tained did not show an inflection point, indicating little, if any, acid character. There was evidence, on the basis of a color change from green to red-orange, of the disproportionation into $UO_2(C_9H_6-NO)_2 \cdot C_9H_6NOH$ and UO_2^{++}. The complexes, $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$ and $Sc(C_9H_6NO)_3 \ C_9H_6-NOH$, gave such broad titration curves that it was not possible to assign an inflection point value to them.

Mixed Chelates.—In all of the solvents used, it was not possible to prepare any of the mixed chelates, i.e., complexes containing a solvate molecule of a different species than the coördinated groups. In most cases, the $UO_2(C_9H_6NO)_2$ disproportionated as was evidenced by the change in color of the solution from green to red-orange.[12] This was similar to the behavior of $UO_2(C_9H_6-NO)_2$ when titrated with potassium methoxide.

The unsolvated thorium complex, $Th(C_9H_6NO)_4$, reacted in a different manner than the unsolvated uranium chelate. When it was digested in a dilute sodium hydroxide solution of 2-methyl-8-quinolinol, no reaction was observed. When the solution was made neutral, an immediate color change from yellow to orange occurred. In weakly acidic solutions, the thorium chelate showed no tendency to disproportionate, but the addition of 2-methyl-8-quinolinol caused an immediate change to the solvated form. Despite the fact that the thorium chelate did not appear to disproportionate, some interchange reaction the solvate position and the normal chelate position was in evidence. The resulting sublimates all proved to be mixtures of the two chelating agents present.

Discussion

It appears that the solvated 8-quinolinol chelates of scandium and thorium are not analogous to the uranium (VI) compound. Using substituted 8-quinolinols with a large group at the 2- or 7-position, it is possible to prepare the unsolvated chelates of scandium and thorium directly from solution while only the solvated uranium chelate is precipitated. With 2-methyl-8-quinolinol, thorium forms $Th(CH_3C_9H_5NO)_4^{18}$ as well as $Th(CH_3C_9H_5NO)_4 \cdot CH_3C_9H_5NOH$,[14] while uranium gives only the solvated chelate. Scandium reacts with 7-[α-anilinobenzyl)-8-quinolinol[19] to give the unsolvated chelate while again, uranium gives only the solvated compound. These reactions suggest that perhaps the solvate molecule in the scandium and thorium chelates is held in a different manner than in the uranium chelate. In basic solution, the normal uranium chelate could easily form a complex anion with 8-quinolinol having the formula, $[UO_2(C_9H_6NO)_3]^{-1}$,[12] giving uranium a coordination number of eight. To form a similar complex anion with the scandium and thorium chelates would require the unlikely cation coördination numbers of eight and ten, respectively.

(18) J. P. Phillips, J. F. Emery and H. P. Price, Anal. Chem., **24**, 1033 (1952).

(19) J. P. Phillips and A. L. Duckwall, THIS JOURNAL, **77**, 5504 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA, AND THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Stereochemistry of Inorganic Complexes. XXVI.[1] The Ammonation of Two Optically Active Cobalt(III) Complexes[2,3]

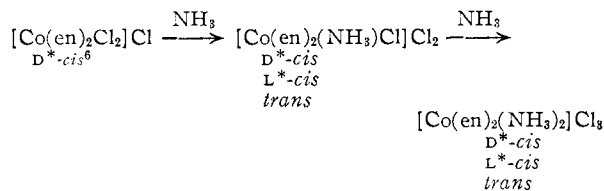BY RONALD D. ARCHER AND JOHN C. BAILAR, JR.

RECEIVED AUGUST 1, 1960

The stereochemical changes involved in the reaction of ammonia with optically active cis-dichlorobis-(ethylenediamine)-cobalt(III) chloride and optically active cis-chloroamminebis-(ethylenediamine)-cobalt(III) chloride have been investigated. It has been found that the "Walden (D* → L*)[4] inversion of the two step ammonation of the dichloro complex[5] occurs in the first step of the ammonation of the dichloro complex at low (liquid ammonia) temperatures. The relative configurations are based on the rotatory dispersion curves and the absorption spectra of the complexes. The ammonation of racemic and D*-cis-chloroamminebis-(ethylenediamine)-cobalt(III) chloride to the corresponding diammine complex occurs with almost complete retention of configuration under a variety of conditions. The ammonation of D*-cis-dichloro-bis-(ethylenediamine)-cobalt(III) chloride gives considerable trans-diammine as well as the cis-diammine. Possible reaction intermediates are discussed for the inversion, which requires an S$_N$2 reaction.

