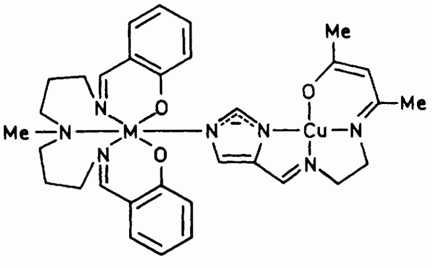
Synthesis and Characterization of Imidazolate-bridged Iron(III)–Copper(II) and Manganese(III)–Copper(II) Binuclear Complexes†

Naohide Matsumoto,* Yonezo Maeda, and Hisashi Okawa
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan
Toshifumi Akui, Tetsuro Kawaji, and Akira Ohyoshi
Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kurokami 2-39-1, Kumamoto 860, Japan
Masahito Kodera, Hiroki Oshio, and Sigeo Kida
Institute for Molecular Science, Okazaki National Institute, Okazaki 444, Japan

Imidazolate-bridged iron(III)–copper(II) and manganese(III)–copper(II) binuclear complexes $[FeL^1CuL^2][BPh_4]$ (**1**) and $[MnL^1CuL^2][BPh_4]$ (**2**) have been prepared and characterized, where H_2L^1 is 4-methyl-*N,N'*-bis(salicylidene)-4-azaheptane-1,7-diamine and H_2L^2 denotes the unsymmetrical quadridentate ligand 4-(6-methyl-8-oxo-2,5-diazanona-1,5-dienyl)imidazole. The magnetic susceptibility data indicated that the spin ground states of the complexes (**1**) and (**2**) are $S = 2$ and $\frac{3}{2}$, respectively, which are produced by antiferromagnetic interaction operating between high-spin iron(III) $S_1 = \frac{5}{2}$ [manganese(III) $S_1 = 2$] and copper(II) $S_2 = \frac{1}{2}$ ions through the L^2 imidazolate group. The Mössbauer spectrum of (**1**) measured at 4.2 K showed a doublet with $\Delta = 1.30$ mm s^{-1} and $\delta_d = 0.49$ mm s^{-1}, consistent with high-spin iron(III). The e.s.r. spectrum of a powdered sample of complex (**1**) measured at 20 K showed no signals, while that of (**2**) showed several signals.

Discrete imidazolate-bridged mixed-metal complexes are of current interest, since such a binuclear structure has been found in the active site of bovine erythrocyte superoxide dismutase (Zn^{II}–Cu^{II})[1] and has been one of the candidate structures for the active site of the resting form of cytochrome *c* oxidase (high-spin Fe^{III}–Cu^{II}).[2] We have reported[3–5] an effective synthetic route to imidazolate-bridged binuclear complexes which have the structural characteristics of the metal enzymes, *i.e.* mixed-metal different co-ordination geometries in the binuclear unit. A copper(II) complex with an unsymmetrical quadridentate ligand bearing an imidazole (or an imidazolate) moiety $[Cu(HL^2)]^+$ (or $[CuL^2]$) plays the key role in producing imidazolate-bridged heterometal binuclear complexes, since $[Cu(HL^2)]^+$ or $[CuL^2]$ can function as an unidentate ligand through the imidazolate nitrogen atom to another metal complex. The key copper compound reacts with a metal complex which can provide a co-ordination site by increasing its co-ordination number or losing a weakly bound ligand to give an imidazolate-bridged binuclear complex. In previous studies[3,4] this synthetic procedure was applied to the homometal system copper(II)–copper(II), and the crystal structures and magnetic properties of the binuclear copper(II) complexes thus obtained were reported.

In this study, the same synthetic principle has been applied to the preparation of imidazolate-bridged mixed-metal systems Fe^{III}–Cu^{II} and Mn^{III}–Cu^{II} which are interesting in view of their magnetism and as model compounds for cytochrome *c* oxidase. The schematic structures of the complexes $[ML^1CuL^2][BPh_4]$ (**1**; M = Fe^{III}) and (**2**; M = Mn^{III}) are shown below. We report here their synthesis, spectral and magnetic properties.



