

observe a partially resolved doublet<sup>10</sup> adjacent to the methyl resonance in the spectrum of the deuterated compound at 120°. Obviously, this doublet arises from the  $-\text{CH}_2-$  protons and confirms the arguments proposed above. Therefore, we conclude that the ligands undergo a rocking and twisting motion at elevated temperatures. This would also explain the observed temperature dependence of the  $\text{Co}(\text{en})_3^{3+}$  complex spectra.

#### Experimental Section

Compounds used in this study were the chloride, sulfate, nitrate, and acetate salts of the  $\text{Co}(\text{en})_3^{3+}$  complex<sup>11</sup> and  $\text{D}[\text{Co}((+)\text{pn})_3]\text{Cl}_3$ .<sup>12,13</sup> The pmr spectra were obtained on a Varian A-60 spectrometer equipped with a variable-temperature probe. The samples were degassed and sealed under vacuum to eliminate any possibility of line broadening by dissolved oxygen. Tetramethylsilane was used throughout as an internal standard.

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(10) The bridgehead proton, which we expect to give an unresolved multiplet, can now be assigned to the broad resonance that is visible as a shoulder on the low-field side of the methylene doublet in the 120° spectrum.

(11) J. B. Work, *Inorg. Syn.*, **2**, 221 (1946).

(12) F. P. Dwyer, A. M. Sargeson, and L. B. James, *J. Am. Chem. Soc.*, **86**, 590 (1964).

(13) A sample of  $\text{D}[\text{Co}((+)\text{pn})_3]\text{Cl}_3$  was kindly supplied by Dr. J. Fujita, Tohoku University, Tohoku, Japan.

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## Lanthanide 2-Hydroxy-2-methylbutanoate Chelate Stabilities<sup>1</sup>

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In an earlier note<sup>2</sup> it was proposed that the picolinate anion bonds to lanthanons in a purely bidentate manner. This conclusion was reached through an application of Bjerrum's theory<sup>3</sup> that ratios of successive step formation constants depend principally upon individual formation and decomposition statistics relating to the  $\text{AB}_{n-1}$  and  $\text{AB}_n$  chelate species. Bjerrum's theory can be expressed generally as  $*P = *K_{n-1}/*K_n = SRT$ , where  $*P$  is the observed ratio of true thermodynamic step formation constants (at infinite dilution or zero ionic strength),  $S$  is the purely statistical contribution,  $T$  is the electrostatic factor, and  $R$  is a general "rest" or "everything else" factor (which includes ligand asymmetry and steric effects).<sup>3</sup>

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2522.

(2) J. E. Powell and J. W. Ingemanson, *Inorg. Chem.*, **7**, 2459 (1968).

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

At ionic strength other than zero, the observed ratio  $P$  depends upon the ionic strength as well as the factors  $S$ ,  $R$ , and  $T$

$$P = K_{n-1}/K_n = (*K_{n-1}/*K_n)f(\mu) = *Pf(\mu) = SRTf(\mu) \quad (1)$$

In the case of the lanthanide picolinate species,<sup>2</sup> it was shown that the  $K_1/K_2$  ratio at  $\mu = 0.1$  was essentially constant at about 4. Thus, the observed values of  $P$  fell between the purely statistical values of 3.27 and 4.92 which one predicts from the supposition that picolinate anion functions bidentately or tridentately, respectively, in its associations with nine-coordinate lanthanons (in aqueous media).  $T$  has been estimated<sup>4</sup> to be about 1.5 and  $f(0.1)$  is about 0.67. Thus, since it is difficult to imagine anything giving rise to an  $R$  factor less than unity, it is clear that picolinate *does not* bond tridentately through the nitrogen atom and both carboxyl oxygen atoms.