Introduction

A previous study[5] has shown that either of two optically active forms of cis-diamminebis-(ethyl-

(1) Number XXV of this series, THIS JOURNAL, **82**, 1524 (1960).

(2) Presented in part at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

(3) In part from the Doctoral Dissertation of R. D. Archer, in partial fulfillment for the Ph.D., University of Illinois, Urbana, Illinois, 1959.

(4) D* and L* refer to absolute configurations, whereas d, l, D and L are designations given to optically active substances by other investigators but have not always implied absolute or even relative configurations.

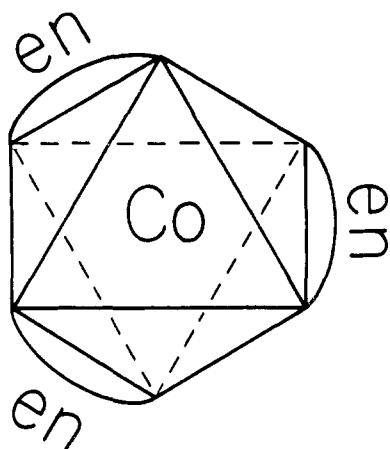(5) J. C. Bailar, Jr., J. H. Haslam and E. M. Jones, THIS JOURNAL, **58**, 2226 (1936).

enediamine)-cobalt(III) chloride can be formed in excess of the other by varying the temperature at which ammonia reacts with optically active cis-dichlorobis-(ethylenediamine)-cobalt(III) chloride. This inversion is complicated by the stereochemical changes possible during the reaction

$$[Co(en)_2Cl_2]Cl \xrightarrow{NH_3} [Co(en)_2(NH_3)Cl]Cl_2 \xrightarrow{NH_3}$$

$$\begin{array}{ccc} D^*\text{-}cis^5 & D^*\text{-}cis & \\ & L^*\text{-}cis & \\ & trans & \end{array}$$

$$[Co(en)_2(NH_3)_2]Cl_3$$

$$\begin{array}{c} D^*\text{-}cis \\ L^*\text{-}cis \\ trans \end{array}$$

Fig. 1.—Absolute configuration of the D*-[Co(en)₃]³⁺ ion[12] (puckering of the chelate rings not shown).

Not more than 10% of the *trans*-diammine was indicated in the over-all two step ammonation of the *cis*-dichloro complex.[5] Haslam[7] has indicated that higher percentages of the *trans* complex are often observed. Both results were based on the precipitation of the slightly soluble *trans*-[Co(en)₂-(NH₃)₂]₂(S₂O₆)₃.

The only other "Walden" or "D*↔L*" inversion which has been observed among the reactions of optically active octahedral complexes is the reaction of carbonate ion with cobalt complexes.[8] Several other inorganic reactions have been thought to show similar inversions, but their solubilities, crystal forms or rotatory dispersions have led to the conclusion that no inversion occurs. A detailed discussion of these non-inverted reactions has been given by Basolo.[9]

Although rotations of the same sign at a particular wave length do not imply the same relative configurations, similar optical rotatory dispersion curves do imply the same relative configuration if considered relative to corresponding absorption peaks.[9,10]

The absolute configuration of the D*-[Co(en)₃]³⁺ ion (originally designated as the *d* ion by Werner[11]) has been determined by means of X-rays.[12] The ethylenediamine rings are puckered[13] and are

(6) In the original reference[5] the D*-dichloro ion was referred to as the *l*-dichloro ion, the designation given the ion by A. Werner, *Ber.*, **44**, 3280 (1911). That the *l*-ion may be designated as the D*-ion in this instance is discussed later in this paper. The symbol *en* designates ethylenediamine.

(7) J. H. Haslam, B. S. Thesis, University of Illinois, 1935.

