the three carbon atoms bonded to the apical phosphorus atom are staggered in such a way that these methylene carbon atoms can approach within the observed value of 2.8 A of each other, much closer than the 4.0 A approach suggested by the van der Waals radius of the methylene group.[32] It should be noted that a diastereomeric form of [Ni(TAP)CN$^+$] can theoretically occur in which two trimethylene chains pucker in one direction and a third trimethylene chain puckers in the opposite direction. Since this diastereomer would require one nonbonding C$\cdots$C distance of only 2.2 A for two methylene carbon atoms attached to the apical phosphorus atom, its possible formation can be precluded by steric considerations as being energetically unfavorable unless there is considerable angular distortion.

The results obtained in this study indicate the need of further structural investigations of five-coordinate metal complexes of d^8 configuration. Insight into the causes of the displacement of the central metal atoms from the equatorial triarsenic planes in the [Ni(TAP)CN$^+$] and the [Pt(QAS)I$^+$] cations could be gained from the synthesis and X-ray structural analysis of the cyanide analog of [Pt(QAS)I$^+$]. A probable rationale is that the observed distortion is a means of minimizing nonbonding atomic repulsions without unduly increasing the metal–ligand bond lengths (thus weakening the metal–ligand bonds). Although the appropriate sums of the van der Waals radii[32] of As (2.0 A), P (1.9 A), and C (1.5 A) suggest nonbonding As$\cdots$As contacts of 4.0 A, As$\cdots$P contacts of 3.9 A, and As$\cdots$CN contacts of 3.5 A in [Ni(TAP)CN$^+$], the observed average nonbonding distances are 4.0, 3.3, and 2.9 A, respectively. A regular trigonal-bipyramidal configuration with the observed Ni–As, Ni–P, and Ni–CN bond lengths would possess nonbonding As$\cdots$P and As$\cdots$CN contacts of 3.2 and 3.0 A, respectively. Hence, in order to minimize the nonbonding interactions, the arsenic atoms are displaced toward the cyanide group, increasing the As–Ni–P angles from 90° to the observed average value of 95°. In [Pt(QAS)I$^+$] the monodentate iodide ligand has a larger van der Waals radius than the apical arsenic atom (2.15 vs. 2.0 A)[32] so that the distortion is in the opposite direction, effectively pulling the central platinum atom below the triarsenic plane. If the minimizing of nonbonding repulsions is the dominant factor in these observed distortions, the central platinum atom in [Pt(QAS)CN$^+$] should likewise be displaced from the plane of the three equatorial arsenic atoms toward the apical arsenic atom.

An X-ray determination of the bromide analog of [Ni(TAP)CN$^+$], which has also been synthesized by Benner, Hatfield, and Meek,[5] is being carried out in order to compare the structural features of the two cations. A comparison of Weissenberg photographs of [Ni(TAP)CN$^+$]ClO$_4{}^-$ and [Ni(TAP)Br$^+$]ClO$_4{}^-$ has indicated that their crystal structures are not isomorphous. On the basis of spectral observations, Meek[33] has suggested that the cation of the latter bromide compound is possibly distorted toward a tetragonal-pyramidal geometry. Detailed structural parameters of [Ni(TAP)Br$^+$]ClO$_4{}^-$ should provide significant information concerning the nature and extent of this molecular deformation.

(32) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, pp 260–261.

(33) D. W. Meek, private communication to L. F. Dahl, 1965.

Racemization and Proton Exchange in the trans,trans-Dinitrobis(N-methylethylenediamine)cobalt(III) Ion

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Abstract: The rates of proton exchange and racemization at the optically active nitrogen centers in the trans,trans-dinitrobis(N-methylethylenediamine)cobalt(III) ion have been measured. Substantial retention of configuration was observed in the proton exchange, $k_D/k_R \sim 90,000$. Rates and activation parameters are compared with previous results. Conformational effects and the significance of the substituents in the 1 and 6 positions of the octahedral ion are also discussed.

Recently complexes of the form [Co(NH$_3$)$_4$sar]$^{2+}$ [1] and [Co(NH$_3$)$_4$N-Meen]$^{3+}$ [2] (sar = sarcosinate anion, N-M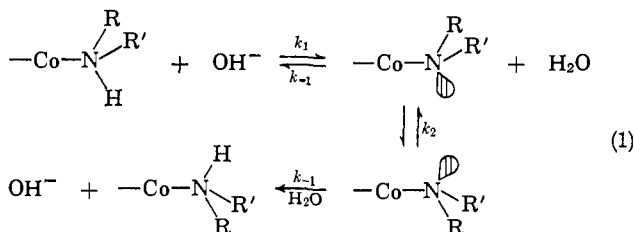een = N-methylethylenediamine) have been resolved into their catoptromers (mirror-image forms) where the sole source of asymmetry resides in the coordinated secondary amine N atom. This is achieved

(1) B. Halpern, A. M. Sargeson, and K. R. Turnbull, J. Am. Chem. Soc., 88, 4630 (1966).

