Racemization and Deuteration at the Asymmetric Nitrogen Center of the N-Methylethylenediaminetetraamminecobalt(III) Ion

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Abstract: The $[Co(NH_3)_4(N\text{-}Meen)]^{3+}$ ion has been resolved into its optical forms and the rates of racemization (k_R) and deuteration (k_D) at the asymmetric nitrogen center have been measured. The ratio k_D/k_R is $\sim 10^5$ and implies that the configuration about the N atom is retained most of the time that the proton is off the quaternary N site. The activation parameters are compared with those for the $[Co(NH_3)_4sar]^{2+}$ (sar = N-methylglycinate) ion, and the additional retention obtained is attributed to the conformational effects in the cobalt N-methylethylenediamine ring.

The rapid rate of inversion of tervalent nitrogen has prevented the resolution of dissymmetric molecules having trigonal nitrogen as the sole center of asymmetry, except in certain fused ring systems.[1] The tetrahedral nitrogen of a protonated tertiary asymmetric amine lacks the lone pair of electrons responsible for the rapid rate of inversion, but the acidity and lability of such ions have prevented their resolution into optical enantiomorphs.[1] Failure to achieve resolutions of secondary amines coordinated to metal ions has led to the belief that the acidity and lability of the amine hydrogen preclude their resolution.[2] Recently, several workers have shown that this is not the case.[3,4] In fact, the rate of hydrogen exchange for many metal complexes is sufficiently slow to allow the resolution of coordinated secondary amines in dilute acid.

Using this fact to advantage, Halpern, Sargeson, and Turnbull[4] successfully resolved the $[Co(NH_3)_4sar]^{2+}$ ion (where sar = N-methylglycinate) and found that the ratio of the rate of hydrogen exchange to the rate of racemization was ~ 4000.[4] The ion $[Co(NH_3)_4(N\text{-}Meen)]^{3+}$ (N-Meen = N-methylethylenediamine, Figure 1) has now been resolved into its optical forms, and this paper is concerned with the rates and mechanism of racemization and deuteration at the asymmetric center of this ion compared with those for $[Co(NH_3)_4sar](NO_3)_2$. The two complexes differ in charge and in the electronic and conformational properties of the chelate. They have a common property in that the chelate N atom is the sole source of optical activity. The Co atom in these complexes merely acts as a chromophoric substituent on the N atom, and in this respect the optical properties of the complexes are important, but this aspect will be discussed elsewhere.[5]

Experimental Section

All materials used were reagent grade. Rotations were measured in 1-dm cells with a Perkin-Elmer 141 polarimeter fitted with a Zeiss monochromator and a quartz-halogen lamp. Proton magnetic resonance spectra were measured using a Perkin-Elmer R10 nmr spectrometer and sodium trimethylsilylpropanesulfonate as the standard reference. The circular dichroism was measured on a Jouan Dichrographe.

Ammonium Disulfitodiammine-N-methylethylenediaminecobaltate(III) Hemihydrate. Ammonium disulfitotetraamminecobaltate(III)[6] (36.0 g) was suspended in water (500 ml), and N-methylethylenediamine (7.4 g) was added slowly with stirring over 15 min. The resulting solution was reduced to half its volume under vacuum. The yellow product was obtained by addition of ethanol, collected, and washed with ethanol and acetone and dried in a vacuum desiccator, yield 36.5 g. *Anal.* Calcd for $NH_4[Co(SO_3)_2(NH_3)_2(N\text{-}Meen)]\cdot 0.5H_2O$: C, 10.17; H, 5.97; N, 19.77. Found: C, 10.22; H, 5.95; N, 20.06.

Dibromodiammine-N-methylethylenediaminecobalt(III) Bromide. $NH_4[Co(SO_3)_2(NH_3)_2(N\text{-}Meen)]\cdot 0\cdot 5H_2O$ (36.0 g) was added slowly with stirring to a hot solution of HBr (140 ml of 40% at 80°) and heated for 5 min. The green crystals which formed on cooling at room temperature were collected after 10 hr and washed with acetone and ethanol. A second fraction, which formed upon addition of *n*-butyl alcohol and cooling, was collected and washed similarly, total yield 28.0 g. A sample was recrystallized for analysis from boiling methanol and dried under vacuum at room temperature. *Anal.* Calcd for $[CoBr_2(NH_3)_2(N\text{-}Meen)]Br\cdot 0.5CH_3OH$: C, 9.94; H, 4.29; N, 13.22. Found: C, 10.06, 9.98; H, 4.34, 4.36; N, 13.29. Several attempts to remove the solvent of crystallization by drying the sample at 80° were unsuccessful.

Tetraammine-N-methylethylenediaminecobalt(III) Bromide Monohydrate. $[CoBr_2(NH_3)_2(N\text{-}Meen)]Br$ (28.0 g) was added slowly to liquid ammonia in a vacuum flask. After evaporation of the ammonia the orange residue was extracted with ethanol and washed with acetone. It was recrystallized from warm HBr (100 ml, 1 *N*) by adding ethanol and cooling. The orange crystals were removed, washed with ethanol and acetone, and air-dried, yield 25.0 g. *Anal.* Calcd for $[Co(NH_3)_4(N\text{-}Meen)]Br_3\cdot H_2O$: C, 7.85; H, 5.27; N, 18.31. Found: C, 7.84; H, 5.28; N, 18.78.

