anions, each with a negative deprotonated amide group, has been demonstrated[7] as the irreversible cobalt(III) reaction product for the cobalt(II)–glycylglycine–oxygen system.

The facile equilibrium with molecular oxygen, the slowness of the irreversible reaction, and the rapid equilibrium resulting in the formation of the oxygenated complex make the Co(II)–DGENTA–oxygen system a convenient oxygen carrier for further study and provide a convenient model for the elucidation of the structure and reaction mechanisms of cobalt(II) peptide oxygen carriers.

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Racemization and Hydrogen Exchange in the *trans*-Bis(diethylenetriamine)cobalt(III) Ion

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The rates of hydrogen exchange and racemization at the secondary N–H center in the *trans*-$[Co(dien)_2]^{3+}$ ion with coupled chelate rings have been measured, and rates and activation parameters are compared with previous results. The close correspondence of the kinetic results with those for the single chelate ring complex $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ of identical cationic charge indicates that the coupling of chelate rings across the secondary N–H center in the dien complex has little effect on either process. It is still difficult however to decide on the details of the nitrogen inversion process. Comparisons with the other asymmetric nitrogen systems previously studied involve variations of more than one structural parameter, but it appears that the electronegative trans substituent X in *sym*-$[Co(trenen)X]^{2+}$ has a greater effect on the kinetics than does the extensive chelate ring coupling.

Introduction

The three geometric isomers of $[Co(dien)_2]^{3+}$ (dien = diethylenetriamine) have recently been separated, and the two dissymmetric forms u-cis[1a] and trans resolved into their optical isomers.[1b] The trans isomer (Figure 1) is of particular interest because the dissymmetry arises essentially from the chiralities of the C_2 related bond pairs in the two dien ligands, as typified and uniquely described[2] by the two secondary N–H bonds at the secondary nitrogen centers.

Coordination of amines to cobalt(III) considerably reduces the rate of nitrogen–hydrogen dissociation from that in corresponding organic quaternary ammonium salts. Coordination of an unsymmetrically substituted secondary amine NHR_1R_2 to a metal generates an asymmetric center at the donor nitrogen atom, and the proton-exchange rate is sufficiently slow at suitably low pH to restrict inversion at that nitrogen center. Optical resolution of the resulting asymmetric complex thus becomes feasible, and a number of such optical separations have now been achieved.

dien is a symmetrically substituted secondary amine so that *trans*-$[Co(dien)_2]^{3+}$ does not contain an asymmetric donor atom. However racemization will result if one of the secondary N–H bonds adopts the alternative disposition (Figure 1). This process is equivalent to inversion of configuration at the asymmetric nitrogen center in the situation $Co\text{–}NHR_1R_2$, and we henceforth use the term "inversion" to describe the analogous configurational change about a secondary nitrogen center in *trans*-$[Co(dien)_2]^{3+}$ despite the absence of asymmetry. This configurational change must involve N–H dissociation and will be accompanied by conformational inversion in each of the adjacent chelate rings.

These phenomena provide an unequivocal method for establishing the geometric configurations of the two dissymmetric forms, since the optical rotatory powers derive from different chiral sources in the u-cis and trans isomers. The u-cis, whose optical activity arises essentially from a configurational effect, should be optically stable in base, but the racemization of the trans isomer should be OH^- catalyzed. It was thus necessary to establish the OH^- dependence of the racemization of the trans isomer, and this prompted the present study of the kinetics of both racemization and hydrogen exchange under a variety of conditions in the hope of further elucidating the mechanistic steps involved in the racemization.

Recently the kinetics of racemization and deuteration have been studied by Buckingham and Sargeson and coworkers for several cobalt(III) complexes where the sole source of asymmetry resides in a coordinated secondary amine N atom. For the three complexes $[Co(NH_3)_4sarc]^{2+}$,[3] $[Co(NH_3)_4(N\text{-Meen})]^{3+}$,[4] and *trans*,*trans*-$[Co(N\text{-Meen})_2(NO_2)_2]^+$[5] (sarc = sarcosinato anion; *N*-Meen = *N*-methylethylenediamine) the rates of proton exchange were several orders of magnitude faster than the respective rates of racemization, and both measured processes were described by rate laws of similar form, $R = k[\text{complex}][OH^-]$.

The two mechanisms which have been proposed by

(1) (a) The three geometric isomers of $[C(dien)_2]^{3+}$ have been designated s-cis (or symmetrical-facial), u-cis (or unsymmetrical-facial), and trans (or meridional). (b) F. R. Keene and G. H. Searle, *Inorg. Chem.*, **11**, 148 (1972); F. R. Keene, G. H. Searle, Y. Yoshikawa, A. Imai, and K. Yamasaki, *J. Chem. Soc. D*, 784 (1970).

(2) F. R. Keene, G. H. Searle, and S. F. Mason, *ibid.*, 893 (1970).

