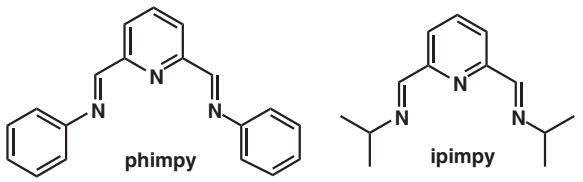
$[Co^{II}(phimpy)_2](ClO_4)_2$ and $[Co^{II}(ipimpy)_2](ClO_4)_2$: New Cobalt(II) Spin Crossover Compounds, and the Role of the Ligand Flexibility in Spin Transition Behavior

Gergely Juhász, Shinya Hayami,* Katsuya Inoue,† and Yonezo Maeda*
Department of Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581
†*Institute for Molecular Science, 38 Saigonaka, Myodaiji, Okazaki 444-8585*

(Received June 5, 2003; CL-030506)

New spin-crossover compounds, $[Co(phimpy)_2](ClO_4)_2$ (**1**) and $[Co(ipimpy)_2](ClO_4)_2$ (**2**) (phimpy = 2,6-bis(*N*-phenylformimidoyl)pyridine and ipimpy = 2,6-bis(isopropyliminomethyl)pyridine) were prepared, and the crystal structures were determined. The magnetic susceptibility measurements showed gradual transition for both compounds, despite the strong intermolecular π stacking in **1**.

The spin-crossover (SC) phenomenon is one of the most well-known examples of bistability in molecular systems.[1] Although the SC transition is due to a molecular origin and it can be observed even in solutions or polymer matrices, the interaction of SC centers can dramatically influence it. Gradual or abrupt-type spin transitions may be observed in the solid state, depending on the absence or presence of cooperativity. The understanding of the cooperative behavior in SC transition can be a key to design materials that are useful for information technology. Some experiments showed that the cooperative interactions play an important role in the LIESST effect,[2] and this approach also helped to find the first iron(III) LIESST compound.[3] There are two techniques that try to enhance the interaction between the spin-crossover molecules; both were applied successfully many times to prepare new materials with an abrupt SC transition or wide hysteresis loop.[4] One possibility is to connect them with covalent bonds i.e. prepare SC polymers. The other way is to connect the molecules with strong intermolecular interactions. The role of intermolecular interactions like π stacking[5] and hydrogen bonds,[6] was studied extensively. However the packing of the molecules in the crystal lattice, which basically determines the geometry of intermolecular interactions, is not easy to control, as it is influenced by many factors. The flexibility of the ligand can be one of the factors that influence the cooperative interaction both directly (because the more flexible the ligand is, the less probable it can mediate the effects of structural changes) and indirectly through the packing structure.



Scheme 1.

We hereby discuss two Co(II) SC compounds: $[Co(phimpy)_2](ClO_4)_2$ (**1**) and $[Co(ipimpy)_2](ClO_4)_2$ (**2**) (where phimpy = 2,6-bis(*N*-phenylformimidoyl)pyridine and ipimpy = 2,6-bis(isopropyliminomethyl)pyridine; Scheme 1). These tridentate ligands are structurally related to 2,2′,2″ terpyridine[7] and bzimpy = 2,6-bis(benzimidazol-2-yl)pyridine[8] ligands; however, phimpy and ipimpy are more flexible. For the comparison of **1** and **2**, magnetic and structural properties are reported and discussed. The ligands phimpy and ipimpy were prepared by condensation of pyridine-2,6-dicaroxaldehyde and the corresponding amine, and the ligands were used without separation for the preparation of Co(II) complexes.[9]

The crystal structure of **1** was determined at 100 K (Figure 1).[10] The structure of **1** consists of mononuclear units of $[Co(phimpy)_2]^{2+}$, ClO_4^- anions and a methanol solvent molecule. The elemental analysis has not confirmed the presence of methanol, which shows that the solvent molecule is weakly bonded, and releases fast from the sample. The two tridentate phimpy ligands coordinate to the Co^{2+} forming a distorted $[CoN_6]$ octahedron. The two phimpy ligands have inequivalent positions.[11] The ligands are not planar; the plane of the phenyl rings is rotated from the plane of the pyridine ring,[12] which shows that there is no extended bond delocalization through the imine group between the aromatic rings. The $[Co(phimpy)_2]^{2+}$ units have a close packing along the crystallographic *a* axis forming chains owing to the intermolecular π–π interaction of the phenyl rings.[13] This stacking means an arrangement of aromatic rings in a face-to-face position, but which is not perfectly parallel.

