Bull. Chem. Soc. Jpn., ***75***, *735–740 (2002)*

Crystal Structures and ^{166}Er Mössbauer Spectra for Some *β*-Diketonatoerbium(III) Complexes

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(Received September 27, 2001)

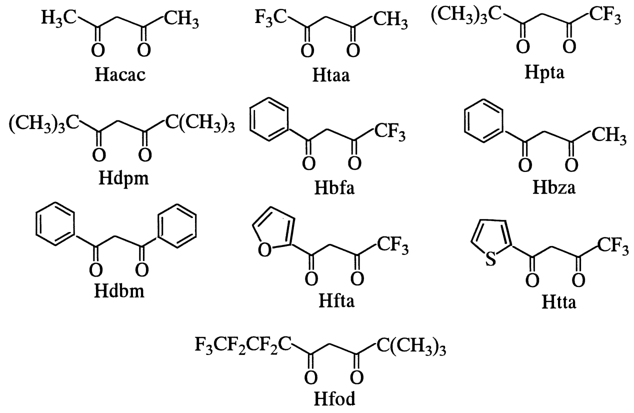
The crystal structures and ^{166}Er Mössbauer spectra for some *β*-diketonatoerbium(III) complexes have been investigated. The geometries around the Er(III) ions in $[Er(dpm)_3(H_2O)]$ (**1**; Hdpm = 2,2,6,6-tetramethyl-3,5-heptanedione), $[Er(pta)_3(H_2O)]$ (**2**; Hpta = 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione) and $[Er_2(pta)_6]$ (**3**) are distorted monocapped trigonal prisms. **3** is a dimeric structure in which one of the chelating oxygen atoms of the pta ligand bridges between the $Er(pta)_3$ fragments. The ^{166}Er Mössbauer spectra for those *β*-diketonatoerbium(III) complexes show paramagnetic relaxation patterns at 12 K. The estimated relaxation time (τ) is spread out from 0.1 to 1 ns. For the seven-coordinated complexes, τ decrease among with a decrease in the Er(III)–Er(III) distance. τ for the six-coordinated complex of $[Er(dpm)_3]$ is as short as 0.4 ns in spite of having a rather long distance of Er(III)–Er(III) ions, suggesting that the τ also depends on the coordination number.

The erbium isotope ^{166}Er has a ($2^+ \rightarrow 0^+$) rotational E2-transition, and the Mössbauer effect of the 80.6 keV transition in ^{166}Er has been effectively applied to investigate the structural and magnetic properties of erbium alloys and intermetallic compounds.[1–5] The spectra for erbium complexes, however, have been scarcely measured. Thus, we started ^{166}Er Mössbauer spectroscopic studies on the structural chemistry of a number of erbium complexes.[6–7] During the course of this study we found that the ^{166}Er Mössbauer spectra were subject to be influenced by a paramagnetic relaxation effect. Few studies on the paramagnetic relaxation phenomenon for erbium compounds have been reported, though the spin relaxation ^{166}Er Mössbauer spectrum has already been reported for $ErFeO_3$ by Nowik and Wickman in 1966.[8]

Two relaxation mechanisms, spin–spin and spin–lattice relaxation, have been indicated, and sometimes the spin–spin distance has been suggested to be important to determine the relaxation time (τ). Therefore we carried out a systematic study using *β*-diketonatoerbium(III) complexes to examine the relation between the spin-spin distances and the relaxation times. We also carried out X-ray structural determinations to obtain the crystal and molecular structures of these complexes. Ten *β*-diketonato ligands were used in this study; their abbreviations are shown in the scheme 1.

Experimental

Materials. All of the complexes were prepared by a modified procedure of Eisentraut and Sievers.[9] The *β*-diketones from Japan Dojin Chemical Institute were used without further purification.



Scheme 1.

A typical procedure is described based on the preparation of dpm complexes, $[Er(dpm)_3]$ and $[Er(dpm)_3(H_2O)]$ (**1**): H(dpm) (3 g, 16.3 mmol) was dissolved into 30 mL of 95% ethanol in a flask. To the solution, NaOH (0.65 g, 16.3 mmol) was added. After stirring about 1 hour, $Er(NO_3)_3 \cdot 6H_2O$ (2.5 g, 5.43 mmol) was added to the flask, and then the flask was sealed, evacuated and stirred for 2 hours. Precipitation was obtained after the volume of the solution was reduced to half and distilled water was added. Single-crystals of $[Er(dpm)_3]$ were obtained by subliming the crude product at 453 K under reduced pressure. Single-crystals of **1** were obtained by keeping the *n*-hexane solution of $[Er(dpm)_3]$ for two days.

