

for the ready hydrolysis of hexachlororhenate(IV) ion in alkaline medium. It also may reflect an inability of chloride ion to stabilize oxidation states lower than four sufficiently well to permit their formation in these circumstances.

It may be mentioned that the two compounds $K_4\text{ReO}_2(\text{CN})_4$ and $K_3\text{Re}(\text{OH})_3(\text{CN})_3$ have not been reported previously. Some evidence for the existence of a red rhenium(IV) compound and a

green rhenium(V) compound also has been given above, but characterization of these materials must await further work.

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The Mechanism of Racemization of the Hexadentate Complex of Cobalt(III) with Ethylenediaminetetraacetic Acid

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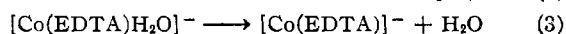
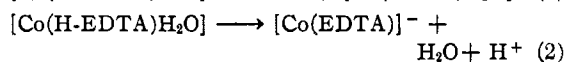
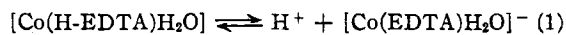
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The rate of racemization of the optically active hexadentate complex of cobalt(III) with ethylenediaminetetraacetic acid, $d\text{-}[\text{Co}(\text{EDTA})]^-$, has been determined as a function of $p\text{H}$ and temperature. Racemization proceeds very slowly in acidic media by a $p\text{H}$ -independent path, for which $\Delta E_a = 40.6$ kcal./mole and $\Delta S^\ddagger = 20.6$ cal./deg. mole. The reaction is explained in terms of a unique intramolecular inversion process. A strong base catalysis of racemization also has been observed, providing a second order path for which $\Delta E_a = 32.7$ kcal./mole and $\Delta S^\ddagger = 54.7$ cal./deg. mole. In view of the structure of the cobalt complex and the details of its reaction in basic media, the possibility exists that the mechanism involves nucleophilic attack by an OH^- ion with simultaneous increase of the coordination number of the central atom to seven and the formation of a symmetrical intermediate.

Introduction

Dwyer, Gyarfás, and Mellor¹ reported that the optically active forms of $[\text{Co}(\text{EDTA})]^-$ are stable in aqueous solutions at 30° for two weeks, and that racemization occurs at 100° with an approximate half-life of 170 minutes. They suggested that the mode of racemization might depend on the breaking of at least one Co–O bond and that racemization could occur at elevated temperatures through a five-coordinate intermediate in which a certain group in the partially dissociated ligand is temporarily replaced by a solvent molecule. Detailed study of the stereochemical model reveals that the multiply connected nature of the ligand requires that any racemization proceeding through a dissociative mechanism must be accompanied by extensive rearrangement or by reduction of the penta- or hexadentate linkage to tetradentate. Also, earlier studies on the conversion of pentadentate cobalt–EDTA complexes

reveal that dissociative mechanisms lead to substitution with complete retention of enantiomeric configuration.^{1–3} Since the attainment of a tetradentate structure must proceed stepwise, the process should be aided by increased hydrogen ion concentrations. This follows from the equilibrium given in equation 1 and the fact that the conversion of $[\text{Co}(\text{H-EDTA})\text{H}_2\text{O}]$ into the hexadentate complex (equation 2) is slower than the corresponding reaction for $[\text{Co}(\text{EDTA})\text{H}_2\text{O}]^-$ (equation 3).^{2,4}



Base acceleration of the substitution reactions of cobalt(III) amines has been explained on the

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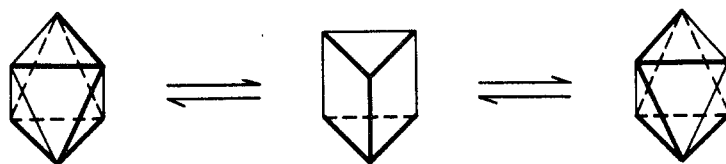
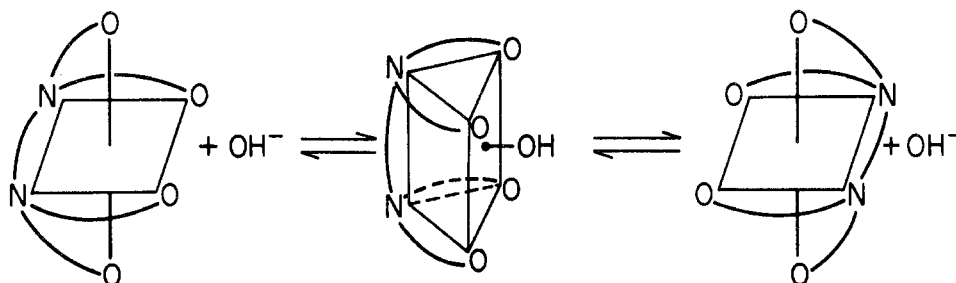
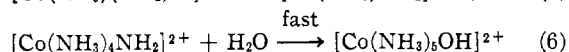
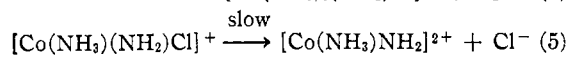
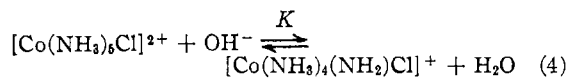
(a) Thermal Racemization of d -CoEDTA $^-$ (b) Base Catalyzed Racemization of d -CoEDTA $^-$.

