Inorganica Chimica Acta, *214* (1993) 97–102

Synthesis and characterization of dicopper(II,II) and diiron(III,III) complexes with a dinucleating tetraimidazole ligand, 1,5-bis[bis(4-imidazolylmethyl)amino]-3-pentanol

Masahito Kodera*

Department of Applied Chemistry, Doshisha University, Kamigyouku, Kyoto 602 (Japan)

Naoki Koura, Sachio Hosohara, Masato Nishimura, Masaaki Ohba and Hisasi Okawa

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812 (Japan)

Sigeo Kida

Kumamoto Institute of Technology, 4-22-1 Ikeda, Kumamoto 860 (Japan)

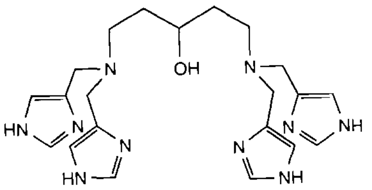
(Received April 3, 1993; revised June 22, 1993)

Abstract

A new dinucleating ligand 1,5-bis[bis(4-imidazolylmethyl)amino]-3-pentanol (Hbipl) has been synthesized. It forms the dicopper(II,II) and diiron(III,III) complexes, $[Cu_2(bipl)Cl](ClO_4)_2 \cdot H_2O$ and $[Fe_2(bipl)(OAc)_2](ClO_4)_3 \cdot H_2O$, which are characterized by elemental analyses, magnetic susceptibility measurements, cyclic voltammetry, and IR and UV–Vis spectroscopies.

Introduction

Dinuclear copper and iron sites containing five or six imidazoles as donor groups play an essential role in binding dioxygen in hemocyanin [1] and hemerythrin [2], respectively, and also the presence of a similar dinuclear site has been suggested for tyrosinase [3]. Hence, in order to provide structural and functional models [4] for such metal proteins, synthesis of chelating agents having imidazoles as donor groups is essentially desirable [5, 6]. Although a large number of dinuclear metal chelates have been synthesized as model compounds for those metal proteins, their donor groups are mostly pyridines, pyrazoles, benzimidazoles, or aliphatic imines or amines because of the difficulty of synthesizing polyimidazole ligands and solubility problems of their metal complexes [7–14], hence only few polyimidazole ligands have been reported [15, 16]. Thus, in order to further the model studies of dioxygen binding metal proteins it is desirable to exploit novel polyimidazole dinucleating ligands. In this paper we report the synthesis and characterization of such a compound, 1,5-bis[bis(4-imidazolylmethyl)amino]-3-pentanol (Fig. 1; abbreviated as Hbipl) and its dinuclear iron(III,III) and copper(II,II) complexes.



Hbipl

Fig. 1. Chemical structure of Hbipl.

Experimental

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be handled, and with great caution.

Materials

All the reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. The following solvents were distilled under Ar before use: methanol from $Mg(OCH_3)_2$, ethanol from $Mg(OC_2H_5)_2$ and acetonitrile from P_2O_5. 4-Formylimidazole [17, 18] and 1,5-diamino-3-pentanol [19] were obtained by the literature methods.

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

Physical measurements

Elemental analyses of carbon, hydrogen and nitrogen were obtained at the Elemental Analysis Service Center of Kyushu University. Analyses of Fe and Cu were made on a Shimadzu AA-660 atomic absorption/flame emission spectrophotometer. Infrared (IR) spectra were recorded on a JASCO IR-810 spectrometer on KBr disks or Nujol mulls. Electronic absorption spectra were measured in acetonitrile with a Shimadzu UV-210 spectrophotometer. ^{1}H NMR spectra (400 MHz) were recorded on a JEOL JNM-GX 400 spectrometer in deuterated dimethyl sulfoxide (DMSO-D6) using tetramethylsilane as the internal standard at 30, 50 and 70 °C. Fast atom bombardment (FAB) mass spectra were obtained with a JEOL JMS-DX300 spectrometer. Solid-state magnetic susceptibility measurements were carried out on a Faraday balance designed in our laboratory in the range 80–300 K. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ [20]. Cyclic voltammograms were obtained in a methanol solution (and acetonitrile solution) containing $N(C_4H_9)_4BF_4$ (0.1 M) as the supporting electrolyte, with an assembly comprising a Hokuto Denko HA501 potentiostat and an HB104 function generator. A glassy-carbon disk ($\phi = 0.3$ mm) and a platinum plate were used as the working electrode and the counter electrode, respectively, and a TOA saturated calomel electrode (SCE) was used as the reference electrode with 1% agar salt bridge (0.1 M KCl).

