

Fig. 5.—The formation curve for the diethylenimine mercuric ion: O, in 0.1*N* AzH<sup>+</sup> and 1*N* NaNO<sub>3</sub> at 15°; ⊙, in 0.3*N* AzH<sup>+</sup> and 1*N* NaNO<sub>3</sub> at 15°; ●, in 1*N* NaNO<sub>3</sub> and variable (AzH<sup>+</sup>), without addition of free Az.

ion. From comparison with the linear free energy plots of Bruehlman and Verhoek<sup>11</sup> ethylenimine appears to complex more strongly than expected for a secondary amine of comparable ionization constant. The spreading factor  $\alpha$  for complexes with silver ion is also low, being comparable to that found for primary amines rather than secondary amines.<sup>11</sup> Thus, all of the available data indicate that the nitrogen of aziridine is little affected in its chemistry by the steric properties of the balance of the three-membered ring.

(4) The ethylenimine ring is quite stable when bonded to a metal in a solid complex. Complexes were stored in a closed container for several months without appreciable change in color and properties.

(11) R. J. Bruehlman and F. H. Verhoek, *THIS JOURNAL*, **70**, 1401 (1948).

TABLE IV<sup>a</sup>  
COORDINATION NUMBERS OF AMINE COMPLEXES

	MeNH <sub>2</sub>	Et-NH <sub>2</sub>	Az
NiI <sub>2</sub>	6	6	6
NiBr <sub>2</sub>	6	4-6	6
NiCl <sub>2</sub>	6	4	4
MnI <sub>2</sub>	6	4 <sup>b</sup>	5
MnCl <sub>2</sub>	6	4	4

<sup>a</sup> The cobalt salts behave similarly; Copper had in all cases the coordination number four. <sup>b</sup> 6 at *T* well below 0°.

Only those with higher vapor pressure (as the chlorides) were gradually losing ethylenimine but apparently without opening of the ring. The presence of metal ions in the Az-solution did not appear to cause a significantly more rapid ring opening.

(5) The strength of the metal-to-nitrogen bond was found in all cases to be lower than that of the corresponding ammonia-complexes. It is not surprising that Az forms weaker complexes, in view of its lower basicity to protons than ammonia. The formation curves have the same shape as those reported by Bjerrum for the ammonia-complexes, to which they are approximately parallel. In the case of mercury, the curve is here much flatter, showing a higher relative stability of the mono-complex; the reason for this is not presently known.

It must be pointed out that all the investigated complexes were formed with metal ions belonging to the "rapid replacement" class. The results of the work on metals whose coordination spheres are "inert" to replacement, namely Cr(III) and Co(III), will be reported in a future publication.

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## Stability Relationships Among the Rare Earth Dipicolinates

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Step-wise stoichiometric formation constants have been determined for the complexes between copper, yttrium, the rare earths and the dipicolinate ion. The measurements have been made in an aqueous perchlorate medium of the ionic strength  $\mu = 0.5 M$  at a temperature of 20°.

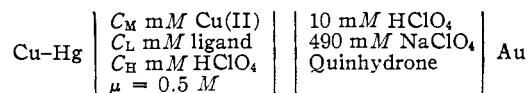
### Introduction

Complex formation between various metal ions and the dipicolinate ion has been studied earlier.<sup>2,3</sup> These measurements now have been extended to include the rare earths and yttrium. It was impossible to use the familiar *pH* method for the determination of the formation constants, because of the low basicity of the dipicolinate ion and because of its very high affinity for the metal ions being studied.

The copper-dipicolinate system was determined by e.m.f. measurements of the concentration of free

central ion, [Cu<sup>+2</sup>], in the solutions of complexes, by means of a copper amalgam electrode. When the complexity of this system was known, that of the others could be determined by a competition method.<sup>4</sup>

**Calculation of Complexity Constants from Measurements of [Cu<sup>+2</sup>] = [M] with the Copper Amalgam Electrode. 1. Cu<sup>+2</sup>-dipic<sup>-2</sup>.**—Experimentally, the e.m.f., *E*, of cells of the following type was measured



(1) Department of Chemistry, University of Lund, Lund, Sweden.