(2) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, ibid., 89, 825 (1967).
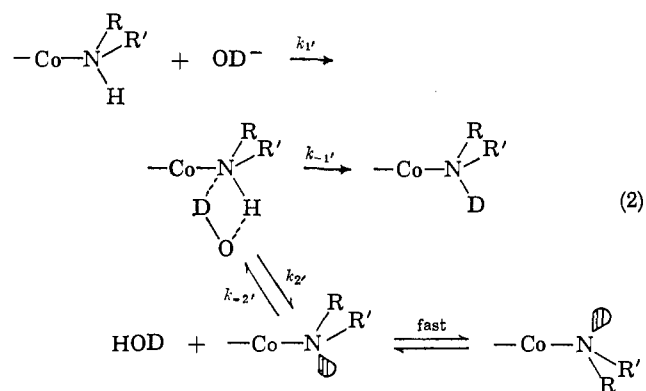
because the $[N_5Co]^{3+}$ moiety makes the *sec*-N atom more basic than is usual for organic quaternary ammonium salts, and the rate of proton exchange is thereby reduced over the rates observed for amines such as dimethylamine.

The rates of racemization and deuteration at the asymmetric center were measured for both the above compounds under a variety of conditions and are compared in Table IV. The most significant results arising from these studies were that the rates of proton exchange were several orders of magnitude faster than the respective rates of racemization and that both reactions obeyed the same rate law $R = k'[\text{complex}][\text{OH}^-]$.
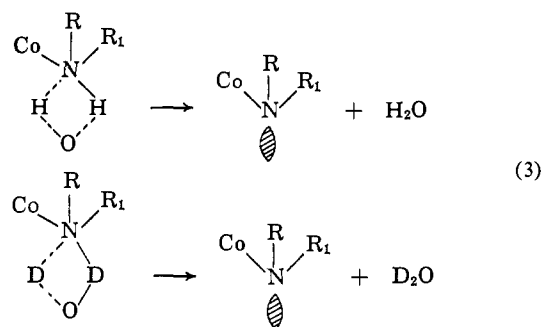
Two possible mechanisms (eq 1 and 2) proposed to account for these results differed mainly in respect to the hydrogen-exchange reaction. In the preferred scheme the N proton was abstracted with OH^-, and the lone pair thereby exposed to the solvent reacted mostly with retention. Reprotonation (k_{-1}) occurred too rapidly for inversion (k_2) to dominate the reaction of the intermediate.

$$-\text{Co}-\overset{\underset{|}{R}}{\underset{H}{N}}\overset{R'}{} + \text{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} -\text{Co}-\overset{\underset{\text{⌀}}{R}}{N}\overset{R'}{} + \text{H}_2\text{O}$$

$$\downarrow k_2$$

(1)

$$\text{OH}^- + -\text{Co}-\overset{H}{\underset{R}{N}}\overset{R'}{} \overset{k_{-1}}{\underset{\text{H}_2\text{O}}{\leftarrow}} -\text{Co}-\overset{\text{⌀}}{\underset{R}{N}}\overset{R'}{}$$

An alternative proposal accounted for retention in the deuteration step by H-isotope interchange in the ion pair (k_1') and for racemization by an ion–solvent dissociation step (k_2').

$$-\text{Co}-\overset{\underset{|}{R}}{\underset{H}{N}}\overset{R'}{} + \text{OD}^- \overset{k_{1'}}{\longrightarrow}$$

$$-\text{Co}-\overset{\underset{|}{R}}{\underset{D~~H}{N}}\overset{R'}{}\underset{O}{} \overset{k_{-1'}}{\longrightarrow} -\text{Co}-\overset{\underset{|}{R}}{\underset{D}{N}}\overset{R'}{}$$

(2)

$$k_{-2'}\diagup\diagdown k_{2'}$$

$$\text{HOD} + -\text{Co}-\overset{\underset{\text{⌀}}{R}}{N}\overset{R'}{} \underset{\text{fast}}{\rightleftharpoons} -\text{Co}-\overset{\text{⌀}}{N}\overset{R'}{\underset{R}{}}$$

Both mechanisms allow for racemization through inversion in the deprotonated intermediate but the isotope effects observed for racemization are not consistent with mechanism 2 without some modification. Under the experimental conditions racemization is measured after the *sec*-N proton has equilibrated with the solvent which means that in H_2O and D_2O respectively the ion–solvent pair dissociation would take the forms in eq 3 and a substantial isotope effect $(k_H/k_D > 2)$ would be expected if separation of the ion–solvent pair were the rate-determining step for racemization. Since this result was not observed, the implication is that ion–solvent pair separation and re-formation also leads to retention of configuration most of the time and that racemization occurs through inversion of the deprotonated intermediate as the rate-determining step. Al-

$$\overset{\underset{\text{Co}}{\diagdown}}{\underset{H}{N}}\overset{R_1}{\underset{\diagdown}{}}\overset{R}{\underset{O}{}}\underset{H}{} \longrightarrow \overset{\underset{\text{Co}}{\diagdown}}{N}\overset{\underset{\text{⌀}}{R_1}}{}\overset{R}{} + \text{H}_2\text{O}$$

