which alters the ratio of product isomers should be readily detectable. If the leaving group is present in the transition state just prior to the addition of water the charge and/or size difference between N_2 ($+N_2O$) and HgX^+ would be expected to manifest itself in affecting the product ratio. The data in fact do show that the product ratio is sensitive to the nature of the process—note, for example, that some of the spontaneous aquations do show differences from the assisted processes. The fact that the alternate modes of inducing aquation lead to the same product ratio indicates that the leaving group has little or no participation in the transition state for the induced reactions. In other words, the data seem to indicate that the same intermediate is formed by mercuric ion or nitrous acid induced aquations.

As has already been pointed out, the stereochemistry of the induced reactions does not agree with that observed for the spontaneous. These differences are most marked for the cis-$[Co(en)_2N_3X]^+$, $trans$-$[Co(en)_2N_3X]^+$, and cis-$[Co(en)_2ClX]^+$ systems. In each case the ratio of the product isomers is different by a factor of at least three from that observed for the corresponding induced reaction, indicating that the mechanisms of the two types of reaction do differ. The stereochemistry observed for the aquation of $trans$-$[Co(en)_2ClX]^+$ provides a further indication

that the leaving group in spontaneous aquations participates in the transition state observed. If the literature values are accurate the $cis:trans$ product ratio changes from 1:2 to 1:4 with the change of Cl^- to Br^- for leaving group.

Using the "linear free energy relationship" to analyze the influence of the leaving group and a Hammond analysis to determine the importance of the entering group, Langford[1d] has concluded that at best both entering and leaving groups are only weakly bonded in the transition state for the aquation of $Co^{III}(NH_3)_5X$. The present evidence for the series $Co^{III}(en)_2YX$ shows that the spontaneous aquation in most cases does not involve an intermediate of the type occurring in the induced reactions, but the evidence also suggests that the induced reactions (which involve better leaving groups) do take place by a common intermediate. According to the present study the activated complexes for the reactions appear to be in the general range of bond making–bond breaking character described by Langford.

CONTRIBUTION FROM VENABLE HALL LABORATORIES, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA 27514

Complexes of Cobalt(III) and Rhodium(III) with a Cyclic Tetradentate Secondary Amine

By JAMES P. COLLMAN[1] AND PETER W. SCHNEIDER

The following complex cations of cobalt(III) and rhodium(III) containing 1,4,7,10-tetraazacyclododecane (cyclen) have been prepared and characterized: $[Co(cyclen)Cl_2]^+$, $[Co(cyclen)Br_2]^+$, $[Co(cyclen)CO_3]^+$, $[Co(cyclen)C_2O_4]^+$, $[Co(cyclen)(NO_2)_2]^+$, and $[Rh(cyclen)Cl_2]^+$. Comparison of the visible absorption spectra of these cyclen complexes with the spectra of corresponding tetraammine, bis(ethylenediamine), triethylenetetramine, and 4-(2-aminoethyl)diethylenetriamine complexes strongly suggests that the cyclen ligand in these complexes adopts a configuration such that the remaining two coordination positions are *cis*. The significantly higher molar absorptivities of the cyclen complexes are discussed in terms of steric constraint and distortion of the octahedral field.

Introduction

Selective N-terminal hydrolyses of simple peptides[2] have been carried out using "pseudo-enzymatic" cationic chelates such as cis-β-$[Co(trien)(OH)(OH_2)]^{2+}$ and cis-$[Co(tren)(OH)(OH_2)]^{2+}$.[3] In the course of

