Inorganica Chimica Acta, 218 (1994) 27–32

Heterodinuclear Ni(II)M(II) (M = Pb, Mn, Fe, Co, Ni, Cu, Zn) complexes of a phenol-based dinucleating macrocycle with dissimilar 4- and 5-coordination sites

Jun Nishio, Hisashi Ōkawa*, Shin-ichiro Ohtsuka and Mie Tomono
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812 (Japan)

(Received August 12, 1993; revised October 12, 1993)

Abstract

An Ni(II)Pb(II) complex $[NiPb(L)](ClO_4)_2 \cdot H_2O$ has been obtained by template reaction, where L^{2-} is the dinucleating macrocycle with two 2,6-di(iminomethyl)-4-methylphenolate entities combined by two lateral chains, $-(CH_2)_2-$ and $-(CH_2)_2NH(CH_2)_2-$, at the imino nitrogens. The Ni and Pb ions are located at the 4-coordination site with the chain $-(CH_2)_2-$ and the 5-coordination site with the chain $-(CH_2)_2NH(CH_2)_2-$ of the macrocycle, respectively. By the use of the Ni(II)Pb(II) complex as the precursor a series of Ni(II)M(II) complexes $[NiM(L)](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) have been obtained in hydrated or solvated forms and characterized by IR, ^1H NMR and UV–Vis spectra, magnetic measurements, and cyclic voltammetry. Cyclic voltammograms of the Ni(II)M(II) complexes show the Ni(II)/Ni(I) reduction at −1.0 to −1.1 V versus SCE. The oxidation of the Fe(II) of the Ni(II)Fe(II) complex occurs at +0.43 V whereas the oxidation of the Mn(II) of the Ni(II)Mn(II) complex and the Co(II) of the Ni(II)Co(II) complex does not occur up to +1.3 V.

Key words: Electrochemistry; Nickel complexes; Macrocyclic ligand complexes

Introduction

It is generally known that metal complexes of macrocyclic ligands (macrocycles) are stabilized thermodynamically and kinetically relative to those of corresponding acyclic ligands (macrocyclic effect [1]). Further, macrocycles can provide a specific geometrical environment for the bound metal ion and thence influence its physicochemical property [2]. The design of macrocycles which can provide dinuclear complexes of a well-defined structure is of importance to mimic dinuclear metallobiosites [3], to search appropriate systems for activating simple molecules [4–6], and to investigate the mutual effect of the two metal centers on their physicochemical properties [7, 8].

In our previous study [9] the dinucleating macrocycle with two 2,6-di(iminomethyl)-4-methylphenolate entities combined by two lateral chains, $-(CH_2)_2-$ and $-(CH_2)_2NH(CH_2)_2-$, at the imino nitrogens (see Fig. 1, abbreviated as L^{2-}) was obtained by the stepwise template reaction as a Cu(II)Pb(II) complex. It is found that the Cu(II)Pb(II) complex is a good precursor for a series of heterodinuclear Cu(II)M(II) (M = Mn, Fe, Co, Ni, Cu, Zn) complexes. In this study the corresponding Ni(II)Pb(II) complex of L^{2-}, $[NiPb(L)](ClO_4)_2$, has been prepared by a similar stepwise template reaction and used to prepare a series of Ni(II)M(II) complexes, $[NiM(L)](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn).

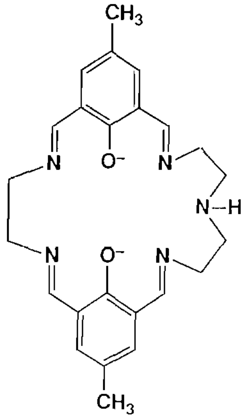

Fig. 1 Chemical structure of the macrocycle L^{2-}.

---

*Author to whom correspondence should be addressed.

