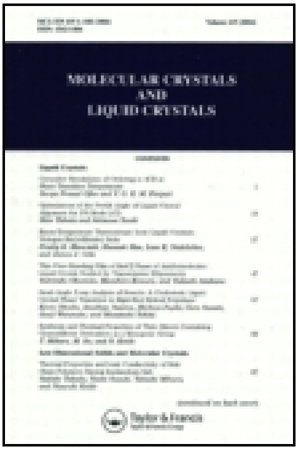

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Structures and Magnetic Properties of Binuclear Iron(III) Spin-Crossover Complexes

Shinya Hayami [a] , Katsuya Inoue [a] & Yonezo Maeda [b]

[a] Institute for Molecular Science, Nishigounaka 38, Myodaiji, Okazaki, 444-8585, Japan

[b] Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka, 812-8581, Japan

Version of record first published: 24 Sep 2006

To cite this article: Shinya Hayami, Katsuya Inoue & Yonezo Maeda (1999): Structures and Magnetic Properties of Binuclear Iron(III) Spin-Crossover Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 573-582

To link to this article: http://dx.doi.org/10.1080/10587259908028898

*Mol. Cryst. and Liq. Cryst.*, 1999, Vol. 335, pp. 573-582
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

# Structures and Magnetic Properties of Binuclear Iron(III) Spin-Crossover Complexes

SHINYA HAYAMI[a], KATSUYA INOUE[a] and YONEZO MAEDA[b]

[a]*Institute for Molecular Science, Nishigounaka 38, Myodaiji, Okazaki 444–8585, Japan and* [b]*Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki 6–10–1, Higashi-ku, Fukuoka 812–8581, Japan*

Binuclear Iron(III) complexes with salten or salen ligands $[\mathrm{Fe_2(salten)_2}(t\text{-L})](\mathrm{BPh_4})_2$ and $[\mathrm{Fe_2(salen)_2}(t\text{-L})(\mathrm{L'})_2](\mathrm{ClO_4})_2$ ($\mathrm{L}^1$ = azobis(4-pyridine) and $\mathrm{L}^2$ = 4,4'(-vinylenebis(pyridine)) were prepared and characterized by Mössbauer spectra and magnetic susceptibilities. The crystal structures of $[\mathrm{Fe_2}\ \mathrm{(salten)_2}(t\text{-L}^1](\mathrm{BPh_4})_2$ (**1**), $[\mathrm{Fe_2(salten)_2}(t\text{-L}^2)](\mathrm{BPh_4})_2$ (**2**) and $[\mathrm{Fe_2(salen)_2}(t\text{–L}^2)(\mathrm{H_2O})_2](\mathrm{ClO_4})_2{\bullet}(t\text{-L}^2){\bullet}\mathrm{H_2O}$ (**3**) were determined. Crystal data for **1** : $C_{98}H_{94}O_4N_{10}B_2Fe_2$, space group $P2_1/c$, $Z$=2, $a$=16.422(7), $b$=16.005(6), c=16.565(8) Å, β=108.47(3)°, $V$=4129(2) Å$^3$, $R$=0.075, $R_w$=0.060. Crystal data for **2** : $C_{100}H_{96}O_4N_8B_2Fe_2$, space group $P2_1/a$, $Z$=2, $a$=16.554(8), $b$=15.877(3), $c$=16.823(3) Å, β=109.20(2)°, $V$=4175(1) Å$^3$, $R$=0.051, $R_w$=0.040. Crystal data for **3**: $C_{52}H_{52}O_{16}N_{12}Cl_2Fe_2$, space group $P\bar{1}$ , $Z$=1, $a$=11.744(4), $b$=15.710(5), $c$=8.177(2) Å, α=94.60(3)°, β=90.29(3)°, γ=110.84(2)°, $V$=4129(2) Å$^3$, $R$=0.075, $R_w$=0.060. The complex $[\mathrm{Fe_2(salen)_2}(t\text{-L}^2)(\mathrm{im})_2](\mathrm{BPh_4})_2{\bullet}3\mathrm{H_2O}$ (**4**) was prepared to compare with the complex **3**. The complexes **1** and **2** exhibited spin-crossover behavior depending on temperature, interexchange the rates of which are rapid compared to the Mössbauer time scale ($10^7$/s). The complex **3** was in the high-spin state and the complex **4** was mixture of the high-spin and low-spin species.

