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Binuclear Metal Complexes. LIII [1]. Synthesis and Properties of Iron(II) and Iron(III) Complexes of Strati-bis Schiff Bases

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Strati-bis iron(II) and iron(III) complexes, $Fe_2(sata)$, $Fe_2(sacta)$, $Fe_2(sata)Cl_2$, *and* $Fe_2(sacta)Cl_2$, *have been prepared and characterized, where* H_4sata *denotes 1,2,3,4-tetrakis(salicylideneamino)-2,3-dimethylbutane and* H_4sacta *1,2-bis(salicylideneamino)-1,2-bis(salicylideneaminomethyl)cyclohexane. In comparison with the relevant mononuclear iron(II) complexes,* $Fe_2(sata)$ *and* $Fe_2(sacta)$ *were shown to be less sensitive to molecular oxygen. Each differential pulse polarogram of the iron(II) and iron(III) complexes revealed two waves attributable to the reduction at the metal. The higher potential wave was tentatively assigned to the one-electron transfer process, Fe(III)–Fe(III)/Fe(III)–Fe(II), of the stacked conformer, while the lower potential wave to the two-electron transfer process, Fe(III)–Fe(III)/Fe(II)–Fe(II), of the non-stacked conformer. The facile reduction of iron(III) in the stacked conformer has been attributed to the emergence of an electron delocalization over the whole molecule due to the stacking of the two coordination planes.*

Introduction

Strati-bis metal complexes are of current interest in studying magnetic, spectral and electrochemical properties of the complexes and mimicing metalloenzymes possessing a stacked dimeric structure [2–10].

In the previous papers of this series [11, 12], we have shown that the Schiff bases, 1,2,3,4-tetrakis(salicylideneamino)-2,3-dimethylbutane (abbreviated as H_4sata) and 1,2-bis(salicylideneamino)-1,2-bis(salicylideneaminomethyl)cyclohexane (H_4sacta), form strati-bis copper(II)–copper(II) and copper(II)–nickel(II) complexes, which showed magnetic, spectral, and electrochemical properties in contrast with those of the mononuclear copper(II) complexes relevant to those strati-bis complexes. The most striking characteristics of those complexes are the facile reduction to the copper(I)–copper(II) and copper(I)–nickel(II) species and considerable stabilization of these reduced species. This can be rationalized in terms of electron delocalization over the whole molecule.

As an extension of these studies, we have prepared binuclear iron(II) and iron(III) complexes of H_4sata and H_4sacta, and examined their properties in comparison with those of the mononuclear iron complexes relevant to the binuclear complexes. The mononucleating ligands relevant to H_4sata and H_4sacta are N,N′-disalicylidene-1,2-propanediamine (H_2salpn) and 1-(salicylideneamino)-1-(salicylideneaminomethyl)cyclohexane (H_2sacda), respectively. The chemical structures of the strati-bis and mononucleating Schiff bases are given in Fig. 1.

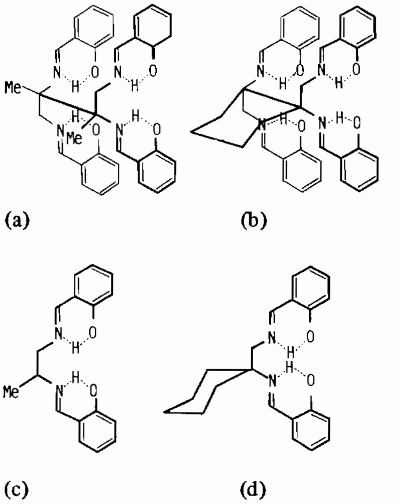

Fig. 1. Chemical structures of (a) H_4sata, (b) H_4sacta, (c) H_2salpn, and (d) H_2sacda.

Experimental

Synthesis

Synthetic methods for H_4sata, H_4sacta, and H_2sacda have been described in the previous paper [11]. Fe(salpn) [13] and Fe(salpn)X (X = Cl, Br) [14]

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were prepared by the methods in the literature. All the iron(II) complexes were synthesized in nitrogen atmosphere by means of a VAC Inert Atmosphere and Vacuum Deposition Equipment Model HE-43-2.

Fe_2(sata)

Iron(II) acetate (0.33 g) and H_4sata (0.53 g) were suspended in absolute methanol (30 cm^3) and the mixture was stirred at room temperature for 12 hours. The black crystalline powder thus formed was collected and dried under reduced pressure. *Anal.* Found: C, 60.76; H, 4.79; N, 8.16%. Calcd for $C_{34}H_{30}N_4O_4Fe_2$: C, 60.92; H, 4.51; N, 8.36%.

