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Stability Constants of the Rare Earth Chelate Species Formed with Some Monocarboxylate Ligands[1]

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The formation constants of the first two chelate species formed by rare earth and yttrium ions with propionate, methoxyacetate, and thioglycolate ligands have been determined by a potentiometric method at 20.0° and an ionic strength of 0.10. The supporting electrolyte was sodium perchlorate. The data indicate that methoxyacetate and thioglycolate (α-mercaptoacetate) ligands behave essentially as monodentate ligands, as do acetate and propionate. It is apparent that the affinity of the simple carboxylic acid ligands for rare earth ions decreases in the order acetate > propionate > isobutyrate. It is also clear that the order of the electron-donating ability of the functional groups studied is $OH >> OCH_3 > SH$. The ionization constants of propionic, methoxyacetic, and thioglycolic acids were determined at 20.0° and an ionic strength of 0.10.

Introduction

Stability trends among the trivalent rare earth ions with polydentate ligands have been studied extensively, but relatively little work has been done in the case of monodentate ligands. The stability constants of the rare earth acetate complexes have been determined at ionic strengths of 0.1[2] and 2.0,[3,4] and the stability constants of the rare earth isobutyrate complexes have been determined at an ionic strength of 0.5,[5] but the rare earth propionate, methoxyacetate, and thioglycolate complexes have not been extensively investigated. This paper is concerned with the determination of the stability constants of the rare earth complexes formed with the latter three ligands at an ionic strength of 0.1 and a temperature of 20° and in comparing the trends with the trends observed for the acetate[2] and isobutyrate[5] complexes.

Experimental

The preparation and standardization of rare earth solutions used in this work were the same as for those solutions used by Kolat and Powell in the determination of the rare earth acetate stability constants.[2]

The propionic acid used in these determinations was purified by fractional distillation followed by dilution to approximately 1 *M*, heating with decolorizing charcoal, and filtering. The other acids were of reagent grade purity and were used without further purification.

An equimolar buffer solution of each acid and its sodium salt was prepared by adding a measured amount of carbonate-free standard sodium hydroxide solution to a roughly known amount of the acid solution. In order to prevent air oxidation of the thioglycolic acid, water purged of oxygen by bubbling in purified nitrogen was used in preparing all solutions, and all measurements of the thioglycolate solutions were made under a stream of nitrogen. An aliquot of the resulting buffer solution was then titrated with carbonate-free standard potassium hydroxide solution prepared by the method of Hiller and Powell[6] in order to determine the free-acid concentration. Both the sodium hydroxide and potassium hydroxide were standardized against accurately weighed amounts of pure HCdHEDTA.[7]

In the case of propionic acid, a series of eleven solutions in which the original total propionate ion concentration ranged from 0.0024 to 0.0700 *M* was prepared. The total rare earth concentration was 0.004 *M* in each sample. A similar series of solutions was prepared for each of the other ligands. The ionic strength was adjusted to 0.1 in each sample using sodium perchlorate as the supporting electrolyte. The samples were then equilibrated in a 20.0° constant temperature bath. After equilibration in the bath, the pH of each solution was measured using a Beckman Model GS expanded scale pH meter with a glass–calomel electrode system. The Beckman Instrument Company regards this instrument as capable of a reproducibility of ±0.003 pH unit. The pH meter was calibrated with a pH 4.0 ± 0.01 buffer and an appropriate correction was made for the acitivity coefficient in computing hydrogen ion concentrations from pH data. The measured pH values fell in the pH region 4.0–5.0 in all cases.

The dissociation constants of the acids were determined at a temperature of 20.0° and an ionic strength of 0.1 at several concentrations of buffer. The average values of the dissociation constants are as follows: propionic acid, 2.21×10^{-5}; methoxyacetic acid, 4.91×10^{-4}; thioglycolic acid, 3.89×10^{-4}.

The first and second successive formation constants of the rare earth propionate, methoxyacetate, and thioglycolate complexes were calculated by the method originated by Fronaeus and Leden.[3,4,8,9] These values are listed in Table I.

Discussion

Among the propionates, the first complexation constants rise steadily from lanthanum through samarium, corresponding to the decrease in ionic radius. However, the europium constant is only slightly higher than the samarium constant and a sharp decrease in stability is noted for the gadolinium constant. This decrease in complex stability near the position in the sequence occupied by gadolinium is noted in virtually all rare earth complex systems. There is a continued downward trend for terbium and dysprosium followed by a leveling off and then a slight rising trend at the end of the series. The yttrium constant was

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[1] Contribution No. 1404. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] R. S. Kolat and J. E. Powell, *Inorg. Chem.*, **1**, 293 (1962).

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

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

[5] W. R. Stagg and J. E. Powell, *Inorg. Chem.*, **3**, 242 (1964).