*Keywords:* spin-crossover; iron(III) complexes

## INTRODUCTION

The first transition metal complexes with $d^4$, $d^5$, $d^6$ and $d^7$ electron configuration are usually classified into two categories according to the strength of ligand field against the mean spin-pairing energy, i.e., high- and low-spin complexes. In some cases, however, if the ligand field strength is comparable to mean spin-pairing energy, the complexes exhibit a spin-state transition as temperature or pressure varies. In particular, a number of spin-crossover iron(II) and iron(III) complexes has been study.[1] The spin-crossover iron(II) complexes have been also achieved spin transition from low-spin to metastable high-spin state by light irradiation at low temperature.[2] This light-induced spin transition effect is termed LIESST (light-induced excited spin-state trapping), the high-spin species remain trapped. The difference in metal-ligand bond length $\Delta r_{HL}$ and the zero-point energy difference $\Delta E^0{}_{HL}$ of the spin-crossover iron(III) complexes, however, are smaller than those of the iron(II) complexes, then the lifetime of the light-induced high-spin state in the iron(III) spin-crossover complexes is very short at low temperature.[3] Recently, ligand-driven light-induced spin changes (LD-LISC) in the spin-crossover iron(II) complexes have been reported by Roux et al.[4] The spin-state transition of the complexes occurs by a new strategy which consists in varying ligand field strength under photochemical *cis-trans* isomerization of ligands, of which phenomenon has been able to be observed by using 4-styrylpyridine derivatives at relatively high temperature.

In this paper, we report the structures, the magnetic properties of **1**, **2**, **3** and **4** with photoisomerization ligands (Scheme 1).

## EXPERIMENTAL SECTION

### Preparation of the Axial Ligands

$L^1$ = azobis(4-pyridine) was prepared as described previously.[5] Anal. Calcd for $C_{10}H_8N_4 \cdot 1/3H_2O$: C, 63.14; H, 4.59; N, 29.46 %. Found: C, 62.75; H, 4.21; N, 29.17 %. 4,4'-vinylenebis(pyridine) ($t$-$L^2$) was supplied from Aldlich Co.

## Preparation of the Complexes

$[Fe_2(salten)_2(t\text{-}L^1)](BPh_4)_2$ (**1**). $H_2$salten was prepared by adding a solution of 3,3'-diaminodipropylamine (0.21 g, 2 mmol) in methanol (25 ml) to a solution of salicylaldehyde (0.49 g, 4 mmol) in methanol (25 ml) under stirring. The solution turned yellow immediately, this solution was stirred at room temperature for 2 h. Then a solution of $Fe(NO_3)\cdot 9H_2O$ (0.81 g, 2 mmol) in *methanol (10 ml) was added dropwise* to this yellow solution, turned to a dark purple. To the solution was added a solution of $t\text{-}L^1$ (0.19 g, 1 mmol) in methanol (10 ml) and stirred for 1 h. Then to the solution was added a solution of sodium tetraphenylborate (2.05 g, 6 mmol) in methanol (10 ml) and stirred for 1 h. The solution was filtered and taken to dryness under reduced pressure at room temperature. The dark purple solid materials were recrystallized from an acetone-ethanol solution. The crystals were washed with ethanol, then ether, and dried under vacuum at room temperature. Anal. Calcd for $C_{98}H_{94}O_4N_{10}B_2Fe_2$ (**1**): C, 73.14; H, 5.89; N, 8.71 %. Found: C, 72.59; H, 5.87; N, 8.58 %. $[Fe_2(salten)_2(t\text{-}L^2)](BPh_4)_2$ (**2**). The preparative method for the complex **2** is similar to that above. Anal. Calcd for $C_{100}H_{96}O_4N_8B_2Fe_2$ (**2**): C, 74.73; H, 6.02; N, 6.97 %. Found: C, 75.14; H, 6.00; N, 6.72 %. $[Fe_2(salen)_2(t\text{-}L^2)(H_2O)_2](ClO_4)_2\cdot(t\text{-}L^2)\cdot H_2O$ (**3**). The preparative method for the complex **3** is similar to that above. Anal. Calcd for $C_{55}H_{52}O_{16}N_{12}Cl_2Fe_2$ (**3**): C, 49.08; H, 3.80; N, 13.18 %. Found: C, 48.66; H, 4.08; N, 13.09 %. $[Fe_2(salen)_2(t\text{-}L^2)(im)_2](BPh_4)_2\cdot 3H_2O$ (**4**). The preparative method for the complex **4** is similar to that above. Anal. Calcd for $C_{84}H_{90}O_7N_{12}B_2Fe_2$ (**4**): C, 67.16; H, 5.91; N, 9.81 %. Found: C, 67.38; H, 5.65; N, 9.82 %.

