Affinity of Lanthanoid(III) Ions for Nitrogen-donor Ligands in Aqueous Solution

By **Robert D. Hancock,* Graham Jackson,** and **Ann Evers,** National Institute for Metallurgy, Private Bag X3015, Randburg 2125, South Africa

A model of the chelate effect is used to predict that lanthanoid(III) ions should form chelated complexes with glycine at pH >6, and bipyridyl complexes resistant to hydrolysis in aqueous solution with $\log K_1 \sim 1$. The values of $\log K(\mathrm{ML}) = 3.26$, $\log K[\mathrm{ML(OH)}] = 8.79$, and $\log K[\mathrm{ML(H)}] = 10.43$ have been obtained in 0.15 mol dm^{-3} $NaClO_4$ at 25 °C for M = $\mathrm{Nd^{III}}$ and L = glycine. At 25 °C in 0.5 mol dm^{-3} $Na[NO_3]$, $\log K_1$(bipyridyl) has been determined for the following lanthanoid(III) ions: La, 0.8; Ce, 0.9; Pr, 0.9; Nd, 0.9; Sm, 0.9; Gd, 0.8; Dy, 0.9. Ultraviolet spectroscopy and n.m.r. line-broadening experiments are used to support the potentiometric studies, which indicate that, in addition to the complexes bound through the carboxylate to protonated glycine, ring closure involving bonding to the nitrogen occurs at higher pH.

IN a recent review [1] it was pointed out that lanthanoid(III) ions appear to have a considerable affinity for nitrogen-donor ligands. This was evidenced by the synthesis of complexes containing weakly basic nitrogen-donor chelates [*e.g.* 2,2′-bipyridyl(bipy) or 1,10-phenanthroline] in the solid state, and the study of complexes with strongly basic nitrogen-donor chelates (*e.g.* ethylenediamine or diethylenetriamine) in non-aqueous solvents.[2] No interaction with ligands containing nitrogen-donor atoms only has been observed to date in aqueous solution,[1] although interactions do occur in mixed-donor chelates when the nitrogens are accompanied by oxygen donors, as in quinolin-8-ol or polyaminocarboxylates.

In recent papers [3,4] a model of the chelate effect was used to estimate formation constants for hydrolysis-prone ammonia complexes. Thus $\log K_1(NH_3)$ for $\mathrm{La^{III}}$ was estimated to be 0.7 from the formation constants of its polyaminocarboxylate complexes. This indicates that no strongly basic nitrogen-donor lanthanum(III) complexes (not even the polyamines) can survive hydrolysis in aqueous solution as in equation (1).

$$[\mathrm{La(NH_3)}]^{3+} + \mathrm{H_2O} \rightleftharpoons [\mathrm{La(OH)}]^{2+} + [\mathrm{NH_4}]^{+} \quad (1)$$

pK_W is taken as 14, the pK_a of ammonia as 9.2, and $\log K_1(\mathrm{OH^-})$ is [5] 5.7 for $\mathrm{La^{III}}$. Account must also be taken of $\log K_{so}$, the solubility product of $\mathrm{La[OH]_3}$, which is −21.9.[5] Tanner and Choppin [6] suggested that even in glycinate ($\mathrm{glyO^-}$) complexes of lanthanoid(III) ions the nitrogen donor is not attached, and that only complexes of the type $[\mathrm{Ln(HglyO)}]^{3+}$, bonded through the carboxyl group alone, are formed. In contrast, Cefola *et al.*[7] considered only the chelated complex to be present in their system, with bonding through both nitrogen and oxygen. While the work of Tanner and Choppin [6] demonstrated clearly that no bonding occurred through the nitrogen in the pH limits at which they worked (pH <6), the chelate-effect model [3] can be used to calculate $\log K_1$(gly) 4.6 for $\mathrm{La^{III}}$, from which we would expect formation of the chelate complex only at pH >6. In support of this, Katzin and Gulyas [8] have found from the circular dichroism spectra of gadolinium(III) complexes of optically active amino-acids, such as alanine, that the amino-group co-ordinates at pH >7. Since our estimate of $\log K_1(NH_3)$ for lanthanoid(III) ions has considerable bearing on the reliability of the derived chelate-effect equations,[3] it was thought that a study of lanthanoid(III) complexes with gly at pH >6, a higher value than used in either ref. 6 or 7, would be useful. So that a u.v. spectroscopic study of the system could also be made, the lanthanoid chosen was $\mathrm{Nd^{III}}$, which should be very similar to $\mathrm{La^{III}}$. The hypersensitive transitions $^4I_{\frac{9}{2}}\rightarrow{}^4G_{\frac{5}{2}}$ and $^4I_{\frac{9}{2}}\rightarrow{}^2G_{\frac{7}{2}}$ can be used [9] to follow complex formation in neodymium(III) complexes. In addition, n.m.r. line-broadening experiments were carried out with sarcosine (*N*-methylglycine, sar) and $\mathrm{Gd^{III}}$, in an attempt to detect attachment of the nitrogen atom.