(3)

$$\overset{\underset{\text{Co}}{\diagdown}}{\underset{D}{N}}\overset{R_1}{\underset{\diagdown}{}}\overset{R}{\underset{O}{}}\underset{D}{} \longrightarrow \overset{\underset{\text{Co}}{\diagdown}}{N}\overset{\underset{\text{⌀}}{R_1}}{}\overset{R}{} + \text{D}_2\text{O}$$

though the mechanisms 1 and 2 are now equivalent for the racemization step, no conclusive evidence has yet been found for the deprotonated intermediate in the hydrogen ion exchange although some ionic strength effects appear to favor this explanation.[2] Deprotonated forms of Co(III) complexes have been established however.[3,4]

Cyclic intermediates similar to those indicated for the deuteration step in (2) have been invoked to account for retention reactions at analogous isoelectronic carbanions. However, they have all been associated with a large negative entropy[5] attributed to the loss of degrees of freedom in the cyclic structure and in this respect they differ from the entropies of activation observed in the cobalt(III) systems.

One of the possible explanations advanced[1] for the large retention factor in the deuteration of the complexes cited was that the adjacent NH_3 group hydrogen bonded to the lone pair of the intermediate until the latter was reprotonated and retention of configuration about the N center was thereby preferred. This possibility seemed feasible since the rate of inversion at the tertiary N in aziridines is reduced in hydrogen-bonding solvents.[6] To test the proposal we have measured the deuteration and racemization of a complex with strongly electronegative groups in the 1 and 6 positions, namely the *trans,trans*-$[\text{Co(N-Meen)}_2(\text{NO}_2)_2]^+$ ion. This ion has the structure shown in Figure 1, where the N-CH_3 groups are *trans* to one another. The structure was
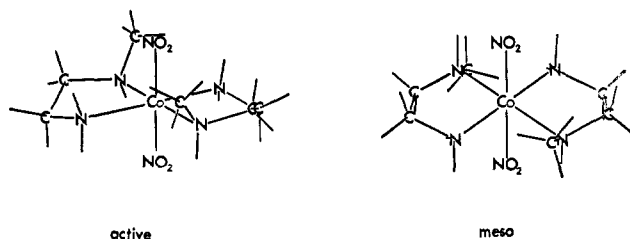

Figure 1. Optically active and *meso* isomers of the *trans,trans*-dinitrobis(N-methylethylenediamine)cobalt(III) ion.

established by a combined pmr and rotatory dispersion study of both the *trans,trans*- and *meso*-$[\text{Co(N-Meen)}_2$-$(\text{NO}_2)_2]^+$ ions and their chloro nitro counterparts, but this aspect of the investigation will be described in a subsequent communication along with the preparation,

(3) R. B. Jordan, I. I. Olsen, and A. M. Sargeson, to be published.
(4) A. R. Manyak, C. B. Murphy, and A. E. Martell, *Arch. Biochem. Biophys.*, **59**, 373 (1955).
(5) A. Streitwieser Jr., R. G. Lawler, and C. Perrin, *J. Am. Chem. Soc.*, **87**, 5383 (1965).
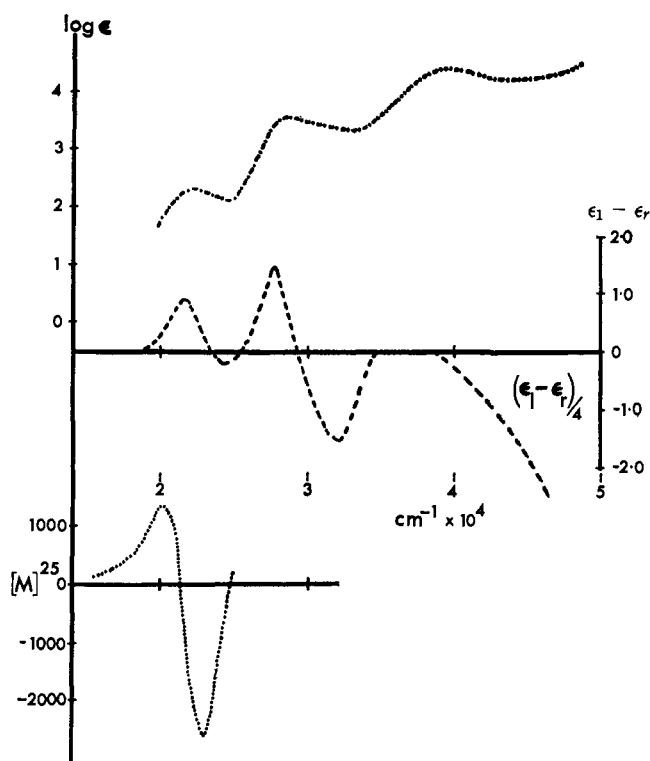(6) A. Lowenstein, J. F. Neumer, and J. D. Roberts, *ibid.*, **82**, 3599 (1960).

Figure 2. The ultraviolet and visible spectrum (-·-·-·), circular dichroism (– – – –), and rotatory dispersion (......) curves for (+)₅₈₉-*trans,trans*-[Co(NO₂)₂(N-Meen)₂]ClO₄.

properties, and structure of the *meso*- and some of the *cis*-dinitro isomers.