Preparation of 1,5-bis[bis(4-imidazolylmethyl)amino]-3-pentanol·hexahydrochloride (Hbipl·6HCl)

2.0 g (10.5 mmol) of 1,5-diamino-3-pentanol and 4.4 g (45.8 mmol) of 4-formylimidazole were dissolved in 40 ml of methanol and the solution was degassed by several cycles of evacuation and refilling with Ar. To this was added 2.8 g (44.4 mmol) of sodium cyanoborohydride and the mixture was stirred for 12 h at room temperature under Ar stream. The reaction mixture was acidified to pH 2 with concentrated hydrochloric acid to decompose the excess amount of sodium cyanoborohydride. Hydrogen gas was vigorously evolved and an insoluble substance was formed. It was removed by filtration, and the filtrate was evaporated to dryness. The residue was dissolved in 30 ml of methanol, filtered to remove the insoluble material, and evaporated to dryness. This treatment was repeated until the insoluble substance was no longer formed. To the resulting methanol solution was added 70 ml of ethanol and the mixture was slowly concentrated to 10 ml to give a white precipitate. It was collected by filtration, washed successively with 10 ml of ethanol and 20 ml of ethyl ether, and dried *in vacuo*. The product was obtained as a hexahydrochloride salt. Yield 6.55 g (95%); m.p. 152–155 °C. *Anal.* Calc. for $C_{21}H_{30}N_{10}O \cdot 6HCl \cdot \frac{1}{2}C_2H_5OH$: C, 38.84; H, 5.78; N, 20.59. Found: C, 38.54; H, 5.77; N, 20.43%. ^{1}H NMR at 30 °C (DMSO-d$_6$, δ (ppm)): 9.23 (2′-H, imidazole, d, 4H), 8.03 (5′-H, imidazole, s, 4H), 4.48 (methylene, bs, 8H), 3.57 (3-H, alkyl chain, bs, 1H), 3.2–3.0 (1,5-H, alkyl chain, m, 4H), 1.94 (2,4-H, alkyl chain, bd, 4H). IR bands (KBr disk, cm^{-1}): 3600–2500(multi, s), 1620(s), 1470(s), 1440(s), 1280(m), 1100(m), 835(s), 630(s). UV data [λ (nm) (ϵ (M^{-1} cm^{-1}))] in CH_3OH: 218 (12 600). FAB mass of Hbipl (*m/z*): 461 $(M+Na)^+$, 439 $(M+H)^+$. High resolution FAB mass spectrum of $(M+H)$ showed isotope peaks as follows, Mass (abundance): 439.268 (100), 440.271 (27.53), 441.273 (3.85), 442.276 (0.37), 443.278 (0.03).

Preparation of $[Cu_2(Cl)(bipl)](ClO_4)_2 \cdot H_2O$ (1)

657 mg (1 mmol) of Hbipl·6HCl were dissolved in 6 ml of methanol. To the solution was added a methanol solution (4 ml) of 750 mg (2.02 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$, and the pH of the mixture was adjusted to pH 4 by adding a methanol solution of sodium hydroxide. Sodium chloride that precipitated was separated by filtration, and the filtrate was diluted with a small amount of ethyl ether and allowed to stand for a few days to afford dark blue crystals. They were collected by filtration and recrystallized from methanol–ethyl ether. Yield 375 mg (51%). *Anal.* Calc. for $C_{21}H_{29}Cu_2Cl_3N_{10}O_9 \cdot H_2O$: C, 30.87; H, 3.82; N, 17.14; Cu, 15.56. Found: C, 30.56: H, 3.61; N, 16.97; Cu, 15.13%. IR bands (KBr, cm^{-1}): 3300(br, s), 3120(s), 3040(m), 2900(m), 1590(m), 1500(s), 1460(s), 1350(m), 1270(s), 1150–1050(vs), 770(m), 620(s). UV–Vis data [λ (nm) (ϵ (M^{-1} cm^{-1}))] in CH_3OH: 216 (17 200) 286 (7000), 643 (250).

