Columnar Structure Formed by Dimeric Fe^{II} Schiff Base Complex: Twisted-Overlap Salophen Platforms and Ferromagnetic Interaction

Zhong Yu, Toshiyuki Shimizu, Toshi Tominaga,
Takashi Okubo, Masahiko Maekawa,
and Takayoshi Kuroda-Sowa*

Department of Chemistry, Faculty of Science
and Engineering, Kinki University,
Higashi-Osaka, Osaka 577-8502

Received March 31, 2009

E-mail: kuroda@chem.kindai.ac.jp

Columnar assembly of dimeric Fe^{II} Schiff base complex based on twisted-overlap orientation of salophen platforms exhibits ferromagnetic interactions at low temperature, which is ascribable to μ-phenoxy-bridged Fe···Fe interactions and π–π interactions.

Metal complexes with salen-type [salen = *N*,*N*′-bis(salicylidene)-1,2-ethylenediamine] Schiff base ligands and their derivatives have undergone extensive research on their promising catalysis for various homogeneous reactions.[1] Recently, their solid-state properties are receiving increasing interest owing to pronounced application in materials science.[2] The current research on spin-crossover (SCO) complexes has attracted our attention to the construction of one-dimensional supramolecular systems by employing a salophen [salophen = *N*,*N*′-bis(salicylidene)-1,2-phenylenediamine] platform as a functional module.[3] Due to the presence of a big aromatic plane and free axial sites on metal centers, it is possible to build up various architectures by extensive hydrogen bonds, aromatic π–π interactions as well as introducing multilinkable modules.[4]

Under this strategy, the complex $[Fe^{II}_2(Cl\text{-}salophen)_2(CH_3OH)_2]$ (**1**) was synthesized by employing N_2O_2 tetradentate Cl-salophen ligand [Cl-salophen = *N*,*N*′-bis(5-chlorosalicylidene)-1,2-phenylenediamine]. Complex **1** exhibits a six-coordinated μ-phenoxy-bridging dimeric structure with a twisted-overlap configuration, revealing a rare instance in similar dimeric metal–salen/salophen species. Crystal structures in relation with the magnetic properties of **1** will be discussed in this report.

Black needle crystals of **1** suitable for X-ray diffraction analysis were isolated from a reaction solution containing $Fe(BF_4)_2\cdot 6H_2O$, Cl-salophen, and pyrazine at room temperature. Single-crystal X-ray diffraction analysis revealed that complex **1** crystallizes in the space group $C2/c$ with two independent dimeric molecules in the asymmetric unit. As shown in Figure 1, the iron(II) atoms are coordinated by tetradentate Cl-salophen ligands in the equatorial plane. The outer axial sites of iron(II) atoms are occupied by oxygen atoms of methanol molecules, while the inner axial sites are occupied by phenolate oxygen atoms of adjacent Cl-salophen moieties. Thus, the iron(II) coordination sphere presents a distorted octahedral six-coordination geometry.

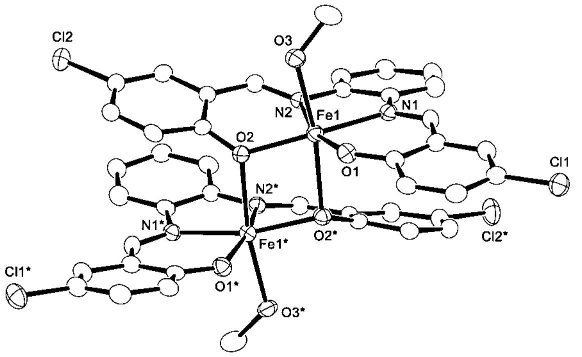


Figure 1. Dimeric molecular structure of **1**. Selected bond parameters: Fe1–O1 = 1.987(2), Fe1–O2 = 2.011(2), Fe1–O3 = 2.192(2), Fe1–N1 = 2.114(3), Fe1–N2 = 2.121(3), Fe1–O2* = 2.289(2) Å; parameters for enantiomers are similar. ORTEP view showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

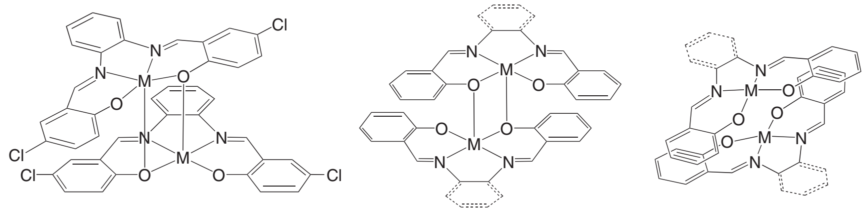
In dimeric **1**, two salophen planes are slightly distorted with the mean deviation from the basal plane of 0.1978 Å. They are nearly parallel (dihedral angle is almost 0°) and overlap each other with a twist angle of approximately 60° between two axial lines along Cl1–Cl2 and Cl1*–Cl2* respectively (Figure 2a). The observed differences in twisted direction (clockwise vs. counterclockwise) confirm configurational distinction between two enantiomers, which were arranged alternately in rows to form a racemic array.

