

## Chelation of Some *Bisazophenyl-β*-diketone Derivatives with Lanthanide Metal Ions

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**Summary.** The chelation behaviour of *bisazo-β*-diketone compounds with La, Ce, Nd, Sm, Gd, Er, and Lu ions was investigated. Composition and stability constants of the chelates have been determined by conductometric and potentiometric techniques. Electronic absorption, IR, and <sup>1</sup>H-NMR spectra as well as molar conductance and elemental and thermal analyses were used to characterize the complexes.

**Keywords.** Lanthanide(III) chelates; *Bisazo-β*-diketone; Conductometry; Potentiometry; Spectrophotometry.

### Komplexierung einiger Lanthaniden mit *Bisazophenyl-β*-diketon-Derivaten

**Zusammenfassung.** Das Komplexierungsverhalten einiger *Bisazophenyl-β*-diketone mit La, Ce, Nd, Sm, Gd, Er und Lu wurde untersucht. Zusammensetzung und Stabilitätskonstanten der Chelate wurden mit konduktometrischen und potentiometrischen Methoden bestimmt. Zur Charakterisierung der Komplexe wurden UV/Vis-, IR- und <sup>1</sup>H-NMR-Spektroskopie sowie molare Leitfähigkeit, Elementaranalyse und thermische Analyse herangezogen.

### Introduction

The chelating properties of *bisazo-β*-diketones towards transition metal ions have been investigated in some detail [1–4]. Many of these compounds act as mordant dyes for different fibers [5]. A survey of the literature reveals that little is known about lanthanide complexes with the same ligands. Therefore we attempted to synthesize and characterize some lanthanide complexes of *bisazo-β*-diketones.

### Results and Discussion

The conductometric titration curves of the *bisazo* dyes with lanthanide ions exhibit four inflections at molar ratios of 0.5, 1.0, 1.5, and 2.0, indicating the existence of 2:1, 1:1, 2:3, and 1:2 (*M:L*) complex species in solution.

The proton-ligand ionization and lanthanide-ligand formation constants of the *bisazo* dyes under investigation were determined by the method of *Irving and Rossotti* [6] as well as by that given by *Mushran et al.* [7]. The proton-ligand

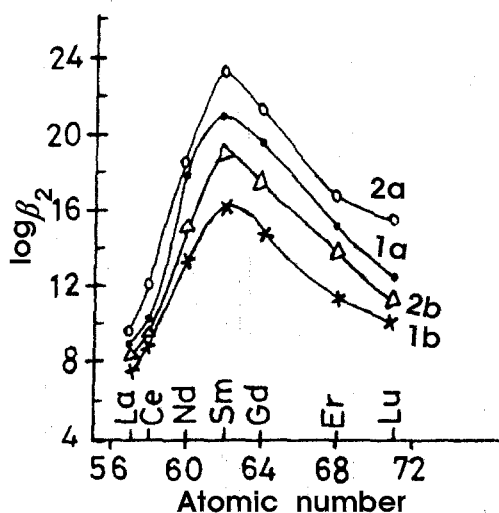


Fig. 1. Relation between  $\log \beta_2$  of the Ln(III) complexes and the atomic number

