five-line multiplet appeared most probably to arise from overlap of three quartets in a 1:1:1 intensity ratio with the further restriction that the triplet splitting be approximately one-half of the value of the quartet splitting. Again it must be stressed that the α-CF$_2$ resonances were always broad and thus it was difficult to obtain accurate data on coupling constants from such resonances. In one compound $(\pi$-C$_5$H$_5$Co(CO)-[(C$_6$H$_5$)$_3$P]C$_3$F$_7$$^+ClO_4$$^-$) the expected quartet pattern could not be resolved. Broadening of these α-CF$_2$ resonances might be a result of relaxation caused by the nuclear quadrupole moment of the cobalt atom or the chlorine atom of the perchlorate group.

The β-CF$_2$ group in some of the perfluoropropyl compounds showed evidence of further splitting. This splitting was generally quite small.

The variation of the chemical shift of the α-CF$_2$ in both the pentafluoroethyl and heptafluoropropyl compounds as a function of the ligand groups was striking. The chemical shift differences of almost 30 p.p.m. seem to parallel basicity of the ligands. In view of previous discussion of the α-CF$_2$ chemical shifts in perfluoroalkyl transition metal complexes[15] such a shift is not surprising. Certainly a variation of the electronic structure in these compounds would be in a regular pattern and the resulting paramagnetic contribution to the chemical shift would also be expected to vary accordingly.


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

By B. BOSNICH, C. K. POON, and M. L. TOBE

1,4,8,11-Tetraazacyclotetradecane (cyclam) has been prepared by the action of 1,3-dibromopropane on 1,3-bis(2'-aminoethylamino)propane. The following complex cations have been characterized: [Co(cyclam)Cl$_2$]$^+$, [Co(cyclam)Br$_2$]$^+$, [Co(cyclam)(NCS)$_2$]$^+$, [Co(cyclam)(NO$_2$)$_2$]$^+$, [Co(cyclam)(N$_3$)$_2$]$^+$, [Co(cyclam)(NH$_3$)$_2$]$^{3+}$, [Co(cyclam)N$_3$Cl]$^+$, and [Co(cyclam)NCSCl]$^+$. Apart from the dichloro complex, only one isomeric form has been obtained, and a comparison of the visible absorption spectra with those of the corresponding bis(ethylenediamine)cobalt(III) complexes suggests that all have a *trans* configuration of the monodentate ligands. The solvolytic equilibrium of the dichloro complex has been studied in aqueous solution and the aquo complexes have been shown to be less stable than those of the corresponding bis(ethylenediamine)cobalt(III) complexes. The possible configurational isomers of these complexes are discussed and a structure is suggested.

Studies of the stereochemical consequences of substitution in octahedral complexes have led to the concept of a trigonal bipyramidal intermediate in the dissociative substitution reactions of the cobalt(III) amine complexes.[1] Most of the data refer to systems containing two ethylenediamine molecules which do not significantly resist any change in the shape of the complex, and it is now desirable to extend the investigations to molecules with greater rigidity due to the presence of macrocyclic quadridentate ligands. Although such cyclic ligands have been known for a long time, most have been of natural origin, *e.g.*, porphyrins, etc., and are highly conjugated. More recently, considerable interest has been aroused by the synthesis of such macrocyclic ligands using a metal ion as a "template,"[2,3] but, in the search for a ligand which would not

differ greatly in its electronic effects from those amines used in previous studies and which did not contain superfluous organic side chains, we were fortunate to find 1,4,8,11-tetraazacyclotetradecane (cyclam)

Cyclam
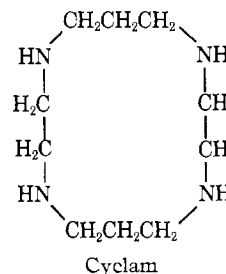
which could be readily synthesized by conventional methods. This compound was first claimed by Van Alphen[4] as a product of the reaction between 1,3-dibromopropane and 1,3-bis(2'-aminoethylamino)-propane in the presence of alkali. More recently,

