© 1998 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 71, 379—383 (1998) 379

Copper(II)–Lanthanide(III) Complexes of Symmetric Dinucleating Macrocycle with Two Phenolate Bridges

Kazuhiro Manseki, Motoko Kumagai, Masatomi Sakamoto,* Hiroshi Sakiyama, Yuzo Nishida, Akira Matsumoto,† Yoshihiko Sadaoka,†† Masaaki Ohba,††† and Hisashi Ōkawa†††

Department of Materials and Biological Chemistry, Faculty of Science, Yamagata University,
Kojirakawa-machi, Yamagata 990

†Laboratory of Chemistry, Faculty of Education, Ehime University, Bunkyo-cho, Matsuyama 790-77

††Department of Materials Science and Engineering, Faculty of Engineering, Ehime University,
Bunkyo-cho, Matsuyama 790-77

†††Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

(Received September 11, 1997)

The first heteronuclear copper(II)–lanthanide(III) complexes, CuLn(fsal-2,2)$(NO_3)_3(H_2O)_n$ ($n=2$ for Ln = Nd and $n=1$ for Ln = Eu and Gd), of a symmetric macrocyclic dinucleating Schiff base ligand, H_2fsal-2,2, which is a condensation product of two molecules of 2,6-diformyl-4-methylphenol and two molecules of ethylenediamine, were synthesized by the reaction of [*N*,*N*′-bis(3-formyl-5-methylsalicylidene)ethylenediaminato]copper(II) and ethylenediamine in the presence of lanthanide(III) ion as a template, where fsal-2,2 denotes the dianion formed by the deprotonation of two phenolic hydroxyl groups in H_2fsal-2,2. The absorption spectra suggested that substrates possessing N- and O-donor groups, such as amino alcohols, are specifically bound at the Cu–Ln center through nitrogen-coordination to the copper site and through oxygen-coordination to the lanthanide site. The fluorescence intensity of Eu(III) decreased drastically upon forming the Cu–Eu complex. A cryomagnetic susceptibility measurement indicated a ferromagnetic spin-spin interaction between Cu(II) and Gd(III) ions.

Heterodinuclear complexes have received much attention, in order to investigate electronic, electrochemical, and magnetic properties arising from the metal–metal interaction,[1] to develop appropriate systems for binding and activating simple molecules,[2] and to mimic the active sites of some metalloenzymes, such as cytochrom c oxidase,[3] hydrogenase,[4] and purple acid phosphatase.[5] Among the various heterodinucleating ligands designed thus far, macrocycles are excellent ligands, because macrocyclic complexes are thermodynamically stabilized and kinetically retarded toward metal dissociation (macrocyclic effect).[6] Especially macrocycles derived from two 2,6-diformyl-4-methylphenols and two diamines have been widely used, since the dinucleating complexes were first reported by Pilkington and Robson,[7] and by one of the present authors.[8] Heteronuclear complexes of these macrocycles with various lateral methylene chain lengths (Fig. 1(b)) are, in general, synthesized by the reaction of diamine with the corresponding mononuclear complex precursors of acyclic ligands (Fig. 1(a)) in the presence of a second metal ion as a template.[9—11] Such a stepwise template reaction makes it possible to prepare the heteronuclear complexes, even when macrocycles are symmetric in their chemical structures.[9,10] However, heteronuclear complexes of a dinucleating macrocycle prepared by the use of lanthanide ions as a template have not been reported, despite the fact that the studies of template syntheses using lanthanide ion are expected to give useful informations about new synthetic methods for the coordination compounds.

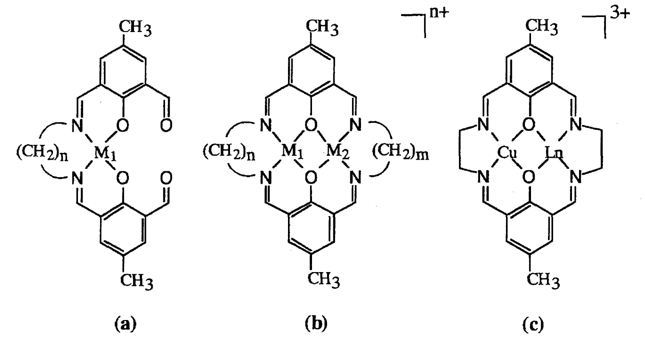

Fig. 1. Chemical structures of mononuclear complexes of acyclic ligands, H_2fsal-*n* (**a**), heteronuclear complexes of macrocycles, H_2fsal-*n*,*m* (**b**), and copper(II)–lanthanide(III) complexes, fsal-2,2-Cu,Ln (**c**).