(2) R. M. Tichane and W. E. Bennet, *THIS JOURNAL*, **79**, 1293 (1957).

(3) G. Anderegg, *Helv. Chim. Acta*, **43**, 414 (1960).

(4) I. Leden, *Acta Chem. Scand.*, **6**, 971 (1952).

$C_M$  and  $C_L$  denote the total concentration of metal ion and ligand. The e.m.f. of the above cell can be written as

$$E = E_k - \frac{RT}{2F} \ln [M]$$

where  $E_k$  is a constant. If the e.m.f. for the special case of  $C_L = 0$ ,  $[M] = C_M$  is denoted by  $E'$ , we obtain

$$E - E' = E_M = \frac{RT}{2F} \ln \frac{C_M}{[M]} \quad (1)$$

From the quantity  $C_M/[M]$  the cumulative stability constants  $\beta_i$  can be calculated by the method of Leden<sup>5,6</sup> as developed by Fronaeus.<sup>7</sup>

If only mono-nuclear and non-acid complexes are formed then

$$\frac{C_M}{[M]} = 1 + \sum_{n=1}^N \beta_n [L]^n = X([L]) \quad (2)$$

where  $[L]$  is the concentration of free (uncomplexed) ligand and  $X([L])$  is an abbreviation of the polynomial  $1 + \sum_{n=1}^N \beta_n [L]^n$  in  $[L]$ . Corresponding values of  $X$  and  $[L]$ , usually found by a method of extrapolation, make it possible to evaluate the constants  $\beta_n$ . The extrapolation method involves a determination of  $E_M$  as a function of  $C_L$  at several different values of  $C_M$ . Using these data, it is possible to plot  $C_L$  as a function of  $C_M$  using different  $E_M$  values as parameters. If only mono-nuclear and non-acidic complexes are present, these curves are of the form:  $C_L = [L] + \bar{n}C_M$ ; *i.e.*, straight lines with the slope given by the average number of complexed ligands,  $\bar{n}$ . By extrapolation to  $C_M = 0$ , the concentration of free ligand  $[L]$  is obtained.

Due to the very strong complexity all intercepts are in this case zero for  $C_L < 2C_M$ . If corresponding values of  $[L]$  and  $X$  are chosen within a range where  $[L]$  can be determined, in this case for  $C_L > 2C_M$ , it is possible to find corresponding values of  $X$  and  $[L]$  in any other region by integration of the differential equation

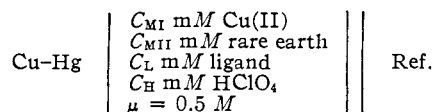
$$\bar{n} = \frac{d \log X}{d \log [L]} \quad (3)$$

The integration gives the result

$$\log \frac{[L]_a}{[L]_s} = \int_{X([L]_s)}^{X([L]_a)} \frac{1}{\bar{n}} d \log X \quad (4)$$

This integration is made graphically by plotting  $1/\bar{n}$  against  $\log X$ .<sup>8</sup>

2. Rare earths-dipic<sup>-2</sup>.—Experimentally the e.m.f. of cells of the following type was measured:



(5) I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

(6) I. Leden, *Potentiometrisk undersökning av några kadmium-salters komplexitet* (Diss.), University of Lund, Sweden, 1943.

(7) S. Fronaeus, *Komplex system hos koppar* (Diss.), University of Lund, Sweden, 1948.

(8) For further details see S. Ahrlund, J. Chatt, W. R. Davies and A. A. Williams, *J. Chem. Soc.*, 264, 276 (1958).

Ref. is the same quinhydrone reference cell as before and the e.m.f. is also here given by the expression (1).

