

Figure 5.—Exchange mechanism, where L represents either acetylacetone or trifluoroacetylacetone.

occurs while the hydrogen is bonded to an oxygen and while both the entering and the leaving ligands are bonded to the metal. Previous work indicates that the proton exchange takes place while the hydrogen is bonded to an oxygen atom rather than to a carbon atom.¹⁸ Because of the large mass difference between zirconium and hafnium, it is expected that the exchange should be faster for zirconium provided that the rate-determining step is the breaking of a metal–oxygen bond (as in step 4). The nmr data show that the acetylacetone exchange is faster for zirconium; therefore, it seems likely that step 4 is the rate-determining step for

(18) A. N. Nesmeyanov, D. N. Kursanov, T. A. Smolina, and Z. N. Parnes, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 598 (1949); *Chem. Abstr.*, **44**, 3917 (1950).

the acetylacetone exchange. There is no detectable difference in the exchange rate of trifluoroacetylacetone with the zirconium or hafnium complexes. For this ligand the rate-determining step must be 2 or 3. Apparently the highly electronegative CF_3 group increases the rate at which the metal–oxygen bonds are broken. It has recently been reported that electronegative groups on the β -diketone ring increase the rate of metal–oxygen bond breaking.¹⁹ It is also possible that the exchange proceeds through a bimolecular attack on the eight-coordinate complex to give a nine-coordinate species. The breaking of a metal–oxygen bond in one of the chelate rings would give the eight-coordinate intermediate shown in Figure 5.

In order for the keto isomer of acetylacetone to exchange rapidly with the metal complex, either the exchange of a proton while it is bonded to a carbon atom or the isomerization of the keto and enol isomers would have to be rapid. Both processes are known to be slow;²⁰ therefore, it is not surprising that exchange with the keto isomer is not observed.

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(19) J. P. Collman and J. Y. Sun, *Inorg. Chem.*, **4**, 1273 (1965).

(20) Reference 18 shows that the first process is slow. The fraction of the enol isomer of β -diketones is often measured by bromine titration; consequently, the isomerization must be slow.

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The Successive Stabilities and Proposed Models of the Rare Earth 1-Hydroxycyclopentanecarboxylic Acid Chelates¹

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The formation constants of the first three chelate species of the tripositive rare earth cations with the 1-hydroxycyclopentanecarboxylic acid ligand (HCPC) have been determined. Some values of K_4 have also been reported where calculable. Measurement was by a potentiometric method at 25°, and the ionic medium was maintained at $\mu = 0.1$ by the supporting electrolyte, sodium perchlorate. The ionization constant of the acid was also determined over the same ligand concentration range. From the stability constant ratios and hydration data of solid species, obtained using a thermobalance technique, an effort has been made to postulate the coordination number in the complex and the dentate character of the ligand, based on the nine-coordinate, trigonal prism +3 model.

Introduction

Recently, many rare earth monocarboxylate complexes have been studied by a potentiometric method.^{2–9} In this investigation a cyclic acid was

chosen in order to investigate any steric effect arising from the presence of an alicyclic ring as compared to

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1832.

(2) (a) A. Sonesson, *Acta Chem. Scand.*, **12**, 165, 1937 (1958); **13**, 998 (1959); **14**, 1495 (1960); (b) R. H. Karraker, "Stability Constants of Some Rare Earth Metal Chelates," Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1961.

(3) G. R. Choppin and J. A. Chopporian, *J. Inorg. Nucl. Chem.*, **22**, 97 (1961).

(4) J. Grenthe, *Acta Chem. Scand.*, **16**, 1695 (1962).

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

(6) R. W. Kolat and J. E. Powell, *ibid.*, **2**, 293, (1962).

(7) H. Deelstra, W. Vanderleen, and F. Verbeek, *Bull. Soc. Chim. Belges*, **72**, 632 (1963).

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

(9) J. E. Powell, R. S. Kolat, and G. S. Paul, *ibid.*, **3**, 518 (1964).