Single-crystals of $[Er(pta)_3(H_2O)]$ (**2**) were obtained by recrystallizing the crude product from *n*-hexane. Single-crystals of $[Er_2(pta)_6]$ (**3**) were obtained from subliming the crude product under reduced pressure at 423–473 K.

All of the samples were dried in vacuum over three days before conducting a chemical analysis and an ^{166}Er Mössbauer measurement. Their chemical analysis was carried out on a Perkin-Elmer Model 2400, and the erbium contents were determined by chelatometric titration. Satisfactory results were obtained.

Structure Determination. The crystal structures of $[Er(dpm)_3]$, **1**, **2** and **3** were determined by single-crystal X-ray analysis. Since the crystal structure of $[Er(dpm)_3]$ has been reported by De Villiers and Boeyens,[10] only the crystallographic and

Table 1. Crystallographic and Experimental Data for **1**–**3**

Complex	**1**	**2**	**3**
MW	735.08	770.76	1505.49
Chem. formula	$C_{33}H_{59}O_7Er$	$C_{24}H_{32}O_7F_9Er$	$C_{48}H_{60}O_{12}F_{18}Er_2$
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$(No.2)	$P\bar{1}$(No.2)	$P2_1/n$(No.14)
a/Å	14.57(1)	13.202(3)	20.108(9)
b/Å	14.85(2)	13.388(3)	13.843(9)
c/Å	11.582(9)	10.006(2)	24.60(1)
α/°	100.06(8)	98.14(2)	
β/°	106.89(7)	109.24(2)	11.82(4)
γ/°	119.05(7)	97.12(2)	
V/Å^3	1941(4)	1625.1(7)	6357(5)
Z	2	2	8
ρ_{obs}/g cm^{-3}	1.26	1.57	1.60
ρ_{cal}/g cm^{-3}	1.25	1.58	1.61
μ(Mo-$K\alpha$)/cm^{-1}	21.95	26.64	27.24
F_{000}	766.00	762.00	30.48.00
No. reflns [$I > 3\sigma(I)$]	4152	5916	6492
No. parameters	370	370	701
R	0.057	0.047	0.050
R_w	0.073	0.067	0.067
GOF	1.22	1.27	1.26
Max shift / error in final cycle	0.75	0.47	0.76
Max residual Peak/ eÅ^3	1.75	3.41	1.42
Min. residual peak/ eÅ^3	−2.13	−0.69	−0.80

$R = \Sigma||F_o|-|F_o||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o{}^2|]^{1/2}$;
$w = [\sigma_c{}^2(F_o) + (p^2/4)F_o{}^2]^{-1}$, GOF $= [\Sigma w(|F_o|-|F_c|)^2/(N_0-N_v)]^{1/2}$.

experimental data of **1**–**3** are summarized in Table 1. The reflection data were collected on a Rigaku AFC5S diffractometer with graphite-monochromated Mo-$K\alpha$ radiation (λ = 71.069 pm) at room temperature. The data were measured using a ω–2θ scan method at a scan speed of 8° min^{-1} in ω and were corrected for the Lorentz absorption, polarization effects and ψ-scan absorption. Three standard reflections were measured every 150 reflections during intensity data collection; no significant degradation was observed.

The space group was determined based on a systematic absence of peaks. The structure for [Er(dpm)$_3$] was solved by a direct method using the SAPI92 program, and those for **1**–**3** were solved by a heavy atom method using the DIRDIFF92 program; the structures were expanded using Fourier techniques. The structures were refined by full-matrix least-squares procedures with anisotropic thermal parameters for non-hydrogen atoms, except for the four terminal carbon atoms (C13, C22, C31, and C46) in **3**. Hydrogen atoms were located at the calculated positions and not refined. All of the calculations were performed using a teXsan crystallographic software package from Molecular Structure Corporation.[11]

X-ray crystallographic files in CIF format for **1**–**3** have been deposited as document No.75020 at the Office of the Editor of Bull. Chem. Soc. Jpn and also deposited at the CCDC, 12 Union Road, Cambridge CB21EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 177648–177651.

