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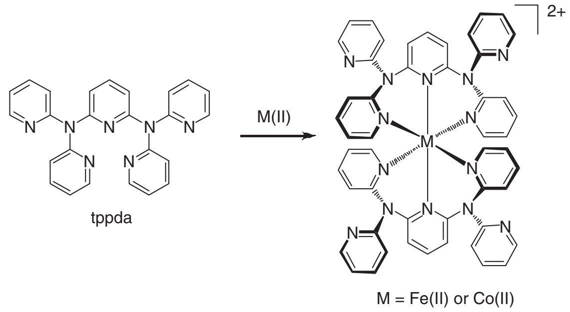
Molecular Structure and Magnetic Properties of Pentapyridyl-based Iron(II) and Cobalt(II) Complexes

Young Hoon Lee,[1] Kazuya Kato,[1] Emi Kubota,[1] Satoshi Kawata,[2] and Shinya Hayami*[1]
[1]*Department of Chemistry, Graduate School of Science and Technology, Kumamoto University,*
2-39-1 Kurokami, Kumamoto 860-8555
[2]*Department of Chemistry, Faculty of Science, Fukuoka University,*
Nanakuma, Jonan-ku, Fukuoka 814-0180

(Received February 24, 2012; CL-120154; E-mail: hayami@sci.kumamoto-u.ac.jp)

Two metal complexes, [Fe(tppda)$_2$](ClO$_4$)$_2$•acetone (**1**) and [Co(tppda)$_2$](PF$_6$)$_2$•MeOH (**2**) were synthesized, and their molecular structures and magnetic properties were also characterized by single-crystal X-ray diffraction analysis and magnetic susceptibility. Both compounds showed that six pyridyl groups of two tppda ligands were coordinated to the central metal ion while the remaining four pyridyl and four *tertiary*-amine substituents existed without coordination. Additionally, the temperature-dependent magnetic susceptibility of both complexes revealed a gradual spin transition for **1** and high-spin state for **2**, respectively.



Scheme 1. Synthetic route of compounds **1** and **2**.

The coordination chemistry of polypyridyl complexes has been studied extensively due to their unique redox properties, and their physical and photochemical features which can be utilized as magnetic switches,[1] fluorescence probes,[2] photocatalysts,[3] molecular devices,[4] dye sensitizers for solar cells,[5] and chemotherapeutic agents.[6] Among them, pyridyl-bridged pentapyridyl compounds have been recently employed in a number of studies in the field of biological activity, spin transition, and metal–organic coordination polymers, usually binding to metal ions as a pentadentate ligand. For instance, Goldsmith et al. have reported [M(PY5)X]$^{2+}$ complexes (M = Mn^{III} or Fe^{III}, PY5: 2,5-bis[methoxydi(2-pyridyl)methyl]pyridine, X = OH or OMe), acting as a lipoxygenase by C–H activation.[7] Sun et al. have also reported that a molecular cobalt pentapyridine catalyst [(PY5Me$_2$)Co(MeCN)]$^{2+}$ (PY5Me: 2,6-bis[1,1-di(2-pyridyl)ethyl]pyridine) could generate hydrogen from water.[8] In addition, a series of polymeric coordination systems with 1-D chains and 2-D networks by M^{II}–X$_2$–M^{II} bridges (M = Zn, Cd, and Hg; X = Cl, Br, and I) have been reported to date.[9]

In particular, polypyridyl compounds are promising candidates in spin-crossover (SCO) not only due to their coordination ability as ligands, but also due to the possibility to induce strong cooperative effect by intermolecular aromatic interaction which can engender much steeper transition curve and hysteresis behavior.[10] Recently, Amoore et al. have reported dinuclear iron(II) complexes [Fe$_2$(ddpp)$_2$(NCS)$_4$] (ddpp: 2,5-bis[di(2-pyridyl)amino]pyridine) exhibiting multistep spin-crossover (SCO) behavior.[11]

Keeping the aforementioned research in mind, we herein describe the crystal structure and magnetic properties of two polypyridyl metal complexes [M(tppda)$_2$]$^{2+}$ (M = Fe^{II} or Co^{II}).