(8) (a) J. C. Bailar, Jr., and W. Auten, THIS JOURNAL, **56**, 774 (1934); (b) J. C. Bailar, Jr., F. G. Jonelis and E. H. Huffman, *ibid.*, **58**, 2224 (1936); (c) J. C. Bailar, Jr., and J. P. McReynolds, *ibid.*, **61**, 3199 (1939); (d) J. C. Bailar, Jr., and D. F. Peppard, *ibid.*, **62**, 820 (1940).

(9) (a) F. Basolo, "Stereochemistry of Hexacovalent Atoms," in "Chemistry of Coördination Compounds," J. C. Bailar, Jr., Editor, Reinhold Publishing Corp., New York, N. Y., 1956, Chapter 8; (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Complexes," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 5.

(10) (a) J. P. Mathieu, *J. chim. phys.*, **33**, 78 (1936); (b) J. Mathieu, *Bull. soc. chim. France*, [5] **3**, 476 (1936); (c) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956); (d) C. Djerassi, "Optical Rotatory Dispersion," McGraw–Hill Book Co., New York, N. Y., 1960.

(11) A. Werner, *Ber.*, **45**, 121 (1912).

(12) (a) Y. Siato, K. Nakatsu, M. Shiro and H. Kuroyo, *Bull. Soc. Chem. Japan*, **30**, 795 (1957); (b) *ibid.*, **30**, 158 (1957).

(13) The non-planarity of these chelate rings is discussed by E. J. Corey and J. C. Bailar, Jr., THIS JOURNAL, **81**, 2620 (1959).
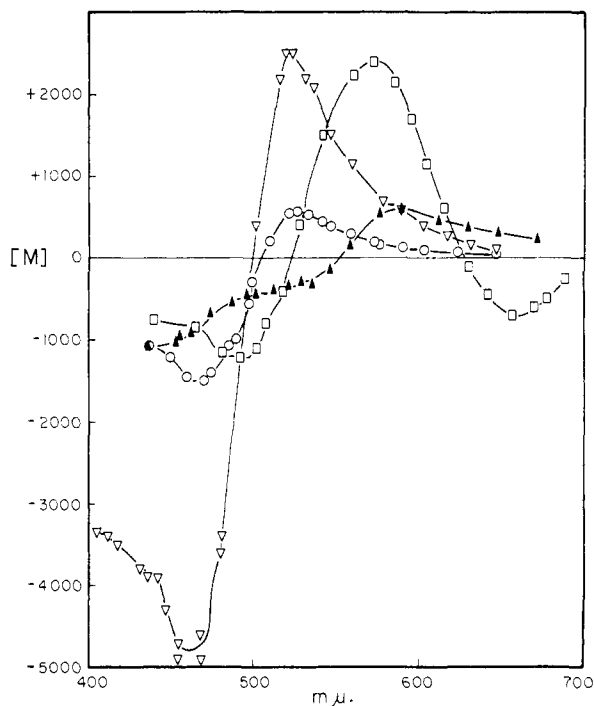

Fig. 2.—Rotatory dispersion curves of several cobalt(III) cations[10a,b]: ▽, D*-[Co(en)₃]⁺³; ▲, D*-[Co(en)₂(NH₃)Cl]⁺²; O, D*-[Co(en)₂(NH₃)₂]⁺³; □, D*-[Co(en)₂Cl₂]⁺ (formerly called *l*-ion).

bonded to cobalt(III) in the relative positions indicated in Fig. 1.

The absolute configurations of the complex ions in the reaction between ammonia and optically active *cis*-dichlorobis-(ethylenediamine)-cobalt-(III) chloride may be determined by a comparison of the rotatory dispersion curves of the complex ions in question with the curve of the D*-[Co-(en)₃]⁺³ ion (see Fig. 2). The similarity of the rotatory dispersion curves of these ions is apparent if the dispersion curves are compared to the visible absorption peaks of the complexes, which are at 470 mμ for the [Co(en)₃]⁺³ and the *cis*-[Co(en)₂-(NH₃)₂]⁺³ ions, at 530 mμ for the *cis*-[Co(en)₂-Cl₂]⁺ ion, and at about 522 mμ for the *cis*-[Co(en)₂-(NH₃)Cl]⁺² ion.[14] This relationship of rotation and absorption is plotted in Fig. 3, in which the curves have been shifted so that the absorption peaks coincide. All four of these ions exhibit optical rotatory dispersion curves which pass from a negative rotation to a positive rotation with increasing wave length in the region of the visible absorption peak