Preparation of $[Fe_2(OAc)_2(bipl)](ClO_4)_3 \cdot H_2O$ (2)

657 mg (1 mmol) of Hbipl·6HCl and 890 mg (2.2 mmol) of $Fe(NO_3)_3 \cdot 9H_2O$ were dissolved in 10 ml of water. The pH of the solution was adjusted to 4 by adding sodium acetate. To the solution was added 740 mg (6 mmol) of sodium perchlorate and the mixture was evaporated to dryness. The residue was dissolved in 50 ml of acetonitrile and insoluble materials were filtered off. To the filtrate was added a small amount of water and the mixture was allowed to stand for 1 day to give brown needles. They were recrystallized from acetonitrile–ethyl ether several times to give 200 mg (yield 20%) of the title complex. *Anal.* Calc. for $C_{25}H_{35}Cl_3Fe_2N_{10}O_{17} \cdot H_2O$: C, 30.53; H, 3.79; N, 14.24; Fe, 11.35. Found: C, 30.39; H, 3.82; N, 13.98; Fe, 12.28%. IR bands (KBr, cm^{-1}): 3400(br, s), 3120(s), 3040(m), 2900(m), 1590(w), 1540(s), 1490(m), 1440(s), 1350(m), 1270(m), 1150–1050(br, vs), 1120, 1110(m), 820(w), 780(w), 630(s).

Results and discussion

Syntheses

A related dinucleating tetraimidazole ligand, 2,6-bis[(bis(1-methylimidazol-2-yl)methyl)aminomethyl]-4-methylphenol (Hbimp), was previously synthesized by Hendrickson and co-workers [15]. Hbimp has two metal binding sites of the N_3O donor set, sharing the phenolic oxygen as the bridge. The two *N*-methylimidazole groups are connected at the 2-position of the imidazole to the amine nitrogen. Hbipl resembles Hbimp in the donor set but differs in the bridging group. Further, the four imidazole groups in Hbipl are not methylated and are connected to the ligand skeleton at the 4-position of the imidazole as is the case of histidine in biological systems. The synthesis of Hbipl was carried out by one-pot reaction as follows (see Scheme 1). 1,5-Diamino-3-pentanol and 4-formylimidazole in the 1:4 molar ratio were reacted in methanol to give a Schiff base *in situ* which was reduced with sodium cyanoborohydride. This method using 4-formylimidazole is a great advantage for introducing two imidazole groups into a primary amine and applicable to the synthesis of various polyimidazole ligands. The formation of Hbipl was confirmed by elemental analyses, ^1H NMR and FAB mass spectra. The high resolution FAB mass spectrum of Hbipl shows a parent peak, $(M+H)^+=439$, that gives the elemental composition, $C_{21}H_{31}N_{10}O$ ($=[H_2bipl]^+$). The ^1H NMR spectrum of Hbipl·6HCl shows well resolved peaks from the pendant imidazoles and broad peaks from the alkyl chain of the diaminopentanol unit at 30 °C. The resolution of the broad peaks was improved at higher tempratures, 50 and 70 °C.