Preparation of ^{166}Ho/Ho$_{0.4}$Y$_{0.6}$H$_2$ Mössbauer Source. The preparation of the ^{166}Ho/Ho$_{0.4}$Y$_{0.6}$H$_2$ source was based on a method reported by Stöhr and Cashion.[12] Ho$_{0.4}$Y$_{0.6}$ (about 200 mg), prepared by an arc melt method, was wrapped with a titanium sheet, which acted as an oxygen getter; moreover, it was also wrapped with a tantalum sheet, and then put into a quartz tube. The alloy was heated to 1273 K for 2 hour in a vacuum and then cooled to 1123 K. Dried hydrogen was passed and kept at 200 Torr for 30 minutes (1 Torr ≈ 133.322 Pa). Ho$_{0.4}$Y$_{0.6}$ alloy reacted almost immediately with the hydrogen. The quartz tube was cooled rapidly by immersing in liquid nitrogen to avoid the formation of trihydrate, Ho$_{0.4}$Y$_{0.6}$H$_3$. The formation of Ho$_{0.4}$Y$_{0.6}$H$_2$ was confirmed by powder X-ray diffraction (XRD).

Ho$_{0.4}$Y$_{0.6}$H$_2$ (55.3 mg) was pelletized into a disc (ϕ10 mm) and sealed using aluminum sheets of high purity. The disc was irradiated in the PN-1 hole of a JRR-3M (neutron flux of 6.0×10^{13} cm^{-2} s^{-1}) at Japan Atomic Energy Research Institute (JAERI) for 9 minutes. ^{166}Ho/Ho$_{0.4}$Y$_{0.6}$H$_2$ of about 1.5 GBq (41 mCi) as a Mössbauer source was obtained. The quality of the source was evaluated by measuring the single line spectrum of an absorber, ErH$_2$ with an absorber thickness of 200 mg Er cm^{-2}. A typical line width was 8.3 ± 0.3 mm s^{-1} at 12 K, which compares well with that reported by Stöhr and Cashion (7.7 mm s^{-1} at 4.2 K with the absorber thickness of 74 mg Er cm^{-2}).[12] Since the half life of ^{166}Ho is as short as 26.9 h, one ^{166}Ho/Ho$_{0.4}$Y$_{0.6}$H$_2$ source could only be used for measurements of 3–4 samples.

^{166}Er Mössbauer Measurement. ^{166}Er Mössbauer spectra were measured using the above ^{166}Ho/Ho$_{0.4}$Y$_{0.6}$H$_2$ source on a Wissel Mössbauer measuring system consisting of MDU-1200,

Table 2. Er–O Bond Distances (Å) in **1**–**3**

Bond distance	**1**	**2**	**3**
Er1–O1	2.213(6)	2.250(4)	2.320(6)
Er1–O2	2.249(7)	2.285(4)	2.303(6)
Er1–O3	2.239(7)	2.306(4)	2.244(7)
Er1–O4	2.322(6)	2.281(4)	2.224(7)
Er1–O5	2.204(7)	2.237(4)	2.227(6)
Er1–O6	2.332(7)	2.268(4)	2.294(7)
Er1–O7	2.336(7)	2.346(7)	2.354(6)
Er2–O1			2.369(6)
Er2–O7			2.345(6)
Er2–O8			2.292(8)
Er2–O9			2.272(6)
Er2–O10			2.240(7)
Er2–O11			2.258(7)
Er2–O12			2.236(6)
Mean	2.271	2.282	2.282

DFG-1200 and MVT-1000. Both the source and the sample containing 200 mg Er cm^{-2} were kept at 12 K in a cryostat equipped with a closed-cycle refrigerator. The 80.57 keV γ-rays were counted with a pure germanium detector. The Doppler velocity was measured with a laser Mössbauer velocity calibrator (Wissel MVC-450) and calibrated by measuring the ^{57}Fe Mössbauer spectrum of α-iron foil. The spectra were analyzed by using the Nowik and Wickman model, except for ErH_2. For ErH_2, curve-fitting was carried out by assuming a Lorentz absorption line shape.

Results and Discussion

Preparation of Complexes. The dimeric structure for lanthanide dpm complexes have been known for La–Dy.[13] The present study shows that the erbium ion could also form a dimeric structure of $[Er_2(pta)_6]$. Since a hydrated dimer structure has been reported for the lanthanide fod complex, $[Pr_2(fod)_6(H_2O)_2]$,[14] we attempted to obtain such a complex. However, no complex was obtained. The small ionic radius of erbium might prevent the hydrated eight-coordinated structure from being adopted.