[6] J. E. Powell and M. A. Hiller, *J. Chem. Educ.*, **34**, 330 (1959).

[7] J. E. Powell, J. S. Fritz, and D. B. James, *Anal. Chem.*, **32**, 954 (1960).

[8] S. Fronaeus, "Komplexsystem hos koppar," unpublished Ph.D. thesis, Library, University of Lund, Lund, Sweden, 1948.

[9] I. Leden, "Potentiometrisk undersökning av nagra kadmiumsalters komplexitet," unpublished Ph.D. thesis, Library, University of Lund, Lund, Sweden, 1948.

TABLE I

FORMATION CONSTANTS OF RARE EARTH COMPLEXES WITH SOME MONODENTATE LIGANDS[a]

$\mu = 0.1\ (NaClO_4)$; 20°

	Thioglycolic acid		Methoxyacetic acid		Propionic acid	
Metal	K_1	K_2	K_1	K_2	K_1	K_2
La	96	10	106	7	78	15
Ce	98	11	114	10	112	17
Pr	106	11	118	15	132	22
Nd	117	16	128	17	157	21
Sm	129	23	134	18	161	31
Eu	117	22	131	20	168	33
Gd	103	20	115	9	122	30
Tb	91	18	111	9	99	39
Dy	86	21	113	12	85	33
Ho	83	21	117	14	90	32
Er	87	21	119	14	87	35
Tm	95	13	119	14	81	33
Yb	96	21	120	19	85	28
Lu	102	20	124	19	100	34
Y	82	19	99	13	75	15

[a] It is estimated that the possible errors in the reported values of K_1 and K_2 may be as great as ±10 and ±20%, respectively.

found to be lower than that of any of the rare earths. With minor variations these are the same general trends as were observed in the acetate series.

In contrast to the propionate series, a maximum stability was attained in the thioglycolate and methoxyacetate series with the samarium complex, and thereafter the same decreasing trend was noted as has been observed for the isobutyrate ligand[5] with a rising trend apparent toward the end of each series. In comparing these trends, one must remember that there is a possible error of ±10% in K_1 and ±20% in the K_2 values, which could account for the lack of exact parallelism in the trends. Among the aliphatic acids, the stability increases in the order isobutyrate < propionate < acetate.

One might expect that the ether group of the methoxyacetate ligand would form fairly strong bonds with the rare earth ions by donating electrons to the rare earth coordination sphere. However, only the methoxyacetate complexes of rare earths heavier than terbium are stronger than the corresponding acetates. Even here the difference is less than the experimental accuracy of the method.

Two possible explanations for this anomaly suggest themselves. (1) Since methoxyacetic acid is a stronger acid than acetic acid, if we suppose that the anions of these acids all form complexes by bonding only through the carboxylate group, then the acetate species should be more stable than the methoxyacetates. From this viewpoint, it appears that the ether group actually does bond weakly to the rare earths, since the loss in complex stability from acetates to methoxyacetates is of considerably lesser magnitude than the loss of affinity for hydrogen ion. (2) Another possibility is that steric factors are introduced when the hydrogen of the hydroxyl group is replaced by a methyl group. If this steric hindrance is such that the oxygen atom is prevented from closely approaching the rare earth, then a good deal of the potential complexing strength is lost.

The rare earth thioglycolate complexes were found to be even less stable than the methoxyacetate complexes even though steric effects, other than that due to the size of the sulfur atom, are not present. As both acids are of similar strength, it appears that little or no contribution to complex stability is made by the sulfur atom. In fact, the detrimental effect of substituting the SH functional group equals or exceeds the detrimental effect due to substituting CH_3 for a hydrogen atom in the acetate ligand.

In the case of the thioglycolate (α-mercaptoacetate) ligand it is possible to make some comparisons with previously reported data. However, since the constants reported by previous investigators were obtained at different temperatures and/or ionic strengths and the supporting electrolytes were different, a critical comparison is not possible. In order that the reader may draw his own conclusions, the various K_1 values are compared in Table II. The reader will notice that the present values fall between the other sets of data. A comparison of the last two columns, in particular, reveals a common trend although there is a considerable difference in magnitudes. An increase in stability with decreased ionic strength is generally observed, so that the lack of agreement is not unexpected.

TABLE II

A COMPARISON OF THE AVAILABLE DATA ON STABILITIES OF 1:1 RARE EARTH THIOGLYCOLATE SPECIES

Ion	K_1 (30°; $\mu = 0.1$)[a]	K_1 (25°; $\mu = 2.0$)[b]	K_1 (20°; $\mu = 0.1$; this work)
La	1.9×10^2	26	96
Ce	1.9×10^2	27	98
Pr	2.5×10^2		106
Nd	3.0×10^2	31	117
Sm		64	129
Eu		56	117
Gd		44	103
Tb		43	91
Dy			86
Ho		21	83
Er		19	87
Tm			95
Yb		21	96
Lu			102
Y		31	82

[a] M. Cefola, A. S. Tompa, A. V. Celiano, and P. S. Gentile, *Inorg. Chem.*, **1**, 290 (1962). [b] J. L. Bear, G. R. Choppin, and J. V. Quagliano, *J. Inorg. Nucl. Chem.*, **24**, 1601 (1962).