Some estimates of the strength of attachment of weakly basic nitrogen donors to lanthanoid(III) ions can also be made using the chelate-effect equations.[3] While it has been found that the stability of complexes of chelating ligands that contain the pyridyl group are anomalously high [3,10] in terms of these equations, the latter can be empirically modified so as to predict these constants correctly. Instead of using $\log K_1$(pyridine) in these equations, $\log K_1$(pyridyl), defined as in equation (2), is used as a measure of the strength of the pyridyl group in chelating ligands. These $\log K_1$(pyridyl)

$$\log K_1(\text{pyridyl}) = \tfrac{1}{2}[\log K_1(\text{bipy}) + \lambda_N - \log 55.5] \quad (2)$$

values replace the 1.152 $\log K_1(NH_3)$ term used previously.[3] λ_N has the same significance as for strong-base ligands,[3] and is set equal to 0.5. A few representative $\log K_1$ values for chelating ligands containing the pyridyl group, calculated as above, together with the observed values, are shown in Table 1.

In a similar way, $\log K_1(\mathrm{NC_5H_4CO_2^-}) = 3.6$ reported [11] for $\mathrm{La^{III}}$ can be combined with $\log K_1(\mathrm{MeCO_2^-}) = 2.5$ (ref. 12) so as to calculate $\log K_1$(pyridyl) = −0.1, from which $\log K_1$(bipy) = 0.9 can be estimated. In contrast to the strong-base nitrogen-donor ligands, substitution of this value together with pK_a(bipy) = 4.5 into equation (1) indicates that bipy complexes of lanthanoid(III) ions should be resistant to hydrolysis. In order to check this prediction of the existence in

TABLE 1

logK_1 for pyridyl-containing chelating ligands, calculated as described in the text and observed. Abbreviations : terpy = 2,2′ : 6′,2″-terpyridine; $NC_5H_4CH_2O^-$ = the anion of 2-hydroxymethylpyridine; $NC_5H_4CO_2H$ = pyridine-2-carboxylic acid

log K_1		(pyridyl)	bipy	terpy	$NC_5H_4CH_2NH_2$	$NC_5H_4CH_2OH$	$NC_5H_4CH_2O^-$	$NC_5H_4CO_2^-$	$NC_5H_3(CO_2)_2^{2-}$
Cu^{II}	calc.	3.4	8.1	12.2	9.4	3.7	11.3	7.0	10.2
	obs.		8.1	~13	9.5	3.7	11.2	7.8	~10
Ni^{II}	calc.	2.9	7.1	10.7	7.3	3.2	8.2	5.9	8.3
	obs.		7.1	10.7	7.2	2.9	~9	6.8	~7
Pb^{II}	calc.	0.9	3.0	4.6	4.5	1.2	9.6	4.8	8.3
	obs.		3.0					4.6	8.7
Mn^{II}	calc.	0.7	2.6	4.1	2.9	1.0	5.9	3.5	5.9
	obs.		2.6	4.4		~1		3.9	5.0

aqueous solution of a complex of lanthanoid(III) ions with a ligand containing nitrogen-donor atoms only a potentiometric study of the bipy complexes of La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, Gd^{III}, and Dy^{III} was undertaken.

