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# ESR and Mössbauer Spectra of Low-spin Iron(III) Complexes with Dimethylglyoxime

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*New low-spin iron(III) complexes with dimethylglyoxime,* $[Fe(dgm)_2(A)_2]B(ph)_4$ *were prepared, where Hdgm represents dimethylglyoxime, and A is imidazole or N-ethylimidazole. ESR spectra of the complexes were of axial symmetry, giving* $g_\parallel = 1.96$ *and* $g_\perp = 2.28$*. From the results, it was assumed that an unpaired electron lies in the* $d_{xy}$ *orbital of the iron atom. The absolute values of the quadrupole splitting,* $|\Delta E|$ *were 2.84 mm/sec for A = imidazole, and 2.79 mm/sec for A = N-ethylimidazole, respectively. A detailed comparison of the* $|\Delta E|$ *values with those of iron(III)–porphyrin complexes led to the conclusion that not only the contribution from the 3d electrons of iron but also that from the external ligand charges should be taken into consideration in order to elucidate the observed* $|\Delta E|$ *values of the low-spin iron(III) complexes.*

## Introduction

From the Mössbauer spectra of $^{57}$Fe, isomer shift (c.s.) and quadrupole splitting (ΔE) are obtained, which are important for the discussion on the oxidation state of iron and the nature of the coordination bonds in iron complexes [1]. The magnitude of the quadrupole splitting is proportional to the electric field gradient (EFG) tensor which interacts with the quadrupole moment of the nucleus. While isomer shift measures the s-electron density at the nucleus, the EFG tensor measures the distortion from the cubic symmetry of the electron distribution and ligands about the Mössbauer atom.

The EFG tensor can be expressed as a sum of the two contributions, $q_{lat}$, the contribution from the external ligand charges, and $q_{val}$, the contribution from the valence electrons [1].

Both $q_{lat}$ and $q_{val}$ terms can, in principle, be calculated using the theoretical expressions [1], if the crystal structure and the valence orbital populations are known. However it is usually difficult to assign a charge to each atom of the ligands, and valence orbital populations are usually not known. Therefore, semiempirical methods such as the additivity model have been proposed to rationalize the observed |ΔE| values of low-spin iron(II) complexes [1–5]. However, only few study has been reported on the observed |ΔE| values of low-spin iron(III) complexes.

In this study we synthesized new low-spin iron(III) complexes with the general formula, $[Fe(dgm)_2(A)_2]B(ph)_4$, where Hdgm represents dimethylglyoxime, and A are imidazole and N-ethylimidazole, and measured their ESR spectra, attempting to elucidate the observed |ΔE| values of iron(III)–dimethylglyoxime complexes in terms of the results of ESR spectra and |ΔE| values of low-spin iron(III)–porphyrin complexes. Hereafter imidazole and N-ethylimidazole are abbreviated as im and etim, respectively.

## Experimental

### *Preparation of the Complexes*

$[Fe(dgm)_2(im)_2]B(ph)_4 \cdot CH_3OH$: To an absolute methanol solution (30 ml) of anhydrous iron(III) chloride (0.5 g), dimethylglyoxime (0.7 g) was added, and the solution was warmed at 60 C for ten minutes. To this solution was added imidazole (0.7 g) and the resulting solution was kept at 60 C for ten minutes and filtered. The filtrate was added to the absolute methanol solution (10 ml) containing sodium tetraphenylborate (1.0 g), and allowed to stand for several hours at room temperature. Brown crystals yielded were filtered and washed with absolute methanol.

According to a method similar to that described above, $[Fe(dgm)_2(etim)_2]B(ph)_4 \cdot CH_3OH$ was also prepared. Found: C, 60.56%, H, 5.99%, N, 14.50%. Calcd. for $[Fe(dgm)_2(im)_2]B(ph)_4 \cdot CH_3OH$: C, 60.50%, H, 5.69%, N, 14.99%. Found: C, 62.25%, H, 6.56%, N, 13.51%. Calcd. for $[Fe(dgm)_2(etim)_2]B(ph)_4 \cdot CH_3OH$: C, 62.39%, H, 6.34%, N, 13.76%.