(**1**) M = Fe^{III}
(**2**) M = Mn^{III}

Experimental

Synthesis.—$[CuL^2]\cdot0.5CHCl_3$. The complex $[Cu(HL^2)][ClO_4]$ was prepared by the method reported previously.[4] The complex (10 mmol) was converted into the deprotonated form $[CuL^2]$ by treating with NaH (10 mmol) in chloroform (50 cm^3). The deprotonated form (imidazolate) was obtained as dark green crystals with 0.5 molecule of chloroform of crystallization. The green colour of the complex changes to red upon loss of the solvent when heated. A mass loss corresponding to $0.5CHCl_3$ was observed at 41—93 °C. The green complex was used for the synthesis of mixed-metal complexes.

$[FeL^1][BPh_4]\cdot2MeOH$. The quinquedentate Schiff-base ligand H_2L^1 was prepared by the reaction of salicylaldehyde and bis(3-aminopropyl)methylamine in the mol ratio of 2:1 in methanol. The ligand solution was used subsequently for the synthesis of the iron(III) complex $[FeClL^1]$.[6] The latter complex (2.21 g, 5 mmol) was dissolved in the minimum amount of chloroform and filtered. To the filtrate was added a methanol solution (100 cm^3) of sodium tetraphenylborate (1.71 g, 5 mmol). The resulting solution was warmed on a water-bath for 20 min and left to stand at ambient temperature for several hours. The black needle crystals which precipitated were collected by filtration, washed with methanol, and dried (Found: C, 71.60; H, 6.85; N, 5.60. Calc. for $C_{47}H_5BFeN_3O_4$: C, 71.50; H, 6.65; N, 5.30%), m.p. 175—177 °C.

$[Fe(mim)L^1][BPh_4]$. To a methanol solution (100 cm^3) of $[FeL^1][BPh_4]\cdot2MeOH$ (789 mg, 1 mmol) was added a methanol solution (10 cm^3) of *N*-methylimidazole (mim) (82 mg, 1 mmol). The solution was warmed on a water-bath for

---

† *Supplementary data available* (No. SUP 56740, 5 pp.): magnetic susceptibility data, e.s.r. spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: G = 10.4 T.

10 min and left to stand for several hours at room temperature. The black needle crystals which precipitated were collected by filtration, washed with methanol, and dried (Found: C, 72.75; H, 6.40; N, 8.60. Calc. for $C_{49}H_{51}BFeN_5O_2$: C, 72.80; H, 6.35; N, 8.65%), m.p. 165 °C, Λ_M 95 S cm^2 mol^{-1} (in acetonitrile).

$[MnL^1][BPh_4]\cdot 2MeOH$. To a solution of ligand (1 mmol) was added a methanol solution (20 cm^3) of manganese(III) acetate dihydrate (268 mg, 1 mmol). The solution was warmed on a water-bath for 10 min and filtered. To the filtrate was added a methanol solution (20 cm^3) of sodium tetraphenylborate (342 mg, 1 mmol). After several hours, the dark green crystals which precipitated were collected by filtration and dried (Found: C, 71.70; H, 6.70; N, 5.40. Calc. for $C_{45}H_{45}BMnN_3O_2\cdot$2MeOH: C, 71.50; H, 6.75; N, 5.30%), m.p. 185 °C, Λ_M 92 S cm^2 mol^{-1} (acetonitrile).

$[Mn(mim)L^1][BPh_4]$. To a hot methanol solution (50 cm^3) of $[MnL^1][BPh_4]\cdot 2MeOH$ (790 mg, 1 mmol) was added *N*-methylimidazole (164 mg, 2 mmol). The solution was warmed on a water-bath for 10 min and filtered. The filtrate was left to stand at ambient temperature. Dark green crystals precipitated and were collected by filtration, washed with methanol, and dried (Found: C, 72.75; H, 6.45; N, 8.25. Calc. for $C_{49}H_{51}BMnN_5O_2$: C, 72.85; H, 6.35; N, 8.25%), m.p. 163 °C, Λ_M 96 S cm^2 mol^{-1} (acetonitrile).

$[FeL^1CuL^2][BPh_4]$ (**1**). The complex can be prepared by methods (*A*) and (*B*).