Experimental Section

Reagents. All materials used were of reagent grade, except N-methylethylenediamine (95%) which was purchased from Fluka. The silver (+)-α-bromo-π-camphorsulfonate (BCS) was made by mixing hot aqueous solutions of NH₄BCS and AgNO₃. On cooling, the silver salt crystallized out.

trans,trans-**Dinitrobis(N-methylethylenediamine)cobalt(III) Chloride Hemihydrate.** An ice-cold solution of N-methylethylenediamine (15.5 g of 95% in 8.8 ml of 11.3 N HCl) was added to a cold solution of CoCl₂·6H₂O (23.8 g in 50 ml of H₂O) and NaNO₂ (14 g) added quickly. The resulting solution was aerated in an ice bath for 0.5 hr, followed by 5 hr at ambient temperature. The residue formed on evaporation at room temperature was ground in methanol and filtered. The filtrate contained the desired product, and the insoluble material (1.3 g) consisted of NaCl and some *meso*-[Co(N-Meen)₂(NO₂)₂]Cl. Ethanol was added to the filtrate, the solution was slowly evaporated, and six fractions of the *trans,trans* product were obtained (total 24 g). *Anal.* Calcd for [Co(NO₂)₂-(N-Meen)₂]Cl·0.5H₂O: C, 20.97; H, 6.16; N, 24.46. Found: C, 21.16; H, 6.16; N, 24.46.

trans,trans-**Dinitrobis(N-methylethylenediamine)cobalt (III) Bromide.** [Co(NO₂)₂(N-Meen)₂]Cl (16 g) was dissolved in methanol (200 ml), and LiBr (9.5 g in 10 ml of methanol) and ethanol (200 ml) were added. On cooling and scratching yellow crystals formed which were collected, washed with EtOH, and dried under vacuum (12.3 g). *Anal.* Calcd for [Co(NO₂)₂(N-Meen)₂]Br: C, 19.01; H, 5.32; N, 22.17. Found: C, 18.90; H, 5.20; N, 22.41. A portion of this bromide salt (3.4 g) was deuterated by dissolving it in D₂O (10 ml of 99.9%), allowing it to stand for 2 days, and then evaporating off the D₂O under vacuum. The process was then repeated with fresh D₂O.

Resolution of *trans*-[Co(NO₂)₂(N-Meen)₂]Cl. All rotations were measured in a 1-dm tube with a Perkin-Elmer spectropolarimeter fitted with a Zeiss monochromator and quartz iodine lamp. A solution of [Co(NO₂)₂(N-Meen)₂]Cl (6.8 g) in water was shaken with AgBCS (3.4 g), filtered, and evaporated to near dryness. The residue was dissolved in methanol (75 ml) and cooled in ice for 1 hr. The crystals were collected, washed with methanol, acetone, and

ether, and air-dried (3.45 g, αD +0.085° for a 0.1% solution in 10⁻³ M HClO₄). The filtrate was reserved for the separation of the (−) isomer. Fractional recrystallization of this product from methanol (60 ml, 50°) gave no improvement in the optical purity. *Anal.* Calcd for (+)-[Co(NO₂)₂(N-Meen)₂]BCS: C, 31.54; H, 5.63; N, 13.80. Found: C, 31.51; H, 5.82; N, 13.44. NH₄BCS may be used as a resolving agent also after seed crystals of the diastereoisomer have been obtained.

(+)₅₈₉-**Dinitrobis(N-methylethylenediamine)cobalt(III) Perchlorate.** (+)-[Co(NO₂)₂(N-Meen)₂]BCS (1.5 g) was ground with NaClO₄ (1 g) in methanol (20 ml) and washed with methanol and air-dried (0.8 g, αD +0.065° for a 0.1% solution in 10⁻³ M HClO₄). *Anal.* Calcd for [Co(NO₂)₂(N-Meen)₂]ClO₄: C, 18.08; H, 5.06; N, 21.09. Found: C, 18.01; H, 5.10; N, 20.90.

(−)₅₈₉-**Dinitrobis(N-methylethylenediamine)cobalt(III) Chloride.** The filtrate left after isolation of the (+) isomer was reduced to 20 ml and cooled for 0.5 hr. The product (0.75 g) gave αD +0.036° for a 0.1% solution in 10⁻³ M HClO₄. Further evaporation to 10 ml and cooling produced a racemic fraction (0.8 g). Further evaporation and the addition of ethanol followed by 2-propanol produced four fractions of (−)-[Co(NO₂)₂(N-Meen)₂]Cl, all of similar activity (total yield 1.4 g, αD −0.070° for a 0.1% solution in 10⁻³ M HClO₄). Recrystallization of the (−) isomer from methanol gave no improvement in optical purity. Addition of 2-propanol saturated with LiCl and finally LiClO₄ to the residual filtrate resulted in fractions of low activity. No evidence for the *meso* isomer was obtained. *Anal.* Calcd for (−)-[Co(NO₂)₂(N-Meen)₂]Cl: C, 20.97; H, 6.16; N, 24.46. Found: C, 21.26; H, 6.23; N, 24.21.