In a system of known complexity  $X$  is a known function of  $[L]$ , and in such a case the concentration of free ligand  $[L]$  can always be calculated from a potentiometric determination of  $[M]$ , provided the total concentration of metal ion,  $C_M$ , is known. The experimental method used here is based on the competition between Cu(II) and another metal ion for the given ligand. Using the known complexity of the copper system, it is possible to calculate  $[L]$  even in the presence of the competing metal ion. This is done as before by a graphical integration when the values of  $\log X$  have been experimentally determined.

The total concentration of ligand  $C_L$  is given by the expression

$$C_L = [L] + \bar{n}_{MI} C_{MI} + \bar{n}_{MII} C_{MII} \quad (5)$$

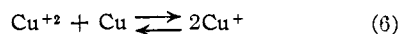
In this equation all quantities except  $\bar{n}_{MII}$  are known. Corresponding values of  $\bar{n}_{MII}$ , from eq. (5), and  $[L]$  have thus been obtained and the formation constants for the unknown system can easily be obtained, either by solving the simultaneous equations of Block and McIntyre<sup>9</sup> or by the method of Fronaeus.

### Experimental

**Chemical.**—All chemicals used were of analytical grade. Stock solutions of the rare earths and yttrium (Lindsay Light and Chemical Company) were prepared and analyzed as before.<sup>10</sup> A stock solution of copper perchlorate was prepared by dissolving the salt (G. Frederick Smith Co.) in water. The copper concentration was determined electrolytically.

A 2% liquid copper amalgam was prepared by electrolysis of an acid copper sulfate solution using mercury (Eastern Smelting and Refining Company, triple distilled) as a cathode. Dipicolinic acid (Aldrich Chemical Company) was purified by recrystallization from water. The purity was checked by an equivalent-weight determination, the agreement between the experimental and theoretical values were within 0.2%. A stock solution of the di-sodium salt was prepared by neutralization of the free acid with NaOH.

**The Potentiometric Measurements.**—The behavior of the copper amalgam electrode has earlier been investigated by several authors.<sup>7</sup> When a solution containing Cu(II) is in contact with metallic copper the disproportionation equilibrium (6) is established.



with the equilibrium constant<sup>7</sup>  $K = \sqrt{[\text{Cu}^{+2}]/[\text{Cu}^+]}$  =  $10^3$ . The quotient  $\text{Cu}^{+2}/\text{Cu}^+$  is concentration dependent and decreases with increasing  $\text{Cu}^{+2}$  concentration. From the value of the equilibrium constant it is seen that the cuprous concentration is negligible for  $C_M > 5mM$  in non-complex solutions. This is not necessarily the case in the complexed solutions. Light absorption measurements by Anderegg<sup>3</sup> on Cu(II)-dipic<sup>-2</sup> solutions which had been standing in the presence of copper amalgam showed no presence of Cu(I). It can thus be concluded that no reduction of Cu(II) takes place and, consequently, that no corrections have to be applied to the total concentration copper,  $C_M$ .

The main measurements were carried out as titrations in the following way: A solution S, of known  $C_M$ ,  $C_H \approx 1 mM$  and with  $C_L = 0$  was prepared in the amalgam half-cell. To this solution successive amounts of the titrant T, were added. The e.m.f. of the cell was read after each addition of T. The readings were repeated until a constant value of the e.m.f. was obtained.

(9) B. P. Block and G. H. McIntyre, *THIS JOURNAL*, **75**, 5667 (1953).

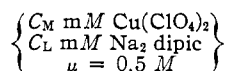
(10) I. Grenthe and W. C. Fernelius, *ibid.*, **82**, 6258 (1960).

