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Synthesis and characterization of iron(III) and iron(IV) complexes of *N*-(2-hydroxyphenyl)salicylamide and homologs

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Abstract

The complexation of tridentate trianionic chelating ligands, *N*-(2-hydroxyphenyl)salicylamide (H_3L^1) and its homologs with a substituent on the 2-hydroxyphenyl moiety (5-CH_3, H_3L^2; 5-Cl, H_3L^3), toward iron ion has been studied. The ligand H_3L^1 formed a high-spin iron(III) complex $K_3[Fe(L^1)_2]$ when treated with $FeCl_3$ in an alkaline solution under open atmosphere. This complex was oxidized with Ce(IV) to a high-spin iron(IV) complex $(NPr_4)_2[Fe(L^1)_2]$. The ligand H_3L^2 formed a low-spin iron(IV) complex $K_2[Fe(L^2)_2]$ under open atmosphere, whereas the ligand H_3L^3 gave a high-spin iron(III) complex $(PBu_4)_3[Fe(L^3)_2]$. The complexes were characterized by means of cyclic voltammetry, electronic spectra and Mössbauer spectra.

Introduction

The study of high-valent transition metal ions has become an attractive subject in coordination chemistry [1, 2] because of the interest in physicochemical properties of such high-valent metal ions and the desire to exploit new metallooxidants in organic syntheses. For this purpose it is essential to design new ligands that can stabilize the higher oxidation states of metal ions. Recent investigations have revealed that the deprotonated amido-nitrogen [3] and phenolic oxygen [4] are such donor atoms, and some chelating ligands comprising these donor atoms can be utilized to synthesize high-valent metal complexes [5–9]. Tridentate ligands *N*-(2-hydroxyphenyl)salicylamide and homologs were utilized for such a purpose in our laboratory [10–12]. They function as both strong σ and π donors with the deprotonated phenolic oxygens and amide nitrogen to stabilize high-valent metal ions such as Mn(IV) [10], Mn(V) [10], Co(IV) [11] and Cu(III) [12]. The aim of this study was to synthesize and characterize iron complexes of *N*-(2-hydroxyphenyl)salicylamide (abbreviated as H_3L^1), *N*-(2-hydroxy-5-methylphenyl)salicylamide (H_3L^2) and *N*-(2-hydroxy-5-chlorophenyl)salicylamide (H_3L^3). The chemical structures of the ligands are given in Fig. 1.

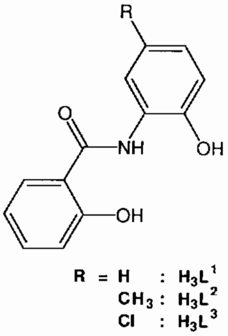

Fig. 1. Chemical structure of the ligands.

Experimental

Materials

All the chemicals were reagent grade and used as received. All solvents were purified in the usual ways before use. Tetrabutylammonium perchlorate used as supporting electrolyte in electrochemical measurements was obtained commercially, recrystallized three times from a mixture of ethyl acetate and n-hexane, and dried *in vacuo*. The ligands H_3L^1–H_3L^3 were obtained as described previously [13].

Preparation

$K_3[Fe(L^1)_2]\cdot 5H_2O$ (*1*)

A mixture of H_3L^1 (460 mg), anhydrous iron(III) chloride (163 mg), and potassium t-butoxide (1120 mg) in dry methanol (20 ml) was stirred, while general

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precautions against atmospheric moisture were taken. After 30 min purple microcrystals precipitated, which were collected by suction filtration, washed with methanol (50 ml), and recrystallized from a methanol/acetonitrile (1:1 in volume) mixture. Yield 78%.

$(NPr_4)_2[Fe(L^1)_2]\cdot 2H_2O$ (2)

H_3L^1 (460 mg) and anhydrous iron(III) chloride (163 mg) were dissolved in a methanolic sodium methoxide solution prepared by dissolving 200 mg of sodium metal in 20 cm^3 of methanol. To the resulting purple solution was added a methanolic solution (10 ml) of $(NH_4)_2Ce(NO_3)_6$ (560 mg), and the mixture was stirred for 20 h. A methanolic solution (10 ml) of tetrapropylammonium bromide (NPr_4Br; 550 mg) was added and the mixture was heated at about 50 °C for 4 h with stirring. The solvent was removed by evaporation under reduced pressure, the residue was dissolved in acetonitrile, and the solution was passed through an alumina column (1.5∅×5 cm). The eluent was concentrated to 10 ml and allowed to stand for a week to give brown crystals. They were separated and recrystallized three times from acetonitrile. Yield 34%.