## RESULTS AND DISCUSSION

Iron(III) complexes of general formula $[Fe_2(salten)_2(L)](BPh_4)_2$ and $[Fe_2(salen)_2(L)(L')_2](ClO_4)_2$ were prepared, where salten is a quinquedentate ligand derived from salicylaldehyde and 3,3'-diaminodipropylamine, and salen is a tetradentate ligand derived from salicylaldehyde and ethylenediamine, and where L is a bidentate axial ligand and L' is a cap molecule.

## Magnetic Properties

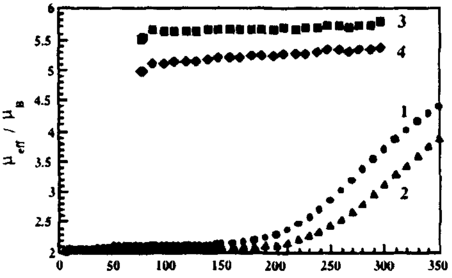

FIGURE 1 Temperature dependence of effective magnetic moments for **1**, **2**, **3** and **4**.

The temperature dependence of the magnetic susceptibilities of **1**, **2**, **3** and **4** were measured in solid state and the effective magnetic moments for the complexes are shown in Fig. 1. The magnetic moments of **1** and **2** increase gradually from ca. 2.1 $\mu_B$ at 150 K to ca. 4.0 $\mu_B$ at 350 K by the temperature increasing, which exhibits spin-equilibrium behavior ($S=1/2 \leftrightarrow S=5/2$). The value of the magnetic moment of **1** at 350 K (ca. 4.4 $\mu_B$) was larger than that of **2**, i.e. the ligand field strength of **2** with $t$-L$^2$ (vinyl group) is stronger than that of **1** with $t$-L$^1$ (azo group). The values of the magnetic moments of **1** and **2** observed at 350 K were smaller than typical values observed for high-spin complexes ($S=5/2$). Therefore there are two possibilities, i.e. the complexes are the mixtures of high- and low-spin species or the complexes show rapid spin-equilibrium behavior. The magnetic behavior for the increasing and decreasing temperature sequences is practically the same, indicating that the spin transition between high- and low-spin states is not associated with a thermal hysteresis. The magnetic moments of **3** and **4** are constant ca. 5.8 $\mu_B$ and ca. 5.4 $\mu_B$, respectively in the tempareture range of 300 to 80 K. The The complex **3** is in the high-spin state and **4** is mixture of the high-spin and low-spin state species.

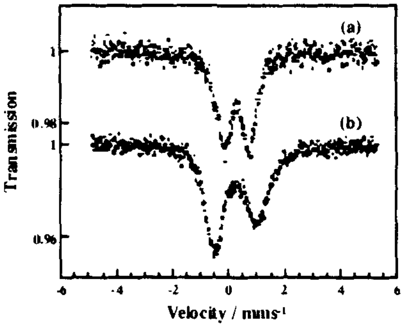

**FIGURE 2. Mössbauer spectra for 1 (a) at 293 K and (b) at 95 K.**

## Mössbauer spectra

The variable temperature Mössbauer spectra of **1**, **2**, **3** and **4** are shown in Figs. 2, 3, 4 and 5, respectively. The typical absorptions for low-spin iron(III) with a large quadrupole splitting ($\Delta E$=1.53 mms$^{-1}$) are observed in the spectrum of **1** at 95 K, and the spin state estimated from the spectrum is agreed with that obtained from the magnetic measurements (2.1 $\mu_B$). The quadrupole splitting, 1.53 mms$^{-1}$ at 95 K is less than that of the iron(III) complexes with salten ligands reported previously (2.72 mms$^{-1}$); the decrease seems to result from the change in $q_{val}$ (the electron field gradient due to lattice distribution of valence electron on the orbitals). On the other hand, the spectrum at 293 K shows only a small quadrupole splitting with an isomer shift ($\delta$) of 0.280 mms$^{-1}$. The spin-state estimated from the Mössbauer parameters ($\delta$=0.280 mms$^{-1}$) and the magnetic moments (3.70 $\mu_B$) is in rapid spin-equilibrium between high- and low-spin states. Spectra for rapid intercrossing between high- and low-spin states have been theoretically calculated by Maeda et. al.[6] It is expected that the relaxation spectra with the end components (spectra for high- or low-spin species) of an antisymmetric doublet could not be reliably analyzed, and then the interconversion rate for **1** could not be calculated from the spectra. However, the interconversion rate