TABLE I  
 EXPERIMENTAL RESULTS FOR THE  $\text{Cu}^{+2}$ -DIPIC $^{-2}$  SYSTEM

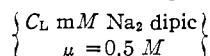
$C_L, mM$	$\log X$	$1/\bar{n}$	$\int \frac{1}{\bar{n}} d \log X$	$[L] M$	$\frac{X-1}{[L]} = X_1, M^{-1}$	$\frac{X_1 - \beta_1}{[L]}, M^{-2}$
2.88	0.062	5.18				
4.91	.155	3.05	7.31	$2.79 \times 10^{-10}$	$1.54 \times 10^9$	
6.82	.272	2.19	7.00	5.68	1.53	
8.63	.378	1.73	6.793	9.07	1.53	
10.34	.509	1.45	6.576	$1.49 \times 10^{-9}$	1.50	
11.97	.650	1.25	6.386	2.32	1.50	
13.52	.812	1.11	6.196	3.59	1.53	
15.48	1.032	0.966	5.967	6.07	1.61	
17.31	1.290	.864	5.732	$1.04 \times 10^{-8}$	1.78	
19.44	1.579	.769	5.496	1.80	2.05	$2.89 \times 10^{16}$
21.43	1.909	.698	5.255	3.13	2.56	3.32
23.28	2.232	.634	5.040	5.12	3.32	3.52
25.00	2.580	.598	4.823	8.47	4.51	3.53
26.61	3.040	.562	4.550	$1.56 \times 10^{-7}$	7.05	3.54
28.13	3.783	.531	4.153	3.96	15.3	3.48
29.55	6.53	.506	2.760	$9.79 \times 10^{-6}$	$3.47 \times 10^{11}$	3.52
30.88	10.55	.500	0.750	$1.00 \times 10^{-2}$	$3.55 \times 10^{13}$	3.55
32.14	11.26	.500	0.395	2.27	8.02	3.53
33.33	11.62	.500				
34.46	11.86	.500				
35.53	12.05 <sup>a</sup>	.500		5.63 <sup>a</sup>	19.9	
36.54	12.21	.500				

<sup>a</sup> Denotes upper integration limit.

In the  $\text{Cu(II)}$ -dipic $^{-2}$  titrations the titrant had the composition



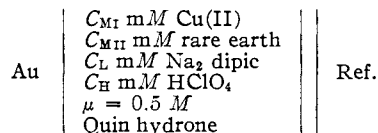
in the rare-earth titrations, the composition was



Titration were made at four different metal-ion concentrations  $C_M = 5, 7.5, 10$  and  $15 \text{ mM}$  in the  $\text{Cu(II)}$  titrations. In the rare earth titrations both  $C_{M\text{I}}$  and  $C_{M\text{II}}$  varied during the titrations. Titrations at two different initial concentrations of rare earth,  $C_{M\text{II}}$  and  $2C_{M\text{II}}$  were made for  $\text{Nd}^{+3}$ ,  $\text{Tb}^{+3}$  and  $\text{Yb}^{+3}$ .

Solutions of the different rare earths and dipicolinic acid gave crystalline precipitates after a few hours standing. A few of these were analyzed and were found to have the composition  $\text{H}_3\text{O} [\text{R}(\text{dipic})_2]$ : e.g.,  $\text{H}_3\text{O} [\text{Ce}(\text{dipic})_2]$  gave  $C = 34.47\%$ ,  $H = 1.80\%$  compared with the theoretical value  $C = 34.36\%$  and  $H = 1.85\%$ . The compounds are high-melting (m.p.  $> 370^\circ$ ) and are probably acid complexes.

$\rho\text{H}$ -Titrations using the cells



were made in the  $\rho\text{H}$ -region of the earlier titrations in order to check the possible occurrence of acid complexes in solution at these  $\rho\text{H}$  values.

The accuracy of the e.m.f. measurements is  $\pm 0.3 \text{ mv.}$  when  $C_L < 2C_M$  and a little bigger,  $\pm 0.6 \text{ mv.}$ , when  $C_L > 2C_M$ .