$K_2[Fe(L^2)_2]\cdot 2.5H_2O$ (3)

This complex was obtained as dark-purple prisms by a method similar to that for $K_3[Fe(L^1)_2]\cdot 5H_2O$. Recrystallization was carried out from a methanol/acetonitrile (1:1 in volume) mixture three times. Yield 21%.

$(PBu_4)_3[Fe(L^3)_2]$ (4)

The ligand H_3L^3 (527 mg), tris(acetylacetonato)-iron(III) (353 mg), and potassium t-butoxide (1150 mg) were dissolved in dry methanol (20 ml), and the mixture was stirred overnight. A methanol solution of tetrabutylphosphonium bromide (PBu_4Br, 680 mg) was added to the resulting brown solution and the stirring was continued for one day. The solvent was removed by evaporation, the residue was dissolved in dry dichloromethane, and the solution was passed through an alumina column (1.5∅×5 cm). The eluent was slowly diffused with ether in a desiccator to give brown microneedles after few days. Yield 57%.

Physical measurements

Elemental analyses for C, H and N were obtained at the Elemental Analysis Service Center, Kyushu University. Analyses of iron were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. IR spectra were recorded on a JASCO IR-810 spectrometer on nujol mulls or KBr disks. Electronic spectra were recorded on a Shimadzu Multipurpose spectrophotometer MPS-2000. Magnetic susceptibilities were determined at room temperature on a Faraday balance equipped with a CAHN-2000 electrobalance. The Faraday balance was controlled by a NEC PC-9801VX2 personal computer and calibrated with $[Ni(en)_3]S_2O_3$ [14] (en = ethylenediamine). Magnetic moments were calculated by the equation $\mu_{eff}=2.828(\chi_A T)^{1/2}$, where χ_A is the magnetic susceptibility corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants. Cyclic voltammograms (CV) were obtained on an apparatus comprising a HA-501 potentiostat/galvanostat, a HB-104 function generator, and a HF-201 coulomb/ampere-hour meter of Hokuto Denko Ltd. Measurements were carried out in dichloromethane or an acetonitrile/methanol mixture containing 0.1 M (1 M = 1 mol dm^{-3}) tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The working electrode was a glassy carbon ($\phi = 3$ mm) electrode. The counter electrode and the reference electrode were a platinum net and a saturated calomel electrode (SCE), respectively. Controlled-potential electrolyses were made on the same instrument using a platinum net as the working electrode. Mössbauer spectra were measured with a constant-acceleration spectrometer (Ausin Science Associates) using a ^{57}Co source diffused into palladium foil. Isomer shifts were given with respect to the centroid of the spectrum of an iron foil enriched with ^{57}Fe.

Results and discussion

Synthesis and general characterization

The three ligands used in this study show a significant diversity in complexation behavior toward iron ion, depending upon the electronic nature of the substituent attached to the '2-hydroxyphenyl' moiety and the reaction condition. The analytical results and magnetic moments (at room temperature and near liquid nitrogen temperature) for the obtained complexes are summarized in Table 1. The metal/ligand ratio is 1/2 for all the complexes, suggesting a pseudo octahedral surrounding about the metal ion like $[Mn(L^n)_2]^{2-}$ and $[Co(L^n)_2]^{3-}$ previously reported [10, 11]. The reaction of H_3L^1 with iron(III) chloride in an aerobic condition formed iron(III) complex $K_3[Fe(L^1)_2]\cdot 5H_2O$ (**1**) whose magnetic moment (5.80 BM at room temperature) is common for high-spin iron(III) ($S = 5/2$). Complex **1** was oxidized with Ce(IV) to give $(NPr_4)_2[Fe(L^1)_2]\cdot 2H_2O$ (**2**) which was characterized as a high-spin iron(IV) complex ($\mu_{eff} = 4.99$ BM). On the other hand, the ligand with methyl substituent, H_3L^2, formed a stable iron(IV) complex $K_2[Fe(L^2)_2]\cdot 2.5H_2O$ (**3**) when reacted with iron(III) chloride under open atmosphere. Its magnetic moment (2.84 BM) is very close to the spin-only value for $S = 1$ (2.83 BM), demonstrating the low-spin state

