the release of the phosphato ligand than would be the case for a proton sited on a nonbridging oxygen. It seems reasonable to postulate that the greater the protonation of the complex the greater is the probability that the bridging oxygen will be protonated. One cannot, of course, rule out the possibility that protonation of the oxygens on phosphorus is sufficient. The activation parameters for the three protonated species are rather similar which fact may be due to a combination of bond weakening and solvation effects.

An insight into the role of water in the hydrolysis of P_3 was perhaps gained by the observation that the hydrolysis rate law for this species is:[3] rate = $k_3 \cdot [P_3]a_W$. This was rationalized in terms of an equilibrium being established between P_3 and an intermediate P_3' consisting of P_3 and a water molecule combined in a seven-coordinated species, *i.e.*

$$P_3 + H_2O \rightleftharpoons P_3' \xrightarrow{k'} Co(NH_3)_5H_2O^{3+} + H_3PO_4$$

$$\text{rate} = k'[P_3']f_{P_3} = k''[P_3]f_{P_3}a_W/f_{P_3}' = k[P_3]a_W$$

where f_{P_3}/f_{P_3}' is assumed to remain constant, f and a_W represent an activity coefficient and the activity of water, respectively, and k is the experimental rate constant. Similar mechanisms have been proposed for the hydrolysis of several other complex cobalt(III) species.[9,10] A dissociative or solvent-assisted dissociative mechanism would also be possible as has been most often postulated. Perhaps one should keep an open mind on this question for these systems.

The $\Delta S^{\ddagger}$ values for both P_2 and P_1 are more negative than that for P_3, which suggests that these species might also hydrolyze *via* an associative mechanism.

The markedly higher $\Delta H^{\ddagger}$ values observed for the hydrolysis and base-catalyzed hydrolysis of $Co(NH_3)_5PO_4^0$ might well be attributable to the fact that no protonation of the bridging oxygen is possible, and consequently a greater cobalt–oxygen bond energy exists than was the case for the protonated analogs. It could be argued that as a result an even greater amount of nucleophilic assistance from the incoming water molecule would be required in the transition state, leading to an associative activation process. The small differences between the base hydrolysis and hydrolysis are worth noting.

The base-catalyzed hydrolysis of $Co(NH_3)_5PO_4^0$ is kinetically consistent with most of the proposed base hydrolysis mechanisms.[11] The zero charge of this complex would presumably reduce the effect of ion pairing with hydroxide to a minimum. Green and Taube[12] have suggested that the slower base-catalyzed hydrolyses of acidopentaamminecobalt(III) complexes may proceed *via* an associative mechanism. In the case of $Co(NH_3)_5PO_4^0$ an associative mechanism would be in keeping with the trend suggested for its protonated analogs, although the $\Delta S^{\ddagger}$ value is not easily explained by any mechanism.

Acknowledgment.—We wish to express appreciation for a grant to Washington State University from the National Science Foundation for support of research participation for college teachers under which this study was in part carried out.

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[9] D. G. Lambert and J. G. Mason, *J. Am. Chem. Soc.*, **88**, 1633, 1637 (1966).

[10] P. J. Staples, *J. Chem. Soc.*, 745 (1964).

[11] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1967, pp 177–193.

[12] M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

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Mechanism of the Reactions of Dihydroxobis(ethylenediamine)cobalt(III) Cations in Highly Basic Aqueous Solution

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The rates of isomerization and of the racemization of the $Co(en)_2(OH)_2^+$ ions have been measured over the temperature range 25–70°. The observed rates are independent of hydroxide concentration. The activation energies for the *cis* → *trans* change and for the *trans* → *cis* change are 29.5 and 28.5 kcal mol^{-1}, respectively. The activation energy for the racemization is not constant over the temperature range. The mechanisms of oxygen exchange with solvent and of stereochemical change are discussed. The mechanism of the latter is intramolecular, and it is proposed that a twisting process is the most likely one.

Introduction

Three studies of the system containing the *cis*- and *trans*-$Co(en)_2(OH)_2^+$ ions are reported in the literature.[1–3] Bjerrum and Rasmussen[1] investigated the equilibrium and estimated the rate constant for *cis* ⇌ *trans* isomerization at 25°. Tong and Yankwich[2] showed that the rate of isomerization at 35° was independent of hydroxide concentration between 1.0 and 0.0005 *M*.

