

Characterizations of Divalent Lanthanoid Iodides in Tetrahydrofuran by UV–Vis, Fluorescence and ESR Spectroscopy

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Abstract

Spectrochemical properties of LnI_2 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) prepared with lanthanoid metal and diiodoethane in THF were characterized by means of UV–Vis, fluorescence and ESR spectroscopy. A comparative investigation has also been made concerning LnI_3 ($\text{Ln} = \text{La}–\text{Lu}$) and the Grignard-type compounds R–Ln–I ($\text{R} = \text{Et}, \text{Ph}; \text{Ln} = \text{Eu}, \text{Yb}$). LnI_2 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) was also prepared from reaction of lanthanoid metal and iodine in THF.

Introduction

In 1977, Namy *et al.* published a new method for the preparation of divalent samarium and ytterbium iodides (SmI_2 , YbI_2) in tetrahydrofuran (THF) [1]. This method appears to be a very convenient way to make THF solutions of divalent lanthanoids. At present, many studies have been carried out for organic syntheses using a THF solution of SmI_2 [2–5]. However, the spectrochemical properties of lanthanoid(II) compounds in organic solvents are not fully known. Investigation of the behavior of lanthanoid ions in the synthetic processes would give reliable information about the reaction mechanisms. Therefore fundamental and systematic studies are needed in order to determine the properties of divalent lanthanoids.

Thus, spectroscopic characterizations of divalent lanthanoid iodides (LnI_2 : $\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) in THF have been made by ultraviolet–visible (UV–Vis), fluorescence and electron spin resonance (ESR) spectroscopy. Furthermore, UV–Vis absorption spectra of trivalent lanthanoid iodides (LnI_3 : $\text{Ln} = \text{La}–\text{Lu}$) in THF have also been investigated in connection with those of LnI_2 . Additionally, another method for the preparation of LnI_2 solutions has been examined.

Experimental

Materials

Lanthanoid metals were powders or ingots from Research Chemicals. Ingots were ground before each

preparation under a nitrogen atmosphere. 1,2-Diiodoethane from Tokyo Kasei was used after suitable treatment (see ref. 2). Ethyl iodide and iodobenzene from Wako Pure Chemicals were used after distillation. THF from Wako Pure Chemicals was distilled under a nitrogen atmosphere over CaH_2 and diethyl ether was distilled over CaH_2 . Other reagents were commercially available and were used without further treatment.

Procedures

All manipulations were carried out under a nitrogen atmosphere.

A typical preparation of a THF solution of SmI_2 (*ca.* 0.06 mol dm^{-3}) is as follows. Samarium metal powder (0.9 g, 6 mmol), diiodoethane (0.85 g, 3 mmol) and a magnetic stirring bar were placed in a 50-cm^3 centrifuge tube and the tube was sealed with a serum cap. After a stream of nitrogen was introduced into the tube, 50 cm^3 of freshly distilled THF was added by syringe. The mixture was stirred overnight at room temperature. Other THF solutions of LnI_2 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Yb}$) were prepared similarly with lanthanoid metal and diiodoethane at a molar ratio of 2:1.

In the above preparation, it was confirmed that iodine can be used instead of diiodoethane.

When ethyl iodide or iodobenzene was used instead of diiodoethane, the formation of divalent lanthanoid Grignard-type compounds, such as R–Ln–I ($\text{R} = \text{Et}, \text{Ph}; \text{Ln} = \text{Eu}, \text{Yb}$), was reported [6]. Therefore their preparations were carried out according to the literature method.

THF solutions of LnI_3 ($\text{Ln} = \text{La}–\text{Lu}$) were obtained when the molar ratio of lanthanoid metal to diiodoethane or iodine was changed to the ratio 2:3.

Clear THF solutions were obtained by decanting or filtration.

Measurements

All measurements were carried out at room temperature. UV–Vis absorption spectra were recorded on a Hitachi 100-50 spectrophotometer using 1-mm or 1-cm quartz cells. Fluorescence spectra were

recorded using a 1-cm quartz cell in the range 200–850 nm on a Hitachi 650-60 fluorescence spectrophotometer with a xenon lamp as a light source. The first-derivative ESR spectra were recorded on a Jeol JES-FE3X spectrometer at X-band frequencies. The g -values were determined with a Mn^{2+}/MgO powder standard ($g_4 = 1.981$).

The concentrations of lanthanoid(II) ions were determined by EDTA titration after the lanthanoid(II) ions were oxidized to the trivalent state by exposure to air.