TABLE 1. Elemental analyses and magnetic moments of iron complexes

Complex	Found (calc.) (%)				μ_{eff} (BM)	
	C	H	N	Fe	r.t.	78 K
$K_3[Fe(L^1)_2]5H_2O$ (**1**)	43.65 (43.65)	3.55 (3.65)	4.05 (3.90)	7.45 (8.40)	5.80	5.68
$(NPr_4)_2[Fe(L^1)_2]2H_2O$ (**2**)	64.80 (65.50)	7.50 (8.30)	5.80 (6.10)	6.10 (6.35)	4.99	4.60
$K_2[Fe(L^2)_2]2.5H_2O$ (**3**)	50.60 (51.00)	3.80 (3.80)	4.35 (4.25)	7.75 (7.80)	2.84	2.53
$(PBu_4)_3[Fe(L^3)_2]$ (**4**)	64.30 (65.55)	8.00 (9.05)	2.75 (2.05)	3.80 4.10)	5.82	5.55

of Fe(IV) ion. The ligand with chloro substituent, H_3L^3, formed a high-spin iron(III) complex $(PBu_4)_3[Fe(L^3)_2]$ (**4**) ($\mu_{eff}=5.82$ BM at room temperature). We attempted to synthesize an iron(IV) complex of $(L^3)^{3-}$ by chemical oxidation of **4** but all our efforts were in vain. The presence of lattice water was evidenced for complexes **1**–**4** by a broad IR band near 3400 cm^{-1} [15] (measured on Nujol mulls). Each magnetic moment of the **1**–**4** was practically independent of temperature down to liquid nitrogen temperature (see Table 1), ruling out the possibility of the operation of a spin-crossover phenomenon for all the complexes in the temperature range 80–300 K.

We have already shown [10] that the donor ability of the ligands increases in the order: $(L^3)^{3-}$ (R=5-Cl) < $(L^1)^{3-}$ (R=H) < $(L^2)^{3-}$ (R=5-CH_3). In the present study the most donative $(L^2)^{3-}$ formed low-spin iron(IV) complex **3**, whereas the least donative $(L^3)^{3-}$ afforded only iron(III) complex **4**. Moderately donative $(L^1)^{3-}$ formed both iron(III) and iron(IV) complexes (**1** and **2**). It is to be noted that the iron(IV) complexes **2** and **3** differ in spin-state, i.e. high-spin for **2** and low-spin for **3**. Six-coordinated iron(IV) complexes generally adopt the low-spin configuration [16, 17] and high-spin iron(IV) complexes seem very rare.

All our efforts to grow single crystals suitable for X-ray analyses were unsuccessful.

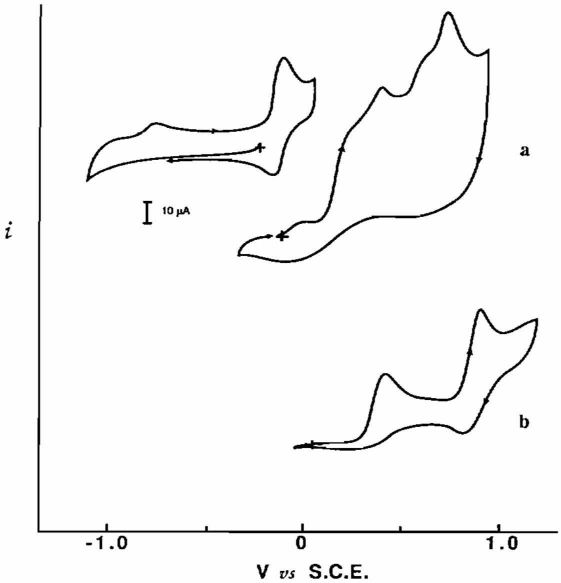

Fig. 2. Cyclic voltammograms of (a) complex **1** in methanol/acetonitrile and (b) complex **2** in dichloromethane: glassy carbon electrode, scan speed 100 mV s^{-1}.