In a more detailed study Kruze and Taube[3] found that during the *cis* ⇌ *trans* isomerization of the Co-

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[1] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952).

[2] J. Y. Tong and P. E. Yankwich, *J. Am. Chem. Soc.*, **80**, 2664 (1958).

[3] W. Kruze and H. Taube, *ibid.*, **83**, 1280 (1961).

$(en)_2(OH)_2^+$ cations only a fraction of one oxygen exchanges for each act of isomerization. They found that the energy of activation was not constant over the temperature range 14–37° and suggested that isomerization involves two paths: one corresponding to breaking of a cobalt–oxygen bond and the other to cobalt–nitrogen bond fission. Both paths permit isomerization, but only Co–O bond fission leads to oxygen exchange with solvent.

This paper presents a study of the racemization and isomerization of $Co(en)_2(OH)_2^+$ ions in highly basic media over an extended temperature range.

Experimental Section

In order to exclude difficulties resulting from impurities in preparation,[1,2] the *cis*- and *trans*-dihydroxo species were generated in solution from $[Co(en)_2CO_3]ClO_4$ and *trans*-$[Co(en)_2OH(OH_2)](ClO_4)_2$, respectively. The *cis*-$Co(en)_2(OH)_2^+$ species was obtained by acid hydrolysis of $[Co(en)_2CO_3]ClO_4$ and subsequent addition of alkali. Both acid hydrolysis and proton removal take place with full retention of configuration.[4] $[Co(en)_2CO_3]ClO_4$ was prepared from an aqueous solution of the chloride[4] by the addition of sodium perchlorate and was recrystallized from warm water. *Anal.* Calcd for $C_5H_{16}ClCoN_4O_7$: C, 17.7; H, 4.8; N, 16.5. Found: C, 17.6; H, 4.6; N, 16.8. The complex, resolved by Dwyer's method,[4,5] had $[\alpha]_D \pm 1250°$.

trans-$Co(en)_2(OH)_2^+$ was generated in solution by dissolving *trans*-$[Co(en)_2OH(OH_2)](ClO_4)_2$ in alkali.[6] (The authors thank Dr. M. L. Tobe for a sample of this compound.)

Spectrophotometric Runs. Method A.—A known weight of *rac*-$[Co(en)_2CO_3]ClO_4$ was dissolved in a known excess of standard perchloric acid and 0.5 ml of this solution was transferred to a known volume of standard sodium hydroxide in a thermostated 1-cm silica cell. The change of absorbance at 27,000 or at 19,200 cm^{-1} was recorded on either a Unicam SP 700 or SP 800 spectrophotometer. The latter was fitted with a scale expansion unit and external recorder. Cell temperatures were measured with a thermocouple and checked against standard NPL thermometers.

Spectrophotometric rate constants were calculated from the formula

$$k_1 + k_{-1} = (2.303/t) \log [(D_0 - D_\infty)/(D_t - D_\infty)] \text{ sec}^{-1}$$

where D_t was the absorbance after t seconds and D_0 was the absorbance at the time of the first reading (which was arbitrarily taken as zero time). By extrapolation back to time of mixing the molar extinction coefficients of pure *cis*-$Co(en)_2(OH)_2^+$ were 103 and 93 at 27,000 and 19,200 cm^{-1}, respectively (lit.[1] values 103.6 and 93).

Method B.—A known weight of *trans*-$[Co(en)_2OH(OH_2)](ClO_4)_2$ was dissolved in standard sodium hydroxide solution thermostated to the desired temperature. The solution was transferred to the thermostated cell in the spectrophotometer. The procedure was then as in method A.

Method C.—A known weight of *trans*-$[Co(en)_2OH(OH_2)](ClO_4)_2$ was dissolved in standard sodium hydroxide solution, and samples were placed in sealed tubes in a thermostat. These were withdrawn at known time intervals and the absorbance at 19,200 cm^{-1} was measured using a Unicam SP 500 spectrophotometer. The extinction coefficients of *trans*-$Co(en)_2(OH)_2^+$ were found to be 53.0 and 53.7 at 19,200 and 26,300 (lit.[1] values 53.0 and 53.9).