(14) Numerous literature references report the absorption peaks of these complexes and agree within a few millimicrons with the values listed above for the first three ions; however, the following peaks have been reported from the *cis*-[Co(en)₂NH₃Cl]⁺² ion: (a) 512 mμ, F. Basolo, THIS JOURNAL, **72**, 4393 (1950); (b) 517 mμ (ν = 58.0 × 10¹³ sec.⁻¹), H. Kuroya, *J. Inst. Polytech. Osaka City Univ., C1*, No. 1, 29 (1950); (c) 522 mμ, this study; (d) 525 mμ, J. P. Mathieu, *Bull. soc. chim. France*, [5] **3**, 463 (1936); (e) 527 mμ, A. V. Ablov and M. P. Filippov, *Zhur. Neorg. Khim.*, **2**, 42 (1957). These discrepancies are not due to anion effects as the 512 and the 527 values are both for the dithionate, nor to solvent changes as it has been found in this study that the complex gives approximately the same peak in methanol and water. Impurities are more likely to be the cause of these differences, as the unresolved complex prepared for this study had a peak at 515 mμ but gave a value of 522 mμ and a better analysis after resolution with α-bromo-*d*-camphor-π-sulfonate.
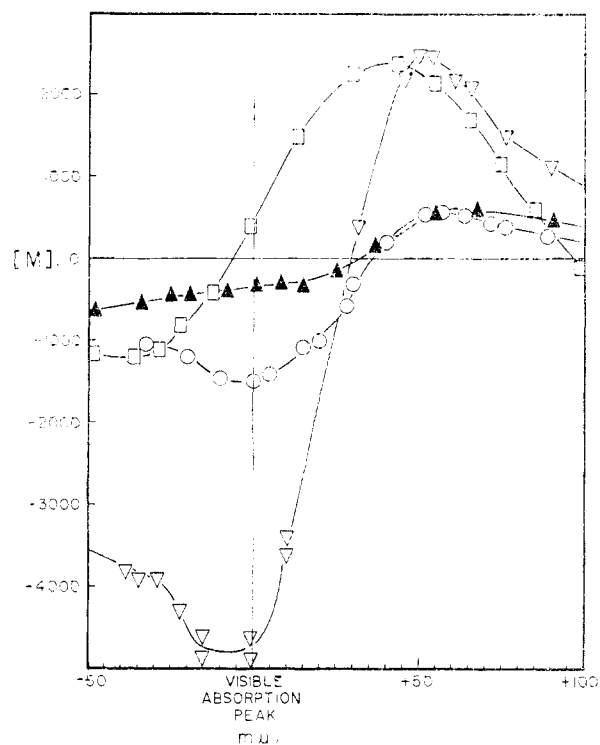
Fig. 3.—Rotatory dispersion curves with respect to the visible absorption peak of the complexes (complexes and symbolism same as Fig. 2).

Fig. 4.—Rotatory dispersion curves of the ammonation products of D*-[Co(en)$_2$Cl$_2$]Cl: ⊚, reaction in liquid NH$_3$ at −50°; ▣, reaction in gaseous NH$_3$ at 80°.

product which has an optical rotatory dispersion curve (Fig. 4, lower curve) which is of similar magnitude to the curve of the product obtained at 80°, but this curve is the inverse of the curve for the product obtained by the reaction at the elevated temperature, the inverse of the curves obtained for the products of ammonation of the D*-dichloroammine complex, and the inverse of the curves of the D*-diammine and D*-chloroammine complexes.

and reach a maximum value at a wave length about 50 mμ greater than the absorption peak. Therefore, it seems logical to designate all of these ions as D*-ions.