### *Measurements*

ESR spectra were measured with a JEOL ESR apparatus model JES-ME-3X using an X-band, DPPH being used as a standard marker. The principal values of g-tensors were calculated according to the usual methods [6, 7]. Magnetic susceptibilities were

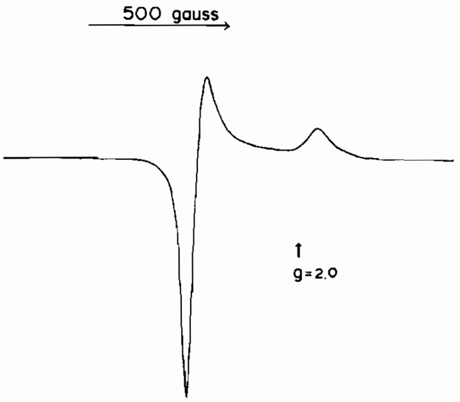

Figure 1. ESR spectrum of $[Fe(dgm)_2(im)_2]B(ph)_4$ (powder, 295 °K).

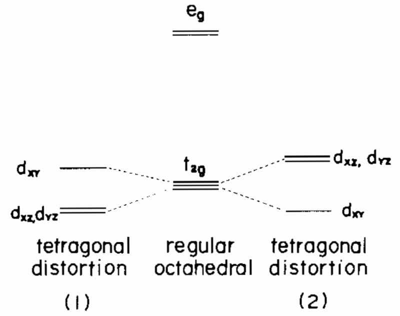

Figure 2. The splitting of 3d orbitals in tetragonal symmetry.

measured by Faraday method, Pascal's constant being used for diamagnetic correction. Mercury tetra(thiocyanato)cobaltate(II) was employed as a standard for magnetic susceptibility. The effective magnetic moments at room temperature were calculated from the expression,

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

where $\chi_A$ is the susceptibility per gram atom of iron.

The Mössbauer spectra were obtained according to the method described in the separate paper [8]. The spectrometer was calibrated by using sodium nitroprusside and metallic iron. Isomer shifts were quoted with respect of the centroid of metallic iron (*cf.* Fig. 3).

## Results and Discussion

### *ESR and Mössbauer Spectra*

The magnetic moments of the complexes obtained in this study were 2.28 BM for A = imidazole and 2.18 BM for A = N-ethylimidazole at room temperature, respectively, indicating that both complexes are of the low-spin type. The structures of these complexes are assumed to be *trans*-(A)-$[Fe(dgm)_2(A)_2]^+$, because bis(dimethylglyoximato)metal complexes generally prefer planar coordination [9].

As shown in Fig. 1, ESR spectra of these complexes are of axial symmetry both in powder and in DMSO frozen solutions, from which $g_\parallel$ and $g_\perp$ were calculated to be 1.96 and 2.28, respectively. There are two possibilities for the ground state configurations of low-spin six-coordinate iron(III) complexes with tetragonal symmetry, as shown in Fig. 2,

(1) $(d_{xz})^2(d_{yz})^2(d_{xy})^1$

and

(2) $(d_{xz})^2(d_{xy})^2(d_{yz})^1$ (or $(d_{yz})^2(d_{xy})^2(d_{xz})^1$).

In fact, the low-spin iron(III) complexes so far studied can be classified into Type-A and Type-B in terms of their ESR spectra, as shown in Table I, and an unpaired electron has assumed to be in the $d_{yz}$ and an unpaired electron has been assumed to be in the $d_{yz}$ and in the $d_{xy}$ orbital for Type-A and Type-B complexes, respectively. It should be noted that for Type-A complexes, $g_z$ is much larger than 2.0 and all the ESR spectra are of the rhombic symmetry, whereas the symmetry and the anisotropy of three g-tensors is small. The features of the ESR parameters of both Type-A and Type-B complexes can be explained in terms of the ligand field theory, as described in the Appendix.

It is clear that the $[Fe(dgm)_2(A)_2]B(ph)_4$ complexes belong to Type-B on the basis of their observed ESR spectra. In order to confirm the above discussion, we have calculated three g-tensors according to Kotani's method [14, 15]. Since the iron(III) atom has a $(3d)^5$ electronic configuration, the low-spin iron(III) complexes can be treated in terms of the $(t_{2g})^1$ configuration. Thus, the wave functions of the lowest Kramers doublet can be written as follows,

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

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

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

In this paper we have calculated the coefficients, $c_1$, $c_2$ and $c_3$, solving the secular equation of the following 3 × 3 spin–orbit matrix,