Fe_2(sacta)

A suspension of iron(II) acetate (0.30 g), H_4sacta (0.51 g) and NaOH pellets (0.14 g) in absolute methanol (40 cm^3) was stirred at room temperature for 12 hours. The black crystalline powder which was precipitated was collected, washed with a small amount of methanol, and dried *in vacuo*. *Anal.* Found: C, 61.83; H, 4.93; N, 7.79%. Calcd for $C_{36}H_{32}N_4O_4Fe_2$: C, 62.09; H, 4.63; N, 8.05%.

Fe(sacda)

This complex was obtained as black prisms by reacting iron(II) acetate (0.30 g) and H_2sacda (0.58 g) in absolute ethanol (30 cm^3). Elemental analysis of this complex was not carried out because of its high sensitivity to atmospheric oxygen.

Fe_2(sata)Cl_2

A mixture of iron(II) chloride tetrahydrate (0.33 g) and H_4sata (0.40 g) in absolute ethanol (30 cm^3) was stirred for 4 hours in an atmosphere of nitrogen and then allowed to stand in the open air overnight. The black prisms which separated were collected and dried over P_2O_5 in a desiccator. *Anal.* Found: C, 52.19; H, 4.26; N, 7.40%. Calcd for $C_{34}H_{30}N_4O_4Cl_2Fe_2 \cdot 2H_2O$: C, 52.54; H, 4.41; N, 7.21%.

Fe_2(sacta)Cl_2

This complex was obtained as black prisms by reacting iron(II) chloride hetrahydrate (0.32 g) and H_4(sacta) (0.40 g) in ethanol (30 cm^3) in a way similar to that for Fe_2(sata)Cl_2. *Anal.* Found: C, 54.70; H, 4.45; N, 6.78%. Calcd for $C_{36}H_{32}N_4O_4Cl_2Fe_2 \cdot 3/2H_2O$: C, 54.44; H, 4.44; N, 7.05%.

Fe(sacda)Cl

This complex was obtained as black prisms by the reaction of anhydrous iron(III) chloride (0.20 g) and H_2sacda (0.40 g) in ethanol (20 cm^3). *Anal.* Found: C, 59.03; H, 5.30; N, 6.38%. Calcd for $C_{21}H_{22}N_2O_2ClFe$: C, 59.25; H, 5.21; N, 6.58%.

Fe_4(sata)$_3$

A methanolic solution (20 cm^3) of Fe_2(sata) (0.30 g) was stirred at room temperature in an open atmosphere. On concentrating the reaction mixture, reddish brown crystals were obtained. *Anal.* Found: C, 64.66; H, 5.09; N, 8.69%. Calcd for $C_{102}H_{90}N_{12}O_{12}Fe_4$: C, 64.50; H, 4.78; N, 8.85%.

Fe_4(sacta)$_3$

This complex was obtained as brown crystals by air-oxidation of Fe_2(sacta) in nearly the same way as that for Fe_4(sata)$_3$. *Anal.* Found: C, 65.94; H, 5.25; N, 8.34%. Calcd for $C_{108}H_{96}N_{12}O_{12}Fe_4$: C, 65.60; H, 4.89; N, 8.50%.

Measurements

All the solutions of the iron(II) complexes for spectral and electrochemical measurements were prepared under nitrogen atmosphere. Electronic spectra were measured on a Shimadzu Multipurpose Spectrophotometer Model MPS-5000 and a Shimadzu UV–VISIBLE Recording Spectrometer Model UV-240 in dichloromethane. Differential pulse polarograms were recorded on a Yanagimoto Voltammetric Analyzer Model P-1000 in dichloromethane containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as the supporting electrolyte, by the use of a three-electrode cell equipped with a glassy carbon as a working electrode, a platinum coil as an auxiliary electrode, and a saturated calomel electrode as a reference electrode. The cell was capped with a silicon rubber with a small hole for gas outlet. During electrochemical measurements a stream of nitrogen was introduced to the cell from the inlet attached to the cell wall to protect the solution from atmospheric oxygen. All the potentials observed were normalized by the use of ferrocene as an internal standard [15] and are given by V *vs.* E_{Fc/Fc^+}(E_{Fc/Fc^+}: oxidation potential of ferrocene). Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated with Hg[Co(NCS)$_4$] [16]. Diamagnetic corrections were carried out with Pascal's constants.

