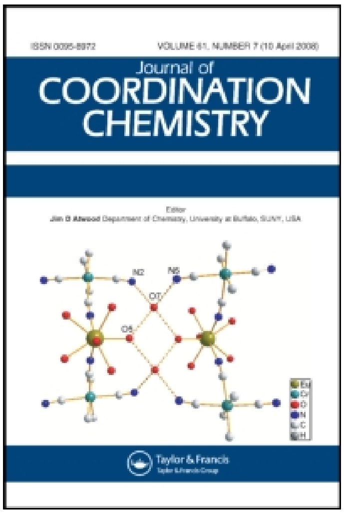

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HYPERSENSITIVITY IN COMPLEXES OF Nd(III) AND Ho(III) WITH DIBASIC AND POLYBASIC LIGANDS

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The hypersensitive transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}{}'\,{}^2G_{7/2}$ in Nd(III) and $^5I_8 \rightarrow {}^5G_6{}'\,{}^5F_1$ in Ho(III) have been studied for lanthanide complexes in aqueous solution with dibasic and polybasic ligands as well as for some mixed ligand complexes. For the dibasic ligands, a linear relation is observed between the oscillator strength of the hypersensitive transition and the sum of the ligand pK$_a$ values. With ligands which contain both N and O coordination sites, the correlation holds when only the basicity of the O sites is considered.

INTRODUCTION

While most $f \rightarrow f$ spectral transitions in lanthanide ions are quite insensitive to the environment about the ion, certain transitions are significantly affected.[1] These 'hypersensitive' transitions are the object of continuing study inasmuch as the source of this hypersensitivity is still not understood. In previous papers from this laboratory we have considered the possible roles of environmental symmetry, metal–ligand covalent bonding and vibronically induced mechanisms.[2–4] We have also reported the observation of a correlation between the acid constant (pK$_a$) of a wide variety of monobasic ligands and the oscillator strength (P) of hypersensitive transitions for 1:1 and 1:2 metal–ligand complexes in aqueous solution.[5] The hypersensitive transitions studied were the $^4I_{9/2} \rightarrow {}^4G_{5/2}{}',\ {}^2G_{7/2}$ in Nd(III) and the $^5I_8 \rightarrow {}^5G_6{}',\ {}^5F_1$ in Ho(III). The existence of such a correlation for monodentate ligands such as F^- as well as chelating ligands such as acetylacetonate would seem to indicate that differences in symmetry are less important than the variation in metal–ligand bond covalency (even though the latter is assumed to be small in lanthanide complexes).

We have extended our study of the effect of complexation on lanthanide hypersensitivity to dibasic and polybasic ligands. The immediate goal was to investigate the generality of the relationship between ligand pK$_a$ and the oscillator strength of the hypersensitive spectral transitions. If this correlation helps to establish the explanation of hypersensitivity, these spectral effects could be important probes in the study of certain aspects of the complexes of the lanthanide ions.

EXPERIMENTAL

The equipment and procedures are identical to those previously described.[5] All reagents were standard analytical grade and, unless otherwise noted, were used as received. The ligands were treated as follows: dipicolinic acid, the aqueous solution was neutralized and recrystallized from water; malonic acid, the aqueous solution was decolorized with activated charcoal; maleic acid was obtained by hydrolysis of maleic anhydride; methyl succinic acid was recrystallized from chloroform; iminodiacetic acid (IMDA), the disodium salt was recrystallized from water/ethanol solution. Stock solutions were prepared either gravimetrically or by standard acid-base titration.

