Mixed-valence Dinuclear Iron Complexes with a Nonadentate Polypyridine Ligand: High-spin Iron(II)–Low-spin Iron(III)†

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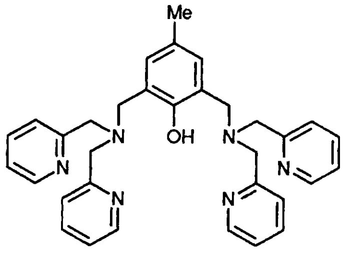
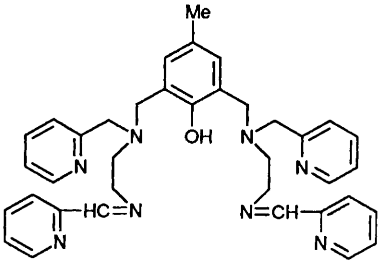
Dinuclear iron(II,III) complexes $[Fe_2L(O_2CMe)][O_2CMe]X_2$ with a nonadentate ligand HL, *i.e.* 4-methyl-2,6-bis[*N*-(2-pyridylmethyl)-*N*-(2-pyridylmethyleneaminoethyl)aminomethyl]phenol, and X = PF_6^- (**1**) or BPh_4^- (**2**) have been prepared. Their Mössbauer spectra consist of two quadrupole doublets due to high-spin iron(II) and low-spin iron(III). The magnetic susceptibilities are consistent with this. Cyclic voltammograms in dried acetonitrile showed a quasi-reversible redox couple with $E_1 = -0.07$ V and an irreversible redox couple with $E_2 = 0.58$ V *vs.* saturated calomel electrode for **1**, corresponding to a comproportionation constant of 1.0×10^{12}. No visible or near-infrared bands due to intervalence electron transitions between iron-(II) and -(III) were observed.

Mixed-valence iron(II,III) complexes have been intensively studied in recent years since it is known that dinuclear iron clusters in the active sites of metalloproteins play an important role in biological systems such as haemerythrin,[1,2] the R2 protein of ribonucleotide reductase,[3] methane monooxygenase,[4–6] and purple acid phosphatase,[7–9] and there is a hope that dinuclear polymers will be able to provide new electronic materials. Studies of synthetic dinuclear $Fe^{II}Fe^{II}$ and $Fe^{II}Fe^{III}$ units[10] which mimic physicochemical properties found for the above proteins are rare in comparison with those of their $Fe^{III}Fe^{III}$ analogues.[11] The complex $[Fe_2(bpmp)(O_2CMe)_2]^{2+}$ {bpmp = 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-methylphenol} and analogues have been investigated;[12,13] when the analogues contain long-chain carboxylate ligands, they show averaged valence states between high-spin Fe^{II} and Fe^{III}.[14,15]

In order to study electronic transitions between atoms of different spin states, the compound HL promising a stronger ligand field than that of bpmp was synthesized and applied to the formation of mixed-valence dinuclear complexes with similar co-ordination moieties. The significant difference between the physical properties of the resulting complexes **1** and **2** and bpmp complexes should provide important insights into the magnetic and electronic interactions of dinuclear iron centres.



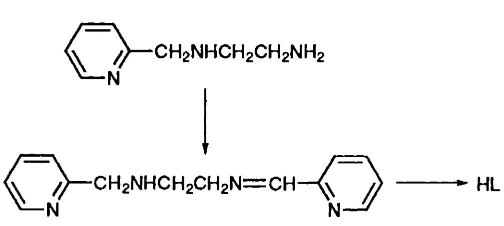
bpmp



HL

Experimental

Materials.—*N*-2-Pyridylmethylethane-1,2-diamine was synthesized according to the literature.[12] 2-Chloroethylamine monohydrochloride (Tokyo Kasei Kogyo; 24 g) was neutralized with saturated aqueous K_2CO_3 (in two 12 g portions to avoid generation of heat; the neutralised portions were recombined). After removal of the precipitated KCl, the base-free solution was added with rapid stirring to a solution of 2-(aminomethyl)pyridine (Tokyo Kasei Kogyo, 44 g) in ethanol. The reaction mixture was then refluxed for 2 h. The ethanol was removed by rotary evaporation, the residue poured onto crushed ice, and the mixture neutralized with 25% KOH followed by an excess of KOH pellets. The dark orange-brown solution was extracted several times with $CHCl_3$. After drying with anhydrous $MgSO_4$ and removal of the $CHCl_3$, the residue was distilled under vacuum. After distillation the product was yellow and yielded a poor NMR spectrum. A colourless non-viscous liquid was obtained by distilling twice. The ^1H NMR spectrum showed peaks at δ 7.0–8.7 (aromatic protons), 3.9 and 2.8 (methylene protons), and 1.6 (amine protons) with area ratios of 4:2:4:3 in agreement with the calculated ratio.