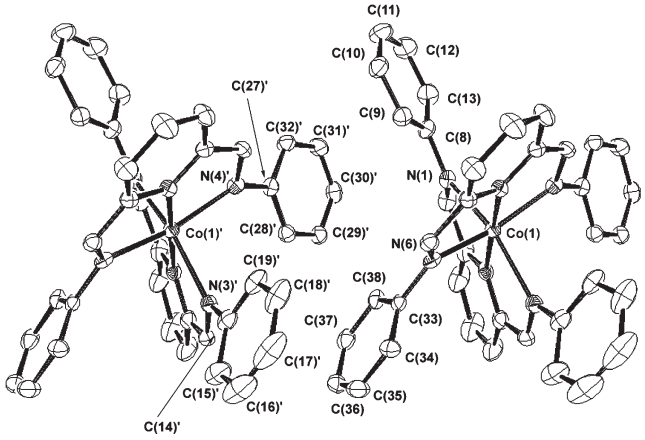


Figure 1. The structure of **1**: the position of two neighbor $[Co(phimpy)_2]^{2+}$ units. The hydrogen atoms are omitted.

The crystal structure of **2** was determined at 100 K (Figure 2).[10] The symmetric unit of **2** consists three crystallographically nonequivalent mononuclear units of $[Co(ipimpy)_2]^{2+}$ and the ClO_4^- anions. Similarly to **1**, the ligands have inequivalent position in the $[CoN_6]$ chromophore, and the Co–N(imine) distances vary between 2.02 and 2.27 Å. Because of the lack of phenyl rings and the apolar character of isopropyl groups, there is no strong interaction between the molecules.

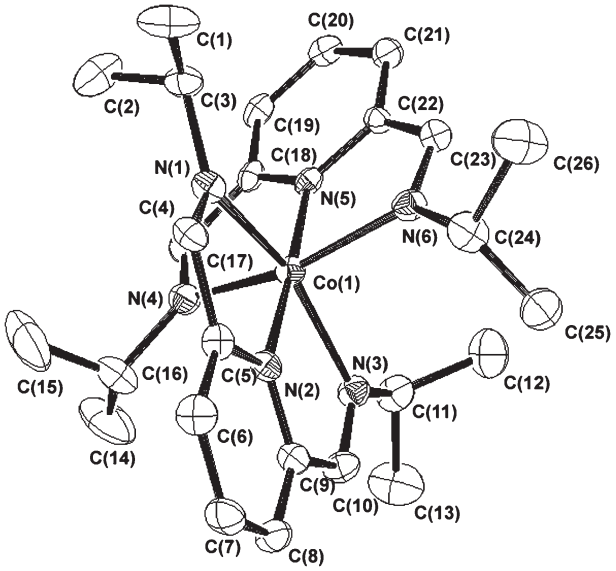


Figure 2. The structure of **2** (one of the three different $[Co(ipimpy)_2]^{2+}$); the hydrogen atoms are omitted for the clarity.

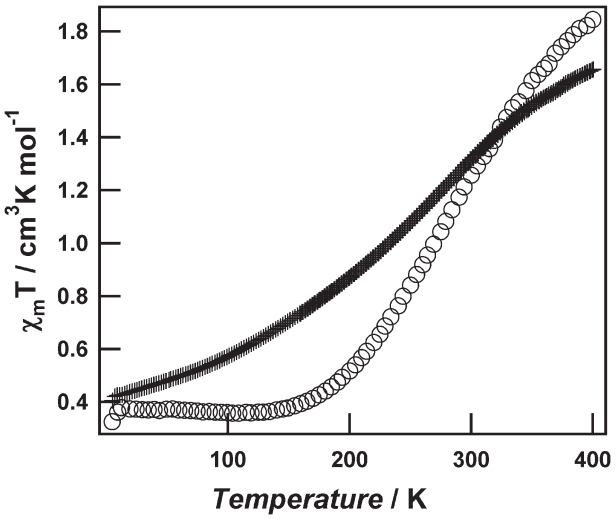


Figure 3. Temperature dependence of the $\chi_m T$ for **1** (+) and **2** (○).

The magnetic susceptibilities for both **1** and **2** were measured over the 5–400 K temperature range (Figure 3). For **1**, the $\chi_m T$ value changes gradually, and the spin-transition is incomplete in the measured temperature range. Repeated susceptibility measurements after annealing showed no change of the transition, which proves that the sample was desolvated during the measurement. The $\chi_m T$ value at 5 K ($0.406\,cm^3K\,mol^{-1}$) is corresponding to the Co(II) LS ($S = 1/2$) state. The value at 400 K ($1.657\,cm^3K\,mol^{-1}$) is somewhat lower than the theoretical spin-only value for Co(II) HS ($S = 3/2$) state. Compound **1** shows a spin-transition without hysteresis and with a transition temperature of $T_{1/2} \approx 275$ K. The extremely gradual transition of **1** is surprising, since SC compounds with π stacking generally show abrupt spin-transitions due to cooperative behavior. However, the release of the solvent can introduce defects into the lattice of **1**, and reduce the domain size during the transition. These defects can also disturb the environment of the complexes, and introduce a statistical distribution to the thermodynamic parameters of the spin-transition. The effects of vacancies and defects were studied and discussed for many iron(II) and iron(III) compounds.[14] In the case of compound **1**, the ligand is very flexible, that is why the intermolecular interactions are more sensitive to the lattice imperfections. The lack of rigidity let the structure be disturbed and distorted even for small perturbations.