0020-1693/94/$07.00
SSDI 0020-1693(93)03779-A

Experimental

Physical measurements

Elemental analyses of carbon, hydrogen and nitrogen were obtained from the Elemental Analysis Service Center at Kyushu University. Metal analyses were made on a Shimadzu AA-660 atomic absorption/flame emission spectrophotometer. IR spectra were recorded on a JASCO IR-810 spectrometer on KBr disks or Nujol mulls. Electronic spectra were recorded on a Shimadzu MPS-2000 spectrometer. ^{1}H NMR (400 MHz) spectra were recorded on a JEOL JNM-GX 400 spectrometer in deuterated dimethyl sulfoxide, using tetramethylsilane as the internal standard. Magnetic susceptibilities of powdered samples were measured on a Faraday balance. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ [10]. Diamagnetic corrections were made with Pascal's constants [11] and effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828[\chi_A T]^{1/2}$. Cyclic voltammograms were recorded on an apparatus comprising an HA-501 potentiostat/galvanostat, an HB-104 function generator and an HF-201 coulomb/amperehour meter of Kokuto Denko Ltd. Measurements were carried out in acetonitrile for oxidation and in dimethyl sulfoxide for reduction, using a three-electrode cell equipped with a glassy carbon working electrode, a platinum coil as the auxiliary electrode, and a saturated calomel electrode as the reference Tetrabutylammonium perchlorate was used as the supporting electrolyte. **Caution.** Tetrabutylammonium perchlorate is explosive especially in acetonitrile and should be handled with great caution.

Syntheses

2,6-Diformyl-4-methylphenol was prepared by the modified Duff reaction [12, 13]. *N,N'*-Ethylenebis(3-formyl-5-methylsalicylideneimine) and *N,N'*-ethylenebis(3-formyl-5-methylsalicylideneiminato)nickel(II) were obtained by the literature method [13]. **Caution.** The perchlorate complexes described below may be explosive and should be prepared in small portions

$[NiPb(L)](ClO_4)_2 \cdot H_2O$ (1)

A suspension of *N,N'*-ethylenebis(3-formyl-5-methylsalicylideneiminato)nickel(II) (1.6 g, 4 mmol) in methanol (30 cm^3) and a solution of $Pb(ClO_4)_2 \cdot 3H_2O$ (1.8 g, 4 mmol) in methanol were mixed and stirred at ambient temperature for 15 min. A methanol solution (20 cm^3) of diethylenetriamine (0.41 g, 4 mmol) was added and the mixture was refluxed for 30 min to form an orange solution from which reddish orange microcrystals separated out. They were dissolved in *N,N*-dimethylformamide (40 cm^3) and the solution was diffused with ether to give red prisms. Yield 2.92 g (82%). *Anal* Found: C, 32.24; H, 3.33; N, 7.92; Ni, 6 62. Calc. for $C_{24}H_{29}Cl_2N_5NiO_{11}Pb$: C, 32.02; H, 3.25; N, 7.78; Ni, 6.52%.

$[NiMn(L)](ClO_4)_2 \cdot H_2O$ (2)

A suspension of **1** (0.89 g, 1.0 mmol) and $MnSO_4 \cdot 6H_2O$ (0.26 g, 1.0 mmol) in methanol (30 cm^3) was stirred for 30 min at boiling temperature and evaporated to dryness. The residue was extracted with acetonitrile (30 cm^3) and the extract was evaporated to dryness. The resulting crude product was dissolved in methanol (30 cm^3) and the solution was diffused with ether to give red prisms. They were separated, washed with ether and dried *in vacuo*. Yield 0.52 g (69%). *Anal.* Found: C, 38.34; H, 4.05; N, 9.34; Mn, 6.95; Ni, 7.51. Calc. for $C_{24}H_{29}Cl_2MnN_5NiO_{11}$: C, 38.54; H, 3.91; N, 9.36; Mn, 7.34; Ni, 7.85%.

$[NiFe(L)](ClO_4)_2 \cdot DMF$ (3)

This complex was obtained by the reaction of **1** (0.89 g, 1.0 mmol) and $FeSO_4 \cdot 7H_2O$ (0.28 g, 1.0 mmol) in methanol under argon, in nearly the same way as that for **2**. The crude product was dissolved in DMF and the solution was diffused with isopropanol to give red crystals. Yield 0.49 g (61%). *Anal.* Found: C, 40.16; H, 4.31, N, 10.60; Fe, 6.87; Ni, 7.08. Calc. for $C_{27}H_{34}Cl_2FeN_6NiO_{11}$: C, 40.28; H, 4.38; N, 10.44; Fe, 6 94; Ni, 7.29%.

