. of data collected	33975	7818	21515
No. of unique data	8487	7818	9004
Goodness-of-fit	0.961	1.058	0.720
R	0.0983	0.0818	0.0763
R _w	0.2774	0.2466	0.2207

were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F². All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [12]. Crystal data and processing parameters for complexes **1a**, **1b** and **2a** are summarized in Table 1. CCDC-667620–667622 contain the supplementary crystal-lographic data for this paper, these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

3. Results and discussions

3.1. Synthesis and characterization of the complexes

The desired ligand 6-difluoro-*N*-(1-(6-(1-methyl-1*H*-benzo[*d*]imidazol-2-yl) pyridine-2-yl)ethylidene)benzenamine (**1**) was easily prepared in moderate yield (65%) through the condensation reactions of 1-(6-(1-methyl-1*H*-benzoimidazol-2-yl) pyridin-2-yl) ethanone and the 2,6-difluoroaniline using our previous method (Scheme 2) [5a], and sufficiently characterized by elemental analysis, ¹H and ¹³C NMR, IR, and ESI mass spectrometry.

The iron complex **1a** was prepared by stirring an ethanol solution of 1 equiv of $FeCl_2 \cdot 4H_2O$ and the corresponding ligand **1** at room temperature under nitrogen (Scheme 2). The obtained complex was precipitated from the reaction solution and separated as blue powders in good yield (79.5%) with good purity. Formation of the complex was confirmed by elemental analysis and IR. In comparison with the IR spectra of the free ligand (1647 cm⁻¹) for C=N group, the stretching vibration in complex **1a** was shifted toward lower frequency of 1591 cm⁻¹ with the reduced intensity, indicating an effective coordination between ligand and metal. Similarly, its cobalt analogue **1b** was conveniently prepared as green powders in 72.7% yield (Scheme 2) with the lower frequency of 1594 cm⁻¹ for C=N along with a decreased intensity.

Though much effort was made in the synthesis of the Schiffbase compound, N-((pyridin-2-yl)methylene)-quinolin-8-amine, pure product could not be obtained due to decomposition of those particular Schiffbase compounds [9,13a]. Therefore, one-pot

method was employed to synthesize its iron complex. The stoichiometric amounts of the 8-amino-quinoline, pyridine-2-aldehyde and the ferrous dichloride were mixed and refluxed in presence of acetic acid for 2 h to afford the corresponding complex **2a** (Scheme 3). The resultant air-stable and green product were precipitated from the reaction solution and collected by filtration, washed with diethyl ether to remove the acetic acid and dried in vacuum. The complex was characterized with elemental analysis and IR spectroscopy. In the IR spectra, the frequency of 1594 cm⁻¹ could be ascribed to the stretching vibration of C=N bond [13c]. Different with **1a** and **1b**, elemental analysis result supported the structure of $L_2Fe^{2+} \cdot 2FeCl_4^-$, perhaps due to the effect of acetic acid, iron atom in the anion part was oxidized to be Fe³⁺, which was further confirmed by single-crystal X-ray analysis.

3.2. Crystal structures

To confirm their structures, the single-crystal X-ray crystallography was employed, and it was confirmed that these complexes exhibit ion-paired structural feathers. However, there are five isolated water molecular for **1a** and one isolated water molecular for **1b**. Because they are disordered in the single crystal, it is difficult to find their hydrogen atoms from different Fourier synthesis. Therefore, the hydrogen atoms were not given in the crystal data.

Single crystals of complexes **1a** and **1b** were individually obtained by slow diffusion of diethyl ether into their methanol solutions under nitrogen atmosphere. The molecular structures are



Fig. 1. (a) Molecular structure of 1a. Hydrogen atoms, and solvent have been omitted for clarity. (b) Simplified structure.

shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in Table 2. The X-ray diffraction analysis revealed that complex **1a** existed as an ion pair comprised of $[FeL_2]^{2+}$ and $[FeCl_4]^{2-}$ (Fig. 1). In the cation part, the iron atom is coordinated by six nitrogen atoms from two ligands, and its coordination geometry at the iron center of $[FeL_2]^{2+}$ can be described as distorted octahedron. The average coordinated Fe-N bond length is 1.946 Å, comparable with other low-spin Fe (II) complexes [10], indicating the low-spin state of **1a** at 293 K, which is in agreement with the magnetic susceptibility measurement. Compared with the iron analogues with bulkier substituents [5a], the Fe-N(imino) bonds are much shorter by about 0.2 Å for 1a. While the N(3)-C(13) distance is 1.279(1) Å, typically for C=N bond, the N(7)-C(37) distance is 1.333(1)Å, a bit longer than normal distance. The two ligands are almost vertical to each other, forming a dihedral angle of 92.0°. The geometry at the iron center of $[FeCl_4]^{2-}$ can be described as a distorted tetrahedron with Fe(2)–Cl distances of 2.228(3)-2.267(3) Å and Cl-Fe(2)-Cl angles of 106.66(2)-112.64(2)°. The distance between Fe(1) and Fe(2) is 8.221 Å.

Compared with **1a**, the structure of complex **1b** showed similar coordination manner. The cobalt atom in the cation of complex **1b** is octahedral, with six coordination bonds to the nitrogen atoms of two ligands. The bond lengths of two C=N bonds are 1.288(8) Å (N(3)–C(13)) and 1.296(8) Å (N(7)–C(34)), respectively. However, the Co–N bonds are longer than its iron analogue **1a** (see Table 2 for comparison), and comparable with the cobalt analogues [5a], indicating that **1b** is in high-spin state, which is further confirmed by the magnetic property. The Co(1)–N bond distances varied, indicating that coordination geometry was not perfectly octahedral. The two ligands are almost vertical to each other, forming a dihedral angle of 98.2°. The geometry at the cobalt center of $[CoCl_4]^{2-}$ can be described as a distorted tetrahedron with Co(2)–Cl distances of 2.272(3)–2.282(3) Å and Cl–Co(2)–Cl angles of 108.22(1)–110.68(1)°. The distance between Co(1) and Co(2) is 8.016 Å.

Although there were some literatures about the analogue salts of **2a** [13], however, no structure was reported before. Crystals of ferrous complex **2a** suitable for X-ray structural determination



Fig. 2. Molecular structure of 1b. Hydrogen atoms, and solvent have been omitted for clarity.

Table 2

Selected bond lengths (Å) and angles (deg) for 1a and 1b

	1a (M=Fe)	1b (M=Co)
Bond lengths		
M(1)-N(1)	1.966(7)	2.100(5)
M(1)-N(2)	1.892(7)	2.075(5)
M(1)-N(3)	1.993(7)	2.209(5)
M(1)-N(5)	1.961(7)	2.104(5)
M(1)-N(6)	1.883(7)	2.054(5)
M(1)-N(7)	1.982(7)	2.162(5)
N(3)-C(13)	1.279(1)	1.288(8)
N(7)-C(34)	1.333(1)	1.296(8)
Bond angles		
N(2)-M(1)-N(1)	79.7(3)	76.8(2)
N(2)-M(1)-N(3)	79.4(3)	74.6(2)
N(1)-M(1)-N(3)	158.9(3)	151.3(2)
N(6)-M(1)-N(5)	80.8(3)	77.45(2)
N(6)-M(1)-N(7)	79.2(3)	74.88(2)
N(5)-M(1)-N(7)	159.5(3)	151.72(2)

were grown from a CH₂Cl₂ solution layered with pentane. The molecular structure is shown in Fig. 3. Selected bond lengths and angles are given in Table 3. The central iron atom was six coordinated, and the geometry around the iron atom could be described as a distorted octahedron in which N(3a), N(3b), N(1a) and N(1b) atoms compose an equatorial plane while the other two nitrogen atoms(N(2a) and N(2b)) occupy the axial position. The Fe(1)-N bond lengths are in the range from 1.881 Å to 1.967 Å, comparable with **1a** and other low-spin $[FeL_2]^{2+}$ complexes [10], indicating the low-spin character of Fe(1). However, there are two $[FeCl_4]^-$ anion part in the structure, suggesting the iron atoms in [FeCl₄]⁻ oxidize to be Fe^{3+} . In the structure of **2a**, the Fe(1) atom locates 0.0127 Å above the equatorial plane towards N(2a). The bond distances of N(2a)-C(10a) and N(2b)-C(10b) are 1.271(1)Å and 1.295(1)Å, respectively, displaying typical C=N double bond character. In ligand A and B, the quinolinyl ring plane and the pyridyl ring plane are almost coplanar with a dihedral angel of 2.8° and 3.1°, respectively. The two ligands are almost vertical to each other, with the dihedral angel of 89.9°. The distances of Fe(1)-Fe(2) and Fe(1)-Fe(3) are 6.602 Å and 10.383 Å, respectively.