formation curves were obtained by plotting the average number of protons attached per ligand ion ( $\bar{n}_A$ ) vs. the  $pH$  value. The method of interpolation at half  $\bar{n}_A$  is employed to evaluate  $pK^H$ . The values of the proton ionization constants  $pK_1^H$  and  $pK_2^H$  of the ligands **1a**, **1b**, **2a**, and **2b** are equal to 10.2 and 5.5, 8.0 and 5.0, 10.9 and 6.7, 8.9 and 5.2, respectively, indicating that the proton ionization constants of the ligands decrease in the order **2a** > **1a** > **2b** > **1b**. The formation curves of the complexes were obtained by plotting the average number of ligands attached per lanthanide ion ( $\bar{n}$ ) vs. the free ligand exponent ( $pL$ ). The maximum  $\bar{n}$  values calculated were found not to exceed two in all lanthanide complexes, indicating the formation of 1:1 and 1:2 (metal:ligand) complexes. A ratio of 1:3 may be excluded due to steric hindrance in accommodating three *bisazo* dye molecules around a lanthanide ion as well as to the effect of the dioxane-water medium in which the lanthanide ions exist as aquo complexes. The stepwise formation constants  $\log K_1$  and  $\log K_2$  are listed in Table 1. The formation constants of the complexes decrease in the order  $\text{Sm}^{3+} > \text{Gd}^{3+} > \text{Nd}^{3+} > \text{Er}^{3+} > \text{Lu}^{3+} > \text{Ce}^{3+} > \text{La}^{3+}$ . The stability of the complexes was also studied as a function of the atomic number of the lanthanide ion (Fig. 1). It was found that the stability constants exhibit a trend commonly found in many other lanthanide complexes [8, 9]. The  $\log \beta_2$  values ( $\log \beta_2 = \log K_1 + \log K_2$ ) increase from lanthanum to samarium, where they reach a maximum, and then fall with increasing atomic number of the heavier lanthanide ions. From Fig. 1, the formation constants of the lanthanide complexes can be seen to decrease in the order **2a** > **1a** > **2b** > **1b** which is due to the change in the structure of the ligands. The relation between the electronegativities [10] as well as the ionic radii [11] of the lanthanide(III) ions and the stability constant of the respective complexes shows that the  $\text{Sm}^{3+}$  complexes have the highest stability (Table 1).

In the UV/Vis region (200–700 nm, *DMF*), the free *bisazo* dyes exhibit three absorption bands within the ranges of 215–220, 248–260, and 380–450 nm which can be assigned to the moderate energy  $\pi \rightarrow \pi^*$  transition representing the  ${}^1L_a \leftarrow {}^1A$  state, the low energy  $\pi \rightarrow \pi^*$  transition due to the  ${}^1L_b \leftarrow {}^1A$  state within

**Table 1.** Formation constants of lanthanide(III) complexes of *bisazo*- $\beta$ -diketones

	<b>1a</b>		<b>1b</b>		<b>2a</b>		<b>2b</b>		$Z^a$	$EN^b$	$1/r^c$
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$			
La <sup>3+</sup>	5.0	4.12	4.35	3.36	5.75	4.00	4.80	3.75	57	1.10	0.943
Ce <sup>3+</sup>	5.76	4.65	5.10	3.86	6.6	5.56	5.38	4.11	58	1.12	0.967
Nd <sup>3+</sup>	9.40	8.65	7.16	6.38	9.63	9.10	8.15	7.00	60	1.14	1.005
Sm <sup>3+</sup>	10.83	10.12	8.50	7.66	12.30	10.96	9.82	9.16	62	1.17	1.037
Gd <sup>3+</sup>	10.15	9.36	7.96	7.00	10.95	10.30	9.25	8.36	64	1.20	1.066
Er <sup>3+</sup>	8.11	7.20	6.50	5.11	8.72	8.20	7.65	6.30	68	1.24	1.135
Lu <sup>3+</sup>	6.86	5.80	5.95	4.40	8.22	7.35	6.40	5.00	71	1.27	1.179

<sup>a</sup> Atomic number; <sup>b</sup> electronegativity (*Pauling*); <sup>c</sup> ionic radius ( $\text{\AA}$ )

the aromatic moieties, and finally to the charge-transfer interaction within the whole molecule. However, the electronic spectra of lanthanide(III) chelates at different  $M:L$  ratios show a red shift (18–39 nm) for the *CT* band in comparison to that of the free ligands, indicating complex formation. In addition, a weak broad new absorption band at 594–646 nm is observed for all chelates, being due to the electronic transitions within the lanthanide ion suborbitals.