PROCEDURE AND RESULTS

The solution concentrations of various metal–ligand complexes were calculated as described in the previous paper[5] using the material balance equation for the total metal (M_t) and total ligand (L_t), solution pH, the metal–ligand stability constants and the acid protonation constants. Since polybasic acids were studied, multiple acid pK$_a$ values had to be taken into account. The equation for the free ligand concentration, L, previously given must be modified by

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substituting β_a for K_a. The equation becomes:

$$\begin{aligned} b\beta_3 L^4 &+ [b\beta_2 + \beta_a\beta_3(3M_T - L_T)]L^3 \\ &+ [b\beta_1 + \beta_a\beta_2(2M_T - L_T)]L^2 \\ &+ [b + \beta_a\beta_1 [M_T - L_T)]L - \beta_a L_T = 0 \end{aligned} \quad (1)$$

where M_T and L_T are the total metal and total ligand concentrations respectively, β_1, β_2, and β_3 are the complexation stability constants, and β_a is the product of the successive ligand proton dissociation constants (i.e. πK_{A_i}). b has a value given by:

$$b = \sum_{n=0}^{p} H^n \beta_{a_{(p-n)}} \quad (2)$$

H is the hydrogen ion concentration and p is the maximum number of protons ionized from the ligand acid; $H^\circ = \beta_{a_0} = 1$. Solving for the free ligand concentration is Eq. (1) and substituting the results into the appropriate stability constant expression, one obtains the concentration for each solution complex. The experimental and calculated oscillator strengths were determined as described in our previous paper using the equation

$$P_{\exp} = \sum_{i=0}^{2} f_i P_{ML_i} \quad (3)$$

where f_i is the calculated mole fraction of the ML_i complex.

The experimental technique consisted of titrating an aqueous metal solution with a buffered ligand solution. Spectroscopic and pH measurements were then made at every titrant point. Figure 1 is a comparison of the spectrum of Nd(III)$_{(aq)}$ and that of Nd(HEDTA)$_{(aq)}$ complex. An example of the experimental data, in this case for Nd(III)-methylsuccinate, is given in Table I; the complete data is available in reference 6. The calculated oscillator strengths for the various complexes studied are tabulated in Tables II and III.

The 1:1 complexes of DTPA, EDTA and DCTA were studied by titrating a 1:1 stoichiometric solution of metal and ligand with standard base. Because of the high stability constants of these complexes, it was assumed that complexation was complete at all pH values studied. In order to eliminate the possi-

