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Synthesis and Magnetic Properties of Iron(III) Complexes with Several Quadridentate Schiff Bases[1]

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New iron(III) complexes containing quadridentate Schiff bases, $[Fe(L)AB]^{n+}$, were prepared, where H_2L represents a quadridentate Schiff base, and A and B, unidentate ligands, such as imidazole, pyridine derivatives, and cyanide ions. The magnetic moments of the complexes are in the range of 1.9—6.0 B.M. at room temperature. Based on the magnetic susceptibilities at various temperatures (90—295 K), these compleses were classified into four types: (1) high-spin ($S=5/2$), (2) low-spin ($S=1/2$), (3) intermediate spin ($S=3/2$), and (4) cross-over complexes, the last of which have a ligand-field strength near the cross-over point of high-spin and low-spin types. From the ESR spectra obtained, the existence of a spin-equilibrium was established for the cross-over complexes.

Iron(III) complexes have a $(3d)^5$ electronic configuration and the energy levels in the octahedral ligand field have been calculated by Tanabe and Sugano.[2] According to their diagram, three types of iron(III) complexes can be expected in the octahedral field, depending upon the strength of the ligand field, that is, high-spin ($S=5/2$), low-spin ($S=1/2$), and cross-over complexes, the last of which have a ligand-field strength near the cross-over point of high-spin and low-spin types. In fact, complexes of these types are known for six-coordinated iron(III) complexes.[3]

For the iron(III) complexes of porphyrin derivatives (abbreviated as H_2por), $[Fe(por)AB]^{n+}$, the magnetic moments depend greatly upon the axial ligands, A and B, and fall in the range of 2.2—5.9 B.M. at room temperature. In seeking to explain the variation in magnetic moments, some authors have claimed the existence of a spin-equilibrium of two spin states in these porphyrin derivatives.[4] However, Harris has carried out numerous calculations on the magnetic properties of iron(III) complexes with tetragonal symmetry and concluded that the anomalous magnetic behavior of heme derivatives should be elucidated in terms of "spin-mixed states."[5,6] For the interpretation of the magnetic properties of the cross-over complexes in more detail, systematic data on many other complexes are necessary. Accordingly, we have attempted to prepare iron(III) complexes with a tetragonal symmetry, by the use of quadridentate Schiff bases (abbreviated as H_2L) as the planar ligands. The prepared complexes have the general formula of $[Fe(L)AB]^{n+}$, where A and B are unidentate ligands, such as imidazole, pyridine derivatives, and cyanide ions.

The Schiff bases and other ligands used in this study are listed in Tables 1 and 2 with their abbreviations, while the structural formulas of their representative Schiff bases are shown in Fig. 1.

Table 1. Abbreviations of the Schiff bases
(Skeletal structures are depicted in Fig. 1.)

Type	X	R	Y	Abbreviation (L)
(a)	H	$-CH_2CH_2-$		salen
	H	1,2-C_6H_4		salphen
	3-CH_3O	$-CH_2CH_2-$		vanen
(b)		$-CH_2CH_2-$	CH_3	acen
		$-CH_2CH_2-$	C_6H_5	bzacen

Table 2. Abbreviations of the unidentate ligands

Ligands	Abbreviation
Imidazole	im
Pyridine	py
4-Aminopyridine	apy
β-Picoline	β-pic
γ-Picoline	γ-pic

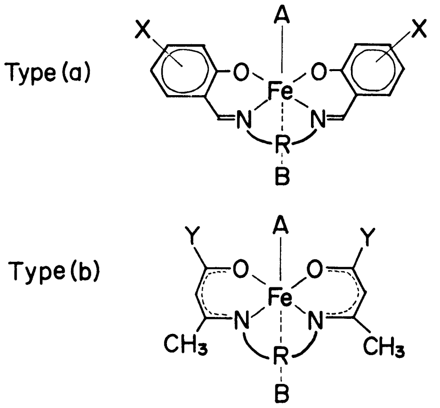

Fig. 1. Iron(III) Schiff base complexes (*cf.* Table 1).