(1) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 215; R. S. Nyholm and M. L. Tobe, "Essays in Coordination Chemistry," Birkhäuser Verlag, Basel, 1964, p. 112, and references therein.
(2) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).
(3) D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **84**, 3248 (1962); G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963).
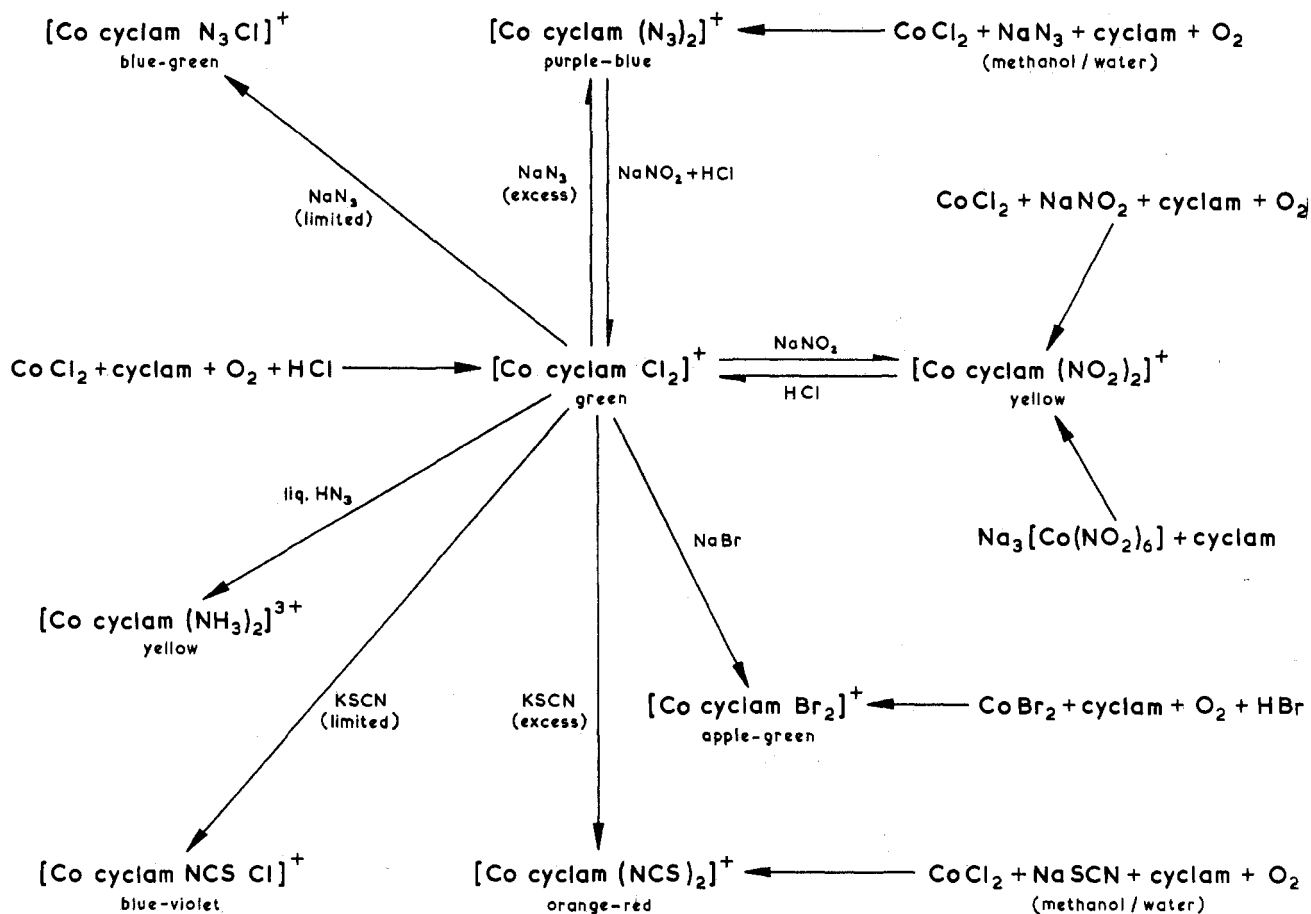(4) J. Van Alphen, *Rec. trav. chim.*, **56**, 343 (1937).

Figure 1.

Stetter and Mayer[5] synthesized the amine by an un-
ambiguous route and showed that the material de-
scribed by Van Alphen contained only a small amount
of the required ligand. We have found that it is more
convenient to use a modification of Van Alphen's
method and isolate the ligand in small yield than to use
the much more elegant, but time consuming, method of
Stetter and Mayer, which had much the same over-all
yield. The infrared spectrum of the ligand was identi-
cal with that reported in the literature,[5] and the nuclear
magnetic resonance spectrum of a chloroform solution
had three main proton resonance bands whose areas
were in the ratio 4:1:1, which is consistent with the
formulation. There are three types of hydrogen:
(i) the four attached to nitrogen, (ii) the sixteen at-
tached to the α carbon atoms, and (iii) the four attached
to the β carbon atoms. All the bands are split, as
would be expected from the spin–spin interactions, and
the band attached to the amine protons is broad because
of quadrupole coupling and possibly because of some
intramolecular hydrogen bonding. The fine structure
does not enable us to determine the configuration of the
free ligand.

Complexes of the Cyclic Tetramine with Cobalt(III).
—The general scheme for the preparation of the com-
plexes is outlined in Figure 1. All are diamagnetic,
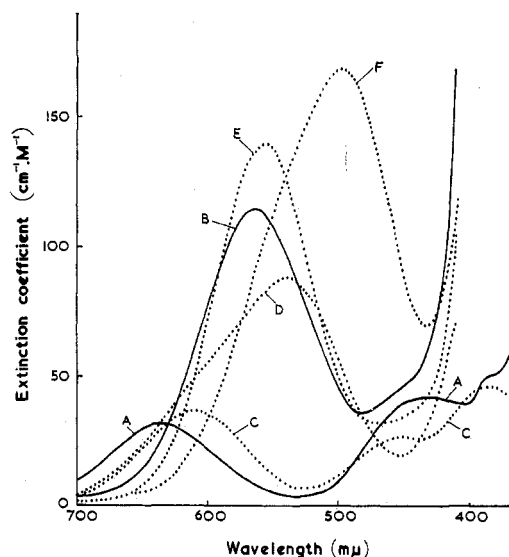as would be expected for a d^6 ion in a strong octahedral

