Synthesis and Reactivities of Binuclear Iron(III) Complexes with Ligands Composed of Two Tridentate Chelating Groups

YUZO NISHIDA*, MASATAKA TAKEUCHI, HIROYUKI SHIMO and SIGEO KIDA

Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812, Japan

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Abstract

Several new binuclear iron(III) complexes were prepared using the binucleating ligands in which two molecules of N,N-bis(2-benzimidazolylmethyl)amine are linked by a polyatomic chain, such as $-(CH_2)_4-$ (L-4), $-(CH_2)_6-$ (L-6), and $-CH_2CH(OH)CH_2-$ H(L-3′), etc., and were characterized in terms of the magnetic measurements and cyclic voltammetry. The complex, $Fe_2(L\text{-}3')(NO_3)_5$ showed subnormal magnetic moments, 4.10 BM at 299 K and 2.22 BM at 87 K, respectively, suggesting the presence of an alkoxo-bridged structure. This complex showed much higher catalytic activity for the O_2 oxidation of N,N,N′,N′-tetramethyl-1,4-diaminobenzene than those of the relevant mononuclear complex and other binuclear complexes studied here which have no alkoxo-bridge. The complex reacts with catechol and hydrogen peroxide to form 1:1 adducts.

Introduction

Transition metal complexes of binucleating ligands are of interest because they provide the opportunity to study the magnetic exchange interaction and multi-electron redox reactions, and possible activation of small molecules (such as O_2 and N_2) between the metal centers. They may also serve as models for some metal proteins [1, 2].

We have been investigating the reactivities of the synthetic binuclear metal complexes to contribute to the elucidation of the functions of metalloproteins, and have reported that many binuclear complexes of copper(II), cobalt(II) and manganese(III) show very high activities in some redox reactions compared with the relevant mononuclear ones [3–13].

In this study we have prepared several novel type binuclear iron(III) complexes with the ligands in which two tridentate chelating groups are linked by a polyatomic chain, as shown in Fig. 1. The complexes were reacted with N,N,N′,N′-tetramethyl-1,4-diaminobenzene (hereafter abbreviated as TMPD), catechol and hydrogen peroxide, and discussed on the reactivities in relation to their possible molecular structures.

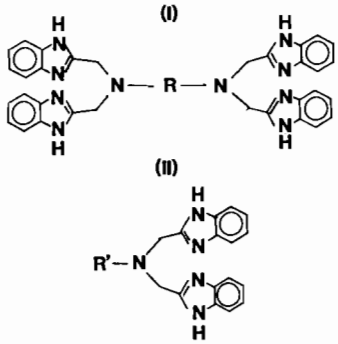

Fig. 1. Chemical structures of the ligands used in this study, and their abbreviations. (I), R = $-(CH_2)_4-$ L-4; R = $-(CH_2)_6-$ L-6; R = $-CH_2C_6H_4CH_2-$ (1,4) L-px and R = $-CH_2CH(OH)CH_2-$ H(L-3′); (II) R′ = H ibz.

Experimental

Preparations

The ligands cited in Fig. 1 were prepared according to the published methods: ibz [14], L-4 [15], L-6 [15], L-px [5] and H(L-3′) [17]. The iron(III) complexes, $Fe(ibz)Cl_3$, **1** [16], $Fe_2(L\text{-}4)Cl_6$, **2** [17] and $Fe_2(L\text{-}3')Cl_5$, **5** [17] were already reported.

$Fe_2(L\text{-}3')(NO_3)_5 \cdot 2C_2H_5OH$, 7

An ethanol solution (100 ml) containing $Fe(NO_3)_3 \cdot 9H_2O$ (0.002 mol), H(L-3′) (0.001 mol) and triethylamine (0.001 mol) was kept standing for 24 hours at room temperature, and the orange needles deposited were recrystallized from an ethanol solution. Found. C, 41.66%, H, 3.89% and N, 18.88%. Calcd. for $Fe_2C_{39}H_{45}N_{15}O_{18}$. C, 41.69%, H, 4.04% and N, 18.70%. Similarly, $Fe_2(L\text{-}3')(NO_3)_5 \cdot 4CH_3OH$, **6** was obtained as orange needles from a methanol solution. Found. C, 40.08%, H, 4.26% and N, 18.02%. Calcd. for $Fe_2C_{39}H_{49}N_{15}O_{20}$. C, 40.40%,

*Author to whom correspondence should be addressed.