In the present work, the syntheses of Cu(II)–Ln(III) complexes (abbreviated as fsal-2,2-Cu,Ln and see Fig. 1(c)) of macrocycle, H_2fsal-2,2, were undertaken by the reaction of the mononuclear Cu(II) complex (abbreviated as fsal-2-Cu) of acyclic ligand, *N*,*N*′-bis(3-formyl-5-methylsalicylidene)ethylenediamine (H_2fsal-2), with ethylenediamine in the presence of some lanthanide(III) (Ln(III)) ions as a template ion; some of their properties which occured due to a co-operative effect of Cu(II) and Ln(III) ions were investigated based on the electronic and fluorescence spectra and magnetic susceptibility measurements.

Experimental

General. 2,6-Diformyl-4-methylphenol was prepared according to a method reported by Ullmann and Brittners.[12] A mononuclear copper(II) complex of *N*,*N*′-bis(3-formyl-5-methylsalicylidene)ethylenediamine ($n = 2$ in Fig. 1(a), abbreviated as fsal-2-Cu), where Cu(II) is located at the N_2O_2-coordination site of ligand, was synthesized by a previously reported method.[8b] All of the chemicals were of reagent grade, and were used as purchased.

Syntheses of Heteronuclear Cu(II)–Ln(III) Complexes, fsal-2,2-Cu,Ln, (Ln = Nd, Eu or Gd). A methanolic solution (2—4 cm^3) of hydrated lanthanide(III) nitrate (1 mmol) was added with stirring to a suspension of mononuclear copper(II) complex, fsal-2-Cu (0.414 g, 1 mmol), in methanol (30 cm^3). After the mixture was stirred at room temperature for 2 h, a methanolic solution (2 cm^3) of ethylenediamine (0.060 g, 1 mmol) was added, and the mixture further stirred at room temperature for 2 h. Thus-obtained complexes were collected by suction filtration, washed successively with methanol and diethyl ether, and then dried in the open air. The yields were 76, 68, and 76% for fsal-2,2-Cu,Nd, fsal-2,2-Cu,Eu, and fsal-2,2-Cu,Gd, respectively.

Measurements. Elemental analyses of carbon, hydrogen, and nitrogen were carried out at the Service Center of Elemental Analysis, Kyushu University. The contents of copper and lanthanide were determined by the EDTA titration of an aqueous solution of copper(II) nitrate and lanthanide(III) nitrate, prepared by dissolving in HNO_3 after the complex was ignited, where the masking reagents were thiourea and ammonium fluoride for copper(II) and lanthanide(III), respectively. The IR spectra were measured with a Hitachi 270-50 spectrophotometer on KBr disks. The electronic spectra were measured with a Shimadzu UV-240 spectrophotometer. Electric-conductivity measurements were carried out with a Horiba conductivity meter (ES-14). Fluorescence spectra were obtained with a Shimadzu RF-540 fluorospectrophotometer. The magnetic susceptibilities were determined with a HOXAN HSM-D SQUID susceptometer in the range of 4.2 to 80 K and with a Faraday balance in the range of 80 to 300 K. Calibrations were made by the use of $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$ for a SQUID magnetometer and $[Ni(en)_3]S_2O_3$ for a Faraday balance. The data were corrected for magnetization of the sample holder and for diamagnetism contributions with Pascal's constants.[13] The effective magnetic moments were calculated by the equation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{M}}T)^{1/2}$, where χ_{M} is the magnetic susceptibility per CuGd unit.