Results and Discussion

Iron(II) Complexes

Mononuclear complexes Fe(salpn) and Fe(sacda) are very air-sensitive and realidy oxidized to iron(III) complexes even in the solid state. On the other hand, the present binuclear complexes Fe_2(sata) and Fe_2(sacta) are fairly stable to air in the solid state, and no appreciable changes in appearance and in weight were observed even when these complexes were exposed to air for a few minutes. However, they were slowly oxidized by atmospheric oxygen with increase in weight and change of color from almost black to brown. The products obtained by exposing solid Fe_2(sata) and Fe_2(sacta) to air for 48 hours were assumed to be Fe_2(sata)O_2 and Fe_2(sacta)O_2

respectively, based on the weight increase and the elemental analysis. However, they were not characterized any further in this study. In solutions Fe_2(sata) and Fe_2(sacta) were both oxidized to Fe_4(sata)$_3$ and Fe_4(sacta)$_3$, respectively, in open atmosphere.

Magnetic moments of Fe_2(sata) and Fe_2(sacta) per one iron atom are 5.42 and 5.46 BM, respectively, which fall in the range of the moments (5.20–5.55 BM [17]) of conventional mononuclear high-spin iron(II) complexes.

Electronic spectra of Fe_2(sata) and Fe_2(sacta) were measured in dichloromethane and are shown in Fig. 2. The figure includes the spectra of Fe(salpn) and Fe(sacda) for comparison. The spectra of the binuclear iron(II) complexes are similar to those of the reference mononuclear iron(II) complexes, except for the shoulder at 16 700 cm^{-1} of Fe_2(sata) and Fe_2(sacta). The appearance of the absorption for the binuclear complexes is presumed to be indicative of an intramolecular interaction between the [FeN_2O_2] chromophores.

Each differential pulse polarogram of Fe_2(sata) and Fe_2(sacta) exhibits two waves (Fig. 3), similarly to those of the Cu(II)–Cu(II) [11] and Cu(II)–Ni(II) [12] complexes of H_4(sata) and H_4(sacta). Since the ligands do not show any reduction waves down to -2.0 V, both waves should be attributed to the reduction at the metal. In an attempt to analyze the electrochemical processes, the measurements of Fe(salpn) and Fe(sacda) were also carried out for comparison. However, the differential pulse polarograms obtained contained some complicated waves, probably due to the contamination of species oxidized by permeating oxygen.

Electrochemical investigations of planar iron complexes with salen-like Schiff bases are very limited. Only N,N′-disalicylidene-2,3-(+)-butanediaminatoiron(III) and its meso-homolog, [Fe{sal(+)-bn}]$^+$ and [Fe{sal(m)bn}]$^+$, were electrochemically studied by a dropping mercury electrode in DMF [18]. The polarograms showed only one reduction wave at ~ -0.35 V *vs.* SCE, attributable to Fe(III)/Fe(II). These potentials correspond well to the second reduction potential of Fe_2(sata) and Fe_2(sacta), if the oxidation potential of ferrocene (E_{Fc/Fc^+}: +0.40 V *vs.* NHE [19]) is taken into account. Thus, similarly to the Cu(II)–Cu(II) [11] and Cu(II)–Ni(II) [12] complexes of H_4sata and H_4sacta, in the cases of Fe_2(sata) and Fe_2(sacta) the stacked and non-stacked conformers are in equilibrium in solution (Fig. 4), and the non-stacked conformer is reduced at -0.8 V by a two-electron transfer process, Fe(III)–Fe(III)/Fe(II)–Fe(II). Hence, the first wave can be reasonably attributed to the reduction of iron(III) of the stacked conformer.

In order to gain insight into the first redox wave, Fe_2(sata) was electrolyzed at -0.7 V. However,

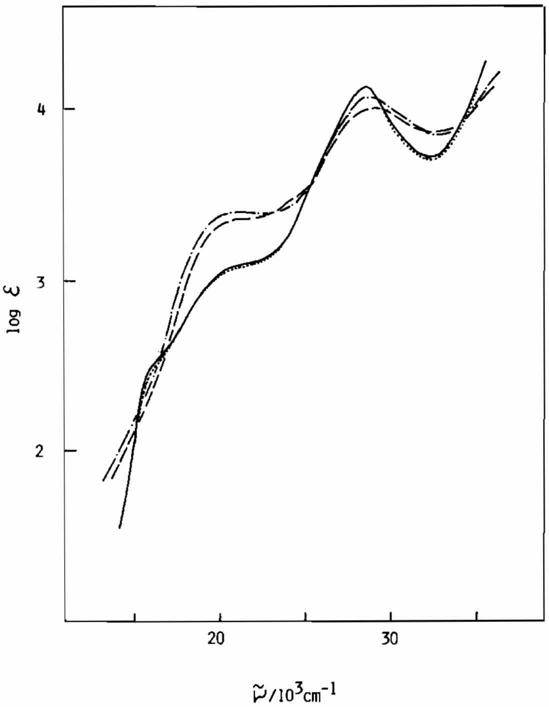

Fig. 2. Electronic absorption spectra of (——) Fe_2(sata), (- -) Fe_2(sacta), (– – –) Fe(salpn), and (– · –) Fe(sacda) in dichloromethane.

