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EPR Spectra of Gadolinium(III)-β-diketonate Complexes

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The electron paramagnetic resonance spectra of some gadolinium(III)-β-diketonate complexes were observed as frozen solutions. The observed spectra differ from each other upon changing the ligands, indicating that a change of the ligand fields and/or coordination structure of the ligands has a great effect on the behavior of the inner 4f electrons. Zero field splitting (ZFS) parameters were estimated by spectral simulations for the $^8\mathrm{S}_{\frac{7}{2}}$ system. The EPR spectral simulations attempted so far indicate that at least the ZFS parameter ($|D|$) for the Gd(hfa)$_3$ complex is much smaller than that for other complexes, such as Gd(acac)$_3$.

Since the rare-earth elements are characterized by their 4f-electrons, how the 4f-electrons contribute to chemical bonds is very important in understanding the chemistry of rare-earth ion complexes. It is thus a very interesting problem to elucidate the role and nature of the 4f-electrons in coordination complexes. If the behavior of the 4f-electrons can be observed directly, it is expected that fruitful information about them would be obtained. The 4f-electrons have paramagnetic properties owing to their electron spin and orbital angular momentum. Electron paramagnetic resonance (EPR)[1] is one of the powerful methods used to directly measure these magnetic properties of 4f-electrons. Though rare-earth ions in metal oxides and ionic crystals of alkali or alkali-earth elements have measured by EPR in order to investigate the effects of crystalfields or lattice constants, few coordination complexes of rare-earth ions have been studied.

In this work, the EPR spectra of some Gd(III)-β-diketonate complexes[2,3] were measured, and the effects of the coordinating ligands investigated. The Gd(III) ion, which has the 4f^7 electronic configuration and $^8\mathrm{S}_{\frac{7}{2}}$ as the energy term of the ground state, easily yields EPR signals, thus making it simple to analyze the spectra, because of the S-state ion for which the orbital angular momentun is quenched. EPR spectral simulations of disordered samples were attempted for $^8\mathrm{S}_{\frac{7}{2}}$ systems.

Experimental

Materials. All of the chemicals used were commercially obtained, and no further purifications were made. Gd(III) complexes were synthesized according to the literature with only small modifications.[4] A 1 : 3 molar ratio of GdCl$_3$ and the ligands were mixed in ethanol; the latter were neutralized by an equimolar base, such as (CH$_3$)$_4$NOH, and the precipitated powders were collected by filtration and dried. Complex formations were confirmed by the IR and EPR spectra.

EPR Measurement. The EPR spectra were observed using a JEOL RE3XG X-band EPR spectrometer with a liquid-nitrogen dewar or a cold gas-flow variable-temperature unit. The typical measurement condition involved a temperature range of 77—120 K, and a microwave power of 5—20 mW. Toluene–ethanol (1 : 1 v/v) frozen solutions of the Gd(III) complexes were used to observe the EPR spectra. This solvent was chosen to make a good glass of randomly oriented sample. The magnetic fields were measured using an EFM-2000AX field meter (Echo Electronics Co., Ltd.), and microwave frequencies were determined by a Mn^{2+} marker.

EPR spectral simulations were performed using original software based on the procedure described below at the Computer Center of Hirosaki University.

Analysis of the EPR Spectra for $^8\mathrm{S}_{\frac{7}{2}}$ Systems

The spin Hamiltonian for $^8\mathrm{S}_{\frac{7}{2}}$ systems was taken as

$$\hat{\mathscr{H}}=\frac{g\beta}{\hbar}\left(B_x\hat{\mathscr{S}}_x+B_y\hat{\mathscr{S}}_y+B_z\hat{\mathscr{S}}_z\right)+\frac{D}{\hbar^2}\left(\hat{\mathscr{S}}_z^2-\frac{1}{3}\hat{\mathscr{S}}^2\right)+\frac{E}{2\hbar^2}\left(\hat{\mathscr{S}}_+^2+\hat{\mathscr{S}}_-^2\right), \qquad (1)$$

where the g value is equal to that of the free spin (g_0= 2.0023); β and $\hbar$ are the Bohr magneton and Plank's constant divided by 2π, respectively. D and E are the zero-field splitting (ZFS) parameters. B_u and $\hat{\mathscr{S}}_u$ (where u=x,y, and z) are the u-direction component of the magnetic-flux densities and that of the electron-spin angular-momentum operators, respectively. $\hat{\mathscr{S}}_+$ and $\hat{\mathscr{S}}_-$ are the usual step-up and step-down operators of the electron spin. Only two interactions, the electron Zeeman (EZ) and ZFS, are included in this Hamiltonian; additional interactions, such as higher-order crystalfield terms, were not considered.