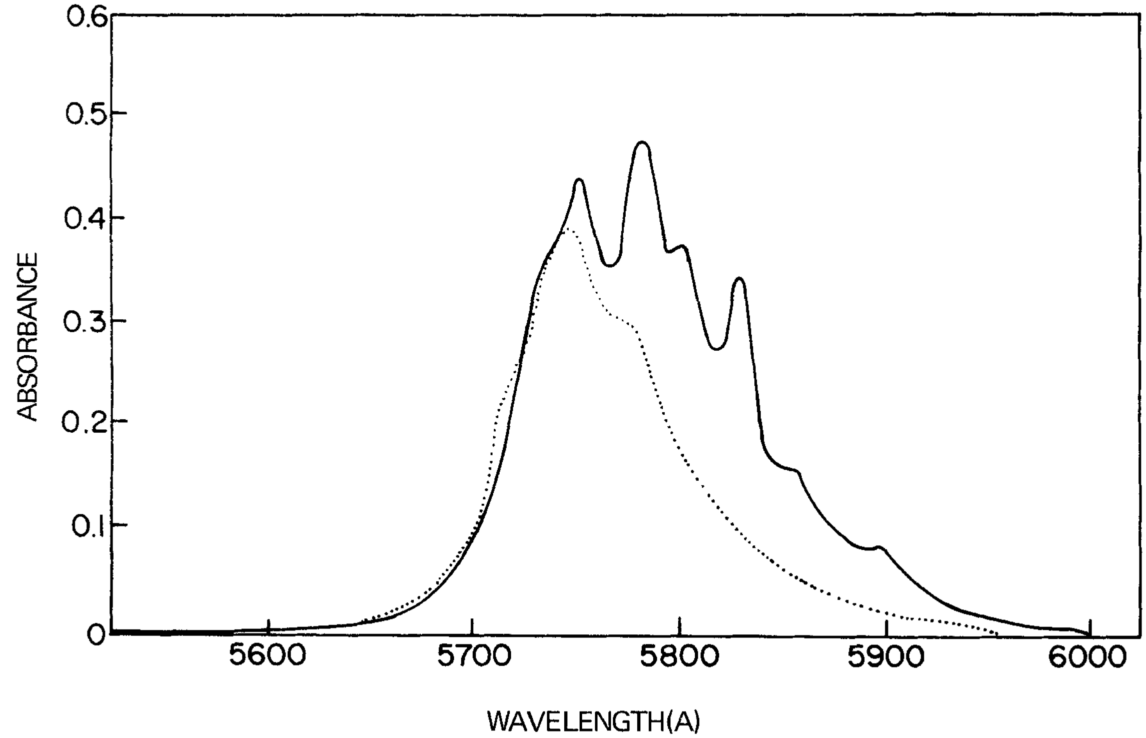

FIGURE 1 Absorption curves for the hypersensitive transition in Nd(III) $^4I_{9/2} \to {}^4G_{5/2}$, $^2G_{7/2}$; Nd$^{+3}_{(aq)}$ —, Nd (HEDTA) ----.

TABLE I
Data for Nd(III) – methyl succinate solutions
$I = 0.1\text{M}$, $T = 23 \pm 2°\text{C}$

Ph	[M]	[ML]	[ML_2]	[ML_3]	[M_T]	[L]	[L_T]	$P_{exp}(\times 10^6)$
Conc(M)2.894	.0114	0.0000	0.0000	0.0000	.01140	0.0000	0.00000	
f_i	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.00000	9.68
Conc(M) 4.816	.0103	.0009	.0000	0.0000	.01126	.0001	.00119	
f_i	.9160	.0837	.0002	0.0000	1.0000	.0422	1.00000	10.13
Conc(M)5.157	.0091	.0020	.0000	0.0000	.01113	.0001	.00236	
f_i	.8180	.1808	.0012	0.0000	1.0000	.0515	1.00000	10.64
Conc(M)5.146	.0081	.0029	.0000	0.0000	.01100	.0002	.00350	
f_i	.7330	.2640	.0029	0.0000	1.0000	.0566	1.00000	11.10
Conc(M)4.955	.0073	.0035	.0001	0.0000	.01088	.0003	.00461	
f_i	.6710	.3241	.0048	0.0000	1.0000	.0576	1.00000	11.49
Conc(M)5.009	.0064	.0043	.0001	0.0000	.01075	.0004	.00570	
f_i	.5931	.3986	.0082	0.0000	1.0000	.0648	1.00000	11.91
Conc(M)4.964	.0052	.0052	.0002	0.0000	.01056	.0005	.09746	
f_i	.4953	.4898	.0149	0.0000	1.0000	.0728	1.00000	12.63
Conc(M)4.932	.0043	.0058	.0002	0.0000	.01036	.0007	.00915	
f_i	.4156	.5611	.0233	0.0000	1.0000	.0811	1.00000	13.06
Conc(M)4.949	.0035	.0063	.0004	0.0000	.01018	.0010	.01079	
f_i	.3420	.6231	.0349	0.0000	1.0000	.0928	1.00000	13.74
Conc(M)4.954	.0029	.0067	.0005	0.0000	.01000	.0013	.01236	
f_i	.2856	.6665	.0478	0.0000	1.0000	.1038	1.00000	14.12
Conc(M)4.977	.0023	.0069	.0006	0.0000	.009828	.0016	.01388	
f_i	.2370	.6995	.0635	0.0000	1.0000	.1168	1.00000	14.41
Conc(M)5.003	.0019	.0070	.0008	0.0000	.009658	.0020	.01535	
f_i	.1974	.7215	.0811	0.0000	1.0000	.1309	1.00000	14.97
Conc(M)5.032	.0016	.0070	.0010	0.0000	.009498	.0024	.01679	
f_i	.1650	.7344	.1005	0.0000	1.0000	.1457	1.00000	15.00

