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ESR Spectra of Low-Spin Iron(III) Complexes with Several Quadridentate Schiff Bases

Y. NISHIDA, S. OSHIO and S. KIDA

Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Japan 812

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ESR spectra of several low-spin six-coordinated iron(III) complexes with the general formula, $[FeLAB]^{n+}$ were measured, where H_2L represents a quadridentate Schiff base and A and B, various unidentate ligands, such as imidazole, pyridine derivatives and cyanide ion. All the ESR spectra obtained are of rhombic symmetry and the g_1, g_2 and g_3 are in the range 2.3 ~ 2.4, 2.1 ~ 2.2 and 1.9 ~ 2.0, respectively. Analysis of the ESR data by Kotani's method has shown that an unpaired electron lies in d_{xy} orbital for all the complexes examined.

Introduction

Low-spin iron(III) complexes have a $(d\epsilon)^5$ electronic configuration with one unpaired electron under octahedral symmetry. However, almost all low-spin iron(III) complexes are distorted from octahedral symmetry to a more or less degree, and the $d\epsilon$ orbitals are split into two or three levels, bringing about the question of estimating the order of energy levels. This question has been investigated by ESR for $[Fe(CN)_6]^{3-}$, [1, 2], $[Fe(bidentate\ ligand)_3]^{n+}$, [3–6] and $[FeporAB]^{n+}$, [7–9], where H_2por represents a porphyrin derivative and A and B, axial ligands such as imidazole, azide ion and cyanide ion, *etc.* The ESR spectra of $[FeporAB]^{n+}$ all display rhombic symmetry independent of axial ligands, and an unpaired electron was assumed to be present in the d_{yz} orbital, this implying that axial ligands do not exert so strong an effect as to change the order of energy levels of $d\epsilon$ orbitals. This assumption was also supported by the NMR studies [10, 11].

Recently we have synthesized a series of iron(III) complexes with quadridentate Schiff bases (abbreviated as H_2L) of the general formula, $[FeLAB]^{n+}$ where A and B represent imidazole, pyridine derivatives or cyanide ion. The complexes were found to involve various types of spin states [12]. Of these complexes, the low-spin complexes showed an ESR spectral pattern quite different from those found for $[FeporAB]^{n+}$, the main features of the spectral pattern being independent of axial ligands so far employed. In this paper we report the result of the detailed analysis of the ESR spectra by the use of Kotani's approach.

The quadridentate Schiff bases used in this study are listed in Table I with their abbreviations, and two representative ligands are illustrated in Fig. 1.

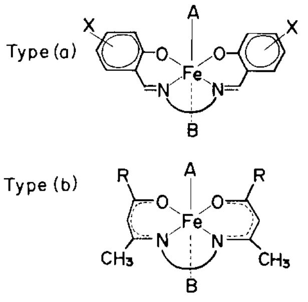

Fig. 1. Iron(III) Schiff base complexes.

TABLE I. Abbreviations of the Ligands.

Quadridentate Schiff Base	X*	R*	Type*	Abbreviation
N,N′-bis(salicylidene)ethylenediamine	H		a	H_2salen
N,N′-bis(3-methoxysalicylidene)ethylenediamine	$3\text{-}CH_3O$		a	H_2vanen
N,N′-bis(1-acetonylethylidene)ethylenediamine		CH_3	b	H_2acen
N,N′-bis(2-benzoyl-1-methylethylidene)ethylenediamine		C_6H_5	b	$H_2bzacen$
Unidentate Ligands				
Imidazole				im
4-Aminopyridine				apy

**Cf.* Fig. 1.

Experimental

Materials

The low-spin iron(III) complexes, $[FeLAB]^{n+}$ were prepared according to the methods described in the preceding paper [13].

Measurements

ESR spectra of the complexes were obtained with a JEOL ESR spectrometer model JES-ME-3X using an X-band. DPPH was used as a standard marker.

Results and Discussion

The ESR measurements of low-spin iron(III) complexes were carried out on the powder samples and DMSO frozen solutions. In the case of DMSO frozen solutions, a little excess of axial ligand was added in order to avoid partial dissociation of the complexes. The ESR spectra of powder samples are very similar to those of DMSO frozen solutions. As representative examples, the spectra of $[Feacen(im)_2]BPh_4$ and $Na[Feacen(CN)_2]$ are shown in Fig. 2. As shown in Fig. 2, three absorptions are found in the range 2700 ~ 3000 gauss. All the spectra of the complexes show rhombic symmetry, and g-values were calculated according to the usual methods [14, 15], and are listed in Table II. It is clear from the Table that g_1, g_2 and g_3 fall in the range 2.3 ~ 2.4, 2.1 ~ 2.25, and 1.9 ~ 2.0, respectively.