Scheme 1

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† *Supplementary data available* (No. SUP 57 105, 4 pp.): infrared and reflectance spectra, temperature dependence of magnetic susceptibility.

Non-SI units employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

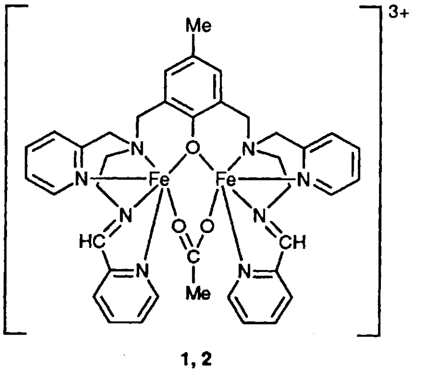
N-(2-pyridylmethyl)-*N*′-(2-pyridylmethylene)ethane-1,2-diamine was prepared as follows. A methanol (100 cm^3) solution of the previous compound (35 g) was added slowly to a methanol (100 cm^3) solution of pyridine-2-carbaldehyde (Tokyo Kasei Kogyo, 25 g) and permitted to stand for 1 h with stirring. The required compound was obtained upon distillation under reduced pressure (5 mmHg, *ca.* 665 Pa) at 150 °C.

4-*Methyl*-2,6-*bis*[*N*-(2-*pyridylmethyl*)-*N*-(2-*pyridylmethyleneaminoethyl*)*aminomethyl*]*phenol* (HL). The above compound (2.4 g) was added to a methanol (50 cm^3) solution of triethylamine (1.02 g). A methanol (50 cm^3) solution of 2,6-bis-(chloromethyl)-4-methylphenol (1.0 g) was added dropwise at < 10 °C. The resulting solution was stirred for 30 min and methanol was removed by evaporation in vacuum. The residue was dissolved in chloroform and washed several times with water. This chloroform solution was dried over anhydrous sodium sulfate and chloroform was removed by rotary evaporation. The residue was used as HL.

Preparations of $[Fe_2L(O_2CMe)][O_2CMe][PF_6]_2$ **1** *and* $[Fe_2L(O_2CMe)][O_2CMe][BPh_4]_2$ **2**.—Complex **1** was prepared using a deoxygenated solvent under a nitrogen atmosphere. A mixture of HL (0.62 g, 1 mmol), acetic acid (0.12 g, 1.2 mmol) and triethylamine (1.02 g, 1 mmol) in methanol (20 cm^3) was added to a mixture of $FeCl_2 \cdot 4H_2O$ (0.24 g, 1.2 mmol) and $NaPF_6$ (0.20 g, 1.2 mmol) in methanol (20 cm^3) with stirring. The solution was stirred and added to a mixture of $FeCl_3$ (0.13 g, 0.8 mmol) and $NaPF_6$ (0.13 g, 0.8 mmol) in methanol (20 cm^3). After the solution was allowed to stand for a few minutes, it was concentrated under vacuum. The dark green crystals obtained were filtered off, washed with ethanol and dried *in vacuo*. They were recrystallized several times from acetonitrile–ethanol (Found: C, 43.75; H, 3.85; Fe, 10.00; N, 9.95. Calc. for $C_{41}H_{45}F_{12}Fe_2N_8O_5P_2$: C, 43.50; H, 4.00; Fe, 9.85; N, 9.90%).

Complex **2** was prepared in similar manner using sodium tetraphenylborate instead of $NaPF_6$ (Found: C, 71.95; H, 5.80; Fe, 7.55; N, 7.40. Calc. for $C_{89}H_{85}Fe_2B_2N_8O_5$: C, 72.25; H, 5.80; Fe, 7.55; N, 7.55%).