To obtain the fully deuterated compound, $[Co(NH_3)_4(N\text{-}Meen)]Br_3\cdot H_2O$ (4.6 g) was dissolved in D_2O (10 ml, 99.9%) and maintained at 40° for 2 days. The D_2O was then evaporated under vacuum and the process repeated. The pmr spectrum in 0.1 *N* DCl showed no evidence of NH signals.

Resolution of $[Co(NH_3)_4(N\text{-}Meen)]Br_3\cdot H_2O$. $Na(+)[Co(C_2O_4)_2en]\cdot H_2O$ (3.6 g) was added to a solution of $[Co(NH_3)_4(N\text{-}Meen)]Br_3\cdot H_2O$ (9.2 g) in HBr (50 ml, 0.04 *N*, at 30°). After 24 hr the orange-purple crystals (fraction A) were collected, washed with methanol and then acetone, and air-dried, yield 4.9 g. *Anal.* Calcd for $(-)[Co(NH_3)_4(N\text{-}Meen)](+)[Co(C_2O_4)_2en]Br_2\cdot H_2O$: C, 15.94; H, 4.75; N, 17.11. Found: C, 16.00; H, 4.68; N, 17.27.

The filtrate was reduced to half its volume under reduced pressure and cooled in an ice bath. The crystals formed (fraction B) were

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(1) R. L. Shriner, R. Adams, and C. S. Marvel, "Organic Chemistry, An Advanced Treatise," 2nd ed, H. Gilman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp 402–413.

(2) J. R. Keubler and J. C. Bailar Jr., *J. Am. Chem. Soc.*, 74, 3535 (1952).

(3) (a) J. W. Palmer and F. Basolo, *J. Phys. Chem.*, **64**, 778 (1960), and references therein; (b) F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Am. Chem. Soc.*, **82**, 1073 (1960).

(4) B. Halpern, A. M. Sargeson, and K. R. Turnbull, *ibid.*, **88**, 4630 (1966).

(5) D. A. Buckingham, L. G. Marzilli, S. F. Mason, and A. M. Sargeson, to be published.

(6) J. C. Bailar, Jr., and D. F. Peppard, *J. Am. Chem. Soc.*, **62**, 105 (1940).

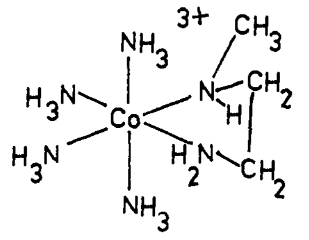
Figure 1. $[Co(NH_3)_4(N\text{-}Meen)]^{3+}$ ion.

collected and treated as above, yield 0.88 g. The total yield was 85%. The filtrate was treated with excess NaI, and optically impure $(+)[Co(NH_3)_4(N\text{-}Meen)]I_3 \cdot H_2O$ (4.15 g, fraction C) was collected and washed as above. Fraction A was recrystallized by dissolving it in HBr (45 ml, 0.1 *N*). After 20 hr at room temperature the crystals (1.9 g) were collected and ground with NaI in a small volume of 0.04 *N* HBr. The yellow crystals formed were collected and shaken with AgBr in HBr (20 ml, 0.04 *N*). The solution was filtered and $Na(+)[Co(C_2O_4)_2en] \cdot H_2O$ (0.7 g) added. After the first fraction of $(-)[Co(NH_3)_4(N\text{-}Meen)](+)[Co(C_2O_4)_2en]Br_2 \cdot H_2O$, which formed at room temperature, was removed a second fraction (0.32 g) was obtained on cooling. This was converted to optically impure $(-)[Co(NH_3)_4(N\text{-}Meen)]I_3 \cdot H_2O$ as above, yield 0.3 g, α_{480} −0.059° for a 0.1% solution in 0.04 *N* HBr. This isomer could be obtained optically pure using $(-)[Co(C_2O_4)_2en]^-$ ion as the resolving agent. Fraction C and a similar fraction from another resolution (6.3 g) were converted to a solution of the bromide salt as above (30 ml), and $Na(-)[Co(C_2O_4)_2en] \cdot H_2O$ (1.8 g) was added. After 5 hr, the diastereoisomer $(+)[Co(NH_3)_4(N\text{-}Meen)](-)[Co(C_2O_4)_2en]Br_2 \cdot H_2O$ was collected, washed with 50% 0.04 *N* HBr–methanol and then methanol, and air-dried, yield 1.88 g. This was dissolved in a minimum volume of 0.1 *N* HCl, filtered, and allowed to stand at room temperature for 3 hr and at 10° for 4 hr. The crystals formed were collected as above (0.88 g) and ground with NaI. The resulting orange crystals were recrystallized to constant rotation from warm 0.1 *N* HCl by adding NaI. The optical form was less soluble than the racemate, α_{480} +0.090° for a 0.1% solution in 0.04 *N* HBr. *Anal.* Calcd for $[Co(NH_3)_4(N\text{-}Meen)]I_3 \cdot H_2O$: C, 6.01; H, 4.03; N, 14.02. Found: C, 6.07; H, 4.00; N, 14.12.