Results and Discussion

UV-Vis Spectral Characterization

The colors of SmI_2 , EuI_2 and YbI_2 in THF were deep blue–green, colorless and light yellow–green, respectively. The UV–Vis spectra of SmI_2 , EuI_2 and YbI_2 in THF are shown in Fig. 1. These spectra are assigned to transitions from $4f^n$ to $4f^{n-1} 5d^1$. The molar extinction coefficient of the band at 341 nm of EuI_2 in THF is about $1600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and

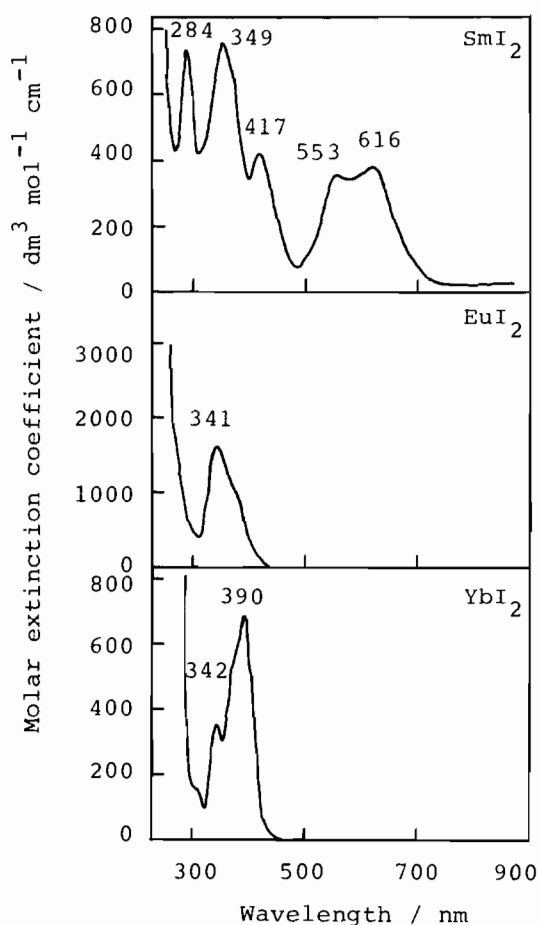


Fig. 1. Absorption spectra of SmI_2 , EuI_2 and YbI_2 in THF.

about twice the maximum molar extinction coefficient of SmI_2 or YbI_2 in THF. On the other hand, all lanthanoid(II) spectra in THF show a shoulder at 370 nm, probably due to iodide ion (I^-). The spectra of these LnI_2 solutions were sensitive to dilution with THF and oxidation by air and water. Occasionally, in the ultraviolet region, the shape of spectrum was apt to change, *i.e.*, shoulders probably due to iodine or lanthanoid(III) ion were observed.

Accordingly, the UV–Vis absorption spectra of the LnI_3 in THF were also measured. Because there is a strong absorption at 365 nm in the above spectra, the bands were observed in the range 500–900 nm. This strong absorption is probably due to iodine (I_2) or triiodide ion (I_3^-) formed from decomposition of diiodoethane in THF. On the other hand, the bands observed in the range 500–900 nm are due to f – f transitions characteristic of the individual lanthanoid(III) ion. Their intensities are weaker than those of LnI_2 . The molar extinction coefficients for the bands of LnI_3 in THF are apparently as large as those in aqueous solution.

The absorption spectra corresponding to Et–Eu–I, Et–Yb–I and Ph–Yb–I in THF are similar to those of the respective LnI_2 . In the spectrum of Ph–Yb–I in THF, the bands due to the phenyl group could be observed at around 250–260 nm.

Fluorescence Spectral Characterization

Excitation and emission spectra of SmI_2 , EuI_2 and YbI_2 in THF are shown in Fig. 2. These emission spectra are due to transitions from $4f^{n-1} 5d^1$ to $4f^n$ and have aspects like the UV–Vis absorption spectra. EuI_2 in THF showed an excitation level (431 nm) close to the emission level (442 nm), and as its emission intensity is very strong, the color was observed to be light lilac in the sunlight.

These fluorescence spectral data are shown in Table I. The emission intensity of the band at 442 nm

TABLE I. Relative Fluorescence Intensities of SmI_2 , EuI_2 and YbI_2 in THF

LnI_2	Wavelength (nm)		Relative emission intensity
	Emission	Excitation	
SmI_2	769	485	0.16
		495	0.15
		736	1.84
EuI_2	442	313	9.66
		431	175
YbI_2	515	324	0.22
		435	1.00 ^a

^aIntensity standard.