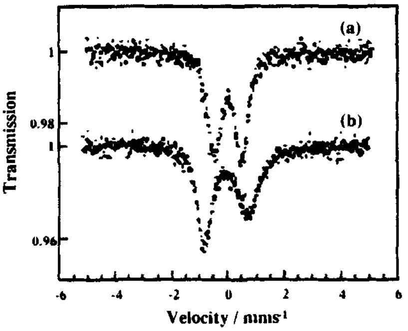

**FIGURE 3** **Mössbauer spectra for 2 (a) at 293 K and (b) at 95 K.**

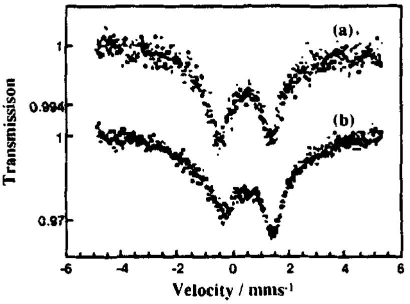

**FIGURE 4** **Mössbauer spectra for 3 (a) at 293 K and (b) at 95 K.**

between high- and low-spin states for **1** (the rate of electronic relaxation of spin transition) is assumed to be faster than the inverse of the lifetime of the excited Mössbauer nuclear state ($10^7$ $s^{-1}$) at 293 K. The Mössbauer spectra of **2** are similar to those of **1**; the spectrum is a large doublet ($\Delta E$=1.53 $mms^{-1}$) at 95 K and is a small doublet ($\Delta E$=0.936 $mms^{-1}$) at 293 K. The spin-state estimated from the Mössbauer parameters ($\delta$=0.194 $mms^{-1}$) and the magnetic moments (2.95 $\mu_B$) is expected to be in the rapid spin-equilibrium between high- and low-spin states. The Mössbauer spectrum for **3** is large quadrupole splitting doublet ($\Delta E$=1.861 $mms^{-1}$) and the value of the isomer shift $\delta$ is 0.416 $mms^{-1}$ at 293 K, and the Mössbauer parameters at 95 K are $\Delta E$=1.854 $mms^{-1}$ and $\delta$=0.515 $mms^{-1}$. The quadrupole splitting values are larger than those of the tipical high-spin iron(III) complexes because of ansymmetry of the axial ligands (pyridine and $H_2O$). The Mössbauer spectra for **4** are observed two doublets at 293 and 95 K. The Mössbauer parameters are $\Delta E$=1.104 $mms^{-1}$ and $\delta$=0.370 $mms^{-1}$ for high-spin species at 293 K, and $\Delta E$=0.953 $mms^{-1}$ and $\delta$=0.450 $mms^{-1}$ for high-spin species and $\Delta E$=2.501 $mms^{-1}$ and $\delta$=0.242 $mms^{-1}$ for low-spin species at 95 K.