Although it has been suspected for some time,<sup>5</sup> the following stability constant data (for the first time) clearly demonstrate that homologs of the glycolate anion (substituted  $\alpha$ -hydroxycarboxylate ligands) can function either bidentately or tridentately, depending on the ionic radius of the presumably nine-coordinate aquated lanthanide cation. (The short nonbonded distance between the two carboxyl oxygen atoms dictates that they do not simultaneously occupy coordination sites on a regular nine- or ten-coordinated lanthanon. It is suggested that tridentate liganacy in this instance involves attachment of the second carboxyl oxygen atom to a hydrogen atom of a coordinated water molecule *via* a hydrogen bond to give a  $-\text{Ln}-\text{O}-\text{H}-\text{O}-\text{C}-\text{O}-$  ring rather than  $-\text{Ln}-\text{O}-\text{C}-\text{O}-$ .) These data in no way discredit the likelihood that the coordination number of the lighter (larger) cations of the series ( $\text{La}^{3+}-\text{Nd}^{3+}$ ) may be 10 rather than 9. At least one regular ten-coordinate array (Archimedean antiprism + 2) leads to the same predicted  $S$  value (4.92) as the nine-coordinate (trigonal prism + 3) array of sites in its associations with tridentate ligands.<sup>2,5</sup> Indeed, it is even likely that a change from nine- to ten-coordination is the factor that permits accommodation of the  $\alpha$ -hydroxycarboxylate ligand as a nominally tridentate entity.

#### Experimental Section

**2-Hydroxy-2-methylbutanoic Acid Buffer.**—Reagent grade 2-hydroxy-2-methylbutanoic acid was obtained commercially and purified further by recrystallization from hot carbon tetrachloride. The purified product (mp 72–73°) was used to prepare buffer stock solutions, 0.1 *N* in HL and 0.1 *N* in KL, in which the precise concentrations of acid and salt were determined by standard stoichiometric techniques.

**Ionization Constants of the Acid.**—Series of 20–25 individual dilutions of the buffer (all adjusted to 0.10 *M* ionic strength by appropriate additions of  $\text{KNO}_3$ ) were prepared. The volumetric flasks were carefully equilibrated in a 25° water bath and the  $\text{pH}_c$  of each was read to a precision of 0.0002 unit, using the

(4) P. G. Manning, *Can. J. Chem.*, **43**, 2911 (1965); **44**, 3057 (1966).

(5) J. E. Powell and D. L. G. Rowlands, *Inorg. Chem.*, **5**, 819 (1966).

TABLE I  
STEP FORMATION CONSTANTS FOR THE 1:1, 2:1, AND 3:1  
2-HYDROXY-2-METHYLBUTANOATO LANTHANIDE CHELATE SPECIES

Element	$10^{-3}K_1$	$10^{-2}K_2$	$10^{-2}K_3$	$K_1/K_2$
La	0.22 (0.20) <sup>a</sup>	0.38 (0.42)	0.2 (0.01)	5.8
Ce	0.32 (0.27)	0.53 (0.54)	0.16 (0.08)	6.0
Pr	0.35 (0.35)	0.59 (0.65)	0.13 (0.12)	5.9
Nd	0.45 (0.41)	0.69 (0.78)	0.21 (0.19)	6.5
Pm				
Sm	0.63 (0.63)	1.40 (1.56)	0.32 (0.34)	4.5 (4.0)
Eu	0.80 (0.81)	2.00 (1.91)	0.40 (0.44)	4.0 (4.2)
Gd	0.88 (0.91)	2.20 (2.29)	0.38 (0.47)	4.0 (4.0)
Tb	1.25 (1.24)	2.99 (3.07)	0.54 (0.55)	4.2 (4.0)
Dy	1.45 (1.55)	3.50 (3.52)	0.53 (0.74)	4.1 (4.4)
Ho	1.72 (1.71)	4.29 (4.21)	0.71 (0.71)	4.0 (4.1)
Er	2.09 (1.97)	5.39 (4.94)	0.96 (0.90)	3.9 (4.0)
Tm	2.32 (2.09)	5.77 (5.29)	(0.84)	4.0 (4.0)
Yb	2.69 (2.56)	6.69 (6.16)	1.08 (1.08)	4.0 (4.2)
Lu	2.79 (2.70)	7.03 (6.87)	1.12 (1.18)	4.0 (3.9)

<sup>a</sup> The data in parentheses are from an unpublished M.S. thesis of J. W. I.