Results and Discussion

General Characterization. The present type of complex can be synthesized for all lanthanide(III) ions. However, this report deals with fsal-2,2-Cu,Nd, fsal-2,2-Cu,Eu, and fsal-2,2-Cu,Gd as the representatives, since the yields of the other complexes were lower (< 30 %) compared with these three complexes. A mononuclear copper(II) complex, fsal-2-Cu, showed two strong and sharp bands attributable to the ν(C=O) and the ν(C=N) around 1670 and 1630 cm^{-1}, respectively. In the Cu(II)–Ln(III) complexes, the band due to the ν(C=O) disappeared and only a strong and relatively broad band could be observed at 1630—1635 cm^{-1} due to the ν(C=N). This indicates the formation of a macrocylclic Schiff base due to a template reaction. From these results and elemental analyses, the compositions of the complexes can be proposed to be dihydrate for fsal-2,2-Cu,Nd and monohydrate for fsal-2,2-Cu,Eu and fsal-2,2-Cu,Gd, as summarized in Table 1. The splitting width of the combination bands in the region of 1700 to 1800 cm^{-1}, which has often been utilized as a diagnosis method of the bonding mode of nitrate ion, was about 30 cm^{-1} for all complexes, suggesting the existence of the bidentate nitrate ion coordinating to the lanthanide ion, though the number of bidentate nitrate ions remains unclear.[14] The molar conductances determined in the 1×10^{-3} mol dm^{-3} DMF solution at 25 °C were 165 S cm^2 mol^{-1} for fsal-Cu,Nd, and 162 S cm^2 mol^{-1} for fsal-2,2-Cu,Eu and fsal-2,2-Cu,Gd, indicating that these complexes behave as 1 : 2 electrolyte in DMF.[15] Evidently, two nitrate ions are released from the coordination-sphere of the lanthanide ion. These heteronuclear complexes, comprising d-transition metal and lanthanide ions with symmetric dinucleating macrocycle, are the first compounds. In similar macrocyclization reactions, lead(II) has been known to be effective as a template ion.[10,11] Also, the effectiveness of lanthanides as a template was shown in this work. The present Cu(II)–Ln(III) complexes are expected to be the precursor of other heteronuclear complexes as well as Cu(II)–Pb(II) complexes, since lanthanide(III) ions are kinetically labile in the ligand-substitution reaction.

Interaction of the d–f Heterometal Center with Organic Substrates. The absorption spectra of fsal-2,2-Cu,Gd were measured in DMF by adding some amino alcohols,

Table 1. Elemental Analyses of Complexes

Complex	Found (%) (Calcd (%))				
	C	H	N	Cu	Ln
fsal-2,2-Cu,Nd ($C_{22}H_{22}N_7O_{11}CuNd(H_2O)_2$)	33.01 (32.85)	3.21 (3.26)	12.05 (12.19)	8.17 (7.90)	18.35 (17.93)
fsal-2,2-Cu,Eu ($C_{22}H_{22}N_7O_{11}CuEu(H_2O)$)	33.52 (33.28)	3.08 (3.05)	12.06 (12.35)	7.96 (8.00)	18.84 (19.14)
fsal-2,2-Cu,Gd ($C_{22}H_{22}N_7O_{11}CuGd(H_2O)$)	33.61 (33.06)	3.26 (3.03)	11.51 (12.27)	7.71 (7.95)	20.14 (19.67)

diols, and amine as a substrate (Fig. 2). The numerical data concerning the d–d band maxima of Cu(II) are summarized in Table 2. It is generally known that the axial coordination of a substrate to the square planar Cu(II) site leads to a red shift of the d–d band maximum, because the energy level of the $d_{x^2-y^2}$ orbital is lowered, where the *x*- and *y*-axes are taken along the N_2O_2-coordinating atoms of the ligand. When 2-aminoethanol or 3-aminopropanol was added as the substrate, the d–d band shifted to a lower energy compared with that of the d–d band in the absence of substrate, whereas the spectra were little affected by adding 1,2-ethanediol or 1,3-propanediol. These facts indicate that the amino alcohols coordinate to the copper at the nitrogen atom.[16] In order to confirm such nitrogen-atom coordination of amino alcohols, the absorption spectrum was measured after the addition of *N*,*N*-dimethylethanolamine as the substrate. Two methyl groups of this substrate are expected to make the nitrogen coordination difficult because of their steric effect. As expected, the d–d band absorption maximum was little influenced, supporting the specific coordination of the nitrogen atom of the amino alcohols to the copper. On the other hand, it cannot be determined only from the absorption spectra how the alcoholic oxygen atom of amino alcohols behaves. However, it is most plausible that such alcoholic oxygen interacts with the lanthanide site through direct coordination or through hydrogen bonding with the solvent molecule and/or water molecule coordinating to the lanthanide ion.[16] Diols, such as 1,2-ethanediol and 1,3-propanediol, may coordinate to lanthanide as the bidentate ligand.