Method (*A*). The complex $[FeClL^1]$ (221 mg, 0.5 mmol) was dissolved in methanol (100 cm^3) and filtered. To the filtrate was added a methanol solution (50 cm^3) of $[CuL^2]\cdot 0.5CHCl_3$ (171 mg, 0.5 mmol) and the mixture was stirred for 30 min at room temperature and then filtered. To the filtrate was added a methanol solution (10 cm^3) of sodium tetraphenylborate (171 mg, 0.5 mmol). The resulting solution was warmed on a water-bath for 5 min and left to stand at room temperature for several hours. Black fine crystals precipitated and were collected by filtration, washed with methanol and diethyl ether, and dried in air.

Method (*B*). To a hot methanol solution (50 cm^3) of $[FeL^1][BPh_4]\cdot MeOH$ (363 mg, 0.5 mmol) was added a methanol solution (30 cm^3) of $[CuL^2]\cdot 0.5CHCl_3$ (171 mg, 0.5 mmol). The mixture was stirred for 5 min on a water-bath and then filtered. After several hours, black fine crystals precipitated and were collected by filtration, washed with methanol and diethyl ether, and dried in air (Found: C, 66.35; H, 5.95; Cu, 6.25; Fe, 5.85; N, 9.60. Calc. for $C_{56}H_{59}BCuFeN_7O_3$: C, 66.70; H, 5.90; Cu, 6.30; Fe, 5.55; N, 9.70%), m.p. 189 °C, Λ_M 94 S cm^2 mol^{-1} (acetonitrile).

$[MnL^1CuL^2][BPh_4]$ (**2**). This complex was prepared similarly to $[FeL^1CuL^2][BPh_4]$ [method (*B*)], but $[MnL^1][BPh_4]\cdot 2MeOH$ instead of $[FeL^1][BPh_4]\cdot 2MeOH$ was used (Found: C, 66.65; H, 5.90; Cu, 6.05; Mn, 5.55; N, 9.80. Calc. for $C_{56}H_{59}BCuMnN_7O_3$: C, 66.75; H, 5.90; Cu, 6.30; Mn, 5.45; N, 9.75%), m.p. 174 °C, Λ_M 87 S cm^2 mol^{-1} (acetonitrile).

Physical Measurements.—Elemental analyses for C, H, and N were obtained at the Technical Service Center of Kumamoto University. Elemental analyses for Fe, Mn, and Cu were carried out on a Hitachi A-508 atomic absorption spectrometer. Melting points were measured on a Yanagimoto micro-melting point apparatus and were uncorrected. Electrical conductivities were measured on a Denki Kagaku Keiki AOC-10 digital conductometer on *ca*. 10^{-3} mol dm^{-3} solutions. Infrared spectra were recorded with a JASCO A-702 spectrophotometer, electronic absorption spectra on a Hitachi UV-323 spectrophotometer in dichloromethane solutions. Magnetic susceptibilities were obtained for 4.3—85 K by use of a HOXAN HSM-2000 SQUID magnetometer and for 85—300 K by the Faraday method. Data were corrected for magnetization of the sample holder and for the diamagnetism of the component atoms by the use of Pascal's constants. The molar effective magnetic moments were calculated by the equation $\mu_{eff.} = 2.828\sqrt{\chi_M T}$. E.s.r. spectra were measured on a JEOL JES-FE2XG spectrometer (*X*-band microwave unit, 100-KHz filed modulation) equipped with an Air Product LTD-3-110 liquid-helium transfer system. The microwave frequency was monitored with a Takeda Riken TR5212 microwave counter, and the resonance magnetic field values of the signals were measured with an n.m.r. filed meter (ECHO Electronics Co.).

Results and Discussion

Synthesis.—Despite great interest in imidazolate-bridged iron(III)–copper(II) binuclear complexes as models for the active site of cytochrome *c* oxidase, few examples are known so far.[7,8] In our synthetic approach to imidazolate-bridged iron(III)–copper(II) binuclear complexes, $[CuL^2]$ was used as the copper(II)-site component, because (1) the imidazolate moiety in this complex is incorporated in an unsymmetrical quadridentate ligand so that the complex can function as an unidentate ligand through the imidazolate nitrogen atom to iron(III), (2) the complex is fairly soluble and stable as mononuclear species of the imidazolate form in common organic solvents. Thus, $[CuL^2]$ is a key material for the synthesis of mixed-metal imidazolate-bridged polynuclear complexes. As the iron(III) site, $[FeL^1][BPh_4]$ or $[FeClL^1]$ was employed, because they can provide a co-ordination site by increasing their co-ordination number or losing a weakly bound ligand, and it is known that the reaction of the complexes with various imidazole derivatives (X) gives six-co-ordinated complexes $[FeXL^1]^+$.[6]