Nicklin et al. have developed a method to interpret the EPR spectra of Gd(III) ions, where the effective g-values are derived from some perturbative procedure with the ZFS interaction being an unperturbative term and EZ interaction being perturbation.[5] They indicated that the effective g-values are given as a function of the ZFS parameters: E/D, D, and the microwave frequency. It is also shown that E/D can be determined by making a comparison with the calculated results and the observed spectra. Nowadays, an EPR spectrometer with multi-microwave frequency is not popular for most reserchers, and the ZFS interactions of the Gd(III) complexes are not large enough to be considered an unperturbed term. Since we could not determine D according to the method described by Nicklin et al., a full-matrix diagonalization is required in order to analyze the powder spectra of the Gd(III) complexes.

In order to simulate the powder pattern EPR spectra of Gd(III) complexes, matrices of the spin Hamiltonian (Eq. 1) with all polar angles (θ and ϕ) should be calculated in order to obtain the energy levels. Instead of searching resonance fields, the eigenfield method was used to obtain them as eigenvalues of the matrices.[6] The spectral line-shape function ($S(B)$) for the full EPR spectra were constructed from the integral of all directions,

$$S(B) = \int_0^{2\pi}\int_0^{\pi/2} L(B - B_{\mathrm{res}}(\theta,\phi))\cdot I(\theta,\phi)\sin\theta \mathrm{d}\theta \mathrm{d}\phi, \quad (2)$$

where B_{res} is the resonance field, L the line-width function, for which a Gaussian-type function was used here, and I the transition intensity.[7] Furthermore, we assumed isotropic transition probabilities, isotropic line-widths, and that the transition probabilities and the line-widths are independent of m_{S}.

Results and Discussion

EPR Spectra. The X-band EPR spectra of Gd(III)-β-diketonate complexes are shown in Fig. 1. These spectra do not show satellites from the natural abundant isotopes Gd-155 (14.8%) and Gd-157 (15.65%), both of which have a nuclear spin (I) of $\frac{3}{2}$. The missing satellites are due to the very large line-width, i.e. the short spin-relaxation time. Thus, the observed structures in the EPR spectra are considered to be the fine structure due to the eight-fold spin multiplicity.

The observed EPR spectra are different from each other due to the change of the ligand. These spectra indicate that 4f-electrons, which are situated in the inner shell and are shielded by the outer 5s and 5p electrons, are affected by the ligand fields and/or coordination strictures. The Gd(hfa)$_3$ complex has different spectrum from the others, where a strong broad signal appears only at 320 mT. However, the other Gd(III) complexes have a similar spectral pattern, showing two sharp peaks at 110 and 220 mT, and have a very broad signal at 250—500 mT. The latter is also similar to the Gd(III) ion dissolved in a solvent as a mixture of ethanol and toluene, in which the ions are considered to be coordinated by alcoholic oxygens. All of the spectra obtained here can be classified in two groups: one is that of the Gd(hfa)$_3$ complex; the other is that of the remaining complexes. The spectrum of the Gd(acac)$_3$ complex is used to represent the latter group in the following arguments.