Electrochemistry

Cyclic voltammograms were measured in an acetonitrile/methanol mixture for **1** and in dichloromethane for **2**–**4**. The iron(III) complex **1** shows a reversible redox couple at −0.13 V (versus SCE) and two irreversible redox waves at about +0.4 and +0.7 V (Fig. 2(a)). The numerical data are summarized in Table 2. The wave at −0.13 V is assigned to the Fe^{III}/Fe^{IV} process, because the wave was found to involve a one-electron transfer based on the controlled-potential electrolysis at +0.05 V. Since the deprotonated ligand shows no redox wave up to +1.2 V [11, 12], the waves at +0.4 and +0.7 V are tentatively assigned to the Fe^{IV}/Fe^{V} and Fe^{V}/Fe^{VI} processes, respectively

$$[Fe(L^1)_2]^{3-} \xrightleftharpoons{-0.13} [Fe(L^1)_2]^{2-} \xrightleftharpoons{+0.4} [Fe(L^1)_2]^{-} \xrightleftharpoons{+0.7} [Fe(L^1)_2]^{0}$$

Recently, an iron(IV) complex of a macrocyclic tetraamido ligand was synthesized and characterized by single-crystal X-ray method [9]. Its precursor iron(III) complex was electrochemically examined to show the Fe^{III}/Fe^{IV} process at +0.645 V versus NHE (= +0.4 V versus SCE). Notably, the Fe^{III}/Fe^{IV} redox potential of **1** (−0.13 V versus SCE) is unusually low compared with that of the tetraamido iron complex.

The iron(III) complex **4** with the chloro substituent shows two quasi-reversible redox couples at +0.43 and +0.95 V which may be assigned to the Fe^{III}/Fe^{IV} and Fe^{IV}/Fe^{V} processes, respectively (Fig. 2(b)). Each po-

TABLE 2. Electrochemical data of complexes[a]

Complex	Fe^{III}/Fe^{IV}			Fe^{IV}/Fe^{V}			Fe^{V}/Fe^{VI}		
	E_{pc}	E_{pa}	$E_{1/2}$[b]	E_{pc}	E_{pa}	$E_{1/2}$[b]	E_{pc}	E_{pa}	$E_{1/2}$[b]
1	−0.10	−0.16	−0.13	0.40			0.74		
4	0.49	0.37	0.43	0.99	0.82	0.95			
2				0.75					
3				0.48					

[a] Volt vs. SCE, scan rate 100 mV s^{-1}, glassy carbon electrode. [b] $E_{1/2} = (E_{pc} + E_{pa})/2$.

tential is shifted to the positive side by *c.* +0.5 V relative to the corresponding potential of **1**. The Fe^{V}/Fe^{VI} process was not observed for **4** in the available potential range.

The cyclic voltammograms of the iron(IV) complexes **2** and **3** are similar to each other in spite of different spin-state and show only one irreversible oxidation wave due to the Fe^{IV}/Fe^{V} process at +0.75 and +0.48 V, respectively. The electrochemical behavior of **2** differs from that of the precursor **1**, probably because the measurements were performed under different conditions. Electrochemical studies support that $(L^1)^{3-}$ and $(L^2)^{3-}$ remarkably stabilize the iron(IV) oxidation state through σ and π donations.

Electronic spectra

Electronic spectra of the complexes **1**–**4** in methanol are given in Fig. 3. They obey Beer's law in the concentration range 1×10^{-3} to 1×10^{-4} mol dm^{-3} and show an absorption band near 20×10^{3} cm^{-1} and some absorption bands of higher intensity in the region higher than 30×10^{3} cm^{-1}. Under an octahedral crystal field, high-spin iron(III) should show only very weak d–d transition bands because of both the Laporte and spin-forbidden rules. Thus, the absorption band at 22×10^{3} cm^{-1} ($\epsilon \sim 5000$ dm^3 mol^{-1} cm^{-1}) found for the iron(III) complexes **1** and **4** cannot be assigned to the d–d transition band. This band may be assigned to a CT transition. The intense absorptions in the region higher than 30×10^{3} cm^{-1} may be assigned to the intra-ligand transitions.

In spite of different spin states the iron(IV) complexes **2** and **3** show no marked spectral difference in the visible region. They show an intense CT band at 21×10^{3} cm^{-1} similarly to the case of the iron(III) complexes **1** and **4**. The d–d transition band of the iron(IV) complexes may be located at the field higher than 25×10^{3} cm^{-1} but concealed by the intense CT and intra-ligand absorption bands.