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H, 4.26% and N, 18.12%. These complexes are soluble in most organic solvents available such as methanol, N,N-dimethylforamide (dmf), N,N-dimethylacetamide and dimethylsulfoxide (dmso), whereas **5** is soluble only in polar solvents, such as dmf and dmso.

$Fe_2(L\text{-}6)Cl_6 \cdot 2H_2O$, 3 and $Fe_2(L\text{-}px)Cl_6 \cdot 3/2H_2O$, 4

These complexes were prepared by a method similar to that described for **2** [17]. Found. C, 46.10%, H, 4.42% and N, 14.02%. Calcd. for **3**. C, 45.77%, H, 4.45% and N, 14.05%. Found. C, 47.66%, H, 3.80% and N, 13.82%. Calcd. for **2**. C, 47.65%, H, 3.90% and N, 13.89%.

Determination of Catalytic Activity of Iron(III) Complexes for O_2 Oxidation of TMPD

The dmf solution (1 ml) of an iron(III) complex and the methanol solution (7 ml) of TMPD were mixed, and the increase of the absorbance at 565 nm of the resulted solution was recorded as a function of time at 288 K, where the concentrations were 2.5×10^{-5} and 2.5×10^{-4} mol dm^{-3} for Fe(III) and TMPD, respectively.

Measurements

The absorption spectra were obtained with a Shimadzu spectrophotometer model UV-240. Cyclic voltammograms were measured with a Yanagimoto P-1000 Voltammetric Analyzer in dmf at 293 K. The concentrations of a complex and supporting electrolyte (tetraethylammonium perchlorate) were about 0.001 and 0.1 mol dm^{-3}, respectively. A three-electrode cell with a glassy carbon as the working electrode and a platinum coil as the auxiliary electrode were used for the measurements. All the potentials were referenced to the redox potential of ferrocene (Fc^+/Fc, +0.4 V *vs.* NHE) [18] as an internal standard.

Results and Discussion

Characterization of Complexes

The magnetic moment of the mononuclear complex **1** is 5.9 BM at 295 K, implying that this complex is of high-spin type. The conductance data (97 ohm^{-1} cm^2 mol^{-1} in 1×10^{-3} mol dm^{-3} methanol solution at 298 K) shows that this complex is a 1:1 electrolyte in the solution [19]. The iron(III) ions in the binuclear complexes, **2**, **3**, and **4** are also of high-spin type [17]. On the other hand, the magnetic moment of **6** is subnormal (μ_{eff} = 4.10 BM at 299 K) and temperature-dependent, as shown in Table I. Based on the magnetic and analytical data, we assume that **6** has an alkoxo-bridged structure, as illustrated in Fig. 2-D. The conductivity measurement on a methanol solution (189 ohm^{-1} cm^2 mol^{-1} for 1×10^{-3} mol dm^{-3} solution at 298 K) reveales that this complex is a 2:1 electrolyte, suggesting a nitrate bridge. The temperature dependence of magnetic susceptibility (90–300 K) of **6** (see Table I) could not be interpreted in terms of the theoretical curve based on the Heisenberg model for a regular octahedron [20]. This may be due to the large deviation of coordination geometry from the regular octahedron.

TABLE I. Temperature Dependence of Magnetic Moment of $Fe_2(L\text{-}3')(NO_3)_5 \cdot 4CH_3OH$.

T/K	μ_{eff}/BM[a]	T/K	μ_{eff}/BM
86.9	2.22	98.8	2.39
112.3	2.57	125.6	2.73
139.1	2.89	152.5	3.03
166.0	3.17	179.2	3.29
192.6	3.40	206.1	3.50
219.6	3.59	233.0	3.68
246.4	3.78	259.5	3.86
273.0	3.94	286.0	4.02
299.3	4.10		

[a] $\mu_{eff} = \sqrt{8\chi T}$.