Method D.—The procedure was as in method C, except that the contents of each tube was run into an excess of standard perchloric acid and the absorbance (now of the $Co(en)_2(OH_2)_2^{3+}$ species) was measured at 20,000 cm^{-1}. The extinction coefficients of *trans*-$Co(en)_2(OH_2)_2^{3+}$ were found to be 32.5, 33.1, and 55.8 at 18,200, 22,500, and 28,900 cm^{-1}, respectively (lit.[1] values 32.8 and 33.2, respectively, for the first two peaks).

Polarimetric Runs.—$(-)_D$-$[Co(en)_2CO_3]ClO_4$ was dissolved in standard perchloric acid and neutralized with a known excess of standard sodium hydroxide. A sample was placed in a thermostated tube in a Zeiss photoelectric polarimeter. Readings of the rotation at 436 nm were taken at known time intervals.

Results

The results of the spectrophotometer runs are given in Table I.[7] It is evident from these results that the variation in the position of equilibrium is outside experimental error, although this is large.[8] The average values of ϵ_∞ and per cent *cis* at equilibrium have been calculated at the temperatures ~70, ~60, ~50, 37.5, and ~25° and are shown in Table II, together with some literature values. The rate of loss of optical activity is shown in Table III.

It can be seen that the *cis* → *trans* change cannot fully account for the loss of optical activity. The specific rate constants k_1(*cis* → *trans*) and k_{-1}(*trans* → *cis*) were calculated using the position of equilibrium shown in Table II. The constant k_1 was then subtracted from k_p to give k_r, the racemization rate: k_r is then twice the inversion rate, k_i. The results are shown in Table IV.

The results in Table IV are shown as Arrhenius plots in Figure 1. It can be seen that log k_1 and log k_{-1} *vs.* the reciprocal of the absolute temperature give straight-line plots whereas log k_i *vs.* $1/T$ gives a curve. The variations of k_1 and k_{-1} with temperature fit the Arrhenius equations

$$k_1 = 2.1 \times 10^{16} \exp(-29{,}500/RT) \text{ sec}^{-1}$$

$$k_{-1} = 3.1 \times 10^{15} \exp(-28{,}500/RT) \text{ sec}^{-1}$$

Discussion

The results of this investigation and those in the literature[1-3] show that the rates of oxygen exchange with solvent, the isomerization, and the racemization of the dihydroxo cations are independent of hydroxide concentration and of ionic strength. The loss of optical activity cannot be accounted for entirely by the *cis* → *trans* change.

Kruze and Taube[3] have shown that during the *cis* ⇌ *trans* isomerization only a fraction of one oxygen exchanges for each act of isomerization and that the exchange rate of the *cis* isomer is about eight times faster than the *cis* → *trans* rate. Most of the oxygen exchange must therefore take place with retention of

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[4] F. P. Dwyer, A. M. Sargeson, and T. K. Reid, *J. Am. Chem. Soc.*, **85**, 1215 (1963).

[5] F. P. Dwyer, A. M. Sargeson, and F. L. Garvan, *ibid.* **83**, 1285 (1961).

[6] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

[7] The proposed equilibrium between the *trans* species is: *trans*-$Co(en)_2(OH)_2^+ + Cl^- \rightleftharpoons Co(en)_2ClOH^+ + OH^-$; see E. A. Dittmar and R. D. Archer, *J. Am. Chem. Soc.*, **90**, 1468 (1968). However this reaction has been shown not to take place: M. E. Farago, B. Page, and M. L. Tobe, *Inorg. Chem.*, **8**, 388 (1969). The isomerization of $Co(en)_2(OH)_2^+$ ions is not catalyzed by chloride; neither does coordinated chlorine in *trans*-$Co(en)_2ClOH^+$ exchange with chloride ion in basic media.

[8] The fact that the per cent of *cis* product is independent of wavelength and of initial configuration indicates that this is a real effect and not just a consequence of variation of ϵ_m with temperature.