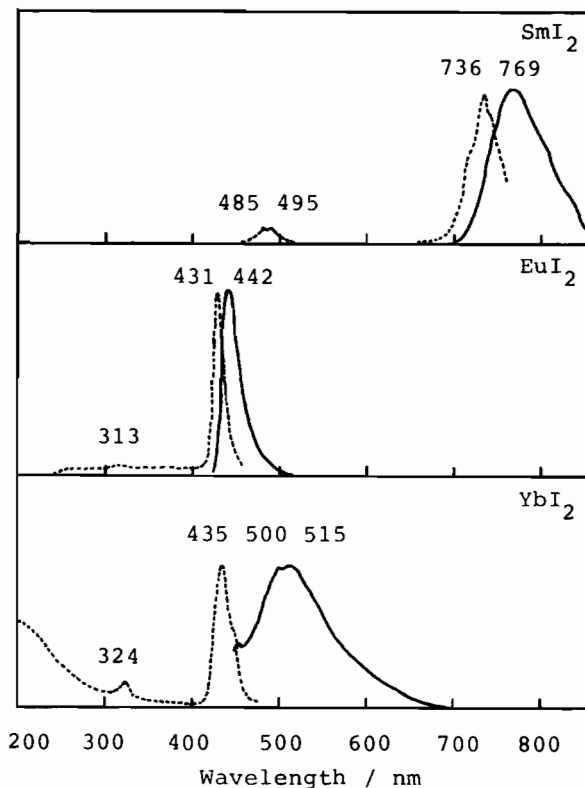


Fig. 2. Excitation (---) and emission (—) spectra of SmI_2 , EuI_2 and YbI_2 in THF.

by excitation at 431 nm of EuI_2 in THF is very strong and 100 times as strong as the maximum intensity of SmI_2 in THF, and 175 times that of YbI_2 in THF.

Excitation and emission spectra corresponding to Et-Eu-I in THF are almost the same as those of EuI_2 . Excitation and emission bands were, respectively, observed at 426 and 441 nm.

ESR Spectral Characterization

ESR spectra at room temperature can be obtained for europium(II) and gadolinium(III) with $4f^7$ configuration. In this study, the ESR spectra of EuI_2 , Et-Eu-I and Ph-Eu-I in THF were measured and are shown in Fig. 3. Additionally, ESR spectra are shown in Fig. 3 for EuBr_2 prepared with the metal and dibromoethane in THF, and for GdI_3 in THF.

The g -value and peak-to-peak width (ΔH_{pp}) are indicated for the europium(II) and the gadolinium(III) species in Table II. It can be seen that EuI_2 in THF has almost the same peak-to-peak width as GdI_3 in THF, but its g -value is slightly different from that of GdI_3 in THF. The peak-to-peak width of EuI_2 in THF is larger than those of Et-Eu-I and Ph-Eu-I , which have the almost same width.

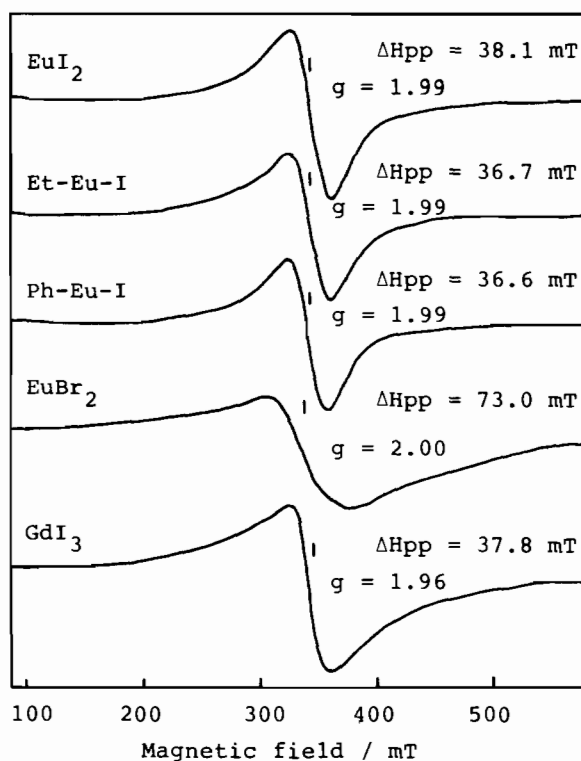


Fig. 3. ESR spectra of EuI_2 , Et-Eu-I , Ph-Eu-I , EuBr_2 and GdI_3 in THF.

