Monatshefte für Chemie 126, 163–171 (1995)

Monatshefte für Chemie
Chemical Monthly

Chelation Behaviour of Lanthanides with some *thio-Schiff* Bases

Y. M. Issa*, H. M. Abdel Fattah, M. M. Omar, and **A. A. Soliman**

Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

Summary. The stability constants of complexes of trivalent Y, La, Ce, Pr, Sm, Gd, Dy, Ho, Er, and Yb ions with some *thio-Schiff* bases have been determined potentiometrically using the *Calvin–Bjerrum* titration technique as modified by *Irving* and *Rossotti* at 25 °C and an ionic strength of 0.1 M (NaCl) in 70% (v/v) aqueous ethanol. 1:1 and 1:2 complexes are formed and evidenced by conductometric studies. The pK_a values of the SH group were correlated with the *Hammet* constants of substituents. The values of the stability constants are correlated with the atomic numbers of the lanthanides and with the sum of the ionization constants of the ligands.

Keywords. Stability constants; Lanthanides; Potentiometry; Conductometry.

Komplexierungsverhalten von Lanthaniden mit einigen *thio-Schiff*schen Basen

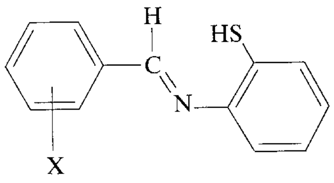
Zusammenfassung. Die Stabilitätskonstanten von Komplexen trivalenter Y-, La-, Ce-, Pr-, Sm-, Gd-, Dy-, Ho-, Er- und Yb-Ionen mit einigen *thio-Schiff*schen Basen wurden potentiometrisch unter Verwendung der von *Irving* und *Rossotti* modifizierten *Calvin–Bjerrum*-Titrationstechnik bei 25 °C und $I = 0.1\ M$ (NaCl) in 70% (v/v) wäßrigem Ethanol bestimmt. Wie konduktometrisch gezeigt werden konnte, treten 1:1- und 1:2-Komplexe auf. Die pK_a-Werte der SH-Gruppen wurden mit den *Hammet*schen Substituentenkonstanten korreliert, die Stabilitätskonstanten mit den Kernladungszahlen der Lanthaniden und mit der Summe der Ionisationskonstanten der Liganden.

Introduction

The complexation ability of lanthanides with *Schiff* bases is limited compared to that of d-block elements. This results in part from the inability of the f-orbitals to form hybrid orbitals which might lead to covalent bonds and also from the fact that the lanthanide ions are rather large compared with those of the d-block elements, thus lowering the electrostatic forces of attraction.

However, there is a recent attention for lanthanide complexes with *Schiff* bases not only due to the simplicity of the *Schiff* base molecule but also to the important applications of both lanthanides and *Schiff* bases [1–7].

A survey of the literature reveals that no work has been done on lanthanide complexes of the *thio-Schiff* bases under investigation. So the present work aims to study the chelation affinity of lanthanide ions with these new *Schiff* bases (**1**) obtained by the condensation of *o*-aminothiophenol with aromatic aldehydes such as benzaldehyde, *p*-chloro-, *p*-N,N-dimethylamino-, *p*-hydroxy-, *p*-nitro-, *p*-methoxy-, *p*-methyl-, and *o*-hydroxybenzaldehyde.



1

X = H (**a**), p-Cl (**b**), p-N(CH$_3$)$_2$ (**c**), p-OH (**d**), p-NO$_2$ (**e**), p-OCH$_3$ (**f**), p-CH$_3$ (**g**), and o-OH (**h**)

Results and Discussion

The ionization constants of *Schiff* bases **1a**–**1h** are calculated from the potentiometric titration curves of hydrochloric acid in presence and absence of the ligands. The pK_a values are obtained directly from their formation curves and also by the average value method [15]. The pK_a values obtained by both methods are given in Table 1 indicating the presence of one pK_a value for **1a**, **1b**, **1c**, **1e**, and **1g** corresponding to the ionization of the SH group and two pK_a values (pK_{a1} and pK_{a2}) for **1d** and **1h**, assignable to the ionization of the OH and SH groups, respectively.