Results

The reaction of ammonia with D*-chloroamminebis - (ethylenediamine) - cobalt(III) chloride yields a predominance of the corresponding D*-diammine ion under a wide variety of conditions as indicated by the optical rotations in Table I. This retention of configuration is noted for reactions as both liquid ammonia and room temperatures. The reaction of the cis-chloroammine complex with gaseous ammonia at 80° is very slow; the optical rotations after one week show no significant changes.

Reaction of D*-[Co(en)$_2$Cl$_2$]Cl with gaseous ammonia at 80° yields a product which has a dispersion curve (Fig. 4, upper curve) which is similar to that of D*-[Co(en)$_2$(NH$_3$)$_2$]Cl$_3$ but shows only a small fraction (approximately 1/10) of the magnitude of the pure D*-diammine complex (Fig. 2). Ammonation of the resolved dichloro complex in methanol at 30° results in a color change from violet to red, the color of the chloroammine complex, within thirty minutes; however, the reaction solution still appears reddish in color after 9-½ days. From rotations at the Na-D-line (Table II) it appears that the D*-dichloro complex has changed to the D*-chloroammine complex, which has in turn been converted partially to the D*-diammine complex.

On the other hand, reaction of liquid ammonia with the D*-dichloro complex at −50° yields a

TABLE I
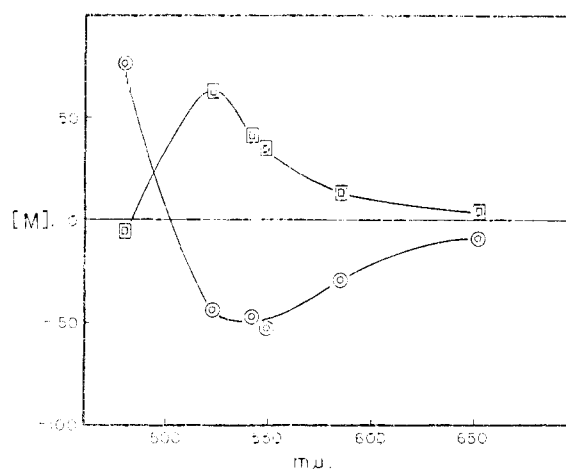
Optical Rotations for the Ammonation of D*-[Co(en)$_2$(NH$_3$)Cl]Cl$_2$[a]

Solvent	Reaction temp., °C.	Reaction time	$[M]^{20}$D	$[M]^{20}$ 554 mμ	$[M]^{20}$ 546 mμ
....	..	....	580 ± 17	0 ± 21	−190 ± 27
Liquid NH$_3$	−37	15 min.	153 ± 12	142 ± 11	74 ± 22
Liquid NH$_3$	−37	30 min.	59 ± 18	315 ± 21	196 ± 22
Liquid NH$_3$	−37	12 hr.	87 ± 11	303 ± 11	298 ± 15
NH$_3$ in CH$_3$-OH (2.7 M in NH$_3$)	30	9.5 days	65 ± 11	120 ± 30	......
Gaseous NH$_3$	80	7 days	550 ± 25	10 ± 30	......
D*-[Co(en)$_2$(NH$_3$)$_2$]Cl$_3$[b]			600	0	−200

[a] The rotations were measured in dilute aqueous solution after removal of the ammonia, except in the case of the MeOH solution of NH$_3$ and complex, which was measured in situ. [b] Ref. 10b.

TABLE II

Ammonation of D*-[Co(en)$_2$Cl$_2$]Cl in Methanol at 30°

Complex concn. (M)	Ammonia concn. (M)	Time	$[M]^{20}$D	Absorption peak[a]
0.0005	0.6	10 min.	633 ± 119	....
.0005	0.6	40 min.	317 ± 104	....
.0024	2.7	9.5 days	126 ± 41	490 mμ

[a] Reaction incomplete in all cases.

The absorption spectrum of the diammine obtained in the reaction between ammonia and the D*-chloroammine complex is almost identical to that reported for the cis-diammine[13a] as indicated in Table III.

