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Coördination Compounds. II. Trends in the Stability of Some Rare Earth Chelates[1]

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This investigation involved a potentiometric study of the chelates formed by the cerium group of rare earth chlorides (lanthanum, cerium, praseodymium, and neodymium) with several types of organic compounds, including the amino, hydroxy, and mercapto analogs of acetic, propionic, benzoic, and succinic acids. The order of decreasing stability for the ligands was aspartic, malic, glycine, thiomalic, anthranilic, glycolic, β-alanine, salicylic, β-hydroxy propionic, β-mercapto propionic, and thioglycolic. The stability of chelates with analogs of acetic, propionic, benzoic, and succinic acids decreases for any given acid as the donor group changes from $-NH_2$ to $-OH$ to $-SH$. Considering acids which contain the same donor group ($-NH_2$ or $-OH$ or $-SH$) decreasing stability is observed in the analogs of succinic, acetic, benzoic, aud propionic acids, in that order, the only exception being thioglycolic acid which, of all the ligands, forms the weakest chelate.

Introduction

Some rare earth chelates of glycine[2] and glycolic,[3,4] aspartic,[2,5] malic,[2,6] and salicylic acids[6] have been prepared previously. They have been examined with respect to their conductivity and as elutriants in ion-exchange and fractional precipitation separations. In these cases, it was indicated that some complexing took place, but usually no attempt was made to determine stabilities of the assumed complexes. The only reported stability measurements were those made by Sonesson[7] with the glycolic acid system. The current study was undertaken to provide the missing data.

Experimental

Materials.—All chemicals employed were reagent grade and were not purified further except for thiomalic acid (Evans Cosmetics Corp.) and aspartic acid (Eastman Kodak Co.) which both were recrystallized from aqueous solution. The rare earth chlorides were 99.9% pure (Lindsay Chemical Co.). β-Hydroxypropionic acid was prepared by dissolving β-propiolacetone in hot water.[8] The KOH (carbonate-free) solutions were prepared by a standard technique.[9]

Analysis.—The acids, with the exception of glycine and β-alanine, were standardized with potassium hydroxide by potentiometric titration. Glycine and β-alanine were standardized by adding 10 ml. of a 35% solution of formaldehyde to 10 ml. of an aqueous solution of the acid[10,11] and then titrating (potentiometrically).

The rare earth chloride solutions were prepared at a concentration of 0.0167 *M* and were standardized by two procedures. In the ion-exchange method[12-14] (cation analysis), 25 ml. of the aqueous rare earth chloride solution was added to a column containing Amberlite IR-120 cation-exchange resin. The eluant (HCl) was titrated with standardized potassium hydroxide using phenolphthalein as the indicator. The Fajans adsorption indicator method[15] was used to standardize the potassium chloride and rare earth chloride solutions, using dichlorofluorescein as the indicator.

Procedure.—The experimental procedure involved a potentiometric titration of the organic acids in the absence and presence of the rare earth chlorides. The acids employed were glycine, glycolic, thioglycolic, β-alanine, β-hydroxy propionic, β-mercapto propionic, aspartic, malic, thiomalic, anthranilic, and salicylic. All organic acids were prepared at a concentration of 0.1 *M*, with the exception of anthranilic acid and salicylic acid which were prepared at 0.01 *M* due to their low solubilities in water.

The ionic strength of the solutions in all cases was adjusted to 0.1 using potassium chloride as a supporting electrolyte and titrations were run in duplicate using 12:1, 3:1, and 1:1 ratios for acid to metal ion concentrations. This was accomplished by introducing 5, 20, or 60 ml. of 0.0167 *M* metal chloride solution into the titration cell in addition to 10 ml. of 0.1 *M* acid solution. The final

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[2] R. C. Vickery, *J. Chem. Soc.*, 2058 (1950).

[3] G. Jantsch, *Z. anorg. u. allgem. Chem.*, **153**, 9 (1926).

[4] D. C. Stewart and J. P. Faris, *J. Inorg. & Nuclear Chem.*, **3-4**, 64 (1956).

[5] D. I. Ryabchikov and E. A. Terent'eva, *Izvest. Akad. Nauk, S.S.S.R. Otdel. Khim. Nauk*, **44**, (1949).

[6] L. Holleck, *Z. Naturforsch.*, **2b**, 81 (1947).

[7] A. Sonesson, *Acta Chem. Scand.*, **13**, 998 (1959).

[8] T. L. Gresham, J. E. Jansen, and F. W. Shaver, *J. Am. Chem. Soc.*, **70**, 998 (1948).

[9] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 339 (1948).