Experimental

Preparations. The quadridentate Schiff bases used in this study were prepared according to the methods described in the literatures.[7]

[Fe(salen)Cl]: This complex was prepared according to the method of Pfeiffer *et al.*[8]

[Fe(acen)Cl]: The H_2acen ligand (1.1 g) dissolved in absolute methanol (20 ml), was added to anhydrous iron(III) chloride (0.8 g) dissolved in absolute methanol (20 ml). To this mixture, triethylamine (1.0 g) was then added. The resulting solution was warmed at 60 °C for ten minutes and subsequently allowed to stand for five hours at room temperature. The purple crystals yielded were filtered and washed with cold absolute methanol.

[Fe(salen)(im)$_2$]B(ph)$_4$: The [Fe(salen)Cl] complex was suspended in absolute methanol (40 ml), and then imidazole (0.6 g) was added to this solution. The solution was warmed at 60 °C for ten minutes and then filtered. Sodium tetraphenylborate (0.7 g) dissolved in absolute methanol (10 ml) was added to the filtrate, and the solution was allowed to

stand overnight at room temperature. The reddish-brown crystals separated were filtered and washed with cold ethanol.

$[Fe(vanen)(im)_2]B(ph)_4$ and $[Fe(salphen)(im)_2]B(ph)_4$: These complexes were prepared according to a procedure similar to that described for $[Fe(salen)(im)_2]B(ph)_4$.

$[Fe(acen)(im)_2]B(ph)_4$, $[Fe(acen)(py)_2]B(ph)_4$, $[Fe(acen)(\beta\text{-}pic)_2]B(ph)_4$, $[Fe(acen)(apy)_2]ClO_4$, and $[Fe(acen)(\gamma\text{-}ipic)_2]ClO_4$: These complexes were prepared according to a method similar to that described above, except that [Fe(acen)Cl] was used, instead of [Fe(salen)Cl], and $NaClO_4$ instead of $NaB(ph)_4$.

$[Fe(salen)CN]\cdot CH_3OH$: Sodium cyanide (0.05 g) dissolved in absolute methanol (15 ml) was added to an absolute methanol solution (15 ml) of $[Fe(salen)(im)_2]B(ph)_4$(0.8 g). This solution was allowed to stand five hours at room temperature. The black precipitate thus yielded was filtered and washed with absolute methanol.

$Na[Fe(salen)(CN)_2]\cdot CH_3OH$: Sodium cyanide (0.1 g) dissolved in absolute methanol (15 ml) was added to an absolute methanol solution containing 0.55 gram of [Fe(salen)Cl], and then the solution was warmed at 60 °C for ten minutes. The solution was evaporated under reduced pressure, and the dicyano complex thus separated was recrystallized from hot absolute methanol. The green crystals thus obtained were filtered and washed with absolute ethanol.

$Na[Fe(acen)(CN)_2]$ and $[Fe(bzacen)(im)CN]$: These complexes were prepared by methods similar to those described for $Na[Fe(salen)(CN)_2]$ and $[Fe(salen)CN]\cdot CH_3OH$ respectively.

$[Fe(bzacen)(im)_2]B(ph)_4$: To a hot absolute methanol solution (40 ml) of anhydrous ferric chloride (0.85 g), H_2 bzacen (1.73 g) and imidazole (2.00 g) were added, the solution was then warmed at 60 °C for ten minutes and filtered. To this filtrate, $NaB(ph)_4$ (1.0 g) was added, and the solution was allowed to stand for five hours. The dark green crystals thus precipitated were filtered and washed with cold absolute methanol.