$[NiCo(L)](ClO_4)_2 \cdot H_2O$ (4)

The reaction of **1** (0.89 g, 1.0 mmol) and $CoSO_4 \cdot 7H_2O$ (0.28 g, 1.0 mmol) in methanol formed **4** as reddish brown crystals. Yield 0.47 g (63%). *Anal.* Found: C, 38.94; H, 3.98; N, 9.53; Co, 7.77; Ni, 7.45. Calc. for $C_{24}H_{29}Cl_2CoN_5NiO_{11}$: C, 38.80; H, 3.80; N, 9.43; Co, 7.93; Ni, 7.89%.

$[Ni_2(L)](ClO_4)_2 \cdot H_2O \cdot i\text{-}PrOH$ (5)

This was obtained as reddish brown microcrystals by the reaction of **1** (0.89 g, 1.0 mmol) and $NiSO_4 \cdot 6H_2O$ (0.28 g, 1.0 mmol) in methanol. They were recrystallized from DMF/isopropanol as described for **3**. Yield 0.48 g (59%). *Anal.* Found: C, 40.04; H, 4.67; N, 8.75; Ni, 14.22. Calc. for $C_{27}H_{37}Cl_2N_5Ni_2O_{12}$: C, 39.94; H, 4.59; N, 8 63; Ni, 14 46%.

$[NiCu(L)](ClO_4)_2 \cdot DMF \cdot H_2O$ (6)

The reaction of **1** (0.89 g, 1.0 mmol) and $CuSO_4 \cdot 5H_2O$ (0.25 g, 1.0 mmol) in methanol formed black crystals. They were recrystallized from DMF/isopropanol as described for **3**. Yield 0.51 g (62%). *Anal.* Found: C, 38.94; H, 4.43; N, 10.08; Cu, 7.52; Ni, 7.14. Calc. for $C_{27}H_{36}Cl_2CuN_6NiO_{12}$: C, 39.08; H, 4.37; N, 10.13; Cu, 7.66; Ni, 7 07%.

[NiZn(L)]$(ClO_4)_2 \cdot 2H_2O \cdot CH_3CN$ (7)

The reaction of **1** (0.89 g, 1.0 mmol) and $ZnSO_4 \cdot 7H_2O$ (0.29 g, 1.0 mmol) in methanol formed orange crystals, which were recrystallized from acetonitrile. Yield 0.55 g (67%). *Anal.* Found: C, 39.10; H, 4.40; N, 10.12; Ni, 6.89; Zn, 8.15. Calc. for $C_{26}H_{35}Cl_2N_6NiO_{12}Zn$: C, 39.09; H, 4.13; N, 10.13; Ni, 7.07; Zn, 7.88%.

Results and discussion

Ni(II)Pb(II) complex (1)

The stepwise template reaction using Ni(II) and Pb(II) ions at the different stages of cyclization was successfully applied to the synthesis of the macrocycle, L^{2-}, giving the Ni(II)Pb(II) complex [NiPb(L)]-$(ClO_4)_2 \cdot H_2O$ (**1**). The macrocycle is unsymmetrical with respect to the two dissimilar coordination sites, i.e. 4-coordination site of N_2O_2 donor set and 5-coordination site of N_3O_2 donor set, sharing the two phenolic oxygens as bridges. It is presumed that the Ni(II) ion is located at the 4-coordination site and assumes an essentially planar configuration. This is supported by the diamagnetic behavior of this complex. The Pb(II) ion at the 5-coordination site of the macrocycle may take a coordination number larger than six together with the perchlorate oxygens, judged from the split ν_3 band of the perchlorate group (1140, 1110 and 1080 cm^{-1}) [14]. In the related Cu(II)Pb(II) complex [CuPb(L)(OAc)]-$(BPh_4) \cdot$DMF (OAc = acetate) the Pb(II) ion at the 5-coordination site assumes an eight-coordiante structure together with bridging acetate oxygens [9].