TABLE II
Oscillator strengths ($\times 10^6$) of Nd(III) complexes in aqueous solutions[a] for the $^4I_{9/2} \rightarrow {}^4G_{5/2}{}'\,{}^2G_{7/2}$ transition

	DTPA	DCTA	EDTA	HEDTA	NTA	IMDA
M	–	–	–	9.79 ± 0.08	9.77 ± 0.05	9.71 ± 0.04
ML	15.25	14.28	18.02 ± 0.07	17.37 ± 0.05	13.03 ± 0.03	12.89 ± 0.16
ML_2	–	–	–	–	13.01 ± 0.20	16.93 ± 2.03
	Dipicolinate	*Methyl Succinate*	*Malonate*	*Maleate*	*Fumarate*	*Sulfate*
M	9.51 ± 0.04	9.61 ± 0.06	9.68 ± 0.10	9.35 ± 0.08	9.66 ± 0.04	9.51 ± 0.07
ML	14.41 ± 0.10	15.32 ± 0.16	14.84 ± 0.52	16.22 ± 0.14	16.22 ± 0.37	13.76 ± 0.31
ML_2	22.49 ± 2.51	22.95 ± 1.55				
	NTA–Malonate	*HEDTA–OH*				
M	–	–				
ML	12.89 ± 0.04	17.51 ± 0.05				
ML_2	14.77 ± 0.21	18.95 ± 0.06				

[a] The values for the oscillator strengths of M under each ligand were determined from equation (3) and were not forced to be equal to the measured aquo value of 9.68×10^{-6}. Errors are listed as 1σ values.

TABLE III
Oscillator strengths (x10^6) of Ho(III) complexes in aqueous solution[a] for the $^5I_8 \rightarrow {}^5G_6{}' \, {}^5F_1$ transition

	DTPA	*DCTA*	*EDTA*	*HEDTA*	*NTA*	*IMDA*
M	–	–	–	5.93 ± 0.13	6.11 ± 0.08	6.13 ± 0.02
ML	12.71 ± 0.03	9.35 ± 0.02	9.92 ± 0.04	14.39 ± 0.09	11.09 ± 0.05	10.34 ± 0.06
ML_2	–	–	–	–	11.73 ± 0.05	14.94 ± 0.26
	Dipicolinate	*Methyl Succinate*	*Malonate*	*Maleate*	*Fumarate*	*Sulfate*
M	5.98 ± 0.07	5.93 ± 0.07	6.14 ± 0.08	6.09 ± 0.04	6.16 ± 0.03	6.05 ± 0.07
ML	14.26 ± 0.26	13.82 ± 0.21	11.86 ± 0.39	11.80 ± 0.16	11.33 ± 0.13	8.89 ± 0.32
ML_2	–	20.29 ± 1.01	18.38 ± 0.96	–	–	–
	NTA–Malonate	*HEDTA–OH*				
M	–	–				
ML	11.12 ± 0.04	13.85 ± 0.14				
ML_2	14.26 ± 0.19	11.17 ± 0.12				

[a] The values for the oscillator strengths listed for M under each ligand were determined from equation (3) and were not forced to be equal to the measured aquo value of 6.12 x 10^{-6}. Errors are listed as 1σ values.

bility of perturbations due to the presence of protonated metal–ligand complexes in these solutions, data from solutions of pH values near 7 were used to calculate the oscillator strengths in Tables II and III. In some cases the oscillator strengths at other pH values did not differ significantly from those near neutrality so average deviations are listed in the tables. The experimental data for DTPA, EDTA and DCTA complexes with Nd(III) and Ho(III) are listed in Tables IV and V.