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

Figure 2.—Visible absorption spectra of (A) *trans*-[Co-
(cyclam)Cl₂]Cl, (B) *trans*-[Co(cyclam)NCSCl]ClO₄, (C) *trans*-
[Co(en)₂Cl₂]Cl, (D) *cis*-[Co(en)₂Cl₂]Cl, (E) *trans*-[Co(en)₂-
NCSCl]ClO₄, (F) *cis*-[Co(en)₂NCSCl]NO₃ in water.

field. The visible absorption spectra are shown in
Figures 2, 3, and 4, where they are compared with the
spectra of the *cis* and *trans* isomers of the corresponding
bis(ethylenediamine)cobalt(III) complexes. In every
case there is a close similarity with the *trans* complex,
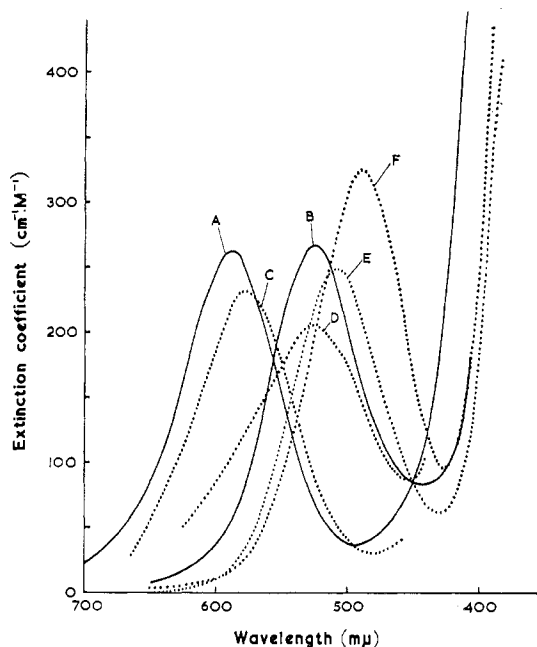and it is on the basis of this evidence that we assign a

Figure 3.—Visible absorption spectra of (A) *trans*-[Co(cyclam)-N₃Cl]ClO₄, (B) *trans*-[Co(cyclam)(NCS)₂]NCS, (C) *trans*-[Co(en)₂N₃Cl]ClO₄, (D) *cis*-[Co(en)₂N₃Cl]ClO₄, (E) *trans*-[Co(en)₂(NCS)₂]Cl, (F) *cis*-[Co(en)₂(NCS)₂]Cl in water.
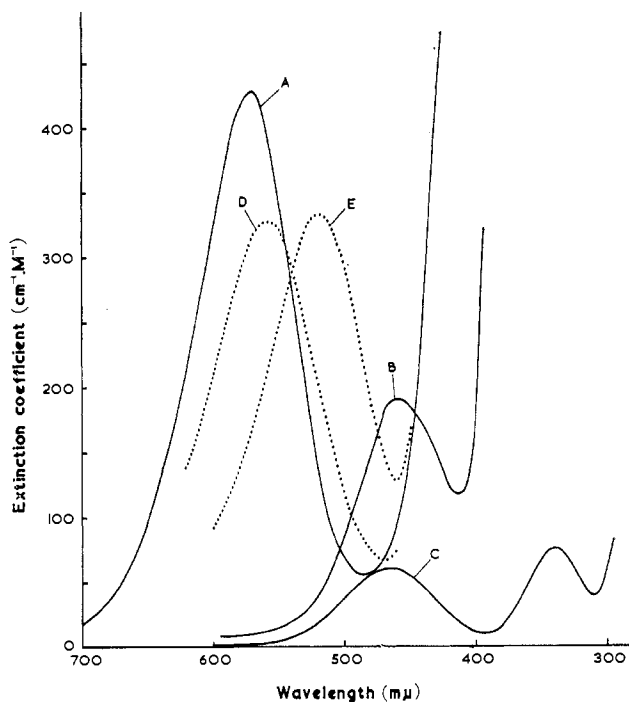

Figure 4.—Visible absorption spectra of (A) *trans*-[Co-(cyclam)(N₃)₂]ClO₄, (B) *trans*-[Co(cyclam)(NO₂)₂]ClO₄, (C) *trans*-[Co(cyclam)(NH₃)₂]Cl₃, (D) *trans*-[Co(en)₂(N₃)₂]ClO₄, (E) *cis*-[Co(en)₂(N₃)₂]ClO₄ in water.

trans configuration to the complex cations. The assignment is most reliable when the spectra of the *cis*- and *trans*-[Co(en)₂XY]ⁿ⁺ have the greatest difference, *e.g.*, in the dihalo, chloroazido, chloroisothiocyanato, and diazido complexes. There is often a small shift of the visible peak to a longer wave length, but this is small enough to indicate that the ligand field

strength of the cyclic amine is not very much different from that of two ethylenediamines.