Table I

Observed Spectrophotometric Rate Constants, $k_1 + k_{-1}$, for the Isomerization of the *cis*- and *trans*-$Co(en)_2(OH)_2^+$ Ions

Starting isomer	Method[a]	Temp, °C	[Complex], m*M*	[$NaClO_4$],[b] *M*	[OH^-], *M*	$k_1 + k_{-1}$, sec^{-1}	ν,[c] kK	ϵ_∞
cis	A	71.0	9.84	0.015	0.0681	5.5×10^{-3}	27.0	73.3
cis	A	71.0	9.84	0.015	0.0515	5.4×10^{-3}	27.0	73.3
cis	A	68.0	4.25	0.025	1.33	4.30×10^{-3}	19.2	68.0
cis	A	68.0	8.50	0.033	1.26	3.83×10^{-3}	19.2	67.5
cis	A	61.0	7.20	0.022	0.044	1.68×10^{-3}	27.0	73.6
cis	A	61.0	7.20	0.022	1.27	1.65×10^{-3}	27.0	73.6
cis	A	61.0	7.20	0.022	3.31	1.64×10^{-3}	27.0	74.0
trans	B	59.1	9.22	0.00	0.067	1.20×10^{-3}	27.0	73.5
trans	B	59.1	9.22[d]	0.00	0.067	1.30×10^{-3}	27.0	73.5
trans	B	50.8	6.95	0.00	0.067	4.4×10^{-4}	27.0	73.4
trans	B	50.8	6.95[d]	0.00	0.067	4.5×10^{-4}	27.0	73.4
trans	B	50.8	6.95[d]	0.00	0.067	4.5×10^{-4}	19.2	68.8
trans	D	50.7	8.00[e]	0.00	0.050	4.4×10^{-4}	20.0	...
cis	A	49.3	9.84	0.015	0.0681	3.81×10^{-4}	27.0	74.5
cis	A	37.5	9.84	0.015	0.0681	6.5×10^{-5}	27.0	75.0
cis	A	37.5	9.84	0.015	0.0515	6.4×10^{-5}	27.0	75.5
trans	B	25.5	9.80	0.00	0.067	7.68×10^{-6}	19.2	71.3
trans	C	24.8	10.5	0.00	1.00	6.52×10^{-6}	19.2	70.5
cis	A	24.6	10.6	0.046	2.32	6.40×10^{-6}	19.2	...
cis	C	24.0	10.6	0.046	2.32	6.32×10^{-6}	19.2	71.5

[a] See text. [b] $NaClO_4$ produced as product of neutralization. [c] Reaction followed at this wave number. [d] In presence of 0.353 *M* NaCl.[7] [e] In presence of 0.40 *M* NaCl.[7]

Table II

Position of Equilibrium for the Isomerization of the $Co(en)_2(OH)_2^+$ Ions

Temp, °C	ϵ_∞ (27 Kk)	% *cis*	ϵ_∞ (19.2 Kk)	% *cis*	Av % *cis*
~70	73.3	38	67.7	37	37.5
~60	73.5	39			39
~50	74.5	41	68.8	40	40.5
37.5	75.2	42			42
37.5[a]					46[a]
35[b]	73.8	39	69.5	40	39.5[b]
~25			71.1	45	45
24.95[a]					46[a]
25.0[c]	75.7	45	71.4	45	45[c]
14.4[a]					46[a]

[a] From ref 3. [b] From ref 2. [c] From ref 1.

Table III

Observed First-Order Rate Constants (k_p) for the Loss of Optical Activity of the (−)D-$Co(en)_2(OH)_2^+$ Ion

Temp, °C	[Complex], m*M*	[NaOH], *M*	10^4k_p, sec^{-1}
69.4	7.6	0.259	69.9
60.8	4.1	0.855	19.0
60.8	5.0[a]	0.855	19.0
60.8	7.8	0.259	19.9
49.3	8.0	0.259	4.16
37.2	7.5	0.259	0.692
24.8	9.9	0.259	0.0936

[a] Run carried out in presence of free ethylenediamine.

Table IV

Specific Rate Constants (sec^{-1}) for the Isomerization and Inversion of the $Co(en)_2(OH)_2^+$ Ions

Temp, °C	$10^4(k_1 + k_{-1})$	% *cis*[a]	10^4k_1	10^4k_{-1}	10^4k_p	10^4k_i
69.4	53[b]	37.5	33.1	19.9	69.9	18.4
61.0	16.5	39.0	10.1	6.44	19.0	4.45
49.3	3.81	40.5	2.27	1.54	4.16	0.945
37.5	0.644	42.0	0.374	0.270	6.692	0.159
24.8	0.0652	45.0	0.036	0.029	0.0936	0.0288

[a] At equilibrium. [b] By interpolation.