Mixed complexes of Nd–HEDTA–OH and Ho–HEDTA–OH were studied by titrating HEDTA solutions of Nd(III) and Ho(III) with standard base. The free OH concentration and the mixed complex concentrations were determined directly from the pH values. The data for P_{ML} in Tables 2 and 3 for the mixed ligand systems refer to the P_{ML} values for Ln–malonate and Ln–HEDTA complexes obtained by analysis of the mixed solutions. The agreement of the values with the values determined for the same *ML* complexes in the binary systems is a further measure of the validity of our analysis.

The reliability of the oscillator strength calculated for the complex species is a function of the error limits of the stability constant and pK_a data. The estimated standard errors are 2–5% for β_1, 5–10% for β_2 and 10–20% for β_3. The pK_{A_i} values have similar errors. In most systems only P_{ML} was determined and in a few P_{ML_2}. Within these errors for β_i and pK_{A_i} limits, the error in the oscillator strengths was not increased beyond that listed in the Tables which is the standard error from the linear regression analysis of Eq. 3. Moreover, the satisfac-

TABLE IV
Experimental data for Nd(III) and EDTA, DCTA, DTPA.
$I = 0.1M$. $T = 23 \pm 2°C$

Ligand	*[Nd]*	*[Ligand]*	*pH*	*P(x10^6)*
EDTA	0.00956	0.00966	1.99	16.96
			2.68	18.02
			6.29	17.95
			10.20	18.09
DCTA	0.00814	0.00819	2.40	13.63
			3.50	14.04
			6.13	14.28
			11.77	15.15
DTPA	0.101	0.0111	1.79	14.24
			2.57	15.45
			4.42	15.25
			8.70	16.01

TABLE V
Experimental data for Ho(III) and EDTA, DCTA, DTPA
$I = 0.1M$, $T = 23.2°C$

Ligand	*[Ho]*	*[Ligand]*	*pH*	*P(x10^6)*
EDTA	0.00921	0.00975	1.96	9.96
			2.66	9.88
			6.09	9.95
			10.29	9.95
DCTA	0.00784	0.00823	2.39	9.33
			3.50	9.33
			6.19	9.37
			11.76	14.57
DTPA	0.00986	0.01040	1.79	12.72
			2.57	13.04
			4.44	12.71
			8.57	12.69
			10.50	12.74

tory agreement between the values of P_M calculated from Eq. 3 and that measured directly for the aquo ion (see footnote in Tables II and III) is a further measure of the validity of the calculation of the P_{ML} and P_{ML_2} values.

DISCUSSION

Dibasic Ligands

Linear correlations with thermodynamic parameters of complexation have been found with both pK_{a_2}[7,8] and $pK_{a_1} + pK_{a_2}$[8,9] for dibasic ligands. In our systems a plot of oscillator strength vs. pK_{a_2} provided poor correlation, whereas one of P vs. ΣpK_{a_i} showed good linearity (Figures 2 and 3). As these plots indicate, the variation of the oscillator strength of the complex with ligand basicity is less for the dibasic than for the monobasic ligands. This cannot be simply an effect of charge as the $ML_2{}^+$ complexes have a strong dependence on pK_a and their oscillator strengths are much larger[5] (e.g., for $pK_a \sim 5$, P_{ML_2} + ~20). Similarly, we cannot explain the difference in the slopes of the ML^{2+} and ML^+ correlations as related simply to mono vs. bidentation because several of the monobasic ligands (glycolate, α-picolinate, acetylacetonate) which fitted the ML^{2+} correlation are most probably bidentate.