(1) Fellow of the Alfred P. Sloan Foundation.
(2) J. P. Collman and D. A. Buckingham, *J. Am. Chem. Soc.*, **85**, 3039 (1963).
(3) The following abbreviations are used in this article: cyclen for 1,4,7,10-tetraazacyclododecane; cyclam for 1,4,8,11-tetraazacyclotetradecane; en for ethylenediamine; trien for triethylenetetramine; tren for 4-(2-aminoethyl)diethylenetriamine; tetramine for any four nitrogen atoms attached to cobalt(III) or rhodium(III); tetraammine for four ammonia molecules in complexes of cobalt(III).
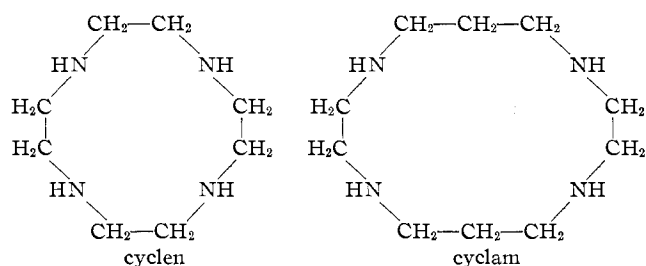
evaluating the scope, mechanism, and utilization of this peptide-cleavage reaction, we decided to investigate other *cis* cobalt(III) complexes containing tetradentate ligands. Two *cis*-coordinated water molecules are necessary to effect peptide hydrolysis. Concurrent mechanism studies using cis-β-$[Co(trien)(OH)(OH_2)]^{2+}$ and cis-$[Co(tren)(OH)(OH_2)]^{2+}$ have been complicated by the nonequivalence of the reactive *cis* positions. Furthermore, two isomeric amino acid complexes can arise from each case.[4] This difficulty would be

(4) L. G. Marzilli, honors paper in chemistry, Brown University, Providence, R. I., 1965.

obviated by the use of a symmetrical, macrocyclic, tetradentate ligand such as cyclen.[3]

While our experiments were in progress, cobalt(III) complexes of a closely related ligand, cyclam,[3] were reported.[5] All of the cyclam complexes described were found to have a *trans* configuration.

Herein we wish to report the preparation and spectral properties of cobalt(III) and rhodium(III) complexes of 1,4,7,10-tetraazacyclododecane (cyclen). These cyclen complexes have a *cis* configuration in contrast to the recently described *trans* cyclam complexes.

$$CoCl_2 + cyclen + O_2 + NaNO_2 \longrightarrow [Co(cyclen)(NO_2)_2]Cl$$
yellow-orange

$$CoCl_2 + cyclen + O_2 \xrightarrow{HCl} [Co(cyclen)Cl_2]Cl$$
violet

[Co(cyclen)Br₂]Br — HBr
dark olive green[8]

[Co(cyclen)CO₃]Cl — Li₂CO₃
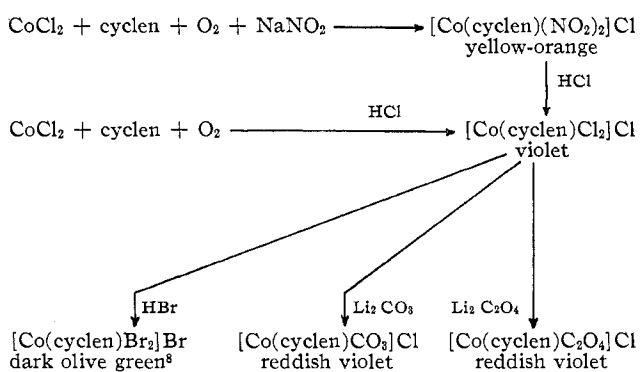reddish violet

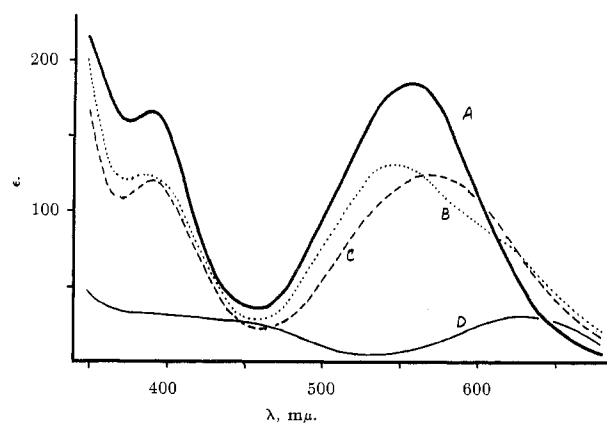[Co(cyclen)C₂O₄]Cl — Li₂C₂O₄
reddish violet

Figure 1.