Crystal Structure for 1. The Er–O bond distances in **1**–**3** are listed in Table 2. The crystal structure of **1** is shown in Fig. 1(a). The cystal structure is isostructural with that of $[Dy(dpm)_3(H_2O)]$ reported by Erasmus and Boeyens.[15] The Er(III) ion is seven-coordinated with three bidentate dpm and one water molecule.

The coordination polyhedron around the Er(III) ion is a slightly distorted monocapped trigonal prism. This configuration is commonly found in many lanthanide β-diketonato monoaqua complexes. The mean Er–O bond distance (2.271 Å) including Er–O7(water) is shorter than that of $[Dy(dpm)_3(H_2O)]$ (2.294 Å). The difference of 0.023 Å compares favorably with the difference of the seven-coordinated ion radius of erbium (0.945 Å) and dysprosium (0.970 Å),[16] and is well interpreted by the lanthanide contraction. The shortest distance of the Er(III)–Er(III) ions is 5.56 Å. It is clearly shorter than that of a six-coordinated complex, $[Er(dpm)_3]$ (9.98 Å), that was reported by De Villiers and Boeyens,[10] and also confirmed in the present study.

The mean bond angle of O–Er–O in the dpm chelate rings is 74.3°. This is almost the same as that of $[Er(dpm)_3]$ (74.1°). The mean bond angle of O–Dy–O (73.6°) in the dpm chelate ring for $[Dy(dpm)_3(H_2O)]$ is slightly smaller than that of **1**. Intermolecular hydrogen bonds exist as in the case of $[Dy(dpm)_3(H_2O)]$.

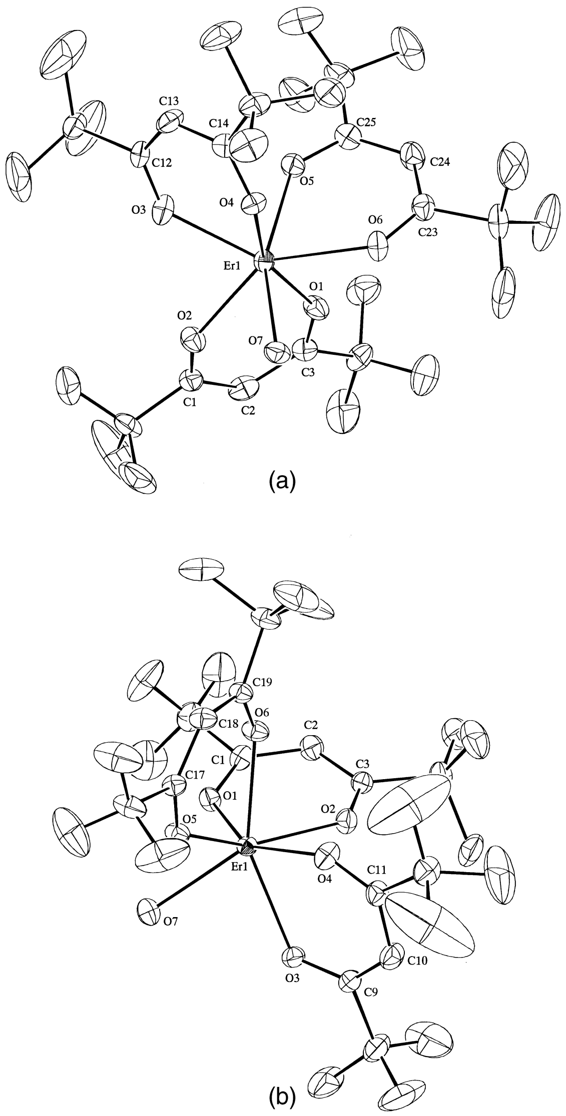


Fig. 1. ORTEP structure of $[Er(dpm)_3(H_2O)]$ (**1**) (1a) and $[Er(pta)_3(H_2O)]$ (**2**) (1b) in 20% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Three types of the complex (nonaqua, monoaqua and dimer) have been reported for the lanthanide dpm complexes. The crystal structures of the monoaqua have been reported for $[Eu(dpm)_3(H_2O)]$ and $[Dy(dpm)_3(H_2O)]$.[13,15] From a consideration of the lanthanide contraction, Erasmus and Boeyens have suggested that the monoaqua complex could not be formed for lanthanide ions heavier than Dy.[15] The present study, however, indicates that the monoaqua complex can be formed for the Er(III) ion, even though the ion radius is smaller than that of Dy(III) ion.