TABLE I
 FORMATION CONSTANTS OF RARE EARTH 1-HYDROXYCYCLOPENTANECARBOXYLATE CHELATE SPECIES

Metal	K_1	K_2	K_3	K_4	K_1/K_2	K_2/K_3	K_3/K_4
La	238 ± 2	47.5 ± 1.1	9 ± 2		5.01	5.28	...
Ce	324 ± 1	67.2 ± 0.7	12 ± 1		4.82	5.60	...
Pr	402 ± 1	83.3 ± 0.5	15 ± 0.5		4.83	5.67	...
Nd	463 ± 3	91.1 ± 1.8	12 ± 2		5.08	7.59	...
Pm	(536) ^a	(110) ^a	(25) ^a				
Sm	615 ± 2	140 ± 1	32 ± 1	12 ± 1	4.39	4.37	2.7
Eu	636 ± 6	157 ± 2	37 ± 2	...	4.05	4.24	...
Gd	698 ± 7	167 ± 5	45 ± 4	31 ± 4	4.18	3.71	1.4
Tb	792 ± 9	230 ± 6	54 ± 4	17 ± 2.5	3.44	4.26	3.2
Dy	958 ± 6	293 ± 4	59 ± 2.5	47 ± 2.5	3.27	4.97	1.3
Ho	1050 ± 6	302 ± 4	74 ± 2.5	31 ± 2	3.48	4.08	2.4
Er	1163 ± 10	381 ± 6	66 ± 3	53 ± 3	3.05	5.77	1.2
Tm	1288 ± 6	409 ± 4	98 ± 2	20 ± 1	3.15	4.17	4.9
Yb	1497 ± 10	474 ± 6	112 ± 1.5	21 ± 1.5	3.16	4.23	5.3
Lu	1663 ± 12	528 ± 7	140 ± 4	35 ± 2	3.15	3.77	4.0
Y	995 ± 10	273 ± 7	69 ± 5	49 ± 4.5	3.64	3.96	1.4
Mean dev	0.7%	1.6%	6.6%	8%			

^a Interpolated values.

the open-chain counterparts. A further and more important consideration was to deduce the coordination number of the chelates formed, based on stability constant and thermal decomposition data.

Early workers, using X-ray analysis to determine crystalline arrangements, have postulated nine-coordinate systems for certain lanthanide compounds. In 1939, Helmholtz¹⁰ deduced the structure of $\text{Nd}(\text{BrO}_3)_3 \cdot 9\text{H}_2\text{O}$ as six water molecules at the corners of a trigonal prism with three more out from the rectangular prism faces. Measurements on $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ¹¹ indicated a structure where all the La-O distances were approximately equal (2.72 Å). This configuration has been further supported by work on $\text{Ln}(\text{C}_2\text{H}_5\text{OSO}_3)_3 \cdot 9\text{H}_2\text{O}$ where Ln is Pr, Er, and Y.¹² Recently, the rare earth EDTA complexes were examined,¹³ and a coordination number of nine was assigned to the elements from lanthanum to samarium, while europium and gadolinium showed a transition to eight-coordination for the remaining elements.

Experimental Section

Preparations.—Rare earth perchlorate solutions were prepared from the oxides as described by Kolat and Powell.⁹ The starting materials were rare earth oxides from the Ames Laboratory of the Atomic Energy Commission with a purity of 99.9% or better. Standardization of these solutions was effected by precipitation of the rare earth as the oxalate and subsequent ignition of the oxalate to the oxide.

The carboxylic acid was synthesized from cyclopentanone (Columbia Organic Chemical Co., Inc.) by a cyanohydrin addition followed by hydrolysis with HCl to the organic acid. The latter was recrystallized from CCl_4 to a melting point of 104.5–105°. Ligand buffer solutions (0.2 M) were prepared by approximately half-neutralizing a weighed amount of the acid with a measured quantity of standard carbonate-free sodium hydroxide. Aliquots of the resulting solutions were then titrated with

standard KOH to determine the concentration of excess ligand acid.

Procedure.—Volumes of buffer ranging from 1.00 to 50.00 ml were added to 100-ml volumetric flasks together with constant amounts of metal ion solutions. To maintain the ionic strength at 0.1 M, calculated quantities of a sodium perchlorate solution were introduced. The supporting electrolyte solution was prepared by the addition of a slight excess of sodium hydroxide pellets to perchloric acid, filtering off insoluble hydroxides, and making the filtrate just acidic again. The molarity was determined by means of an H^+ -form ion-exchange resin and standard sodium hydroxide.