Powell and Burkholder[10] have made a suggestion which could be the basis of the difference in slope of the ML^{2+} and ML^+ lines in Figures 2 and 3. These authors have proposed that in lanthanide-EDTA complexes, a strongly hydrogen-bonded water structure exists involving the metal ion and the *non-coordinated* oxygen atoms of the ligand. Such a network could weaken the metal–ligand interaction and cause a decrease in the oscillator strength of the hypersensitive transitions of the cation. Consistent with this idea is the observation that kojate, which forms ML^{2+}, has uncomplexed oxygen atoms and showed a lower value of P than the other monobasic ligands.[5]

A second point of interest in the dibasic ligand systems is the comparison of the maleate and fumarate complexes. Maleate, the cis isomer, would be expected to show a correlation of P vs (pK_{a_1} + pK_{a_2}) but fumarate, the trans isomer, similarly

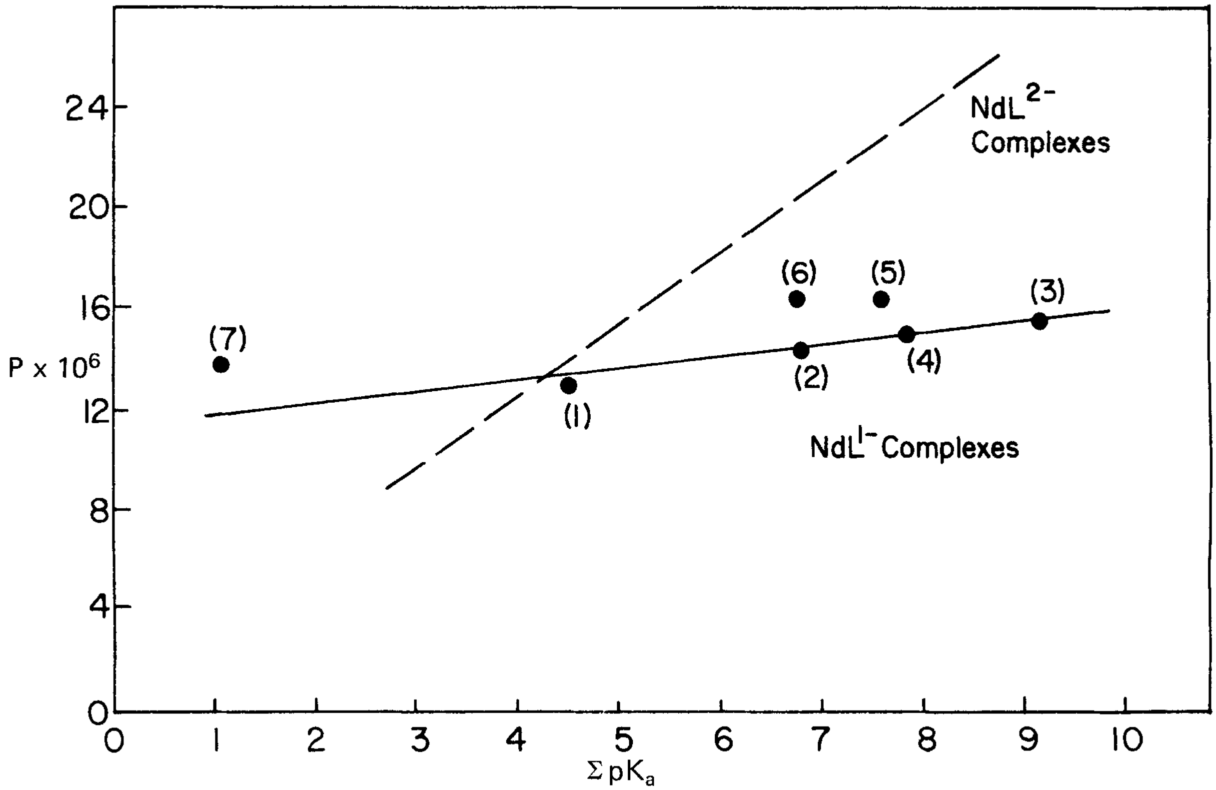

FIGURE 2 Plot of the oscillator strength, P, of the 1:1 complexes of Nd(III) vs. the ΣpK_A of the ligand acid.