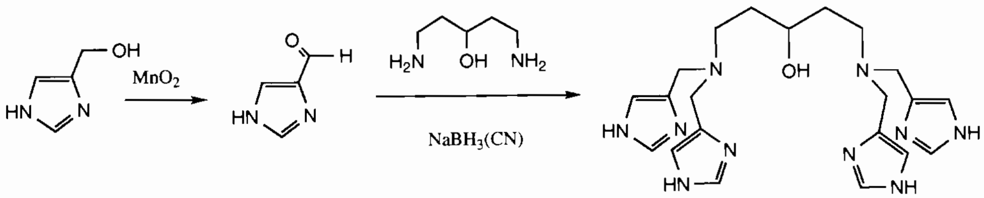
Complexation of the Hbipl towards metal ions was very sensitive to the pH of the reaction medium. The dicopper(II,II) complex, **1**, was obtained when the pH of the methanolic solution was adjusted to 4. At a pH higher than 4, deprotonation of the imidazole proton occurs resulting in the formation of insoluble materials. The elemental analysis of **1** accords with the calculated values of chemical formula, $[Cu_2(C_{21}H_{29}N_{10}O)Cl](ClO_4)_2\cdot H_2O$, suggesting a dinuclear structure bridged by the endogenous alkoxide and exogenous chloride ions. The iron complex, **2**, was also obtained when the pH of the reaction mixture was adjusted to *c*. 4 using sodium acetate. The elemental analysis of **2** suggests a μ-alkoxo-bis(μ-acetato) diiron(III,III) core structure. In spite of many efforts we were unsuccessful in obtaining large single crystals suitable for X-ray crystallography.

Dicopper(II,II) complex, 1

The electronic spectrum of **1** consists of three bands at 216 (ϵ 17 000), 287 (7000) and 643 (250 M^{-1} cm^{-1}) nm with a shoulder near 700 nm. The highest energy band is assigned to the imidazole π–π^* transition. The band at 287 nm can be assigned to an imidazole $\pi(N)\rightarrow d\sigma$ charge-transfer transition [21]. The band at 643 nm and the shoulder near 700 nm are assigned to d–d transition bands of the copper(II) ion. The spectral feature in the visible region suggests a distorted square-pyramidal geometry about the copper(II) ion [8b]. Alkoxo- [22] and phenolato-bridged [23] dicopper(II,II) complexes generally show a $O\rightarrow d\sigma$ LMCT band in the near-UV region. However, complex **1** showed no appreciable band. Recently, Handa *et al.* have reported that the LMCT band is characteristic of a di-μ-hydroxo- or di-μ-alkoxo-dicopper(II,II) core with a significant electrostatic interaction between the bridging oxygens [24]. The spectral feature of **1** is similar in d–d band frequency to that of the Cl^- adduct of half-met hemocyanin, which exhibits no charge-transfer transition band in the visible region [25].

The cyclic voltammogram of **1** shows an irreversible couple near 0 V versus SCE (E_{pa} +0.08, E_{pc} −0.12 V) which is tentatively assigned to the reduction $Cu_2(II,II)\rightarrow Cu_2(I,II)$ (Fig. 2(a)). The high potential probably reflects the distorted five-coordinate geometry about the copper ion.

The temperature-dependence of the magnetic susceptibility of **1** was measured over the range 80–300 K (see Fig. 3). The magnetic moment per one copper(II) ion is 1.75 μ_B at room temperature and decreases slightly with decreasing temperature to 1.72 μ_B at 80 K, suggesting the operation of a very weak antiferromagnetic interaction between the two copper(II) ions. To the best of our knowledge dinuclear copper(II) complexes bridged by an alkoxo and a chloro group have not been reported. Some dinuclear copper(II) complexes with a phenoxo and a chloro bridge are known [26a] and in the complexes of Schiff bases derived from 2,6-diformyl-4-methylphenol and glycine or alanine a weak antiferromagnetic interaction is observed. In



Scheme 1.