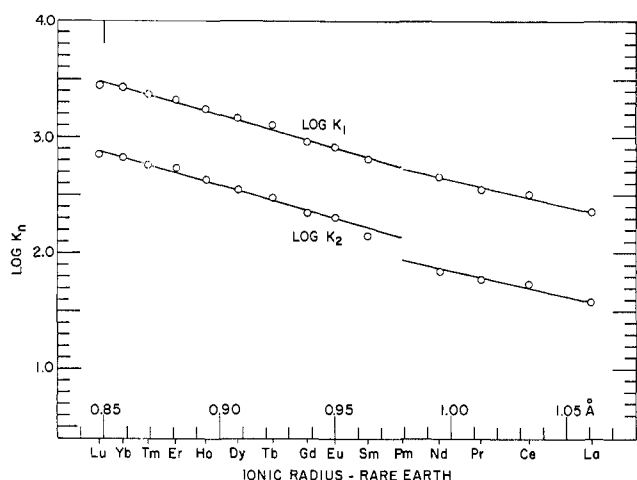


Figure 1.—Stabilities of the 1:1 and 2:1 2-hydroxy-2-methylbutanoatolanthanide chelate species.

Beckman research pH meter, Model 1019, standardized *vs.* precisely known concentrations of mineral acid (likewise at  $\mu = 0.100$  ( $\text{KNO}_3$ )).  $K_a$  was determined as a slightly variable linear function of ligand anion concentration by means of a least-squares program developed in this laboratory. The variable ionization parameter at  $25^\circ$ ,  $\mu = 0.100$  ( $\text{KNO}_3$ ), was found to be  $K_a = (1.86 - 2.4[\text{L}^-]) \times 10^{-4}$  up to  $[\text{L}^-] = 0.03 M$ .

**Stability Constant Determinations.**—In the case of each rare earth, a similar series of 25 dilutions of acid-salt buffer was prepared in 100-ml volumetric flasks to which 4.00 ml of 0.100 *M* rare earth nitrate ( $[\text{R}^{3+}]/[\text{NO}_3^-] = 0.333$ ) and appropriate varying amounts of  $\text{KNO}_3$  had been introduced. The resulting solutions were all at ionic strength 0.100 (after diluting to volume) and 0.004 *M* in total rare earth, but each contained a different known amount of HL-KL buffer. After equilibrating at  $25^\circ$ , the  $\text{pH}_c$  of each solution was read to 0.0002 unit, using the Beckman research pH meter (although the reproducibility of the machine is probably no better than 0.001 unit). The  $\beta_n$  values and individual stepwise formation constants  $K_n$  were computed on the 360/60 IBM computer.

### Results and Discussion

Values of  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_1/K_2$  for the individual rare earth chelate species are tabulated in Table I. Although it was apparent that 1:4 rare earth chelate species were formed in the case of the heavier rare

earths (Sm-Lu), the  $K_4$  values found were not considered sufficiently precise to warrant publication.

If one disregards data for the lighter (larger) lanthanons when  $\log K_n$  values are plotted *vs.* ionic strength, the Lu-Sm  $\log K_1$  points may be fitted on one straight line and the corresponding  $\log K_2$  values may be fitted to another line parallel to the first but 0.60 log unit lower. The Nd-La  $\log K_1$  and  $\log K_2$  data approximate a similar pair of parallel straight lines separated by 0.78 log unit. That is, the  $K_1/K_2$  ratios for the heavier lanthanides (Lu-Sm) and the lighter lanthanides (Nd-La) are distinctly different and average about 4.0 and 6.0, respectively.