Figure 2.—Visible absorption spectra of (A) *cis*-[Co(cyclen)Cl₂]⁺, (B) *cis*-α-[Co(trien)Cl₂]⁺, (C) [Co(tren)Cl₂]⁺, (D) *trans*-[Co(en)₂Cl₂]⁺.
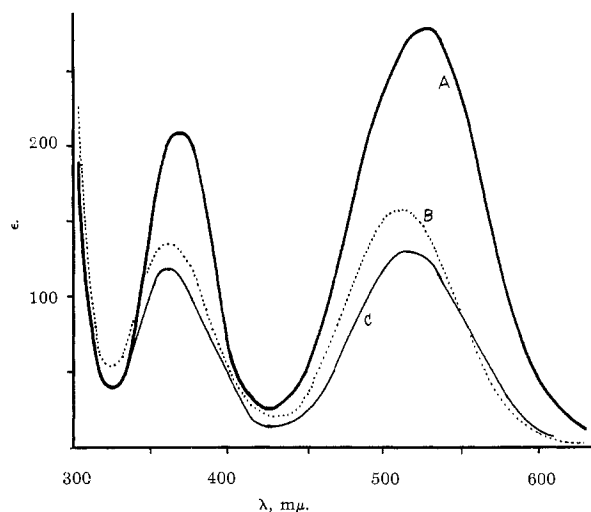

Figure 3.—Visible absorption spectra of (A) [Co(cyclen)CO₃]⁺, (B) β-[Co(trien)CO₃]⁺, (C) [Co(en)₂CO₃]⁺.

Results and Discussion

Cyclen was synthesized by the method of Stetter and Mayer.[6] It was isolated as the tetrahydrochloride, which can be purified easily and in higher yields by recrystallization from hydrochloric acid than by distillation from sodium.[6]

The cobalt(III) cyclen compounds were obtained following the general methods for the preparation and interconversion[7] of cobalt(III) amine complexes (Figure 1).[8-11]

In Figures 2-4 and Table I,[12-22] visible and ultraviolet spectral data are given and compared with the corresponding tetraammine,[3] bis(ethylenediamine), trien, and tren compounds. Apart from small shifts in the absorption maxima to longer wavelength in the cyclen complexes, there is a close similarity in character and shape of the spectra of cobalt(III) and rhodium(III) cyclen complexes with those of the *cis* isomers of other tetramine[3] compounds. Based on this evidence, the

monodentate ligands (chloride and bromide) in these cyclen complexes can be assigned a *cis* configuration (Figure 2, Table I).

The spectral difference between *cis* and *trans* dinitro complexes is less clear-cut. However, it has been shown recently that infrared spectroscopy can be used to differentiate between *cis*-α, *cis*-β, and *trans* isomers of several cobalt(III) trien complexes.[10] The infrared spectra of all of the cobalt(III) cyclen complexes show,

(5) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

(6) H. Stetter and K.-H. Mayer, *Chem. Ber.*, **94**, 1410 (1961).

(7) See, *e.g.*, G. H. Searle, Ph.D. Thesis, Australian National University, Canberra, A.C.T., Australia, 1963.

(8) The "green color" in dibromocobalt(III) tetramine complexes does not necessarily mean that the complex has the *trans* configuration. Linhard and Weigel⁹ report *cis*-[Co(en)₂Br₂]⁺ to be dichroic dark olive-green. Recently, Buckingham¹⁰ provided infrared evidence that the green *trans*-[Co(trien)Br₂]Br isomer prepared by Selbin and Bailar¹¹ is mainly *cis*-α-contaminated by *cis*-β-[Co(trien)Br₂]Br.

(9) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **271**, 101 (1952).

(10) D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

(11) J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **82**, 1524 (1960).

(12) J.-P. Mathieu, *Bull. Soc. Chim. France*, **3**, 463 (1936).

(13) R. C. Brasted and C. Hirayama, *J. Phys. Chem.*, **63**, 780 (1959).

(14) F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950).

(15) G. H. Searle, Ph.D. Thesis, Australian National University, Canberra, A.C.T., Australia, 1963.