Complex **1** shows a well-resolved ^1H NMR spectrum. Because of the unsymmetrical nature of the macrocycle L^{2-} with respect to the two coordination sites, the two ring protons appear at separate fields 7.88 and 7.52 ppm. On the other hand, only one azomethine proton signal with the intensity corresponding to two protons (2H) is observed at 8.62 ppm. This may be assigned to the azomethine proton of the 4-coordination site. The azomethine proton of the 5-coordination site may be obscured probably due to the lability of the proton [15–19]. A broadening of the azomethine signal is seen in **7** (NiZn) also (see below). As for the protons of the chain $=NCH^{\alpha}H^{\beta}CH^{\gamma}H^{\delta}-NH-CH^{\delta}H^{\gamma}CH^{\beta}H^{\alpha}N=$, the H^{α} and H^{β} signals are observed as broad bands at 4.21 and 4.01 ppm, respectively, and the H^{γ} and H^{δ} signals as broad bands at 5.80 and 5.60 ppm, respectively. The protons of the ethylene lateral chain of the 4-coordination site are observed as an AB quartet (3.93, 3.89, 3.57, 3.53 ppm). Such NMR spectral features of **1** are in accord with the X-ray crystallographic result for the Cu(II)Pb(II) complex of L^{2-} [9] where the central amino nitrogen of the 5-coordination site is associated with the donation to the Pb so that both the lateral chains are strained. The methyl proton signal is seen as a singlet at 2.29 ppm.

The visible spectrum of **1** in DMF shows intense bands at 327 ($\epsilon = 7900\ M^{-1}\ cm^3$) and 394 ($9600\ M^{-1}\ cm^3$) nm, that are assigned to the π–π^* transition associated with the azomethine group and a d–π^* transition, respectively [20]. A d–d band of the Ni(II) ion is seen as a shoulder at 540 nm, that is nearly the same wavelength as that (548 nm) of *N,N'*-ethylenebis(3-formyl-5-methylsalicylideneiminato)nickel(II) [13].

Ni(II)M(II) complexes (2–7)

The conversion of the Ni(II)Pb(II) complex (**1**) into a series of heterodinuclear Ni(II)M(II) (M = Mn (**2**), Fe (**3**), Co (**4**), Ni (**5**), Cu (**6**), Zn (**7**)) complexes by transmetallation was achieved in tolerable yields when stoichiometric amounts of **1** and a transition metal(II) sulfate were reacted in methanol. The magnetic moments at room temperature and electronic spectral data in acetonitrile of **2**–**7** are summarized in Table 1.

The magnetic moment of **2** (NiMn) is 5.86 μ_B (per molecule) that is common for high-spin Mn(II) ion. The magnetic moments of **3** (NiFe), **4** (NiCo), **5** (NiNi) and **6** (NiCu) are also common for high-spin Fe(II), Co(II), Ni(II) and Cu(II) complexes, respectively. Complex **7** (NiZn) is diamagnetic. These facts clearly demonstrate that the Ni(II) ion is diamagnetic in all the complexes.

It should be noted that the magnetic moments of **3** and **4** (4.85 and 4.25 μ_B, respectively) are low relative to those of high-spin octahedral Fe(II) and Co(II) complexes (the moments 5.2–5.5 and 4.7–5.2 μ_B, respectively, have been reported [21]). The crystal structure analysis for [CuMn(L)(AcO)]BPh_4 has revealed a highly distorted geometry about the Mn(II) owing to the steric requirement of the 5-coordination site [9]. Such a distortion of the configuration about the M(II) must be the case of the present Ni(II)M(II) complexes, giving rise to the reduction of the orbital contribution to the overall magnetic moment. In our previous cryomagnetic studies on the Cu(II)Co(II) complexes of L^{2-}, small *g* values (2.25–2.32) were evaluated for the Co(II) ion [9].