Chemically there is a considerable difference between the behavior of these complexes and those of ethylenediamine. The *trans*-[Co(cyclam)Cl₂]⁺ is much more stable with respect to the corresponding aquo complex than *trans*-[Co(en)₂Cl₂]⁺. The position of the equilibrium

$$trans\text{-}[Co(cyclam)Cl_2]^+ + H_2O \underset{\longleftarrow}{\overset{K}{\longrightarrow}}$$
$$trans\text{-}[Co(cyclam)ClH_2O]^{2+} + Cl^-$$
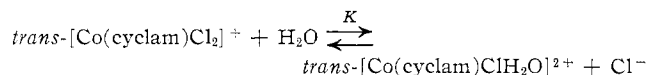
in 0.01 N HNO₃ and in water at 80° has been studied by direct titration of the ionic chloride and the results are collected in Table I. In the absence of added acid the equilibrium moves further to the right. When the *trans*-[Co(en)₂Cl₂]⁺ cation is allowed to reach aquation equilibrium under similar conditions, but at 30°, no dichloro complex is present and 75% of the complex is in the form of the diaquo cation, even when the original complex was supplied as the chloride. Increase in temperature forces the equilibrium further toward the diaquo complex, as does an increase in pH.[6] A qualitative similarity has been observed with the other chloro complexes and the dibromo complex, but the equilibria have not been examined in detail. The kinetics and mechanism of the aquation, anation, and other substitution reactions of these complexes are now being studied and will be reported shortly. Because of the reduced stability of the aquo cyclam complexes we observe a behavior in aqueous solution that is somewhat reminiscent of the substitution reactions of the bis(ethylenediamine)cobalt(III) complexes in nonaqueous solution. We have been unable to isolate these aquo complexes in solid crystalline forms, presumably because of the facile anation reaction, but we have been able to characterize and study them adequately in solution.

Table I

Equilibrium Measurements for the Reaction[a]

$$trans\text{-}[Co(cyclam)Cl_2]^+ + H_2O \underset{\longleftarrow}{\overset{K}{\longrightarrow}}$$
$$trans\text{-}[Co(cyclam)ClH_2O]^{2+} + Cl^-$$

| Solvent	[Co(cyclam)-Cl₂]⁺ₑₙᵢₜ, mM	[Cl⁻]ᵢₙᵢₜ, mM	[Cl⁻]fᵢₙₐₗ, mM	10³K, M
0.01 N HNO₃	1.81[b]	1.81	3.01	5.9
0.01 N HNO₃	3.28[c]	0.93	3.10	6.0
0.01 N HNO₃	5.92[b]	5.92	8.38	6.0
Water	2.26[b]	2.26	4.48	...[d]
Water	3.40[c]	1.16	4.20	...[d]
Water	4.16[b]	4.16	7.34	...[d]

[a] Equilibrium is reached after 24 hr. at 80.0°. [b] Complex supplied as the chloride. [c] Complex supplied as a mixture of the chloride and the nitrate. [d] The position of equilibrium depends upon the pH which depends upon the concentration of aquo complex and which was not controlled.

A number of attempts have been made to prepare the *cis* isomers of these complexes. Evaporation of an aqueous solution of *trans*-[Co(cyclam)Cl₂]⁺ yields only the original material and at no stage is there any color change that would be indicative of the formation of

(6) J. P. Mathieu, *Bull. soc. chim. France*, **3**, 2121 (1936).

cis chloro or aquo complexes. The oxidation of a solution containing cobalt(II) chloride, sodium bicarbonate, and the ligand yields an ill-defined material that is probably the *trans* aquocarbonato (or hydroxobicarbonato) complex and the same compound is formed in the reaction between the ligand and sodium tris-(carbonato)cobaltate(III). Furthermore, the reaction between the ligand and sodium cobaltinitrite yields a dinitro complex that is identical in every respect with that prepared by the action of sodium nitrite on the dichloro complex. In none of the preparations starting from *trans*-[Co(cyclam)Cl$_2$]$^+$ is there any indication of the presence of a second component that is isomeric with the main crop. Spectrophotometric studies of the solution reactions of these complexes also give no indication of the presence of more than one product in a single-stage reaction. However, we have recently been able to isolate a purple-violet crystalline material in very small yield from crude *trans*-[Co(cyclam)Cl$_2$]$^+$. This complex can be converted quantitatively to the *trans* dichloro complex and may very well be the *cis* isomer. The characterization of this complex and a study of its reactions and derivatives is now in progress and will be reported in a later paper.

The Configuration of the Coordinated Ligand.— Apart from the, as yet, uncharacterized violet complex obtained in the preparation of the *trans* dichloro chloride, all the complexes are *trans* isomers and all of their substitution reactions occur with complete retention of configuration. The designation *trans* does not fully characterize the complex since the cyclic ligand will have a number of possible distinct configurations; these are discussed briefly below and the principles will apply to any cyclic tetradentate ligand whose donor atoms are tetrahedral when coordinated. In 1,4,8,11-tetraazacyclotetradecane, each nitrogen, when coordinated, is an asymmetric center, and five distinct non-enantiomeric combinations can be produced. When the nitrogens are coordinated to the corners of a square the hydrogen attached to each nitrogen is approximately axial and it is convenient to discuss the problem in terms of the direction in which the N–H bond points rather than to use the sign of the helicity of each nitrogen. The five forms can be represented diagramatically as follows
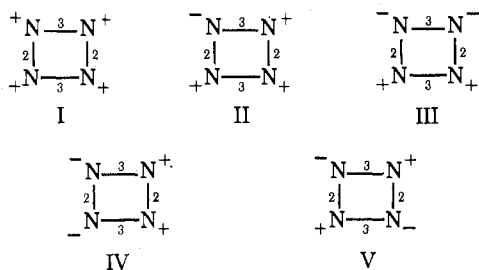
In these diagrams the plus refers to a hydrogen that points above the plane and a minus to one that points below. The number of carbon atoms in the linking chains are also represented.