[10] L. Katzin and J. Sullivan, *J. Phys. and Colloid Chem.*, **55**, 346 (1951).

[11] S. Sorenson, *Biochem. Z.*, **7**, 43 (1907).

[12] G. E. Boyd, J. Schubert, and A. W. Adamson, *J. Am. Chem. Soc.*, **69**, 2818 (1947).

[13] S. H. Harris and E. R. Tompkins, *ibid.*, **69**, 2793 (1947).

[14] F. H. Spedding and J. E. Powell, *ibid.*, **76**, 2545 (1954).

[15] R. F. Lumb and A. E. Martell, *J. Phys. Chem.*, **57**, 690 (1953).

volume was adjusted to 100 ml. with 0.1 *M* KCl. The titrations were carried out in a nitrogen atmosphere and at a temperature of 30.0 ± 0.1°, using a 200-ml. flask with five necks to accommodate the tube delivering nitrogen, a mercury seal stirrer, a microburet, and glass and calomel extension electrodes connected to a Beckman Model G *p*H meter.

The equations employed in the calculation of the acid dissociation and chelate formation constants have been reported previously in the literature.[16] Two important factors considered were whether the rare earth chlorides form chloro-complexes and/or undergo hydrolysis, since the formation of chloro-complexes would lead to low values for stability constants, whereas hydrolysis would yield high values. From previous experiments the effect of chloro-complexing[17-23] and/or hydrolysis[21,24] on the light rare earth chlorides can be considered to be negligible below *p*H 6. The data used in the determination of stability constants were taken from the region of $pH < 6$. In making these calculations, the mean activity coefficient of the hydrogen ion in potassium chloride[25-27] and in cerous chloride[28] and lanthanum chloride[29,30] was taken into consideration. The value used was 0.8.

Discussion

The calculated values of the acid dissociation constants obtained from the averaging of 5–10 separate determinations are listed in Table I. The values of log K_1 were obtained from the 3:1 acid to metal curves, using Bjerrum's method.[31] Log K_2 and log K_3 values were obtained from the 12:1 acid to metal curves. Log K_3 values were not obtained for any of the monocarboxylic acids because precipitation occurred above $\bar{n}$ values of 2. For the acids, β-alanine, salicylic, and anthranilic, log K values were obtained by the algebraic method owing to precipitation below $\bar{n}$ values of 0.5. The values of the formation constants obtained are listed in Tables II and III.

The order of decreasing stability for the ligands was aspartic, malic, glycine, thiomalic, anthranilic, glycolic, β-alanine, salicylic, β-hydroxy propionic, β-mercapto propionic, and thioglycolic. The error limits are ±5% for K_1, ±10% for K_2, and ±20% for K_3. This corresponds to the errors: ±0.02 for log K_1, ±0.05 for log K_2, and ±0.1 for log K_3.

TABLE I

DISSOCIATION CONSTANTS OF MONOBASIC AND DIBASIC ACIDS[a]

Monobasic acid	pK_a values	Dibasic acid	pK_a values
Glycine	9.53	Aspartic	3.79
Glycolic	3.70		9.63
Thioglycolic	3.55	Malic	3.22
β-Alanine	10.55		4.78
β-Hydroxy-propionic	4.49	Thiomalic	3.15
			4.68
β-Mercapto-propionic	4.27		
Anthranilic	4.86		
Salicylic	2.88		

[a] $\mu = 0.1$; temperature, 30°.

The stability of chelates with analogs of acetic, propionic, benzoic, and succinic acids decreases for any given acid as the donor group changes from $-NH_2$ to $-OH$ to $-SH$. This decrease parallels the order of decreasing basicity of the ligand in any given series. Considering acids which contain the same donor group (NH_2 or OH or SH), decreasing stability is observed in the analogs of succinic, acetic, benzoic, and propionic acids, in that order, the only exception being thioglycolic acid, which forms the weakest chelate of all the ligands.

The chelate stabilities of the amino and hydroxy analogs of acetic acid were found to be higher than the corresponding analogs of propionic acid. However, the stability of β-mercapto propionic acid was higher than thioglycolic acid. This anomaly may be explained by taking into consideration the size of the lanthanide ion and the large size of the sulfur atom as compared to nitrogen and oxygen. Trials with atomic models show that the mercapto group in thioglycolic acid is closer to the carboxyl group than in β-mercapto propionic acid, with the resulting introduction of strain in the five-membered chelate ring. Such strain would have the tendency to reduce the stability of the chelate. The situation is analogous to that found by Irving and Fernelius[32] in their study on the formation constants of some

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(16) S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5052 (1952).