Trinitroammine(N-methylethylenediamine)cobalt(III) Monohydrate. NaNO₂ (0.33 g) was added to [CoBr₂(NH₃)₂N-Meen]Br² (1 g) in methanol (30 ml) and stirred at −20° for 5 min. The volume was reduced by boiling to 8 ml and the solution cooled. The yellow crystals which formed on scratching were washed with water, methanol, and then acetone. The product was shown to be a nonelectrolyte by electrophoresis. *Anal.* Calcd for [Co(NO₂)₃-NH₃(N-Meen)]·H₂O: C, 11.77; H, 4.94; N, 27.45. Found: C, 11.58; H, 4.64; N, 27.78.

Kinetic Studies. The methods employed in this investigation for following the rates of racemization and hydrogen isotope exchange have been detailed in a previous paper dealing with the [Co(NH₃)₄N-Meen]³⁺ ion.² Since both reactions proceed at slower rates for the [Co(NO₂)₂(N-Meen)₂]⁺ ion when compared to the [Co(NH₃)₄N-Meen]³⁺ ion, higher pH buffers were required in this study. Acetate buffer (0.2 M) and glycine–NaOH buffer (0.05 M) were employed for the deuteration and racemization reactions, respectively. In all cases the addition of the complex to the buffer did not change the pH. Light was excluded as far as possible.

Results

Preparation. The preparation of the *trans,trans*-dinitro complex from the aerial oxidation of a mixture of Co²⁺ (1 mole), N-Meen (2 moles), NaNO₂ (2 moles), and HCl (1 mole) occurred readily, and a small amount of the *meso* isomer was also formed. An attempt to prepare the [Co-*trans*-(NO₂)₂(NH₃)₂N-Meen]Br complex, which contains only one asymmetric N center, by treating [Co-*trans*-Br₂(NH₃)₂N-Meen]Br with NaNO₂ in methanol gave [Co(NO₂)₃NH₃N-Meen] as the major product.

Spectra. The visible and ultraviolet absorption spectra, the rotatory dispersion curve, and the circular dichroism curve of (+)₅₈₉-*trans,trans*-[Co(NO₂)₂-(N-Meen)₂]ClO₄ are given in Figure 2. The pmr spectra of the protonated and deuterated ions and of the *meso,trans,trans* isomer are given in Figure 3, and the assignments of the absorptions are given in Table I. The principal difference between the spectra for the two isomers occurs for the methyl doublet arising from coupling with the N proton.

The absorption band at 346 mμ in Figure 2 is consistent with the *trans*-dinitro configuration since the *cis*-dinitro isomers absorb in the vicinity of 330 mμ which

Table I. Assignment of Chemical Shifts[a] (ppm) for the Pmr Spectra of the *trans,trans*-[Co(N-Meen)₂(NO₂)₂]⁺ Ions

	A racemic	B racemic-d₆	C meso
–CH₃	2.25	2.25	2.40
–CH₂CH₂–	2.2–3.2	2.2–3.2	2.4–3.2
HOD	4.7	4.7	4.7
–NH₂	5.35	. . .	5.3
–NH	~5.7	. . .	5.3

[a] Sodium trimethylsilylpropane sulfonate as reference; 60-Mc spectra P-E R10 spectrometer. All solutions were ~0.1 M in complex and 0.06 N in DCl.

coincides with the pattern found for the *cis-* (325 mμ) and *trans-* (347 mμ) [Co(en)₂(NO₂)₂]⁺ ions[7] and for *cis-*[Co-(−)-(pn)₂(NO₂)₂]⁺.[8] For the *meso,trans,trans* isomer ϵ_{max} occurs at 354 mμ. The optical properties of the complexes will be discussed in more detail in a subsequent communication.

Hydrogen isotope exchange was followed by the collapse of the methyl doublet to a singlet as the *sec*-NH was deuterated or *vice versa*. Plots of log [(peak height)$_t$ − (peak height)$_\infty$)] *vs.* t were linear over at least two half-lives, and the Arrhenius plots were also linear in the range studied. The deuteration rate constants are given in Table II. There was no evidence of the pres-

Table II. Rate Constants for H and D Exchange[a]

pH	Temp, °C	k_{obsd} × 10⁴, sec⁻¹	$k_{H \text{ or } D}$ × 10⁻⁴, M^{-1} sec⁻¹
3.62	34.3	0.05	6.2
4.41	34.3	0.30	6.1
4.78	34.3	0.70	6.0
5.92	34.3	9.83	6.1
3.62	45.0	0.26	. . .
3.62	45.0	0.26	. . .
3.62	55.0	1.19	. . .
3.62	55.0	1.24	. . .
5.95[b]	34.3	7.97	9.4
5.95[b]	34.3	7.70	9.1

[a] 1 M KCl, 0.2 M acetate buffer, 0.05 M complex. [b] D₂O, K_{D_2O} = 0.195K_w, pD 6.35.

ence of appreciable amounts of the *meso* isomer either in the rate plots or in the pmr spectra, and the pmr spectra of the active isomer and the racemate were identical. The rate law for deuteration is the same as that obtained in previous examples

$$R = k_D[\text{complex}][\text{OH}^-]$$

The H isotope effect, k_H/k_D, was ~1.5, but there is some uncertainty in evaluating pD absolutely in the acidity range used.