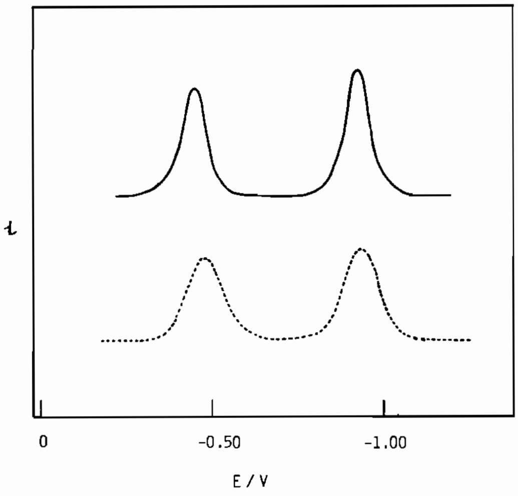

Fig. 3. Differential pulse polarograms of (——) Fe_2(sata) and (- - -) Fe_2(sacta) in dichloromethane.

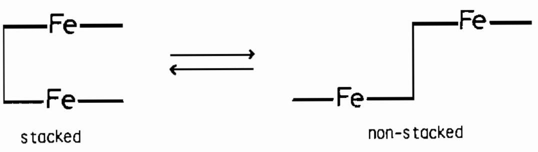

Fig. 4. Schematic representation of the stacked and non-stacked conformers of the iron(II) complexes.

the oxidized solution showed essentially the same electronic spectrum as that of $Fe_4(sata)_3$. Although no direct evidence for the first process is available, we tentatively assigned it to the one-electron transfer process, Fe(III)–Fe(III)/Fe(III)–Fe(II), judging from the fact that the stacked conformer of the Cu(II)–Cu(II) [11, 12], Cu(II)–Ni(II) [12], and Mn(II)–Mn(II) [20] complexes reveals one-electron transfer to form a mixed-valence species. The facile reduction of the iron(III) of the stacked conformation compared with that of the non-stacked one can be attributed to the emergence of an electron delocalization over the whole molecule of this conformation.

Iron(III) Complexes

Magnetic moments of $Fe_2(sata)Cl_2$ and $Fe_2(sacta)Cl_2$ per iron atom at room temperature are 5.72 and 5.71 BM, respectively, which are common for high-spin iron(III) complexes. It is known that Fe(salen)Cl and Fe(salpn)Cl have a dimeric structure bridged by the phenolic oxygen atoms and show a reduced magnetic moment even at room temperature, owing to an antiferromagnetic spin-exchange interaction [21–23]. Because of the structural requirement of the ligands, it is unlikely that $Fe_2(sata)Cl_2$ and $Fe_2(sacta)Cl_2$ take a dimeric structure bridged by the phenolic oxygen. Cryomagnetic measurements for $Fe_2(sata)Cl_2$ revealed a monotonous decrease in magnetic moment to 5.51 BM when temperature was lowered to the liquid nitrogen temperature. A small change in the magnetic moment implies that an antiferromagnetic spin-exchange interaction is weak even if it operates within the molecule.

Electronic spectra of $Fe_2(sata)Cl_2$ and $Fe_2(sacta)Cl_2$ resemble those of Fe(salpn)Cl and Fe(sacda)Cl, respectively [Fig. 5]. The concentration dependence of the spectrum of $Fe_2(sata)Cl_2$ was examined in the range 2×10^{-4}–4×10^{-5} mol dm^{-3}. Practically no spectral change was detected, indicating no dissociation of the apical chloride ion at least in this concentration range in dichloromethane. On the other hand, a solution of $Fe_2(sata)Cl_2$ in methanol assumed a reddish brown color and showed a spectrum similar to that of $Fe_4(sata)_3$. The same trend was observed for $Fe_2(sacta)Cl_2$. It is likely that $Fe_2(sata)Cl_2$ and $Fe_2(sacta)Cl_2$ undergo dissociation and structural change in polar solvents.