Measurements. Magnetic susceptibilities were measured over the range from the temperature of liquid nitrogen to room temperature by the Faraday method, Pascal's constants being used for diamagnetic correction. Mercury(II) tetrathiocyanatocobaltate(II), $HgCo(NCS)_4$ was employed as the standard for magnetic susceptibility. The effective magnetic moments at room temperature were calculated from the expression:

$$\mu_{\mathrm{eff}} = 2.828\sqrt{T\cdot\chi_A}$$

where χ_A is the susceptibility per gram atom of iron.

The ESR spectra of polycrystalline samples and DMSO-frozen solutions were measured with a JEOL ESR spectrometer model, JES-ME-3X using an X-band. DPPH was used as the standard marker.

The absorption spectra were measured with a recording spectrophotometer model, Hitachi EPS-2, at room temperature.

Results and Discussion

Characterization of New Complexes. Table 3 gives the analytical data, color, and magnetic moments of the complexes. The structures of the new complexes are assumed to be *trans* (A, B)-$[Fe(L)AB]^{n+}$, because the quadridentate Schiff bases used in this study prefer the planar coordination, furthermore, $Na[Fe(salen)(CN)_2]$ shows only one sharp band, at 2105 cm^{-1}, in the infrared spectrum.

The magnetic moments of the complexes depend greatly on the Schiff bases and axial ligands; they fall in the range of 1.9—6.0 B.M. at room temperature. On the basis of magnetic susceptibilities at various temperatures (90—295 K), the **1**—**3** and **4**—**8** complexes are high-spin and low-spin types, respectively. The **9**—**13** complexes show intermediate magnetic moments (2.5—5.0 B.M.) between high-spin and low-spin values; accordingly, they may be assumed to be cross-over complexes. The interpretation of the magnetic data on the assumption of a dimeric structure such as $[Fe(salen)Cl]_2$[9] is impossible, because all the complexes can assume six-coordination without any bridged structure.

Judging from the magnetic data of the series $[Fe(L)(im)_2]^{n+}$ complexes shown in Table 3, the spin-pairing abilities of planar Schiff bases appear to be of the following order: $H_2acen > H_2bzacen > H_2salen \approx H_2salphen$. Thus, it was revealed that a small change in the planar

TABLE 3. ANALYTICAL DATA AND MAGNETIC MOMENTS

No.	Complexes	C Calcd (Found)	H Calcd (Found)	N Calcd (Found)	Color	Magnetic moments (B.M.) 295 K	80 K
(**1**)	$[Fe(salen)(im)_2]B(ph)_4$	71.06(71.57)	5.44(5.50)	10.81(10.84)	brown	5.89	5.37
(**2**)	$[Fe(salphen)(im)_2]B(ph)_4$	72.74(72.42)	5.13(5.04)	10.18(10.06)	brown	5.97	5.58
(**3**)	[Fe(acen)Cl]	45.96(45.84)	5.79(5.79)	8.93(8.89)	purple	5.85	5.56
(**4**)	$Na[Fe(salen)(CN)_2]\cdot CH_3OH$	53.17(53.24)	4.23(4.21)	13.05(13.22)	green	1.87	1.74
(**5**)	$Na[Fe(acen)(CN)_2]$	47.61(46.65)	5.14(5.26)	15.86(15.40)	green	2.11	2.00
(**6**)	$[Fe(acen)(im)_2]B(ph)_4$	68.77(68.35)	6.32(6.36)	11.46(11.46)	green	2.17	1.91
(**7**)	$[Fe(acen)(apy)_2]ClO_4$	46.70(46.22)	5.34(5.29)	14.85(14.68)	green	2.29	2.14
(**8**)	[Fe(bzacen)(im)CN]	62.91(62.56)	5.28(5.31)	14.11(13.84)	green	1.99	1.80
(**9**)	$[Fe(vanen)(im)_2]B(ph)_4$	68.83(68.65)	5.54(5.61)	10.03(10.03)	dark purple	5.03	3.57
(**10**)	$[Fe(bzacen)(im)_2]B(ph)_4$	72.82(72.31)	5.88(5.88)	9.80(9.87)	brownish green	4.79	2.23
(**11**)	$[Fe(acen)(py)_2]B(ph)_4$	73.12(72.36)	6.40(6.35)	7.42(7.38)	green	3.31	2.30
(**12**)	$[Fe(acen)(\beta\text{-pic})_2]ClO_4$	51.13(50.52)	5.72(5.66)	9.94(9.87)	brownish green	2.51	1.93
(**13**)	$[Fe(acen)(\gamma\text{-pic})_2]B(ph)_4$	73.56(73.09)	6.69(6.62)	7.16(7.11)	brownish green	3.64	2.04