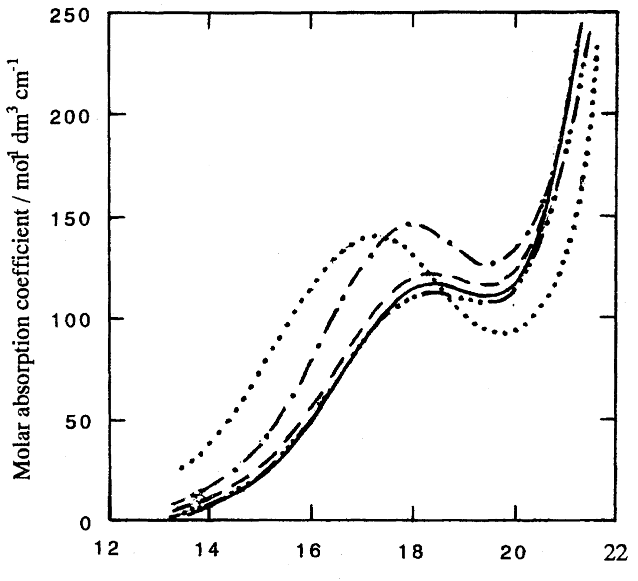

Fig. 2. Typical absorption spectra of fsal-2,2-Cu,Gd in DMF solution of various additives. Concentration of fsal-2,2-Cu, Gd is 2.00×10^{-3} mol dm^{-3}. (—): without additive; (- -): with 1,2-ethanediol(5.62×10^{-2} mol dm^{-3}); (····): with 2-aminoethanol(6.30×10^{-2} mol dm^{-3}); (-·-): with 3-aminopropane(1.93×10^{-2} mol dm^{-3}); (-···-): with *N*,*N*-dimethylaminoethanol(2.23×10^{-2} mol dm^{-3}).

Magnetic Property. The gadolinium(III) complex is quite suitable for understanding its magnetic data, since the ground state of Gd(III) is $^8S_{7/2}$ and the level of the lowest excited state is very high in energy, i.e., the contributions of the orbital angular momentum and the anisotropic effect do not need to be taken into account. These inherent natures of Gd(III) have led to energetic studies on the magnetic property of heteronuclear complexes comprising a d-transition metal and lanthanide ions in the last decade in order to elucidate mechanism of the magnetic interaction between these two metal ions and to develop new magnetic materials.[17] Also, in the present work, the magnetic property of fsal-2,2-Cu,Gd complex was investigated.

Figure 3 shows the temperature dependences of the magnetic susceptibilities per CuGd unit (χ_M), the reciprocal magnetic susceptibilities ($1/\chi_M$), and the effective magnetic moments (μ_{eff}). The Weiss constant was estimated to be +1.4 K, indicating a ferromagnetic interaction. The effective magnetic moment at 290.2 K is 8.17 μ_B, which is very close to the spin-only value (8.12 μ_B) calculated from the equation $\mu_{eff} = (\mu_{Cu}^2 + \mu_{Gd}^2)^{1/2}$, derived by assuming that a magnetic interaction between Cu(II) ($S_{Cu} = 1/2$) and Gd(III) ($S_{Gd} = 7/2$) is absent. The magnetic moment gradually increases from 8.17 μ_B at 290.2 K to the maximum value (8.84 μ_B) at 7.9 K with decreasing the temperature, and then decreases to 8.61 μ_B at 4.2 K. The maximum value (8.84 μ_B) is close to the spin-only value (8.94 μ_B) for the spin-state $S = 8/2$, which arises from a ferromagnetic spin-coupling of the present spin system ($S_{Cu} = 1/2$ and $S_{Gd} = 7/2$). Thus, the observed magnetic behavior clearly indicates the operation of an intramolecular ferromagnetic spin-coupling between Cu(II) and Gd(III). The decrease in the moment below 7.9 K may be due to an