(16) J. P. Collman, W. R. Roper, and S. A. Young, unpublished results.

(17) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 311 (1956).

(18) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **267**, 113 (1951).

(19) B. Adell, *Acta Chem. Scand.*, **5**, 54 (1951).

(20) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 3193 (1963).

(21) [Rh(tren)Cl₂]NO₃ was prepared by the method of S. A. Johnson and F. Basolo, *Inorg. Chem.*, **1**, 925 (1962).

(22) The error in the ε values is estimated to be ±5–10%; the error in the wavelength, to be ±5 mμ, in the cyclen and tren complexes.

TABLE I

COMPARISON OF THE ELECTRONIC SPECTRA OF A SERIES OF *cis*-TETRAMINE COMPLEXES

Complex	Solvent	λ, mμ	ϵ	λ, mμ	ϵ	Ref
cis-[Co(NH$_3$)$_4$Cl$_2$]$^+$	H$_2$O	540	45			12, 13
cis-[Co(en)$_2$Cl$_2$]$^+$	H$_2$O	530	78	380	69	13
	H$_2$O	535	100	390	78	12, 14
cis-α-[Co(trien)Cl$_2$]$^+$	Dil HClO$_4$	539	130	381	135	15
[Co(tren)Cl$_2$]$^+$	30% HCl	565^{22}	125	390	120	16
cis-[Co(cyclen)Cl$_2$]$^+$	30% HCl	560^{22}	185	390	165	
cis-[Co(en)$_2$Br$_2$]$^+$	H$_2$O	560	110			9
cis-[Co(cyclen)Br$_2$]$^+$	Concd HBr	570	180	390	170	
cis-[Co(NH$_3$)$_4$CO$_3$]$^+$	H$_2$O	520	102	363	105	12, 17
cis-[Co(en)$_2$CO$_3$]$^+$		515	135	364	123	17
β-[Co(trien)CO$_3$]$^+$	H$_2$O	507	178	358	140	15
[Co(cyclen)CO$_3$]$^+$	H$_2$O	530	280	368	210	
[Co(NH$_3$)$_4$C$_2$O$_4$]$^+$		510	81	357	129	17
[Co(en)$_2$C$_2$O$_4$]$^+$		500	113	355	144	17
[Co(cyclen)C$_2$O$_4$]$^+$	H$_2$O	520	245	365	205	
cis-[Co(NH$_3$)$_4$(NO$_2$)$_2$]$^+$	H$_2$O	445	158	324	4170	18
cis-[Co(en)$_2$(NO$_2$)$_2$]$^+$	H$_2$O	435	182			19
cis-α-[Co(trien)(NO$_2$)$_2$]$^+$	H$_2$O	434	214	323	4670	15
[Co(tren)(NO$_2$)$_2$]$^+$	H$_2$O	440	229	320	4670	16
cis-[Co(cyclen)(NO$_2$)$_2$]$^+$	H$_2$O	445	355	320	4460	
cis-[Rh(en)$_2$Cl$_2$]$^+$		350	130	292	170	20
cis-[Rh(trien)Cl$_2$]$^+$		350	101	304	198	20
[Rh(tren)Cl$_2$]$^+$	H$_2$O	370	300	302	315	21
cis-[Rh(cyclen)Cl$_2$]$^+$	H$_2$O	365	535	302	430	

apart from those regions where additional absorptions of the mono- and bidentate ligands are found, only minor variations such as shifts lying within the experimental errors, differences in the relative intensities, and the resolution of the absorption peaks. Since in the solid state the vibrational modes of metal–amine chelate rings are affected by (i) the orientation of the chelating ligand about the central metal atom, (ii) the spatial configuration of the individual chelate rings and nonbonded interaction between them, and (iii) the ionic interaction or hydrogen bonding between the cation, anion, and lattice-bound water,[10] the infrared spectra provide further evidence for a *cis* configuration in all of these cyclen complexes. Further, in the cases of carbonato- and oxalatocobalt(III) tetramine complexes where a *cis* configuration has to be assumed because of the nature of the bidentate ligands, the visible

Figure 4.—Visible absorption spectra of (A) [Co(cyclen)C$_2$O$_4$]$^+$, (B) [Co(en)$_2$C$_2$O$_4$]$^+$.

absorption spectra display the same similarity (Figures 3 and 4).