Measurements.—Magnetic susceptibility measurements were made using an electrobalance type 2002 (Cahn Instrument) by the Faraday method. The temperature was controlled in the range 80–300 K using a model 3700 digital temperature controller (Scientific Instruments); $HgCo(NCS)_4$ was used as a calibrant. The effective magnetic moments were calculated by the formula $\chi_{eff} = 2.83\ (\chi_m T)^{\frac{1}{2}}$ where χ_m is the molar susceptibility after applying diamagnetic corrections. Mössbauer spectra were measured with an S-600 constant-acceleration spectrometer (Austin Science Associates). The data were stored in a 1024-channel analyser, type IT-5200 (Inotech Inc.). A 10 mCi cobalt-57 source diffused into palladium foil was used. The spectra were fitted by a Lorentzian line shape using a least-squares method at the Computer Center, Kyushu University, and the velocity scales were normalized to iron foil at room temperature. Cyclic voltammetry of the complexes in acetonitrile was carried out on an AC/DC Cyclic Polarograph P-900 (Yanaco) at 293 K under an argon atmosphere. A standard three-electrode system (BAS) was employed comprising a glassy carbon working electrode, a $Ag-Ag^+-MeCN-NBu_4ClO_4$ (RE-5, BAS), reference and a platinum counter electrode. Ferrocene was used as a standard and the values measured were referenced to the saturated calomel electrode (SCE). Absorption and reflectance spectra were recorded with a Shimadzu UV-3100PC self-recording spectrophotometer in the region 300–2600 nm. Infrared spectra were taken on a JASCO FT/IR-5000 spectrometer as KBr pellets, ESR spectra on a X-band spectrometer [FEX (JEOL) calibrated with MnO in MgO] and a fast atom bombardment (FAB) mass spectra with a JEOL JMS-SX/SX 102A tandem mass spectrometer. Microanalyses for C, H and N were performed at the Elemental Analysis Center, Kyushu University and for Fe by atomic absorption spectroscopy.



1, 2

Results and Discussion

Chemical Structure of the Complexes.—Infrared spectra of complexes **1** and **2** are available as SUP 57105. In the case of **1**, the $\nu_{sym}(CO_2^-)$ stretching vibrations of the acetate group are observed at 1429 and 1481 cm^{-1} and ν_{asym} of co-ordinated acetate at 1580 cm^{-1}; ν_{asym} of unco-ordinated acetate is observed at 1605 cm^{-1}, and the C=N stretching vibration of the Schiff base at 1702 cm^{-1}. Similar bands are observed for **2**. Both iron atoms have N_4O_2 octahedral donor sets, and are bridged with phenoxo and carboxylato oxygen atoms.

Complex **1** in a glycerin (propane-1,2,3-triol)–dimethylformamide matrix was subject to FAB mass spectroscopy and showed significant peaks in the mass range 1000–1135 (see Fig. 1). The peak at *m*/*z* 1131 is assigned to the molecular ion (M^+), and peaks at *m*/*z* 1102–1104 to $[M - CO]^+$ which may be formed by partial elimination of unco-ordinated $MeCO_2^-$. These data support the formulation $[Fe_2L(O_2CMe)][O_2CMe][PF_6]_2$.

Mössbauer spectroscopy was applied to the diiron mixed-valence complexes at 297 K. The spectra (Fig. 2) consist of a quadrupole doublet of iron(II) and another doublet of iron(III). The isomer shift of 0.33 mm s^{-1} observed for the iron(III) doublet is 0.10–0.17 mm s^{-1} smaller than that of iron(III) in the high-spin mixed-valence complex $[Fe_2(bpmp)(ena)_2][BF_4]_2$ (Hena = heptanoic acid) and the quadrupole splitting of 0.96 mm s^{-1} is twice that observed for $[Fe_2(bpmp)(ena)_2][BF_4]_2$,[14] indicating that the iron(III) species of **1** is in the low-spin state. The isomer shift of 0.96 mm s^{-1} and quadrupole splitting of 2.64 mm s^{-1} for the other doublet are characteristic of high-spin iron(II). The corresponding parameters of **2** are as follows: isomer shift 0.28 mm s^{-1}, quadrupole splitting 1.11 mm s^{-1} for Fe^{III}; and isomer shift 0.99 mm s^{-1}, quadrupole splitting 2.52 mm s^{-1} for Fe^{II}. An essential point to be deduced from the