The effect of substituents X was investigated by plotting $pK_{a\mathrm{SH}}$ values *vs.* *Hammett* substitution constants σ_x (Fig. 1). The linear plot was statistically analyzed applying the least squares method [16]. The slope (ρ) is negative indicating that electron withdrawing groups decrease the $pK_{a\mathrm{SH}}$ values, *i.e.* increase the ionization of such compounds, and *vice versa*. However, the correlation coefficient value of 0.59 indicates that the SH group is not directly influenced by the variation of the substituents on the aromatic ring. This may be explained on the basis of the noncoplanar structure assumed for the molecules [17].

Table 1. pK_a values of **1a**–**1h**

	pK_a				mean pK_a		$-\Delta G^\circ$ (kJ/mol)	
	pK_{a1}		pK_{a2}		pK_{a1}	pK_{a2}	pK_{a1}	pK_{a2}
	1st method	2nd method	1st method	2nd method				
1a	10.12	10.12	–	–	10.12	–	57.68	–
1b	9.25	9.25	–	–	9.25	–	52.71	–
1c	10.18	10.18	–	–	10.17	–	57.98	–
1d	5.15	5.15	9.05	9.06	5.15	9.06	29.34	51.66
1e	9.00	9.00	–	–	9.00	–	51.29	–
1f	9.70	9.60	–	–	9.65	–	55.01	–
1g	9.50	9.46	–		9.48	–	54.05	–
1h	9.32	9.30	10.34	0.35	9.30	10.35	53.00	58.98

1st method: interpolation of $\bar{n}_A$ values; 2nd method: $\log \bar{n}_A/1-\bar{n}_A$ or $\log \bar{n}_A - 1/2 - \bar{n}_A$ *vs.* *pH*

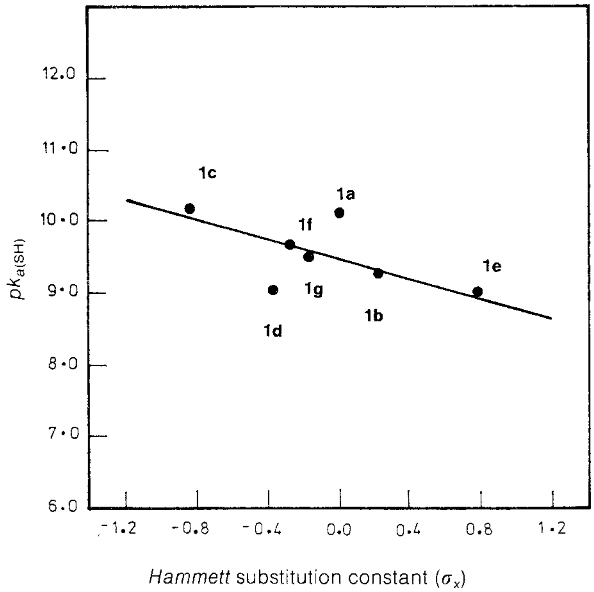
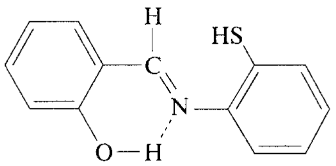


Fig. 1. $pk_{a(SH)}$ *vs.* σ_x plot for **1a–1g**

It is also of interest to notice the large difference in pK_{a1} (OH group) values of **1d** and **1h** which are found to be 5.15 and 9.30, respectively. This can be attributed to the participation of the OH group of **1h** in intramolecular hydrogen bonding which decreases the acidity of the OH group [18–20].



The respective metal ions with the ligands **1a–1h** (mixture 3) were titrated against NaOH. A displacement was noticed in the metal titration curves with respect to the ligand titration curve indicating the release of protons due to complex formation.

Values of $\bar{n}$ and pL were calculated using a Casio FX-700 programmable calculator. The maximum $\bar{n}$ values calculated for metal–ligand systems were found not to exceed 2 for all complexes indicating the formation of only 1:1 and 1:2 species.