Table 2. Absorption Maxima of d–d Bands of fsal-2,2-Cu,Gd in DMF Solution of Various Additives[a]

Additive (Concentration/mol dm^{-3})	ν_{max}/10^3 cm^{-1} (ε/mol^{-1} dm^3 cm^{-1})
None	18.40 (118)
1,2-Ethanediol (5.61×10^{-2})	18.40 (122)
1,3-Propanediol (2.65×10^{-2})	18.40(122)
2-Aminoethanol (6.30×10^{-2})	17.24 (141)
3-Amino-1-propanol (3.06×10^{-2})	17.92 (143)
3-Aminopropane (1.93×10^{-2})	17.97 (145)
N,*N*-Dimethylaminoethanol (2.23×10^{-2})	18.35 (113)

a) Concentration of fsal-2,2-Cu,Gd is 2.00×10^{-3} mol dm^{-3}.

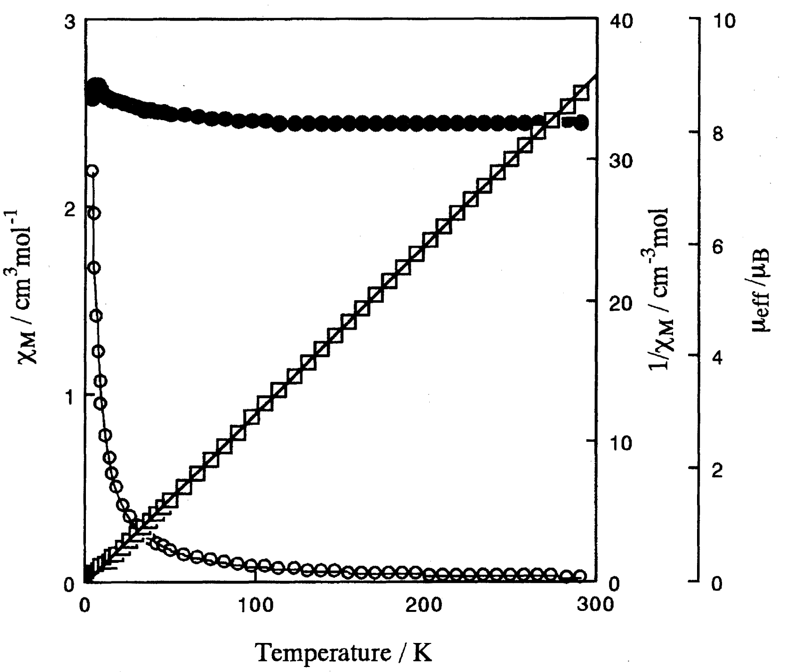

Fig. 3. Temperature dependence of χ_M (○), $1/\chi_M$ (□), and μ_{eff} (●) of fsal-2,2-Cu,Gd. χ_M and μ_{eff} are magnetic susceptibility and effective magnetic moment per CuGd unit, respectively.

intermolecular antiferromagnetic interaction. The magnetic data were analyzed on the basis of the following spin-only expression, including a correction term (θ) of intermolecular interaction, using a spin-Hamiltonian defined as $H = -2JS_{Cu} \cdot S_{Gd}$:

$$\chi_M = \frac{4Ng^2\beta^2}{k(T-\theta)} \frac{15+7\exp(-8J/kT)}{9+7\exp(-8J/kT)}.$$

The best-fit was attained with parameters of g=2.00, J=+2.1 cm^{-1}, θ=−0.3 K. The positive J-value is consistent with the intramolecular ferromagnetic interaction described just above, and the value of +2.1 cm^{-1} is comparable to those previously reported for the Cu(II)–Gd(III) systems.[17,18]