Comparison of the electronic spectra of a series of tetramine complexes (Table I) reveals a remarkable change in the molar absorptivity (ϵ). These differences are especially pronounced for the absorption band at the longest wavelengths. Comparing the ligands in the order of four ammonias, two en, trien, tren, and cyclen, the ϵ values increase by a factor of about 4 in the *cis*-dichlorocobalt(III) complexes, by 3 in the oxalato-, by 2.7 in the carbonato-, and by 2.2 in the *cis*-dinitro-complexes. An increase in ϵ by a factor of 4 is found in *cis*-dichlororhodium(III) complexes in exchanging two en by cyclen.

Theory[23] suggests that the intensities of d–d transitions should be enhanced by increasing the asymmetry of the ligand field. There is experimental support for this proposition.[24] It seems reasonable that the rise in ϵ values accompanying the more rigid tetramine ligands is caused by increasing distortion of the octahedral field. Each additional ethylene bridge would be expected to result in further steric constraint. This hypothesis is further strengthened by comparing the ϵ values of the trien and tren complexes of cobalt(III) and rhodium(III). Linear trien is more flexible than branched tren. The ϵ values of the *cis*-dichlorocobalt-(III) trien and tren complexes are about the same (130 and 125). On the other hand, the arrangement of these ligands around the larger rhodium(III) results in a greater distortion by tren than by trien. The ϵ values of the rhodium(III) complexes differ by a factor of 3.
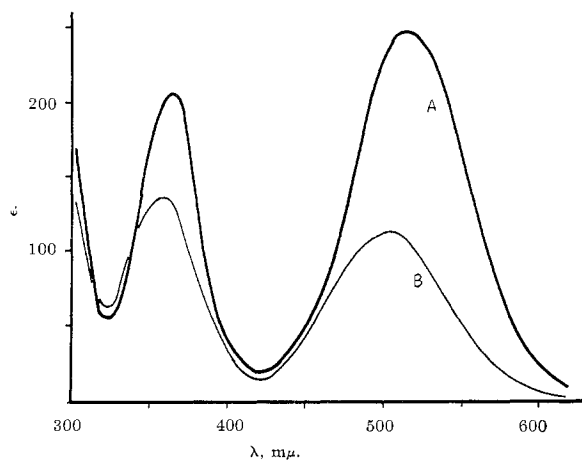
(23) See, *e.g.*, F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955), or F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, Inc., New York, N. Y., 1963, pp 231 ff.

(24) R. L. Belford and W. A. Yeranos, *Mol. Phys.*, **6**, 121 (1963); P. W. Schneider and H. Brintzinger, *Helv. Chim. Acta*, **47**, 1717 (1964).

COMPARISON OF THE ELECTRONIC SPECTRA OF A SERIES OF
trans-TETRAMINE COMPLEXES

Complex	λ, mμ	ϵ
trans-[Co(NH₃)₄Cl₂]⁺	630	43
trans-[Co(en)₂Cl₂]⁺	620	38
trans-[Co(cyclam)Cl₂]⁺	~630	~35
trans-[Co(NH₃)₄(NO₂)₂]⁺	441	235
trans-[Co(en)₂(NO₂)₂]⁺	430	186
trans-[Co(cyclam)(NO₂)₂]⁺	~460	~185
trans-[Co(en)₂(NCS)₂]⁺	505	275
trans-[Co(cyclam)(NCS)₂]⁺	~520	~265
trans-[Co(NH₃)₄(N₃)₂]⁺	570	372
trans-[Co(cyclam)(N₃)₂]⁺	~575	~425

In Table II,[25] data are listed for some *trans* tetramine complexes of cobalt(III). No significant differences in the ϵ values are observed in going from *trans* tetra-ammine to *trans* cyclam complexes. These ϵ values are generally smaller than those from the corresponding *cis* complexes as is expected from the presence of a center of symmetry in the *trans* complexes. A distorting effect by the ethylene bridges in both the cyclam and bis-(ethylenediamine) complexes can destroy the C_4 axis, but as long as the distortion along the edges of the tetragonal plane occurs symmetrically, the center of inversion is retained.