The reaction of $[FeClL^1]$ or $[FeL^1][BPh_4]$ with $[Cu(HL^2)][ClO_4]$ (imidazole form) in the presence of triethylamine or sodium methoxide as a base generally leads to ill characterized materials contaminated by $Fe(OH)_3$, though good results were obtained when this method was applied to the copper(II)–copper(II) system.[3,4] This is presumably due to the fact that the addition of triethylamine or sodium methoxide to the mixed solution of $[FeClL^1]$ or $[FeL^1][BPh_4]$ and $[Cu(HL^2)][ClO_4]$ results in the precipitation of $Fe(OH)_3$ rather than deprotonation of the imidazole proton of $[Cu(HL^2)]^+$. In order to avoid this, the deprotonated complex $[CuL^2]$ (imidazole form) was first isolated and used for the synthesis of the iron(III)–copper(II) binuclear complex (**1**). Mixing $[FeL^1][BPh_4]\cdot 2MeOH$ with $[CuL^2]$ in methanol leads to the formation of crystalline (**1**). The same synthetic procedure was applicable to the synthesis of $[MnL^1CuL^2][BPh_4]$ (**2**). The elemental analyses of compounds (**1**) and (**2**) thus obtained are consistent with the 1:1 (M:Cu) formulation. The molar electrical conductances of complexes (**1**) and (**2**) in acetonitrile are 94 and 87 S cm^2 mol^{-1}, respectively, consistent with 1:1 electrolytes.[9]

Electronic Absorption Spectra.—$[FeL^1CuL^2][BPh_4]$ (**1**). The co-ordination of the imidazolate nitrogen atom of $[CuL^2]$ to the iron(III) of $[FeL^1]^+$ is easily detected from the electronic spectrum of complex (**1**). The electronic spectrum of $[FeL^1CuL^2][BPh_4]$ (**1**), along with those of the component and reference complexes $[CuL^2]$, $[FeL^1][BPh_4]$, and $[Fe(mim)L^1][BPh_4]$, are shown in Figure 1, where all spectra were measured in dichloromethane solutions at room temperature. All iron(III) complexes exhibit two strong absorptions (ε 3 000—6 000 dm^3 mol^{-1} cm^{-1}) in the region 340—700 nm assignable to charge-transfer transitions, while $[CuL^2]$ exhibits a broad absorption at 540 nm (ε = 210 dm^3 mol^{-1} cm^{-1}) assignable to a *d–d* transition. The component iron(III) complex

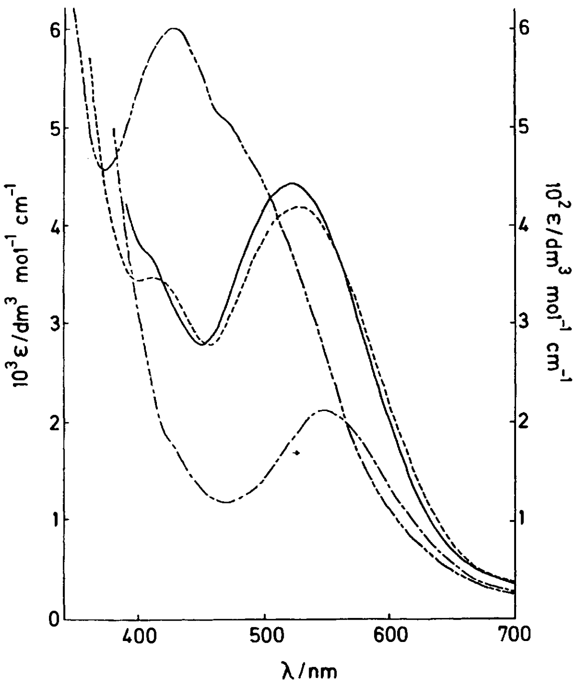


Figure 1. Electronic absorption spectra of $[FeL^1CuL^2][BPh_4]$ (—), and the component and reference complexes $[FeL^1][BPh_4]\cdot 2MeOH$ (— · · —), $[CuL^2]\cdot 0.5CHCl_3$ (— · —), and $[Fe(mim)L^1][BPh_4]$ (· · · · ·) in dichloromethane at room temperature