It is possible, in concept, to turn each of these *trans*

forms into one or two *cis* analogs by a simple displacement of a nitrogen along an edge of the octahedron, although certain of these forms are sterically impossible and others are somewhat strained. By using Dreiding Stereomodels the amount of strain was assessed qualitatively and the results are collected in Table II, where it can be seen that all five *trans* forms are possible, although it is difficult to place the four nitrogens of V at the corners of a square. The *cis* isomers are much more sensitive to the configuration of the ligand and only derivatives of II and V can readily leave two *cis* positions vacant. Some idealized structures are shown in Figure 5.

TABLE II

QUALITATIVE ESTIMATION OF FEASIBILITY OF THE VARIOUS ISOMERS OF THE OCTAHEDRAL COMPLEXES OF 1,4,8,11-TETRAAZACYCLOTETRADECANE^a

Configuration of ligand	I	II	III	IV	V
trans	XX	XX	XX	XX	—
cis	X^b	XX^c	— —	—	XX

^{a} XX = strain-free with no repulsion between atoms; X = strain-free with possible interatomic repulsion; — = strained with distorted bond angles; — — = not possible. The most satisfactory arrangements are boxed. ^{b} There are two forms depending upon whether the four N–H bonds point (a) toward the monodentate ligands, or (b) away from them. Only the first form is sterically possible. ^{c} Two forms must be considered but only the one with three of the four N–H bonds pointing toward the monodentate ligands is possible.

At this stage it is not possible to decide directly the configuration of the ligand in the *trans* complexes described above. Only in the case of configuration I would a chemical test provide experimental proof since, in the *trans* dichloro complex, the two chlorines would be nonequivalent because the ligand, taking the form of a basket, points all four amine hydrogens toward one of the chlorines. Chloride exchange studies, which will be reported elsewhere, give no evidence for nonequivalence. The nickel(II) complexes of this ligand provide some indication of the configuration of the cobalt(III) complexes. The structure of [Ni(cyclam)Cl$_2$] has been determined,[7] and the ligand shown to have configuration III with the four nitrogens at the corners of a square. The chloride, bromide, iodide, and perchlorate are not isomorphous, but the ease with which they can be converted one into the other suggests that they all have the same configuration of the ligand and that the structural and infrared spectra differences are due to the different spatial relationships between the same square-planar complex unit and the anions, whether coordinated or not. The infrared spectra, which are discussed in the next paper,[8] show some interesting relationships. Those of *trans*-[Co(cyclam)Cl$_2$]Cl and [Ni(cyclam)I$_2$] are very similar

(7) B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.* (London), 97 (1965).

(8) B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **4**, 1109 (1965).

(a) *trans* (I)

(b) *trans* (II)

(c) *trans* (III)
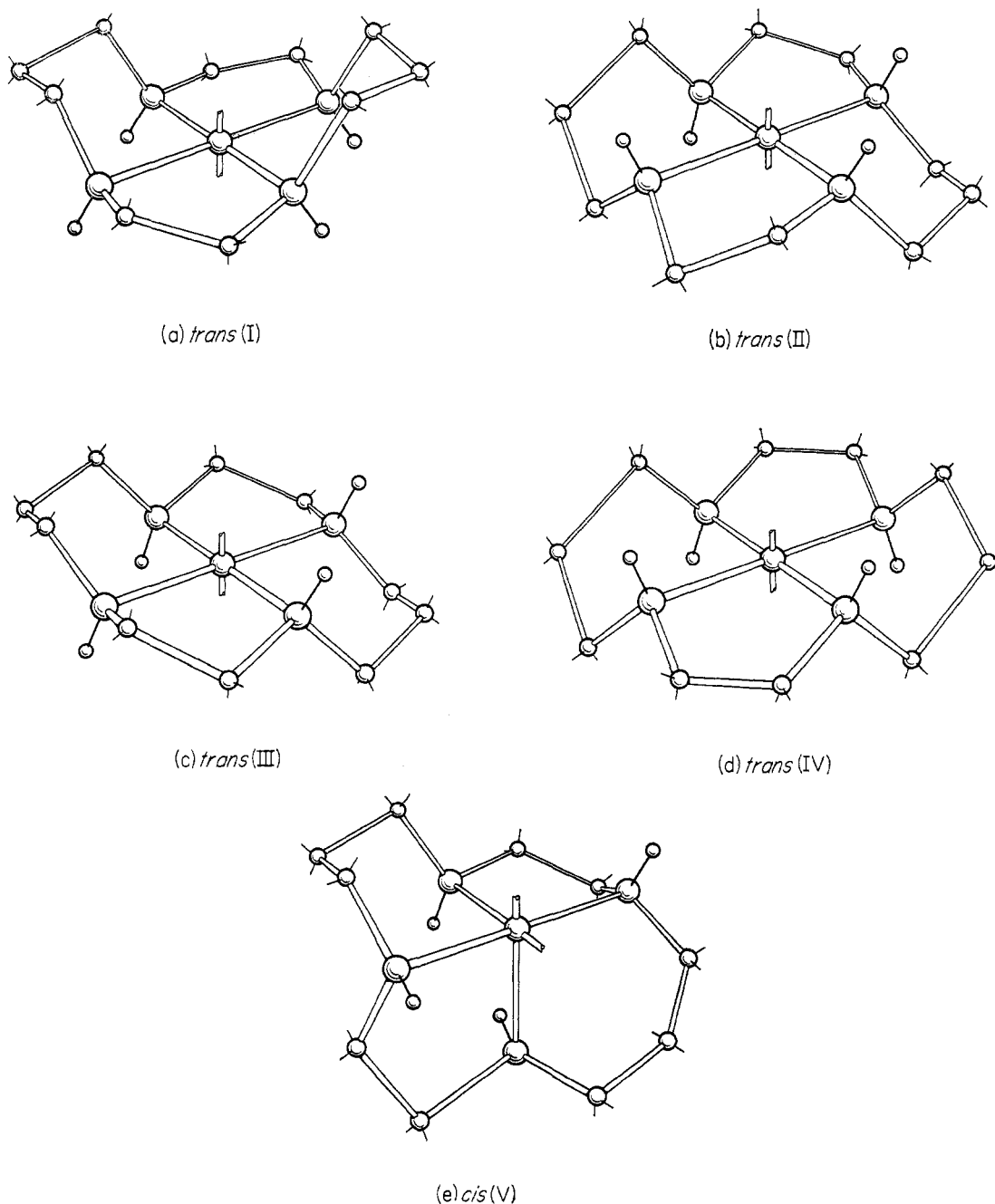
(d) *trans* (IV)