From the stability constant values reported here for methoxyacetate and thioglycolate complexes of the rare earth ions and those for the rare earth glycolates, lactates, and α-hydroxyisobutyrates, which definitely function as bidentate ligands, one may conclude that the order of electron-donating ability of the functional groups toward rare earth ions is $OH >> OCH_3 > SH$.

In view of the fact that Cefola, Tompa, Celiano, and Gentile[10] give a pK value of 3.55 for the ionization

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(10) M. Cefola, A. S. Tompa, A. V. Celiano, and P. S. Gentile, *Inorg. Chem.*, **1**, 290 (1962).

of thioglycolic acid at 30° and an ionic strength of 0.10, corresponding to an ionization constant of 2.82×10^{-4} compared to our 20° value of 3.89×10^{-4}, it is consistent that the rare earth complex stability constants observed at 30° are larger than those observed at 20° at a comparable ionic strength.

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The Kinetics of Formation of Some Divalent Transition Metal–Dye Complexes, Studied by the Temperature-Jump Relaxation Method

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The kinetics of reaction of pyridine-2-azo-*p*-dimethylaniline (I) with bivalent cobalt, nickel, copper, zinc, and cadmium have been measured by the temperature-jump relaxation method. The values for the second-order formation constant are compared with kinetic data for the reaction of other ligands with these metals, and the importance of dissociation of water from the metal aqua ion in the formation reaction is further substantiated.

Introduction

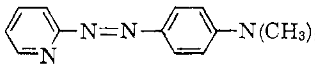
Divalent metal ions of the first transition series (vanadium–zinc) form metal complexes with simple ligands rapidly. The second-order formation rate constants are now known for the manganese–zinc series and especially for the slower reacting Ni(II) ion with a number of ligands.[2] These values have been determined by flow, relaxation, and competitive methods[3] and in some cases from a combination of dissociative rate and thermodynamic data. More information is required however, especially for the earlier members, bivalent vanadium and chromium, and for zinc (for comparison with cadmium) as well as the determination of Arrhenius parameters.

In the application of the temperature-jump method[4,5] to a metal–complex equilibrium

$$M + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML \qquad K, \text{ formation constant} \qquad (1)$$

One of the prerequisites for success is that the increase of temperature of some 10° promotes an easily detectable change in the concentration of one of the species present in the equilibrium.

This is most simply achieved by using a ligand (L) which does not complex too strongly with the metal. Since spectral is the most convenient detection method, it should also have a high molar extinction coefficient or produce a complex ML with a high absorption. This enables dilute solutions to be used with concomitant slower relaxation times (see Results). Examination of the literature for quantitative thermodynamic data[6] reveals that few metal–ligand systems fulfill these requirements, however. Nevertheless the dye, pyridine-2-azo-*p*-dimethylaniline (I), does chelate



I

weakly in aqueous solution with transition metal ions ($5 < K < 10^6$), and the complexes have strong absorption bonds ($\epsilon \sim 3 \times 10^4$) at about 550 mμ, shifted some 80 mμ from those of the free ligand.[7] In addition, there is a small, but calculably sufficient, heat of reaction. Finally, if experiments are performed in the neutral pH region, protonated forms of the dye are not important ($pK_1 \sim 4.5$) and equilibria involving these (which may even be rate-controlling) need not be considered.[8] Consequently the reaction rate constants k_1 and k_{-1} were determined from measurements on the cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) *mono* complexes of I. Unfortunately, vanadium(II), chromium(II), and silver(I) ions rapidly decolorized the dye and could not be investigated. With iron(II), some slow color changes were observed on addition of the dye; without further investigation, it was therefore decided not to include this ion in the temperature-jump experiments.

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(2) M. Eigen and R. G. Wilkins, to be published.

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(5) For recent uses of this powerful method in complex ion reactions, see (a) oxidation–reduction processes: J. Halpern, R. J. Legare, and R. Lumry, *J. Am. Chem. Soc.*, **85**, 680 (1963); H. Diebler, *Ber. Bunsen Gesellschaft Phys. Chem.*, **67**, 396 (1963); (b) substitution reactions: G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962); *J. Phys. Chem.*, **67**, 528 (1963).

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(8) Compare, G. Czerlinski, H. Diebler, and M. Eigen, *Z. physik. Chem.* (Frankfurt), **19**, 246 (1959).