(3) B. Halpern, A. M. Sargeson, and K. R. Turnbull, *J. Amer. Chem. Soc.*, **88**, 4630 (1966).

(4) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 825 (1967).

(5) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89**, 3428 (1967).

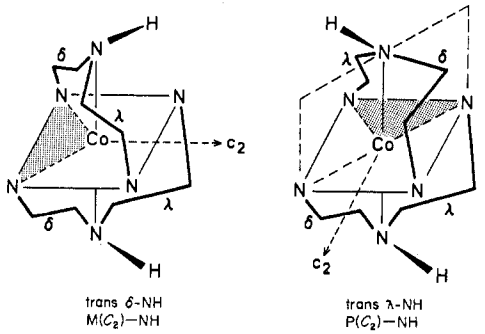

Figure 1.—Optical isomers of *trans*-$[Co(dien)_2]^{3+}$.[1,2]

the previous authors[4,5] to account for all these results are shown in Figure 2, where the part chelate ring indicated may be either *N*-Meen or sarc. The preferred scheme A involves abstraction of the N proton with OH^- (k_1). The alternative mechanism B proposes formation of an ion pair with OD^- (k_3) and ion–solvent dissociation (k_4). The two mechanisms are equivalent for the racemization step as given by inversion of the deprotonated intermediate k_2. In

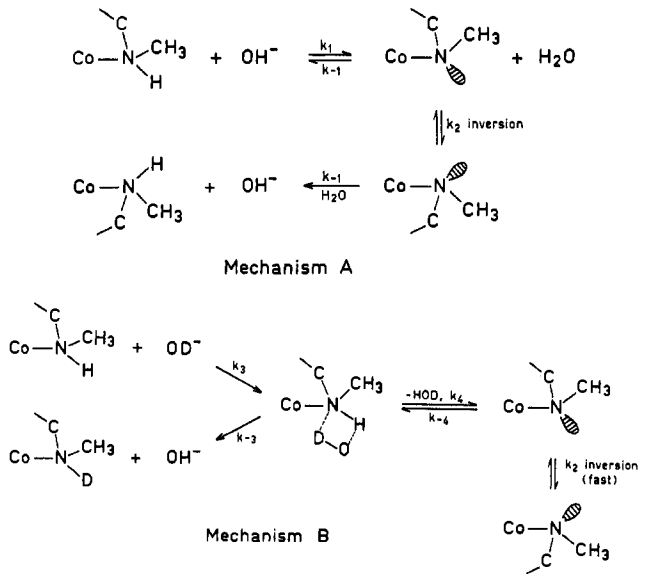

Figure 2.—Alternative mechanisms for hydrogen exchange and racemization at an asymmetric nitrogen center.

mechanism B ion–solvent pair separation is required for racemization for which k_4 could thus be the rate-determining step, but this step is not required for exchange to occur with retention of configuration k_{-3}. The absence of a substantial isotope effect $k_{deuteration}/k_{protonation}$ (k_D/k_H) for the exchanges, as would be expected for the step k_4,[5] gave support for the former mechanism, and circumstantial evidence also supporting mechanism A has been expounded.[4,5] Results of measurements of retention ratio $k_{protonation}/k_{racemization}$ during exchange in nonaqueous solutions have also been interpreted on the basis of mechanism A.[6]

The previous studies cited above are confined to complexes involving an asymmetric donor nitrogen center in the bidentate ligands *N*-Meen or sarc. The chelate ring in the sarcosine complex is essentially planar[7] so that a ring conformational change is not involved. Mechanisms A and B as drawn in Figure 2 do not specifically consider inversion of the single chelate ring conformation in the *N*-Meen complexes, and k_2 in Figure 2 refers only to the nitrogen inversion which is the essential step for racemization. The ring conformation must invert however if the methyl substituent is to remain in the preferred equatorial disposition with respect to the overall plane of the ring in the *N*-Meen complexes.[4,5] The increase in $\Delta H^{\ddagger}$ and in retention ratio for the *N*-Meen complexes compared to the sarc complex was attributed to the additional energy required to invert the *N*-Meen ring conformation as well as the N center.[4,5] In the studies mentioned, no decision could be made as to the time relationship between conformational interchange and inversion at the nitrogen atom during the observed racemization, and Figure 2 is noncommittal on whether the ring inversion precedes, postcedes, or is synchronous with k_2.[4,5]

A subsequent study of hydrogen exchange and racemization of (+)D-*sym*-$[Co(trenen)N_3]^{2+}$ (trenen = 4-(aminoethyl)-1,4,7,10-tetraazadecane) attempted to clarify the issue of the interaction between conformational interchange and nitrogen inversion.[8] This complex has coupled ring conformations (Figure 3, X

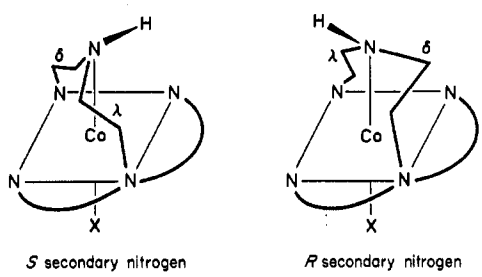

Figure 3.—Optical isomers of *sym*-$[Co(trenen)X]^{2+}$. This geometric isomer of the trenen complex may be alternatively designated $[Co(sec\text{-}trenen)X]^{2+}$ where X is trans to the secondary amine group.