Racemization Studies. A Cambridge pH meter (±0.005 pH unit) was used to measure the pH of the buffer at the temperature used for the rate studies (Table IV). The acetate buffer was found to be temperature independent, and the pH value at 35° was used for all temperatures. The reaction mixtures were all ~0.2% in complex and had the same pH as the buffer. The ionic strength $\mu = 1$ was maintained with KCl. All rotations were initially of the order of 0.1 to 0.15°. Rates were reproducible to ±5%, and individual measurements were accurate to ±0.002°. The rotation was followed to zero between 400 and 700 mμ for at least one run in each buffer system. The acetate buffer in D_2O was prepared from anhydrous sodium acetate and acetic anhydride. The solution gave the predicted pH and the $[D^+]$ was calculated using the empirical formula pD = pH + 0.4.[7]

Hydrogen-exchange studies were followed with the nmr spectrometer, and the rate constants were reproducible to within ±5% for $[H^+]$ or $[D^+]$ greater than 0.003 *N*. The stock acid solutions were titrated potentiometrically against standard base. All solutions were 0.167 *M* in complex. The peak height of the methyl signal of the deuterated complex in D_2O was used as a standard to allow for variations in resolution of the spectrometer with time. The pmr spectra of this standard solution showed that the complex decomposes less than 5% in 5 months at 34.3°. The nmr tubes were kept in the preheater of the spectrometer for runs at 34.3° and in a water bath for other temperatures. In the latter the tubes were cooled quickly and the spectra taken immediately. For both the racemization and hydrogen-exchange studies the temperature was kept constant to ±0.1°.

Results

Rotatory dispersion, circular dichroism, and visible and ultraviolet absorption curves for the isomer $(+)[Co(NH_3)_4(N\text{-}Meen)]I_3 \cdot H_2O$, $[\alpha]^{25}_{490}$ +100°, are given in Figure 2. The maximum optical rotation appears at 490 mμ, and this wavelength was used to follow the racemization rates in acetate and collidine–HCl buffers at $\mu = 1$. All rates were followed for at least two half-lives and plots of log α_{490} against time gave straight lines. It is apparent from Figure 2 that the deuteration takes place with retention of configuration.

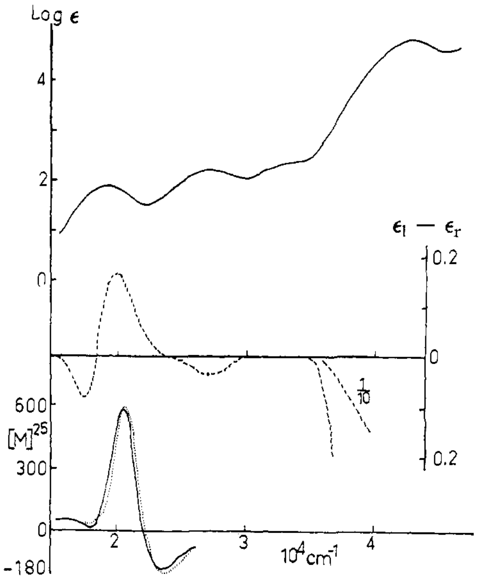

Figure 2. Absorption spectrum, circular dichroism (CD), and rotatory dispersion (RD) curves for the $(+)[Co(NH_3)_4(N\text{-}Meen)]^{3+}$ ion in water. The dotted RD curve is for the deuterated complex ion in D_2O.

Proton Magnetic Resonance Spectra. The pmr spectra of $[Co(NH_3)_4(N\text{-}Meen)]Br_3 \cdot H_2O$ and $[Co(ND_3)_4(N\text{-}Meen)(D_3)]Br_3 \cdot D_2O$ are given in Figure 3, measured in D_3O^+ and D_2O, respectively. The absorptions in the spectra were assigned as indicated in Table I. The most significant peaks are those due to the methyl group split by the adjacent N proton. In the deuterated complex the doublet collapses to a singlet, and this change allows the deuteration rate at this N atom to be measured specifically. Part of a typical set of data is given in Figure 4. It was more accurate, however, to measure the rate of protonation of the deuterated complex in H_2O since the broad water signal did not interfere and since pD has to be evaluated empirically.[7] The peak height at the center of the doublet was measured and plots of log [(peak height)$_\infty$ − (peak height)$_t$] against time gave straight lines for at least two half-lives.

Table I. Chemical Shifts (δ)[a] in D_2O at 34.3°

	B	A
$-CH_3$	2.38	2.30
$-CH_2CH_2-$	2.90	2.95
NH_3		3.57
$-NH_2$		5.30
$>NH$		5.80

[a] Sodium trimethylsilylpropanesulfonate as reference.

Rate Constants. The observed rate constants k_{obsd} determined by the above methods are listed in Tables II and III, and the derived rate constants k_D and k_R

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[7] R. Lumry, E. L. Smith, and R. R. Glantz, *J. Am. Chem. Soc.*, 73, 4330 (1951); P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, 64, 188 (1960).