The values of $\log\beta_1$ and $\log\beta_2$ and their mean values for the complexes of the trivalent Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, and Yb ions with the *Schiff* bases under investigation are given in Table 2.

It is clear from Table 2 that **1h** has the highest affinity for chelation with the lanthanide ions among the used *Schiff* bases. This is attributed to the presence of an additional coordinating site (phenolic OH group). On the other hand, **1e** was found to have the lowest ability for chelation. This can be explained by the presence of the NO_2 group which has a strong electron withdrawing effect resulting in a decrease in electron density on the nitrogen atom and hence in a decrease of stability constants of the formed complexes.

In general, the values of $\log\beta_1$ and $\log\beta_2$ reflect the affinities of the used *Schiff* bases for chelation with the lanthanide ions and are comparable with those reported

Table 2. Comulative data of $\log\beta_1$ and $\log\beta_2$ values for complexes of **1a–1h** with lanthanide metal ions in 70% ethanol-water at 25 °C

	Stability constant															
	1a		**1b**		**1c**		**1d**		**1e**		**1f**		**1g**		**1h**	
	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$	$\log\beta_1$	$\log\beta_2$
Y	11.31	20.94	7.26	15.34	9.13	18.59	8.44	17.47	7.47	14.50	8.45	16.60	8.34	16.79	14.17	25.59
La	8.42	15.79	8.59	15.17	9.73	19.29	7.13	11.77	6.06	13.60	7.76	14.38	7.58	14.37	11.13	21.27
Ce	9.22	17.69	8.23	16.83	9.14	18.19	8.26	14.98	7.24	14.63	8.35	16.59	7.75	14.69	11.36	21.11
Pr	8.43	16.37	8.53	16.30	7.99	16.30	7.90	13.62	6.08	13.97	8.41	15.01	8.78	16.85	12.34	23.41
Nd	7.97	15.61	8.46	15.87	7.97	16.19	8.33	14.70	6.04	13.68	11.37	22.18	8.52	14.52	12.71	23.68
Sm	8.39	16.52	8.10	15.22	8.04	16.35	7.62	13.86	6.29	13.75	8.87	17.60	7.89	15.28	12.10	23.10
Gd	7.86	15.76	8.58	16.19	8.03	16.41	7.36	13.24	5.87	14.23	8.98	17.20	7.92	15.47	12.72	24.49
Dy	8.36	15.69	8.53	16.09	9.12	18.78	9.37	15.06	6.14	13.57	7.78	15.22	8.28	15.33	11.12	22.15
Ho	8.38	16.44	7.33	14.32	7.98	16.27	8.69	15.53	6.33	14.16	10.11	17.80	8.22	16.22	13.39	25.27
Er	8.01	14.85	7.88	14.77	8.06	16.09	8.86	14.02	6.06	13.72	8.77	16.88	8.33	15.54	12.05	22.44
Yb	8.35	15.56	7.92	15.03	9.54	19.11	6.50	10.59	6.00	13.55	7.85	14.83	8.22	16.10	11.15	21.00

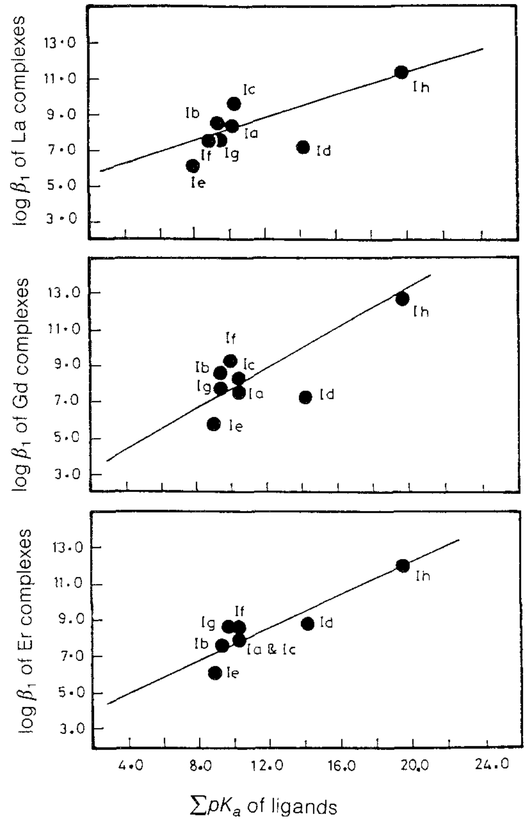


Fig. 2. log β_1 of La(III), Gd(III), and Er(III) complexes with **1a–1h** *vs.* $\sum pK_a$ of ligands