The mode of bonding of the *bisazo* dyes to the lanthanide ions was elucidated by investigating the IR spectra of the chelates  $2M:1L$ ,  $1M:1L$  and  $1M:2L$  as compared to those of the free ligands. The bands observed at 3400, 3360, 3480, and 3440  $\text{cm}^{-1}$ , assigned to  $\nu(\text{OH})$  in the spectra of the free ligands **1a**, **b** and **2a**, **b**, are broadened; their positions are shifted to higher wavenumbers (20–35  $\text{cm}^{-1}$ ). This behaviour may be attributed to the participation of the enolic OH group of the *bisazo*- $\beta$ -diketones in chelation with the lanthanide ion. The new broad, weak, or medium intensity band observed at 3210–3160  $\text{cm}^{-1}$  in the IR spectra of all chelates is probably due to  $\nu(\text{OH})$  of the water molecule. The bending  $\nu(\text{OH})$  bands at 1365, 1358, 1368, and 1360  $\text{cm}^{-1}$  of the free ligands exhibit a shift of 8–15  $\text{cm}^{-1}$  to lower wavenumbers values on complexation. This behaviour is due to the liberation of the enolic OH group of the ligand from hydrogen bond formation through chelation with lanthanide ions. The  $\nu(\text{C}=\text{O})$  bands at 1648, 1675, 1640, and 1672  $\text{cm}^{-1}$  of the free ligands exhibit a shift of 5–13  $\text{cm}^{-1}$  to lower or higher wavenumbers on complexation which may be taken as evidence for the participation of the C=O group in coordination. The  $\nu(\text{N}=\text{N})$  bands at 1418, 1412, 1415, and 1425  $\text{cm}^{-1}$  of the free ligands are not affected by complexation. This indicates that the N=N group does not contribute to the chelation. Thus, the chelation occurs through the carbonyl or carbonyl-enol form of the ligands. The new bands appearing in the ranges of 530–500 and 360–332  $\text{cm}^{-1}$  are assigned to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{Cl})$ , respectively [12].

The <sup>1</sup>H NMR spectrum of **2a** was compared with those of its La<sup>3+</sup> chelates in *DMSO*-*d*<sub>6</sub> at  $M:L$  ratios of 2:1, 1:1, and 1:2. The signal of the protons of the enolic OH groups of free **2a** are found at 14.98 ppm and disappears in the presence of D<sub>2</sub>O. It is broadened and shifted to higher field (0.4–1.2 ppm) upon chelation. The aromatic protons resonate at 7.88–7.30 ppm for free **2a**. Chelation causes a downfield by  $\sim 0.8$  ppm, accompanied by an obvious decrease and broadening of

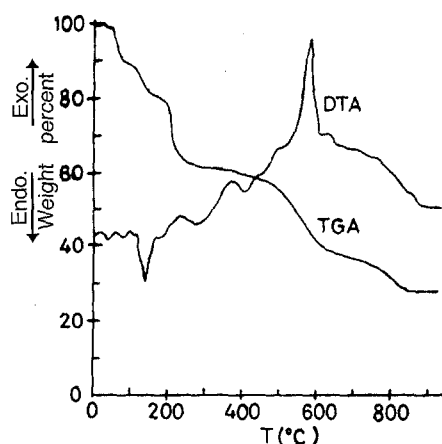


Fig. 2. Thermogram of gadolinium with ligand **2a** (1:1)

their envelope, indicating the formation of a covalent bond between the lanthanum ion and the oxygen atom of the enolic OH group. In most of the NMR spectra of  $\text{La}^{3+}$  chelates, a new signal is found at 4.1 ppm, originating from water molecules coordinated to the lanthanum ion in the complex.

The values of molar conductance ( $\Lambda_m, \text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ ) of the chelates in DMF (Table 3) show that all 1M:2L complexes are non-electrolytes. On the other hand, the molar conductance values of 1:1 and 2:1 complexes indicate an ionic nature of the chelates and the presence of  $\text{Cl}^-$  outside the coordination sphere which is confirmed by the precipitation of AgCl by addition of  $\text{AgNO}_3$ .