(17) R. E. Connick and S. W. Mayer, *ibid.*, **73**, 1176 (1951).

(18) S. Datta and M. Dee, *Indian J. Phys.*, **10**, 163 (1936).

(19) R. M. Diamond, K. Street, and G. T. Seaborg, *J. Am. Chem. Soc.*, **76**, 1461 (1954).

(20) T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

(21) F. H. Spedding and J. Dye, *J. Am. Chem. Soc.*, **76**, 879 (1954).

(22) F. H. Spedding, P. E. Porter, and J. M. Wright, *ibid.*, **74**, 2055 (1952).

(23) E. J. Wheelright, F. H. Spedding, and G. Schwarzenbach, *ibid.*, **75**, 4196 (1953).

(24) R. S. Tobias and A. B. Garrett, *ibid.*, **80**, 3532 (1958).

(25) H. S. Harned, *ibid.*, **48**, 326 (1926).

(26) H. S. Harned and M. J. Cook, *ibid.*, **59**, 1291 (1937).

(27) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., Third Edition, 1958, p. 457.

(28) C. M. Mason and D. B. Kellam, *J. Phys. Chem.*, **38**, 689 (1934).

(29) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

(30) M. Randall and G. E. Breckenridge, *ibid.*, **49**, 1435 (1927).

(31) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(32) R. J. Irving and W. C. Fernelius, *J. Phys. Chem.*, **60**, 1427 (1956).

Table II

log Stability Constants of Monobasic Acids with Lanthanum, Cerium, Praseodymium, and Neodymium Chlorides at 30°

	$LaCl_3$		$CeCl_3$		$PrCl_3$		$NdCl_3$	
Acid	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2	log K_1	log K_2
Glycine	3.23	2.92	3.40	3.00	3.64	3.32	3.71	3.30
Glycolic	2.68	2.42	2.84	2.45	2.98	2.69	3.07	2.81
Thioglycolic	2.27	2.35	2.28	2.36	2.40	2.44	2.48	2.52
β-Alanine	2.43[a]		2.63[a]		2.92[a]		3.04[a]	
β-Hydroxypropionic	2.58	2.49	2.61	2.60	2.65	2.58	2.80	2.72
β-Mercaptopropionic	2.30	2.40	2.41	2.48	2.56	2.49	2.58	2.49
Anthranilic	3.14		3.18		3.22		3.23	
Salicylic	2.64[a]		2.66[a]		2.68[a]		2.70[a]	

[a] Algebraic method.

Table III

log Stability Constants of Dibasic Acids with Lanthanum, Cerium, Praseodymium, and Neodymium Chlorides at 30°

	$LaCl_3$			$CeCl_3$			$PrCl_3$			$NdCl_3$		
Acid	log K_1	log K_2	log K_3	log K_1	log K_2	log K_3	log K_1	log K_2	log K_3	log K_1	log K_2	log K_3
Aspartic	4.84	3.42	...	5.13	3.65	2.75	5.23	3.84	2.72	5.40	4.08	3.06
Malic	4.73	3.22	2.68	5.00	3.28	2.75	5.04	3.40	2.80	5.12	3.64	2.92
Thiomalic	3.01	2.57	2.27	3.22	2.88	2.53	3.31	2.86	2.59	3.38	2.99	2.57

of the first row transition elements with S-alkyl carboxylic acids, where six-membered sulfur rings were more stable than the five-membered analogs for several of the metal ions.

In general, log K_1 is greater than log K_2 for a given chelate. However, the difference in the values of the two constants usually is quite small, indicating that there is almost as strong a tendency to form the double-ring chelate as a single-ring chelate. With the mercapto analogs of acetic and propionic acids, log K_2 is equal to or slightly higher than log K_1. This anomalous order, for related mercapto chelates, also was observed by Irving and Fernelius. Log K_2 is greater than log K_1 in only a few cases.[33-36]

Anthranilic and salicylic acid can form six-membered rings with the lanthanides. To attempt a correlation of the stabilities of the analogs of benzoic acid with the corresponding analogs of acetic and propionic acids is difficult because as the donor group changes many other changes occur in the ligand simultaneously, such as base strength, ring size, steric factors, and resonance.[37] The stabilities of anthranilic acid and salicylic acid are less than the analogs of acetic acid, and higher than the analogs of propionic acid. An analogous situation was discovered by Schwarzenbach,[38,39] who found that a six-membered aliphatic ring bound calcium ions less effectively than a six membered ring through the benzene ring.