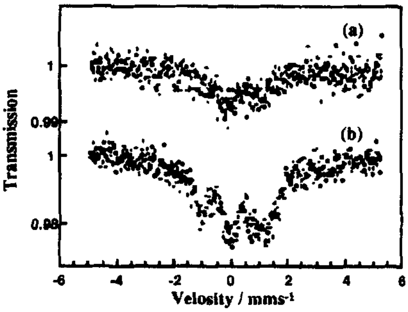

**FIGURE 5 Mössbauer spectra for 4 (a) at 293 K and (b) at 95 K.**

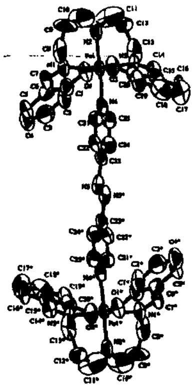

**FIGURE 6 ORTEP view of the cation for 1. All hydrogen atoms are omitted for clarity.**

## Structures of the Complexes

The ORTEP views of the complexes **1**, **2** and **3** are shown in Figs. 6, 7 and 8, respectively. The complex **1** crystallizes in the $P2_1/c$ monoclinic space group (Z=2). Two iron atoms are bridged by an azobis(4-pyridine). The moiety of diazo (N=N) of the cation of **1** sits on a center of symmetry, the two nitrogen atoms of the diazo moiety (N(5) and N(5*)) are *trans* geometry. The iron atom of binuclear complexes have a pseudooctahedral coordination with a *trans* geometry for the two salicylideneiminato moieties (N(1) and N(3)), in which the basal plane comprises the $N_2O_2$ donors of these two moieties, and the two axial positions are occupied by the secondary amine nitrogen atom of 3,3'-diaminodipropylamine moiety and the nitrogen atom of azobis(4-pyridine). The basal plane defined by Fe, O(1), O(2), N(1) and N(3) assumes a slight tetrahedral distortion, the deviations of the constituent atoms from the least-squares plane $FeO_2N_2$ being from -0.14 to 0.04 Å, and the dihedral angle between the planes Fe-O(1)-N(1) and Fe-O(2)-N(3) is 7.5°. Two salicylideneiminato-moieties contrast a shallow 'cave', in which the azobis(4-pyridine) ligand is positioned. The iron atoms of the complex are in the center of an approximately octahedral geometry, with two oxygen atoms (O(1) and (O(2)) being *trans* to each other, imino nitrogen atoms (N(1) and N(3)) being *trans*, and amine and pyridine nitrogen atoms (N(2) and N(4)) being *trans*. The values of the bond

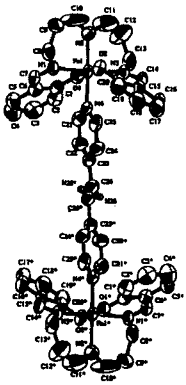

**FIGURE 7 ORTEP view of the cation for 2. Some hydrogen atoms are omitted for clarity.**

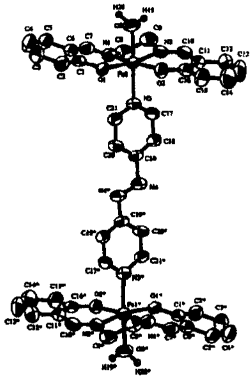

**FIGURE 8 ORTEP view of the cation for 3. Some hydrogen atoms are omitted for clarity.**

distances Fe-O (1.89 Å) and Fe-N (2.03 Å) are intermediate between the typical values of the bond distances for high-spin complexes Fe-O (1.91 Å) and Fe-N (2.16 Å) and low-spin complexes Fe-O (1.88 Å) and Fe-N (1.98 Å). The ORTEP view of **2** is shown in Fig. 7 and the complex **2** crystallizes in the $P2_1/a$ centric space group (Z=2). The structure of **2** is similar to that of **1**. The ORTEP view of **3** is shown in Fig. 8 and the complex **3** crystallizes in the $P\bar{1}$ centric space group (Z=1). Two iron atoms are briged by an azobis(4-pyridine) and two water molecules coordinate to another sites. The moiety of diazo (N=N) of the cation of **3** sits on a center of symmetry, the two nitrogen atoms of the diazo moiety (N(4) and N(4*)) are *trans* geometry. The values of the bond distances Fe-O (1.90 Å) and Fe-N (2.13 Å) are values of the typical high-spin complexes. One azobis(4-pyridine) and one water molecule are contained in the crystals.

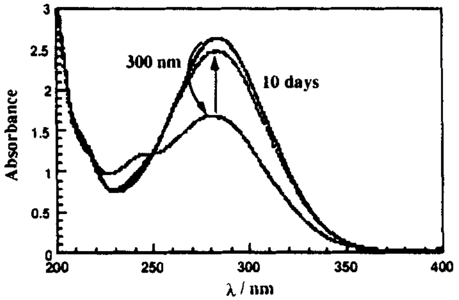

**FIGURE 9** Absorption spectra for *t*-L[1] ligand in acetonitrile solution; (a) before light irradiation at 300 nm, (b) after irradiation, (c) 10 days after irradiation.