Proceeding from the reasonable hypothesis that tripositive lanthanons are either nine-coordinate or that the larger cations (La-Nd) are ten-coordinate while the rest are nine-coordinate in aqueous media, one is led by the relative magnitude of the change in average  $K_1/K_2$  ratios to the assumption that 2-hydroxy-2-methylbutanoate functions tridentately in bonding to large lanthanons but only bidentately to the smaller ones (Sm-Lu). It is highly significant that  $6.0/4.0 = 4.92/3.27$ , since 4.92 is the purely statistical ratio predicted for the first two consecutive step formation constants on the basis of a tridentate ligand and either a nine- or a ten-coordinate cation while 3.27 is the ratio calculated for a bidentate ligand and a nine-coordinate cation. It is apparent that  $P/S = RTf(0.1) = 1.22$  in either case; thus it may be presumed that tridentate and bidentate ligancies are associated, in this instance, with identical electrostatic and steric factors. Considering this and noting further that  $\log K_1$  values for the lighter lanthanons (La-Nd) deviate upward very little from an extension of the straight line drawn through the other points, one supposes that formation of a third attachment (in changing from bidentate to tridentate behavior) involves nothing more than formation of a hydrogen bond between the second (previously uninvolved) carboxyl oxygen atom and an adjacent molecule of coordinated water. This supposition, based on lack of evidence (in the  $\log K_1$  trend) that entropy

has increased, is consistent with the observation that separation of carboxyl oxygen atoms, in general, is insufficient to allow both atoms to coordinate directly with a single metal cation in lieu of water molecules.

The value of  $f(\mu)$  at  $\mu = 0.1$  (the activity correction to the  $K_1/K_2$  ratio in this case) is estimated to be about 0.67, assuming that

$$\log \gamma_i = -0.509Z_i^2 \left\{ \sqrt{\mu}/(1 + 2\sqrt{\mu}) - 0.2\mu \right\}$$

This assumption yields  $RT = 1.83$ , setting a practical upper limit of 1.83 on the coulombic factor  $T$ , since it is difficult to imagine an  $R$  factor ever less than unity because steric and asymmetry factors tend to attenuate affinity of the acceptor for subsequent ligands. Following this line of argument, previous data of Powell and Rowlands (average  $K_1/K_2 = 4.93$  for elements La–Nd and 3.29 for elements Tb–Lu) establish an even smaller upper limit of 1.5 on the coulombic factor for the case of lanthanide associations with 1-hydroxycyclopentanecarboxylate, an analogous ligand. The present findings and those of Powell and Rowlands could be correlated rather simply by assuming that  $T = 1.5$ , as Manning has proposed.<sup>4</sup> For this assumption to be valid it would be necessary that the rest factor  $R$  (primarily steric in origin) be unity in the case of small "tied together" alkyl groups as in 1-hydroxycyclopentanecarboxylate, but greater when the alkyl substituents of the  $\alpha$ -hydroxycarboxylate entity are bulky and/or free to cause local disturbances by rotating. In the present case,  $R$  would then be 1.22, because the ethyl radical is not linear and can rotate about its attachment to the  $\alpha$ -carbon atom. While the smaller ratios of Powell and Rowlands strongly suggest that  $T$  does not exceed a value of 1.5 in these systems, the possibility that the coulombic factor is actually somewhat less than this maximum figure cannot be ruled out. Consequently, it may be that  $R$  actually exceeds unity in the case of HCPC and is correspondingly greater than 1.22 in the case of the HMBA anion. Certainly it appears safe to assume that  $1.0 < T < 1.5$  for the process  $\text{Ln}^{3+} \rightarrow \text{LnL}^{2+} \rightarrow \text{LnL}_2^+$ , that  $1.0 < R < 1.5$  in the case of HCPC, and that  $1.22 < R < 1.83$  with HMBA.

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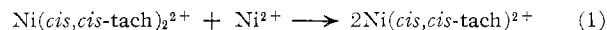
### Hindered Ligand Systems. III. Kinetics of the Dissociation of the Nickel(II) Complex of *cis,cis*-1,3,5-Triaminocyclohexane

BY R. F. CHILDERS AND R. A. D. WENTWORTH

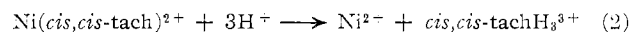
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The bis complexes of *cis,cis*-1,3,5-triaminocyclohexane,  $M(\text{cis,cis-tach})_2^{2+}$  ( $M = \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}$ ), were recently prepared and characterized.<sup>1</sup> As with the

bis complexes<sup>2</sup> of Co(III) and Rh(III), all available evidence indicated that the ligands are bonded to the trigonal faces of an octahedron. In addition, it was found that in the case of Ni(II) only, it was possible to prepare and isolate the mono complex according to



(with waters of hydration omitted). Subsequent studies of this new species led to the discovery of its extraordinary kinetic stability in the presence of mineral acids. The half-life of the reaction



in 5 *M* HNO<sub>3</sub> is about 7 min at 25°. In contrast, the dissociation of  $\text{Ni}(\text{dien})^{2+}$ <sup>3</sup> in solutions of the same acidity is nearly instantaneously complete.