Fig. 1.

basis of the S_N1cb mechanism⁵ as detailed in the example below.



The assumption that this represents the most probable mode of interaction of the hydroxide ion with complexes of cobalt(III) would lead to the prediction that the rate of racemization of d -[Co(EDTA)] $^-$ should be insensitive to hydroxide ion. The absence of ionizable hydrogen atoms on the donor atoms of the tetranegative ligand demands this conclusion if attention is restricted to such mechanisms.

The data contained herein stand in sharp contrast to these expectations. At temperatures above 80°, in acidic media, the racemization proceeds slowly and in accord with the first order law, without decomposition or appreciable side reaction. As shown in Table I, the rate is independent of pH over the range from 2 to 4. A pK value of about 3 has been found for the free carboxyl group in the pentadentate complex. Consequently, if a dissociative mechanism were involved, the pentadentate intermediate should give rise to a pH

dependence within the range studied. Also, a dissociative process should be associated with a negative entropy of activation.^{2,3} The data reported here reveal a positive entropy change of 20.6 cal./deg. mole. The activation energy is 40.6 kcal./mole.

TABLE I
RATE OF RACEMIZATION OF [Co(EDTA)] $^-$ IN ACIDIC MEDIA

T , °C.	pH	k , hr. $^{-1}$
100	2.0	0.015
100	3.0	.014
100	4.0	.014
90	2.0	.0032
90	3.0	.0032
90	4.0	.0032
85	2.0	.0013

Bailar⁶ has proposed an intramolecular mechanism for the racemization of d -[Co(EDTA)] $^-$. This scheme (Fig. 1a) does not require the breaking of Co-O bonds and, accordingly, should be insensitive to pH in the acid region. Further, the stretching of at least four metal-ligand bonds in forming the symmetrical transition state might easily give rise to the high activation energy observed. It appears highly likely that this is the appropriate mechanism for the racemization of [Co(EDTA)] $^-$. Although it has been pointed out that such an intermediate might form without

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley, New York, N. Y., 1958; R. G. Pearson, H. H. Schmidtke, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 4434 (1960).

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extension of the bond distances, such an occurrence would require all adjustments to be made by reconstituting the conformations of the five chelate rings. Extension of the metal ligand bonds would permit more equitable distribution of strain.

The data summarized in Table II also militate against the dominant role of dissociative processes in the racemization of $[\text{Co}(\text{EDTA})]^-$, since there obviously exists a relatively rapid path which is dependent in the first order on the concentration of hydroxide ion. The activation energy is 32.7 kcal./mole and the entropy of activation is 54.7 cal./deg. mole.

TABLE II
RATE OF RACEMIZATION OF $[\text{Co}(\text{EDTA})]^-$ IN BASIC MEDIA

T, °C.	(OH ⁻)	$k_2, M^{-1} \text{ min.}^{-1}$
35	2.14×10^{-4}	33.9
35	1.83×10^{-2}	31.1
35	1.02×10^{-1}	32.5
		k_2 (av.) 32.5 ± 1.4
44	1.72×10^{-4}	141
44	3.80×10^{-4}	166
		k_2 (av.) 154 ± 13
53	6.17×10^{-5}	624
53	9.12×10^{-5}	634
		k_2 (av.) 629 ± 5

A promising explanation of the base-catalyzed path involves the assumption that a seven-coördinate symmetrical intermediate is formed, as shown in Fig. 1b. The very large positive entropy may be associated, in part, with desolvation of the attacking hydroxide ion. The apparent nucleophilic attack of hydroxide ion on the central atom of $[\text{Co}(\text{EDTA})]^-$ and the likelihood of intramolecular racemization without dissociation in acidic

media are of particular interest since the reactions of cobalt(III) usually are described in terms of unimolecular dissociation mechanisms.

An alternate possibility has not been adequately eliminated. As Basolo⁷ has suggested, attack on the acyl carbon atom of a coördinated carboxyl group might conceivably alter the system sufficiently to promote intramolecular rearrangement. The results of experiments designed to test this possibility will be reported along with studies on the kinetics of the base hydrolysis reaction.

Experimental

Optically active potassium ethylenediaminetetraacetatocobaltate(III) 2-hydrate was prepared by the method of Dwyer and Garvan,⁸ using optically active *cis*-dinitro-bis-(ethylenediamine)-cobalt(III) bromide as a resolving agent. The pH of the reacting solution was adjusted with nitric acid, or a suitable buffer, and the ionic strength of the solution was adjusted with nitrate salts. The stoppered flask containing this solution was placed in a thermostat and the samples were withdrawn periodically for the measurement of optical rotations.

The optical rotations were determined with a precision of $\pm 0.003^\circ$ using a Rudolph Model 80 photoelectric polarimeter, and the ratio of the rotation at a given time to that of a sample withdrawn immediately after the initiation of the reaction was taken as a measure of the extent of the reaction. Most of the rotations were measured using a Hanovia Xeon high pressure arc at a wave length of 450 m μ or by using a mercury lamp at a wave length of 436 m μ . The latter is more convenient. The zero of the polarimeter was determined using the racemate at the same concentration as was used in measuring rotation. A one-decimeter tube was used for all readings.

Acknowledgment.—The financial support of the National Science Foundation is gratefully acknowledged.

(7) F. Basolo, private communication.

(8) F. P. Dwyer and F. L. Garvan, *Inorg. Syntheses*, **VI**, 192 (1960).