## Irradiation Effects

The photo-induced electronic spectra for ligands *t*-L[1] and *t*-L[2] were measured in acetonitrile solution at room temperature with a high-pressure mercury lamplight 300 nm obtained by using of a 34U band-path filter and

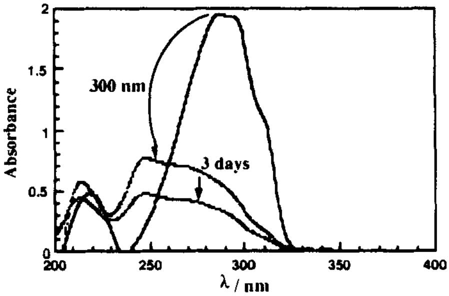

**FIGURE 10** Absorption spectra for *t*-L[2] ligand in acetonitrile solution; (a) before light irradiation at 300 nm, (b) after irradiation, (c) 3 days after irradiation.

are shown in Figs. 9 and 10, respectively. The photoisomerization ligand *t*-$L^1$ has the absorption maximum at 300 nm before light irradiation, while the decrease in absorbance at 300 nm and the increase in the absorbance at 250 nm are observed after irradiation (Fig. 9). The spectral pattern is back to that of the before irradiation after 10 days. Fig. 10 shows the absorption spectra for *t*-$L^2$ and the spectral patterns change by the irradiation. However, the irradiated spectrum isn't back to that of the before the irradiation. The *cis* isomer of *t*-$L^2$ may be stable compared with that of *t*-$L^1$.

## CONCLUSIONS

Binuclear iron(III) complexes **1** and **2** exhibited rapid spin-equilibrium behavior at room temperature. The average bond lengths of Fe-O and Fe-N for **1** and **2** are 1.88(1) and 1.98(1) Å, respectively, and the values are intermediate between the typical values of the bond distances for high- and low-spin complexes. The structures of **1** and **2** form binuclear iron(III), and the moieties of diazo (N=N) and vinyl (CH=CH) sit on a center of symmetry of the complexes. The spin-crossover iron(III) complexes **1** and **2** may be able to observe spin transition by photoisomerization in the near future.

### Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 10146101) from the Ministry of Education, Science Sports and Culture, Japan.

## *References*

[1] M. S. Hadded, W. D. Federer, M. W. Lynch, and D. N. Hendrickson, *J. Am.Chem. Soc.*, **102,** 1468 (1980); E. König, G. Ritter, and S. K. Kulshreshtha, *Chem. Rev.*, **4,** 19 (1985); M. F. Tweedle, and L. J. Wilson, *J. Am, Chem. Soc.*, **98,** 4824 (1976); Y. Maeda and Y. Takashima, *Comments Inorg. Chem.*, **7,**44 (1988); C. Roux, J. Zarembowitch, J. P. Itié, A. Polian, and M. Verdaguer, *InorgChem.* **35**574 (1996); J. A. Real, E. Bousseksou, and F. Varret, *Science*, **268,** 265 (1995); N. Matsumoto, S. Ohta, C. Yoshimura, A. Ohyoshi, S. Kohata, H. Okawa, and Y. Maeda, *J. Chem. Soc., Dalton trans.*, (1985) 2575; S. Ohta, C. Yoshimura, N. Matsumoto, H. Okawa, and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, **59,** 155 (1986); D. Boinnard, A. Bousseksou, A. Dworkin, J. M. Savariault, F. Varret, and J. P. Tuchagues, *Inorg. Chem.*, **33,** 271 (1994); J. Kröber, E. Codjovi, O. Kahn, F. Groliére, and C. Jay, *J. Am. Chem.Soc.*, **115,** 9810 (1993).

[2] A. Hauser, *Chem. Phys.Lett.*, **124,** 543 (1986); P. Gütlich, A. Hauser, and H. Spiering, *Angew, Chem., Int. Ed. Engl.*, **33,** 2024 (1994).

[3] S. Schenker, A. Hauser, and R. Dyson, *Inorg. Chem.*, **35,** 4676 (1996).

[4] C. Roux, J. Zarembowitch, B. Gallois, T. Granier, and R. Claude, *Inorg. Chem.*, **3 3,** 2273 (1994); M. L. Boillot, C. Roux, J. P. Audiére, A. Dausse, and J. Zarembowitch, *Inorg.Chem.*, **35,** 3975 (1996).

[5] D. A. Baldwin, A. B. P. Lever, and R. V. Parish, *Inorg. Chem.*, **8,** 107 (1969).

[6] Y. Maeda, H. Oshio, K. Toriumi, and Y. Takashima, *J. Chem. Soc., Dalton Trans.*, (1991) 1227.