A more detailed study of the dissociation of  $\text{Ni}(\text{cis,cis-tach})^{2+}$  in 0.5–5 *M* HNO<sub>3</sub> has now been completed and the results are reported herein.

#### Experimental Section

$\text{Ni}(\text{cis,cis-tach})(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ .—The preparation of this compound was previously described.<sup>1</sup> However, eq 1 tends to be reversed in hot alcohol, which is the prescribed solvent for recrystallization, and the desired product is inevitably contaminated with small quantities of the bis complex. This occurrence was prevented by recrystallizing the mono complex from 95% alcohol containing excess  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . Generally, large prismatic crystals of the desired compound were obtained from the slow evaporation of saturated solutions. The complex could be obtained more rapidly by removing the solvent with a rotary evaporator. This technique provided poorly formed crystals which, however, were quite satisfactory for kinetic purposes. In either case the crystals were washed with a small quantity of water, followed by alcohol and then ether.

The spectrum of this compound in aqueous solution (with the ionic strength adjusted to 1.00 with NaNO<sub>3</sub>) consists of bands at 361 ( $\epsilon$  11.2), 588 ( $\epsilon$  9.2), and 969 m $\mu$  ( $\epsilon$  8.8).

**Kinetic Measurements.**—The initial studies were conducted in HNO<sub>3</sub> solutions with  $[\text{H}^+] \geq 1$  *M*. In each run a precisely weighed quantity of the complex was dissolved in about 3 ml of H<sub>2</sub>O, followed by addition of 5–15 *M* HNO<sub>3</sub>. Later studies were conducted at  $[\text{H}^+] < 1$  *M* in solutions whose ionic strength was adjusted to 1.00 with NaNO<sub>3</sub>. These solutions were prepared by dissolving a precisely weighed quantity of the complex in a thermostated stock solution which contained the desired quantities of HNO<sub>3</sub> and NaNO<sub>3</sub>. All samples were then well mixed and transferred to a thermostated sample cell in the spectrophotometer. The "zero time" spectrum was then recorded (approximately 4 min after dilution).

In the absence of any bis complex, isobestic points were observed at  $385 \pm 1$  ( $\epsilon$  4.9),  $468 \pm 1$  ( $\epsilon$  0.33), and  $686 \pm 2$  m $\mu$  ( $\epsilon$  1.8) throughout a kinetic run. If the compound had not been recrystallized in the presence of excess  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , true isobestic points did not exist through the early stages of a reaction. Using the absorbancy at 575 m $\mu$ , the pseudo-first-order rate constant was derived from the equation  $\ln [(A_t - A_\infty)/(A_0 - A_\infty)] = -k_{\text{obs}}t$ . In the initial studies of the dissociation at  $[\text{H}^+]$  between 1 and 5 *M*, rate plots generally showed a slight curvature through about the first 25–50% of the reaction but were then linear to at least 94% completion. The major portion of the curvature was traced to local heating caused by dilution of relatively concentrated acid solutions. An additional cause was traced to the method of recrystallization since the crystals used in these runs were not recrystallized from solu-

(2) R. A. D. Wentworth and J. J. Felten, *J. Am. Chem. Soc.*, **90**, 621 (1968).

(3) In this paper the following abbreviations have been used: dien, bis(2-aminoethyl)amine (diethylenetriamine); dapa, bis(3-aminopropyl)amine; ptn, 1,2,3-propanetriamine.

(1) R. A. D. Wentworth, *Inorg. Chem.*, **7**, 1030 (1968).