= azido) and it was felt that the conformations of the two rings abreast of the asymmetric nitrogen (conformations designated δ and λ[9] in Figure 3) would invert synchronously with configurational inversion at the asymmetric center. The close correspondence between observed activation energies for racemization of this system and of $(+)_{480}[Co(NH_3)_4(N\text{-Meen})]^{3+}$ was then taken to imply that inversion at the N center and conformational interchange might coincide for puckered ring systems generally. However the trenen complex has multiple ring coupling at the tertiary nitrogen atom also, and this would confer some restriction on the conformational interchange in question (about the secondary N atom). The portion of the trenen ligand comprising the interlocked rings (δ and λ) about the asymmetric nitrogen in *sym*-$[Co(trenen)N_3]^{2+}$ should be closely similar stereochemically to each dien ligand in *trans*-$[Co(dien)_2]^{3+}$ (compare Figures 1 and 3). This latter complex is free of the restriction mentioned, however, and is also a better basis for comparison with $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ on account of similar cation charge and the absence of the electronegative azido

(6) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **90**, 6028 (1968).

(7) H. C. Freeman and I. E. Maxwell, *Inorg. Chem.*, **9**, 649 (1970).

(8) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **8**, 1595 (1969).

(9) *Ibid.*, **9**, 1 (1970).

substituent. The comparison of the kinetic patterns for the dien and trenen complexes may be expected to give some further information on the effects of cation charge and azido substituent however.

Experimental Section

(+)D-*trans*-[Co(dien)$_2$](NO$_3$)$_3$·H$_2$O.—The racemic chloride was resolved with Ag(+)[Co(en)(mal)$_2$]·2H$_2$O as described earlier.[1] The active bromide thus obtained was converted to the nitrate by passage of a solution in 0.01 *M* HNO$_3$ through an exchange resin in the nitrate form. The eluate was concentrated on a rotary evaporator, and crystallization was completed by the addition of ethanol. *Anal.* Calcd for (+)D-*trans*-[Co(C$_4$H$_{13}$N$_3$)$_2$](NO$_3$)$_3$·H$_2$O: C, 20.5; H, 6.0; N, 26.8. Found: C, 20.6; H, 5.7; N, 26.5.

Deuterated (±)-*trans*-[Co(dien-d_5)$_2$]Cl$_3$·xD$_2$O.—A sample of racemic chloride–2.5-water was dissolved in D$_2$O (99.8%), and after standing at 80° for 1 hr the D$_2$O–H$_2$O was evaporated off under vacuum. The process was repeated with fresh D$_2$O, and the pmr spectrum showed that deuteration was essentially complete.

Buffer Solutions.—The buffer solution for each pH was made up using 2,4,6-collidine (freshly distilled) and the appropriate amount of HNO$_3$,[10] and sufficient solid NaNO$_3$ was added to adjust the ionic strength of this solution to μ = 1.9 *M*. The solid complex, when added for each racemization run, contributed a further 0.1 *M* to the ionic strength.

Racemization Kinetics.—(+)-*trans*-[Co(dien)$_2$](NO$_3$)$_3$·H$_2$O (0.075 g) was dissolved in collidine–HNO$_3$ buffers (10 ml) giving solutions 0.016 *M* in complex, with ionic strength adjusted to 2.0 *M* with NaNO$_3$. Racemization was conveniently followed at the Hg line 546.1 nm which is coincident with the first peak of the ORD curve.[1] Rotations were measured on a Perkin-Elmer 141 MC polarimeter in a 1-dm cell jacketed to ±0.1° from a water bath. Initial rotations were about α_{546} +0.14°, and individual measurements were accurate to ±0.002°. In the slower runs light was excluded between readings and each run was followed to at least 2 half-lives.

The pH of each solution was obtained with a Radiometer Model 22 pH meter (±0.005 pH unit) by measurement of the kinetic solution at the run temperature after each run was completed (the collidine buffer is temperature dependent). Rates were reproducible to ±5% with the accuracy limited by the pH determination.

Hydrogen-Exchange Kinetics.—The deuteration runs were carried out on racemic *trans*-[Co(dien)$_2$]Cl$_3$·2.5H$_2$O in D$_2$SO$_4$–D$_2$O, and the corresponding deuterated compound was used for the protonation studies in H$_2$SO$_4$ solutions. The stock acid solutions were titrated potentiometrically against sodium tetraborate. Pmr spectra were measured using a Varian T-60 nmr spectrometer with sodium trimethylsilylpropanesulfonate as the external reference standard. All solutions were 0.33 *M* in complex, whence μ = 2.0 *M*. The nmr tubes were kept in the probe of the spectrometer throughout the runs at 34.9° and in a constant-temperature water bath for the higher temperatures. In these latter runs the tubes were withdrawn from the bath at suitable times and cooled quickly to 35°, and the N–H region of the spectrum was recorded immediately.