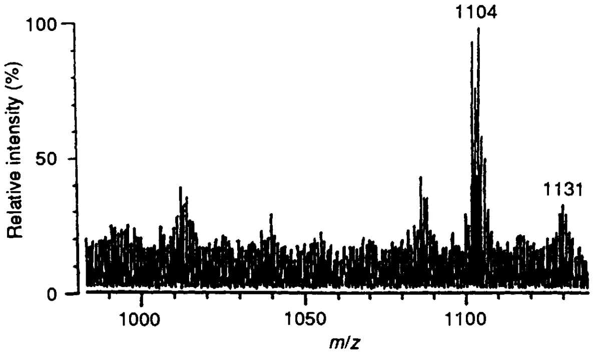


Fig. 1 Positive-ion FAB mass spectrum of complex **1** in a glycerin–dimethylformamide matrix

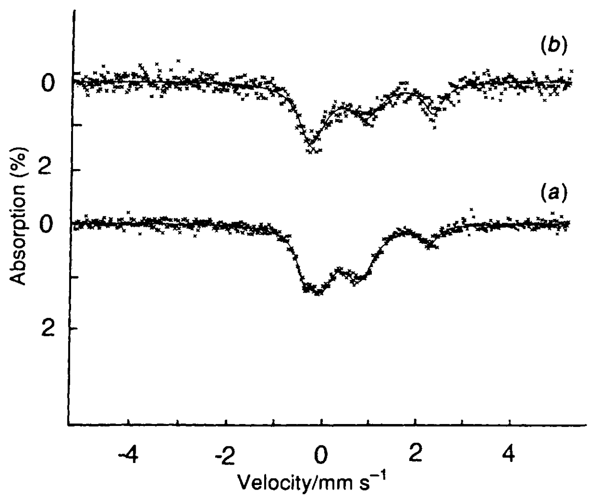


Fig. 2 Mössbauer spectra of (*a*) complex **1** and (*b*) **2** at 297 K

Mössbauer spectra is that **1** and **2** are mixed-valence complexes of high-spin iron(II) and low-spin iron(III) centres, consistent with the magnetic susceptibilities.

Physicochemical Properties.—Magnetic susceptibility measurements of complexes **1** and **2** were made on powder samples in the temperature range 80–300 K. The temperature dependence of the magnetic susceptibility per two iron atoms for **1** is shown in Fig. 3 and that for **2** is available as SUP 57105. The μ_{eff} values of the complexes are 6.09 (**1**) and 6.01 (**2**) μ_B per 2Fe at 290 K and decrease with decreasing temperature. The molar magnetic susceptibility for a dimer is given by equation (1) based on the

$$\chi_m = \frac{N^2\beta^2g^2}{4kT} \times \frac{10x^5 + 35}{2x^5 + 3} + N_\alpha \qquad (1)$$

Heisenberg model $H = -2JS_1 \cdot S_2$ ($S_1 = 2$ and $S_2 = \frac{1}{2}$) where $x = \exp(-J/kT)$, other symbols have their usual meanings, and the temperature-independent paramagnetism was assumed to be zero. The cryomagnetic property of **1** is consistent with high-spin iron(II) and low-spin iron(III) centres using the parameters $g = 2.80$ and $J = -19.9$ cm^{-1} as shown by the solid line in Fig. 3. The iron(III) may be in the low-spin state due to the strong ligand field generated by the N_4O_2 donor set. The discrepancy factors defined as $\chi_i = [(\chi_{obs} - \chi_{calc})^2/(\chi_{obs})^2]^{\frac{1}{2}}$ were 2.52×10^{-3} for **1** and 7.3×10^{-3} for **2** with $g = 2.7$ and $J = -20.0$ cm^{-1}. The J values obtained show that magnetic interaction between the iron atoms is very weak and comparable to values reported for other *m*-phenoxo-bridged complexes.[12,13] This is, to our knowledge, the first example of magnetic susceptibility measurements for high-spin iron(II)–low-spin iron(III) mixed-valence complexes. Two pathways are considered for such magnetic interaction: an s-orbital pathway leading to ferromagnetic interaction and a p-orbital pathway leading to antiferromagnetic interaction. The J values observed show that the latter pathway predominates.