correlates P with $pK_{a_1} + pK_{a_2}$ even though chelation is not possible and only one carboxylate group can be involved in the *ML* complex. The explanation would seem to lie in the fact that the carbonyl and ethylene double bonds in fumarate form a conjugated system which provides a pathway for electron density to 'flow' from one carbonyl group to the other in the *trans* structure. As a result, the monodentate fumarate can exhibit much the same basicity toward the metal ion as can the bidentate maleate. This same model has been proposed independently by Choppin, Dadgar and Stampfli[8] to explain thermodynamic data from complexation reactions, and by Diaz and Taube[11] to explain the very fast redox reaction rates found with fumarate ions. The similarity of P for the fumarate and maleate complexes is another illustration of the much greater influence on the oscillator strength of ligand basicity compared to complex symmetry. The fact that the sulfate complexes fit the correlation well further emphasizes this.

A third interesting point related to Figures 2 and 3 is that the ΣpK_a for IMDA does not include the pK_a attributable to the nitrogen protonation. Using the one reported carboxyl pK_a for IMDA[12] and approximating the second carboxyl pK_a as being the average of the NTA and EDTA values (1.89 and 1.99 respectively), the resulting $pK_1 + pK_2$ $(1.95 + 2.58 = 4.53)$ places the observed IMDA oscillator strengths on the dibasic ligand correlation line. *Including* the nitrogen pK_a (9.33) destroys the correlation. It was found that the α-picolinate complexes correlated with the other monobasic ligands only when the $pK_{a'}$ for the carboxylate group was used.[5] It would seem that the metal–nitrogen interaction has little influence on the spectral intensities when compared to metal–oxygen bonding.

In connection with this discussion we may note that although the Nd dipicolinate behavior is consistant with the above arguments, the Ho–dipicolinate oscillator strength is considerably greater than that expected from the carboxyl group pK_a values alone which may be due to the Ho–nitrogen interaction. In crystals of Yb-dipicolinate, the metal–nitrogen bond distances (2.33 and 2.41 Å) are considerably smaller than those in the comparable Yb–IMDA complexes (2.67 Å).[13] It is conceivable