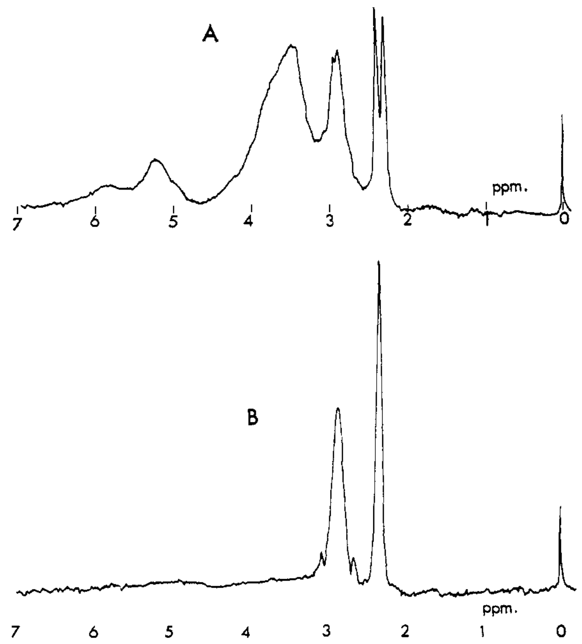

Figure 3. Pmr spectra for (A) $[Co(NH_3)_4(N\text{-}Meen)]Br_3$ in 0.1 *N* D_2SO_4 and (B) $[Co(ND_3)_4(N\text{-}Meen)(D_3)]Br_3$ in D_2O.

were calculated using $K_W = 1.95 \times 10^{-14}$ [8] in 1 *M* KCl at 34.3° and $K_{D_2O} = 0.195K_W$ [9] $= 3.80 \times 10^{-15}$. Both the racemization and hydrogen-exchange processes follow the same rate law

$$R = k[\mathrm{Co}][\mathrm{OH}^-]$$

and the average value of k_D in DCl solutions was $3.0 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$, and for racemization in 2,4,6-collidine–HCl buffer k_R was $2.45 \times 10^2\ M^{-1}\ \mathrm{sec}^{-1}$. The ratio $k_D/k_R = 1.23 \times 10^5$ is ~30 times greater than that reported for the $[Co(NH_3)_4sar]^{2+}$ ion. The rate of deuteration was first order in $[OD^-]$ from 3.13×10^{-3} to 0.132 *N* DCl, and the rate of racemization was first order in $[OH^-]$ from pH 5.92 to 7.97.

Table II. Rate Constants for Hydrogen Exchange in $[Co(N\text{-}Meen)(NH_3)_4]Br_3$ at 34.3° in DCl or HCl[a]

$[H^+]$ or $[D^+]$, *M*	k_{obsd}, sec^{-1}	$10^{-7}k_{calcd}$, $M^{-1}\ \mathrm{sec}^{-1}$
0.00631 (H^+)	3.36×10^{-5}	1.1[b]
0.00631 (H^+)	3.15×10^{-5}	1.0[b]
0.0631 (H^+)	3.21×10^{-6}	1.0[b]
0.00313 (D^+)	3.50×10^{-5}	2.9[c]
0.00313 (D^+)	3.61×10^{-5}	3.0[c]
0.00313 (D^+)	3.71×10^{-5}	3.1[c]
0.0329 (D^+)	3.43×10^{-6}	3.0[c]
0.0658 (D^+)	1.77×10^{-6}	3.1[c]
0.1316 (D^+)	8.95×10^{-7}	3.1[c]

[a] $\mu = 1.0\ M$. [b] $k = (0.693/t_{1/2})([H^+]/1.95 \times 10^{-14})$. [c] $k = (0.693/t_{1/2})([D^+]/3.80 \times 10^{-15})$.

Isotope Effects. The ratio of rates of hydrogen exchange for $[Co(NH_3)_4(N\text{-}Meen)]^{3+}$ in H_2O and D_2O ($k_D/k_H \sim 3$) (Table II) is intermediate between those previously reported (~1.5)[3b] and that found for the $[Co(NH_3)_4sar]^{2+}$ ion (~7).[4]

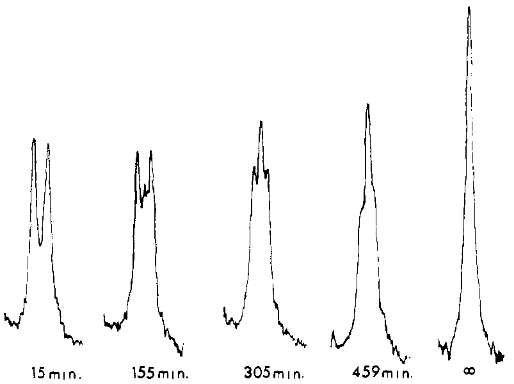

Figure 4. Change in methyl pmr signal with time in 0.03 *N* DCl at 34.3°

The observed rate of racemization (Table IV) in acetate–D_2O buffer is 1.1 times as great as that in acetate–H_2O buffer at the same temperature (40°), when allowance is made for different acid concentrations and different acid dissociation constants for the two solvents. This inverse isotope effect was also found for the $[Co(NH_3)_4sar]^{2+}$ ion.[4] However, the isotope effect is small and there is some uncertainty in defining pD. For these reasons, therefore, no great reliance can be placed on this value.