Fluorescence Property. Some lanthanide ions and their complexes exhibit a characteristic fluorescence of each lanthanide, and a few studies on the effect of the co-existing metal ions or their complexes upon the fluorescence of lanthanides have been reported.[19] The fluorescence of fsal-2,2-Cu,Eu was measured in DMF; the spectrum is shown in Fig. 4, together with the spectrum of Eu(NO$_3$)$_3$·6H$_2$O. Europium(III) nitrate apparently exhibits fluorescence bands attributable to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transitions around 590, 615, 650, and 700 nm, respectively. These bands are almost quenched in fsal-2,2-Cu,Eu. It is generally accepted that the luminescence decreases due to the radiationless energy loss through the excited state of other molecules which are located near to the exciting species.[20] From this consideration and the observed results, it is presumed that the fluorescence of fsal-2,2-Cu,Eu is drastically quenched by energy transfer from the excited Eu(III) to the Cu(II) complex moiety through the bridging oxygen atoms, followed by a radiationless energy loss, as previously discussed.[16a—16d,21] Of course, also, the fluorescence decrease due to the absorption of a large part of exciting light by the complex itself can not be neglected.

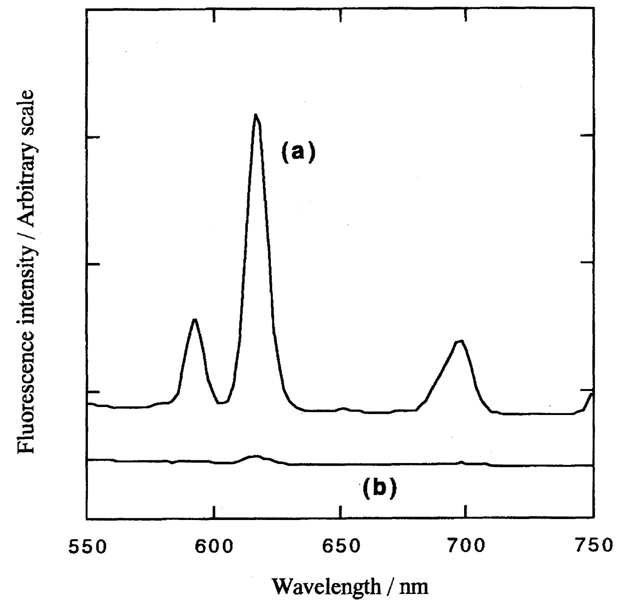

Fig. 4. Fluorescence spectra of Eu(NO$_3$)$_3$·6H$_2$O (**a**) and fsal-2,2-Cu,Eu (**b**) in DMF. Concentration of Eu(NO$_3$)$_3$·6H$_2$O and fsal-2,2-Cu,Eu is 2.00×10^{-4} mol dm^{-3}. Exciting wavelength is 394 nm. Slit width of excitation side and emission side are 20 and 5 nm, respectively. Ordinate scale is ×32.

The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, "New Developments of Rare Earth Complexes" (No. 06241106) from The Ministry of Education, Science and Culture.

References

1) a) O. Kahn, *Struct. Bonding (Berlin)*, **68**, 89 (1987); b) U. Casellato, P. A. Vigato, and M. Vidali, *Coord. Chem. Rev.*, **23**, 31 (1977); c) P. Zanello, S. Tamburini, P. A. Vigato, and G. A. Mazzocchin, *Coord. Chem. Rev.*, **77**, 165 (1987); d) C. Fraser and B. Bosnich, *Inorg. Chem.*, **33**, 338 (1994); e) C. Fraser, R. Ostrander, A. L. Rheingold, C. White, and B. Bosnich, *Inorg. Chem.*, **33**, 324 (1994); f) D. G. McCollum, L. Hall, C. White, R. Ostrander, A. L. Rheingold, J. Whelan, and B. Bosnich, *Inorg. Chem.*, **33**, 924 (1994); g) D. G. McCollum, C. Fraser, R. Ostrander, A. L. Rheingold, and B. Bosnich, *Inorg. Chem.*, **33**, 2383 (1994).

2) a) S. Gambarotta, F. Arena, C. Floriani, and P. F. Zanazzi, *J. Am. Chem. Soc.*, **104**, 5082 (1982); b) F. Arena, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, **25**, 4589 (1986); c) P. A. Vigato, S. Tamburini, and D. E. Fenton, *Coord. Chem. Rev.*, **106**, 25 (1990).

3) a) S. C. Lee and R. H. Holm, *J. Am. Chem. Soc.*, **115**, 11789 (1993); b) G. Palmer, G. T. Babcock, and L. E. Vickery, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 2206 (1976).