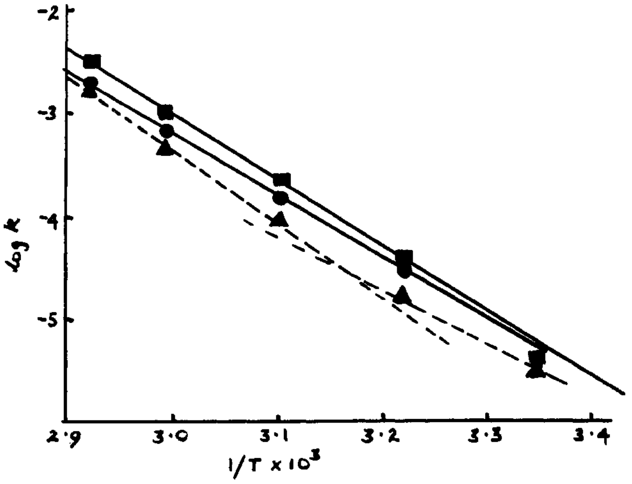

Figure 1.—Arrhenius plots for isomerization and racemization of $Co(en)_2(OH)_2^+$: ■, *k*(*cis* → *trans*); ●, *k*(*trans* → *cis*); ▲, *k*(inversion).

configuration, and most of the isomerization without exchange of oxygen with the solvent. It was suggested[3] that one path for isomerization involves opening of the ethylenediamine chelate ring. This mechanism has also been suggested[9] for the isomerization of the $Co(en)_2NH_3OH^{2+}$ cations, where rearrangement has been shown to take place without exchange of any of the attached ligands.

It was pointed out by Tobe[9] that for complexes of the type $Co(en)_2XOH^{n+}$, the strength of the Co–X bond determines which of two reactions takes place. These reactions can be hydrolysis where X is lost (X = Cl, Br, or NCS) or ring opening where X is strongly bound (X = NH_3, OH).

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(9) D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962).

In acid solution the diaquo ions $Co(en)_2(OH_2)_2^{3+}$ isomerize with water exchange, by slow acid hydrolysis.[3] In neutral solution (pH 7–8) the cations are in the form of the hydroxoaquo species $Co(en)_2OH(OH_2)^{2+}$, and the reactions become much more rapid.[2,3] In highly basic media, the isomerization becomes slow again and independent of hydroxide concentration.

There are several ways in which oxygen could be exchanged for solvent in neutral and basic media. It is not possible, however, from the kinetics to distinguish[10] (i) between aquation of the hydroxoaquo species and base-catalyzed hydrolysis of the diaquo species (at pH 7–8) or (ii) between spontaneous Co–OH fission and base-catalyzed hydrolysis of the hydroxoaquo species (in basic media). However, in basic solution the lack of effect of ionic strength or of base concentration and the fact that oxygen exchange with solvent takes place with retention of configuration lead to the conclusion that the reaction is spontaneous Co–OH fission. If the reaction were base-catalyzed hydrolysis of $Co(en)_2OH(OH_2)^{2+}$ *via* formation of an amide group, water would be the leaving group (less strongly σ bonded). The trigonal-bipyramidal intermediate would then be identical[11] with that for the base hydrolysis of complexes of the type $Co(en)_2OHX^+$. Where X = Cl or Br, this reaction takes place in the *trans* isomer with almost 100% steric change.[12] In the case of the dihydroxo cations, however, reaction must take place with retention of configuration.

Exchange of Oxygen with Solvent.—A possible mechanism for the exchange of oxygen with solvent would be the formation, by dissociation of OH^-, of a trigonal bipyramid stabilized by π bonding[13a] from the remaining hydroxo ligand. Intermediate A is likely to be formed from both *cis* and *trans* starting materials[13b] (intermediate B cannot readily be formed from the *trans* isomer). In order to reduce steric retention *via* intermediate A, it is necessary to restrict the entry of OH^- (or H_2O) to near the leaving group.