Table III. Rate Constants for the Racemization of $[Co(N\text{-}Meen)(NH_3)_4]I_3$ at 34.3°

pH	k_{obsd}, sec^{-1}	k_{calcd}, $M^{-1}\ \mathrm{sec}^{-1}$ [c] $\times 10^{-2}$
5.92[a]	3.58×10^{-6}	2.4
6.38[b]	1.07×10^{-5}	2.3
7.22[b]	8.13×10^{-5}	2.5
7.52[b]	1.60×10^{-4}	2.4
7.52[b]	1.54×10^{-4}	2.6
7.97[b]	4.71×10^{-3}	2.5

[a] 0.2 *M* acetate buffer, 1 *M* KCl. [b] 0.05 *M* collidine buffer, 1 *M* KCl. [c] $k = (0.693/t_{1/2})([H^+]/1.95 \times 10^{-14})$.

Table IV. Temperature Dependence of the Racemization Rate Constants for $[Co(N\text{-}Meen)(NH_3)_4]I_3$

pH	Temp, °C	k_{obsd}, sec^{-1}
8.12[b]	20.0	3.00×10^{-5}
8.08[b]	25.0	8.56×10^{-5}
7.97[b]	30.0	1.75×10^{-4}
7.97[b]	30.0	1.70×10^{-4}
7.97[b]	34.3	4.17×10^{-4}
5.92[a]	34.3	3.85×10^{-6}
5.92[a]	40.0	1.19×10^{-5}
5.92[a]	45.0	2.83×10^{-5}
5.95[c]	40.0	6.79×10^{-6}

[a] 0.2 *M* acetate buffer, 1 *M* KCl. [b] 0.05 *M* collidine buffer, 1 *M* KCl. [c] 0.2 *M* acetate buffer, 1 *M* KCl, D_2O.

Activation Parameters. The rate of hydrogen isotope exchange was studied over the temperature range 34.3–55.0° in both H_2O and D_2O (Table V). The rate of racemization was studied from 20 to 45° in both acetate and collidine–HCl buffers (Table IV). In all instances plots of log *k* against $1/T$ were linear and $\Delta H^{\ddagger}$ was evaluated from the slope (Table VI). $\Delta S^{\ddagger}$ was

[8] H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **55**, 2194 (1933).

[9] W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **32**, 1397 (1936).

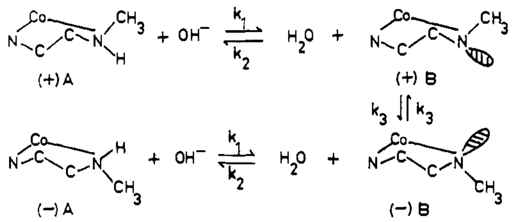

Figure 5.

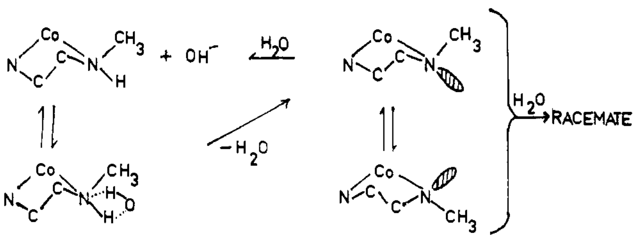

Figure 6.

calculated assuming the transmission coefficient was unity, although some data are available for the inversion of aziridines which suggests that the transmission coefficients for these molecules are less than unity.[10]

Table V. Temperature Dependence of H Exchange

Temp, °C	$k_{obsd} \times 10^5$, sec^{-1} *a*	*b*
34.3	0.343	0.321
45.0	1.54	. . .
50.0	3.21	3.30
55.0	6.60	6.66

[a] Deuteration in 0.0329 *N* DCl. [b] Protonation in 0.0631 *N* HCl.

Table VI. Rate Constants and Activation Parameters for $[Co(NH_3)_4(N\text{-Meen})]^{3+}$ and $[Co(NH_3)_4sar]^{2+}$ Ions

Reaction	Solvent	$k_D{}^a$ or k_R,^{a} M^{-1} sec^{-1}	$E_{a,obsd}$ kcal/mole	$\Delta H^{\ddagger}_{calcd}$, kcal/mole	$\Delta S^{\ddagger}$, eu
	(a) $[Co(NH_3)_4(N\text{-Meen})]^{3+}$				
H exchange	D_2O	2.97×10^7	28.1	13.8	21
D exchange	H_2O	1.04×10^7	28.7	15.4	24
Racemization	Collidine buffer	2.52×10^2	38.3	24.2	31
Racemization	Acetate buffer	2.37×10^2	37.2	23.8	30
	(b) $[Co(NH_3)_4sar]^{2+}$				
H exchange	D_2O	6×10^7	28	13.5	21
Racemization	Acetate buffer	1.7×10^4	32.5	18.6	21

[a] Corrected for K_W at 34.3°.

In the evaluation of $\Delta H^{\ddagger}$ account has been taken of ΔH for the dissociation of H_2O and D_2O over the temperature range used and of the change in pH of the collidine–HCl buffer with change in temperature. The pH of the acetate buffer was temperature independent.

Discussion

The rate laws for racemization and hydrogen exchange are consistent with the formation of a common intermediate as shown in Figure 5 but do not require it. An alternative formulation arises (Figure 6) if H exchange occurs from interchange in the ion pair and if racemization occurs from ion–solvent pair dissociation.