It was not possible to assess peak areas using the instrument integrator due to its instability over the broad N–H peak and with time. Relative peak areas were obtained by making three tracings of the peak recorded at each time (smoothing out noise) onto paper of uniform thickness, sketching in the base line, and cutting out. The triplicate paper pieces were weighed together (weights corresponding to maximum peak areas were about 0.25 g). This procedure averaged out variations caused by subjective judgements in making the tracings.

Results

Hydrogen Isotope Exchange.—The pmr spectrum of *trans*-[Co(dien)$_2$]Cl$_3$·2.5H$_2$O in D$^+$–D$_2$O is given in Figure 4. The band assignments follow from the peak area ratios NH:NH$_2$:CH$_2$ = 1:4:8 as determined previously.[1] The >NH peak is also shown at the higher

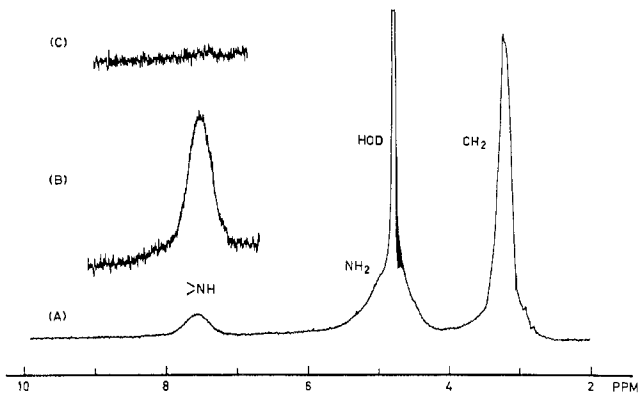

Figure 4.—Pmr spectrum of *trans*-[Co(dien)$_2$]$^{3+}$ in D$^+$–D$_2$O: (A) complete spectrum; (B) >NH peak at amplitude increased 8 times, initially; (C) after deuteration complete (10 half-lives).

amplitude at which the deuteration runs were followed, and it is evident (Figure 4C) that after ~10 half-lives exchange was essentially complete. The exchange was followed in both directions, by measurement of peak area of the >NH signal at appropriate times. Plots of log [(peak area)$_t$ − (peak area)$_\infty$] *vs.* t were linear (within the errors) over at least 2 half-lives for the deuteration runs in D$_2$SO$_4$–D$_2$O. Protonation runs of the deuterated sample in aqueous H$_2$SO$_4$ solutions were more difficult to measure due to the large HOD peak lying close to the >NH signal under these conditions. The HOD background tail under the NH had to be extrapolated subjectively for each recording, and the experimental points in the plot of log [(peak area)$_\infty$ − (peak area)$_t$] *vs.* t (peaks background corrected) were more scattered. All rate constants were computed by least-squares analysis of the experimental points up to 2 half-lives for each run. The number of points used in the computation was at least 8 but was usually about 12. Rate constants for the exchanges are listed in Tables I and II. k_D and k_H were obtained by k_D =

TABLE I
RATE CONSTANTS FOR DEUTERATION IN D$_2$SO$_4$–D$_2$O OF SECONDARY N–H IN *trans*-[Co(dien)$_2$]Cl$_3$·2.5H$_2$O[a]

[D$^+$], *M*	Temp, °C	$10^{-3}k_D$, M^{-1} sec^{-1}	[D$^+$], *M*	Temp, °C	$10^{-3}k_D$, M^{-1} sec^{-1}
0.100–0.00100	34.9	1.04 ± 0.05	0.0300	40.0	1.43
0.0100	34.9	0.60[b]	0.0300	45.0	2.23
0.0100	34.9	1.68[c]	0.0300	50.0	3.0

[a] [Co] = 0.33 *M*; μ = 2.0 *M* (no supporting electrolyte added). [b] [Co] = 0.167 *M*; μ = 2.0 *M*; [KCl] = 1.0 *M*. [c] [Co] = 0.167 *M*; μ = 1.0 *M* (no supporting electrolyte added).

TABLE II
RATE CONSTANTS FOR PROTONATION IN H$_2$SO$_4$ OF SECONDARY N–D IN DEUTERATED *trans*-[Co(dien-d_5)$_2$]Cl$_3$·xD$_2$O[a]

[H$^+$], *M*	Temp, °C	$10^{-3}k_H$, M^{-1} sec^{-1}	[H$^+$], *M*	Temp, °C	$10^{-3}k_H$, M^{-1} sec^{-1}
0.0098	34.9	0.35	0.098	45.0	0.80
0.098	40.0	0.71	0.098	50.0	1.10

[a] [Co] = 0.33 *M*; μ = 2.0 *M* (no supporting electrolyte added).