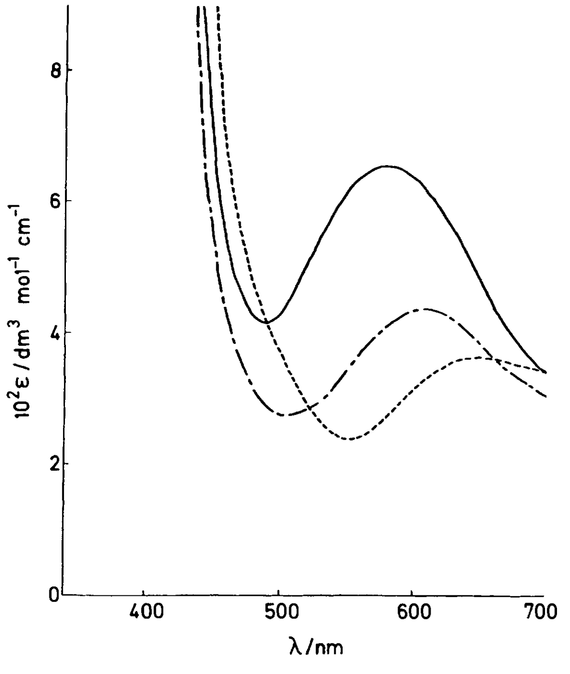


Figure 2. Electronic absorption spectra of $[MnL^1CuL^2][BPh_4]$ (——), and the component and reference complexes $[MnL^1][BPh_4]\cdot 2MeOH$ (· · · · ·) and $[Mn(mim)L^1][BPh_4]$ (— · —) in dichloromethane

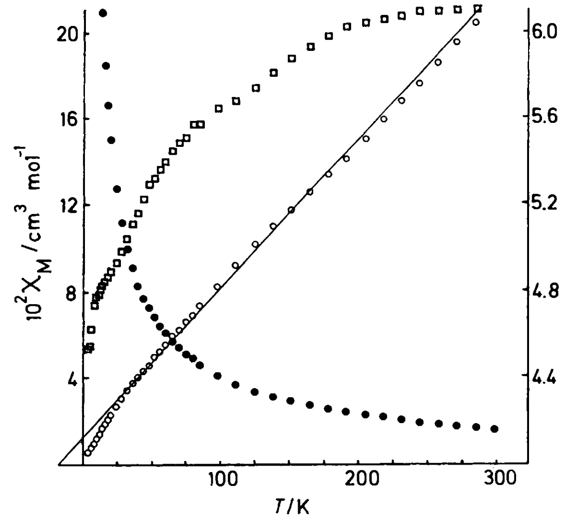


Figure 3. Temperature dependence of the molar magnetic susceptibility (●), reciprocal magnetic susceptibility (○), and effective magnetic moment (□) for $[FeL^1CuL^2][BPh_4]$

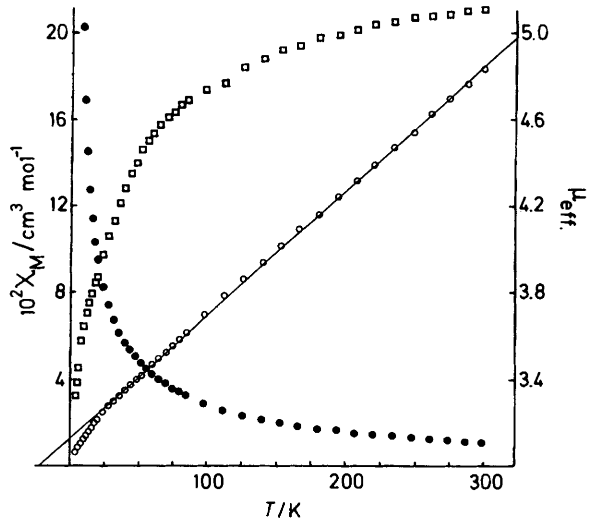


Figure 4. Temperature dependence of the molar magnetic susceptibility (●), reciprocal magnetic susceptibility (○), and effective magnetic moment (□) for $[MnL^1CuL^2][BPh_4]$