### Results

A summary of the experimental results for the  $\text{Cu}^{+2}$ -dipic $^{-2}$  system is given in Table I. The complexity constants have been calculated using the method of Fronaeus.<sup>7,8</sup> As the known upper integration limit values of  $\log X = 12.05$  and  $[L] = 5.63 \text{ mM}$  were used. The values of  $\beta_1 = (1.53 \pm 0.02) \times 10^9$  and  $\beta_2 = (3.52 \pm 0.04) \times 10^{16}$  so obtained are in good agreement with Anderegg's

data at the ionic strength  $\mu = 0.1 M$ . Because of the strong complexity  $\beta_2$  can be calculated directly in the region where  $C_L > 2C_M$ . In this region  $C_M = [\text{Cu}(\text{dipic})_2]$  and  $[L] = C_L - 2C_M$ . The  $\beta_2$  value obtained in this way is the same as the value obtained by the first method.

**The Rare Earth and Yttrium-Dipic $^{-2}$  Systems.**—The experimental results and calculations for one of the titrations, the  $\text{Nd}^{+3}$ -dipic $^{-2}$  titration, are given in Table II. From corresponding values of  $\bar{n}_{M\text{II}}$  and  $[L]$  the formation constants were obtained by solving simultaneous equations according to Block and McIntyre.<sup>9</sup>

 TABLE II  
 EXPERIMENTAL RESULTS FOR THE  $\text{Nd}^{+3}$ -DIPIC $^{-2}$  SYSTEM

Ligand, ml.	$C_L, mM$	$E_M, \text{mv.}$	$\bar{n}_{\text{Cu}^{+2}}$	$\bar{n}_{\text{Nd}^{+3}}$	$[L] M$
0.00		0.0			
1.50	12.00	14.1	0.671	0.441	$1.35 \times 10^{-9}$
1.75	13.73	17.4	.762	.543	1.91
2.00	15.38	21.4	.860	.635	2.77
2.25	16.98	25.9	.952	.735	4.02
2.50	18.52	31.2	1.063	.810	6.66
3.00	21.43	44.0	1.269	.980	$1.60 \times 10^{-8}$
3.50	24.14	58.9	1.490	1.131	3.75
4.00	26.67	76.4	1.681	1.321	9.02
4.50	29.03	97.9	1.834	1.561	$2.37 \times 10^{-7}$
4.75	30.16	110.5	1.894	1.707	4.05
5.00	31.25	125.8	1.942	1.865	7.53
5.25	32.31	144.5	1.972	2.048	$1.70 \times 10^{-6}$
5.50	33.33	164.5	2.00	2.230	3.59
5.75	34.33	183.4	2.00	2.449	7.69
6.00	35.29	204.2	2.00	2.672	$1.72 \times 10^{-5}$
6.25	36.23	233.9	2.00	2.888	5.57
6.50	37.14	290.9	2.00	2.992	$5.31 \times 10^{-4}$
6.75	38.03	319.4	2.00		$1.64 \times 10^{-3}$

All the experimental results are summarized in Table IV where the logarithms of the consecutive