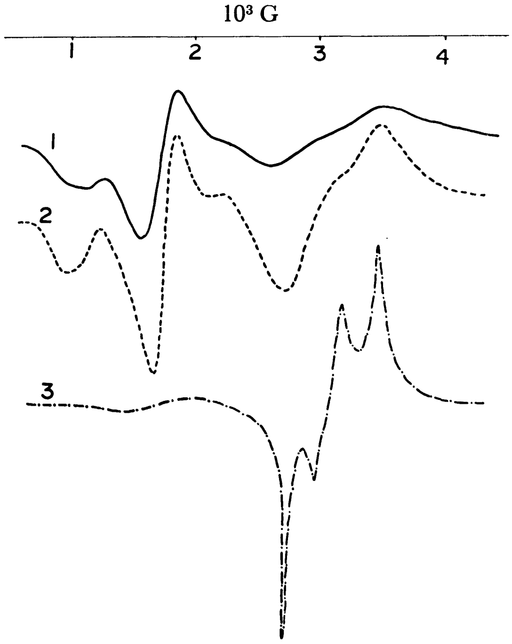

Fig. 2. Powder ESR spectra of [Fe(vanen)(im)$_2$]B(ph)$_4$ (X-band).
1: 244 K, 2: 184 K, 3: 77 K.

ligands exerts a large effect on the electronic configuration of the ground state of the iron(III) ion. From the magnetic data of the series of acen complexes shown in Table 3, the order of spin-pairing ability is: CN$>$imidazole$>$apy$>$$\beta$-pic$>py>$$\gamma$-pic. The order of the pyridine derivatives agrees with neither the order of basicity of pyridine nitrogen nor the spectrochemical series. These facts suggest that the choice of the spin state of [Fe(L)AB]$^{n+}$ depends not only on the ligand field strength, but also on the crystal lattice energy and the steric effect of the ligands.

Cross-over Complexes. In Fig. 2, the ESR spectra of [Fe(vanen)(im)$_2$]B(ph)$_4$ at various temperatures are shown. In Fig. 3, the ESR spectra of [Fe(salen)(im)$_2$]B(ph)$_4$(high-spin type) and Na[Fe(salen)(CN)$_2$](low-spin type) are shown. In the ESR spectrum of [Fe(salen)(im)$_2$]B(ph)$_4$, some absorptions are observed over the wide range of 1000—3000 G. This is characteristic of high-spin complexes.[10,11] On the other hand, in the case of Na[Fe(salen)(CN)$_2$], some peaks are observed at about 3000 gauss. The small anisotropy of *g*-values suggests that the electronic configuration of the ground state is $(d_{xz})^2(d_{yz})^2(d_{xy})^1$.[12]

In the ESR spectra of [Fe(vanen)(im)$_2$]B(ph)$_4$ and [Fe(bzacen)(im)$_2$]B(ph)$_4$,[1] some peaks are observed at about 3000 gauss and in the range of 1000—2700 G. As the temperature is lowered, the relative intensities of the absorptions change dramatically, as may be seen in Fig. 2, although the positions of the absorptions do not change. This fact indicates two or more spin states exists in these complexes in the temperature range investigated; undoubtedly one of them is $S=1/2$.

