Stabilities of Rare Earth Chelates of 5-Sulphosalicylic Acid

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The spectrophotometric and potentiometric study of complex formation between gadolinium ions and 5-sulphosalicylic acid (SSA) has been reported in an earlier paper.(1) It was observed that at pH lower than 7, the reaction between the metal ion and the ligand results in the formation of a protonated complex of the type MHL in equilibrium with the usual ML complex; between pH 7 and 9, however, ML_2 species are predominantly present in solution. We have now studied the reaction of SSA with other rare earths. The data of stability constants obtained will be discussed in this paper in terms of the bonding in these complexes.

Experimental

The stability constants were determined at 20°C and at constant ionic strength of 0.1 M. The technique used for the potentiometric and the spectrophotometric measurements was similar to that described earlier.(1) The spectrophotometric measurements were made at pH 6.0 which was much below the pH of hydrolysis in each case. The spectra of all the rare earth complexes with this ligand were similar; two maxima were observed. The wavelengths corresponding to them are given in Table 1. At the wavelength of 340 mμ and the concentration chosen, the metal perchlorate had negligible absorption. The ligand, however, had finite absorption and during the evaluation of the stability constants the values of the optical density were corrected for this absorption by Beer's law.

The results obtained for all the rare earth complexes were remarkably similar. In the range of pH investigated (5 to 10), both 1 : 1 and 1 : 2 complexes are formed with this ligand. Below pH 7, the reaction is of the type

$$M+HL \underset{}{\overset{k}{\rightleftharpoons}} MHL \underset{}{\overset{k'}{\rightleftharpoons}} ML+H$$

The equilibrium constants k and k' have been evaluated in each case by exactly the same manner as described

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1) N. V. Thakur, S. M. Jogdeo and C. R. Kanekar, *J. Inorg. Nucl. Chem.*, **28**, 2297 (1966).

TABLE 1. WAVELENGTHS OF MAXIMUM ABSORPTION IN THE ULTRAVIOLET FOR RARE EARTH COMPLEXES OF SSA at pH 6.0

Metal ion	Wavelength of maximum absorption, mμ	
Ce^{3+}	252	308
Pr^{3+}	254	310
Nd^{3+}	252	310
Sm^{3+}	254	317
Eu^{3+}	252	314
Gd^{3+}	252	315
Tb^{3+}	254	318
Dy^{3+}	253	317
Ho^{3+}	253	317
Er^{3+}	253	317
Tm^{3+}	254	319
Yb^{3+}	253	316
Lu^{3+}	253	319

in the previous paper1) using both potentiometric and spectrophotometric data. The values of k were also calculated independently from the potentiometric data alone assuming the equilibrium of MHL and ML and this served as a further check on the reliability of the previous calculations.

The values of the stability constant (K_1) for the reaction $M+L \rightleftharpoons ML$ have been calculated using the relation

$$K_1 = k \cdot k' \cdot K_1^H$$

where K_1^H is the first proton ligand stability constant ($10^{11.72}$), involving the phenolic group. The values of K_2 for the reaction $ML+L \rightleftharpoons ML_2$ have been also calculated. The data of k, k', K_1, K_2 and ($K_1 \cdot K_2$) are given in log units in Table 2.

Discussion

There is considerable evidence that rare earths form compounds involving ionic bonds and that the "f" orbitals are not generally involved in bond formation as they are considerably shielded from the influence of the ligand orbitals. If bonds are ionic, one expects Born's energy relationship to be valid and that, for the complexes of various rare earths, the values of stability constants should increase linearly with e^2/r where r is the radius of the rare earth ion. Such a relationship has been tested for a number of rare earth complexes.2-5) Moeller *et al.*6) have reviewed the present state of our knowledge on this subject.

Briefly, the work so far reported indicates that, although the bonding may be predominantly ionic in all the rare earth complexes and the electrostatic description may be fairly adequate for the complexes of the cerium earths, other factors such as steric effect, crystal field stabilisation, the coordination of water molecules in addition to that of the ligand around the rare earth ion and the possibility of $f\pi$-$p\pi$ bonding may be important in the formation of complexes of heavier rare earths. In the light of the previous work the data of the stability constants for SSA complexes can now be examined. The data obtained in this work for k, K_1 and K_2 for various rare earth sulphosalicylates have been plotted in Fig. 1 against e^2/r. For this purpose the values of crystal radii given by

TABLE 2. STABILITY CONSTANTS OF RARE EARTH-SSA COMPLEXES AT 20°C AND CONSTANT IONIC STRENGTH (0.1 M)

Metal ion	pk'	$\log k$	$\log K_1$	$\log K_2$	$\log K_1 \cdot K_2$
Ce^{3+}	6.82	1.93	6.83	5.57	12.40
Pr^{3+}	6.63	1.99	7.08	5.61	12.69
Nd^{3+}	6.42	2.09	7.39	5.62	13.01
Sm^{3+}	6.30	2.23	7.65	5.93	13.58
Eu^{3+}	6.11	2.26	7.87	6.03	13.90
Gd^{3+}	6.20	2.06	7.58	6.07	13.65
Tb^{3+}	5.77	2.47	8.42	6.19	14.61
Dy^{3+}	5.35	2.42	8.29	6.60	14.89
Ho^{3+}	5.55	2.23	8.40	6.75	15.15
Er^{3+}	5.69	2.12	8.15	6.30	14.45
Tm^{3+}	5.65	2.27	8.34	6.61	14.95
Yb^{3+}	5.67	2.30	8.35	6.81	15.16
Lu^{3+}	5.76	2.47	8.43	7.03	15.46

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2) R. Harder and S. Chaberek, *J. Inorg. Nucl. Chem.*, **11**, 197 (1959).