However, the absorption spectra of the diammine products obtained from the dichloro starting ma-

TABLE III

ABSORPTION SPECTRA OF [Co(en)₂(NH₃)₂]Cl₃

Complex	mμ	log ε	mμ	log ε
cis[a]	338	1.55	470	1.52
trans[a]	338	1.78	470	1.81
D*-[Co(en)₂(NH₃)Cl]Cl₂ plus NH₃ (−37°) (12 hr.)	335	1.51	467	1.51
D*-[Co(en)₂Cl₂]Cl plus NH₃ (80°) (7 days)	338	1.80	468	1.85
D*-[Co(en)₂Cl₂]Cl plus NH₃ (−50°) (1 day)[b]	..	..	486	1.76
D*-[Co(en)₂Cl₂]Cl plus NH₃ (−75°) (4 min.)[c]	334	1.84	468	1.84

[a] Ref. 14a. [b] Reaction incomplete. [c] Reaction catalyzed—catalytic agent undetermined.

terial indicate predominantly *trans*-diammine products.

Attempted precipitation of *trans*-[Co(en)₂(NH₃)₂]₂(S₂O₆)₃ from the product obtained by the ammonation of *cis*-[Co(en)₂(NH₃)Cl]Cl₂ with liquid ammonia was unsuccessful.

Discussion

The results of the optical rotatory dispersion measurements point to a D*↔L* inversion in the low temperature ammonation of the dichloro complex. No D*↔L* inversion has been noted for either step of the reaction at room temperature or above.

The absorption spectra also suggest retention of configuration for the second step of the low-temperature reaction and a change in configuration for the over-all reaction, thereby implying a change in the first step. A comparison of the extinction coefficients suggests a complete conversion from *cis* to *trans* during the over-all reaction; however, the optical rotatory dispersion measurements show that at least 10% of the product is in the *cis* form. If any racemization has occurred, even more *cis* must exist at the end of the reaction. Therefore, log ε's quoted for the *trans*-diammine by Basolo[14a] must be low, probably due to contamination by the *cis*-diammine complex.

The scarcity of such Walden inversions in inorganic complexes has been explained by both valence bond and crystal field theories. Basolo and Pearson[9b] as well as Brown, Ingold and Nyholm[15] have pointed out the necessity of S_N2 mechanisms in order that an octahedral complex might undergo a Walden inversion.

Using valence bond theory, Taube[16] has noted that, in general, inner orbital octahedral complexes are inert if the three inner d orbitals not used in bonding possess electrons, the complexes being reluctant to add another electron donor group. Cobalt(III) complexes have these three d orbitals completely filled and, therefore, resist an S_N2 mechanism.

A crystal field description by Basolo and Pearson[9b] shows a larger loss in crystal field stabilization energy (CFSE) for a d^6 system, such as cobalt (III), in going to the seven-coördinate pentagonal bipyramid than in going to the five-coördinate

(15) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

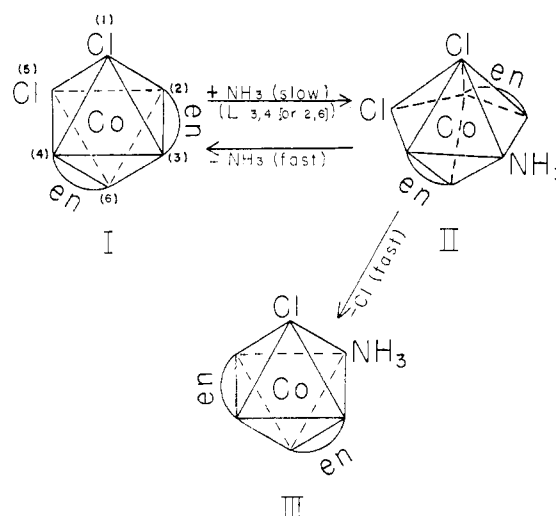(16) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

Fig. 5.—A possible octahedral Walden inversion mechanism for the D*-[Co(en)₂Cl₂]⁺ ion.

tetragonal pyramid. However, the five-coördinate trigonal bipyramid requires an even greater loss of CFSE than does the pentagonal bipyramid, and these are the two logical intermediates used to explain the very common *cis* ↔ *trans* conversions. (The five-coördinate tetragonal pyramid allows only retention of configuration.)