TABLE I. ESR Parameters of Low-spin Iron(III) Complexes

| Type | Complexes | g-values | Ref. |
|---|---|---|---|
| A | Hemoglobin-$N_3$ | $g_z = 2.80$, $g_x = 1.72$, $g_y = 2.22$ | 10 |
|  | Myoglobin-imidazole | $g_z = 2.91$, $g_x = 1.53$, $g_y = 2.26$ | 11 |
|  | Myoglobin-cyanide | $g_z = 3.45$, $g_x = 0.93$, $g_y = 1.89$ | 11 |
| B | $[Fe(mnt)_3]^{3-}$ | $g_\parallel = 1.967$, $g_\perp = 2.113$ | 12 |
|  | $[Fe(terpy)_2]^{3+}$ | $g_\parallel = 1.76$, $g_\perp = 2.54$ | 13 |

TABLE II. Mössbauer Data of Iron(III) Complexes (295 °K).

| Complexes | Ground State Configuration | Observed $\lvert\Delta E\rvert$ (mm/sec) | Ref. |
|---|---|---|---|
| $[Fe(dgm)_2(im)_2]B(ph)_4$ | $(d_{xz})^2(d_{yz})^2(d_{xy})^1$ | 2.84 | This work |
| $[Fe(dgm)_2(etim)_2]B(ph)_4$ | $(d_{xz})^2(d_{yz})^2(d_{xy})^1$ | 2.79 | This work |
| $[Fe(tpp)(im)_2]Cl$ | $(d_{xy})^2(d_{xz})^2(d_{yz})^1$ [a] | 2.12 | 20 |
| Hemin-imidazole | $(d_{xy})^2(d_{xz})^2(d_{yz})^1$ [b] | 2.17 | 20 |

[a] Ref. 21. [b] Ref. 22.

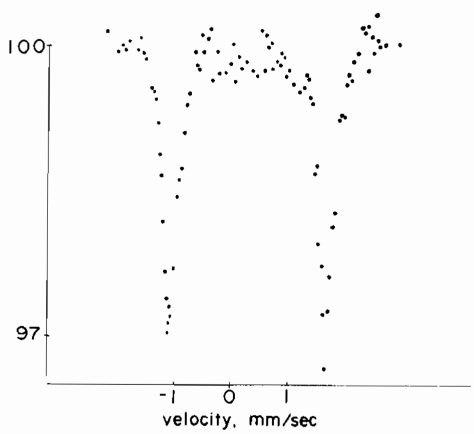

Figure 3. Mössbauer spectrum of $[Fe(dgm)_2(im)_2]B(ph)_4$ (powder, 295 °K).

$$\begin{array}{ccc}
(yz)^{+} & (xz)^{+} & (xy)^{-} \\
\hline
\Delta_1 & -\frac{i}{2}\lambda & \frac{1}{2}\lambda \\
\frac{i}{2}\lambda & \Delta_2 & -\frac{i}{2}\lambda \\
-\frac{1}{2}\lambda & \frac{i}{2}\lambda & \Delta_3
\end{array}$$

where λ is the spin–orbit coupling constant for 3d orbital. As the results, $g_\parallel$ and $g_\perp$ were calculated to be 1.94 and 2.26 on the assumption that $\Delta_1 = \Delta_2 = 3000\ cm^{-1}$, $\Delta_3 = 0$, and $\lambda = -400\ cm^{-1}$, $|c_1|$, $|c_2|$, and $|c_3|$ being calculated to be 0.07, 0.07, and 0.995, respectively. From the above discussion, it was concluded that an unpaired electron lies in the $d_{xy}$ orbital of the iron atom in $[Fe(dgm)_2(A)_2]B(ph)_4$ complexes.

In Fig. 3, the Mössbauer spectrum of $[Fe(dgm)_2(im)_2]B(ph)_4$ obtained at room temperature is shown. The absolute values of the quadrupole splitting, $|\Delta E|$ were found to be 2.84 mm/sec for A = imidazole and 2.79 mm/sec for A = N-ethylimidazole, respectively. In Table II, the Mössbauer data of some low-spin iron(III) complexes of $[FeN_6]$ type are summarized. It is clear that the observed $|\Delta E|$ values of $[Fe(dgm)_2(A)_2]^+$ complexes (hereafter abbreviated as DGM-complexes) are considerably larger than those of iron(III)–porphyrin complexes (hereafter, POR-complexes).