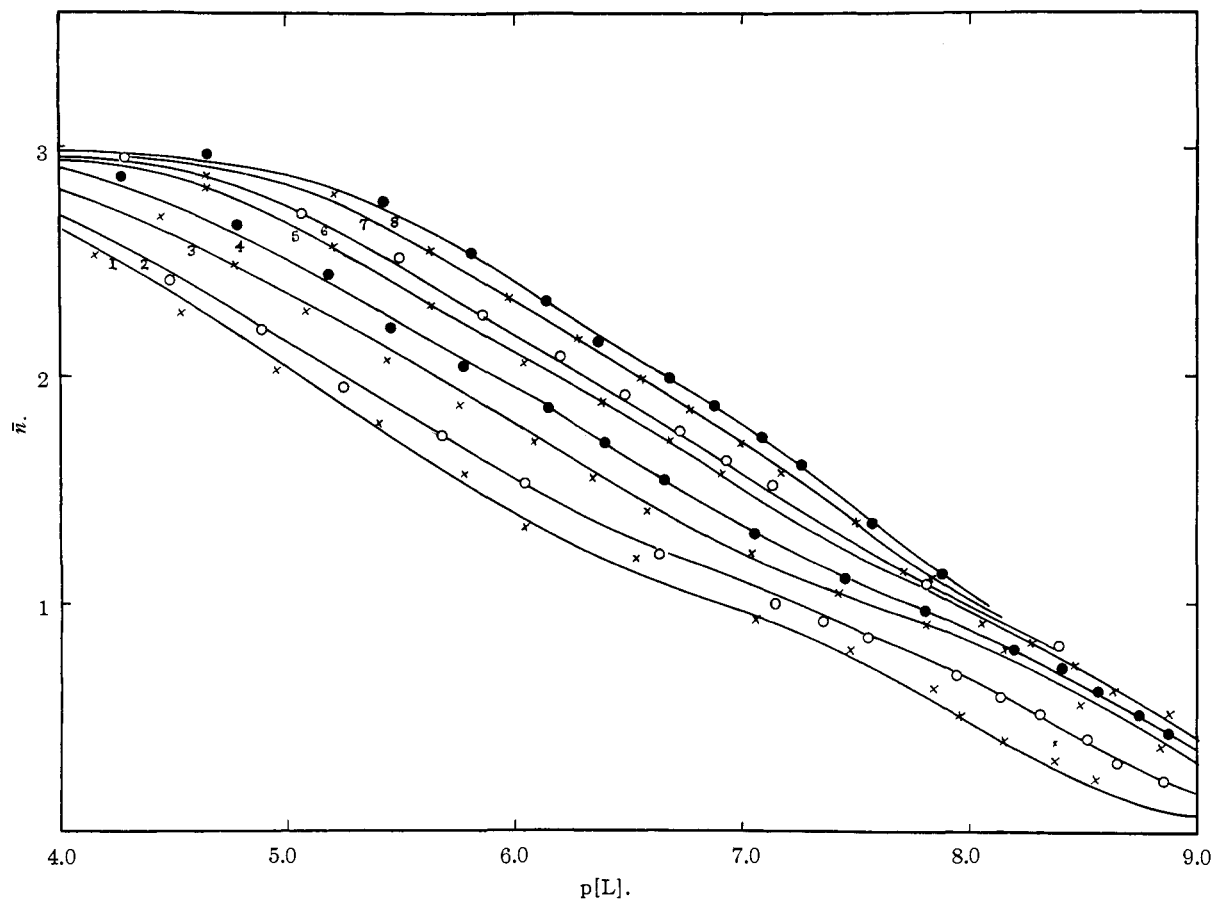


Fig. 1.— $\bar{n} = f(p[L])$  for the rare earths from  $\text{La}^{+3}$  to  $\text{Tb}^{+3}$ . The experimentally determined points are marked according to the scheme in the figure; the full-drawn curves are the formation function calculated from the constants: curve 1 (x)  $\text{La}^{+3}$ ; curve 2 (o)  $\text{Ce}^{+3}$ ; curve 3 (x)  $\text{Pr}^{+3}$ ; curve 4 (●)  $\text{Nd}^{+3}$ ; curve 5 (x)  $\text{Sm}^{+3}$ ; curve 6 (o)  $\text{Eu}^{+3}$ ; curve 7 (x)  $\text{Gd}^{+3}$ ; curve 8 (●)  $\text{Tb}^{+3}$ .

formation constants,  $\log K_i$ , and the logarithm of the total complexity,  $\log \beta_3$ , for the different metal ions are given. The error limits are the maximum deviations from the mean values of the different constants obtained by solving simultaneous equations for several different sets of  $\bar{n}_{\text{MII}} - [L]$  values.

The complex formation functions  $\bar{n} = f(p[L])$ , where  $p[L] = -\log[L]$ , for most of the systems investigated are given in Figs. 1 and 2. In the first figure the experimentally determined values of  $\bar{n}_{\text{MII}} - p[L]$  have been included. In the second figure these data are only given for ytterbium.

The full-drawn curves in both the figures are the formation curves calculated from the constants in Table IV. The agreement between the experimentally determined points and the full-drawn curves is as good for the systems, for which these data have not been included in the figures, as for the ones where they have.