The results of thermal analyses of 2M:1L, 1M:1L, and 1M:2L  $\text{Gd}^{3+}$  chelates with ligands **2a** and **2b** are summarized in Table 2. All investigated  $\text{Gd}^{3+}$  complexes degrade in three stages, as shown by the TG curves, from which the percentage of coordinated water molecules was calculated. Each inflection on the TG curve is accompanied by either an endo- or exothermic peak on the DTA curve corresponding to certain phase transformations (Fig. 2 for Gd-**2a** (1:1) as an example). The first step in the decomposition sequence at 70–105°C corresponds to the loss of physically bound water molecules from the crystal lattice, whereas the second step within the temperature range of 125–200°C represents the removal of

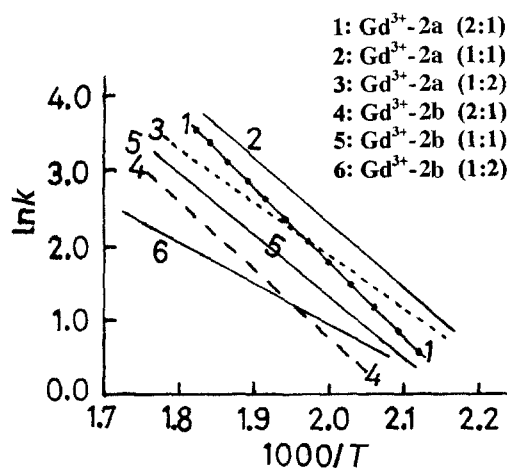


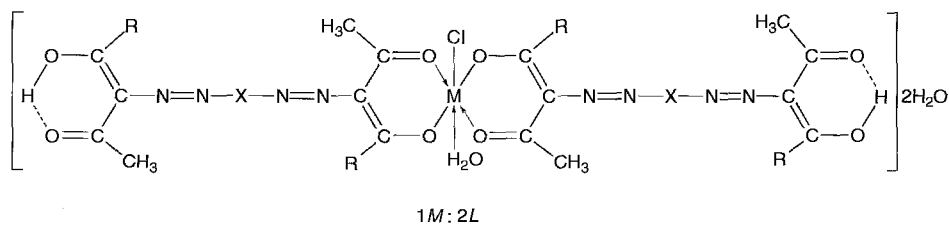
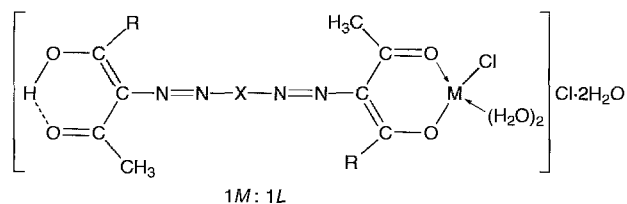
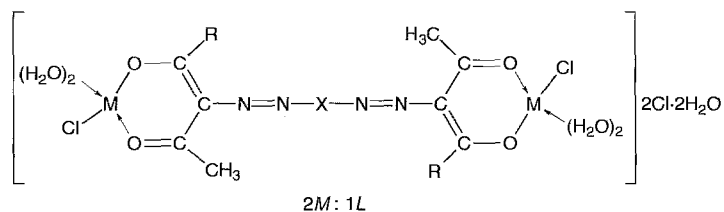
Fig. 3. Arrhenius plots constructed from DTA thermograms

**Table 2.** Thermogravimetric analysis of gadolinium(III) complexes

	$M:L$	Metallic residue (%)	Decomp. temp. ( $^{\circ}\text{C}$ )	$\Delta E_a$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	% $M$		% $\text{H}_2\text{O}$		No. of $\text{H}_2\text{O}$ molecules
					calcd.	found	calcd.	found	
$\text{Gd}^{3+}$ - <b>2a</b>	2:1	40.3	400	83.10	35.23	35.0	12.11	11.9	6
	1:1	28.3	350	69.80	24.98	24.6	11.45	11.5	4
	1:2	19.7	330	59.36	17.4	17.1	5.76	5.4	3
$\text{Gd}^{3+}$ - <b>2b</b>	2:1	35.7	420	75.77	30.93	31.0	10.63	10.7	6
	1:1	24.1	380	68.96	20.86	20.9	9.56	9.3	4
	1:2	15.5	365	43.74	13.65	13.4	4.52	4.2	3