$[FeL^1][BPh_4]$ has two absorptions at 430 (ε = 6 020) and at 480 (ε = 4 870 dm^3 mol^{-1} cm^{-1}), while the *N*-methylimidazole complex $[Fe(mim)L^1][BPh_4]$ has two strong absorptions at 414 (ε = 3 450) and 528 (ε = 4 200 dm^3 mol^{-1} cm^{-1}). These facts indicate that the spectral change is due to co-ordination of the imidazole nitrogen atom to the iron(III) of $[FeL^1]^+$. The electronic spectrum of $[Fe(mim)L^1][BPh_4]$ is similar to that of $[FeL^1CuL^2][BPh_4]$ in the absorption maxima and coefficients. This implies that the imidazolate nitrogen atom of $[CuL^2]$ co-ordinates to the iron(III) in the mixed-metal complex (**1**). Since the imidazolate moiety of $[CuL^2]$ is incorporated in the quadridentate ligand, the spectral data indicate that there is an iron(III)–copper(II) binuclear structure bridged through an imidazolate group even in dichloromethane solution.

$[MnL^1CuL^2][BPh_4]$ (**2**). The electronic spectra of $[MnL^1CuL^2][BPh_4]$ and its component and reference complexes measured in dichloromethane are shown in Figure 2. The spectrum of the manganese(III) site exhibits a broad absorption at 646 nm (ε = 360 dm^3 mol^{-1} cm^{-1}) assignable to a *d–d* transition. The *d–d* transition of the *N*-methylimidazole adduct $[Mn(mim)L^1][BPh_4]$ shifts to lower wavelength at 608 nm (ε = 440 dm^3 mol^{-1} cm^{-1}), although there is no drastic difference between these two spectra as observed for the corresponding iron(III) complexes. The spectrum of [MnL^1-CuL^2][BPh$_4$] exhibits a broad absorption at 578 nm (ε = 650 dm^3 mol^{-1} cm^{-1}) which is roughly consistent with superimposition of the spectrum of the copper(II) site [CuL^2] on that of the manganese(III) reference complex [Mn(mim)L^1][BPh$_4$].

Magnetic Properties.—The magnetic properties of complexes (**1**) and (**2**) are shown in Figures 3 and 4, respectively, in the forms of plots of χ_M *vs.* T, $1/\chi_M$ *vs.* T, and $\mu_{eff.}$ *vs.* T, where χ_M is the molar magnetic susceptibility, $\mu_{eff.}$ the molar effective magnetic moment, and T the temperature. The numerical values of T, χ_M, and $\mu_{eff.}$ are given in SUP 56740. The plots of $1/\chi_M$ *vs.* T are nearly linear in the temperature range 50—300 K and obey the Curie–Weiss law [$\chi_M = C(T + \theta)$] with positive Weiss constants. This suggests that there is an intra- or/and intermolecular antiferromagnetic interaction.

[FeL^{1}CuL^2][BPh$_4$] (**1**). The molar effective magnetic moment at room temperature is 6.1. This value is nearly equal to the spin-only value (6.16) of a binuclear system ($S_1 = \frac{5}{2}$, $S_2 = \frac{1}{2}$) assuming non-magnetic interaction between two magnetic centres. Upon cooling, the molar magnetic moment decreases from 6.11 at 297 K to 4.53 at 4.3 K. In the plot of $\mu_{eff.}$ *vs.* T there seems to be a point of inflection at *ca.* 25 K. At this temperature the magnetic moment is 4.9, consistent with the spin-only value (4.90) expected for a system with $S = 2$. The rather abrupt decrease of $\mu_{eff.}$ below 25 K is due to a zero-field splitting of the ground state $S = 2$. The magnetic data indicate that the spin state of the iron(III) in this complex is high spin ($S = \frac{5}{2}$) and the spin ground state of (**1**) is $S = 2$ due to an antiferromagnetic interaction operating between a high-spin iron(III) ($S = \frac{5}{2}$) and a copper(II) ion ($S = \frac{1}{2}$). The Mössbauer spectrum at liquid-helium temperature shows a doublet with $\Delta E = 1.30$ mm s^{-1} and $\delta_d = 0.49$ mm s^{-1}, indicating that the iron(III) is high spin even at 4.2 K. The *X*-band e.s.r. spectrum of a powdered sample of (**1**) at 20 K showed no signals. This may be consistent with the magnetically deduced conclusion that the ground state of complex (**1**) is $S = 2$. On the other hand, the spectrum of a frozen solution (dichloromethane) at 20 K showed signals at 1 650 G characteristic of high-spin iron(III) and a signal at 3 230 G assignable to that of $S = \frac{1}{2}$ copper(II) in a tetragonal field. These signals can be attributed to the species [FeL^1]$^+$ and [CuL^2] produced by partial dissociation of the imidazolate-bridged species in dichloromethane solution.