To the best of our knowledge, such a dimeric salophen complex has not been reported so far, although various dimeric complexes with salen or salophen ligands have been reported. These dimeric complexes mostly present centrosymmetric architectures with approximately 180° twist angle, and usually exhibit step-ladder mode in μ-phenoxy-bridging species (Figure 2b)[5–9] or offset-overlap mode in non-bridging species (Figure 2c).[10]

Furthermore, those dimeric analogs with substituents on terminal phenyl rings usually have an anti-parallel orientation on ligand units owing to the mutual repulsions between substituents of adjacent moieties,[7–9] even some salen species with flexible backbone completely lose the planarity of ligand.[8,11]

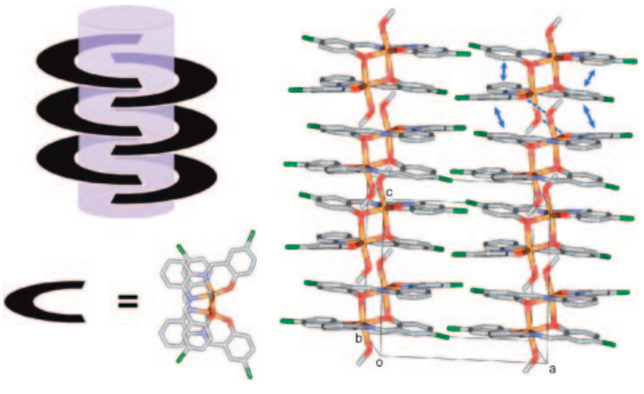
Whereas in the case of complex **1**, iron centers are doubly bridged by two μ-phenolate oxygen atoms from adjacent Cl-salophen ligands to form a Fe–O–Fe–O square, in which the bridging Fe–O bond distances are slightly larger than the values (2.117–2.205 Å) in step-ladder iron–salen species without substituents.[6] It is possible to infer that a complex with rigid Cl-salophen backbone will suffer great repulsive forces between terminal Cl atoms if it adopts Fe–O bridging step-ladder geometry. Consequently, the parallel-twist orientation of Cl-salophen ligand can be understood as the result of stabilizing selection of configuration, which is arranged to

Published on the web October 8, 2009; doi:10.1246/bcsj.82.1274



(a) (b) (c)

Figure 2. Geometries of the dimeric molecules: (a) twisted-overlap, (b) step-ladder, and (c) offset-overlap architectures. M = metal ions. Outer-axial coordination are omitted for clarity.



(a) (b)

Figure 3. (a) The columnar assembly mode of complex **1**. (b) One-dimensional structure of **1** assembled through hydrogen bond (O1···O3^i: 2.661(3) Å; dashed lines) and π–π interactions (closest distances: C3···C17^i: 3.310(5) Å, C13···C15*: 3.275(4) Å; double-headed arrows). Symmetry codes: (i) $-x+1$, $-y$, $-z+1$.

allow not only minimizing steric repulsions between substituents but also maintaining a planar salophen. The planarity of the ligand unit further favors π–π stacking and magnetic interactions between ligand platforms.

In complex **1** crystals, the dimeric molecules are packed to create columnar structure resulting from a steric semicyclic conformation (Figure 3a), in which the parallel overlap salophen platforms construct a rigid outer wall of a hollow cylinder. The Fe–O–Fe–O square of each molecule is mutual parallel to build a columnar cavity with about 3 Å internal diameter. The neighboring dimeric enantiomers are stacked alternately along the *c* axis to form a columnar assembly by hydrogen bonds and inter-dimer π–π interactions (Figure 3b). Columnar assembly displays the tubular structure, which orientates the Fe···Fe interactions along the hollow channels.

It is worth noting that the precedented dimeric complex instead of polymer is obtained in the presence of the linkable ligand pyrazine, which indicates the relatively weak donor ability of pyrazine. The molar ratio of Fe:Cl-salophen:pyrazine used in the present synthesis was 1:1:1. Synthesis of desired polymer complex is now underway by using a large excess amount of pyrazine.