All pH measurements were recorded at $25.00 \pm 0.05^\circ$ with a Beckman Research pH meter, using glass and calomel electrodes. The latter contained a saturated KCl solution. The Model 1019 has a claimed relative accuracy of ± 0.001 pH unit over any range of 3 pH units. To avoid activity coefficient corrections, standardization of the pH meter was carried out frequently with a hydrochloric acid solution of known pH adjusted to $\mu = 0.1$ M with sodium perchlorate.

The calculated formation constants and their ratios are reported in Table I.¹⁴

Solid Chelates.—The method of preparation used was to stir overnight stoichiometric (3:1) quantities of the ammonium salt of the 1-hydroxycyclopentanecarboxylate (HCPC) (pH ~6.0) in solution with six-hydrated rare earth chlorides, the latter having been oven dried at 60°. The precipitates were filtered under vacuum and washed with distilled water until chloride free. The solids were air dried before igniting samples in porcelain crucibles to determine their rare earth contents. Thermal decomposition of individual salts was carried out for 14 hr, using the thermobalance technique, over a temperature range of 25–500°. Knowing the initial and final weights of the sample and oxide, respectively, the hydration numbers were estimated from the recorded weight losses and are presented in Table II.

Method of Calculation

The β_n values for each rare earth were computed on an IBM 7074 computer from the data from 20 to 25 solutions per metal ion. The measured change in

(10) L. J. Helmholtz, *J. Am. Chem. Soc.*, **61**, 1544 (1939).

(11) E. B. Hunt, R. E. Rundle, and A. J. Stosick, *Acta Cryst.*, **7**, 106 (1954).

(12) D. R. Fitzwater and R. E. Rundle, *Z. Krist.*, **112**, 362 (1959).

(13) J. E. Hoard, L. Byungkook, and M. D. Lind, *J. Am. Chem. Soc.*, **87**, 1612 (1965).

(14) Detailed tables of data have been deposited as Document No. 8763 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$2.50 for photoprints, or \$1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

TABLE II
HYDRATE LEVELS AND TEMPERATURES ($^{\circ}\text{C}$) AT WHICH
DEHYDRATION COMMENCES OBSERVED DURING THE THERMAL
DECOMPOSITION OF RARE EARTH
1-HYDROXYCYCLOPENTANECARBOXYLATE HYDRATES

Metal	3H ₂ O	2.5H ₂ O	2H ₂ O	1.5H ₂ O	1H ₂ O	Dehy- dration achieved	Onset of degra- dation
La				35		110	222
Ce				37		109	143
Pr				37		112	238
Nd				35		110	220
Pm							
Sm		86				115	197
Eu		65			86	136	170
Gd		76			96	147	179
Tb	66		93		124	149	176
Dy	77				115	151	175
Ho	85				122	157	177
Er	91				127	145	173
Tm	95					137	174
Yb	96					141	182
Lu	98					143	178
Y	93				113	151	202

hydrogen ion afforded a ready means of determining the degree of complex formation when the metal ion and ligand concentrations were known. The theoretical treatment of these calculations was presented by Leden^{15a} and Fronaeus^{15b} and has been reviewed by Sonesson¹ and Rossotti and Rossotti.¹⁶ The original computer program¹⁷ was written for β_1 , β_2 , and β_3 systems and has been modified for the present studies to include the calculation of β_4 values. The procedure consists of a least-squares curve fitting of a polynomial equation which has coefficients equal to the successive stability constants. From the experimental data, \bar{n} , the Bjerrum ligand number, and $[\text{A}^-]$, the total anion concentrations, were calculated, using individual dissociation constants (K_a) for each measured sample. The proper K_a values ranging from 1.13 to 1.03×10^{-4} , were interpolated from a plot of K_a against $[\text{A}^-]$ arrived at by a separate experiment.