(e) *cis* (V)

Figure 5.—Idealized structures of the strain-free octahedral complexes of 1,4,8,11-tetraazacyclotetradecane.

and suggest an almost identical relationship between the complex unit and its environment, even though there is an extra ion in the cobalt(III) complex and the magnetic properties of the nickel(II) complex indicate considerable tetragonal distortion.

The general observation of complete retention of configuration accompanying the substitution reactions of these complexes can be explained in the light of the configuration of the ligand. Only in the case of form II are the *cis* and *trans* isomers of comparable stability and only here can one expect a *cis* ↔ *trans* change to result from a single-edge displacement. In all other cases one geometric isomer is considerably more strain-free than the other, so that isomerization must require that the edge displacement is accompanied by,

or consequent to, an inversion of configuration of one or more of the nitrogen atoms. This can be achieved by deprotonation of the amine followed by protonation with inversion, a process that becomes more rapid as the pH of the solution increases. Conversion of *trans-*III to *cis*-V (or *vice versa*) requires the inversion of two nitrogens and the formation of the less stable form II as an intermediate.

The configuration of the free ligand deserves some comment, for, although the nitrogens should be able to invert their configuration readily, the relatively high melting point and the ease with which crystals are formed suggests that only one configuration is present. It has been suggested that there is extensive intramolecular hydrogen bonding between the nitro-

gens,[5] but the form suggested, which is indicated diagramatically as VI, is sterically impossible since adjacent nitrogens are not easily able to hydrogen bond either because they are too close or because they are wrongly oriented. Curtis[2] has made some alternative suggestions for his cyclic amine hydrates, but it seems
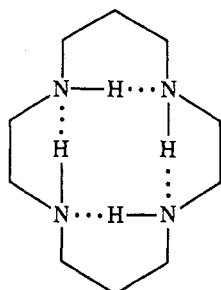
VI

that it is possible to write a structure for the anhydrous amine involving diagonal hydrogen bonding across the ring, leaving two lone pairs pointing out of the compact molecule, Figure 6. This would be consistent
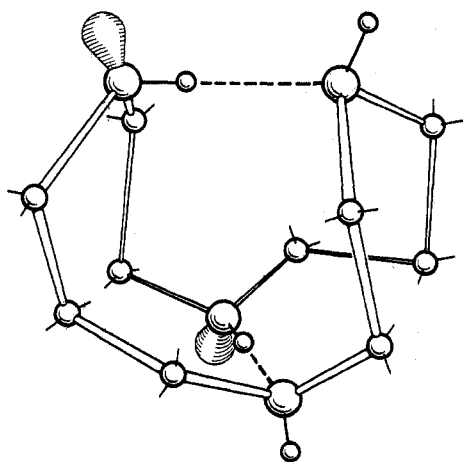

Figure 6.—Possible structure of 1,4,8,11-tetraazacyclotetradecane showing the two intramolecular hydrogen bonds and the two available lone pairs.

with the observations that the four-stage protonation of the nitrogens falls into two pairs of steps, one weakly basic, the other strongly basic,[2,9] rather than a fairly equally separated sequence that is observed for the open-chain tetramine. It is interesting to note that if the hydrogen-bonded structure shown in Figure 6 is opened up to place the four nitrogens at the corners of the square, the ligand will have the form designated as III. This may explain why the *trans* complexes that have been isolated do not contain more than one isomeric form of the ligand.