Crystal Structure for 2. The molecular structure of **2** is similar to that of **1** (Fig. 1(b)). The Er(III) ion is also seven-coordinated with three bidentate pta ligands and one water molecule. To our knowledge, this is the first example that the crys-

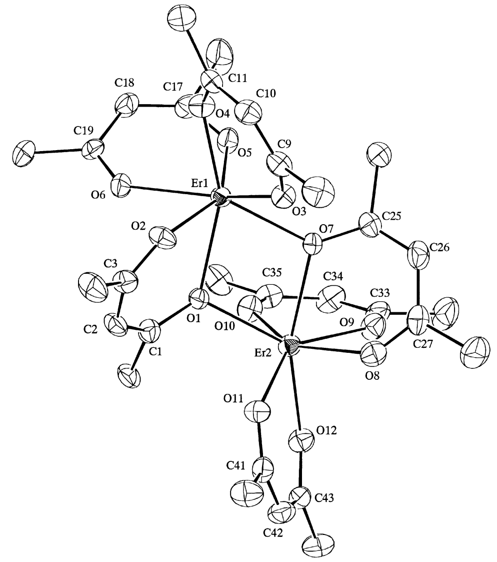


Fig. 2. ORTEP structure of [$Er_2(pta)_6$] (**3**) in 20% probability ellipsoids. Carbon atoms in methyl groups, fluorine atoms and hydrogen atoms have been omitted for clarity.

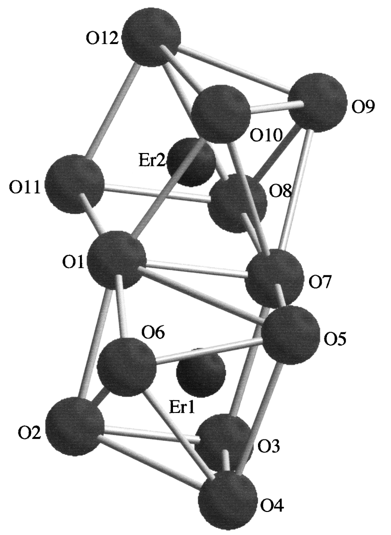


Fig. 3. The coordination geometry of the Er_2O_{12} system in [$Er_2(pta)_6$] (**3**).

tal structure of lanthanide pta complex has been reported.

The coordination polyhedron around the Er(III) ion is also similar to that of **1**. The mean bond distance of Er–O (2.282 Å) is slightly longer than that of **1** (2.271 Å). The shortest distance of the Er(III)–Er(III) ions for **2** is 5.87 Å, being shorter than that of [$Er(dpm)_3$], but slightly longer than that of **1**. The mean bond angle of O–Er–O (75.2°) in the pta chelate rings is larger than that of **1** (74.3°). Intermolecular hydrogen bonds also exist, as in the cases of **1** and $Dy(dpm)_3 \cdot H_2O$.

Crystal Structure for 3. **3** has a dimeric structure, as shown in Fig. 2. Each Er(III) ion is seven-coordinated; one of the chelating oxygen atoms of the pta ligand bridges $Er(pta)_3$ fragments, serving as the seventh ligand atom. This type of dimeric structure has been observed in lanthanide dpm complexes, [$Ln_2(dpm)_6$] (Ln = La–Dy).[13] Due to this bridging, the pta chelate rings containing the bridging atoms experience large deformation.

The coordination geometry of the Er_2O_{12} in the dimeric structure of [$Er_2(pta)_6$] is shown in Fig. 3. Each Er(III) ion is surrounded by a slightly distorted monocapped trigonal prism. This is similar to that of [$Ln_2(dpm)_6$] (Ln = La–Dy). The bond distances between the Er(III) ion and each bridging oxygen atom (O1, O7 (Er1–O1 = 2.320 Å, Er1–O7 = 2.354 Å, Er2–O1 = 2.369 Å, Er2–O7 = 2.345 Å)) are much longer than the Er–O mean bond distance (2.282 Å). The Er–O mean bond distance of 2.282 Å in **3** is the same as that of **2** (2.282 Å), but longer than that of **1** (2.271 Å) and [$Er(dpm)_3$] (2.224 Å). The shortest distance of the Er(III)–Er(III) ions is 3.82 Å, being the intramolecular Er1–Er2 distance, and the shortest intermolecular distance is 10.20 Å. The mean bond angle of O–Er–O in the pta chelate rings is 74.7°.