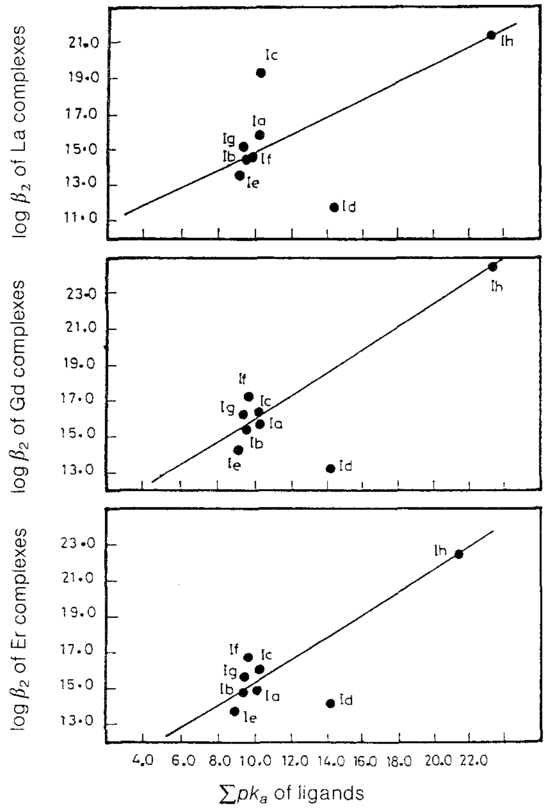


Fig. 3. log β_2 of La(III). Gd(III), and Er(III) complexes with **1a–1h** *vs.* $\sum pK_a$ of ligands

Table 3. Dependence of $\log \beta_1$ and $\log \beta_2$ of La(III), Gd(III), and Er(III) complexes with **1a**–**1h** on pK_a

	$\sum pK_a$	$\log \beta_1$			$\log \beta_2$		
		La	Gd	Er	La	Gd	Er
1a	10.12	8.42	7.86	8.01	15.79	15.76	14.85
1b	9.25	8.59	8.59	7.88	15.17	16.19	14.77
1c	10.17	9.73	8.03	8.06	19.29	16.41	16.09
1d	14.21	7.13	7.36	8.86	11.77	13.24	14.02
1e	9.00	6.06	5.87	6.06	13.60	14.23	13.72
1f	9.65	7.76	8.98	8.77	14.38	17.20	16.88
1g	9.48	7.58	7.92	8.33	14.37	15.47	15.54
1h	19.65	11.13	12.72	12.05	21.27	24.49	22.44
Slope (ρ)		0.26	0.42	0.40	0.43	0.67	0.58
Intercept (C)		5.30	3.66	3.92	10.78	8.94	9.34
St. deviation (s)		1.34	1.33	0.84	8.29	2.52	1.88
Corr. coeff. (r)		0.62	0.78	0.89	0.51	0.73	0.78

for some oxygen-containing *Schiff* bases [20]. This affinity may be attributed to the simple structure of the used ligands and consequently little steric hindrance in the formed 1:1 and 1:2 complexes.

The relation between the sum of the ionization constants of **1a**–**1h** and the stability constants of their complexes with trivalent La, Gd, and Er ions are represented graphically in Figs. 2 and 3. There is a linear relation between $\sum pK_a$ of the respective ligands and $\log \beta$ of their complexes. Therefore, *Schiff* bases with higher $\sum pK_a$ are expected to form more stable complexes. In the case of **1d**, a high $\sum pK_a$ is related to low $\log \beta_1$ and $\log \beta_2$ values compared with **1h**. This can be explained on the basis that the OH group of **1d** does not participate in chelation due to geometrical considerations, whereas the OH group of **1h** affords an additional 6-membered ring and hence increases the stability of the complexes.