The ligand tppda (tppda: *N,N,N′,N′*-tetrapyridin-2-ylpyridine-2,6-diamine) was synthesized following a literature method.[9] The iron(II) and cobalt(II) complexes were obtained by the complexation of tppda with Fe(ClO$_4$)$_2$ in acetone as a purple crystal **1** and Co(BF$_4$)$_2$ in the presence of NH$_4$PF$_6$ in methanol as a yellow crystal **2** under slow ether diffusion, respectively (Scheme 1).[12,13]

Single-crystal X-ray analyses for **1** and **2** were successfully carried out at 200 and 100 K, respectively and the respective crystals adopt a monoclinic $C2/c$ space group for **1** and a monoclinic $P2_1/c$ space group for **2**.[15] As shown in Figure 1a, the solid-state structure of **1** exhibits that the central iron(II) ion is coordinated by six nitrogen atoms of two tppda ligands with a pseudo-octahedral geometry. Two bridged pyridyl groups are placed in axial position (1.996(3)–2.011(3) Å) and four terminal pyridyl groups are symmetrically positioned in equatorial sites (1.9972(16)–2.0027(19) Å), respectively while the remaining four terminal pyridyl groups exist without coordination. Additionally, four tertiary amines do not coordinate to metal ion in order to avoid the formation of steric hindrance. Two counter anions (ClO$_4^-$) and one acetone molecule are also present around the complex cation with a variety of weak intermolecular interactions. The average Fe–N bond length of **1** (2.001 Å) indicates that the complex is in the high-spin state.

Similar coordination behavior was observed for the cobalt(II) complex **2** (Figure 1b), while it shows a significantly distorted octahedral geometry compared to that of **1**. The Co–N bond lengths of two bridged pyridyl groups occupying axial sites are in the range of 2.135(3)–2.173(3) Å, and four terminal pyridyl substitients present on equatorial position are at a distance of 2.104(3)–2.150(3) Å, respectively. The axial N–Co–N bond angle involving the bridged pyridyl moiety is close to linear (176.58(9)°) whereas the equatorial N–Co–N angles are considerably out of 180° (171.80(9) and 170.97(9)°). Two PF$_6^-$ anions and one methanol molecule are also present around the complex cation forming a diversity of weak intermolecular interactions.

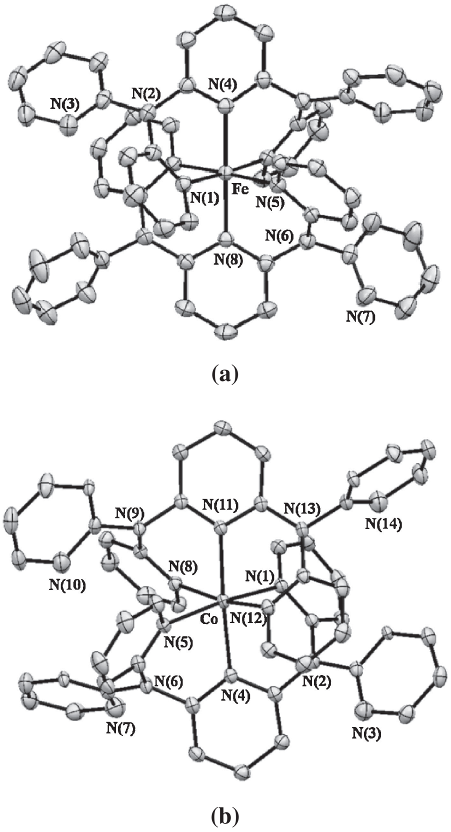


Figure 1. ORTEP drawings of (a) **1** and (b) **2** showing 50% probability displacement ellipsoids. The hydrogen atoms, counter anions, and solvent molecules are omitted for clarity.

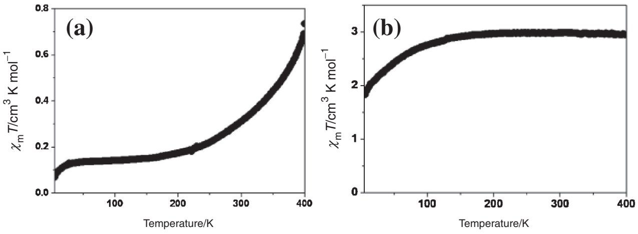


Figure 2. $\chi_m T$ versus T plots for the complexes (a) **1** and (b) **2**.