### *Evaluation of the ΔE Values*

The ΔE value for $^{57}Fe$ can be calculated according to the equation [1],

$$\Delta E = e^2qQ\left(1 + \frac{\eta^2}{3}\right)^{1/2} \tag{3}$$

where Q, e, eq and η are the quadrupole moment of the $^{57}Fe$ atom, protonic charge, electric field gradient and assymetric parameter, respectively. Because η is smaller than 1.0 (therefore, $(1 + \eta^2/3)^{1/2} < 1.15$), ΔE is nearly proportional to q, which is expressed as a summation of $q_{val}$ and $q_{lat}$,

$$q = (1 - R)q_{val} + (1 - r_\infty)q_{lat} \tag{4}$$

TABLE III. Calculated $\Delta E_{lat}$ and $\Delta E_{val}$.

| Complexes | $\Delta E_{lat}$[a] (mm/sec) | Observed $\lvert\Delta E\rvert$ (mm/sec) | Sign[b] | $\Delta E_{val}$[c] (mm/sec) |
|---|---|---|---|---|
| $[Fe(dgm)_2(im)_2]B(ph)_4$ | 0.24 | 2.84 | – | –3.08 |
| $[Fe(dgm)_2(etim)_2]B(ph)_4$ | 0.24 | 2.79 | – | –3.03 |
| $[Fe(tpp)(im)_2]Cl$ | 0.48 | 2.12 | + | +1.64 |
| Hemin-imidazole | 0.48 | 2.17 | + | +1.69 |

[a] Calculated from equation (7) and (3). [b] Estimated sign for observed $\lvert\Delta E\rvert$ values, deduced from equation (6) and the relation $\lvert\Delta E_{val}\rvert > \lvert\Delta E_{lat}\rvert$. [c] Calculated from equation (5).

where $(1 - R)$ and $(1 - r_\infty)$ are the Sternheimer antishielding factors [1]. From equation (3) and (4), we obtain,

$$\Delta E = \Delta E_{val} + \Delta E_{lat} \qquad (5)$$

where $\Delta E_{val}$ and $\Delta E_{lat}$ are the quadrupole splittings due to $q_{val}$ and $q_{lat}$, respectively.

The $q_{val}$ contribution from d electrons can be written by using $N_i'$s,

$$q_{val} = k[N_{x^2-y^2} - N_{z^2} + N_{xy} - \frac{1}{2}(N_{xz} + N_{yz})] \qquad (6)$$

where $K = 4/7\ \langle r^{-3}\rangle_{3d}$ and $N_i$ is an electron population for each d-orbital [1].

According to the equation (6), $\Delta E_{val}$ are calculated to be $-K$ and $K/2$ for the $[FeN_6]$ type complexes with the ground state configuration of $(d_{xz})^2(d_{yz})^2$-$(d_{xy})^1$ and $(d_{xy})^2(d_{xz})^2(d_{yz})^1$, respectively, where $(N_{x^2-y^2} - N_{z^2})$ is assumed to be zero. This means that the $\lvert\Delta E\rvert$ values of DGM-complexes are estimated to be twice larger than those of POR-complexes, however experimental values do not accord with the estimation (*cf.* Table II). Therefore in order to take $\Delta E_{lat}$ into consideration, we have calculated the $q_{lat}$ according to the point charge model [1]

$$q_{lat} = \sum_j \frac{P_j(3\cos^2\theta_j)}{r_j^3} \qquad (7)$$

where $P_j$ is the charge on the j-th ligand atom, and $(r_j, \theta_j)$ are the position coordinates. Fortunately the detailed molecular orbital calculations have been reported for DGM- and POR-complexes [16–18]. According to their results, there is a rather large difference in the net charge on the coordinated nitrogen atoms in DGM- and POR-complexes; *i.e.*, in DGM-complexes the net charge on the nitrogen atoms is nearly zero, on the other hand, the average net charge on the coordinated nitrogen atoms of POR-complexes is about –0.18 [16–18]. Using their results, we calculated the $\Delta E_{lat}$ due to the oxygen and nitrogen atoms for DGM- and POR-complexes, respectively. As a result, $\Delta E_{lat}$ was calculated to be 0.24 mm/sec and 0.48 mm/sec for DGM- and POR-complexes, respectively, where the following values were used; $r_{Fe-O} = 3.1$ Å, $r_{Fe-N} = 2.0$ Å, $P_{oxygen} = -0.44$, $P_{nitrogen} = -0.20$, $(1 - r_\infty) = 12$ [1], $Q = 0.29$ barn, and the contribution from the imidazole molecule was neglected.