An alternative mechanism would be a bimolecular attack by hydroxide or water or a dissociation in which there is a contribution from bond making, as in rhodium(III) complexes.[14] Bonds between ligands and Rh(III) are on the whole more covalent than those to Co(III). Strong σ bonding of the two hydroxide ligands and the four amine groups may make the cobalt(III) center, in this instance, more like rhodium(III).

Whether there is appreciable bond making or not in the transition state, the incoming group must enter *cis* to the leaving group. It would be expected that a leaving hydroxide group would greatly disturb the solvent shell on that side, allowing easy entry for the incoming group. If the incoming group were solvent water, then a proton transfer from the incoming group to the departing hydroxyl group would result in further bond weakening and facilitate bond breaking (Figure 2).

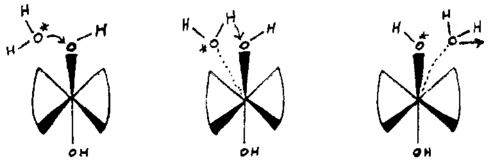

Figure 2.—Oxygen exchange of *cis*-$Co(en)_2(OH)_2^+$ by water attack and proton transfer.

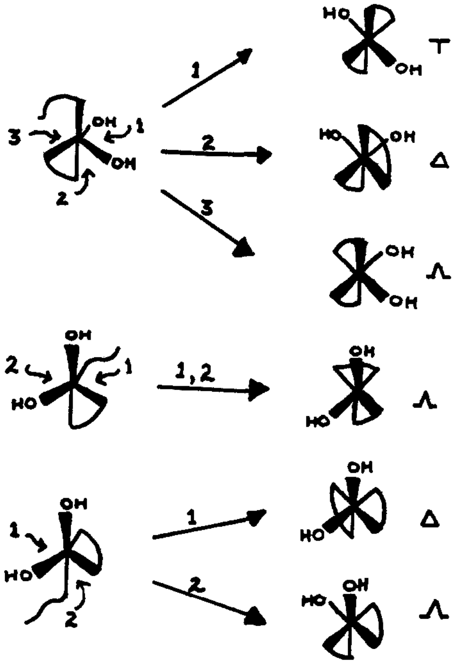

Figure 3.—Isomerization and racemization of $Co(en)_2(OH)_2^+$ *via* a trigonal bipyramid formed by cobalt–nitrogen fission, starting from Λ *cis*.

Stereochange by Intramolecular Mechanism.—There are two possible mechanisms for stereochange without exchange of oxygen with the solvent: twist or bust. In the former none of the six cobalt–ligand bonds is broken, whereas in the latter, cobalt–nitrogen bond fission occurs. Stereochange *via* the opening of an ethylenediamine chelate ring would result from the trigonal-bipyramidal intermediates shown in Figure 3.

The first intermediate in Figure 3 allows isomerization whereas racemization can occur through both the first and the last intermediates. So that isomerization should not be accompanied by exchange of oxygen with solvent, it is necessary that the coordination position be left vacant and not filled by a water molecule. Although this mechanism has been suggested in the diaquobis(oxalato)chromium(III) system,[15] the ring opening of the carbonato group, by cobalt–oxygen fission,[16] is found to take place with the uptake of an OH group.[17]

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[10] C. K. Poon and M. L. Tobe, *Inorg. Chem.*, **7**, 2398 (1968).

[11] R. B. Jordan and A. M. Sargeson, *ibid.*, **4**, 433 (1965).

[12] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).

[13] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, New York, N. Y., 1967: (a) p 186; (b) p 263.

[14] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).

[15] J. Agett, I. Mawston, A. C. Odell, and B. E. Smith, *J. Chem. Soc., A*, 1413 (1968).

[16] C. A. Andrade and H. Taube, *J. Am. Chem. Soc.*, **86**, 1328 (1964).

[17] H. Scheidegger and G. Schwarzenbach, *Chimia* (Aarau), **19**, 169 (1965); M. E. Farago, *Coord. Chem. Rev.*, **1**, 66 (1966).