EXPERIMENTAL

Glycine (B.D.H., AnalaR) was recrystallised from water and bipy (E. Merck, Guaranteed) was recrystallised from light petroleum. Pyridine-2-carboxylic acid (Merck) was used for studying the effect of co-ordination to Nd^{III} on the hypersensitive *f–f* transitions, for comparison with the spectra of the glycine complex. Neodymium stock solutions were prepared by dissolving the oxide (Merck, 99.9%) in the appropriate acid. The salts $La[NO_3]_3 \cdot 6H_2O$ (Merck, Guaranteed) and $Ce[NO_3]_3 \cdot 6H_2O$ (Merck, Extra pure) were used for the preparation of stock solutions of these ions. The nitrates of the other lanthanoids were obtained (Guaranteed, 99.9%) from K & K Chemicals, Plainview, New York. The stock solutions of Nd^{III}, La^{III}, and Ce^{III} were standardised by ethylenediaminetetra-acetate (edta) titration, but this was not possible for the other lanthanoids because of the small quantities of the metal salt available, and the high concentration required in the study with bipy.

The potentiometric study was carried out using a glass electrode and the procedure described before.[13] Ultraviolet spectra were recorded on a Beckman Acta MIV spectrophotometer, n.m.r. spectra on Varian A60 and S-60T spectrometers. A stock solution of Gd^{3+} as the nitrate was made up in D_2O, as was a stock solution of sar. The pH values of these solutions were adjusted using Na[OD], and measured with a radiometer pHM 64 pH meter, no corrections being made for the activity of deuterium. Care was taken to avoid saturation effects, and samples were kept for 10 min to attain thermal equilibrium before spectra were recorded.

RESULTS AND DISCUSSION

(*a*) Nd^{III}*–Glycine Potentiometry*.–Figure 1 shows a plot of $\bar{n}$ against log [gly], with the gly : Nd^{III} ratio varying from 12 : 1 to 2 : 1. The solid lines are theoretical curves calculated on the basis of the formation constants obtained. The data were analysed using the computer program MINIQUAD,[14] and the formation constants obtained at 25 ± 0.1 °C in 0.15 mol dm^{-3} $Na[ClO_4]$ are as shown in Table 2.

Using the constants given in Table 2, a species distribution diagram can be calculated (Figure 2). This shows clearly that only at pH >6 is an appreciable quantity of the ML species formed. The important point in Table 2 is logK_1(gly) = 3.26 for Nd^{III}. Using the Davies[15] form of the extended Debye–Hückel equation, we calculate logK_1(gly) = 4.00 at infinite dilution, which is in reasonable agreement with the expected value of 4.6.

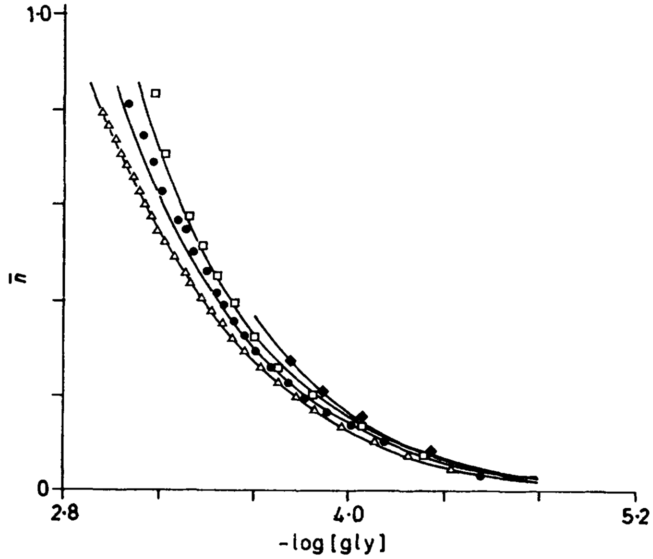

FIGURE 1 Titration curves of the Nd^{III}–glycine system in 0.15 mol dm^{-3} $Na[ClO_4]$, showing $\bar{n}$ (the average number of ligands bound to the metal ion) plotted against −log[gly]. Total Nd^{III} is 0.006 747 mol dm^{-3} for all curves. [gly] : $[Nd^{III}]_T$ = 16.64 (△), 10.42 (●), 6.52 (□), and 5.05 : 1 (◆). The curves are not superimposed because of the formation of ML(OH) species

(*b*) *N.M.R. Line-broadening Experiments*.—It was found that at pH <5.5 the methylene protons are preferentially broadened. This means that in the complex they are closer to the Gd^{III} ion than are the *N*-methyl