A possible occurrence of polynuclear complexes was checked by making the titrations for  $\text{Nd}^{+3}$ ,  $\text{Tb}^{+3}$  and  $\text{Yb}^{+3}$  at two different metal-ion concentrations. The experimental results for  $\text{Yb}^{+3}$  at the two different concentrations  $C_{\text{MII}} = 9.14 \text{ mM}$  and  $C_{\text{MII}} = 16.75 \text{ mM}$  are given in Fig. 2. It is obvious that  $\bar{n} = f(p[L])$  is not a function of  $C_{\text{MII}}$  at these metal-ion concentrations and that consequently no measurable amount of polynuclear

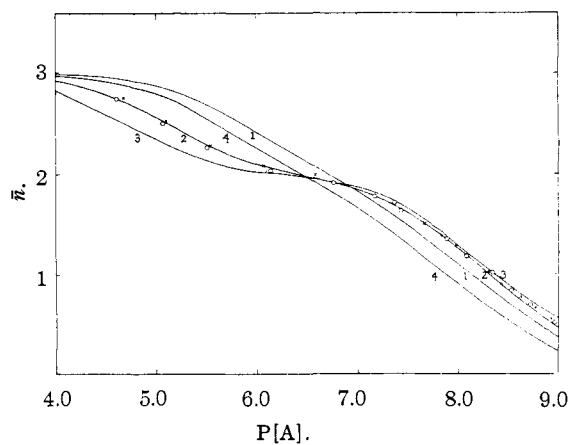


Fig. 2.— $\bar{n} = f(p[L])$  for  $\text{Ho}^{+3}$ ,  $\text{Yb}^{+3}$ ,  $\text{Lu}^{+3}$  and  $\text{Y}^{+3}$ . The experimentally determined points for  $\text{Yb}^{+3}$  at two different metal ion concentrations  $C_{\text{MII}} = 9.14 \text{ mM}$  (x) and  $C_{\text{MII}} = 16.75 \text{ mM}$  (o) have been included. Curve 1,  $\text{Ho}^{+3}$ ; curve 2, ( $C_{\text{MII}} = 9.14$ , x,  $C_{\text{MII}} = 16.75$ , o)  $\text{Yb}^{+3}$ ; curve 3,  $\text{Lu}^{+3}$ ; curve 4,  $\text{Y}^{+3}$ .

complexes is present. The same behavior was shown both by  $\text{Nd}^{+3}$  and  $\text{Tb}^{+3}$  and it is reasonable to suppose that the same is the case for the other rare earths.

TABLE III

LIGAND TITRATIONS OF Tb<sup>+3</sup>-DIPIC<sup>-2</sup>  
The initial volume of the solution S is 11 ml.;  $v$  is the amount of titrant added

Ligand, ml.	Ct, mM	E, mv.	[H <sup>+</sup> ], mM	[H <sup>+</sup> ], (11 + v), mM	[H <sup>+</sup> ], (11 + v), corr. mM
0.00	0.00	54.5	1.16	1.28	1.28
1.25	10.20	60.5	0.912	1.12	1.28
1.50	12.00	61.5	.876	1.10	1.29
1.75	13.73	62.5	.842	1.07	1.28
2.00	15.38	63.9	.797	1.04	1.28
2.25	16.98	65.1	.773	1.02	1.29
3.00	21.43	69.1	.649	0.909	1.27
3.25	22.81	70.5	.614	.875	1.27
3.50	24.14	72.0	.578	.838	1.26
4.00	26.67	75.0	.514	.771	1.25
4.50	29.03	78.1	.454	.704	1.24
4.75	30.16	79.7	.427	.673	1.24
5.00	31.25	81.3	.400	.640	1.24
5.25	32.31	83.9	.361	.587	1.22
5.50	33.33	86.0	.332	.548	1.21
5.75	34.33	90.0	.284	.476	1.17
6.00	35.24	104.0	.163	.277	1.00
6.25	36.23	170.9	.115	.198	0.95

The experimental results of a ligand titration are given in Table III. Because of the presence of a slight excess of sodium hydroxide ( $\sim 0.3$  mM) in the titrant, the hydrogen ion concentration in column 5 must be corrected for the amount neutralized by this excess base. This has been done in column 6 and the very good constancy of this corrected hydrogen-ion concentration shows that no appreciable amount of acid complexes is formed at these pH values. This is certainly not the case at lower pH values as is indicated by the precipitates mentioned before.