^{166}Er Mössbauer Spectra. Figure 4 shows the ^{166}Er Mössbauer spectra for [$Er(dpm)_3$], **1**, **2** and **3** at 12 K. Figure 5 shows the ^{166}Er Mössbauer spectra for aquatris(β-diketonato)erbium(III) at 12 K. All of the spectra show paramagnetic relaxation Mössbauer spectra. The Mössbauer parameters obtained using the Nowik and Wickman model are summarized in Table 3. Since the absorption shapes of the spectra for [$Er(dpm)_3$] and [$Er(dbm)_3(H_2O)$] are very poor, their spectra were analyzed by fixing the line width (Γ_{exp}) to 8.0 mm s^{-1}. Considering the absorption shape of their spectra and their structural features, the obtained Mössbauer parameters are reasonable. In Fig. 5 the spectra is shown in the order of the decrease of the spin relaxation time downward, except for the dbm complex at the bottom, as described below.

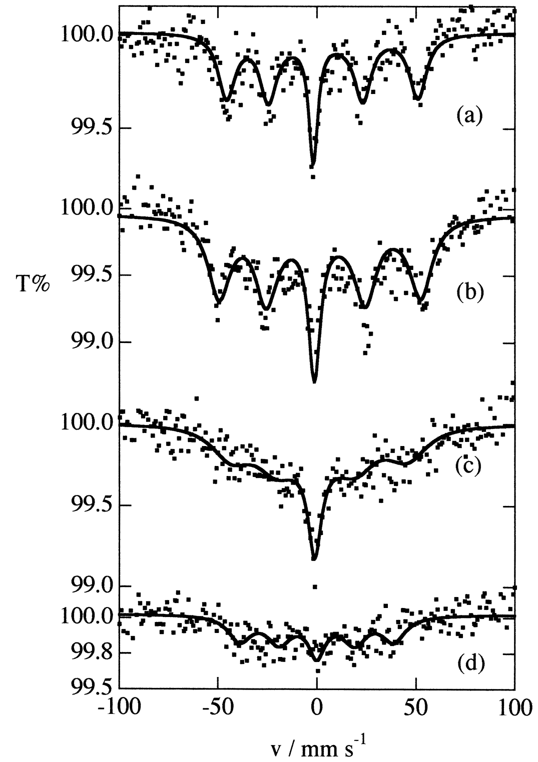


Fig. 4. ^{166}Er Mössbauer spectra for (a) [$Er(pta)_3(H_2O)$] (**2**), (b) [$Er(dpm)_3(H_2O)$] (**1**), (c) [$Er_2(pta)_6$] (**3**) and (d) [$Er(dpm)_3$] at 12 K.

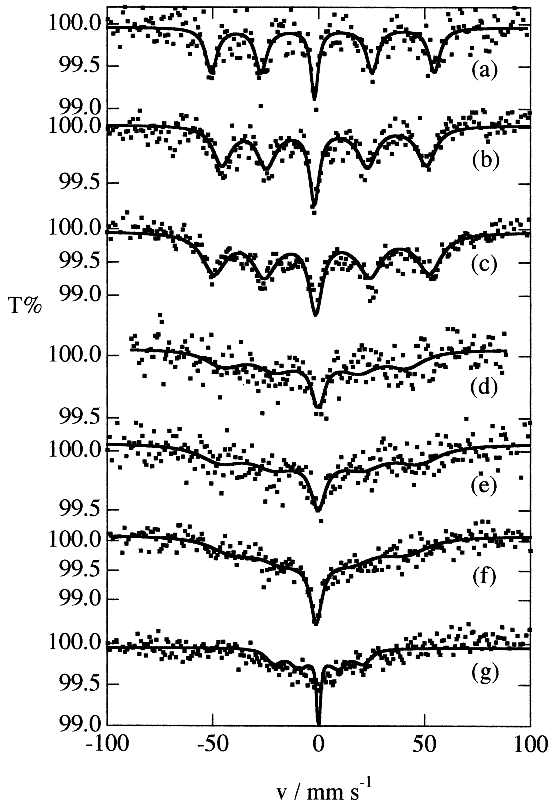


Fig. 5. ^{166}Er Mössbauer spectra for the aqua tris(β-diketonato)erbium(III) complexes at 12 K. (a) [Er(fod)$_3$(H$_2$O)], (b) [Er(pta)$_3$(H$_2$O)] (**2**), (c) [Er(dpm)$_3$(H$_2$O)] (**1**), (d) [Er(acac)$_3$(H$_2$O)], (e) [Er(bfa)$_3$(H$_2$O)], (f) [Er(taa)$_3$(H$_2$O)], (g) [Er(dbm)$_3$(H$_2$O)].