Racemization of the *trans,trans* isomer occurs if either N center inverts since the *meso* isomer is produced for each primary act of inversion. However, no evidence of appreciable amounts of the *meso* form was obtained, and it is clear from the pmr spectra that amounts of *meso* in excess of 10% at most would be

(7) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).
(8) G. A. Barclay, E. Goldschmeid, N. C. Stephenson, and A. M. Sargeson, *Chem. Commun.*, 540 (1966).
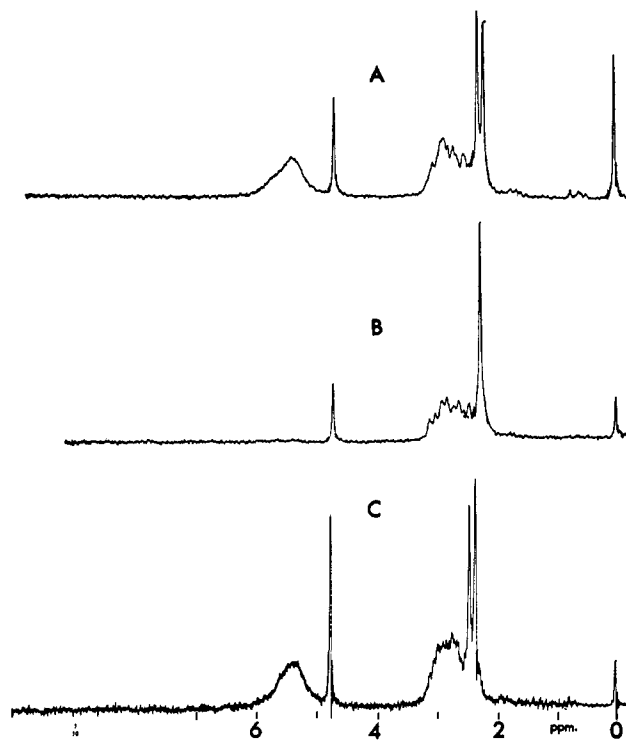
Figure 3. The pmr spectra of the *dl* isomer (A); (B), A deuterated; and the *meso* isomer (C) of the *trans,trans*-[Co(Meen)₂(NO₂)₂]⁺ ion.

detected. We conclude therefore that the active isomer is more stable than the *meso* form by ~1.0 kcal/mole. Racemization was followed at 500 mμ, and one reaction was followed completely to zero rotation (±0.001°) and then scanned from 400 to 700 mμ to ensure that no activity remained at any wavelength. The total loss of activity under these conditions is required by the *trans*-dinitro isomer, but the *cis*-dinitro form should only mutarotate. The plots of log $\alpha°$ *vs.* t were linear over at least three half-lives, and the rate constants obtained are given in Table III. The data were limited to a small

Table III. Rate Constants for Racemization[a]

pH	Temp, °C	k_{obsd} × 10⁵, sec⁻¹	k_R, M^{-1} sec⁻¹
9.10	25.0	0.296	0.235[b]
9.60	25.0	0.895	0.225,[b] 0.230,[c] 0.227[d]
10.23	25.0	3.790	0.223[b]
9.45	30.0	2.14[b]	. . .
8.87	34.3	1.50	1.04[b]

[a] 1 M KCl, 0.05 M glycine–NaOH, K_w (25°) = 1 × 10⁻¹⁴, K_w (34.3°) = 1.95 × 10⁻¹⁴. [b] 0.1% in complex concentration. [c] 0.05% in complex. [d] 0.2% in complex.

pH range (9.10 to 10.23) since the reaction was extremely slow at lower pH values, and at higher pH (>11) competing hydrolysis to the hydroxo nitro complex complicated the kinetics. In the pH range 10.3–11, ion pairing between the buffer glycinate ion and the complex also complicated the analysis of the kinetics although good pseudo-first-order rate plots were obtained.

The rate law was the same as that obtained for the previous complexes, namely

$$R = k_R[\text{complex}][\text{OH}^-]$$

Only one rate was observed which also indicates the absence of the active *trans,cis* isomer and agrees with the pmr spectrum, Figure 3. The H isotope effect was not examined because of the uncertainty in evaluating OD^- in the range used for the experiments.

Discussion

Essentially the same pattern for the kinetics was observed as for the previous studies, and the two electronegative groups in the 1 and 6 positions do not reduce the retention effect in the deuteration process at the asymmetric centers, Table IV. The hydrogen-bonding mechanism outlined in the introductory section and in ref 1 therefore cannot obtain. The effect of the cobalt orbitals on the ratio k_D/k_R seems likely to be small since the filled nonbonding orbitals give rise to a repulsive term when interacting with the N "lone pair," and the empty antibonding orbitals are at much higher energy levels. Moreover, both sets of orbitals are approximately spherical in their distribution in "domains," and they should show little or no stereochemical preference.