Preliminary ESR spectra of powdered complexes **1** and **2** were measured at 290 and 78 K (Fig. 4). Rhombic signals ($g_1 = 1.92$, $g_2 = 2.21$ and $g_3 = 2.58$) observed at 78 K for **2** are assigned to low-spin iron(III) ($S = \frac{1}{2}$) and a signal at $g = 4.3$ to mononuclear rhombic high-spin iron(III) present as an impurity produced by slight decomposition of the complexes. Similar spectra with rhombic signals have been reported for low-spin iron(III) complexes.[16] These ESR spectra are quite different from that observed for $[Fe_2(bpmp)(ena)_2][BF_4]_2$ for which no signal was observed at >78 K.[14] This is indicative of no apparent interaction (within the ESR time-scale) between two metal orbitals of the complexes in the ground state. Broad spectra are observed at about $g = 4.3$ and 2.0 at 290 and 78 K for **1**, assigned to high-spin iron(III) of impurities or decomposed species.

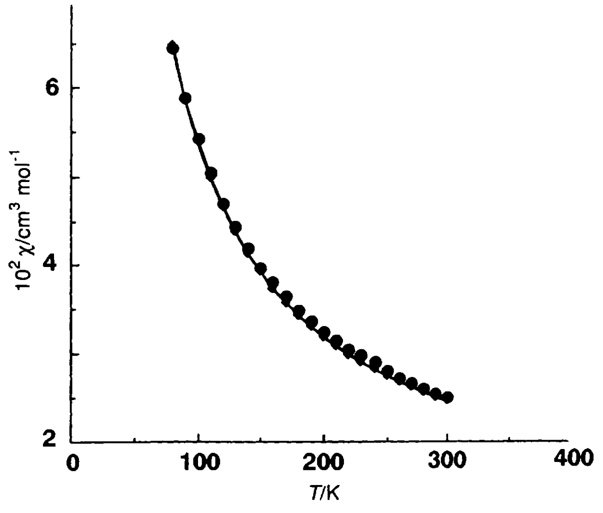
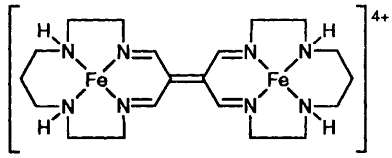


Fig. 3 Temperature dependence of the molar magnetic susceptibility for complex **1**. The solid line is a theoretical fit to the Heisenberg model with parameters given in the text

The cyclic voltammograms of the complexes in acetonitrile solution with 0.1 mol dm^{-3} tetra-*n*-butylammonium perchlorate are shown in Fig. 5. Two redox couples for **1** are observed in acetonitrile previously refluxed over NaH and distilled from P_2O_5 and then distilled from CaH_2 in an argon atmosphere. A quasi-reversible redox couple $E_1 = -0.07$ V ($\Delta E_p = 0.11$ V) *vs.* SCE is assigned to the couple $Fe^{II}Fe^{II}$–$Fe^{II}Fe^{III}$ and an irreversible redox couple $E_2 = 0.58$ V ($\Delta E_p = 0.10$ V) *vs.* SCE to $Fe^{II}Fe^{III}$–$Fe^{III}Fe^{III}$. The values observed for **2** were −0.05 ($\Delta E_p = 0.10$) and 0.60 V ($\Delta E_p = 0.11$ V) *vs.* SCE. These redox couples correspond to one-electron electrochemical processes at both of the redox sites and the values are similar to those observed for $[Fe_2(bpmp)(O_2CMe)_2][BF_4]_2$ (−0.05 and 0.60 V *vs.* SCE). From the separation of the redox potentials, $E_2 - E_1 = (RT/F) \ln K$, the comproportionation constant K at 293 K of reaction (2) can be calculated. The K values obtained for **1**

$$Fe^{II}Fe^{II} + Fe^{III}Fe^{III} \longrightarrow 2Fe^{II}Fe^{III} \qquad (2)$$

and **2** were *ca.* 1.0×10^{12} and 0.9×10^{12}, respectively, comparable to that for $[Fe_2(bpmp)(ena)_2][BF_4]_2$[14] but smaller than that for the low-spin valence-averaged complex $[\mathbf{3}(MeCN)_4]^{4+}$ ($E_1 = 0.95$ and $E_2 = 1.45$ V relative to Ag^+–Ag).[19]