Experimental

1,3-Bis(2'-aminoethylamino)propane was prepared by allowing 1,3-dibromopropane to react with 1,2-diaminoethane in ethanol in the presence of potassium hydroxide according to the method of Van Alphen.[10] The impure fraction boiling at 125–

(9) K. H. Mayer, Dissertation, München, 1960, pp. 25, 26.

(10) J. Van Alphen, *Rec. trav. chim.*, **55**, 835 (1936).

140° (4 mm.) was used in the next step without further purification.

1,4,8,11-Tetraazacyclotetradecane was prepared by a modification of the method of Van Alphen.[4] 1,3-Bis(2'-aminoethylamino)propane (40 g.) and 1,3-dibromopropane (50 g.) were dissolved in ethanol (4 l.) and heated under reflux for 3 hr., during which time the mixture became pale brown; 3 l. of the solvent was distilled off and potassium hydroxide (35 g.) dissolved in hot ethanol (500 ml.) was added. The solution was refluxed for a further 1.5 hr. and the solid potassium bromide filtered off. The remaining ethanol was distilled off under reduced pressure and the viscous residue poured from the residual potassium hydroxide. Another portion of the open-chain tetramine (100 g.) was added and the mixture fractionally distilled under vacuum. The cyclic tetramine passed over at 132–140° (4–8 mm.) as a solid crystalline material in the open-chain tetramine distillate and could be filtered off from this at the end of the distillation. The crude solid was recrystallized from dioxane and obtained as white needle crystals (2.5 g.), m.p. 173° (sealed tube), sublimes at 125°.

Anal. Calcd. for $C_{10}H_{24}N_4$: C, 59.95; H, 12.08; N, 27.97. Found: C, 59.86; H, 12.33; N, 27.81.

trans-**Dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Chloride.**—Cobalt(II) chloride hexahydrate (2.4 g.) dissolved in methanol (30 ml.) was added to a solution of the cyclic amine (2.0 g.) in methanol (20 ml.) and air was bubbled through the brown solution for 1 hr. Concentrated hydrochloric acid (3 ml.) was added and the color changed to deep green. Air was bubbled through the solution for a further hour and then the solution was filtered and evaporated to dryness. The green residue was recrystallized from the minimum amount of water at 80°, and the green needle crystals were filtered off and washed with acetone and ether (2.8 g.).

Anal. Calcd. for $[Co(C_{10}H_{24}N_4)Cl_2]Cl$: N, 15.3; total Cl, 29.15; ionic chloride, 9.7. Found: N, 15.5; total Cl, 28.5; ionic chloride, 9.65.

The **nitrate** was prepared by adding excess ammonium nitrate to a saturated solution of the chloride and was recrystallized from the minimum amount of hot water.

Anal. Calcd. for $[Co(C_{10}H_{24}N_4)Cl_2]NO_3$: C, 30.6; H, 6.1; N, 17.9; Cl, 18.1; Co, 15.0. Found: C, 30.5; H, 6.0; N, 17.8; Cl, 18.1; Co, 14.9.

The insoluble **perchlorate** was prepared in an analogous way using sodium perchlorate.

Anal. Calcd. for $[Co(C_{10}H_{24}N_4)Cl_2]ClO_4$: C, 27.9; H, 5.6; N, 13.0; Cl, 24.8. Found: C, 26.5; H, 5.6; N, 13.0; Cl, 24.7.

trans-**Dibromo(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate.**—*trans*-[Co(cyclam)Cl₂]ClO₄ (1.0 g.) was dissolved in water (50 ml.) containing lithium carbonate (5 g.), and the resulting red solution was filtered and treated with concentrated hydrobromic acid (10 ml.) and then perchloric acid (5 ml.). The solution was warmed for a few minutes whereupon light apple-green crystals started to form. The mixture was allowed to cool to room temperature and the crystalline complex filtered off, washed with water and acetone, and dried (1 g.). The compound explodes on heating and it was not possible to obtain a reliable analysis for carbon.

Anal. Calcd. for $[Co(C_{10}H_{24}N_4)Br_2]ClO_4$: C, 23.1; H, 4.6; N, 10.8; Cl, 6.9; Br, 30.9. Found: C, 21.7; H, 4.6; N, 10.7; Cl, 7.0; Br, 30.5.

An identical material was obtained from cobalt bromide and the ligand using the method described above for the dichloro complex and finally adding lithium perchlorate.

trans-**Diisothiocyanato(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Thiocyanate. Method 1.**—Cobalt(II) chloride hexahydrate (0.30 g.) was mixed with sodium thiocyanate (0.30 g.) dissolved in water (20 ml.) and added to a solution of the ligand (0.25 g.) in methanol (50 ml.). Air was bubbled through the solution for 12 hr. after which time the red solution was filtered and evaporated to a volume of 10 ml. in the presence of more sodium thiocyanate (5 g.). On cooling bright orange crystals

separated and were filtered off, washed with a little ice-cold water, and dried in a stream of air (0.2 g.).