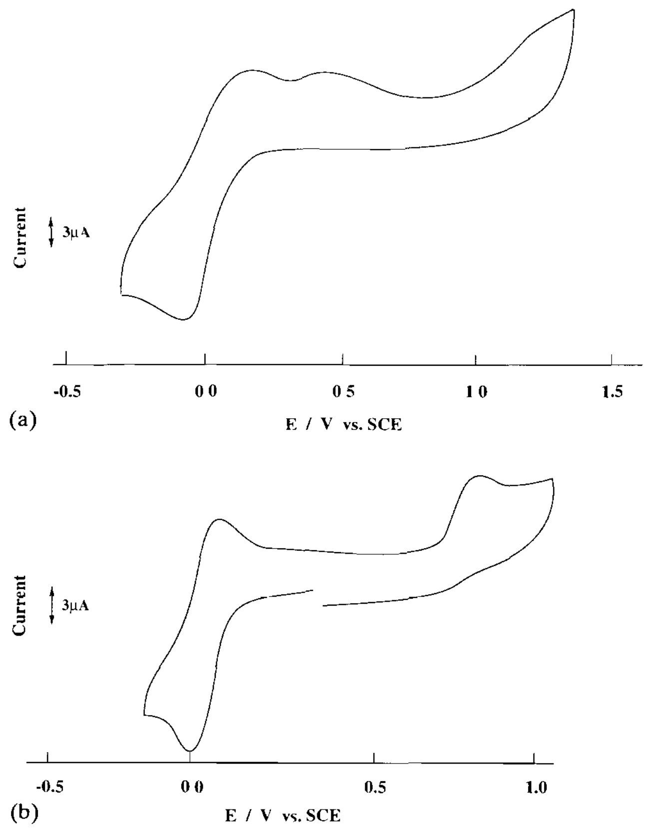


Fig. 2. (a) Cyclic voltammogram of (a) **1** in methanol, (b) **2** in acetonitrile.

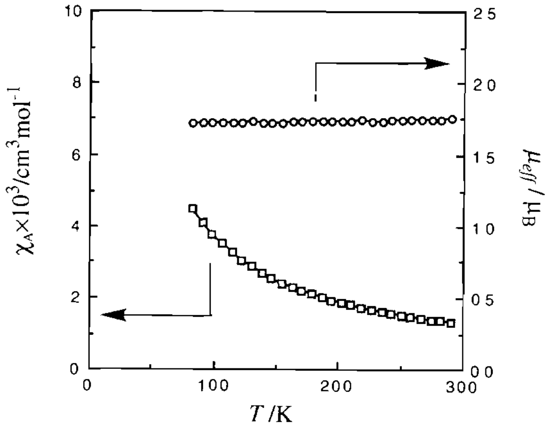


Fig 3. Plots of the temperature dependence of the magnetic susceptibility χ_A (□) and the effective magnetic moment μ_{eff} (○).

$[Cu_2Cl_6]^{2-}$ with large cations a significant ferromagnetic interaction is observed [26b]. It appears that in **1** the alkoxo and the chloro bridges interact counter complementarily with two copper(II) ions to give rise to a weak magnetic interaction.

Diiron(III,III) complex, 2

Complex **2** shows IR bands at 1540, 1490 and 1440 cm^{-1} which are typical of a bridging acetate group. This adds support to the μ-alkoxo-μ-bis(acetato)-diiron(III,III) core structure. The visible absorption spectrum of **2** in acetonitrile shows a weak band near 600 nm which may be assigned to a charge-transfer band from the alcoholic oxygen to the iron(III) ion.

The cyclic voltammogram (Fig. 2(b)) of **2** shows a reversible redox wave at −50 mV versus SCE and an irreversible anode peak at 750 mV versus SCE. In this study our attention was focused on the wave at −50 mV. Based on the potentiostatic reduction at −50 mV versus SCE, showing one-electron reduction, the wave is assigned to the Fe_2(II,III)/Fe_2(III,III) process. The reduced solution shows absorption bands at 533 (ϵ 600), 670 (240) and 1000 (90 M^{-1} cm^{-1}) nm, as shown in Fig. 4. The bands at 533 and 670 nm may be assigned to LMCT bands or d–d bands of the iron(II) ion. The band at 1000 nm is assignable to the intervalence band according to the literature [9, 27, 28]. The reactivity of the diiron(II,III) complex towards molecular oxygen was studied spectroscopically at room temperature and it was found that the diiron(II,III) complex was fairly stable in the open atmosphere but reoxidized to the diiron(III,III) complex after several hours.