At the present time we have not attempted peptide-cleavage reactions using these cyclen complexes. The difficulty in preparing reasonable quantities of the cyclen ligand probably exceeds any advantage that these cyclen complexes might have in application to the peptide-cleavage reactions; however, this ligand should be useful in mechanistic studies.

Experimental Section

1,4,7,10-Tetraazacyclododecane Tetrahydrochloride (cyclen·4HCl).—1,4,7,10-Tetraazacyclododecane was prepared according to the method of Stetter and Mayer[5] by reduction of 14 g of 1,4-ditosyl-6,11-dioxo-1,4,7,10-tetraazacyclododecane with 7 g of lithium aluminum hydride. The crude, dark brown cyclic amine was dissolved in 50 ml of 20% hydrochloric acid and extracted with benzene and ether to remove some of the colored impurities. The aqueous layer was further decolorized by treatment with charcoal. Following filtration, the solution was concentrated on a hot plate until crystals started to form and then stored in the refrigerator overnight. The off-white crystalline product was collected by filtration. After two recrystallizations from 10–20% hydrochloric acid, 6.2 g (65%) of white crystals was obtained, mp 255–259°. *Anal.* Calcd for C₈H₂₄N₄Cl₄: C, 30.2; H, 7.6; N, 17.6; Cl, 44.6. Found: C, 30.2; H, 7.6; N, 17.2; Cl, 44.5.

cis-Dinitro(1,4,7,10-tetraazacyclododecane)cobalt(III) Chloride.—A stream of carbon dioxide free air was passed for 12 hr through a solution containing cyclen·4HCl (635 mg, 2 mmoles), lithium hydroxide (145 mg, 6 mmoles), cobalt(II) chloride hexahydrate (475 mg, 2 mmoles), and sodium nitrite (145 mg, 2.1 mmoles) in 150 ml of water. Yellow-brown crystals were obtained after concentration of the solution to about 15 ml. These were recrystallized from a minimum amount of hot water, yield 450 mg (62%). *Anal.* Calcd for [Co(C₈H₂₀N₄)(NO₂)₂]Cl: C, 26.8; H, 5.6; N, 23.5; Cl, 9.9. Found: C, 26.7; H, 5.9; N, 22.3; Cl, 10.2.

cis-Dichloro(1,4,7,10-tetraazacyclododecane)cobalt(III) Chloride (1.5)Hydrate.—A mixture of *cis*-[Co(cyclen)(NO₂)₂]Cl (450 mg, 1.25 mmoles) and 10 ml of concentrated hydrochloric acid was evaporated to dryness on a steam bath, and the violet residue was then recrystallized from concentrated hydrochloric acid, yield 330 mg (72%). *Anal.* Calcd for [Co(C₈H₂₀N₄)Cl₂]Cl·1.5H₂O: C, 26.3; H, 6.4; N, 15.3; Cl, 29.1. Found: C, 26.2; H, 6.3; N, 15.6; Cl, 29.1.

Attempts to prepare [Co(cyclen)Cl₂]Cl in a direct manner by aeration of cobalt(II) chloride and cyclen, followed by treatment of the solution with hydrochloric acid, proved to be less satisfactory, because of the presence of CoCl₄²⁻ ions, which are difficult to remove by recrystallization.

cis-Dibromo(1,4,7,10-tetraazacyclododecane)cobalt(III) Bromide.—A mixture of cyclen·4HCl (475 mg, 1.5 mmoles), lithium hydroxide (145 mg, 6 mmoles), and cobalt(II) chloride hexahydrate (475 mg, 2 mmoles) in 150 ml of water was aerated for 75 min. Concentrated hydrobromic acid (30 ml) was added, and the solution was evaporated to dryness on a steam bath. Evaporation with concentrated hydrobromic acid was repeated twice. The residue was then triturated with ethanol, filtered, and then recrystallized twice from concentrated hydrobromic acid; yield 150 mg (21%) of dark olive-green crystals. *Anal.* Calcd for [Co(C₈H₂₀N₄)Br₂]Br: C, 20.4; H, 4.3; N, 11.9; Br, 51.0. Found: C, 20.2; H, 4.3; N, 12.2; Br, 51.1.