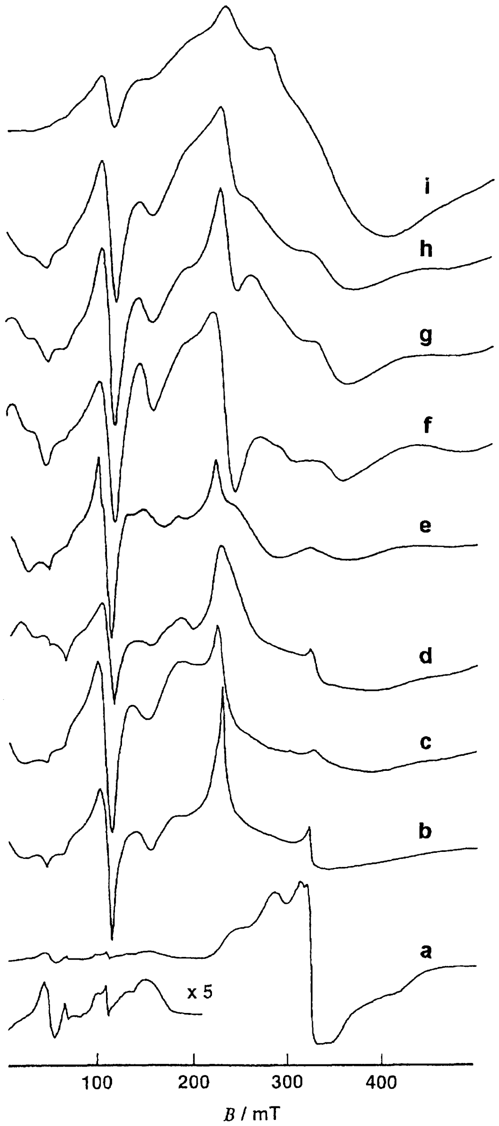

Fig. 1. EPR spectra of Gd(III)-β-diketonate complexes. (a) Gd(hfa)$_3$, (b) GdCl$_3$, (c) Gd(acac)$_3$, (d) Gd(thd)$_3$, (e) Gd(dbm)$_3$, (f) Gd(fta)$_3$, (g) Gd(tta)$_3$, (h) Gd(tfa)$_3$, (i) Gd(paa)$_3$. Typical measurement condition for (a)—(e): microwave frequency, 9.01 GHz; temperature, 77 K; 100 kHz field modulation, 0.2 mT$_{\mathrm{p-p}}$. And that for (f)—(i): microwave frequency, 9.2 GHz; temperature, 120 K; 100 kHz field modulation, 2 mT$_{\mathrm{p-p}}$.

The ZFS parameter ($|D|$) of the Gd(hfa)$_3$ complex has been estimated to be smaller than that of the Gd(acac)$_3$ complex (vide infra). It is interesting that the Gd(III) complex, with hfa$^-$ as a ligand, which has an extremely small pK_{a} value,[8] has very small $|D|$. It is considered that the electron densities on the donating oxygens of the hfa$^-$ ligand are very small for the electron-withdrawing nature of fluorines; thus, this ligand gives a weaker ligand field than do the others. It is shown that the electron spins of the Gd(III) ions are not very much perturbed by a weak ligand field. In other words, these results clearly indicate that the 4f-electrons are affected by the strength and geometry of the ligand field.

Spectral simulations were performed by the method described above; typical results are shown in Figs. 2 and 3. Although these simulation spectra don't show perfect agreement with the observed spectra, the qualitative information about the 4f-electrons can be obtained. The calculated angular variations of the resonance fields show that they are concentrated at 200—450 mT in the X-band when $|D|$ is small. It may give a spectrum similar to that for the Gd(hfa)$_3$ complex (Fig. 2). However, when $|D|$ is large, the resonance fields, which are spread to a higher field, give broad EPR signals above 300 mT. Furthermore, the EPR signal peaks at 110 and 220 mT are given by the turning points and/or stationary points of the resonance fields (see the calculated results for the angular-dependence of the resonance fields), which are shown in the Gd(acac)$_3$ complex (Fig. 3).

The EPR spectra for the Gd(III) ions in ionic crystals with a high site-symmetry, such as octahedral or cubic for alkali halide, alkali-earth oxide or etc., have been interpreted by Hamiltonian which includes the 4-th and 6-th order ligand field terms (i=4 or 6 in Eq. 3).[9,10)]

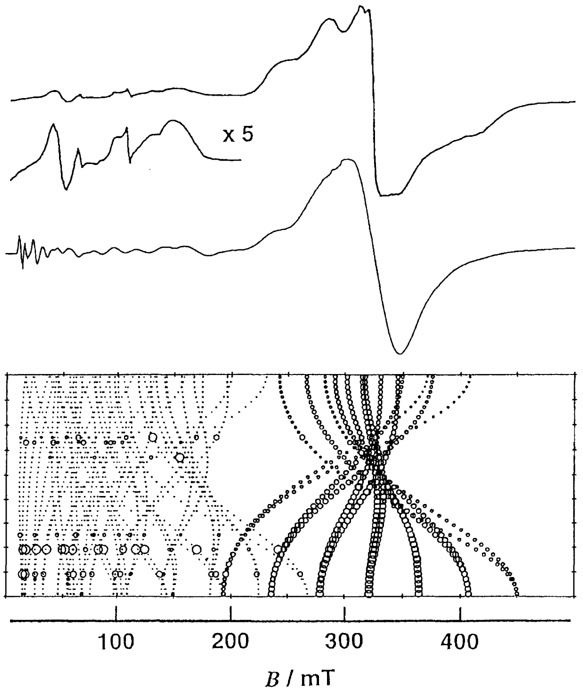

Fig. 2. Observed and simulated EPR spectra for Gd(hfa)$_3$ complex, and angular θ dependence of resonance fields. Solid line: observed spectra. Mw. frequency, 9.005 GHz, mw. power, 5 mW, field modulation, 100 kHz, 0.2 mT$_{\text{p-p}}$, and temperature, 77 K; thin line: simulated spectra. D=0.6 GHz, E=0.06 GHz, (E/D=0.1), and line-width 500 MHz. The resonance fields are shown for both $\phi=0$ and $\phi=\pi/2$, and the size of circles indicate the transition probabilities.