TABLE II. ESR Parameters for EuI_2 , Et-Eu-I , Ph-Eu-I , EuBr_2 and GdI_3 in THF

	Parameters	
	g -value	ΔH_{pp} (mT)
EuI_2	1.99	38.1
Et-Eu-I	1.99	36.7
Ph-Eu-I	1.99	36.6
EuBr_2	2.00	73.0
GdI_3	1.96	37.8
EuCl_2^{a}	1.990	17.0
GdCl_3^{a}	2.016	48.0

^aData of EuCl_2 and GdCl_3 in H_2O [7].

Summary and Additional Remarks

Properties concerning color, UV-Vis absorption, fluorescence and ESR spectra are collected in Table III for SmI_2 , EuI_2 and YbI_2 prepared with lanthanoid metals and diiodoethane in THF. It should be emphasized in this study that the same results are obtained also using iodine instead of diiodoethane. These properties are applicable for the investigation of the behavior of lanthanoid(II) ions in organic

TABLE III. Spectroscopic Characterization of SmI₂, EuI₂ and YbI₂ in THF

	SmI ₂	EuI ₂	YbI ₂
Color	dark blue–green	colorless (light lilac)	light yellow–green
UV–Vis absorption ^a (nm)	284(700), 349(720), 417(400), 553(320), 616(350)	341(1600)	342(330), 390(640)
Fluorescence excitation (nm)	736	431	435
emission (nm)	769	442	515
intensity	weak	very strong (blue)	very weak
ESR g-value		1.99	
ΔH _{pp} (mT)		38.1	

^aValues in parentheses are molar extinction coefficients (dm³ mol⁻¹ cm⁻¹).

synthetic processes. For example, when using a THF solution of SmI₂, detection of the absorption bands at 553 and 616 nm of Sm(II) is easy [8].

Few studies on lanthanoids(II) in solution have been carried out because of their instability. Most published studies for lanthanoids(II) are about their properties in solids, such as CaF₂, SrF₂ and BaF₂ [9–11].

Namy *et al.* [12] reported UV–Vis absorption wavelengths of SmI₂ and YbI₂ in THF. The latest reports on the UV–Vis absorption spectra for LnI₂ in THF and other solvents have been presented by Kamenskaya *et al.* [13, 14]. The results obtained in this study are in good agreement with their results. However, in the spectrum of EuI₂ in THF, differences were indicated with respect to the absorption shoulders due to iodine (I₂) and the molar extinction coefficients.

References

- J. L. Namy, P. Girard and H. B. Kagan, *Nouv. J. Chim.*, **1**, 5 (1977).
- P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, **102**, 2693 (1980).
- H. B. Kagan, J. L. Namy and P. Girard, *Tetrahedron*, **37**, Suppl. 1, 175 (1981).
- J. L. Namy, J. Souppe and H. B. Kagan, *Tetrahedron Lett.*, 765 (1983).
- J. Souppe, L. Danon, J. L. Namy and H. B. Kagan, *J. Organomet. Chem.*, **250**, 227 (1983).
- D. F. Evans, G. V. Fazakerley and R. F. Phillips, *J. Chem. Soc. A*, 1931 (1971).
- O. Kashiwagi, H. Nakamura, T. Isobe and T. Tarutani, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, **11**, 257 (1978).
- Y. Okaue and T. Isobe, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, **16**, 25 (1987).
- D. L. Wood and W. Kaiser, *Phys. Rev.*, **126**, 2079 (1962).
- P. P. Feofilov and A. A. Kaplyanskii, *Opt. Spektrosk.*, **12**, 493 (1962); *Opt. Spectrosc.*, **12**, 272 (1962).
- A. A. Kaplyanskii and P. P. Feofilov, *Opt. Spektrosk.*, **13**, 235 (1962); *Opt. Spectrosc.*, **13**, 129 (1962).
- J. L. Namy, P. Girard, H. B. Kagan and P. E. Caro, *Nouv. J. Chim.*, **5**, 479 (1981).
- A. N. Kamenskaya, N. B. Mikheev and N. P. Kholmogorova, *Zh. Neorg. Khim.*, **28**, 2499 (1983); *Russ. J. Inorg. Chem.*, **28**, 1420 (1983).
- A. N. Kamenskaya, *Zh. Neorg. Khim.*, **29**, 439 (1984); *Russ. J. Inorg. Chem.*, **29**, 251 (1984).