The NMR spectral features of **7** (NiZn) differ from that of **1** (NiPb). In **7** the ring protons are practically equivalent and appear as a singlet at 7.62 ppm whereas two imine proton signals are observed at separate fields 8.62 and 8.20 ppm. The signal at 8.20 ppm is considerably broadened probably due to the same reason as that for **1**. The protons of the lateral chains are seen as three broad signals at 3.81 (4H), 3.63 (4H), and 2.99 (4H) ppm. They can be assigned to $=NCH_2CH_2NHCH_2CH_2N=$, $=NCH_2CH_2N=$ and $=NCH_2CH_2NHCH_2CH_2N=$, respectively. The NMR spectral features observed suggest a fast conformational

TABLE 1. Magnetic moments at room temperature and electronic spectral data (in acetonitrile) of the Ni(II)M(II) complexes

	μ_{eff}/μ_B	UV–Vis λ(nm) (ϵ(M^{-1} cm^3))
[NiMn(L)](ClO_4)$_2$·1.5H_2O (**2**)	5.86	382 (10800), 535sh
[NiFe(L)](ClO_4)$_2$ DMF (**3**)	4.85	382 (10800), 465sh, 530sh
[NiCo(L)](ClO_4)$_2$·H_2O (**4**)	4.25	386 (10300), 537 (130), 1160 (7)
[NiNi(L)](ClO_4)$_2$·H_2O·iPrOH (**5**)	3.25	383 (11100), 525sh, 1020 (12)
[NiCu(L)](ClO_4)$_2$·DMF·H_2O (**6**)	1.83	386 (10100), 541 (210)
[NiZn(L)](ClO_4)$_2$·2H_2O CH_3CN (**7**)	dia.	386 (10900), 525sh

sh = shoulder.

change of the lateral chains relative to the time scale of NMR spectroscopy. To allow such a fast conformational change of the lateral chains, the amino nitrogen of the 5-coordination site must be free from the coordination to the Zn(II) ion in solution. The methyl proton signal is seen as a singlet at 2.31 ppm.

The electronic spectra of **2**–**7** each show one intense band at 384 ± 2 nm in the near-UV region. This band can be assigned to the intraligand π–π^* transition band associated with the azomethine group, by analogy with the Cu(II)M(II) complexes of L^{2-} [9]. The d–π^* band found for **1** is not resolved in **2**–**7**. The ligand field bands appear in the visible region longer than 450 nm. Complex **2** shows one absorption band at 535 nm attributable to the d–d band of the Ni(II) ion [9]. No appreciable absorption band due to the Mn(II) ion is seen in accord with the high-spin state of the metal ion. Similarly, **7** shows only one absorption band due to the Ni(II) ion at 525 nm. Complex **3** shows an additional band at 465 nm which can be assigned to a d–d component of the Fe(II). A similar band has been observed for the Cu(II)Fe(II) complex of L^{2-} [9]. For complex **4** a d–d component of the Co(II) is seen at 1160 nm and for **5** a d–d component of the high-spin Ni(II) at the 5-coordination site is seen at 1020 nm. Complex **6** shows a well-resolved band at 541 nm with a higher extinction coefficient 210 M^{-1} cm^3. This band may be the superposition of a d–d component of the high-spin Ni(II) and a d–d component of the Cu(II). It should be emphasized that the Cu(II)Ni(II) complex with Cu(II) at the 4-coordination site and Ni(II) at the 5-coordination site shows two d–d bands at 527 and 1015 nm. Thus, the Cu(II)Ni(II) and Ni(II)Cu(II) complexes, which differ in the arrangement of the metal ions at the 4- and 5-coordination sites of L^{2-} (coordination position isomers), are available using [CuPb(L)](ClO_4)$_2$ and [NiPb(L)](ClO_4)$_2$ as the precursors, respectively.

In Fig. 2 typical cyclic voltammograms of the Ni(II)M(II) complexes are given. The numerical data are summarized in Table 2.