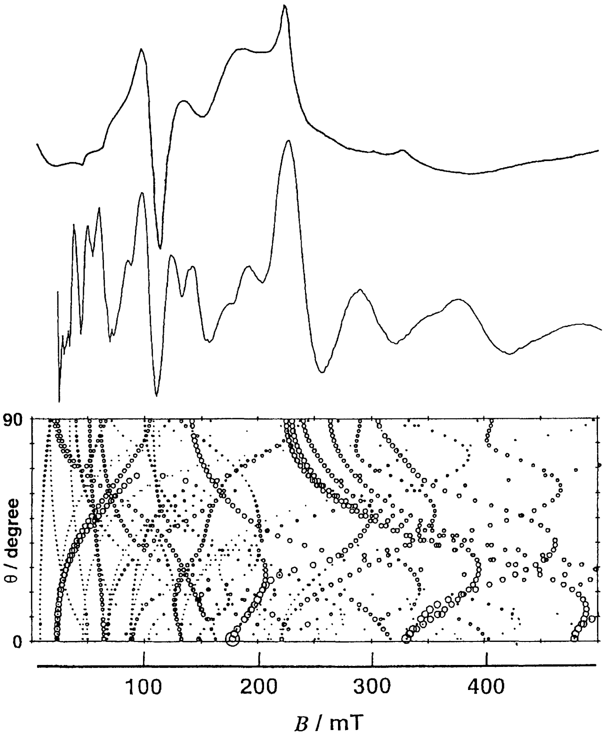

Fig. 3. Observed and simulated EPR spectra for Gd(acac)$_3$ complex, and angular θ dependence of resonance fields. Solid line: observed spectra. Mw. frequency, 9.01 GHz, mw. power, 5 mW, field modulation, 100 kHz, 0.2 mT$_{\text{p-p}}$, and temperature, 77 K; thin line: simulated spectra. D=2.2 GHz, E=0.33 GHz, (E/D=0.15), line-width 500 MHz. The resonance fields are shown for both $\phi=0$ and $\phi=\pi/2$, and the size of circles indicate the transition probabilities.

$$\hat{\mathscr{O}}_i = \sum_{k=0,2,3,4,6;\ i\geq k} b_i^k \hat{\mathscr{O}}_i^k \quad (i=2,4,6), \qquad (3)$$

where $\hat{\mathscr{O}}_i^k$s are the spin operators, and the b_i^ks are their coefficients, which are measurements of the ligand-field interactions. However, the 2nd order terms ($\hat{\mathscr{O}}_2$) are very important and dominant for Gd(III) ions in coordination complexes, because they may have lower symmetry.[5,11,12)] In our case, the EPR spectra of the Gd(III)-β-diketonate complexes can be explained by using the Hamiltonian given in Eq. 1.

The simulated EPR spectra did not agree perfectly well with the observed ones. Neglecting the higher order terms of the ligand field energies in the Hamiltonian or the effect of the orbital angular momentum, which is not completely quenched, is considered to cause these disagreements. However, the reported b_4^0 and b_6^0 values for the Gd(III) ion doped in metal oxides, etc., are much smaller than b_2^0 ($\equiv D$, in our notation).[11,12)] The small shift in the g-value from that of the free spin, which results from the remaining orbital angular momentum, would not affect the powder pattern spectra very much. Another reason for the above disagreement may be a disorder in the structure of the Gd(III) complexes in a frozen solution. A disorder in the structure would also cause inhomogeneous broadening. The coordination number and structure may be changed by the coordinated solvent, ethanol or contaminated water. The spectral line-width used in the simulation was very large, i.e. 500 MHz in the cases of Gd(hfa)$_3$ and Gd(acac)$_3$ complexes (Figs. 2 and 3). This line-width is about ten-times larger than that of normal copper(II) complexes. A large spin multiplicity would produce a very short spin-lattice relaxation time, giving large line-widths. The anisotropy in the line-width and that in the transition probability, which also affects the spectral pattern, were not considered in our spectral simulations. Since there are great difficulties concerning the above effects, we do not discuss them more. However, since they may be important problems concerning the EPR spectra of rare-earth complexes, we are studying them.