$k_{obsd}/[OD^-] = k_{obsd}[D^+]/K_{D_2O}$ and $k_H = k_{obsd}[H^+]/K_w$. The constants used were $K_w = 2.11 \times 10^{-14}$ for 2 *M* KCl at 34.9°[11] and values of K_w for the other

(10) R. M. C. Dawson, D. C. Elliott, W. H. Elliott, and K. M. Jones, "Data for Biochemical Research," 2nd ed, Oxford University Press, London, 1969, p 491.

(11) H. S. Harned and W. J. Hamer, *J. Amer. Chem. Soc.*, **55**, 2194 (1933).

temperatures were also calculated for 2 *M* KCl using data from the same source.[11] K_{D_2O} was taken as 0.195 K_w for zero ionic strength.[12] The assumption has been made that the ratio 0.195 does not change significantly with ionic strength or temperature, as zero ionic strength is the only condition for which strictly comparable values of K_{D_2O} and K_w have been determined.[13] The constancy of k_D over nine runs with D^+ concentration varied over the range 10^{-1} to 10^{-3} *M* at constant temperature (average value 1.04×10^8 M^{-1} sec^{-1} with spread ± 0.05 at 34.9°) establishes the rate law to be the same as that for the previously studied bidentate complexes, $R = k_D[complex][OD^-]$. The average value of k_H under the same conditions is 0.35×10^8 M^{-1} sec^{-1} at 34.9° giving the isotope effect as $k_D/k_H = 3.0$. Our results indicated that rate constants for the deuterations were reproducible to within 10%, all replicate values being within 5% of the mean. Data for a typical deuteration run are plotted in Figure 5.

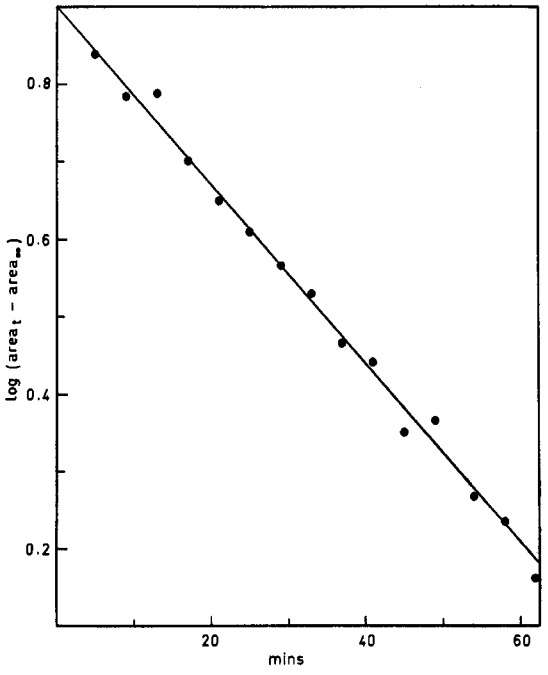

Figure 5.—Rate plot for a typical deuteration run ($[D^+] = 10^{-3}$ *M*, 34.9°, $k_{obsd} = 4.43 \times 10^{-4}$ sec^{-1}).

The accuracy and precision were less than this however for protonation (within 7% of the mean). All determinations were run in duplicate or triplicate, and Tables I and II list only the mean values.

Racemization.—The rates of racemization were measured in buffer solutions at constant ionic strength ($\mu = 2.0$ *M*) over almost the complete pH range 7.08–8.27 of the collidine–HNO_3 buffer system at various temperatures, Table III. Pseudo-first-order plots of log α_{546} *vs.* *t* were linear to at least 3 half-lives, and lines of best fit were drawn visually through the large number of points for each run. Several runs were followed to zero rotation over the visible range ($>10t_{1/2}$), and the constancy of the visible spectrum indicated that in the reaction times any hydrolysis or isomerization was insignificant. Chromatographic analysis on SP C-25 Sephadex[1] of a solution which had completely racemized

(12) W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936).
(13) *Chem. Soc., Spec. Publ.*, **No. 17**, 39 (1964).