The temperature dependence of the magnetic susceptibility for the single crystal of both complexes was measured in the form of the $\chi_m T$ vs. T curve, where χ_m is the molar magnetic susceptibility and T the temperature. The $\chi_m T$ value of **1** is equal to 0.13 cm^3 K mol^{-1} at 35 K, showing that about 4% of iron(II) ions still remain in the high-spin states. The decrease of $\chi_m T$ below 35 K is due to zero-field splitting. It is almost constant to 180 K and then gradually increased to 0.74 cm^3 K mol^{-1} (HS fraction: 25%) at 400 K (Figure 2a). On the other hand, the $\chi_m T$ value of **2** at 400 K is 2.95 cm^3 K mol^{-1}, showing higher than the spin-only value of uncoupled high-spin cobalt(II) ion resulting from the orbital contribution of the octahedral cobalt(II) ion.[14] The $\chi_m T$ value smoothly decreased from 2.95 cm^3 K mol^{-1} at 400 K to 2.87 cm^3 K mol^{-1} at 130 K and then decreased more rapidly at low temperature until it reached 1.83 cm^3 K mol^{-1} at 5 K (Figure 2b). The Co···Co distance is in the range of 11.795–11.839 Å, and antiferromagnetic interaction between Co···Co cannot be expected. Thus, the decrease is caused by zero-field splitting.

In summary, we have succeeded in synthesizing two pentapyridyl-based iron(II) and cobalt(II) complexes. Their molecular structures revealed that two tppda ligands were coordinated octahedrally to the central metal ion while the remaining four terminal pyridyl groups and four tertiary amines were present without coordination. The temperature-dependent magnetic susceptibility of both complexes showed a gradual spin transition for the iron(II) complex and high-spin state for the cobalt(II) complexes, respectively.

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12 Synthesis of **1**: A solution of $Fe(ClO_4)_2\cdot 6H_2O$ (0.02 g, 0.06 mmol) in methanol (5 mL) was added to a methanol solution of tppda (30 mL, 0.05 g, 0.12 mmol). The mixture was stirred at room temperature for 2 h and the purple solution was concentrated to 5 mL under reduced pressure and left it under the diffusion of diethyl ether vapor slowly. Purple-colored crystals suitable for X-ray structure analysis were obtained. Yield: 0.04 g. Visible spectrum (in ethanol): λ_{max}/nm ($\log(\varepsilon_{max}$/M^{-1} cm^{-1})) 547 (1.95), 370 (3.53, sh). IR (KBr, cm^{-1}): 3429 (–OH), 3071 (Ar–H), 842 (PF_6^-). Anal. Calcd for $C_{53}H_{44}Cl_2FeN_{14}O_9$: C, 55.46; H, 3.86; N, 17.08%. Found: C, 55.6; H, 3.81; N, 17.20%.

13 Synthesis of **2**: To a solution of tppda (0.05 g, 0.12 mmol) in methanol (30 mL), a mixture of $Co(BF_4)_2\cdot 6H_2O$ (0.02 g, 0.06 mmol) and NH_4PF_6 (0.025 g, 0.15 mmol) in methanol (30 mL) was added slowly. The orange solution was stirred at room temperature for 2 h and the solution was concentrated under reduced pressure until around 5 mL. The resulting solution was left under the diffusion of diethyl ether vapor slowly. Yellow-colored crystals suitable for X-ray structure analysis were obtained several days later. Yield: 0.05 g. Visible spectrum (in ethanol): λ_{max}/nm ($\log(\varepsilon_{max}$/M^{-1} cm^{-1})) 417 (2.94). IR (KBr, cm^{-1}): 3060 (Ar–H), 1675 (C=O), 1090 (ClO_4^-). Anal. Calcd for $C_{51}H_{42}CoF_{12}N_{14}OP_2$: C, 50.38; H, 3.48; N, 16.13%. Found: C, 50.41; H, 3.44; N, 16.18%.

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