Discussion

The thermal decomposition results seem to substantiate a coordination number of nine for the rare earth HCPC species. From lanthanum to neodymium there is an apparent loss of 1.5 water molecules. However, these are probably not coordinated waters because of the low temperature (36°) at which dehydration commences. So it may be assumed that, if nine-coordination prevails, there are three tridentate ligands electrostatically bonded to the central cations.

Yttrium and the rare earths from terbium to erbium form chelates containing three molecules of water. Thulium, ytterbium, and lutetium chelates show the trihydrate, but no stable lower hydrates are apparent. From the observed stoichiometries of the freshly prepared chelates, the cations from terbium through lute-

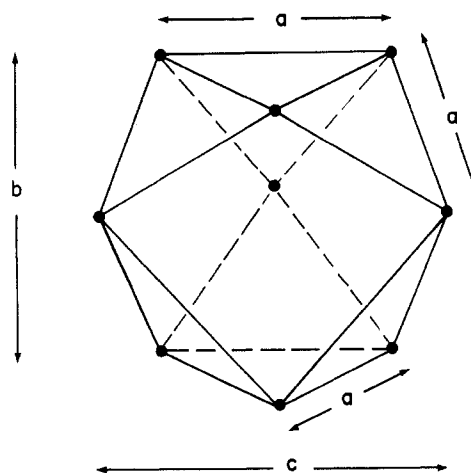


Figure 1.—Trigonal prism +3 scale model. The distances from the geometric center to the nine coordination sites are equivalent ($=0.866a$). $b = 1.291a$; $c = 1.500a$.

tium appear to be nine-coordinate also, but form chelates in which the ligand is attached bidentately.

With samarium, europium, and gadolinium the data indicate the presence of 2.5 waters. Probably with these elements, owing to their decreasing cationic radii, the ligand exhibits a mixture of bidentate and tridentate bonding, as borne out by the ratios in Table I. Hoard and his co-workers¹³ have concluded that europium and gadolinium EDTA complexes are transitional between a nine-coordinated samarium complex and a terbium complex which is eight-coordinated.

This evidence supports a model with nine coordination sites as a basis for discussing the statistical ratios of the stability constants. The model chosen is the trigonal prism with three additional coordination sites projecting from rectangular prism faces; see Figure 1.

The theoretical K_1/K_2 ratio for a tridentate ligand coupling with this arrangement of coordination sites is 4.92, which agrees remarkably well with the 4.93 ± 0.12 average observed for the rare earths from lanthanum through neodymium, while the average value of 3.29 ± 0.19 from terbium through lutetium is in accordance with the theoretical statistical ratio (3.27) that should be observed if the ligand attached bidentately rather than tridentately to this configuration of coordination sites.

With this array of coordination sites and the assumption of tridentate bonding, whenever any two of the triangularly disposed clusters of three sites have been occupied by donor oxygen atoms of the ligand, the three coordination sites remaining are not located at the apices of an equilateral triangle. However, if one ignores this and assumes that the third ligand can bond in a tridentate fashion, the statistical correspondence of $K_1:K_2:K_3$ should be $(8/1):(13/8):(1/3)$. The statistical contribution to the K_2/K_3 ratio would then be $39/8 = 4.875$. When one considers the fact that some strain is of necessity introduced when the last tridentate ligand is accommodated, the values of K_2/K_3 varying from 5.28 (lanthanum) to 7.59 (neodymium) do not appear unreasonable.

(15) (a) I. Leden, Doctoral Dissertation, University of Lund, 1943; (b) S. Fronaeus, Doctoral Dissertation, University of Lund, 1948.

(16) F. J. C. Rossotti and H. Rossotti, "Determination of Stability Constants," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(17) W. R. Stagg and J. E. Powell, USAEC Report IS-727, 1963.