The active site of the respiratory enzyme cytochrome *c* oxidase has been postulated to contain an high-spin iron(III) linked to a Cu^{II} through a bridging group, in which these two metal ions are strongly magnetically coupled ($J > -200$ cm^{-1})[2] and the metal enzyme is e.s.r. silent. As the bridging group, an imidazolate group,[2] oxygen,[10] or sulphur atom[11] has been postulated. The present complex (**1**) can be a model compound for the enzyme in the sense that the complex assumes a binuclear structure containing a high-spin iron(III) linked to copper(II) through an imidazolate bridge, the ground state of the complex is $S = 2$, and the complex is e.s.r. silent.

[MnL^{1}CuL^2][BPh$_4$] (**2**). The molar effective magnetic moment at room temperature is 5.1. This value is nearly equal to the spin-only value (5.20) of a binuclear system ($S_1 = 2$, $S_2 = \frac{1}{2}$) assuming non-magnetic interaction between the two magnetic centres. Upon cooling, the molar effective magnetic moment decreases from 5.11 at 299 K to 3.31 at 4.3 K. There seems to be a point of inflection at *ca.* 20 K. At this temperature, $\mu_{eff.}$ is 3.86 which is consistent with the spin-only value (3.87) expected for a system with $S = \frac{3}{2}$. The rather abrupt decrease of $\mu_{eff.}$ below 25 K is due to a zero-field splitting of the ground state. The magnetic data indicate that the spin state of the manganese(III) in complex (**2**) is high spin ($S = 2$) and an antiferromagnetic interaction between a high-spin manganese(III) and a copper(II) ion is operating. E.s.r. spectra of a powdered sample and of a frozen dichloromethane solution at 20 K were measured (SUP). The spectrum of the powdered sample exhibits several broad resonances probably due to the spin ground state of $S = \frac{3}{2}$, although their assignments have not yet been made.

Acknowledgements

This work was carried out as a Joint Research Program of the Institute for Molecular Science, Okazaki National Institute. We are indebted for financial support from the Ministry of Education, Science and Culture of Japan.

References

1 J. S. Richardson, K. A. Thomas, B. H. Rubin, and D. C. Richardson, *Proc. Natl. Acad. Sci. U.S.A.*, 1975, **72**, 1349.
2 M. F. Tweedle, L. J. Wilson, L. Garcis-Iriguez, G. T. Babcock, and G. J. Palmer, *J. Biol. Chem.*, 1978, **253**, 8065.
3 N. Matsumoto, H. Murakami, T. Akui, J. Honbo, H. Okawa, and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1609.
4 N. Matsumoto, T. Akui, H. Murakami, J. Kanesaka, A. Ohyoshi, and H. Okawea, *J. Chem. Soc., Dalton Trans.*, 1988, 1021.
5 N. Matsumoto, J. Kanesaka, A. Ohyoshi, M. Nakamura, S. Kohata, and H. Okawa, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3056.
6 N. Matsumoto, S. Ohta, C. Yoshimura, A. Ohyoshi, S. Kohata, H. Okawa, and Y. Maeda, *J. Chem. Soc., Dalton Trans.*, 1985, 2575.
7 S. E. Desseens, C. L. Merrill, R. J. Saxton, R. L. Ilaria, J. W. Lindsey, and L. J. Wilson, *J. Am. Chem. Soc.*, 1982, **104**, 4357.
8 C. T. Brewer and G. A. Brewer, *Inorg. Chem.*, 1987, **26**, 3420.
9 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
10 R. J. Saxton, L. W. Olson, and L. J. Wilson, *J. Chem. Soc., Chem. Commun.*, 1982, 984.
11 C. K. Schauer, K. Akabori, C. M. Elliot, and O. P. Anderson, *J. Am. Chem. Soc.*, 1984, **106**, 1127.

Received 3rd *May* 1988; *Paper* 8/01716F