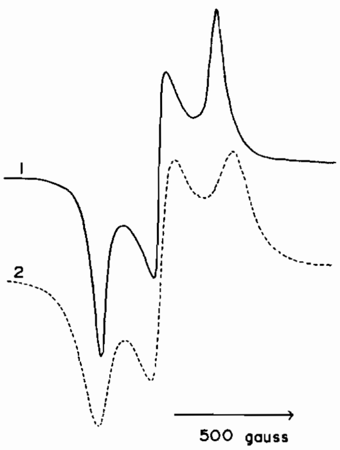

Fig. 2. Powder ESR spectra (X-band) at room temperature. 1: $Na[Feacen(CN)_2]$; 2: $[Feacen(im)_2]BPh_4$.

TABLE II. ESR Parameters of Low-Spin Iron(III) Complexes with Schiff Bases and Porphyrin Derivatives.

Complexes	g_3	g_2	g_1	Temperature
$Na[Fesalen(CN)_2]$	1.99	2.15	2.25	295 K
$[Fevanen(im)_2]BPh_4$	1.89	2.21	2.44	77 K
$[Feacen(im)_2]BPh_4$	1.94	2.14	2.36	295 K
$[Feacen(apy)_2]ClO_4$	1.91	2.10	2.31	295 K
$Na[Feacen(CN)_2]$	1.96	2.13	2.32	295 K
$[Febzacen(im)_2]BPh_4$	1.94	2.10	2.40	77 K
$[FebzacenCN(im)]$	1.94	2.09	2.35	295 K
Hemoglobin azide [8]	$g_z = 2.80, g_x = 1.72,$ $g_y = 2.22$			20 K
Myoglobin imidazole [9]	$g_z = 2.91, g_x = 1.53,$ $g_y = 2.26$			20 K
Myoglobin cyanide [9]	$g_z = 3.45, g_x = 0.93,$ $g_y = 1.89$			20 K

TABLE III. The Best Fit Values of c_1, c_2 and c_3 of Eqn. (1).

Complexes	c_1	c_2	c_3
$Na[Fesalen(CN)_2]$	0.063	−0.041	−0.997
$[Fevanen(im)_2]BPh_4$	0.115	−0.068	−0.991
$[Feacen(im)_2]BPh_4$	0.092	−0.044	−0.995
$[Feacen(apy)_2]ClO_4$	0.081	−0.034	−0.996
$Na[Feacen(CN)_2]$	0.082	−0.038	−0.996
$[Febzacen(im)_2]BPh_4$	0.102	−0.035	−0.994
$[FebzacenCN(im)]$	0.089	−0.030	−0.996

According to Kotani's approach [16], the lowest Kramers doublet of octahedral low-spin iron(III) complexes is described as follows, using hole formalism within $(d\epsilon)^1$ electronic configuration

$$\begin{aligned}\Psi^+ &= c_1 d_{yz}^{\ +} + ic_2 d_{xz}^{\ +} + c_3 d_{xy}^{\ -}\\ \Psi^- &= -c_1 d_{yz}^{\ -} + ic_2 d_{xz}^{\ -} + c_3 d_{xy}^{\ +}\end{aligned} \qquad (1)$$

in which the coefficients, c_1, c_2 and c_3 are taken to be real. Using the above wave functions, the principal components of g-tensors are calculated,

$$\begin{aligned}g_x &= 2|\{(c_2 + c_3)^2 - c_1^2\}|\\ g_y &= 2|\{(c_1 - c_3)^2 - c_2^2\}|\\ g_z &= 2|\{(c_1 + c_2)^2 - c_3^2\}|\end{aligned} \qquad (2)$$

where absolute values are used to ensure that g_x, g_y and g_z are positive quantities.

Substituting the observed values for g-values of the equation (2) and using the relation (3),

$$c_1^2 + c_2^2 + c_3^2 = 1 \qquad (3)$$

we obtained the best fit values of c_1, c_2 and c_3 for all the complexes by the least squares method, which are given in Table III. In our calculation the orbital reduction factors have been taken to be unity, which is permissible in view of the incompleteness of the theory as pointed out by Griffith [17]. From Table III, it is clear that $|c_3|$ is much larger than $|c_1|$ and $|c_2|$ for all the complexes obtained in this study. This means that an unpaired electron in these complexes is mainly in the d_{xy} orbital, independent of the axial ligands. It should be noticed that an unpaired electron lies in the d_{yz} orbital in iron(III) porphyrin complexes irrespective of the axial ligands [7–11].

From the above facts it may be concluded that the axial ligands do not exert so strong effect as to change the order of energy levels of dϵ orbitals, and the splitting of dϵ orbitals is mainly determined by the planar ligands, such as Schiff bases and porphyrin in iron(III) complexes.

The most remarkable difference in the Schiff base and the porphyrin complexes is the anisotropy of g-values. As shown in Table II, the anisotropy of g-values in porphyrin complexes is much larger than that of Schiff base complexes. Another remarkable difference is that the ESR spectra of porphyrin complexes can be obtained only at very low temperature (below 100 K), while we can measure the ESR spectra of Schiff base complexes at room temperature with ease. These differences may be attributed to the different electronic configuration of ground states of Schiff base and porphyrin complexes.

Our conclusion on the ground state configuration of Schiff base iron(III) complexes deduced from the ESR spectra has been shown to be supported by our recent study on the values of quadrupole splitting. The details on this discussion will be published elsewhere [18].

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