Carbonato(1,4,7,10-tetraazacyclododecane)cobalt(III) Chloride (1.5)Hydrate.—A solution of [Co(cyclen)Cl₂]Cl·1.5H₂O (300 mg, 0.8 mmole) and lithium carbonate (150 mg, 2 mmoles) in 15 ml of water was heated for 6 hr at 85°. Calcium chloride (120 mg, 1.1 mmoles) was added, and the mixture was allowed to stand overnight. The calcium carbonate was removed by filtration, and the filtrate was then concentrated to about 2 ml. Upon careful addition of 4 ml of ethanol and 2 ml of acetone, a red gum was formed which solidified after treating several times with absolute ethanol. Recrystallization from water–ethanol yielded 150 mg (52%) of reddish violet crystals. *Anal.* Calcd for [Co(C₈H₂₀N₄)CO₃]Cl·1.5H₂O: C, 30.6; H, 6.6; N, 15.8. Found: C, 30.4; H, 6.7; N, 15.7.

Oxalato(1,4,7,10-tetraazacyclododecane)cobalt(III) Chloride Monohydrate.—A solution of [Co(cyclen)Cl₂]Cl·1.5H₂O (365 mg, 1 mmole), lithium hydroxide (48 mg, 2 mmoles), and oxalic acid (125 mg, 1 mmole) in 20 ml of water was refluxed for 75 min. The mixture was filtered while hot, and after addition of 2 ml of concentrated hydrochloric acid, the filtrate was evaporated until crystallization began. Some violet [Co(cyclen)Cl₂]Cl which crystallized first was filtered off, and product was then precipitated by addition of alcohol and acetone. Recrystallization from water–ethanol yielded 110 mg (29%). *Anal.* Calcd for [Co(C₈H₂₀N₄)C₂O₄]Cl·H₂O: C, 32.3; H, 6.0; N, 15.1. Found: C, 32.4; H, 6.2; N, 15.0.

cis-Dichloro(1,4,7,10-tetraazacyclododecane)rhodium(III) Chloride Dihydrate.—A solution of cyclen·4HCl (320 mg, 1 mmole), lithium hydroxide (70 mg, 3 mmoles), and rhodium(III) chloride trihydrate (265 mg, 1 mmole) in 20 ml of water was heated to reflux. After 10 min, 0.1 ml of 10% hydrazine[26] solution was added. The initially formed orange-yellow precipitate was removed from the hot solution by filtration, and the filtrate was concentrated to 15 ml. A solution of lithium hydroxide (18 mg, 0.75 mmole) in 10 ml of water was added slowly to this filtrate and the solution was then refluxed overnight. Some metallic rhodium which was formed was filtered off, and the bright yellow filtrate was evaporated slowly to dryness. The residue was taken up in 3 ml of water and the product precipitated by addition of 8 ml of ethanol. Recrystallization from water–ethanol gave 196 mg (47%) of bright yellow crystals. *Anal.* Calcd for [Rh(C₈H₂₀N₄)Cl₂]Cl·2H₂O: C, 23.0; H, 5.8; N, 13.4. Found: C, 23.1; H, 5.8; N, 13.8.

Visible and ultraviolet absorption spectra were measured

(25) Data for tetraammine and bis(ethylenediamine) complexes from ref 17; for cobalt(III) cyclam complexes from graphs in ref 5.

(26) R. D. Gillard, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, 1951 (1965).

with a Perkin-Elmer 202 spectrophotometer; infrared spectra were measured with a Perkin-Elmer 237B grating spectrophotometer, using the KBr-disk technique. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill., and Triangle Chemical Laboratories, Inc., Chapel Hill, N. C.