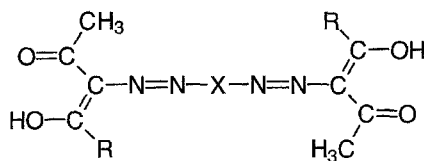
coordinated water molecules, leading to the formation of anhydrous chelates. It is followed by the removal of chloride atoms from the chelates in the temperature range of 230–290 $^{\circ}\text{C}$ . The inflection of the  $TG$  curve at a temperatures range above 310 $^{\circ}\text{C}$  indicates the decomposition of the organic part of the chelate in the last step, leaving gadolinium oxide as a metallic residue at the final temperature. The energy of activation ( $\Delta E_a$ ) of the thermal decomposition of the chelates has been evaluated from the thermograms as shown previously [13, 14]. *Arrhenius* plots were constructed (Fig. 3), and  $\Delta E_a$  was obtained from the slope (Table 2).

The above analytical data agree satisfactorily with the expected formula represented as given below (for  $X$  and  $R$ , see Experimental).



## Experimental

The *bisazo* compounds were prepared as reported previously [15, 16]. After recrystallization from dilute acetic acid, their purities were confirmed by elemental analyses as well as by IR and  $^1\text{H}$  NMR spectra [15]. The ligands have the following structures:



	X	R
<b>1a</b>	<i>m</i> -phenylene	Me
<b>1b</b>	<i>m</i> -phenylene	Ph
<b>2a</b>	<i>p</i> -phenylene	Me
<b>2b</b>	<i>p</i> -phenylene	Ph

Stock solutions of ligands (dioxane, 0.1M), and lanthanide(III) chloride (bidistilled water, 0.1M) were prepared. The lanthanide(III) chelates were synthesized by refluxing a mixture of appropriate amounts of stock solutions for about 4 h. The solid chelates were filtered off, washed with ethyl alcohol, dried, and then subjected to elemental analysis. The C, H, N elemental analyses were performed at the Microchemical Analysis Unit, Cairo University. Lanthanides and chloride ions were analyzed by *EDTA* titration after decomposition of the chelates according to a reported procedure [17, 18]. The analytical data along with the electrolytic conductance values of  $1 \times 10^{-3}M$  lanthanide chelates in *DMF* are given in Table 3.

For potentiometric titrations, three mixtures were prepared: (a) 5 ml 0.1 M  $\text{HClO}_4$  + 5 ml 1.0 M  $\text{NaClO}_4$ ; (b) mixture (a) + 25 ml 0.001 M ligand; (c) mixture (b) + 2 ml 0.01 M lanthanide(III) ion. Mixtures a, b, and c were made up to 50 ml with a mixture of bidistilled water and dioxane (50% v/v). These mixtures were then titrated potentiometrically [19] against 0.02 M KOH containing 50% (v/v) dioxane at  $25 \pm 0.2^\circ\text{C}$  using an Orion Research 601 A *pH*-meter. The average number of protons  $\bar{n}_A$  associated with the ligands at various *pH* values, the average number of ligands  $\bar{n}$  attached to a metal ion, and the free ligand exponent *pL* were calculated using the equations given by *Irving* and *Rossotti* [6]. The methods used for calculating successive stability constants of the complexes were interpolation at half  $\bar{n}$ , correction term, and successive approximation methods [6, 7].

Conductometric titrations of 50 ml  $1 \times 10^{-3}M$  ligand solutions (dioxane-water 50% v/v) with  $1 \times 10^{-2}M$  lanthanide(III) ion solutions (dioxane-water 50% v/v) were carried out using a YSI Model 32 conductivity bridge.

The UV/Vis spectra of  $3 \times 10^{-5}M$  ligands and their chelates were recorded against solvent blanks using matched silica cells on a Perkin Elmer  $\lambda$  3B spectrophotometer. The IR spectra ( $200\text{--}4000\text{ cm}^{-1}$ ) were measured as KBr discs using a Beckman IR 4200 double beam spectrophotometer.  $^1\text{H}$  NMR spectra were run on a Varian EM 390-90 spectrometer in *DMSO*- $d_6$ ; chemical shifts are reported relative to *TMS* as internal standard.