The electrochemical behavior of **2** differs from that reported for related diiron complexes of bimp [27] and 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol (bpmp) [28]. The Fe_2(II,III)/Fe_2(III,III) couples for Fe_2–bipm and Fe_2–bpmp were reported to occur at 435 and 690 mV versus SCE, respectively. Thus, the diiron(II,III) state of **2** is destabilized relative to those of Fe_2–bimp and Fe_2–bpmp. It appears that the diiron(II,III) state is stabilized by the phenolate bridge in both Fe_2–bimp and Fe_2–bpmp, because the phenolate group is a weak base compared with the alkolate group. In the case of Fe_2–bpmp the pyridine groups whose vacant MOs can act as an electron-acceptor may con-

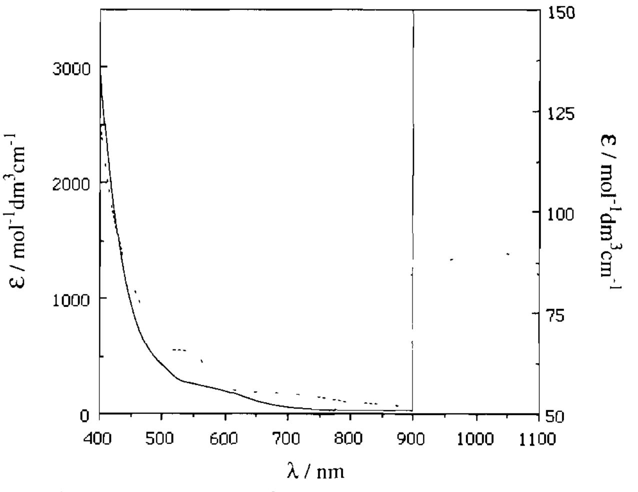


Fig 4. Electronic absorption spectra of **2** (——) and its one-electron reduced complex (– – –).

tribute further to the stabilization of the diiron(II,III) state.

The magnetic moment of **2** is 4.42 μ_B (per one Fe(III)) at room temperature, suggesting an antiferromagnetic interaction between the two iron(III) ions. Its cryomagnetic property (80–300 K), however, could not be interpreted in terms of the isotropic Heisenberg model. Curiously, the magnetic moment tends to increase with decreasing temperature and the value at 80 K is 4.72 μ_B. The origin of this unusual magnetic behavior of the complex remains unknown, and will be studied in the future through its molecular structure.

References

1 W.P J. Gaykema, W.G.J. Hol, J.M. Vereijken, N.M. Soeter, H.J Bak and J J. Beintema, *Nature (London), 309* (1984) 23.

2 R.E Stenkamp, L.C. Sieker and L.H. Jensen, *J Mol Biol, 100* (1976) 23; D.M. Kurtz, Jr., D.F. Shriver and I.M. Klotz, *Coord Chem Rev, 24* (1977) 145, R.E. Stenkamp, L.C Sieker, L.H Jensen, J D. McCallum and J. S-Loehr, *Proc Natl Acad Sci U S A, 82* (1985) 713; R.E. Stenkamp, L C Sieker and L.H Jensen, *J. Am Chem. Soc, 106* (1984) 618.

3 M. Jimenez, K. Kameyama, W L. Maloy, Y. Tomita and V.J. Hearing, *Proc Natl Acad Sci. U S A, 85* (1988) 3830.

4 T.M. Sorrell, *Tetrahedron, 45* (1989) 3; F. Mani, *Coord Chem Rev., 120* (1992) 325; D.M. Kurtz, Jr., *Chem Rev, 90* (1990) 585

5 C.C Tang, D. Davalian, P. Huang and R. Breslow, *J Am Chem Soc, 100* (1978) 3918.

6 C.L. Merrill, L.J. Wilson, T.J. Thamann, T M. Loehr, N.S. Ferris and W.H. Woodruff, *J Chem Soc, Dalton Trans,* (1984) 2207

7 V. McKee, J V Dagdigian, R. Bau and C.A. Reed, *J Am Chem Soc, 103* (1981) 7000; V. McKee, M. Zvagulis, J.V. Dagdigian, M.G. Patch and C A Reed, *J Am Chem Soc, 106* (1984) 4765; V. McKee, N. Zvagulis and C.A. Reed, *Inorg Chem., 24* (1985) 2914, M.G. Patch, H Choi, D.R. Chapman, R Bau, V. McKee and C.A. Reed, *Inorg. Chem, 29* (1990) 110.