The results are treated statistically using the least squares method [16]. The regression of the lines may be represented as $\log \beta_1 = C_1 + \rho \sum pK_a$ or $\log \beta_2 = C_2 + \rho \sum pK_a$, where the values of C and ρ are given in Table 3. The plots have correlation coefficients of 0.62, 0.78, and 0.89 for $\log \beta_1$ and 0.51, 0.73, and 0.78 for $\log \beta_2$ for $\log \beta_2$ of La, Gd, and Er complexes, respectively. Such values indicate the dependence of the stability constants of the complexes on $\sum pK_a$ of the ligand. This favours the assumption that the reaction between the metal ions and the *Schiff* bases proceeds through proton elimination. Thus, for ligands **1a**–**1g**,

$$M(H_2O)_n^{3+} + HL \rightleftharpoons ML(H_2O)_{n-2}^{2+} + H^+$$
$$ML(H_2O)_{n-2}^{2+} + HL \rightleftharpoons ML_2(H_2O)_{n-4}^{+} + H^+$$

and for ligand **1h**,

$$M(H_2O)_n^{3+} + H_2L = MHL(H_2O)_{n-3}^{2+} + H^+$$
$$MHL(H_2O)_{n-3}^{2+} + H_2L = M(HL)_2(H_2O)_{n-6}^{+} + H^+$$

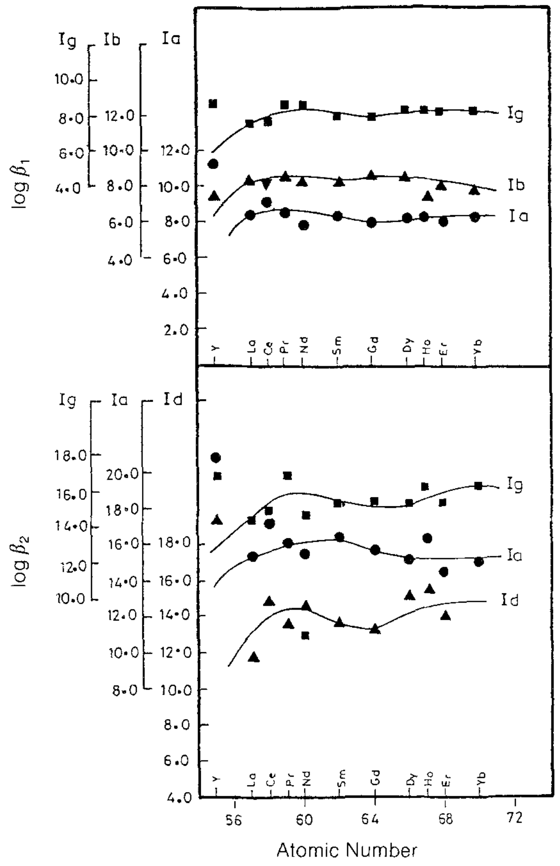


Fig. 4. Relation between log β_1 and log β_2 of the Ln(III) complexes with some *Schiff* bases in 70% ethanol-water mixture and atomic number

The corresponding ΔG values lie between -40.63 and $-145.88\,\mathrm{kJ\cdot mole^{-1}}$ indicating the high stability of the complexes formed and the spontaneous nature of the complexation reaction.

The stability of the complexes was also studied as a function of the atomic number of the lanthanide ion (Fig. 4). It is found that the stability constants exhibit a trend commonly found in many other lanthanide complexes [21–23]. They increase from lanthanum to neodymium where they reach a maximum and then fall at gadolinium (gadolinium break) [23] after which they increase again in the heavier lanthanides with increasing of atomic number. The increase in stability constants in the lighter lanthanides can be explained on the basis of the electrostatic attraction between the lanthanide cation and the ligand which increases as the crystal radius decreases. In the heavier lanthanides, additional factors are also of importance. One of these is the expected increase in covalency as a consequence of the increase of electronegativity with the decrease in the size of the central ion. Other factors are based on the fact that the formation constant really measures a displacement equilibrium between the hydrated ion and the ligand. Of these factors, the smoothing effect of hydration on the crystal radii, the rupture of *Ln*–H_2O bonds, the formation of new bonds and the retention of water in the product are undoubtedly important in determining the measured stability of the heavier lanthanides [23]. The deviation of Y is attributed to the fact that it is not an f-block element.