The estimated ZFS parameter ($|D|$) for the Gd(acac)$_3$ complex is similar in the order to the previously reported values of 1.4—3.1 GHz for that of the Gd(III) ions in metal oxide and in ionic crystals of alkali or alkali-earth elements.[5,9—12] Compared with these data, it is very interesting that the $|D|$ value for the Gd(hfa)$_3$ complex is very small.

Coordination Structure of Gd(III) Complexes. Our results concerning the EPR spectra are discussed here from the viewpoint of the coordination structure of rare-earth complexes. X-ray structural analyses for some rare-earth-β-diketonate complexes, are used in our argument. Rare-earth complexes don't have only a 6-coordinated octahedral structure, also possibly to take a 7- or 8-coordinated structures due to their large ionic radii and steric effects of the ligands. For example, Y(acac)$_3$ and La(acac)$_3$ complexes with two coordinating H_2O have an 8-coordinated square antiprism structure (Fig. 4 (left));[13,14] Yb(acac)$_3$, with a single coordinating water molecule, has a 7-coordinated monocapped trigonal prism structure (Fig. 4 (middle)).[15] Although these complexes do not have a spherically symmetric coordination structure, the former has approximately axial symmetry, and the latter C_2 symmetry. If the Gd(III) complexes have such structures as those of the Y(III) and La(III) complexes, the ZFS parameter ($|D|$) must be non-zero.

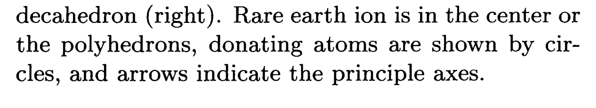

Fig. 4. Coordination structures of square anitiprism (left), monocapped trigonal prism (middle), and dodecahedron (right). Rare earth ion is in the center or the polyhedrons, donating atoms are shown by circles, and arrows indicate the principle axes.

The Y(III) complex with hfa$^-$ as a ligand has been reported to take four β-diketonate ligands, which construct an 8-coordinated dodecahedron-coordinating structure (Fig. 4 (right)).[16] This form is nearly spherically symmetric for the first coordinated sphere. If the Gd(III) complex with hfa$^-$ as a ligand has the same structure in solution, it gives a very small $|D|$ and a weak ligand field, also resulting in a small $|D|$.

Conclusion

In this work, the EPR for some Gd(III)-β-diketonate complexes were measured in order to obtain the spectra due to the 4f-electrons. The main features of the spectra could be interpreted based on the EZ and ZFS interactions, as shown by the spin Hamiltonian in Eq. 1. However, the simulated spectra did not necessarily correspond well with the observed ones. There may be five reasons for these disagreement, i.e. (1) neglecting the higher ligand field terms, (2) the effect of the remaining orbital angular momentum, (3) a disorder in the coordination structure, (4) an improper line-width used in simulation, and (5) an anisotropy in the transition probability. The spectral simulations attempted so far indicate that at least the ZFS parameter ($|D|$) for the Gd(hfa)$_3$ complex is much smaller than that for the other complexes, such as Gd(acac)$_3$. These results are caused by the weak ligand field of the hfa$^-$ and/or pseudo-spherically symmetric coordination structure.

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References

1) Abbreviations: EPR, electron paramagnetic resonance; ZFS, zero field splitting; EZ, electron Zeeman.

2) Ligands: Hhfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; Hacac, 2,4-pentanedione or acetylacetone; Hthd, 2,2,6,6-tetramethyl-3,5-heptanedione; Hdbm, dibenzoylmethane; Hfta, 4,4,4-trifluoro-1-(2-furoyl)-1,3-butanedione; Htta, 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione; Htfa, 1,1,1-trifluoro-2,4-pentanedione; Hpaa, 3-phenyl-2,4-pentanedione.

3) Complexes: Gd(hfa)$_3$, tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)gadolinium(III); Gd(acac)$_3$, tris(2,4-pentanedionato)gadolinium(III); Gd(thd)$_3$, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)gadolinium(III); Gd(dbm)$_3$, tris(dibenzoylmethanato)gadolinium(III); Gd(fta)$_3$, tris(4,4,4-trifluoro-1-(2-furoyl)-1,3-butanedionato)gadolinium(III); Gd(tta)$_3$, tris(4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedionato)gadolinium(III); Gd(tfa)$_3$, tris(1,1,1-trifluoro-2,4-pentanedionato)gadolinium(III); Gd(paa)$_3$, tris(3-phenyl-2,4-pen-

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