Thermogravimetric analyses (*TG-DTA*) were performed on a STA 409 Netzsch TGA-DTA Analyzer in the range of  $25\text{--}900^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  in air.

**Table 3.** Elemental analysis and molar conductance data

	M:L	% C		% H		% N		% M		% Cl		% H <sub>2</sub> O		$A_m$ (ohm <sup>-1</sup> . cm <sup>2</sup> ·mol <sup>-1</sup> )
		calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	
[(Gd <sub>2</sub> ·1a)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	21.52	21.3	1.81	1.8	6.28	6.3	35.23	35.3	15.88	16.0	12.11	12.5	100.8
[(Gd·1a)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	30.52	30.4	2.73	2.8	8.90	9.0	24.98	24.8	11.26	11.1	11.45	11.6	50.0
[(Gd·21a)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	42.54	42.5	3.80	3.7	12.41	12.5	17.40	17.5	3.92	4.0	5.76	5.8	8.2
[(Gd <sub>2</sub> ·1b)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	30.71	30.5	1.99	2.0	5.51	5.4	30.93	31.0	13.94	14.0	10.63	10.8	99.2
[(Gd·1b)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	41.43	41.1	2.81	2.9	7.43	7.4	20.86	20.7	9.41	9.5	9.56	9.7	48.6
[(Gd·21b)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	54.22	54.2	3.68	3.7	9.73	9.6	13.65	13.5	3.08	3.0	4.52	4.8	7.8
[(La <sub>2</sub> ·2a)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	22.45	22.4	1.89	1.9	6.55	6.6	32.45	32.4	16.56	16.5	12.63	12.9	128.8
[(La·2a)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	31.44	31.3	2.81	2.6	9.17	9.2	22.73	22.6	11.60	11.6	11.79	12.0	60.2
[(La·22a)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	43.42	43.3	3.88	3.8	12.66	12.6	15.69	15.6	4.00	4.1	5.88	6.0	8.1
[(Nd <sub>2</sub> ·2a)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	22.17	22.2	1.86	1.9	6.47	6.5	33.28	33.3	16.36	16.2	12.47	12.8	129.3
[(Nd·2a)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	31.16	31.2	2.78	2.8	9.09	9.0	23.39	23.5	11.50	11.6	11.69	11.7	54.8
[(Nd·2a)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	43.16	43.1	3.86	3.9	12.59	12.4	16.20	16.2	3.98	4.0	5.85	6.0	8.6
[(Sm <sub>2</sub> ·2a)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	21.86	21.8	1.84	1.8	6.38	6.4	34.21	34.2	16.13	16.1	12.30	12.7	182.3
[(Sm·2a)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	30.86	30.7	2.76	2.7	9.00	8.9	24.15	24.0	11.39	11.4	11.58	11.9	65.1
[(Sm·22a)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	42.86	42.7	3.83	3.8	12.50	12.3	16.77	16.8	3.95	4.0	5.81	6.0	9.8
[(Gd <sub>2</sub> ·2a)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	21.52	21.5	1.81	1.7	6.28	6.1	35.23	35.2	15.88	15.9	12.11	12.4	173.0
[(Gd·2a)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	30.52	30.5	2.73	2.7	8.90	8.8	24.98	24.8	11.26	11.3	11.45	11.8	62.7
[(Gd·22a)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	42.54	42.4	3.80	3.8	12.41	12.5	17.40	17.4	3.92	3.8	5.76	6.0	9.3
[(Lu <sub>2</sub> ·2a)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	20.70	20.6	1.74	1.8	6.04	6.0	37.70	37.7	15.28	15.1	11.65	11.9	168.1
[(Lu·2a)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	29.69	29.6	2.65	2.6	8.66	8.6	27.03	27.0	10.95	11.0	11.14	11.4	60.6
[(Lu·22a)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	41.72	41.6	3.73	3.6	12.17	12.2	18.99	19.0	3.85	3.6	5.65	5.9	8.8
[(La <sub>2</sub> ·2b)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	31.86	31.8	2.06	2.0	5.72	5.9	28.34	28.3	14.47	14.5	11.03	11.4	142.0
[(La·2b)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	42.46	42.2	2.88	2.9	7.62	7.6	18.89	18.9	9.64	9.6	9.80	10.0	58.6
[(La·22b)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	55.10	55.0	3.74	3.7	9.89	9.7	12.26	12.3	3.13	3.1	4.59	4.9	7.3
[(Nd <sub>2</sub> ·2b)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	31.51	31.5	2.04	2.0	5.66	5.8	29.11	29.1	14.31	14.3	10.91	11.0	147.0
[(Nd·2b)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	42.16	42.1	2.86	2.9	7.57	7.4	19.47	19.5	9.57	9.6	9.73	10.0	59.0
[(Nd·22b)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	54.84	54.8	3.73	3.7	9.84	9.7	12.67	12.7	3.11	3.1	4.57	4.8	7.7
[(Gd <sub>2</sub> ·2b)·2Cl·4H <sub>2</sub> O]·2Cl·2H <sub>2</sub> O	2:1	30.71	30.6	1.99	2.0	5.51	5.5	30.93	31.0	13.94	14.0	10.63	11.0	132.0
[(Gd·2b)·Cl·2H <sub>2</sub> O]·Cl·2H <sub>2</sub> O	1:1	41.43	41.0	2.81	2.7	7.43	7.4	20.86	20.6	9.41	9.5	9.56	9.8	54.3
[(Gd·22b)·Cl·H <sub>2</sub> O]·2H <sub>2</sub> O	1:2	54.22	54.1	3.68	3.5	9.73	9.8	13.65	13.5	3.08	3.0	4.52	4.8	8.0