TABLE III
RATE CONSTANTS FOR RACEMIZATION OF (+)-*trans*-$[Co(dien)_2](NO_3)_3 \cdot H_2O$ IN COLLIDINE–HNO_3 BUFFERS[a]

Temp, °C	pH	$10^4 k_{obsd}$, sec^{-1}	$10^{-2}k_R$, M^{-1} sec^{-1}	Temp, °C	pH	$10^4 k_{obsd}$, sec^{-1}	$10^{-2}k_R$, M^{-1} sec^{-1}
25	8.27	1.30	0.69	35	7.76	4.94	4.1[c]
30	7.51	0.586	1.23	35	7.68	2.84	2.9[d]
30	7.92	1.25	1.29	35	6.42	0.086	1.54[e]
35	7.20	0.769	2.3	40	7.31	2.89	4.7
35	7.42	1.24	2.3	40	7.55	4.87	4.6
35	7.46	1.51	2.5	40	6.44	0.297	3.6[e]
35	7.75	2.76	2.3	45	7.08	4.17	8.7
35	8.12	6.89	2.5	45	7.15	4.75	8.4
35	7.67	1.81	1.86[b]	45	6.45	0.865	7.7[e]
35	7.62	2.85	3.3[c]				

[a] [Co] = 0.016 *M*; $\mu = 2.0$ *M* (supporting electrolyte $NaNO_3$). [b] [Co] = 0.008 *M*; $\mu = 2.0$ *M* ($NaNO_3$). [c] [Co] = 0.016 *M*; $\mu = 1.0$ *M* ($NaNO_3$). [d] [Co] = 0.008 *M*; $\mu = 1.0$ *M* ($NaNO_3$). [e] Phosphate buffer HPO_4^{2-}, $H_2PO_4^-$; [Co] = 0.016 *M*; $\mu = 2.0$ *M* ($NaNO_3$).

failed to detect any other species. $k_R = k_{obsd}/[OH^-]$ was calculated using values of K_w as mentioned above. The constancy of k_R over the pH range 7.20–8.12 (average value with standard deviation $(2.36 \pm 0.09) \times 10^2$ M^{-1} sec^{-1} at 35°) confirmed that only the one reaction was being observed and that the rate law was as previously, $R = k_R[complex][OH^-]$.

Activation Parameters.—Activation energies E_a for the three processes were computed by least-squares analysis of the Arrhenius plots of k_R, k_D, and k_H, where these rate constants from the individual runs have been calculated allowing for the temperature variation of K_w or K_{D_2O}. Figure 6 shows the Arrhenius plots for the

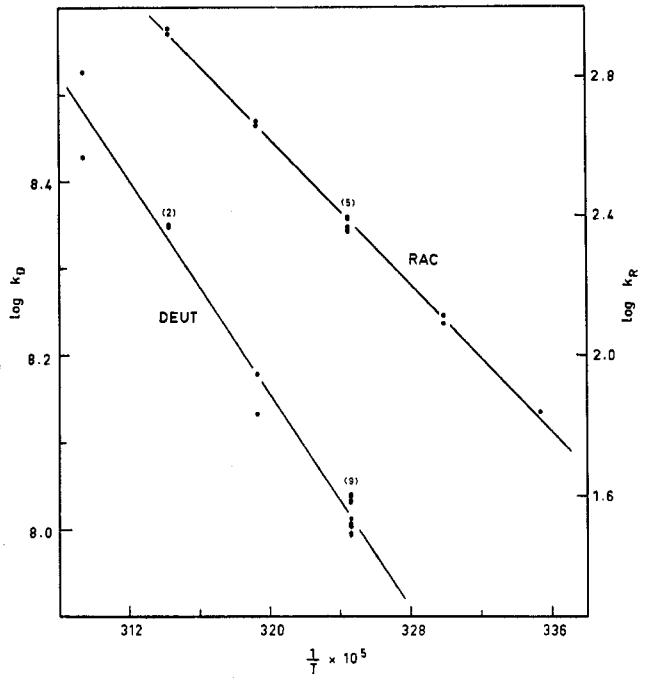

Figure 6.—Arrhenius plots for deuteration and racemization of *trans*-$[Co(dien)_2]^{3+}$. Figures in parentheses are the numbers of points at each temperature.

deuteration and racemization. The activation parameters calculated for the three processes ($\Delta H^{\ddagger} = E_a - 0.60$ kcal mol^{-1}) are given in Table IV. Errors listed were obtained from the standard errors in the least-squares analyses.

TABLE IV
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR SECONDARY N–H HYDROGEN EXCHANGE AND RACEMIZATION

Reaction	Medium	Temp, °C	$k_{D,H,\text{ or }R}$, M^{-1} sec^{-1}	$\Delta H^{\pm}$, kcal mol^{-1}	$\Delta S^{\pm}$, eu
		trans-$[Co(dien)_2]^{3+}$			
Deuteration	D_2SO_4	34.9	1.0×10^8	13.5 ± 1	22 ± 3
Protonation	H_2SO_4	34.9	0.35×10^8	13.4 ± 2	20 ± 7
Racemization	Collidine–HNO_3	35.0	2.4×10^2	23.5 ± 0.4	29 ± 2
		$[Co(NH_3)_4(N\text{-Meen})]^{3+}$			
Deuteration	DCl	34.3	3.0×10^7	13.8	21
Protonation	HCl	34.3	1.0×10^7	15.4	24
Racemization	Collidine–HCl	34.3	2.5×10^2	24.3	31
	Acetate buffer	34.3	2.4×10^2	23.8	30
		sym-$[Co(trenen)Cl]^{2+}$			
Deuteration	DCl	34	5.6×10^9	13.7[a]	31
		sym-$[Co(trenen)N_3]^{2+}$			
Deuteration	DCl	34	1.3×10^9	...	...
Racemization	Tris–$HClO_4$ buffer	34	5.7×10^2	22.7	28

[a] Reference 8 states that $\Delta H^{\pm}$ for deuteration of the chloro and "activation energy" for racemization of the azido complexes are 28 and 36 kcal mol^{-1}, respectively. It appears from the context that these values are both $E_{a,obsd}$ and the $\Delta H^{\pm}$ and $\Delta S^{\pm}$ parameters in the above table have been calculated accordingly.