The hydroxide ligand has a high inductive effect operating through the σ bond, π-antibonding properties,[18] and low ligand field strength.[19] The high inductive effect is responsible for the low pK_a of the amino group.[13a] The weakening of the Co–N bonds by this effect alone would tend to favor a *bust* mechanism; however, the Co–O bonds, in addition, would tend to be weakened by the repulsive π bonding. It seems possible that in compounds of cobalt(III) containing four nitrogen donors and two hydroxide ligands there are favorable conditions for the twist mechanism. An intramolecular mechanism has also been suggested for isomerization in the dihydroxotriethylenetetraminecobalt(III) series.[20]

Three twist mechanisms for octahedral chelate complexes have been proposed by Rây and Dutt,[21] Bailar,[22] and Springer and Sievers.[23] It has been pointed out[23] that the Rây and Dutt and the Springer and Sievers twists are special cases of the Bailar twist and that they will give transition states which differ only in the orientation of the chelate rings about the trigonal prism.[24]

The four trigonal prismatic transition states which result from the twisting of a species of the type $Co(en)_2X_2$ are shown in Figure 4. Springer and Sievers' twist is represented by I, and that of Rây and Dutt by II and III. These three intermediates permit intramolecular *cis* → *cis* changes. Only the fourth which may exist in mirror image forms permits *cis* $\rightleftharpoons$ *trans* changes.

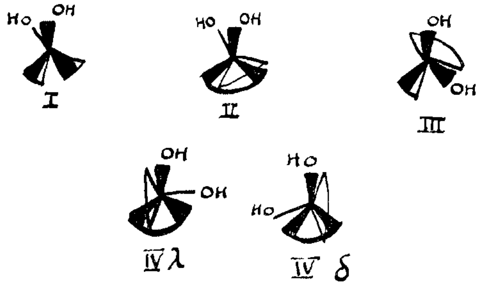

Figure 4.—Four trigonal-prismatic transition states **resulting** from the twist of species of the type $Co(en)_2X_2$.

Serpone and Fay[24] have analyzed the twisting mechanism and this analysis is extended below. Following their numbering,[24] the four *imaginary* C_3 axes of a complex of the type *cis*-$Co(en)_2X_2$ are shown in Figure 5.

The twisting mechanism involves the displacement of three of the donor atoms on one octahedral face (the lower) through 120°, with respect to the three donor atoms of the upper octahedral face. The twisting process may be carried out about any of the four imaginary axes in Figure 5 and may be in a clockwise (c) or an anticlockwise (a) direction. (Anticlockwise (rather than the more usual counterclockwise) is used in order to make the abbreviations comprehensible.) The starting material may be *cis* Λ,[25] *cis* Δ, or *trans;* the axis may be A1, A2, A3, or A4; and the transition state may be any of the prisms I, II, III, or IV shown in Figure 4. Rotation about the axis A3 or A4, which results in racemization *via* intermediate III, is illustrated in Figure 6. Starting from the Λ enantiomer an anticlockwise rotation about either A3 or A4 produces first intermediate III and then the mirror-image Δ enantiomer. Conversely a clockwise rotation of the Δ form about A3 or A4 produces the Λ form. Rotation about the axis A3 or A4 does not permit *cis* $\rightleftharpoons$ *trans* changes.

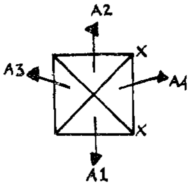

Figure 5.—View of *cis*-$Co(en)_2X_2$ along a fourfold axis showing four imaginary C_3 axes: A1, A2, A3, A4.

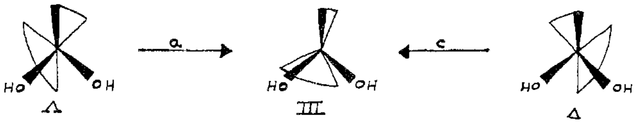

Figure 6.—Racemization of $Co(en)_2(OH_2)^+$ by rotation about axes A3 and A4, *via* trigonal prism III.