Table 3. ^{166}Er Mössbauer Parameters of the β-Diketonato-erbium(III) Complexes at 12 K

Complex	e^2qQ mm s^{-1}	Γ_{exp} mm s^{-1}	τ ns	H_{eff} T
[Er(fod)$_3$(H$_2$O)]	6.1	4.1	1.0	711
[Er(pta)$_3$(H$_2$O)] (**2**)	7.0	5.6	0.5	654
[Er(dpm)$_3$(H$_2$O)] (**1**)	4.3	8.0$^{a)}$	0.4	690
[Er(dpm)$_3$]	0.1	8.0$^{a)}$	0.4	525
[Er(dbm)$_3$(H$_2$O)]	−0.1	8.0$^{a)}$	0.3	294
[Er(fta)$_3$]	−2.4	8.3	0.2	640
[Er(acac)$_3$(H$_2$O)]	−2.7	7.5	0.2	598
[Er(tta)$_3$(H$_2$O)$_2$]	1.8	8.0$^{a)}$	0.2	(316)
[Er$_2$(pta)$_6$] (**3**)	3.6	8.4	0.1	621
[Er(bfa)$_3$(H$_2$O)]	1.0	7.0	0.1	651
[Er(taa)$_3$(H$_2$O)]	2.0	6.8	0.1	582
[Er(bza)$_3$(H$_2$O)$_2$]	−4.0	5.7	0.1	(433)

a). The line-widths (Γ_{exp}) was fixed at 8.0 mm s^{-1}.

The relative absorption intensity for each complex is less than 1%, being much smaller than that of ionic compounds and alloys having a few percent absorption.[1–5] This indicates that the recoilless fraction of these complexes is very small, even at 12 K. The spectra show a wide variety of absorption shapes depending on the relaxation time (τ); a broad single absorption peak exists when τ is short, and five-line absorption peaks occurs when τ is long. The estimated τ is spread out from 0.1 to 1 ns.

The estimated τ for **3** is 0.1 ns, whereas those for **1** and **2** are 0.4 and 0.5 ns, respectively. This is the same order as the increase in the shortest distances of the Er(III)–Er(III) ions: 3.82 Å for **3**, 5.58 Å for **1** and 5.87 Å for **2**. Thus, τ correlates well to the shortest distance of the Er(III)–Er(III) ions. In other words, spin-spin relaxation is important in these systems. This was confirmed by examining the Mössbauer spectra for the monoaqua complexes (see below). Interestingly, τ for [Er(dpm)$_3$] is, however, unexpectedly short (0.4 ns), though the shortest distance of the Er(III)–Er(III) ions (9.98 Å) is prominently longer than that of the other dpm and pta complexes. This is interpreted as meaning that τ is dominated by not only the shortest distance of Er(III)–Er(III) ions, but also by the coordination number. Although we can not explain this completely at this stage, the difference in the coordination number could lead to the difference in the energy level of the Er(III) ion through a crystal field effect, causing the difference in τ. Indeed, τ for Er(III)-edta complexes also depends on the coordination number.[17]

Since τ depends on the coordination number, we focus our interest on seven-coordinated complexes. As already shown, the coordination numbers for the erbium atom in the two monoaqua complexes are seven, since the water molecule participates in the coordination. This can be safely extended to other monohydrate complexes, though the crystal structures are not known. The XRD patterns for [Er(dbm)$_3$(H$_2$O)] are indicated to be isostructural to hexagonal, [Ho(dbm)$_3$(H$_2$O)][18] having a monocapped octahedral coordination with C_3 symmetry, whereas complexes **1** and **2** are triclinic. Thus, [Er(dbm)$_3$(H$_2$O)] is excluded in the following discussion. Indeed, the Mössbauer spectrum for [Er(dbm)$_3$(H$_2$O)] is clearly different from that of other seven-coordinated complexes. However, this suggests that the electronic configuration may play an important role in paramagnetic relaxation.