**References**

- [1] Das Mohon PN, Sumor OP, Trivedia CP (1973) *J Inorg Nucl Chem* **35**: 316
- [2] Abu-El-Wafa SM, El-Sabakh EA, El-Sayed GM (1987) *Egypt J Chem* **30**: 17
- [3] Rys P, Uniger H, Zo (1970) *Fundamental of the Chemistry and Application of Dyes*. Wiley, New York, p 45
- [4] Dessouki HA, Issa RM, Moustafa MM (1989) *Acta Chim Hung* **126**: 653
- [5] Legg N (1958) *Brit* **800**: 145
- [6] Irving H, Rossotti HS (1953) *J Chem Soc*: 3397; (1954) 2904
- [7] Mushran SP, Prakash OM, Murti RAM (1973) *J Inorg Nucl Chem* **35**: 2119
- [8] Dutt NK, Nag K, Seshadri T (1969) *J Inorg Chem* **31**: 3177
- [9] Moeller T (1963) *The Chemistry of the Lanthanides*. Chapman and Hall, London, p 20
- [10] Abd El-Rahman AI, Omar MM, El-Ansary AL (1989) *Egypt J Chem* **32**: 237
- [11] Cotton FA, Wilkinson G (1972) *Advanced Inorganic Chemistry. A Comprehensive Text*, 3rd edn. Wiley Eastern Limited, New Delhi, p 1057
- [12] Mohan M, Tandon JP, Gupta NS (1981) *J Inorg Nucl Chem* **43**: 1223
- [13] Wendlant WW (1963) *J Inorg Nucl Chem* **25**: 833
- [14] Thomas J, Clarke TA (1968) *J Chem Soc A*: L 157
- [15] Issa RM, Ghoneim AK, Deifallah EM, Moustafa MM (1994) *J Indian Chem Soc* **71**: 377
- [16] Vogel AI (1978) *A Textbook of Practical Organic Chemistry*, 4th edn. Longmans, London, pp 687–720
- [17] Srivastava AK, Rana VB, Mohan M, Swami MP, Jain PC (1975) *J Inorg Nucl Chem* **87**: 723
- [18] Bassett J, Denney RC, Jeffery GH, Mendham J (1978) *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th edn. Longman, London, pp 257–344
- [19] Sarin R, Munshi KNJ (1972) *Inorg Nucl Chem* **34**: 581

*Received October 23, 1996. Accepted (revised) January 7, 1997*