4) a) R. T. Volbeda, M.-H. Charon, C. Piras, E. C. Hatchikian, M. Frey, and J. C. Fontecilla-Camps, *Nature*, **373**, 580 (1995); b) R. T. Hembre, J. S. McQueen, and V. W. Day, *J. Am. Chem. Soc.*, **118**, 798 (1996).

5) a) N. Strater, T. Klabunde, P. Tucker, H. Witzel, and B. Krebs, *Science*, **268**, 1489 (1995); b) J. L. Beck, M. J. McArthur, J. D. Jersey, and B. Zerner, *Inorg. Chim. Acta*, **153**, 39 (1988); c) J. L. Beck, L. A. McConachie, A. C. Summors, W. N. Arnold, J. D. Jersey, and B. Zerner, *Biochim. Biophys. Acta*, **869**, 61 (1986).

6) J. D. Lamb, R. M. Izatt, J. J. Christensen, and D. J. Eatough, "Coordination Chemistry of Macrocyclic Compounds," ed by G. A. Melson, Plenum Press, New York (1979), p. 145.

7) N. H. Pilkington and R. Robson, *Aust. J. Chem.*, **23**, 2225 (1970).

8) a) H. Ōkawa and S. Kida, *Inorg. Nucl. Chem. Lett.*, **7**, 751 (1971); b) H. Ōkawa and S. Kida, *Bull. Chem. Soc. Jpn.*, **45**, 1759 (1972).

9) a) R. R. Gagne and C. L. Spiro, *J. Am. Chem. Soc.*, **102**, 1443 (1980); b) R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies, and A. K. Shiemke, *J. Am. Chem. Soc.*, **103**, 4073 (1981); c) S. L. Lambert, C. L. Spiro, R. R. Gagne, and D. N. Hendrickson, *Inorg. Chem.*, **21**, 68 (1982).

10) M. Tadokoro, H. Ōkawa, N. Matsumoto, M. Koikawa, and S. Kida, *J. Chem. Soc., Dalton Trans.*, **1991**, 1657.

11) a) J. Nishio, H. Ōkawa, S. Ohtsuka, and M. Tomono, *Inorg. Chim. Acta*, **218**, 27 (1994); b) H. Ōkawa, J. Nishio, M. Ohba, M. Tadokoro, N. Matsumoto, M. Koikawa, S. Kida, and D. E. Fenton, *Inorg. Chem.*, **32**, 2949 (1993); c) M. Tadokoro, H. Sakiyama, N. Matsumoto, M. Kodera, H. Ōkawa, and S. Kida, *J. Chem. Soc., Dalton Trans.*, **1992**, 313.

12) F. Ullmann and K. Brittners, *Chem. Ber.*, **42**, 2539 (1909).

13) E. A. Boudreaux and L. N. Mulay, "Theory and Applications of Molecular Paramagnetism," John Willey & Sons, New York (1976), p. 491.

14) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 4th ed, John Wiley & Sons, New York (1986), p. 256.

15) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

16) a) M. Sakamoto, T. Ishikawa, Y. Nishida, Y. Sadaoka, A. Matsumoto, Y. Fukuda, M. Sakai, M. Ohba, H. Sakiyama, and H. Ōkawa, *J. Alloys Compounds*, **238**, 23 (1996); b) M. Sakamoto, Y. Nishida, A. Matsumoto, Y. Sadaoka, M. Sakai, Y. Fukuda, M. Ohba, H. Sakiyama, N. Matsumoto, and H. Ōkawa, *J. Coord. Chem.*, **38**, 347 (1996); c) M. Sakamoto, Y. Nishida, K. Ohhara, Y. Sadaoka, A. Matsumoto, and H. Ōkawa, *Polyhedron*, **14**, 2505 (1995); d) M. Sakamoto, M. Ohsaki, K. Yamamoto, Y. Nakayama, A. Matsumoto, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **65**, 2514 (1992); e) M. Sakamoto, M. Hashimura, K. Matsuki, K. Tajima, K. Ishizu, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **64**, 2835 (1991); f) Y. Aratake, H. Ōkawa, E. Asato, H. Sakiyama, M. Kodera, S. Kida, and M. Sakamoto, *J. Chem. Soc., Dalton Trans.*, **1990**, 2941; g) M. Sakamoto, T. Ishimori, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **61**, 3319 (1988).