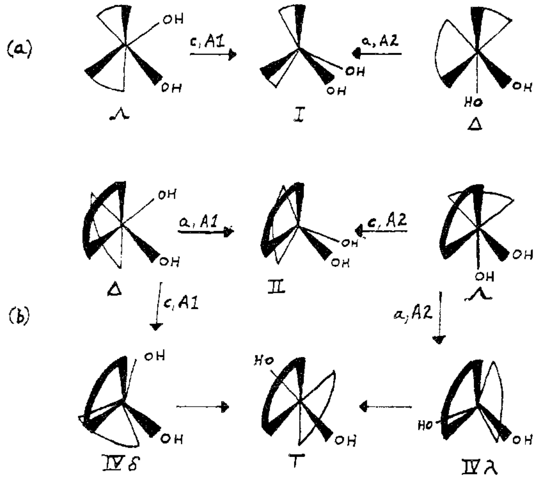

Figure 7.—Steric change of $Co(en)_2(OH)_2^+$ by rotation about axes A1 and A2: (a) racemization *via* trigonal prism I; (b) racemization *via* trigonal prism II and isomerization *via* trigonal prism IV.

Figure 7 shows twists around axis A1 or A2. The Λ isomer may only rotate about axis A1 in a clockwise direction and the Δ isomer is restricted to anticlockwise rotation about axis A2. These twists produce race-

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[18] C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, pp 24, 51.

[19] W. E. Hatfield, J. F. Anders, and L. J. Rivela, *Inorg. Chem.*, **4**, 1088 (1965).

[20] E. Kyono, L. J. Boucher, and J. C. Bailar, *J. Am. Chem. Soc.*, **87**, 4458 (1965).

[21] P. Rây and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1948).

[22] J. C. Bailar, *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

[23] C. S. Springer and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).

[24] N. Serpone and R. C. Fay, *ibid.*, **6**, 1835 (1967).

[25] The nomenclature used for absolute configuration is that of T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

mization *via* intermediate I and are illustrated in Figure 7a. The Λ isomer may twist about axis A2, however, in both clockwise and anticlockwise directions (Figure 7b), giving racemization and isomerization *via* intermediates II and IV, respectively. Similarly the Δ isomer rotates about axis A1 in both directions. It should be noted that the isomerization ($cis \rightleftharpoons trans$) process goes by way of IV, which is either IVδ or IVλ, which give rise to or are evolved from the Δ or Λ *cis* form, respectively.

The data in Figure 1 now seem consistent with a twist mechanism. Isomerization is *via* one type of intermediate, IV, whereas racemization may involve three intermediates, all of which make a contribution to the over-all reaction. The extent of the contribution varies with temperature and, hence, the variable energy. Recently Bradley[26] has suggested a *twist* mechanism in the racemization of *cis*-dialkoxybis(acetylacetonato)-titanium(IV) complexes, where the activation energy tends to increase with the bulk of the alkoxy group.

Intramolecular Interactions between Ligands.—Recently two types of interaction have been suggested: one for the Co(cyclam)OH$(OH_2)^{2+}$ system[10] and one for the *cis*-Co$(en)_2$OH$(OH_2)^{2+}$ system.[21] For the latter compound, Gillard[27] has attempted to link the large Cotton effect of *cis*-Co$(en)_2$OH$(OH_2)^{2+}$ with its fast isomerization. He suggests a preequilibrium ion pair, with a hydroxyl ion linking the aquo and hydroxo ligands giving a quasi-tris complex. Such a preequilibrium would however give kinetics indistinguishable from that of the reaction of the Co$(en)_2(OH)_2^{2+}$ species (*vide infra*), and neither racemization nor the isomerization of this latter compound is fast.

Tobe[10] has suggested that in complexes containing a secondary nitrogen, the fast isomerization of complexes of the type $CoA_4OH(OH_2)^{2+}$ (where A = cyclam or tren) involves an intramolecular proton transfer from nitrogen to oxygen. With a secondary amine the exchange process would lead to inversion of configuration on the nitrogen. Such an inversion would allow steric change to take place in the octahedral moiety, and if this steric change is unfavored, then the intramolecular interaction would facilitate steric change about the cobalt.

There seems to be no *a priori* reason why such an interaction should not occur with a primary nitrogen. It seems possible therefore that the intervention of a water molecule between the aquo and hydroxo groups of *cis*-Co$(en)_2$OH$(OH_2)^{2+}$ could hold the coordinated hydroxide in such a position that one of the lone pairs points toward the hydrogen of a neighboring amine. An intramolecular proton jump would thus be facilitated, producing an amido group and steric change about the cobalt.

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(26) D. C. Bradley and C. E. Holloway, *J. Chem. Soc., A*, 282 (1969).

(27) R. D. Gillard, *ibid., A*, 1945 (1968).