The first mechanism requires the intermediate to react with the solvent with retention most of the time since $k_2 >> k_3$, while the second proposes that retention arises from interchange in the ion pair and also possibly by the intermediate and solvent reacting with retention. The deprotonated intermediate is the same in each case and leads to a racemic product by inversion of the configuration about the tertiary N atom. There is no conclusive evidence so far for the common intermediate in Figure 5 ((+)- and (−)B) for both deuteration and racemization, but there is good evidence for deprotonated intermediates of this type.[11–13] When a strong electron-withdrawing group is present such as in the $Co(NH_3)_5NH_2SO_3]^{2+}$ ion, a proton can be titrated off the complex (pK = 6.17 ± 0.01 at 10°). Also, the compound $Na[Co(glygly)_2]$ in which two protons have been removed is well characterized.[14] That racemization does occur is a good indication that a deprotonated intermediate exists for this reaction since optically active quaternary ammonium salts of the form $[NR_1R_2R_3R_4]^+$ are optically stable, whereas tertiary amines invert readily. Evidence for a common intermediate might be obtained if a competitor for the lone pair could be introduced, leading to a preponderance of noninverted product over inverted product, and this aspect of the problem is now being pursued.

On the other hand, evidence exists for ion-pair formation between complexes of this type and hydroxide ion[15] ($K \approx 2$, $\mu = 1$) so that the mechanism in Figure 5 may need slight modification to include this possibility as a preequilibrium. It has been observed that the deuteration rates decrease with decreasing positive charge on the complex (~10-fold for each unit of charge).[3,5] This is consistent with the increasing difficulty of removing positive charge from the cationic complexes as the charge decreases. Also it is known[16] that the deuteration rate for $Co(NH_3)_6{}^{3+}$ is relatively insensitive to ionic strength, whereas the ion-pair association constant for OH^- and this cation is strongly dependent on ionic strength.[15] This suggests that the ion-pair interchange mechanism is not important in the deuteration process.

The isotope effects for racemization in both this complex and the sarcosine complex are small and possibly inverse which is consistent with the intermediate proposed and the fact that H abstraction is not rate determining. However, the isotope effects do indicate that H abstraction is rate determining for H exchange.

Generally we feel that these results can be rationalized more successfully using the mechanism in Figure 5 although the mechanism in Figure 6 cannot be completely excluded.

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(11) R. G. Pearson, H. H. Schmidtke, and F. Basolo, *ibid.*, **82**, 4434 (1960).

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(13) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **88**, 5443 (1966).

(14) A. R. Manyak, C. B. Murphy, and A. E. Martell, *Arch. Biochem. Biophys.*, **59**, 373 (1955).

(15) J. A. Caton and J. E. Prue, *J. Chem. Soc.*, 671 (1956).

(16) H. Block and V. Gold, *ibid.*, 966 (1959).

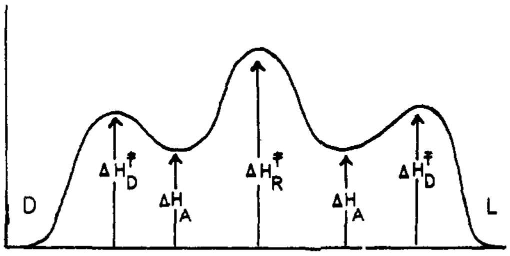

Figure 7. Enthalpy–reaction coordinate profile for racemization.

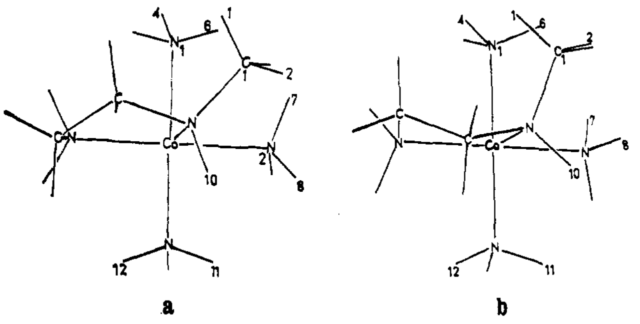

Figure 8. The two N-Meen conformations used in the conformational analysis (see text).

It follows that the rate laws for the first mechanism are

For deuteration

$$R = k_1[\text{complex}][\text{OD}^-]$$

For racemization

$$R = k_3\frac{K_A}{K_W}[\text{complex}][\text{OH}^-]$$

where K_A = [complex-H][H$^+$]/[complex] $\approx 10^{-14}$–10^{-15}.[17]

It follows that $k_R \approx k_3$ for 1 M [OH$^-$] (within one or two orders of magnitude), k_3 being the inversion rate constant for the deprotonated intermediate. The enthalpy profile for the processes is that in Figure 7.

Unfortunately ΔH_A for the deprotonation of the complex is not known because the pK_A is not measurable in aqueous solution,[16] but clearly the height of the inversion barrier ($\Delta H_R^{\ddagger} - \Delta H_A$) must be greater than ($\Delta H_R^{\ddagger} - \Delta H_D^{\ddagger}$) $\sim$ 10 kcal/mole. Using $k_R \approx 10^2$ M^{-1} sec^{-1} and $K_A \sim 10^{-15}$, the inversion rate constant k_3 ($\sim 10^3$ sec^{-1}) compares favorably with those measured for amines,[18] amides,[19] and several N-methylaziridines,[10,20] which have rate constants between 10^2 and 10^5 sec^{-1} and activation energies from 6 to 20 kcal/mole.