3) E. J. Wheelwright, F. H. Spedding and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953).

4) L. C. Thompson, *J. Inorg. Nucl. Chem.*, **24**, 1083 (1962).

5) D. Fleischer and J. E. Powell, USAEC-IS-1121, Ames Laboratory, Iowa State University of Science and Technology (1965).

6) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel and W. J. Randall, *Chem. Revs.*, **65**, 1 (1965).

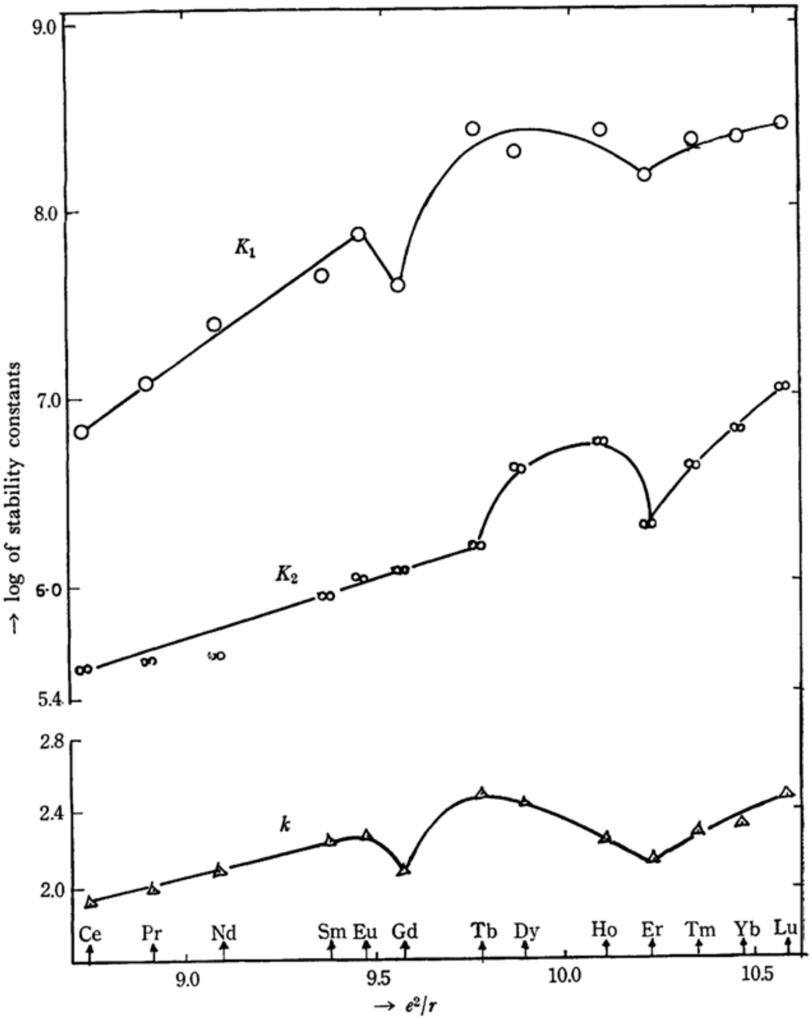

Fig. 1. Graph of stability constants (log units) for rare earth-SSA complexes as a function of ionic potential e^2/r.

Zachariasen⁷⁾ have been used. It is seen that the stability constants show in general a monotonic increase with decreasing ionic radius and the increase is approximately linear for the cerium earths (Ce^{3+} to Eu^{3+}). For complexes of rare earths heavier than gadolinium, however, the relationship between log of the stability constant and e^2/r is definitely non-linear. The observed stability constants for the rare earths heavier than gadolinium are in general less than expected from the extrapolation of the straight line observed for the complexes of the lighter rare earths. The progressively smaller radii of these rare earths may impose an increasing steric hindrance to the ligands and thus effect may partly account for the decrease. In the SSA complexes there are only two possible bonding sites and the chelate ring would utilise both these points. If the steric effect is to be operative there should be a change in the number of coordinated atoms. One is, therefore, led to speculate that the number of water molecules coordinated to the rare earths heavier than gadolinium in SSA complexes may be different from the number attached in complexes of the lighter rare earths. This speculation cannot be tested as the data for ΔH° and ΔS° for the formation of these complexes is not available. It is reasonable to expect that the steric effect, if present, should be pronounced for the formation of 1 : 2 complex because two chelate rings have to be formed. However, the ratios of K_1/K_2 for the heavier rare earth complexes are not appreciably different from the corresponding ratios for the complexes of the lighter rare earths. It appears, therefore, that the steric effect alone cannot account for the observed departure from the Born relationship and

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7) W. H. Zachariasen in G. T. Seaborg and J. J. Katz, eds., "The Actinide Elements," McGraw Hill Book Co., New York (1954), Chap. 18

other factors must be considered. One of them appears to be the interaction of the 4-f orbitals with the ligand orbitals. This may produce different degrees of stabilisation for the various rare earth complexes. To test whether such interactions are significant in rare earth complexes of SSA, it is necessary to study the magnetic susceptibilities of these complexes in the solid state. Such work is in progress.

The values of $\log k$ for the SSA complexes are comparatively lower than Fleischer's data[5) for ethylglycolates (EG), ethylmethylglycolates (EMG) and diethylglycolates (EEG) (Ce^{3+} to Lu^{3+} $\log k$ (EG) 2.45—3.14; (EMG) 2.47—3.45; (EEG) 2.05—3.25; (SSA) 1.93—2.47). This is probably because SSA complex involves a six membered ring while glycolates form five membered rings.

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