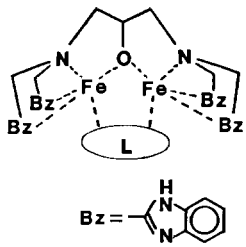

Fig. 2. Assumed structure of 1:1 adduct of $Fe_2(L\text{-}3')(NO_3)_5$- and L. A: L = O_2; B: L = catechol; C: L = H_2O_2; D: L = NO_3^-.

In Fig. 3, the cyclic voltammograms of **1**, **3**, and **6** are shown. The mononuclear complex **1** exhibits one cathodic and one anodic peak separated by ΔE = 120 mV, which should correspond to the redox reaction of Fe^{3+}/Fe^{2+} couple. It is noteworthy that two redox couples were observed forthe binuclear complexes **2**, **3** and **4**, as exemplified by **3** in Fig. 3. The potential ($=\frac{1}{2}(E_{pa} + E_{pc})$) of one redox process at −0.4 V (*vs.* Fc^+/Fc) of **3** is similar to that observed for **1**. On the other hand, another one is observed at more positive potential (−0.25 V *vs.* Fc^+/Fc).

Okawa *et al.* [21] reported that two redox processes were observed in the cyclic voltammograms of the strati-bis type binuclear copper(II) complexes, and concluded that the emergence of the redox process at the positive potential side originates from the electron delocalization due to the overlapping of two coordination planes. In this case, however, the stacking between two iron(III) complexes seems to be difficult because of the steric hindrance between

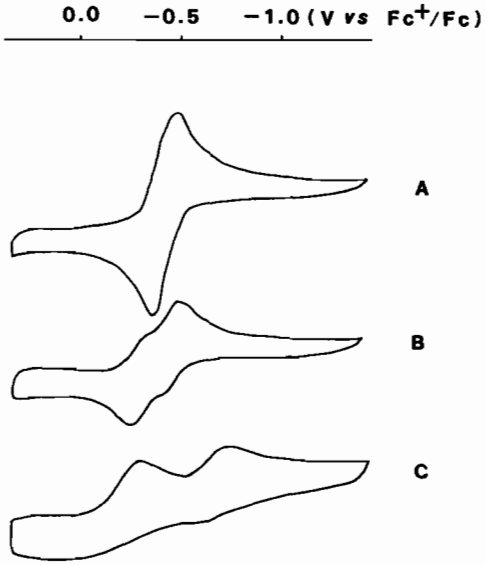

Fig. 3. Cyclic voltammograms (in dmf at 293 K, scan rate = 40 mV/sec): A: $Fe(ibz)Cl_3$; B: $Fe_2(L\text{-}6)Cl_6$; C: $Fe_2(L\text{-}3')(NO_3)_5 \cdot 4CH_3OH$.

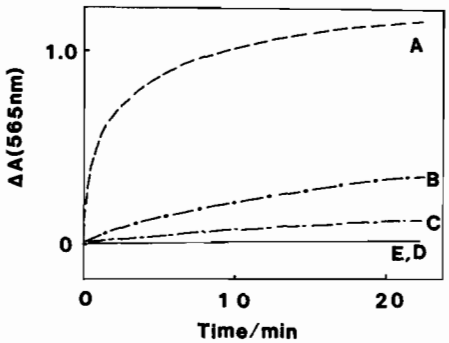

Fig. 4. Time course of $TMPD^+$ formation in the presence of the iron(III) complex. (in dmf/methanol = 1/7 solution, 288 K, $[Fe^{3+}] = 2.5 \times 10^{-5}$ mol dm^{-3}, [TMPD] = 2.5×10^{-4} mol dm^{-3}): A: $Fe_2(L\text{-}3')(NO_3)_5 \cdot 4CH_3OH$; B: $Fe_2(L\text{-}6)Cl_6$; C: $Fe(ibz)Cl_3$; D: $Fe_2(L\text{-}4)Cl_6$; E: $Fe_2(L\text{-}px)Cl_6$.

them, so that other origins should be considered to explain the present results.