Discussion

The kinetic results obtained for the hydrogen exchanges and racemization follow the general pattern previously observed for the asymmetric nitrogen center complexes, and the OH^- catalysis of the racemization allows the geometric configuration of this particular geometric isomer of $[Co(dien)_2]^{3+}$ to be unequivocally assigned as trans.[1]

The close similarity in activation parameters between the dien, *N*-Meen, and trenen complexes, as compared in Table IV, strongly indicates a common mechanism. We are thus led to conclude that the coupling of two puckered chelate rings across the secondary N atom in Co(dien) confers no additional constraint on the nitrogen "inversion" over that in the single-ring case of Co(*N*-Meen). We infer also that the additional ring coupling around the tertiary N in the *sym*-$[Co(trenen)N_3]^{2+}$ complex (Figure 3) places no additional restriction on inversion at the secondary N center.

The present results do not allow a firm decision to be made as to whether nitrogen inversion and conformational interchange are synchronous processes or not. Certainly in the Co(*N*-Meen) case inversion and ring interchange are not required to be synchronous,[4] and conformational change or distortion could occur subsequent to deprotonation but prior to nitrogen inversion. In the present system, as in *sym*-$[Co(trenen)N_3]^{2+}$,[8] Dreiding models imply that it is difficult to invert at the N center without inverting at least one of the ethylenediamine (en) rings, but even this is not required by the results. However recent X-ray studies on coupled en ring systems[14] reveal departures from the idealized structures implied by Dreiding models (fixed bond angles) so that caution must be exercised in the use of such models for mechanistic predictions.

It might be argued that if synchronous conformational interchange does not occur in Co(*N*-Meen), the similarity in $\Delta H^{\pm}$ (racemization) for these three systems suggests inversion of only one ring in each of the dien and trenen complexes during the nitrogen inversions, equivalent to configurational interchange only of the methyl and hydrogen substituents in Co(*N*-Meen) (without conformational change). If ring conformational change does occur synchronously in the Co(*N*-Meen) system, then on this basis both rings would have to invert synchronously in Co(dien). While it seems likely therefore that one ring in Co(dien) inverts synchronously with the nitrogen inversion, the same uncertainties remain for the second ring as in the previous comments[4] on the $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ results.

The concurrent inversion of both chelate rings in one dien ligand of *trans*-$[Co(dien)_2]^{3+}$ would produce a deprotonated intermediate having substantial eclipsing of these chelate rings.[8] From the known energy barriers between the staggered and eclipsed conformers of ethane and methylamine,[15] the energy barrier to formation of the eclipsed deprotonated intermediate for the dien complex may be assessed as $\sim$14 kcal mol^{-1}. On this basis alone we feel that this symmetrical intermediate is unlikely, and such an intermediate has been discounted also in the base hydrolysis of *sym*-$[Co(trenen)Cl]^{2+}$ where the product retains optical activity[8] and in the racemization of $[Pt(N\text{-Meen})(en)]^{2+}$ [16] where the high retention ratio k_D/k_R dictated against a symmetrical π-bonded intermediate.[17] We propose therefore that in the conformational interchanges associated with the nitrogen inversion in *trans*-$[Co(dien)_2]^{3+}$, the two coupled rings will not invert simultaneously. This consideration is distinct from whether or not the inversion of one of the rings is synchronous with nitrogen inversion.

In comparing racemization and exchange rates for the various complexes, account has to be taken of the number of active centers in each molecule and the relationship between inversion at each center and the observed racemization. The significant comparison should be between inversion rates related to a single center, k_i.

trans,trans-$[Co(N\text{-Meen})_2(NO_2)_2]^+$, with two reactive centers, requires inversion of one center in each

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molecule to form the inactive meso form, so that $k_R = k_i$. However, with both *trans*-$[Co(dien)_2]^{3+}$ (two reactive centers) and $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ (one asymmetric center) only one center per two molecules need invert to form racemate, so that $k_R = 2k_i$. The inversion rates k_i are thus essentially similar for these latter ions of identical charge (allowing for the [Co] and μ differences), while that for *sym*-$[Co(trenen)N_3]^{2+}$ ($k_R = 2k_i$) may be slightly higher (Table IV).