Variable-temperature magnetization measurements have been performed on fresh microcrystalline samples solidified with eicosane wax in the temperature range 4–280 K under 0.01 T. The temperature dependence of the $\chi_M T$ product is plotted in Figure 4. The $\chi_M T$ product of **1** at room temperature

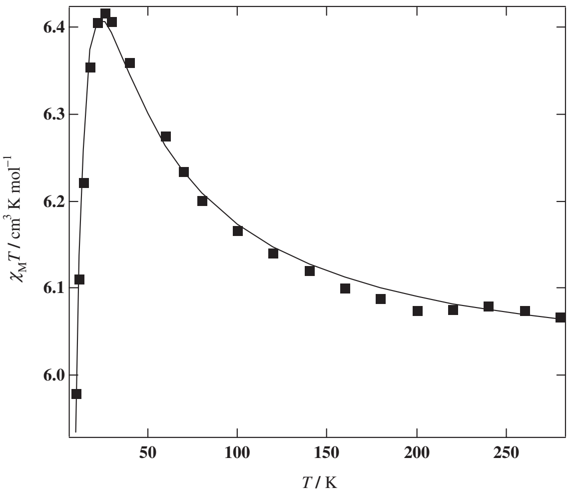


Figure 4. The $\chi_M T$ vs. T plot for complex **1** (■). Line is a least-square fitting using equation stated in the text.

is 6.1 cm^3 K mol^{-1}, consistent to the existence of two HS iron(II) ions with $S = 2$. With decreasing temperature, it increases gradually to show a peak maxima (6.4 cm^3 K mol^{-1}) at around 25 K, then decreases at lower temperatures. Since the iron(II) ion can be treated as Heisenberg-like in its behavior,[12] except at very low temperature where some anisotropy may be important, we carried out data-fitting for the observed data above 10 K by using a simple spin Hamiltonian (eq 1) for a dimer model:

$$\hat{H} = -2JS_1S_2 + g\mu_B(S_1 + S_2)B \tag{1}$$

where g is Lande's g-factor, μ_B is the Bohr magneton, and B is magnetic field. In order to reproduce the low-temperature features, the interdimer interaction is introduced as zJ'. The best fit is shown in Figure 4 as a solid line with parameters $g = 1.998$, $J = 1.7$ K, and $zJ' = -0.2$ K. The weak ferromagnetic interaction observed in **1** is reasonably understood with possible interaction pathways, i.e., through a bridging Fe–O–Fe–O square. Furthermore, the extensive π–π interactions also contribute to the metal interactions resulting from short Fe···Fe distance [3.2828(7) Å] in dimeric structures.

In summary, complex **1** exhibits a particular twisted-overlap dimeric configuration in iron Schiff base complexes, which strikes a balance between ligand planarity and substituent steric repulsion within the molecule. Columnar assembly generates the tubular structures based on the buiding block of Cl-salophen platforms, suggesting possible application to porous magnetic materals. The presence of ferromagnetic interaction at low temperature can be understood by considering the unique arrangement of dimeric structure and crystal packing mode. Further work is being conducted on a series of salophen platforms to achieve improved magnetic properties and to clarify the role of pyrazine in the reaction system.

Experimental

The Schiff base ligand Cl-salophen was synthesized according to previously published procedures.[13] A solution of $Fe(BF_4)_2 \cdot 6H_2O$ (0.2 mmol, 67.4 mg) and antioxidant L-(+)-ascorbic acid (0.2 mmol, 35.2 mg) in methanol (10 mL) was layered over a dichloromethane solution (10 mL) containing Cl-salophen (0.2 mmol, 77.1 mg) and pyrazine (0.2 mmol, 16 mg). Black block crystals of **1** suitable for single-crystal X-ray diffraction were obtained after three weeks at room temperature. Anal. Calcd for $C_{42}H_{32}Cl_4Fe_2N_4O_6$ (942.24): C, 53.54; H, 3.42; N, 5.95%. Found: C, 53.14; H, 3.45; N, 5.92%.