3

Electronic Spectra.—One of the most interesting properties of transition-metal mixed-valence species is that they often exhibit an optical transition in the visible or near-infrared region due to intramolecular electron transitions between different oxidation states. Electronic absorption and reflectance spectra were measured at room temperature for **1** and **2** (SUP 57105), but no appreciable absorption was observed in the region 500–2600 nm except for a peak at 600 nm; the complex $[Fe_2(bpmp)(ena)_2][BF_4]_2$ shows a broad peak at 1200–1600 nm due to an intramolecular electron transition. The peak at 600 nm may be tentatively assigned to d–d transitions of iron(III) and/or

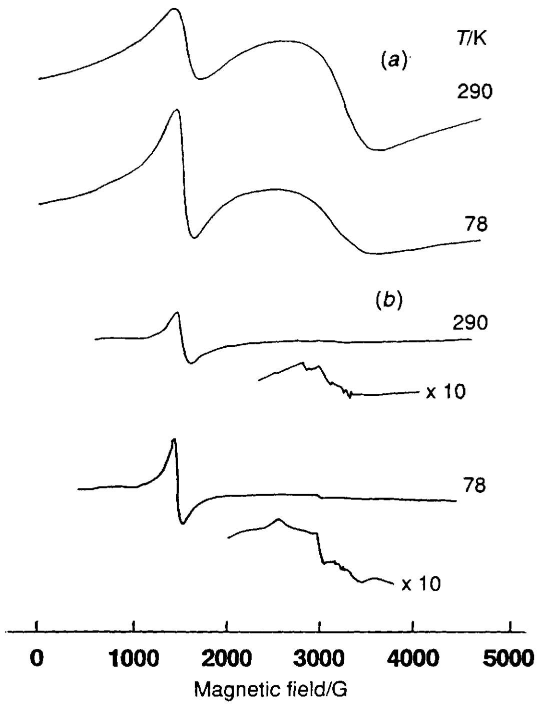


Fig. 4 The ESR spectra of (*a*) complex **1** and (*b*) **2** at 78 and 290 K obtained under the following conditions: microwave frequency, 9.4 GHz; microwave power, 5 mW; modulation frequency, 100 kHz; modulation amplitude, 10 G; instrumental gain, 1 × 100 or 1 × 1000

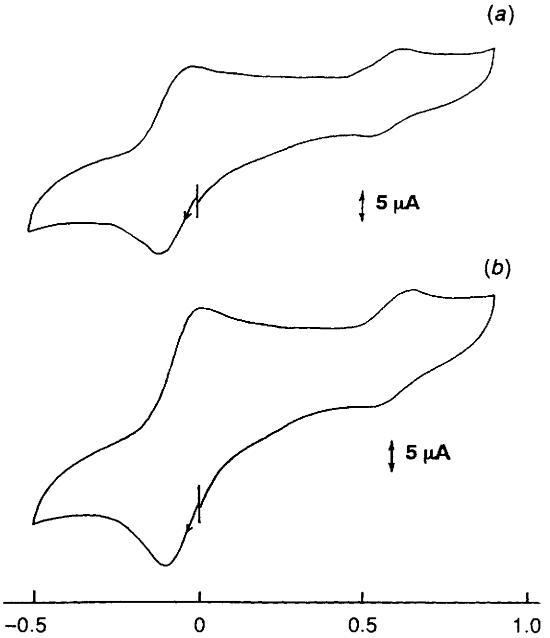


Fig. 5 Cyclic voltammograms for (*a*) complex **1** and (*b*) **2** at 297 K, using a scan rate of 100 mV s^{-1}

charge-transfer transitions of phenolate to the half-filled d_π* orbital of iron(III) because the full width at half maximum is very narrow, 2000 cm^{-1}. According to Hush's theory[18] the widths at half-maximum of intramolecular electron transition bands are usually broad, about 5000 cm^{-1}. An electron transition process between high-spin Fe^{II} and high-spin Fe^{III} occurs by addition to and removal of one electron from a t_{2g} orbital. An electron of the t_{2g} orbital is also correlated with electron transition between low-spin iron(II) and low-spin iron(III).[17] In contrast, electron transition between high-spin iron(II) and low-spin iron(III) is complicated, involving an excitation to antibonding orbitals (e_g). Therefore much energy may be needed and the transition probabilities of the electrons become small. Mixed-valence complexes **1** and **2** are of class I, according to Robin and Day's classification (firmly trapped electron).[19]

Acknowledgements

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