17) a) I. Ramade, O. Kahn, Y. Jeannin, and F. Robert, *Inorg. Chem.*, **36**, 930 (1997); b) J.-P. Costes, F. Dahan, A. Dupuis, and J.-P. Laurent, *Inorg. Chem.*, **35**, 2400 (1996); c) C. Benelli, A. J. Blake, P. E. Y. Milne, J. M. Rawson, and R. E. P. Winpenny, *Chem. Eur. J.*, **1**, 614 (1995); d) M. Andruh, I. Ramade, E. Codjovi, O. Giullou, O. Kahn, and J. C. Trombe, *J. Am. Chem. Soc.*, **115**, 1822 (1993); e) M. Andruh, O. Kahn, J. Sainto, Y. Dromzee, and S. Jeannin, *Inorg. Chem.*, **32**, 1623 (1993); f) C. Benelli, A. C. Farbretti, and A. Giusti, *J. Chem. Soc., Dalton Trans.*, **1993**, 409; g) U. Casellato, P. Guerriero, S. Tamburini, P. A. Vigato, and C. Benlli, *Inorg. Chim. Acta*, **207**, 39 (1993); h) O. Guillou, P. Bergerat, O. Kahn, E. Bakalbassis, K. Boubekeur, P. Batsil, and M. Guillot, *Inorg. Chem.*, **31**, 110 (1992); i) A. J. Blake, P. E. Y. Milne, P. Thornton, and R. E. P. Winpenny, *Angew. Chem., Int. Ed. Engl.*, **30**, 1139 (1991); j) C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou, and L. Pardi, *Inorg. Chem.*, **29**, 1750 (1990); k) A. Benelli, C. Benelli, A. Caneschi, A. Dei, and D. Gatteschi, *Inorg. Chem.*, **25**, 572 (1986); l) A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei, and D. Gatteschi, *J. Am. Chem. Soc.*, **107**, 8128 (1985).

18) a) M. Sakamoto, M. Kumagai, H. Sakiyama, Y. Nishida, Y. Sadaoka, A. Matsumoto, M. Ohba, and H. Ōkawa, *Synth. React. Inorg. Met.-Org. Chem.*, **27**, 567 (1997); b) M. Sakamoto, Y. Nishida, K. Ohhara, A. Matsumoto, M. Ohba, H. Sakiyama, N. Matsumoto, and H. Ōkawa, *Synth. React. Inorg. Met.-Org. Chem.*, **25**, 705 (1995); c) M. Sakamoto, M. Hashimura, K. Matsuki, N. Matsumoto, K. Inoue, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **64**, 3639 (1991); d) N. Matsumoto, M. Sakamoto, H. Tamaki, H. Ōkawa, and S. Kida, *Chem. Lett.*, **1990**, 853.

19) a) N. Higashiyama, Y. Izumi, and G. Adachi, *Inorg. Chim. Acta*, **207**, 233 (1993); b) N. Higashiyama and G. Adachi, *Chem. Lett.*, **1990**, 2029; c) G. Adachi, H. Nakamura, T. Mishima, and J. Shiokawa, *Chem. Express*, **2**, 727 (1987); d) V. G. Berner, D. W. Darnall, and E. R. Birnbaum, *Biochem. Biophys. Res. Commun.*, **66**, 763 (1975); e) V. Valzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).

20) G. E. Buono-Core, H. Li, and B. Marciniak, *Coord. Chem. Rev.*, **99**, 55 (1990).

21) a) M. Sakamoto, K. Yamamoto, A. Matsumoto, Y. Nishida, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **67**, 2707 (1994); b) M. Sakamoto, K. Yamamoto, M. Osaki, A. Matsumoto, and H. Ōkawa, *J. Alloys Compounds*, **192**, 42 (1993); c) M. Sakamoto, K. Matsuki, R. Ohsumi, Y. Nakayama, A. Matsumoto, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **65**, 2278 (1992); d) M. Sakamoto, M. Hashimura, Y. Nakayama, A. Matsumoto, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **65**, 1162 (1992).