The values of τ are much different among the monoaqua complexes. The order of τ is as follows: [Er(fod)$_3$(H$_2$O)] > [Er(pta)$_3$(H$_2$O)] (**2**) > [Er(dpm)$_3$(H$_2$O)] (**1**) > [Er(acac)$_3$(H$_2$O)] > [Er(bfa)$_3$(H$_2$O)] ≈ [Er(taa)$_3$(H$_2$O)]. This indicates that τ depends on the substituent. The substituents (R$_1$, R$_2$) of the β-diketone (R$_1$COCH$_2$COR$_2$) in the above order are (C$_3$F$_7$, *t*-Bu), (CF$_3$, *t*-Bu), (*t*-Bu, *t*-Bu), (CH$_3$, CH$_3$), (Ph, CF$_3$) and (CF$_3$, CF$_3$). This order is essentially that of a decrease in the bulkiness of the substituents. Since the distance of the Er(III)–Er(III) ions depends on the size of the substituents, we can expect that τ depends on the intermolecular distance of the Er(III)–Er(III) ions as a result. Since we could not determine the shortest distance of the Er(III)–Er(III) ions due to unsuccessful results concerning the single-crystal X-ray structure determination on other complexes, we measured the densities of the crystals, while expecting that the density of the crystal would reflect the intermolecular distance of the Er(III)–Er(III) ions. Such an attempt was, however, unsuccessful. No correlation between τ and the density was observed. This would be reasonable, since the packing of the molecules in the crystal is not always the same, and substitution of a hydrogen atom by a fluorine atom could result in an increase in the density.

Since the Mössbauer spectra showing a long τ give well-resolved five-line absorption, we can obtain the value of the quadrupole coupling constant (e^2qQ) with good accuracy. Judging from the absorption shape, the values of e^2qQ for **1**, **2**, [Er(dpm)$_3$] and Er(fod)$_3$·H$_2$O are considerably reliable. Interestingly, the values for the monoaqua complexes, except for [Er(dbm)$_3$(H$_2$O)], are obviously larger than that of the anhydrous complex of [Er(dpm)$_3$]. The coordination polyhedron around the Er(III) ion in [Er(dpm)$_3$] is a trigonal prism.[9] This suggest that there would be some difference in the population of the f orbitals between the six- and seven-coordinated complexes. This is reasonable, since the local symmetry around the Er(III) ion is higher for a trigonal prism than that for a monocapped trigonal prism. The e^2qQ value of [Er(dbm)$_3$(H$_2$O)] is clearly smaller than that of the other monoaqua complexes. This indicate that the local symmetry around the Er(III) ion in [Er(dbm)$_3$(H$_2$O)] is higher than that of the other monoaqua complexes, and is in good agreement with the C_3 symmetry coordination structure, since [Er(dbm)$_3$(H$_2$O)] is isostructural with [Ho(dbm)$_3$(H$_2$O)].

Concerning the values of the effective internal magnetic field (H_{eff}), most of the values range between 500 and 720 T, being close to that of metallic erbium (742 T). The reliability of the smaller values for [Er(tta)$_3$(H$_2$O)$_2$] and [Er(bza)$_3$(H$_2$O)$_2$], given in parentheses in the Table 3, is rather low.

Conclusion

Nonaqua and monoaqua complexes of Er(III) ion for dpm and pta can be prepared under different recrystalization conditions. The crystals of **1** and **2** have seven-coordinated complexes in which the water molecule participates to the coordination. **3** has a dimeric structure in which two pta molecules bridge the Er(III) ion centers, completing the seventh coordination. A rather rare prismatic six coordination in [Er(dpm)$_3$] is also confirmed. Each ^{166}Er Mössbauer spectrum shows a paramagnetic relaxation spectrum. The relaxation time (τ) estimated by the Nowik and Wickman model is spread out from 0.1 to 1.0 ns. The relationship between the values of τ and the shortest distances of the Er(III)–Er(III) ions for the seven-coordinated complexes has been observed; τ becomes shorter along with a decrease in the distance of the Er(III)–Er(III) ions. τ also depends on the coordination number.

A part of this study is supported by the Inter-University Joint Research Program for the Common Use of JAERI Facilities and by Grants-in-Aid for Scientific Research (10440020) from the Ministry of Education, Science, Sports and Culture to M. Takeda. We acknowledge very much to Dr. Hisao Kobayashi of Faculty of Science, Tohoku University for allowing us to use his program based on Nowik and Wickman paramagnetic relaxation model.

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