Table IV. A Comparison of Data for Deuteration and Racemization at Asymmetric Nitrogen Centers

Reaction	k, M^{-1} sec^{-1} 34.3°	$E_{a,\text{obsd}}$, kcal/ mole	$\Delta H^{\ddagger}_{\text{calcd}}$, kcal/ mole	$\Delta S^{\ddagger}$, eu
a.	*trans,trans*-[Co(NO₂)₂(N-Meen)₂]⁺			
H exchange	9.3×10^4			
D exchange	6.1×10^4	29.3	15.9	15
Racemization	1.04	42.3	28.4	34
b.	[Co(NH₃)₄N-Meen]³⁺			
H exchange	3.0×10^7	28.1	13.8	21
D exchange	1.0×10^7	28.7	15.4	24
Racemization	2.4×10^2	37.2	23.8	30
c.	[Co(NH₃)₄sar]²⁺			
H exchange	6×10^7	28	13.5	21
Racemization	1.7×10^4	32.5	18.6	21

It is now pertinent to review the results of all these racemization and deuteration studies in relation to the mechanisms proposed previously. The common features are (1) the same rate law for both racemization and deuteration, namely, specific OH^- catalysis; (2) substantial retention of configuration in all instances; (3) $E_{a,\text{obsd}} \sim 28$ kcal/mole for the deuteration regardless of the charge on the complex and the substituents; (4) no dependence of racemization rate on the complex concentration. Although specific OH^- catalysis might imply a preference for the ion-pair interchange of the H isotopes, we believe that it merely means that OH^- is more efficient than other nucleophiles in water. For instance, in some cobalt(III)-triethylenetetramine complexes, a term in the rate law for the mutarotation at an asymmetric N center appears which is independent of [H⁺] and presumably H_2O abstracts the proton required

to observe the mutarotation.[9] Also the racemization of the *trans,trans*-[Co(NO₂)₂(N-Meen)₂]⁺ ion has been observed in dimethyl sulfoxide and methanol solutions catalyzed by triethylamine. These observations show that other bases do abstract the *sec*-N proton, and a detailed account of this work will be reported subsequently. These factors coupled with the remarks in the introductory section still leave the deprotonated intermediate as the preferred mechanistic step for deuteration.

One factor which has not been discussed in this context before is the approximately constant rate of reprotonation of "lone pairs" at O and N centers ($\sim 10^{10-11}$ M^{-1} sec^{-1}) for a wide variety of compounds.[10] This general observation, if it holds here, requires k_1 to be the rate-determining step in the isotope exchange reaction (1) and suggests that the acid dissociation constant (K_a) for the dinitro complex is $\sim 10^{-19}$ and that a smaller k_D reflects a smaller K_a. The difference in the rates of deuteration and racemization for the *trans*-dinitro and the [Co(NH₃)₄N-Meen]³⁺ ions, respectively, may be accounted for at least partly by a difference in K_a, and the ~ 600-fold increase from the + to the 3+ ion does not seem unlikely as a result of this factor. A statistical factor of 2 appears in the rates for the dinitro ion since there are two reactive centers. However, in the racemization steps, the rate of racemization equals the rate of inversion at a N center for the dinitro ion but is half the inversion rate for the tetraammine complex. If a comparison between the inversion and H exchange rates is made, these factors alter the k_D/k_R ratios quoted above.

Another common factor between these two ions is the conformational effect involved in the Co-N-Meen ring. An examination of the Dreiding molecular models of the *meso* form of the dinitro complex suggests it should be less stable than the active isomers since, in the arrangement (Figure 1b) where the CH₃ groups are most equatorial (most stable conformation), the adjacent NH₂ and NH protons are eclipsed. In the active isomers not only are the CH₃ groups equatorial but the rings are staggered in relation to one another. However, the conformational calculations (as carried out in ref 2) give practically zero energy difference between the two forms *meso* and *active* when the H,H interactions are minimized but amount to 1.0 kcal/mole in favor of the *active* isomer when the sum of all the H,O, H,H, H,N, and H,C interactions is minimized. This conclusion is qualitatively in agreement with the experimental observations on the relative stability of the isomers.

Since the rate of proton exchange is much faster than the racemization step, the formation of the *meso*-deprotonated intermediate is not inconsistent with the final product being the *racemate trans,trans*-dinitro ion. Subsequent reaction of the *meso* form to the inverted isomer would not affect the racemization rate. Also preliminary pmr studies on the *meso* isomer show that deuteration is fast and at pD 10.1 the methyl singlet at 2.40 ppm of the *meso* form disappears and that due to the *active* isomer 2.25 ppm grows synchronously ($t_{1/2} = 23$ min). Assuming the same rate law for the *meso* as for the *active* isomer, the rate of inversion of the *meso* $\rightarrow$ *active* is ~ 10 times faster than the

(9) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 6, 1032 (1967).

(10) E. F. Caldin, "Fast Reactions in Solution," John Wiley and Sons Inc., New York, N. Y., 1964, p 263.

racemization of the active form in D_2O. This difference in inversion rates explains the failure to detect the *meso* form in the racemic product and implies that the energy difference between the isomers is ~ 1.3 kcal/mole.