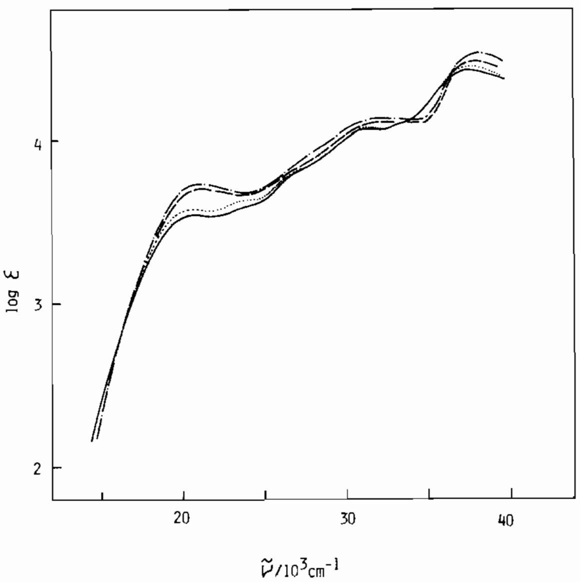

Fig. 5. Electronic absorption spectra of (——) $Fe_2(sata)Cl_2$, (- - - -) $Fe_2(sacta)Cl_2$, (– – –) Fe(salpn)Cl, and (– · –) Fe(sacda)Cl in dichloromethane.

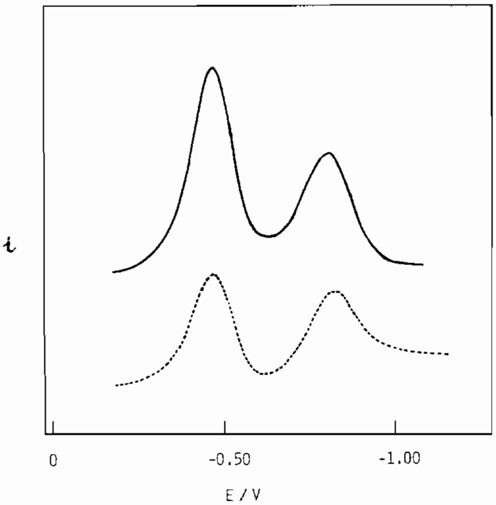

Fig. 6. Differential pulse polarograms of (——) $Fe_2(sata)Cl_2$ and (- - - -) $Fe_2(sacta)Cl_2$ in dichloromethane.

Differential pulse polarograms of $Fe_2(sata)Cl_2$ and $Fe_2(sacta)Cl_2$ are shown in Fig. 6. Similarly to the cases of the iron(II) complexes, each polarogram showed two reduction waves at ~-0.47 and ~-0.80 V, both being attributed to the reduction at the iron. Polarograms of $Fe(salen)N_3$ and its homologs have been measured by dropping mercury electrode in DMF, where the Fe(III)/Fe(II) reduction occurred at -0.5—-0.6 V *vs.* SCE [18]. These reduction potentials correspond to the potential of the second wave of the present complexes. Further, we have measured differential pulse polarograms of Fe(salpn)X (X = Cl, Br) and Fe(sacda)Cl for comparison. The results indicate that the reduction of iron(III) occurs around -0.8—-0.9 V depending upon the apical donor group (Table I). These reduction potentials are practically the same as that of the second wave of the present complexes. Based on these facts and by analogy with the conclusion for the iron(II) complexes, we may conclude that the present iron(III) complexes exist as the stacked and non-stacked conformers, where the stacked conformer is reduced at -0.47 V by one-electron transfer process to the Fe(III)–Fe(II) species and the non-stacked species

TABLE I. Reduction Potentials of Binuclear Iron(III) Complexes, $Fe_2(sata)Cl_2$ and $Fe_2(sacta)Cl_2$, and Related Mononuclear Complexes.

Complexes	$E_{1/2}$	
$Fe_2(sata)Cl_2$	−0.47	−0.80
$Fe_2(sacta)Cl_2$	−0.46	−0.81
Fe(salpn)Cl		−0.89
Fe(salpn)Br		−0.78
Fe(sacda)Cl		−0.91

at −0.80 V by two-electron transfer process to the Fe(II)–Fe(II) species.

The magnetic moments of $Fe_4(sata)_3$ and $Fe_4(sacta)_3$ per iron atom at room temperature are *ca.* 5.7 BM, which showed little decrease when temperature was lowered to liquid nitrogen temperature. These complexes exhibited a differential pulse polarogram showing only one reduction wave near −1.50 V. This suggests that all iron(III) ions in these complexes are equivalent. However, the detailed structures of the complexes are unknown at present.

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