Catalytic Activity of the Complexes for the O_2 Oxidation of TMPD

It is known that TMPD is only very slowly oxidized by atmospheric oxygen in solution, but the rection is very much accelerated by the presence of some metal complexes [3, 6, 7]. The catalytic activities of the present complexes have also been subjected to the investigation. The reaction was monitored by measuring the absorbance at 565 nm due to $TMPD^+$ formed, the results being shown in Fig. 4. It should be noted that the binuclear complex, **6** (and also **5** and **7**) exhibited an eminent catalytic

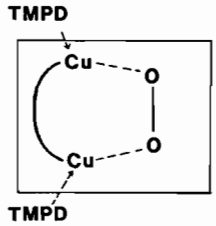

Fig. 5. A model for the reaction of TMPD and the intermediate complex formed from binuclear copper complex and O_2 molecule.

activity among the binuclear iron(III) complexes used in this study.

We reported previously that some binuclear copper(II) complexes showed high catalytic activities for the oxidation of TMPD by O_2 molecule, and pointed out the importance of the intermediate complex formation such as that illustrated in Fig. 5 for the emergence of the catalytic activity; in other words, the determining factor of the catalytic activity is the capability of forming a path for the two-electron transfer process from two copper ions to an O_2 molecule [7, 12]. In the present case, complex **6** (and **5** and **7**) exhibited an eminent catalytic activity among the binuclear complexes studied here. This should be attributed to its alkoxo-bridged structure which can accomodate O_2 molecules, as illustrated in Fig. 2-A. For the other binuclear complexes which have no alkoxo-bridge, the Fe–Fe distance cannot be kept constant so that the formation of the intermediate O_2 complex depends on the steric hindrance between the two coordination spheres and the length of the polyatomic chain. This should greatly reduce the chance to form the intermediate complex. Thus, the present results can be reasonably interpreted in terms of the same principle as that proposed for the copper(II) complexes [12].

Reactions with Catechol or Hydrogen Peroxide

In the previous paper we reported that **1** reacts with catechol to form a green solution, giving a new broad absorption in the range 700–900 nm [16]. It was assumed that this was caused by the chelation of the catechol to the iron(III) ion. The present binuclear iron(III) complexes, except for **5**, **6** and **7**, underwent similar color changes; when catechol was added to a solution of the complex, the color changed from orange to dirty green (*cf.* Fig. 6-D). The product formed by this reaction did not seem to be a simple species since the peak position and contour of the band varied with the complex/catechol ratio, and a definite ratio could not be obtained for the chromophore formed in the solution by the continuous variation method. In contrast to this, the mixed solution of **6** and 4-methylcatechol exhibited a sharper band at 720 nm (see Fig. 6-B)

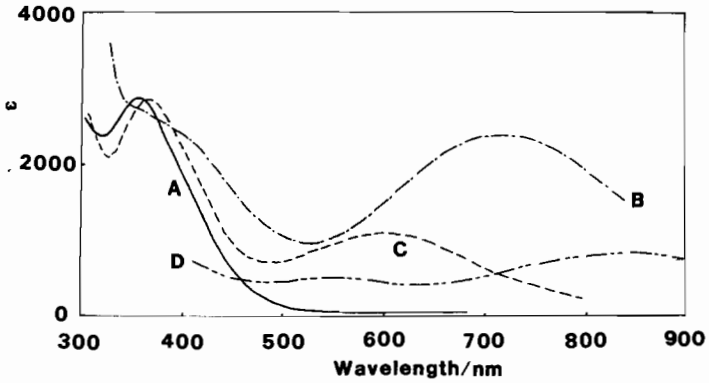

Fig. 6. Absorption spectra (in methanol at 288 K): A: $Fe_2(L\text{-}3')(NO_3)_5 \cdot 4CH_3OH$, **6**; B: **6** + 4-methycatechol([catechol]/[Fe^{3+}] = 10); C: **6** + H_2O_2([H_2O_2]/[Fe^{3+}] = 10); D: **2** + 4-methycatechol([catechol]/[Fe^{3+}] = 10).