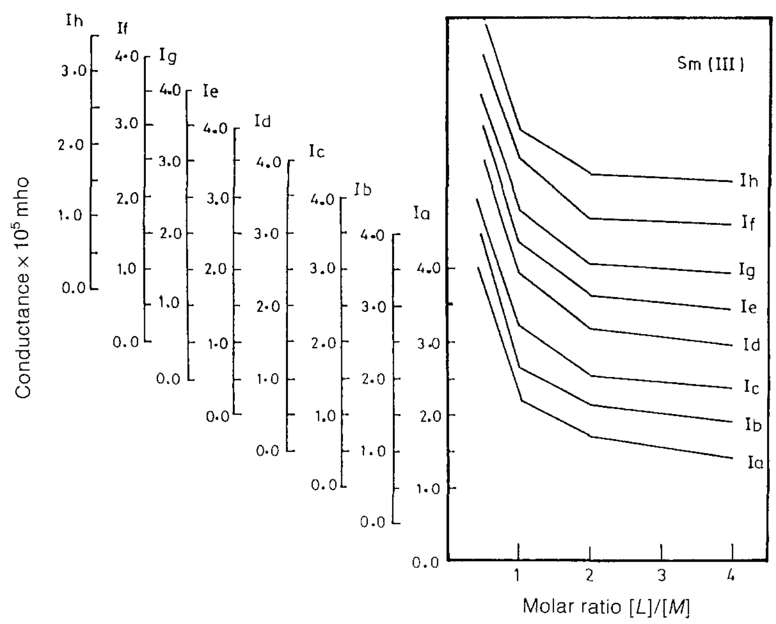


Fig. 5. Conductometric titration curves of **1a–1h** with Sm(III)

The conductometric titration curves (see Fig. 5 for a representative one) for the investigated complexes show two breaks at molar ratios of 1:1 and 1:2 (metal ion: ligand), which is in accordance with the results obtained from the *pH*-metric titrations. However, a higher molar ratio (1:3) may be excluded, owing to steric hindrance in accommodating three *Schiff* base molecules around a metal ion. This may also be attributed to the effect of the alcohol-water medium in which the lanthanide metal ions exist as aquo complexes. Further coordination by a third ligand may therefore be inhibited by the strongly bound water molecules.

Experimental

The chemicals used in the present work were laboratory pure grade. The water used was always twice distilled from all-glass equipment.

The *Schiff* bases were prepared by reflux condensation of *o*-aminothiophenol with the appropriate amount of aldehyde in ethyl alcohol [8]. The ligands obtained were recrystallized from dilute acetic acid till constant metlting point; their purity was confirmed by elemental analysis to be above 99.5%.

Solutions (0.001 *M*) of the ligands **1a–1h** were prepared in freshly distilled ethanol. All lanthanide(III) perchlorate solutions (0.001 *M*) were prepared in bidistilled water and standardized by conventional procedures [9]. A 0.01 *M* solution of hydrochloric acid was prepared and standardized against standard sodium carbonate solution. Sodium chloride (1.0 *M*) was used to keep the ionic strength constant. A solution of sodium hydroxide (0.20 *M*) (Merck) was used as titrant. It was standardized by recommended procedures [10].

Three mixtures were prepared as follows:

(1) 3 ml 0.10 *M* HCl + 5 ml 1.0 *M* NaCl + 35 ml ethanol
(2) 3 ml 0.10 *M* HCl + 5 ml 1.0 *M* NaCl + 20 ml ethanolic solution of the ligands **1a–1h** + 15 ml ethanol
(3) 3 ml 0.10 *M* HCl + 5 ml 1.0 *M* NaCl + 20 ml ethanolic solution of the ligands + 5 ml 0.001 *M* metal ion solution + 15 ml ethanol

The volume was made up to 50 ml with distilled water to obtain 70% alcoholic solutions.