A possible mechanism for the Walden inversion observed in this study is shown in Fig. 5. Because of the high electron density along the edge of the complex,[9b] the ammonia molecule probably approaches *via* one of the *trans* faces (faces 3,4,6 and 2,3,6 of structure I of Fig. 5) before becoming part of the seven coördinate intermediate. A similar intermediate which gives somewhat better bond angles has been suggested by Asperger and Ingold.[17] The energy required for the rearrangement of atoms to form either of the suggested intermediate helps to account for the scarceness of such inversions in reactions of octahedral complexes.

A "*trans*-attack" of the optically active [Co(en)₂Cl₂]⁺ ion leads either to inversion (as shown in Fig. 5) or to a *trans* product (if attack leads to edge 3,6 being part of the five-membered plane). The other six faces, attack upon which lead to retention of configuration, are all *cis* to at least one of the chloride ions. Apparently, the negatively charged chloride ions help repel the electron pairs of ammonia molecules from attacking these faces. The two faces "*trans*" to the chloride ions are surrounded by relatively neutral hydrocarbon and amine groups and are more susceptible to attack. At higher temperatures either the repulsion of the *cis* faces is sufficiently overcome to allow for more "*cis*-attack," or a dissociation mechanism is more prevalent.

A dissociation mechanism can account for the *trans* and D*-*cis* products observed at higher temperatures if one assumes a trigonal bipyramid intermediate with the remaining chloride ion in the trigonal plane. The large amount of *trans* product for this first step of the reaction at these elevated temperatures is again undoubtedly due to the re-

(17) S. Asperger and C. K. Ingold, *J. Chem. Soc.*, 2862 (1956).

pulsion between the chloride ion and the electron pair of the ammonia. The ammonia adds predominantly between the ethylenediamine molecules, which results in a *trans* configuration. The D*-*cis* product occurs only when ammonia adds adjacent to the chloride of the trigonal bipyramid or when a tetragonal pyramid is the intermediate.

It is interesting to note that a tetragonal pyramid is the most logical intermediate for the second step of the reaction because of its almost complete retention of configuration but rather unlikely for the first step at low temperatures.

A comparison of the analogous reactions in water are interesting. The aquation (acid hydrolysis) of *trans*-[Co(en)$_2$(NH$_3$)Cl]$^{+2}$ occurs with retention of configuration[18] (as is also noted for the corresponding ammonation) and is believed to involve largely *cis*-displacement. On the other hand, aquation of *cis*-[Co(en)$_2$Cl$_2$]$^+$ is thought to take place predominantly *via* an S$_N$1 mechanism,[9b,17] which does not allow a D*$\leftarrow$L* inversion as has been noted for the analogous ammonation. The greater polarizability and greater base strength of ammonia may account for this difference.

A kinetic study in liquid ammonia is now in progress in an attempt to determine the thermodynamic constants of possible competing mechanisms.

Experimental

Synthesis of Dichlorobis-(ethylenediamine)-cobalt(III) Chlorides.—The *trans*-dichlorobis-(ethylenediamine)-cobalt-(III) chloride was prepared as described by Bailar[19] with a slight modification—oxygen was bubbled into the cobalt(II) solution through a sintered glass gas bubbler for 1.5 to 2 hr. (longer bubbling for up to 4 hr. does not appreciably alter the yield) instead of bubbling air through the solution for 10 to 12 hr. The *cis*- and D*-*cis*-dichlorobis-(ethylenediamine)-cobalt(III) chlorides were also prepared by the method described by Bailar[19] with comparable yields.

Anal. (resolved *cis* complex) Calcd. for CoC$_4$H$_{16}$N$_4$Cl$_3$: C, 16.83; H, 5.65. Found: C, 16.80; H, 5.66; [M]$_D$ = 2380 ± 75°.

Synthesis of Chloroamminebis-(ethylenediamine)-cobalt-(III) Chlorides.—The *cis*- and the D*-*cis*-chloroamminebis-(ethylenediamine)-cobalt(III) chlorides were prepared by the directions of Work[20] with similar yields.

Anal. (resolved *cis*-chloroammine complex) Calcd. for CoC$_4$H$_{19}$N$_5$Cl$_3$: C, 15.88; H, 6.33; N, 23.15. Found: C, 15.92; H, 6.25; N, 22.95; [M]$_D$ = 580 ± 17°.