In the racemization step not only does the arrangement about the N invert but the Co–N-Meen ring must also interchange its conformation so that in the *meso* intermediate both methyl groups are in equatorial positions.[2] It could not be decided, however, if the conformational interchange precedes or antecedes the inversion act, but regardless of which of these possibilities pertains, $\Delta H_R{}^{\pm}$ should exceed that found for the tetraammine sarcosinato ion, where little or no conformational effect exists. This aspect of the problem has been discussed previously[2] for the $[Co(NH_3)_4N\text{-Meen}]^{3+}$

ion where $\Delta H_R{}^{\pm}$ exceeded that for the sarcosinato ion by ~ 5 kcal/mole. In the present instance $\Delta H_R{}^{\pm}$ exceeds that for the sarcosinato ion by ~ 10 kcal/mole which agrees with the rationalization in terms of the conformational effect. However, the relative magnitude of these values is uncertain in relation to the enthalpy of deprotonation of the complex ion since a rationalization of $\Delta H_R{}^{\pm}$ in terms of the conformational effects alone assumes that the enthalpy of deprotonation is reasonably constant for the complexes considered.

Solvation of Chromium(III) Ion in Acidic Water–Ethanol Mixed Solvents[1,2]

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Abstract: The solvation of chromium(III) ion in acidic water–ethanol mixed solvents has been studied at 50.0 and 75.0°. Separation by ion-exchange methods of individual, differently solvated species, $Cr(OH_2)_{6-n}(OHC_2H_5)_n{}^{3+}$ ($n = 0, 1, 2,$ and 3), present in equilibrated solutions with mole fraction of ethanol up to ~ 0.95 allows calculation of equilibrium quotients for stepwise replacement by ethanol of water in the first coordination shell of chromium: $Cr(OH_2)_{7-j}(OHC_2H_5)_{j-1}{}^{3+} + C_2H_5OH = Cr(OH_2)_{6-j}(OHC_2H_5)_j{}^{3+} + H_2O$. Values of the equilibrium quotients, Q_j (involving the ratio of activities of the solvent components), show a medium dependence, increasing with increasing ethanol content of the solvent. The ratio of activity coefficients of differently solvated chromium(III) ions is not, therefore, constant as the solvent composition varies. Values extrapolated to pure ethanol as solvent (for 75°) are $Q_1{}^0 = 0.42 \pm 0.01$, $Q_2{}^0 = 0.128 \pm 0.005$, and $Q_3{}^0 \cong 0.042$. Values of $\bar{n}$, the average number of ethanol molecules bound per chromium(III), are the same within experimental error, at 50 and 75°, indicating that the enthalpy change associated with the solvent replacement reaction is small (0 ± 0.5 kcal mole^{-1}). The rate of aquation of $Cr(OH_2)_5(OHC_2H_5)^{3+}$ has been studied in aqueous 4.4 M perchloric acid at 39.6°, under which conditions the first-order rate constant is 2.16×10^{-5} sec^{-1}. Problems associated with correlation of $\bar{n}$ data and solvent composition to obtain equilibrium quotient values are discussed.

Direct evaluation of primary solvation of chromium(III) ion in mixed solvents is possible because of the slowness of exchange with the environment of ligands bonded to this metal ion. In earlier studies, the solvation of chromium(III) ion in acidic water–methanol solutions has been established.[3] The present study of chromium(III) in acidic water–ethanol solutions[4] resembles these published studies on the water–methanol system in its general plan: values of $\bar{n}$, the average number of ethanol molecules bound per chromium(III)

ion, have been determined as a function of solvent composition. In addition, quantitative separation by an ion-exchange procedure of individual differently solvated chromium(III) species, $Cr(OH_2)_{6-n}(OHC_2H_5)_n{}^{3+}$ ($n = 0, 1, 2,$ and 3), has been accomplished in the present study; this allows evaluation of equilibrium quotients for the solvent displacement reactions

$$Cr(OH_2)_{7-j}(OHC_2H_5)_{j-1}{}^{3+} + C_2H_5OH =$$
$$Cr(OH_2)_{6-j}(OHC_2H_5)_j{}^{3+} + H_2O$$
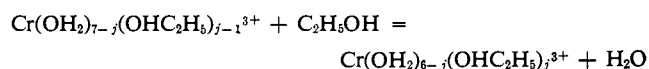
with $j = 1, 2,$ and 3 as a function of solvent. The solvent dependence of the equilibrium quotients is appreciable, with the stability of ethanol-containing species being enhanced in solutions of increasing ethanol content. Separation of individual, differently solvated species has allowed also measurement of the spectrum of the individual species ($n = 0, 1,$ and 2) and the direct evaluation of the rate of aquation of monoethanolchromium(III) ion.

(1) Based upon the Ph.D. thesis of D. W. Kemp, University of Colorado, Aug 1966. Presented in part before the Analytical Division, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 13, 1966.

(2) This work was supported by the National Science Foundation (Grant GP-680).

(3) (a) J. C. Jayne and E. L. King, *J. Am. Chem. Soc.*, **86**, 3989 (1964); (b) R. J. Baltisberger and E. L. King, *ibid.*, **86** 795 (1964).

(4) C. K. Jørgensen, *Acta Chem. Scand.*, **8** 175 (1954). This study of slow spectral changes in water–ethanol solutions of chromium(III) nitrate is not amenable to a quantitative interpretation.