Assuming that 1) the principal axes of EFG tensors coincide with the molecular axes, and 2) the signs of the experimentally obtained $\lvert\Delta E\rvert$ agree with the prediction deduced from equation (6), we can evaluate $\Delta E_{val}$ according to equation (5), the results being shown in Table III. It should be noted that the calculated $\Delta E_{val}$ for DGM-complexes are roughly twice as large as those of POR-complexes, which is consistent with the prediction deduced from equation (6), and that the values are very close to the experimentally obtained $\Delta E$ value of $[Fe(terpy)_2]$-$(ClO_4)_3$ (–3.05 mm/sec at room temperature [13].

The complex, $[Fe(terpy)_2](ClO_4)_3$ is one of the low-spin $[FeN_6]$ type complexes and it has been confirmed that an unpaired electron localizes in the $d_{xy}$ orbital in terms of the ESR spectrum [13]. Because the six coordinated nitrogen atoms are roughly equivalent in $[Fe(terpy)_2]^{3+}$, $\Delta E_{lat}$ may be assumed to be zero, and accordingly the observed $\Delta E$ value can practically be reduced to $\Delta E_{val}$.

From the above discussion, we may conclude that (a) one can reasonably interprete observed $\lvert\Delta E\rvert$ values of DGM- and POR-complexes in terms of $q_{val}$ and $q_{lat}$, and (b) $\Delta E_{val}$'s of low-spin $[FeN_6]$ type complexes are roughly estimated at –3.0 mm/sec, when an unpaired electron localizes in the $d_{xy}$ orbital of the iron atom.

## Appendix

According to quantum mechanics, the g factor for an orbitally singlet ground state is calculated by the equation [19]

$$g_i = 2 - 2\lambda \sum_n \frac{|\langle\psi_n|\hat{L}_i|\psi_o\rangle|^2}{E_n} (i = x, y, z) \qquad (A\text{-}1)$$

where $E_n$ is the energy separation between the ground state and excited state, and $\psi_o$ and $\psi_n$ are the wave functions of the ground state and excited state, respectively. Thus the orbital contribution to g factor is mainly determined by the term, $|\langle\psi_n|\hat{L}_i|\psi_o\rangle|^2/E_n$.

When an unpaired electron lies in the $d_{yz}$ orbital of the iron(III) atom, $\psi_o$ is written as $(d_{yz})$ in terms of the $(t_{2g})^1$ hole formalism. The orbitals, $d_{x^2-y^2}$ and $d_{z^2}$ are the $e_g$-orbitals in the regular octahedral symmetry, and the energy gaps (= $E_n$ in equation (A-1)) between $d_{yz}$ and these two orbitals are large (at least $15 \times 10^3 \times \text{cm}^{-1}$), therefore the contributions from these two orbitals are neglected in Kotani's approach. On the other hand, $d_{xy}$ is one of the $t_{2g}$ orbitals in the octahedral symmetry and the energy separation between $d_{yz}$ and $d_{xy}$ is small (roughly $0 \sim 4 \times 10^3$ cm$^{-1}$). Thus it is estimated that $g_y$ should be larger than $g_x$ by the following relations,

$$\begin{aligned} \hat{L}_x|d_{yz}> &= i|d_{x^2-y^2}> + i\sqrt{3}|d_{z^2}> \\ \hat{L}_y|d_{yz}> &= i|d_{xy}> \qquad \text{(A-2)} \\ \hat{L}_z|d_{yz}> &= -i|d_{xz}> \end{aligned}$$

which is consistent with the experimental results (*cf.* Table I). Since $d_{xz}$ is also one of the $t_{2g}$ orbital in octahedral symmetry, the fact that $g_z$ is larger than 2.0 in POR-complexes can be explained in the same manner as described above.

In the case of the ground state configuration $(d_{xz})^2(d_{yz})^2(d_{xy})^1$, $g_y$ can be equal to $g_x$, provided that $d_{xz}$ and $d_{yz}$ orbitals are degenerate. In this case $g_z$ will be very close to 2.0, because of the following relations,

$$\begin{aligned} \hat{L}_x|d_{xy}> &= i|d_{xy}> \\ \hat{L}_y|d_{xy}> &= -i|d_{yz}> \qquad \text{(A-3)} \\ \hat{L}_z|d_{xz}> &= 2i|d_{x^2-y^2}>. \end{aligned}$$

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