H₂O–H₂O exchange is undoubtedly more rapid than ligand–2H₂O exchange. Also one end of a bidentate ligand will frequently detach momentarily without the second bond breaking. Furthermore, if two similarly charged ligands were to attach originally side by side, a strong tendency would exist for one of the two addends to “walk rapidly” around to the other side of the coordination sphere merely by “stepping” into holes momentarily vacated by water molecules. If such an event occurs rapidly with respect to ligand–2H₂O exchange, then the predicted correspondence of $K_1:K_2:K_3$ with bidentate bonding on our nine-coordinate model would be (18/1):(11/2):(4/3). The K_2/K_3 ratio would, therefore, be $33/8 = 4.125$. If the value of K_2/K_3 for erbium (which appears to be out of line) is omitted, the average K_2/K_3 ratio for the heavier lanthanons (samarium through lutetium) and yttrium is 4.18 ± 0.24 .

Although it is apparent that LnA₄ species do exist in the cases of the heavier rare earths, the wide variance in K_3/K_4 ratios precludes their use in inferring structure.

The stability trend for the 1:1 lanthanide HCPC species (Figure 2) closely resembles that of the mono-alkyl-substituted glycolates. The stability order of the chelates for the rare earth is *t*-butylglycolate < isopropylglycolate < ethylglycolate < HCPC < dimethylglycolate (α -hydroxyisobutyrate). However, a comparison of the stabilities of the 1:1 lanthanide chelates of HCPC with its most closely related open-chain analog (diethylglycolate)¹⁸ reveals a startling anomaly. The latter chelating agent shows reduced stability from lanthanum to neodymium but becomes greater from europium to lutetium. One is led, therefore, to hypothesize that, while the dentate character of the lanthanide–HCPC ligand changes from tridentate at neodymium to bidentate at terbium, the reverse is possibly true for the diethylglycolate species. The K_1/K_2 ratios obtained for lanthanum, praseodymium, and neodymium diethylglycolates are 3.4, 3.1, and 3.1, respectively, which are compatible with the value of 3.27 expected for bidentate behavior. For the heavy rare earths, gadolinium through lutetium (including yttrium), the K_1/K_2 ratios for diethylglycolate average

(18) J. E. Powell, G. S. Paul, B. D. Fleischer, W. R. Stagg, and Y. Suzuki, USAEC Report IS-900, 1964.

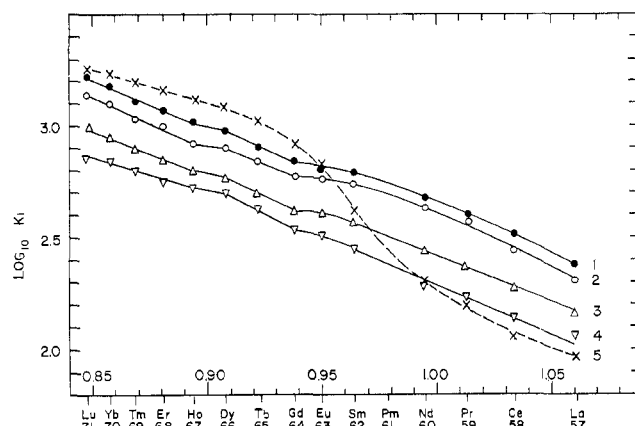


Figure 2.—Logarithm of the stability constant of the 1:1 rare earth chelate vs. ionic radius: (1) 1-hydroxycyclopentanecarboxylate, (2) ethylglycolate, (3) isopropylglycolate, (4) *t*-butylglycolate, (5) diethylglycolate.

8.0, which is consistent with tridentate behavior (theoretical is 4.92), if one considers the additional steric blocking effect of the bulky ethyl groups as the ionic radius of the central cation decreases. The HCPC ligand apparently exhibits little steric effect because the ends of its “ethyl” groups are bonded. This prevents rotation of the alkyl groups and the subsequent blocking of adjacent coordination sites. One is led to the conclusion that the bond angle between the alkyl substituents is wider in diethylglycolate than in the HCPC ligand and that the separation of the hydroxyl and carboxyl groups is therefore less, so that tridentate bonding with diethylglycolate becomes possible with the smaller heavy rare earth cations and no longer possible for the larger light rare earth cations.

In summary, the evidence presented here substantiates the theory that the rare earth HCPC chelates have a common coordination number of nine. A change in dentate character of this ligand from tridentate to bidentate is apparent in going from the lighter to the heavier rare earths, indicating a dependence on the decreasing atomic radius. The dentate character in the case of diethylglycolate, however, appears to be reversed.

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