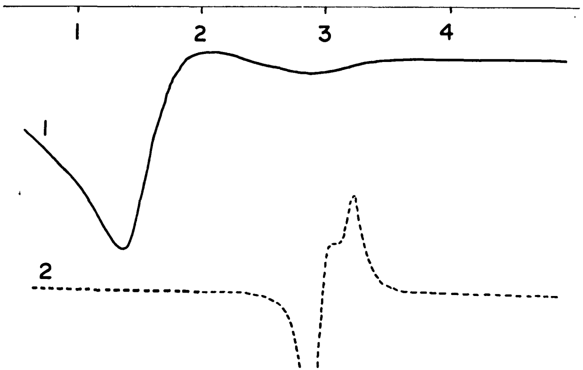

Fig. 3. Powder ESR spectra (X-band, at 244 K).
1: [Fe(salen)(im)$_2$]B(ph)$_4$ (high-spin complex),
2: Na[Fe(salen)(CN)$_2$] (low-spin complex).

Harris[5,6] investigated the magnetic properties of heme derivatives and concluded that the magnetic behavior of complexes with intermediate magnetic moments at room temperature should be explained in terms of "spin-mixed states." However, the presently obtained ESR spectra are not compatible with his prediction. Rather, the magnetic behavior of the **9**—**13** complexes should be interpreted in terms of a spin-equilibrium between two or more spin states. We further attempted to confirm the spin-equilibrium by the use of the Mössbauer spectra. However, clear peaks were not observed for high-spin complexes; therefore, the existence of spin-equilibrium could not be verified by the Mössbauer spectra.

Absorption Spectra. As shown in Table 3, the colors of the low-spin complexes differ from those of the high-spin complexes. In general, the Lambert-Beer law can not be applied to solutions of these complexes, probably because of the partial dissociation of axial ligands. Therefore, a small excess of axial ligands was added to the methanol solutions of the complexes. In Fig. 4, the absorption spectra of [Fe(salen)(im)$_2$]B(ph)$_4$, Na[Fe(acen)(CN)$_2$], and [Fe(bzacen)(im)$_2$]B(ph)$_4$ are shown. The low-spin Schiff base complexes are generally green or blue, perhaps because of the absorptions at

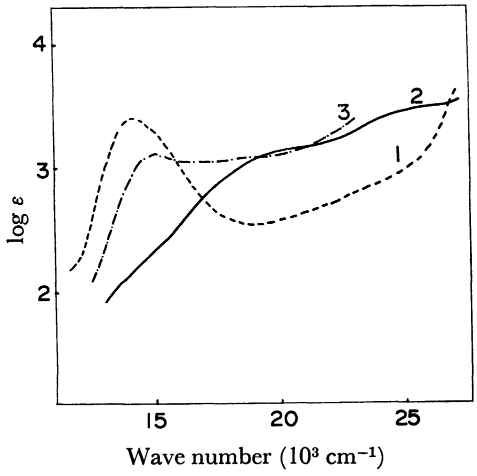

Fig. 4. Absorption spectra of iron(III) Schiff base complexes (at 295 K, in methanol solution).
1: Na[Fe(acen)(CN)$_2$] (low-spin type, 1.9×10^{-4} M),
2: [Fe(salen)(im)$_2$]B(ph)$_4$ (high-spin type, 2.7×10^{-4} M),
3: [Fe(bzacen)(im)$_2$]B(ph)$_4$ (cross-over complex, 4.4×10^{-4} M).

14—16$\times 10^3$ cm^{-1} (log $\varepsilon \approx 3$). Such absorptions are not observed for high-spin complexes. These bands may be attributed to the charge-transfer transitions between metal and Schiff bases, because this absorption is independent of axial ligands. On the other hand, the absorption spectrum of [Fe(bzacen)(im)$_2$]B(ph)$_4$ seems to be a superposition of high-spin and low-spin types; this is consistent with the results of the ESR spectra.

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