This estimate is similar to that estimated for the [Co(NH$_3$)$_4$sar]$^{2+}$ ion ($\sim 10^4$ sec^{-1}), and it is now of some interest to compare the properties of the two systems (Table VI). They differ in over-all charge and in the electronic and conformational properties of the chelates. It might be expected that the 2+ sarcosinato complex ion would exchange the proton more slowly than the 3+ N-methylethylenediamine chelate. However, the inverse is found, although both complex ions have comparable deuteration rates. This apparent inconsistency might be explained by the influence of the electronegative carboxyl group on the sarcosine NH. Removal of charge from the N center should increase the rate of deprotonation.

The different rates of racemization (a factor of 30) probably involve these factors partly, but in addition we propose they are closely related to the chelate conformations. The sarcosinatocobalt ring has little conformational deformation out of the N–Co–O plane, but the Co–N-methylethylenediamine ring is markedly puckered, and some discussion of the conformational aspects of this complex ion is relevant.

Although the axial equatorial nature of the protons on the C atoms is analogous to that in cyclohexane the relationship is not so marked for the substituents on the N atoms. There is ~20° difference in position for the methyl group in the different conformations and our calculations of the magnitude of the nonbonded atomic interactions show that the structure in Figure 8a is more stable than that in 8b, mainly because the methyl group is more distant from the axial NH$_3$ on the Co atom.

Using the equation of Hill,[21] the energy difference was calculated to be 4 kcal/mole when each conformer was in its most stable rotational configuration, *i.e.*, with the maximum distances between the most significant nonbonding interactions (Figure 8).[22] Interaction of the methyl group with all adjacent ammonia molecules was considered, and account was taken of every interaction which differed for the two conformers. Distances were measured using Dreiding models, and those greater than 3.20 A were ignored.

These factors are significant in the racemization process because not only does the N atom invert but the conformation must invert also. The difference between the activation energies for racemization of the sarcosine and the N-Meen complex (~4–5 kcal/mole) is attributed to this conformational factor, namely that additional energy is required to invert the conformer as well as the N center, which means that the retention to inversion ratio is increased for the Meen complex over that for the sarcosinato complex ion. The effect is partly offset by an entropy difference between the racemization and deuteration processes for the former. It is not possible to say whether the conformational interchange precedes or antecedes inversion at the N atom or whether the processes are synchronous.

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[22] Atoms found to be significant in the calculations are as numbered in Figure 8. Distances (in Ångstroms) used were as follows and those that are starred were most significant. Figure 8a: more stable, H_1H_6, 3.20; H_2H_4, 2.35; H_2H_7*, 2.00; H_2H_8*, 2.00; H_6H_7*, 1.92; $H_{10}H_{11}$, 2.40; $H_{10}H_{12}$, 2.60; $H_{10}H_8$, 2.70; H_4C_1, 2.70; H_8C_1*, 2.50; H_3C_1, 2.70; H_2N_2*, 2.20; H_1N_1, 2.70; H_2N_1, 2.80. Figure 8b; less stable, H_1H_4*, 1.72; H_1H_6, 2.50; H_2H_6*, 1.72; H_2H_4, 2.50; H_2H_7, 3.10; H_2H_8, 2.30; H_6H_7, 2.35; H_6H_8, 2.70; $H_{10}H_8$, 2.35; $H_{10}H_{11}$, 2.50; H_8H_{11}, 3.00; H_4C_1*, 2.32; H_8C_1*, 2.32; H_4N_1*, 2.32; H_2N_1*, 2.32.

It can be asserted, however, that they need not be synchronous, and if the change takes place in steps then the energy profile (Figure 7) must be altered to account for the additional conformational isomers of the deprotonated intermediates.

Acknowledgments. We wish to thank Dr. J. Fildes for the microanalyses, Dr. S. F. Mason for the CD spectrum, and Mr. R. Watts for a computer program. The technical assistance of Mr. S. Brown and Mr. H. Satrapa is also acknowledged.

Ligand-Exchange Reactions of Bis(*cis*-1,2-disubstituted ethylene-1,2-dithiolato)nickel Complexes

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Abstract: Ligand exchange reactions between complexes of the type $[MS_4C_4R_4]^z$ and $[MS_4C_4R_4']^z$, $R \neq R' = C_6H_5$, CF_3, CN, for the nickel group metals are described. In acetonitrile, dichloromethane, and acetone it was found that the mixed species $[M(S_2C_2R_2)(S_2C_2R'_2)]^z$, detected by polarography, was preferentially formed. Because the reorganization reactions were slow at room temperature, it was possible to isolate the mixed species from the equilibrium mixtures and also to devise a direct preparation of a mixed species.

There has been considerable interest in the chemistry of (*cis*-1,2-disubstituted ethylene-1,2-dithiolato)-metal complexes. Much of the current work, however, has been concerned with their characterization,[1] their magnetic properties, and the attempts[2] to elucidate their detailed electronic configurations.