The three mixtures were titrated potentiometrically [11] against 0.20 *M* NaOH at 25 °C using a Chemtrix Model 62 A *pH*-meter. The appropriate volume of ethanol was added to keep the ratio of 70% (v/v) constant to avoid precipitation of the *Schiff* bases during the titration. The *pH* readings are corrected for the medium according to *Bates* [12]. The curves are plotted accordingly. The $\bar{n}_A$, $\bar{n}$, and *pL* values were calculated using the method described by *Irving* and *Rossoti* [13]. Successive stability constants were calculated by interpolation at $\bar{n}$ values, application of a correction term, and successive approximation [14].

Conductometric titration were carried out at 25 °C in ethanol-water (70% (v/v)) solution using a DB 12 conductivity meter model LBR at a frequency of 3 KHz to confirm the molar ratio (*M*:*L*) obtained by the potentiometric titration.

References

[1] Erioksen T. E., Grenthe I., Puigdomench I. (1987) Inorg. Chem. Acta **126**: 131

[2] Lajunen L. H. J., Choppin G. R. (1986) Inorg. Chem. Acta **119**: 83

[3] Barsoum B. N., Naom M. M. (1986) Indian J. Chem. **25**: 457

[4] Masoud M. S., Ibrahim N. A., Abou Ali S. A., Ali G. Y., Abed I. M. (1986) Indian J. Chem. **25A**: 389

[5] Mehta P., Mathur P., Mehta R. K. S. (1985) Z. Phys. Chem. (Leipzig) **266**: 1163

[6] Saxena R. S., Gupta A. (1984) Indian J. Chem. **23A**: 786

[7] Mohanty N. K., Patnaik R. K. (1983) Indian J. Chem. **22A**: 820

[8] Savich J. A., Pikaev A. K., Lebedev I. A., Spitsyn V. I. (1959) Mat. Mekh., A Storn, Fiz Khim **1**: 225 (CA: 53, 1334b)

[9] Kolthof I. M., Elvin P. J. (1963) Treatise on Analytical Chemistry, **P. II**, Chap. 8, p. 58

[10] Vogel A. I. (1962) Textbook of Quatitative Inorganic Analysis Including Elementary Instrumental Analysis, 2nd edn. Longmans, London

[11] Sarin R., Munshi K. N. J. (1972) Inorg. Nucl. Chem. **34**: 581

[12] Bates R. G., Paabo M., Robinson R. A. (1972) J. Phys. Chem. **34**: 581

[13] Irving H., Rossoti H. S. (1954) J. Chem. Soc., 2904

[14] Irving H., Rossoti H. S. (1953) J. Chem. Soc., 3397

[15] Nayan R., Dey A. K. (1972) Indian J. Chem **10**: 109

[16] Jaffe H. H. (1953) Chem. Rev. **53**: 191

[17] El-Ansary A. L., Darwish N. A., Issa Y. M., Hassib H. B. (1990) Egypt. J. Chem. **33**: 129

[18] Minkin V. I., Zahdanov Yu. A., Garnoveskii A. D., Sadekov I. D. (1966) Zh. Khim. **40**: 677 (CA: 65, 4784)

[19] Minkin V. I., Bern V. A., Malysheva E. N., Zahdanov Yu. A., Sadekov I. D. (1969) Rects. Sposob. Nost. Org. Soedin. **6**: 34 (CA: 71, 101163)

[20] Ranganthan H., Ramsam T., Ramswamy D., Santappa M. (1986) Indian J. Chem. **25**: 127

[21] Pokhariyal G. P. (1988) J. Indian Chem. Soc. **65**: 596

[22] Dutt N. K., Nag K., Seshadri T. (1969) J. Inorg. Chem. **31**: 3177

[23] Moeller T. (1963) The Chemistry Of The Lanthanides. Chapman & Hall, London

Received April 4, 1994. Accepted (revised) May 24, 1994