The complexes **2**, **3**, **4** and **7** exhibit a quasi-reversible couple at −1.06 ± 0.03 V (versus SCE) that may be ascribed to the reduction of the Ni(II) center based on coulometry for **1**. Complex **5** (NiNi) shows two quasi-reversible couples at −1.01 and −1.23 V. The former potential corresponds to the reduction of the Ni(II) of **2**, **3**, **4** and **7**, but we tentatively assign this wave to the reduction of the Ni(II) at the 5-coordination site and the wave at −1.23 V to the reduction of the Ni(II) at the 4-coordination site. Our assignments are based on the facts that (i) the Cu(II)Ni(II) complex of L^{2-}, possessing the Ni(II) ion at the 5-coordination site, shows the reduction of the Ni(II) at −0.92 V under similar conditions and (ii) in the case of the Cu(II)Cu(II) complex of L^{2-} the reduction of the Cu(II) at the 4-coordination site, that occurs after the reduction of the Cu(II) at the 5-coordination site, appears at *c.* 0.25 V negative potential relative to that of the Cu(II)M(II) complexes [9]. It is natural that the reduction of the Cu(II) at the 4-coordination site is more difficult in Cu(II)Cu(II) complex than in the Cu(II)M(II) complexes because the reduction accompanies the charge change from 1+ to 0 in the former ($[Cu^{II}Cu^{I}]^+ \rightarrow [Cu^{I}Cu^{I}]^0$) whereas the reduction accompanies the charge change from 2+ to 1+ in the latter ($[Cu^{II}M^{II}]^{2+} \rightarrow [Cu^{I}M^{II}]^+$). Complex **6** shows an irreversible redox behavior with cathodic peaks at −0.34 and −1.15 V, which may be attributed to the reductions at the Cu and Ni centers, respectively.

In the sweep in the positive potential, all the complexes showed an irreversible wave near +1.3 V. A similar wave has been found for the Cu(II)M(II) complexes and attributed to the oxidation of the ligand based on electrochemical and spectral studies [9]. In the cyclic voltammogram of **3** (NiFe) a quasi-reversible couple appears at +0.43 V that is assigned to the oxidation of the Fe(II) [9]. On the other hand, **2** (NiMn) and **4** (NiCo) show no wave attributable to the oxidation of the Mn(II) and Co(II) ions in the potential region up to +1.3 V. As discussed previously [9] the M(II) at the 5-coordination site adopts a six-coordinate geometry highly distorted from a regular octahedron. Such a distortion of configuration could be the main reason for the stabilized Mn(II) and Co(II) in **2** and **4**.

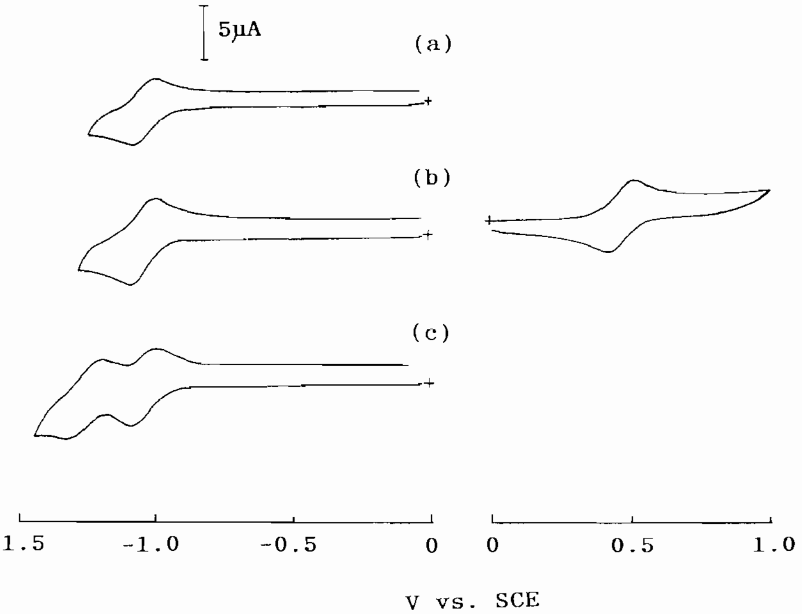

Fig 2. Cyclic voltammograms of **2** (NiMn) (a), **3** (NiFe) (b), and **5** (NiNi) (c): glassy carbon electrode, scan rate 50 mV s^{-1}, conc. 1×10^{-3} M, in DMSO for reduction and in acetonitrile for oxidation.

TABLE 2. Electrochemical data of Ni(II)M(II) complexes

Complex	Reduction (in DMSO)		Oxidation (in CH_3CN)
	Ni(II)/Ni(I)	M(II)/M(I)	M(II)/M(III)
2	−1.05 (70)		
3	−1.03 (80)		+0.43 (80)
4	−1.05 (80)		
5	−1.23 (110)	−1.01 (60)	
6	−1.15cp	−0.34cp	
7	−1.09 (90)		

Glassy carbon electrode, scan rate 50 mV s^{-1}, conc. 1×10^{-3} M, peak separation in parentheses; cp = cathodic peak

Acknowledgement

The authors thank Mr Masaaki Ohba for his help in the magnetic susceptibility measurements.