Transition Metal Complexes of 3,3'-Diaminodipropylamine: Stability Constants

By A. Vacca, D. Arenare, and P. Paoletti

The basicity constants of 3,3'-diaminodipropylamine (dpt) were determined in 0.1 M KCl at 25.0° and were found to be greater than those of 2,2'-diaminodiethylamine (den). The equilibria between dpt and the bivalent transition metal ions from Mn(II) to Zn(II) were investigated under the same conditions. In the case of Mn(II) and Fe(II) the precipitation of hydroxides prevented the measurement of the complex formation constants. Co(II), Ni(II), and Zn(II) form 1:1 complexes for which the formation constants were measured. In the case of Ni(II) the existence of 1:2 complex was demonstrated spectrophotometrically and its formation constant was measured potentiometrically. The reflectance spectrum of the octahedral complex [Ni(dpt)₂](ClO₄)₂ was recorded. In the presence of excess ligand, the ions Cu(II) and Zn(II) do not form 1:2 complexes, but hydroxo complexes of formulas [Cu(dpt)(OH)]⁺ and [Zn(dpt)(OH)]⁺ for which the stability constants were determined. The formation of [Cu(dpt)(OH)]⁺ was also confirmed by conductometric titrations. The metal complexes of dpt are less stable than the corresponding complexes of den, and this is consistent with the strain energies in the chelate rings.

Introduction

It is known that six-membered chelate rings are less stable than the analogous five-membered rings.[1] For example, the formation constants of the complexes formed by nickel and copper with 1,3-diaminopropane or β-aminoethylpyridine are smaller than the corresponding values for the complexes with ethylenediamine and picolylamine.[2] 3,3'-Diaminodipropylamine (dpt) is a triacid base which can form metal complexes having six-membered chelate rings.

The purpose of the present investigation was to measure the three basicity constants of dpt and the formation constants of its complexes with the bivalent metal ions from Mn(II) to Zn(II), at 25.0° in 0.1 M KCl. This enabled us to make a comparison with the corresponding values, under the same conditions of temperature and ionic medium, for 2,2'-diaminodiethylamine (den).[3,4] Some of the den complexes such as [Cu(den)]²⁺ and perhaps [Zn(den)]²⁺ form monohy-

$$HN \underset{CH_2CH_2CH_2NH_2}{\overset{CH_2CH_2CH_2NH_2}{<}} \qquad HN \underset{CH_2CH_2NH_2}{\overset{CH_2CH_2NH_2}{<}}$$

dpt   den

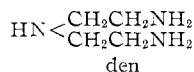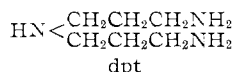droxo complexes.[4] We therefore attempted to find out if the complexes [M(dpt)]²⁺ are also able to bind

hydroxide ions and if such ability is related to the stability of the simple polyamine complex.

Fernelius and others[5] have confirmed the existence of 1:1 complexes with the ions Co(II), Ni(II), and Cu(II) for which they have measured the stability constants at 30° in 1 M KNO₃. Furthermore, the solid complexes [Ni(dpt)₂](NO₃)₂,[6] [Ni(dpt)₂](ClO₄)₂, and [Ni(dpt)₂](BF₄)₂[7] have been isolated, showing that dpt, in spite of considerable steric hindrance, is capable of forming a 2:1 complex with the Ni(II) ion, at least in the solid state. It appeared therefore of some interest to extend the investigation of the equilibria in aqueous solution between dpt and the bivalent transition metal ions, in order to ascertain whether other complexes existed than those found by Fernelius.

Experimental Section

Materials.—Reagent grade metal chlorides were used for the preparation of approximately 0.4 M stock solutions. The solution of ferrous chloride was made *ca.* 0.01 M in hydrochloric acid and reduced with hydrogen in the presence of indigo tetrasulfonate as indicator and of several drops of 2% suspension of colloidal palladium. This solution was kept under hydrogen. The solutions of the other metal chlorides were slightly acidified with HCl in order to prevent hydrolysis. The concentrations of the metal ions in the different solutions were determined using conventional methods. The concentration of the hydrochloric acid was determined potentiometrically.

Nitrogen was purified by passing over pyrophoric copper at 100°. An alcoholic solution of commercial 3,3'-diaminodipropylamine (Fluka) was treated with an excess of concentrated

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