TABLE 2

Stability constants for the species $Nd_p(gly)_qH_r$ at 25 °C and I = 0.15 mol dm^{-3} $Na[ClO_4]$. σ = standard deviation in log β, *n* = number of titration points

p	*q*	*r*	log β	*n*	3σ	Ref.
0	1	1	9.533	65	0.006	*a*
0	1	2	11.878	65	0.009	*a*
1	1	1	10.430			*b*
1	1	0	3.26	90	0.09	*a*
1	1	−1 [c]	−4.96	90	0.09	*a*
1	0	−1 [c]	−8.38			5

[a] This work. [b] Determined spectroscopically (see text). [c] A ' minus proton ' is an hydroxide ion.

protons, indicating bonding through the carboxylate only, in agreement with the formation-constant study in ref. 6. At higher pH values the methyl resonances also broaden, until the two resonances are equally broad. This agrees with the results of Katzin *et al.*,[8] that at pH >7 a chelate complex is formed involving bonding to the nitrogen atom as well as the carboxylate group.

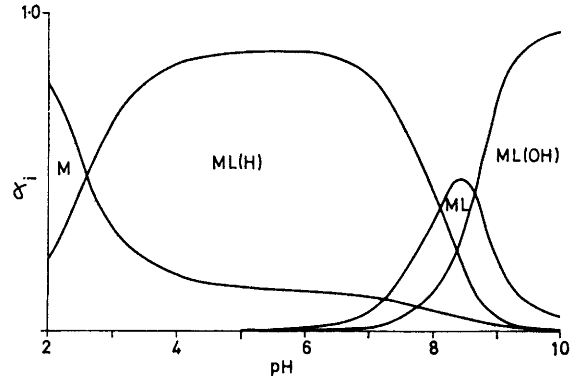

FIGURE 2 Species-distribution diagram for neodymium(III)–glycine complexes in 0.1 mol dm^{-3} glycine, where the concentration of Nd^{III} is much lower than that of glycine. Data calculated using formation constants in Table 2. α_i = fraction of total metal present as species indicated

(*c*) *Ultraviolet Spectroscopy*.—For comparison with the glycine system, the Nd^{III}–$NC_5H_4CO_2^-$ system was also studied, since here Thompson[11] had shown potentiometrically that bonding through the nitrogen occurs. The spectra of this system as a function of pH are seen in Figure 3(*a*). There are two inflection points in a plot of absorbance against pH, one at pH ~1 and another at pH ~ 4.5. These correspond to the formation of the ML$_n$ complexes. Because of the much lower pK_a of $NC_5H_4CO_2^-$ as compared with gly, no region of existence of the ML(H) complexes is observed. The results of this experiment were analysed using the SPEFO facility of the LETAGROP[16] computer program, and logK_n($NC_5H_4CO_2^-$) values obtained as follows in 2 mol dm^{-3} Na[ClO$_4$] at 25 °C: logK_1 = 3.87, logK_2 = 2.96, and logK_3 = 1.75.

The effect of pH on the u.v. spectrum of 0.025 mol dm^{-3} Nd^{3+} in the presence of 0.25 mol dm^{-3} gly is seen in Figure 3(*b*). At pH 1 the spectrum is that of Nd^{3+} alone. As the pH rises, the intensity of the $^4I_{\frac{9}{2}}\rightarrow{}^4G_{\frac{5}{2}}$ and $^4I_{\frac{9}{2}}\rightarrow{}^2G_{\frac{7}{2}}$ transitions increases until at pH ~3.4, when there is little further change until pH ~ 5.5. This must correspond to the complete formation of the ML(H) complex. At pH >5.5 there is another change in the absorption spectrum, corresponding to deprotonation of the nitrogen and chelation. This change is not the same as that which occurs in the absence of gly, so is not due to hydrolysis of the metal ion. The results of the above experiments were subjected to analysis using LETAGROP,[16] and a value of logβ_{MLH} = 0.93 obtained, which is in reasonable agreement with values for other lanthanoid(III) ions.[6]

(*d*) *Potentiometry on* Ln^{III}–bipy *Complexes*.—The pK_a of bipy was determined at 25 °C in 0.5, 1, and 1.5 mol dm^{-3} Na[NO$_3$]. These are as follows, with literature[5] values for comparison (3σ in parentheses):