References

1 D.K. Cabbiness and D.W. Margerum, *J Am. Chem. Soc., 91* (1969) 6540; J.D. Lamb, R.W. Izatt, J.J. Christensen and D.J. Eatough, in G.A. Melson (ed.), *Coordination Chemistry of Macrocyclic Compounds,* Plenum, New York, 1979, p. 145.

2 J.F. Endicott and B. Durham, in G.A. Melson (ed.), *Coordination Chemistry of Macrocyclic Compounds,* Plenum, New York, 1979, p. 393.

3 D.A. Fenton, *Adv. Inorg Bioinorg. Mech., 2* (1983) 187.

4 P.A. Vigato, S. Tamburini and D.E. Fenton, *Coord Chem Rev, 106* (1990) 25.

5 S. Gambarotta, F. Arena, C. Floriani and P.F Zanazzi, *J. Am. Chem. Soc, 104* (1982) 5082; F. Arena, C. Floriani, A.C. Villa and C. Guastini, *Inorg. Chem., 25* (1986) 4589.

6 M. Sakamoto, M. Takagi, T. Ishimori and H. Ōkawa, *Bull. Chem Soc Jpn., 61* (1988) 1613; M. Sakamoto, T. Ishimori and H. Ōkawa, *Bull. Chem. Soc. Jpn, 61* (1988) 3319, Y. Aratake, H. Ōkawa, E. Asato, H. Sakiyama, M. Kodera, S Kida and M. Sakamoto, *J. Chem Soc., Dalton Trans,* (1990) 2941.

7 O Kahn, *Struct. Bonding (Berlin), 68* (1987) 89.

8 U. Casellato, P.A. Vigato and M. Vidali, *Coord Chem Rev., 23* (1977) 31; P. Zanello, S. Tamburini, P A. Vigato and G.A Mazzocchin, *Coord Chem Rev, 77* (1987) 165.

9 H. Ōkawa, J. Nishio, M. Ohba, M. Tadokoro, N. Matsumoto, M. Koikawa, S. Kida and D.E. Fenton, *Inorg Chem, 32* (1993) 2949.

10 N.F. Curtis, *J Chem Soc.,* (1961) 3147.

11 P.W. Selwood, *Magnetochemistry,* Interscience, New York, 1956, pp. 78 and 91.

12 D.A. Denton and H Suschitzky, *J Chem. Soc,* (1963) 4741.

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

14 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 2nd edn., 1970, p. 175.

15 K. Motoda, H. Sakiyama, N. Matsumoto, H. Ōkawa and S. Kida, *Bull Chem. Soc Jpn, 65* (1992) 1176.

16 S. Tamburini, P.A. Vigato, D. Chiarello and P. Traldi, *Inorg Chim Acta, 156* (1989) 271.

17 M.G.B. Drew, J. Nelson and S.M. Nelson, *J. Chem Soc, Dalton Trans,* (1981) 1678.

18 R Menif and A.E Martell, *J Chem. Soc, Chem Commun,* (1989) 1521, R. Menif, A.E. Martell, P J. Squattrito and

A Clearfield, *Inorg Chem*, *29* (1990) 4723, M.P. Ngwenya, D. Chen, A.E. Martell and J Reibenspies, *Inorg Chem*, *30* (1991) 2732.

19 H. Adams, N.A Bailey, D.E. Fenton, R.J. Good, R. Moody and C.O.R de Barbarin, *J. Chem. Soc*, *Dalton Trans*, (1987) 207; D E. Fenton, S.J. Kitchen, C.M. Spencer, S. Tamburini and P A. Vigato, *J Chem. Soc., Dalton Trans*, (1988) 685.

20 B. Bosnich, *J Am. Chem Soc*, *90* (1968) 627.

21 A.T. Casey and S. Mitra, in E.A. Boudreaux and L.N Mulay (eds.), *Theory and Applications of Molecular Paramagnetism*, Wiley, New York, 1976, p 135.