8 (a) K.D. Karlin, J.C. Hayes, Y. Gultneh, R.W Cruse, J.W. McKown, J.P. Hutchinson and J. Zubieta, *J Am. Chem Soc., 106* (1984) 2121; K.D. Karlin, M.S. Haka, R W. Cruse, G.J. Meyer, A Farooq, Y Gultneh, J C. Hayes and J. Zubieta, *J. Am Chem Soc, 110* (1988) 1196; K.D Karlin, Z Tyeklar, A. Farooq, M.S. Haka, P. Ghosh, R.W. Cruse, Y. Gultneh, J.C. Hayes, P.J. Toscano and J. Zubieta, *Inorg Chem, 31* (1992) 1436; (b) T.N. Sorrell, D L Jameson and C.J. O'connor, *Inorg Chem., 23* (1984) 190; Y Nishida, H Shimo, H. Maehara and S Kida, *J Chem Soc, Dalton Trans,* (1985) 1945, H.P. Berends and D W. Stephan, *Inorg. Chem, 26* (1987) 749; S Schindler, D.J. Szalda, and C. Creutz, *Inorg Chem, 31* (1992) 2255

9 M. Suzuki, A Uehara and K. Endo, *Inorg Chim Acta, 123* (1986) L9; A.S. Borovik, B.P. Murch, L. Que, Jr., V. Papaefthymiou and E. Munck, *J Am Chem Soc., 109* (1987) 7190; S. Menage, B A. Brennan, C.J.-Garcia, E Munk and L. Que, Jr, *J Am Chem Soc, 112* (1990) 6423

10 J.L. Sessler, J.W. Silbert and V. Lynch, *Inorg. Chem, 29* (1990) 4143.

11 T.N. Sorrell and V.A. Vankai, *Inorg Chem., 29* (1990) 1687. T.N. Sorrell, V A. Vankai and M.L. Garrity, *Inorg. Chem, 30* (1991) 207; T N Sorrell and M L. Garrity, *Inorg Chem, 30* (1991) 210.

12 C. Mealli, C.S. Arcus, J.L. Wilkinson, T J. Marks and J.A. Ibers, *J Am. Chem. Soc., 98* (1976) 711, N. Kitajima, T. Koda and Y Moro-oka, *Chem Lett.,* (1988) 347; N. Kitajima, T. Koda, S Hashimoto, T. Kitagawa and Y. Moro-oka, *J. Chem Soc, Chem. Commun,* (1988) 151; N Kitajima, K. Fujita and Y. Moro-oka, *J. Am Chem Soc, 111* (1989) 8975; N. Kitajima, T. Koda, Y. Iwata, Y. Moro-oka, *J Am Chem. Soc, 112* (1990) 8833; N. Kitajima, T. Koda, S. Hashimoto, T. Kitagawa and Y. Moro-oka, *J. Am. Chem. Soc, 113* (1991) 5664.

13 W.H. Armstrong and S.J. Lippard, *J Am Chem Soc., 105* (1983) 4837; W.H. Armstrong, A. Spool, G.C. Papaefthymiou, R. B. Frankel and S.J. Lippard, *J Am Chem Soc., 106* (1984) 3653; W H. Armstrong and S.J. Lippard, *J Am Chem Soc, 106* (1984) 4632; J.R. Hartman, R.L. Rardin, P. Chaudhuri, K. Pohl, K. Wieghardt, B. Nuber, J. Weiss, G.C. Papaefthymiou, R B. Frankel and S.J. Lippard, *J. Am. Chem Soc, 109* (1987) 7383.