Apparatus.—Rotatory dispersion measurements were made on instruments reading directly to 0.001°. Both a Schmidt and Haensch polarimeter with a monochromator and a Rudolph Photoelectric Spectro-Polarimeter were used. Jacketed cells with path lengths of one and two decimeters were used. All rotations are reported as molecular rotations, [M].

The absorption measurements were taken on a Cary Recording Spectrophotometer, Model 14, with one cm. matched quartz cells.

Constant low temperatures were maintained with a small heater, a Fenwal thermoregulator, Dry Ice cold fingers and a methanol bath in a large Dewar flask.

Ammonation of Optically Active Complexes.—Refrigeration grade ammonia, distilled from a vessel containing sodium, was used in this study. Moisture was excluded by the use of potassium hydroxide or mercury traps during all experiments and by flashing the reaction vessels with gaseous ammonia prior to their cooling for an experiment. Wherever appropriate, the complex was dissolved in liquid ammonia just above the melting point of ammonia ($-77°$) and warmed to the reaction temperature in the constant temperature bath. At the end of the reaction period, the excess liquid ammonia was flashed off; the precipitate was dried at room temperature *in vacuo* for two days and then dissolved in water to make the appropriate measurements. The ammonia concentrations in methanol were determined by titration with standard hydrochloric acid solution.

Ammonation of Racemic *cis*-Chloroamminebis-(ethylenediamine)-cobalt(III) Chloride.—Three grams (3 g., 0.01 mole) of racemic *cis*-[Co(en)$_2$(NH$_3$)Cl]Cl$_2$ was allowed to react with 500 cc. of liquid ammonia for two weeks. One-half gram (0.5 g.) of the resulting yellow-orange precipitate was dissolved in 100 cc. of water and 50 cc. of a saturated solution of sodium dithionate (saturated in 5% acetic acid) was added. Only a few fine crystals (less than a mg.) of the very slightly soluble *trans*-[Co(en)$_2$(NH$_3$)$_2$]$_2$(S$_2$O$_6$)$_3$ were isolated, even with seeding. However, 0.4 g. of the *cis*-[Co(en)$_2$(NH$_3$)$_2$](I$_x$)$_3$ complex was isolated by the addition of an excess of potassium periodide solution to the filtrate.

(18) M. L. Tobe, *J. Chem. Soc.*, 3776 (1959).

(19) J. C. Bailar, Jr., *Inorg. Synthesis*, **2**, 222 (1946).

(20) J. B. Work, Ph.D. Thesis, University of Illinois, 1942, p. 44.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF UTAH STATE UNIVERSITY, LOGAN, UTAH]

The Interaction of Molybdenum with Riboflavin and Flavin Mononucleotide

BY J. T. SPENCE AND JACQUES TOCATLIAN[1]

An investigation of the complexing properties of molybdenum has led to a study of the interaction of molybdenum (V) and (VI) with FMN, riboflavin and mannitol. Polarimetric studies have indicated a strong complex is formed in acidic solution between molybdenum (VI) and FMN. The complex was found to contain two molybdenums per FMN. Riboflavin probably forms a similar complex. Mannitol was found to complex with molybdenum (VI) in the same ratio as FMN and an apparent stability constant was calculated. No evidence was found for a complex of molybdenum (V) with FMN or mannitol. Kinetic studies indicated FMN acts as a catalyst for the oxidation of Mo (V) to Mo (VI) by oxygen. Results are interpreted as indicating the ribitol side chain of FMN is involved in complex formation with Mo (VI). The biological implications with regard to molybdenum containing enzymes are discussed.

An investigation in this Laboratory of the interaction of molybdenum with compounds of biochemical interest has led to a study of complexes of molybdenum with FMN (flavine mononucleotide) and riboflavin. Molybdenum has been reported to be present in four enzymes,[2-5] all of which contain

(2) A. L. Shug, P. W. Wilson, D. E. Green and H. R. Mahler, THIS JOURNAL, **76**, 3355 (1954).

(3) W. J. D. Nicholas and A. Nason, *J. Biol. Chem.*, **207**, 353 (1954).