Mössbauer spectra

Powder state Mössbauer spectra were obtained at room temperature for all the complexes **1**–**4** and at 78 K for **1** and **2**. The spectra of **1** and **2** at 78 K are essentially identical to those at room temperature, respectively. Typical spectra are shown in Fig. 4 and the isomer shifts (δ_{Fe}) and quadrupole splitting parameters (ΔE_Q) are summarized in Table 3. The iron(III) complex **1** shows a broad unresolved spectrum (Fig. 4) from which the quadrupole splitting and the isomer shift are evaluated at 0.315 and 0.453 mm/s, respectively, based on computer analyses. The iron(III) complex **4** showed a well-resolved Mössbauer spectrum of $\delta_{Fe} = 0.401$ and $\Delta E_Q = 0.565$ mm/s. High-spin iron(III) complexes often show a small quadrupole splitting because of small electric gradient from d-electrons [18]. The relatively large quadrupole splitting of **1** and **4** suggests a distorted configuration about the central iron(III) ion. The isomer shifts of **1** and **4** are common for iron(III) complexes of an N_2O_4 donor set [19].

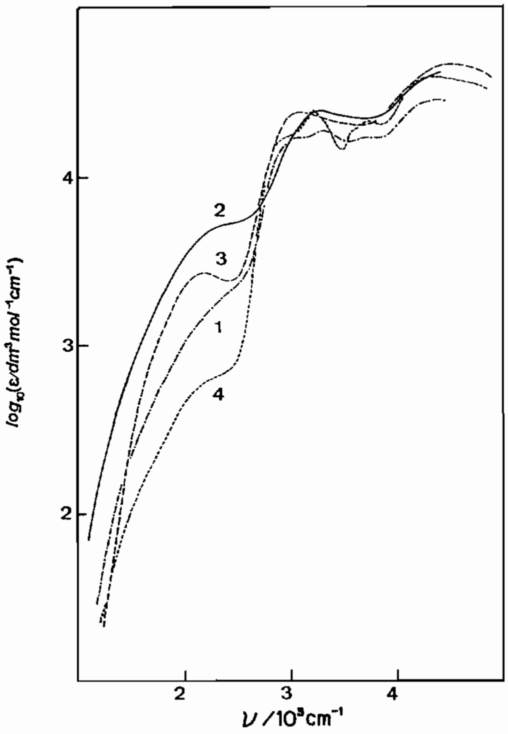

Fig. 3. Electronic spectra of the complexes **1**–**4** in methanol.

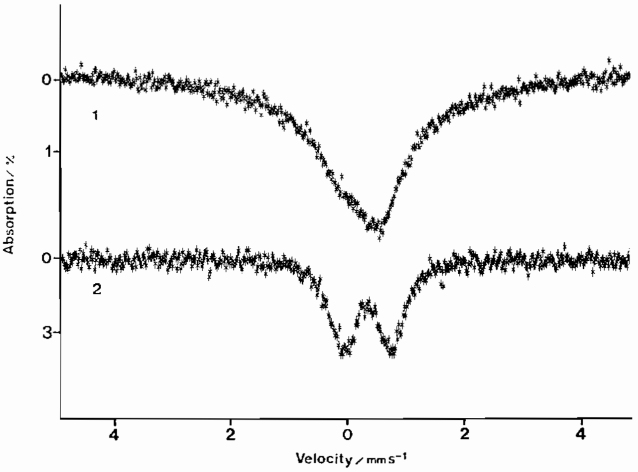

Fig. 4. Mössbauer spectra of **1** and **2** recorded on powder samples at room temperature.

TABLE 3. Mössbauer parameters of iron complexes

Complex	ΔE_Q (mm s^{-1})	δ_{Fe} (mm s^{-1})
1 (high-spin Fe(III))	0.315[a] 0.310[b]	0.453[a] 0.559[b]
4 (high-spin Fe(III))	0.565[a]	0.401[a]
2 (high-spin Fe(IV))	0.824[a] 0.878[b]	0.358[a] 0.451[b]
3 (low-spin Fe(IV))	0.828[a]	0.365[a]

[a]At room temperature. [b]At 78 K.

The Mössbauer spectra of the iron(IV) complexes **2** and **3** evidently differ from those of the iron(III) complexes **1** and **4** and show a large quadrupole splitting and a smaller isomer shift [20] when compared at room temperature. This is consistent with the general trend that iron(IV) complexes show a larger quadrupole splitting (*c.* 1–2 mm/s) because of a large electric gradient of the $(3d)^4$ electronic configuration irrespective of its high- or low-spin state and a small isomer shift because of the decreased shielding effect from the iron nucleus. The quadrupole splittings found for **2** and **3** are rather small. This is probably because the electric gradient arising from the distortion of the iron configuration compensates the electric gradient from d-electrons. As judged from the δ_{Fe} and ΔE_Q values of **2** and **3**, it seems hard to distinguish between high-spin and low-spin iron(IV) complexes based on Mössbauer spectroscopy.

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