A succinic acid analog possibly may form either a bidentate or tridentate lanthanide chelate. Chaberek and Martell[16] have reported tridentate chelates formed between aspartic acid and the first row transition metal ions, whereas Lumb and Martell[15] have observed that aspartic acid forms only bidentate chelates with alkaline earth ions. For the alkaline earth chelates, the stability of the aspartate chelate was only 0.2 log unit higher than the glycinate chelate, and this small increase was attributed to the inductive effect of the negative carboxylate group in aspartic acid which can lend stability to the structure by increasing the basicity of the donor group toward the metal ion.

A comparison of the stability constants for the aspartate, malate, and thiomalate chelates of the lanthanides with the corresponding analogs of acetic and propionic acids show large differences (approximately 1.8, 2.0, and 0.8 log units, respectively, for aspartate, malate, and thiomalate) in K_1 values. These differences are too large to be attributed solely to the inductive effect of an

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(33) C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.* **60**, 384 (1956).

(34) R. J. Bruehlman and F. A. Verhoek, *J. Am. Chem. Soc.*, **70**, 1401 (1948).

(35) E. Gonick, W. C. Fernelius, and B. E. Douglas, *ibid.*, **76**, 4671 (1954).

(36) P. Krumholz, *ibid.*, **71**, 3654 (1949).

(37) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

(38) G. Schwarzenbach, H. Ackermann, and P. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1949).

(39) G. Schwarzenbach, A. Willi, and R. D. Bach, *ibid.*, **30**, 1303 (1947).

additional carboxylate ion in either a five- or six-membered bidentate. It is reasonable to assume that the succinic acid analogs form tridentate chelates since it is known that chelates become more stable as the number of chelate rings in the molecule increases.[37] The chelate stability constants for the series of metals with a given ligand is linearly related to the ionic radii of the metal in the series.

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Acetate Complexes of the Rare Earth and Several Transition Metal Ions[1]

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The first two complex-formation constants of acetate anion with trivalent rare earth and divalent copper, zinc, cadmium, and lead ions have been determined. The temperature was controlled at 20° and an ionic strength of 0.1 was used. Hydrogen ion concentrations were measured using a glass electrode.

Introduction

It is a well known fact that trivalent lanthanon ions exhibit extensive hydrolysis when placed in an aqueous medium. Thus, when neutral rare earth salts are dissolved in water, a distinct lowering of the *p*H is noted. The extent of the lowering depends on the concentration of the rare earth salt and the particular rare earth. Since the ionic radius decreases from lanthanum to lutetium, the heavier the rare earth the greater is the tendency to hydrolyze.

Measurements made on rare earth solutions often must be corrected for hydrolysis. The necessity for correction frequently can be eliminated by making the measurements in solutions in which hydrolysis has been suppressed by the addition of excess hydrogen ions. This is conveniently achieved by introducing an acid buffer into the solution. It has been found that acetic acid–sodium acetate buffer systems provide the *p*H necessary to prevent hydrolysis of dilute rare earth solutions. This buffer has been used in the determination of stability constants of rare earth chelates with ethylenediamine-N,N,N′,N′-tetraacetic acid (EDTA) and N′-hydroxyethylethylenediamine-N,N,N′-triacetic acid (HEDTA).[2] Since the measurement of stability constants involves either direct or indirect determination of free metal ion concentrations, it is imperative to consider the possibility of complex formation between the various metal ions and the buffer ligand.

Sonesson has shown that complexes between the lanthanons and acetate do form.[3–5] He determined the stepwise formation constants of rare earth–acetate species at an ionic strength of 2.0, but data for lower ionic strengths are not available. The present investigation, therefore, considers the magnitude of these formation constants at an ionic strength of 0.1.

In many systems used to determine chelate stability constants, competing metal ions are involved.[2] For this reason the stepwise formation constants of the acetate complexes of divalent copper, zinc, cadmium, and lead ions also have been included in the present investigation.

The determination of the acetate formation constants has an additional purpose. The variation in stability of the complexes formed with members of the rare earth sequence thus far has been studied extensively only for the case of polydentate ligands, and the observed trends have not yet been explained satisfactorily. The distinct drop in stability at gadolinium is presently

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[2] (a) E. J. Wheelwright, F. H. Spedding, and G. Schwarzenbach, *J. Am. Chem. Soc.*, **75**, 4196 (1953); (b) F. H. Spedding, J. E. Powell, and E. J. Wheelwright, *ibid.*, **78**, 34 (1956).

[3] A. Sonesson, *Acta Chem. Scand.*, **12**, 165 (1958).

[4] A. Sonesson, *ibid.*, **12**, 1937 (1958).

[5] A. Sonesson, *ibid.*, **14**, 1495 (1960).