14 K. Wieghardt, K. Poul and W. Gebert, *Angew Chem, Int Ed. Engl, 22* (1983) 727; K Wieghardt, K. Poul and D Ventur, *Angew Chem., Int Ed Engl., 24* (1985) 392; P. Chaudhuri, K. Wieghardt, B. Nuber and J. Weiss, *Angew Chem, Int Ed Engl, 24* (1985) 778, R. Hotzelmann, K. Wieghardt, U Florke, H -J. Haupt, D.C. Weatherburn, J. Bonvoishin, G. Blondin and J.-J Girerd, *J Am Chem Soc., 114* (1992) 1681

15 K J Oberhausen, J F. Richardson, R.M. Buchanan, J.K. McCusker, D N Hendrikson and J.-M. Latour, *Inorg. Chem, 30* (1991) 1357.

16 T.N. Sorrell and A.S. Borovik, *J. Am. Chem. Soc, 109* (1987) 4255, F -J. Wu, D.M. Kurtz, Jr., K.S. Hagen, P.D. Nymann, P. Debrunner and V.A Vankai, *Inorg Chem., 29* (1990) 5174; V.A. Vankai, M G. Newton, *Inorg Chem, 31* (1992) 343. J.L Sessler, J.D. Hugdahl, V Lynch and B Davis, *Inorg Chem, 30* (1991) 334 W B. Tolman, R.L. Rardin and S.J. Lippard, *J Am Chem Soc, 111* (1989) 4532, W.B Tolman, S Liu, J.B Bentsen and S.J. Lippard, *J Am Chem. Soc, 113* (1991) 152, R.L Rardin, P Poganiuch, A Bino, D.P. Goldberg, W B. Tolman, S Liu and S J. Lippard, *J Am Chem. Soc, 114* (1992) 5240

17 J.R. Totter and W.J. Darby, *Org. Synth, 3* (1955) 460.

18 A.R. Battersby, M. Nicoletti, J. Stauton and R. Vleggaar, *J Chem Soc, Perkin Trans I,* (1980) 43

19 I. Murase, M Hatano, M. Tanaka, S. Ueno, H. Okawa and S. Kida, *Bull Chem Soc Jpn., 55* (1982) 2404.

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

21 T.C. Fawcett, E.E. Bernarducci, K.K Jespersen and H.J. Schugar, *J Am Chem Soc, 102* (1980) 2598; J.V. Dagdgian, V McKee and C.A. Reed, *Inorg Chem, 21* (1982) 1332.

22 Y Nishida and S Kida, *J Inorg Nucl Chem., 38* (1976) 451

23 H Okawa, M. Tadokoro, Y Aratake, M. Ohba, K. Shindo, M. Mitsumi, M Koikawa, M. Tomono and D E. Fenton, *J Chem Soc, Dalton Trans,* (1993) 253.

24 M. Handa, T. Idehara, K Nakano, K. Kasuga, M. Mikuriya, N. Matsmoto, M. Kodera and S. Kida, *Bull. Chem Soc. Jpn, 65* (1992) 3241.

25 R S. Himmelwright, N.C. Eickman and E I Solomon, *J Am Chem Soc., 101* (1979) 1576.

26 (a) H. Okawa, S. Kida, Y Muto and T. Tokii, *Bull Chem. Soc Jpn*, *45* (1972) 2480; H. Okawa, T. Tokii and S. Kida, *Bull. Chem Soc Jpn*, *46* (1973) 1462; (b) C Chow, R D Willett and B.C. Gerstein, *Inorg. Chem*, *13* (1975) 205.

27 M.S Mashuta, R J. Webb, K J. Oberhausen, J.F. Richardson, R M. Buchanan and D.N. Hendrikson, *J. Am. Chem Soc*, *111* (1989) 2745; R.M. Buchanan, M.S Mashuta, J.F. Richardson, K J Oberhausen and D.N. Hendrikson, *Inorg Chem*, *29* (1990) 1299.

28 A.S. Borovik and L. Que, Jr., *J Am Chem. Soc*, *110* (1988) 2345, A S. Borovik, V Papaefthymiou, L.F Taylor, O P. Anderson and L. Que, Jr, *J Am Chem Soc*, *111* (1989) 6183.