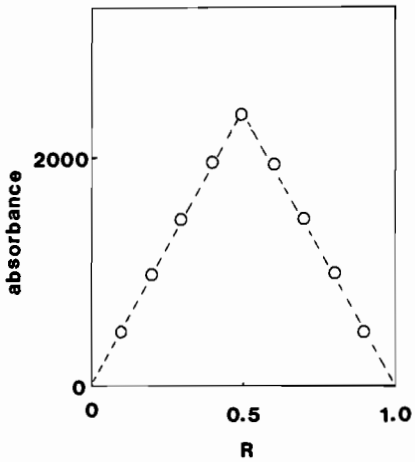

Fig. 7. The absorbance at 720 nm in the **6** and 4-methylcatechol system (in methanol at 288 K). R denotes the ratio of [**6**]/([**6**] + [catechol]).

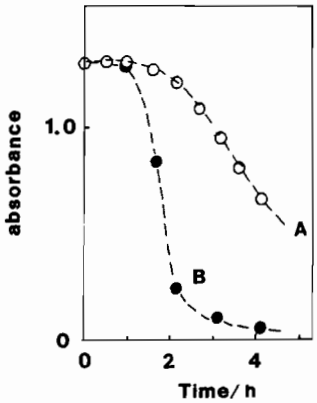

Fig. 8. Time course of the blue-species formed from **6** and H_2O_2 (methanol solution at 288 K): A: [Fe^{3+}] = [H_2O_2] = 1×10^{-3} mol dm^{-3}; B: solution (A) + 2,4-di-tert-butylphenol([phenol] = 2×10^{-2} mol dm^{-3}).

whose peak position and contour was not changed by the variation of the complex/catechol ratio, and the complex/catechol ratio was invariably determined as 1:1 (see Fig. 7). The most probable structure of the 1:1 adduct is illustrated in Fig. 2-B.

We have already reported that many binuclear copper(II) complexes show high catalytic activities for the decomposition of hydrogen peroxide [11, 13]. In this study we have found that **1** decomposes hydrogen peroxide. When hydrogen peroxide was added to the orange solutions of **1**, **2**, **3** and **4**, no color change was observed. In contrast to this, orange methanol solutions of **6** were turned blue by the addition of hydrogen peroxide, yielding a new absorption band at 600 nm (ϵ/Fe = 1300), as shown in Fig. 6-C. Similar color changes were also observed in the solutions of dmf, dimethylacetamide, and dmso. In aqueous solution the color changed from orange to violet (band maximum, 550 nm). The continuous variation method investigation has revealed that the blue-species is due to the formation of the 1:1 adduct of **6** and hydrogen peroxide. Thus it is reasonable to assume that the blue-species is a peroxide adduct of the binuclear iron(III) complex [22], as illustrated in Fig. 2-C, similar to the catechol adduct (Fig. 2-B). Based on the resonance Raman measurements, the O_2 complex of the binuclear iron(II) complex (*e.g.*, oxy-hemerythrin) can be alternatively formulated as a peroxide adduct of the iron(III) complex [23]. Similar results were also obtained for the oxy-hemocyanin [24, 25] and oxy-tyrosinase [26]. Thus, we may conclude that the blue-species obtained in this study is the first model compound for the oxy-hemerythrin.

The facile formation of the 1:1 complex formation between **6** and catechol or hydrogen peroxide supports the assumption of facile formation of the intermediate O_2 complex for **6**, as proposed in Fig. 2-A.

The blue-species thus formed gradually changed to orange (*cf.* Fig. 8-A), and this solution was again changed to blue by the addition of hydrogen peroxide. As shown in Fig. 8-B, the addition of 2,4-di-tert-butylphenol accelerated the decomposition

of the blue-species. After standing the methanol solution (25 ml) containing **6** (5×10^{-6} mol), H_2O_2 (1×10^{-3} mol) and 2,4-di-tert-butylphenol (5×10^{-4} mol) for 4 days at room temperature, we could isolate the corresponding 3,5-di-tert-butylquinone [27] (yield 5.2% based on the phenol). The formation of the quinone was not detected when **1** was used instead of **6**, suggesting that the blue-species reacts with the phenol to produce the catechol [28].

In conclusion, the eminent properties of magnetism, reactivity and catalytic activity of **6** (and also **5** and **7**) should be due to the unique alkoxo-bridged structure of this complex.

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