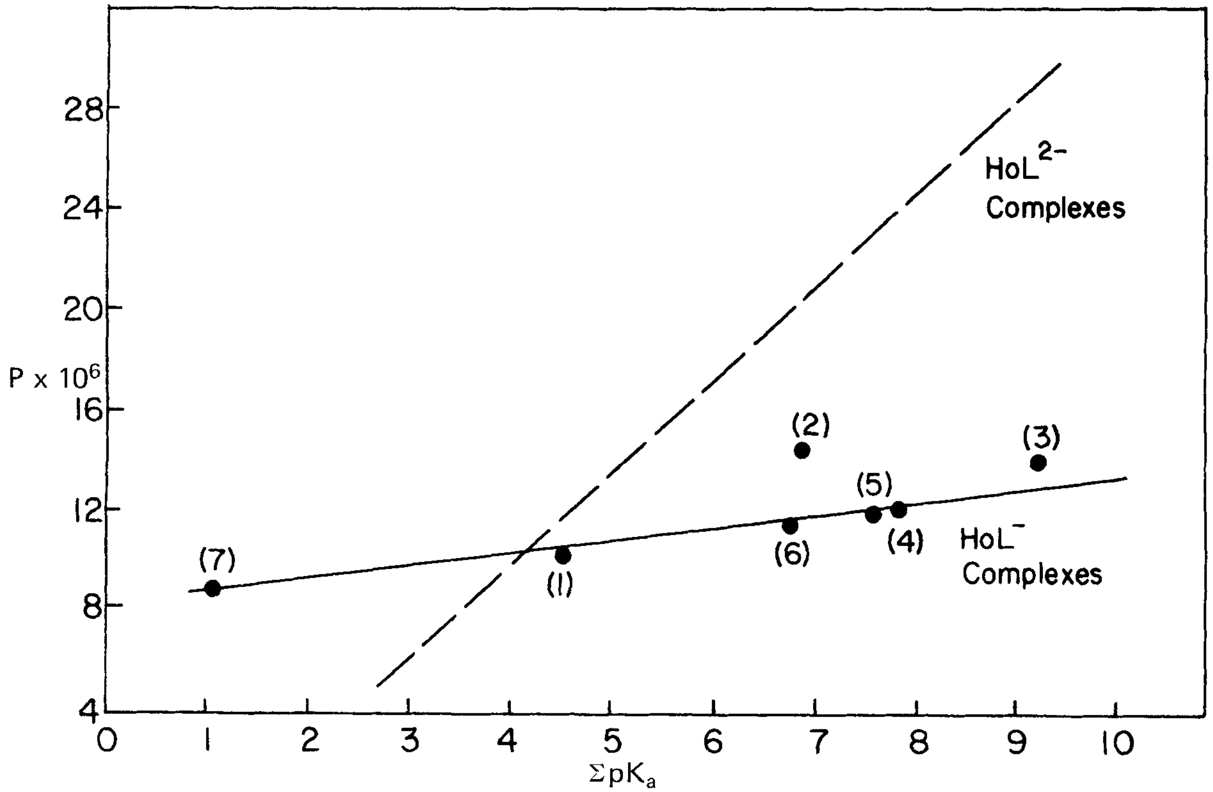

FIGURE 3 Plot of the oscillator strength, P, of the 1:1 complexes of Ho(III) vs. the ΣpK_A of the ligand acid.

that the nitrogen interaction for the dipicolinate complex could be larger than for either the α-picolinates or the aminocarboxylates. Molecular models indicate that because the steric configuration of the dipicolinate anion is rigidly determined by its aromatic ring the heterocyclic nitrogen has little freedom of movement and when both carboxyl groups are bonded to a lanthanide ion, the nitrogen is necessarily drawn close to the metal. On the other hand, the α-picolinate or polyaminocarboxylate anions have greater freedom of movement with few such steric restrictions and the nitrogen bonding sites need not be so close to the metal ion when the carbonyl groups are coordinated.

Aminopolycarboxylates

The complexes of NTA, HEDTA, EDTA, DCTA and DTPA show no correlation between ΣpK_{a_i} and P_{ML}. However, the pK_a values in the literature include the nitrogen deprotonation and, as our correlations of the complexes of α-picolinate, dipicolinate and IMDA indicate, only carboxylate dissociation values should be included in the ΣpK_{a_i}. However, when we omit the nitrogen deprotonation values and assign reasonable values for the unreported carboxylate deprotonation, we still fail to obtain any correlation between P_{ML} and ΣpK_a. From Tables II and III we see that the order of oscillator strengths is:

Nd: EDTA>HEDTA>DTPA>DCTA>NTA
Ho: HEDTA>DTPA>NTA>EDTA>DCTA

We can offer no satisfactory explanation for these sequences nor for the fact that they differ for Nd(III) and Ho(III). These ligands vary in total basicity, in the number of coordinating groups, in their steric limitations, etc. The order of oscillator strengths must reflect several of these factors but a wider variety of ligand systems would have to be investigated before any conclusions could be reached.

The values of P_{ML} do not vary widely; for Nd(III), from 13.03 for NTA to 18.02 for EDTA; for Ho(III), from 9.35 for DCTA to 14.39 for HEDTA. These values are quite comparable to the values for ML complexes of the dibasic ligands but have a more limited range than the oscillator strengths of the *ML* complexes of the monobasic ligands. The mixed ligand systems (NTA-malonate and HEDTA-OH) have values of *P* in the same range as the polydentate ligand complexes. Further research is required before these observations can be interpreted.

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