Na[NO$_3$] Medium:	0.5 mol dm^{-3}	1 mol dm^{-3}	1.5 mol dm^{-3}
pK_a (bipy):	4.575 (0.006)	4.625 (0.009)	4.653 (0.009)
lit.:[5]	4.51	4.67	

Because of the low solubility of bipy (*ca.* 0.03 mol dm^{-3}), the $\bar{n}$ values in these titrations did not rise above 0.15. The values of logK_1(bipy) obtained in 0.5 mol dm^{-3}

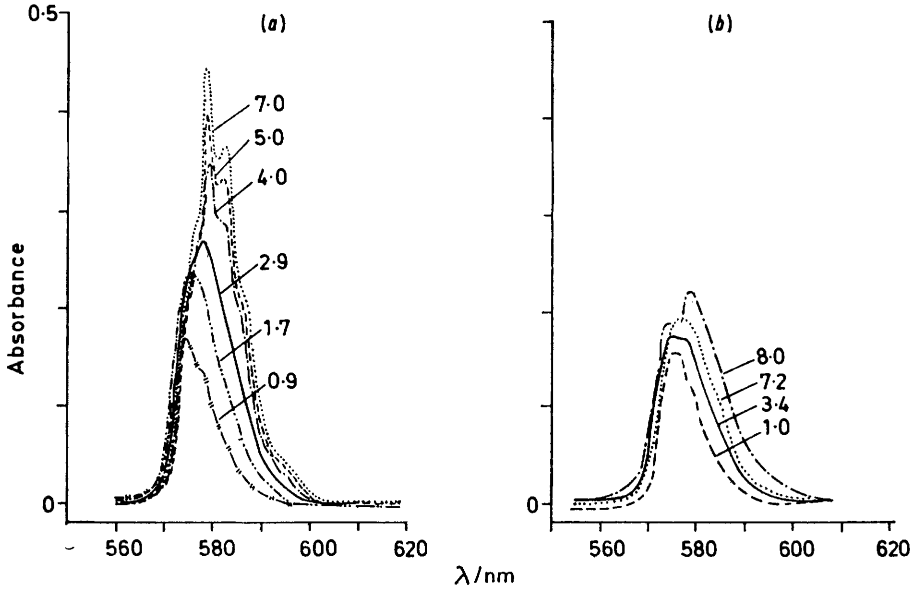

FIGURE 3 Effect of (*a*) pyridine-2-carboxylic acid (0.294 mol dm^{-3}) and (*b*) glycine (0.25 mol dm^{-3}) on the $^4I_{\frac{9}{2}}\rightarrow{}^2G_{\frac{7}{2}},{}^4G_{\frac{5}{2}}$ transitions of Nd[ClO$_4$]$_3$ (0.025 mol dm^{-3}) as a function of pH. The pH for each spectrum is indicated

$Na[NO_3]$ at 25 °C for the lanthanoid(III) ions studied here are as follows ($\sigma = 0.1$).

Ln	La	Ce	Pr	Nd	Sm	Gd	Dy
$\log K_1$ (bipy):	0.8	0.9	0.9	0.9	0.9	0.8	0.9

These values are in reasonable agreement with those expected from the formation constants of the $NC_5H_4CO_2^-$ complexes, *i.e.* about one log unit. $\log K$(bipy) was also determined for La^{III} in 1 mol dm^{-3} $Na[NO_3]$, where it was found to be 0.44. Assuming a linear dependence of $\log K_1$ on ionic strength indicates a value of $\log K_1$(bipy) of 1.16 for La^{III} at infinite dilution. The unusual inverse dependence of $\log K$ on ionic strength for a neutral ligand suggests that nitrate is also complexed to the Ln^{III} ion, competing directly with bipy for co-ordination sites, or forming mixed complexes in which the bipy is less strongly held than in the pure bipy complex.

The experimental results in this paper agree reasonably well with the predictions made on the basis of our model of the chelate effect. However, the value of $\log K_1$(gly) for Nd^{III} is somewhat lower than might have been expected. As will be discussed in a future paper, this relates to the significance of the λ term in equations such as (2). Calculations using an empirical force field have shown that the significance of this term is essentially steric for complexes of polydentate ligands. This means that its estimation will have to be reconsidered in steric terms rather than in the way in which it has been estimated previously.[3,4]

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