#### Discussion

The logarithm of the first constant,  $\log K_1$ , shows the same deviations from the expected increase in stability with increasing atomic number as found before.<sup>10</sup> The logarithm of the second constant increases through the entire series, though the mean differences in  $\log K_2$  between consecutive elements are smaller for the elements after gadolinium. The logarithm of the third constant increases to terbium, is constant for terbium, dysprosium and then decreases. The total effect of this behavior is a maximum for the total complexity

TABLE IV

THE LOGARITHMS OF THE FORMATION CONSTANTS  $K_1$ , AND  $\beta_3$  WITH MAXIMUM RANDOM ERRORS INDICATED

Metal ion	$\log K_1$	$\log K_2$	$\log K_3$	$\log \beta_3$
Cu <sup>+2</sup>	9.14 ± 0.01	7.37 ± 0.02		
La <sup>+3</sup>	7.98 ± .01	5.81 ± .04	4.27 ± 0.02	18.06
Ce <sup>+3</sup>	8.34 ± .02	6.08 ± .03	4.38 ± .02	18.80
Pr <sup>+3</sup>	8.63 ± .02	6.47 ± .01	4.84 ± .02	19.94
Nd <sup>+3</sup>	8.78 ± .02	6.72 ± .02	5.06 ± .03	20.56
Sm <sup>+3</sup>	8.86 ± .03	7.02 ± .01	5.35 ± .01	21.23
Eu <sup>+3</sup>	8.84 ± .01	7.14 ± .02	5.51 ± .02	21.49
Gd <sup>+3</sup>	8.74 ± .01	7.32 ± .03	5.77 ± .03	21.83
Tb <sup>+3</sup>	8.68 ± .03	7.43 ± .04	5.92 ± .03	22.03
Dy <sup>+3</sup>	8.69 ± .02	7.49 ± .02	5.95 ± .01	22.13
Ho <sup>+3</sup>	8.72 ± .02	7.51 ± .01	5.85 ± .01	22.08
Er <sup>+3</sup>	8.77 ± .01	7.62 ± .04	5.74 ± .01	22.13
Tm <sup>+3</sup>	8.83 ± .03	7.71 ± .02	5.50 ± .02	22.04
Yb <sup>+3</sup>	8.85 ± .04	7.76 ± .03	5.12 ± .01	21.73
Lu <sup>+2</sup>	9.03 ± .06	7.77 ± .06	4.68 ± .02	21.48
Y <sup>+3</sup>	8.46 ± .01	7.27 ± .02	5.61 ± .02	21.34

in the same region as is seen from the  $\log \beta_3$  values in the last column of Table IV.

The decrease in  $\log K_3$  probably arises because the progressively smaller radii of the rare earths impose increasing steric hindrance by the interaction between the ions and the ligands. This effect should be most pronounced on the addition of the third ligand because of the presence of two bulky groups. Steric effects have been noted before.<sup>11</sup> As has been pointed out by Betts and Dahlinger,<sup>12</sup> a steric effect probably causes a change in the number of coordinated carboxyl groups in the EDT-EDTA complexes of the rare earths, one carboxyl group less is coordinated after gadolinium.

If the irregularities in  $\log K_1$  were caused by a steric factor, this would be present and even more pronounced on the addition of the second ligand, thus causing variations in  $\log K_2$  similar to but stronger than the variations in  $\log K_1$ . As is seen from Table IV this is not the case, a confirmation of views given previously.<sup>10</sup>

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