For **2**, the $\chi_m T$ value has gradual temperature dependence in the 200–400 K range. The $\chi_m T$ value at 5 K ($0.365\,cm^3K\,mol^{-1}$) is corresponding to the Co(II) LS state, and the value at 400 K ($1.845\,cm^3K\,mol^{-1}$) is corresponding to the HS state, which indicates an almost complete spin-transition without hysteresis, with a spin-transition temperature of $T_{1/2} \approx 290$ K. This gradual transition is expected, since there is no strong intermolecular interaction between the molecules as shown by the crystallographic measurement discussed above.

In summary, new SC compounds, **1** and **2**, were prepared and characterized by means of magnetic susceptibility measurements and X-ray crystallography. An extremely gradual spin-transition was found for **1** in spite of the presence of π stacking between the SC molecules. Intermolecular interactions have little effect on the gradual spin-transition of **2** in agreement with the crystal structure.

We thank Prof. T. Shinmyouzu (Kyushu Univ.) for use of the X-ray diffractometer (Rigaku IP RAPID). This work was supported by Kyushu University Foundation, Casio Foundation and Tokuyama Foundation.

References and Notes

1 a) O. Kahn, in "Molecular Magnetism," VCH Publishers, Inc., New York, NY (1993). b) P. Gütlich, A. Hauser, and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, **33**, 2024 (1994). c) P. Gütlich and A. Hauser, *Coord. Chem. Rev.*, **97**, 1 (1990).
2 a) A. Hauser, J. Jeftic, H. Romstedt, R. Hinek, and H. Spiering, *Coord. Chem. Rev.*, **190**, 471 (1999). b) A. Hauser, *Chem. Phys. Lett.*, **192**, 65 (1992). c) L. Capes, J. F. Letard, and O. Kahn, *Chem.—Eur. J.*, **6**, 2246 (2000).
3 S. Hayami, Z.-Z. Gu, M. Shiro, Y. Einaga, A. Fujishima, and O. Sato, *J. Am. Chem. Soc.*, **122**, 7126 (2000).
4 J. S. Miller and M. Drillon, in "Magnetism: Molecules to Materials," WILEY-VCH Verlag GmbH, Weinheim (2001).
5 a) J.-F. Letard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau, and O. Kahn, *Inorg. Chem.*, **37**, 4432 (1998). b) S. Hayami, Z.-Z. Gu, H. Yoshiki, A. Fujishima, and O. Sato, *J. Am. Chem. Soc.*, **123**, 11644 (2001).
6 S. Hayami, Z.-Z. Gu, Y. Einaga, Y. Kobayashi, Y. Ishikawa, Y. Yamada, A. Fujishima, and O. Sato, *Inorg. Chem.*, **40**, 3240 (2001).
7 J. S. Judge and W. A. Baker, Jr., *Inorg. Chim. Acta*, **1**, 68 (1967).
8 R. Boca, P. Baran, L. Dlhán, H. Fuess, W. Haase, F. Renz, W. Linert, I. Svoboda, and R. Werner, *Inorg. Chim. Acta*, **260**, 129 (1997).
9 Elemental Analyses Calcd. for $C_{38}H_{30}N_6Cl_2CoO_8$ (**1**): H: 3.65, C: 55.09, N: 10.14%; Found H: 3.66, C: 54.95, N: 10.18%. Calcd. for $C_{26}H_{38}N_6Cl_2CoO_8$ (**2**): H: 5.53, C: 45.09, N: 12.13%; Found H: 5.53, C: 44.96, N: 12.06%.
10 Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-000000. Copies of the 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; or deposit@ccdc.cam.ac.uk).
11 The Co(1)–N(4) and Co(1)–N(6) bond distances (Co–imine) [2.025, 2.023 Å] and C(1)–N(5) bond distance (Co–pyridine) [1.860 Å] are significantly shorter than the corresponding distances for the other ligand [2.246, 2.220, and 1.924 Å respectively].
12 The torsion angle of the C(8)–C(13) phenyl ring compared the pyridine ring is 43.11°, for the C(14)–C(19) is 52.08°, for the C(28) C(32) is 49.57°, and for the C(33)–C(38) is 52.75°.
13 Representative distances: C(18′)–C(34): 3.548 Å, C(15′)–C(35): 3.583 Å, C(31′)–C(13): 3.590 Å.
14 a) E. König, G. Ritter, W. Irler, and H. A. Goodwin, *J. Am. Chem. Soc.*, **102**, 4681 (1980). b) M. S. Haddad, W. D. Federer, M. W. Lynch, and D. N. Hendrickson, *Inorg. Chim. Acta*, **20**, 131 (1981).

Published on the web (Advance View) August 27, 2003; DOI 10.1246/cl.2003.882