These complexes have been shown[3] to undergo discrete one-electron-transfer reactions and, as a result, most of the subsequent synthetic work has been concerned with the isolation of the various members of the electron-transfer series. It has been tacitly assumed that these complexes are not labile and do not undergo ligand-exchange reactions. In this paper we show that ligand exchange does occur for the planar complexes of the nickel group, and we describe the isolation of mixed ligand species of the type $[Ni(S_2C_2R_2)(S_2C_2R'_2)]^z$, $z = -1, -2$; $R \neq R' = CF_3$, C_6H_5, and CN.

Experimental Section

Preparation of Compounds. The starting materials were prepared by the previously published procedures.[3] All melting points are uncorrected.

$[(C_2H_5)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CF_3)_2\}]$. A mixture of 0.40 g (0.62 mmole) of $[(C_2H_5)_4N][NiS_4C_4(CF_3)_4]$ and 0.42 g (0.62 mmole) of $[(C_2H_5)_4N][NiS_4C_4(C_6H_5)_4]$ was refluxed in 50 ml of acetone for 12 hr. The mixed ligand species was separated from this equilibrium mixture by the following procedure. A 15-ml portion of 2-butanol was added to this solution, and then most of the acetone (*ca.* 45 ml) was removed under reduced pressure without external heating. This caused the small amount of $[(C_2H_5)_4N][NiS_4C_4(C_6H_5)_4]$ to separate. The mixture was filtered and the residual acetone was removed from the filtrate. The product crystallized during 15 min. It was collected and washed with two 5-ml portions of cold 2-butanol, followed by two 5-ml portions of *n*-pentane. It was twice recrystallized from acetone–2-butanol by this procedure to give 0.1 g of pure $[(C_2H_5)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CF_3)_2\}]$ as brown needles (mp 159–161°).

Anal. Calcd for $C_{26}H_{30}F_6NNiS_4$: C, 47.50; H, 4.60; N, 2.13; S, 19.51; F, 17.34. Found: C, 47.50; H, 4.70; N, 2.20; S, 19.28; F, 17.19.

$[(C_4H_9)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]$. A mixture of 0.50 g (0.61 mmole) of $[(C_4H_9)_4N]_2[NiS_4C_4(CN)_4]$ and 0.33 g (0.61 mmole) of $[NiS_4C_4(C_6H_5)_4]$ was refluxed for 6 hr in 150 ml of acetone. The solvent was removed *in vacuo*, and the resultant solid was washed with two 30-ml portions of methanol. The residue was dissolved in 150 ml of acetone–2-butanol (2:1 v/v). The acetone was stripped off and the mixture was filtered. The dropwise addition of *n*-pentane (*ca.* 5 ml) to the filtrate induced crystallization. The product was recrystallized twice from acetone–2-butanol to give 0.2 g of shiny black needles of pure $[(C_4H_9)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]$, mp 158–159°.

Anal. Calcd for $C_{34}H_{46}N_3NiS_4$: C, 59.73; H, 6.78; N, 6.15; S, 18.76. Found: C, 59.50; H, 6.83; N, 6.19; S, 18.96.

$[(C_2H_5)_4N][Ni\{S_2C_2(C_6H_5)_2\}\{S_2C_2(CN)_2\}]$. This compound was made from an equimolar mixture of either $[NiS_4C_4(C_6H_5)_4]$ and $[(C_2H_5)_4N]_2[NiS_4C_4(CN)_4]$ or $[(C_2H_5)_4N][NiS_4C_4(CN)_4]$ and $[(C_2H_5)_4N][NiS_4C_4(C_6H_5)_4]$, by a procedure similar to that described above, as shiny black needles, mp 160–161°.

Anal. Calcd for $C_{26}H_{30}N_3NiS_4$: C, 54.66; H, 5.29; N, 7.35; S, 22.45. Found: C, 54.30; H, 5.30; N, 7.55; S, 22.32.

$[(C_4H_9)_4N]_2[Ni\{S_2C_2(CF_3)_2\}\{S_2C_2(CN)_2\}]$. A solution of 1.5 g (6.6 mmoles) of $(CF_3)_2C_2S_2$ in 10 ml of benzene was added to a suspension of 1.5 g (2.1 mmoles) of $[(C_6H_5)_3P]_2NiS_2C_2(CN)_2$ in 40 ml of the same solvent. The mixture was refluxed for 5 min and then the solvent was removed under reduced pressure. The residual oil was treated with 30-ml portions of *n*-pentane to extract the small amounts of $[NiS_4C_4(CF_3)_4]$. The residue was treated with 50 ml of ethanol, and the mixture was filtered after 30 min to remove $(C_6H_5)_3PS$.

The dark brown filtrate was treated with 5 ml of hydrazine. To the resulting red solution was added 1.35 g (4.2 mmoles) of $[(C_4H_9)_4N]Br$ dissolved in 10 ml of ethanol. Sufficient water was added to induce crystallization. The crude product separates slowly on standing. It was dissolved in 10 ml of acetone, treated with 25 ml of 2-butanol, and then most of the acetone was removed under reduced pressure. After 5 min the mixture was filtered to remove small amounts of $[(C_4H_9)_4N]_2[NiS_4C_4(CN)_4]$. The filtrate was concentrated to 15 ml under reduced pressure, causing the product to separate as small red platelets. This ma-

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