3.3. Magnetic research

In research of magnetic properties, temperature can exert great influence. With the change of temperature, their spin crossover



Fig. 3. Molecular structure of 2a. Hydrogen atoms have been omitted for clarity.

Table 3	
Selected bond lengths (Å) at	nd angles (deg) for 2a

Bond lengths Fe(1)–N(1A) 1.951(7) Fe(1)–N(1B)	
Fe(1)–N(1A) 1.951(7) Fe(1)–N(1B)	
	1.967(7)
Fe(1)–N(2A) 1.881(7) Fe(1)–N(2B)	1.904(7)
Fe(1)–N(3A) 1.955(6) Fe(1)–N(3B)	1.935(7)
N(2A)-C(10A) 1.271(1) N(2B)-C(10B)	1.295(1)
Bond angles	
N(2A)-Fe(1)-N(1A) 83.1(3) N(2B)-Fe(1)-N(1B)	83.1(3)
N(2A)-Fe(1)-N(3A) 82.2(3) N(2B)-Fe(1)-N(3B)	80.7(3)
N(1A)-Fe(1)-N(3A) 165.3(3) N(3B)-Fe(1)-N(1B)	163.8(3)

were observed for some octahedral coordination iron complexes [10,11]. Temperature dependence of magnetic measurements for complexes **1a**, **1b** and **2a** were investigated in the temperature range 5–300 K under a magnetic field of 1T and were shown in Figs. 4–6, respectively. It was notably that all these complexes composed of anion part and cation part, and contributions from each part should be put into consideration.

For complex **1a**, the x_mT value in 300 K is 0.98 emu mol⁻¹ K indicating the iron(II) with low-spin state in the cation part, which is in good agreement with the X-ray analysis result, and the anion part [FeCl₄]²⁻ will be responsible for non-zero x_mT values. With lower temperature, the x_mT value gradually decreased and in 60 K the value becomes 0.69 emu mol⁻¹ K. The decrease of x_mT value below 30 K is due to the zero-field splitting and/or intermolecular antiferromagnetic interactions in the paramagnetic impurities. Fitting the values to the Curie–Weiss law $[1/x_m = (T - \theta)/C]$ gives Curie constant C = 0.98 emu mol⁻¹ K and Weiss constant $\theta = -20.05$ K.

For complex **1b**, the x_mT value in 300 K is 4.97 emu mol⁻¹ K, much higher than complex **1a**, indicating that the cobalt complex **1b** is in the high-spin state (S = 3/2) in accordance with other high-spin cobalt complex [100]. When the temperature decreased, the x_mT value for **1b** decreased. However, the x_mT value is still higher than 3.00 emu mol⁻¹ K even in 5 K, indicating that no spin-crossover phenomenon took place. Fitting the values to the Curie–Weiss law gives Curie constant C = 5.03 emu mol⁻¹ K and Weiss constant $\theta = -9.17$ K.

For complex **2a**, the x_mT value at 300 K is 2.12 emu mol⁻¹ K, indicating that about two thirds of the molecules are in the highspin states due to the ratio of Fe(III) to Fe(II) in **2a**, and the x_mT value is nearly constant when temperature goes down to 50 K,



Fig. 4. Magnetic susceptibility of complex 1a.



Fig. 5. Magnetic susceptibility of complex 1b.



Fig. 6. Magnetic susceptibility of complex 2a.

followed by sudden decrease below 50 K, which could be attributed to the zero-field splitting and/or intermolecular antiferromagnetic interactions in the paramagnetic impurities. Fitting the values to the Curie–Weiss law gives Curie constant C = 2.29 emu mol⁻¹ K and Weiss constant $\theta = -4.56$ K.

4. Conclusions

In general, by controlling the bulkiness of the substituent of 2-(benzoimidazolyl)-6-iminopyridines and *N*-((pyridin-2-yl)methylene)-quinolin-8-amine derivatives, the ion-paired complexes were formed containing metal(II) ligated by two tridentate (N^N) ligands and tetrachlorometallic anions. Observed the different spin states for iron complex (**1a**) and cobalt complex (**1b**), the iron complex **1a** showed a magnetic property changes within single-crystal-to-single-crystal transformation. Therefore, metal complexes containing tridentate N^N N ligands would be excellent candidates as molecular sensors with high potential.

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