Statistical factors do not enter into the H-exchange rate measurements so that the deuteration rates for the two 3+ complexes differ threefold (Table IV) as do the retention ratios k_D/k_i, 2.5×10^5 for $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ and 8×10^5 for *trans*-$[Co(dien)_2]^{3+}$. These ratios for the 3+ complexes are considerably less than for *sym*-$[Co(trenen)N_3]^{2+}$, $k_D/k_i = 4.6 \times 10^6$. This factor cannot be correlated with the charge difference and it is difficult to associate with some restriction on conformational interchange in the trenen complex since the k_i rates are similar, so that it is probably to be ascribed to the electronegative azido substituent. Although the two highly electronegative groups did not appear to increase the retention ratio in *trans,trans*-$[Co(N\text{-Meen})_2(NO_2)_2]^{+}$ [5] ($k_D/k_i = 9 \times 10^4$), the nitro groups are cis to the asymmetric centers in this instance. It seems likely that the azido group is exerting a *trans effect* in *sym*-$[Co(trenen)N_3]^{2+}$, enhancing k_D and k_D/k_i. This may not be a general effect however, since estimates of N–H exchange rates at both "angular" and "planar" secondary nitrogen donor sites in α-$[Co(trien)NH_3Cl]^{2+}$ [18] and the various configurations of β-$[Co(trien)gly]^{2+}$ [19] (trien = triethylenetetramine; gly = glycinato anion) indicate that both detailed ring geometry and position of electronegative substituent affect these rates, but so far few generalizations have emerged.

Other features found common with previous observations are an isotope effect for exchange similar to that in $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ ($k_D/k_H \approx 3$)[4] and a decrease of racemization rate in phosphate buffers (Table III) associated with ion pairing.

A feature not observed previously[3,5] however is a small dependence of all rates on complex concentration, and the effect of ionic strength on all rates is larger than previously noted[3] (Tables I and II). These features may be rationalized on the basis of ion pairing. Ion association of Cl^- (or NO_3^-) may restrict access of the catalyzing base to the exchangeable proton or reduce the effective positive charge on the complex moiety, so that the ion pair would be less reactive toward exchange (on both mechanisms A and B) and the racemization rate would be consequently diminished also. Slower rates would thus result from increasing μ or by adding KCl to maintain μ constant when [complex] is reduced. Such interactions may be rather specific[20] so that the smaller effects noted by the previous workers need not be surprising, despite the larger specific effect of phosphate on the $[Co(NH_3)_4sarc]^{2+}$ system.[3]

The parallel effects of varying [complex] and μ on both the exchange and racemization rates are more consistent with mechanism A, involving a common intermediate for both processes, than with mechanism B (Figure 2), so that we concur with the remarks of the previous authors. The conceptual difference between the alternative mechanisms is small however.

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Mechanism and Steric Course of Octahedral Aquation. XV.[1] The Acid-Catalyzed Hydrolysis of *trans*-Diacetatobis(ethylenediamine)cobalt(III) Ions

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The aquation of *cis*- and *trans*-$[Co(en)_2(OAc)_2]^+$ (en = 1,2-diaminoethane, OAc = acetate) is acid catalyzed and in both cases obeys the rate law $-d \ln [Co(en)_2(OAc)_2]/dt = kK[H^+](1 + K[H^+])^{-1}$. The cis isomer is considerably more labile than the trans as a result of larger values of k and K. The acid dependence arises from a preequilibrium protonation which, in the case of the trans isomer, has been examined independently by spectrophotometry. The *trans*-diacetato cation yields both *cis*- and *trans*-$[Co(en)_2OAc(H_2O)]^{2+}$ in the ratio found at equilibrium (75% cis, 25% trans) even when the aquation is faster than the subsequent isomerization. The *cis*-diacetato complex aquates with complete retention of configuration. The rates of approach to equilibrium of *cis*- and *trans*-$[Co(en)_2(OAc)H_2O]^{2+}$ are independent of acid concentration; $k_{isom} = 2.5 \times 10^{-5}$ sec^{-1} at 25° (0.01 M $HClO_4$), $\Delta H^{\ddagger} = 28.5 \pm 0.4$ kcal mol^{-1}, and $\Delta S^{\ddagger} = +15.6 \pm 1.6$ cal deg^{-1} mol^{-1}. In strong acid, the $[Co(en)_2(OAc)H_2O]^{2+}$ species aquate further to form *cis*-$[Co(en)_2(H_2O)_2]^{3+}$.

Introduction

Many years ago it was shown that the rates and steric courses of solvolytic displacement of X from *trans*-$[Co(en)_2AX]^{n+}$ were very sensitive to the nature of A.[2] In general, configuration is retained in the act of solvolysis, but when A is a potential π donor, aquation is accompanied by stereochemical change. The number of ligands producing this effect is severely restricted, *e.g.*, A = OH, Cl, Br, and –NCS (and –NHR presumably since base hydrolysis often leads to stereochemical

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