Crystal data for **1**: $C_{42}H_{32}Cl_4Fe_2N_4O_6$, $M_r = 942.24$, monoclinic, space group $C2/c$, $a = 13.345(11)$ Å, $b = 22.916(17)$ Å, $c = 12.746(10)$ Å, $\alpha = 90°$, $\beta = 91.735(11)°$, $\gamma = 90°$, $V = 3896(5)$ Å^3, $Z = 4$, $F(000) = 1920$, $T = 117.1$ K, $D_{calcd} = 1.606$ g cm^{-3}, μ (Mo Kα) $= 1.074$ cm^{-1}. Data collections were performed on RIGAKU/MSC Mercury CCD diffractometer (Mo Kα, $\lambda = 0.71069$ Å) with θ-ranges of $3.1 < \theta < 27.5°$ at 117.1 K. The structures were solved with direct methods (SIR-97)[14] and refined by full-matrix least-squares (SHELXL-97),[15] giving for **1** a final $R1$ value of 0.0732 for 263 parameters and 3804 unique reflections with $I > 2\sigma(I)$ and $wR2$ of 0.1822 for all 4436 reflections.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-722160 for **1**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

This work was supported in part by a Grant-in-Aid for Science Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 18033054). The authors are grateful to Kinki University for financial support.

References

1 a) T. Katsuki, *Chem. Soc. Rev.* **2004**, *33*, 437. b) P. G. Cozzi, *Chem. Soc. Rev.* **2004**, *33*, 410. c) D. A. Atwood, M. J. Harvey, *Chem. Rev.* **2001**, *101*, 37. d) Y. N. Ito, T. Katsuki, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 603.

2 a) B. Weber, R. Tandon, D. Himsl, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1159. b) B. Weber, E. Kaps, J. Weigand, C. Carbonera, J.-F. Letard, K. Achterhold, F. G. Parak, *Inorg. Chem.* **2008**, *47*, 487. c) L. Salmon, P. Thuery, E. Riviere, S. Miyamoto, T. Yamato, M. Ephritikhine, *New J. Chem.* **2006**, *30*, 1220. d) A. W. Kleij, *Chem.—Eur. J.* **2008**, *14*, 10520.

3 A. Nabei, T. Kuroda-Sowa, T. Okubo, M. Maekawa, M. Munakata, *Inorg. Chim. Acta* **2008**, *361*, 3489.

4 S. J. Wezenberg, A. W. Kleij, *Angew. Chem., Int. Ed.* **2008**, *47*, 2354.

5 a) H. Miyasaka, R. Clerac, T. Ishii, H.-C. Chang, S. Kitagawa, M. Yamashita, *J. Chem. Soc., Dalton Trans.* **2002**, 1528. b) H.-L. Shyu, H.-H. Wei, Y. Wang, *Inorg. Chim. Acta* **1999**, *290*, 8. c) R. Karmakar, C. R. Choudhury, G. Bravic, J.-P. Sutter, S. Mitra, *Polyhedron* **2004**, *23*, 949.

6 a) J. L. Resce, J. C. Fanning, C. S. Day, S.-J. Uhm, A. F. Croisy, L. K. Keefer, *Acta Crystallogr., Sect. C* **1987**, *43*, 2100. b) C. H. Yang, J. A. Ladd, V. L. Goedken, *J. Coord. Chem.* **1988**, *19*, 235. c) A. Geiß, H. Vahrenkamp, *Eur. J. Inorg. Chem.* **1999**, 1793. d) Z. L. You, H. L. Zhu, *Acta Crystallogr., Sect. E* **2004**, *60*, m1046.

7 a) T. Akitsu, Y. Takeuchi, Y. Einaga, *Acta Crystallogr., Sect. C* **2005**, *61*, m324. b) Z. Lü, M. Yuan, F. Pan, S. Gao, D. Zhang, D. Zhu, *Inorg. Chem.* **2006**, *45*, 3538.

8 M.-A. Muñoz-Hernández, B. Sannigrahi, D. A. Atwood, *J. Am. Chem. Soc.* **1999**, *121*, 6747.

9 A. W. Kleij, M. Kuil, M. Lutz, D. M. Tooke, A. L. Spek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Inorg. Chim. Acta* **2006**, *359*, 1807.

10 Z. Chu, W. Huang, L. Wang, S. Gou, *Polyhedron* **2008**, *27*, 1079.

11 C. J. Sanders, P. N. O'Shaughnessy, P. Scott, *Polyhedron* **2003**, *22*, 1617.

12 B. J. Kennedy, K. S. Murray, *Inorg. Chem.* **1985**, *24*, 1552.

13 a) D. F. Rohrbach, W. R. Heineman, E. Deutsch, *Inorg. Chem.* **1979**, *18*, 2536. b) R. D. Archer, H. Chen, L. C. Thompson, *Inorg. Chem.* **1998**, *37*, 2089.

14 SIR97, Program for the Solution of Crystal Structures: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.

15 G. M. Sheldrick, *SHELXL-97: Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1997**.