Method 2.—*trans*-[Co(cyclam)Cl₂]NO₃ (0.3 g.) was dissolved in warm water (20 ml.) and treated with a solution of sodium thiocyanate (5 g.) in water (10 ml.). The insoluble thiocyanate of the dichloro complexes was precipitated and the suspension was heated on a steam bath for 0.5 hr., whereby a clear bright red solution was formed. This was evaporated to 10 ml. and the crystals obtained on cooling were treated as in method 1.

Anal. Calcd. for [Co(C₁₀H₂₄N₄)(SCN)₂]SCN: C, 36.0; H, 5.5; N, 22.6. Found: C, 35.7; H, 5.9; N, 22.6.

trans-**Dinitro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate. Method 1.**—*trans*[Co(cyclam)Cl₂]NO₃ (0.5 g.) dissolved in water (100 ml.) together with sodium nitrite (2 g.) was heated on a steam bath for 1 hr. Excess sodium perchlorate was added to the golden yellow solution and crystals of the dinitro perchlorate started to separate. These were filtered from the cooled solution and washed with ethanol and dried (0.4 g.).

Method 2.—Sodium hexanitrocobaltate(III) (0.4 g.) dissolved in water (50 ml.) was added to a solution of the ligand (0.2 g.) in water (20 ml.) and the mixture warmed on a steam bath for 0.5 hr. During this time the color of the solution lightened. Addition of sodium perchlorate caused the yellow perchlorate to separate.

Anal. Calcd. for [Co(C₁₀H₂₄N₄)(NO₂)₂]ClO₄: C, 26.6; H, 5.3; N, 18.7; Cl, 7.9. Found: C, 24.2; H, 5.4; N, 18.8; Cl, 7.9.

An identical complex can be prepared by the air oxidation of a solution of cobalt(II) chloride, sodium nitrite, and the ligand and the subsequent addition of sodium perchlorate.

trans-**Diazido(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Perchlorate. Method 1.**—Cobalt(II) chloride hexahydrate (0.30 g.) together with sodium azide (0.40 g.) was dissolved in water (10 ml.) and added to a solution of the ligand (0.25 g.) in water (20 ml.). Air was bubbled through the solution for 5 hr. and the dark violet solution was treated with more sodium azide (1 g.) and evaporated to a volume of 10 ml. Addition of sodium perchlorate to the cooled solution yielded blue-purple crystals that were filtered off and washed with a little ethanol and dried (0.2 g.).

Method 2.—*trans*-[Co(cyclam)Cl₂]Cl (0.5 g.) was dissolved in hot water (20 ml.) and sodium azide (0.8 g.) was added and the mixture stirred. The dark green solution, which turned bluish violet almost immediately, was allowed to boil for 15 min. On cooling bluish violet crystals of the diazido azide separated and were filtered off and washed with alcohol and ether. The yield could be increased by adding more sodium azide to the mother liquor. The azide could be recrystallized from the minimum amount of boiling water; yield 0.35 g. The azide was dissolved in 10 ml. of boiling water and solid sodium perchlorate was added to the hot solution. Brownish purple crystals started to separate almost immediately and precipitation was complete on cooling. The perchlorate (0.3 g.) was filtered off and washed with alcohol and ether. An analytically pure sample was obtained after a recrystallization from boiling water.

Anal. Calcd. for [Co(C₁₀H₂₄N₄)(N₃)₂]ClO₄: C, 27.1; H, 5.5; N, 31.6; Cl, 8.0; Co, 13.3. Found: C, 27.1; H, 5.4; N, 31.5; Cl, 7.9; Co, 13.3.

Diammine(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Chloride.—Finely ground *trans*-[Co(cyclam)Cl₂]Cl (0.5 g.) was suspended in liquid ammonia (50 ml.) and the green complex immediately went red. This suggested the formation of a chlo-

roammine complex as an intermediate, but we were unable to isolate it as the change to the yellow diammine complex was very rapid. The suspension was shaken from time to time and the ammonia allowed to boil off. The resulting yellow solid was dissolved in warm water (10 ml.) and the solution filtered. Addition of concentrated hydrochloric acid (20 ml.) to the boiling solution caused fine needles of the diamminechloride to precipitate. These could be recrystallized from boiling concentrated hydrochloric acid. The crystals were washed with alcohol and dried; yield 0.5 g.

Anal. Calcd. for [Co(C₁₀H₂₄N₄)(NH₃)₂]Cl₃: C, 30.0; H, 7.6; N, 21.0; Cl, 26.6. Found: C, 30.1; H, 7.9; N, 21.2; Cl, 27.0.

trans-**Chloroazido(1,4,8,11-tetraazacyclotetradecane)cobalt-(III) Perchlorate.**—*trans*-[Co(cyclam)Cl₂]Cl (1.0 g.) was dissolved in the minimum quantity of warm methanol, and, when the solution was brought back to room temperature, excess sodium azide was added and the mixture stirred. Pale green crystals of *trans*-[Co(cyclam)Cl₂]N₃ separated and were filtered off as soon as possible and washed with small quantities of cold water to remove any excess sodium azide. The azide of the complex was suspended in methanol (50 ml.) and the mixture was heated gently until all the solid had dissolved and the solution had turned blue. This was then cooled in an ice bath and excess sodium perchlorate was added in order to precipitate a blue solid which proved to be a mixture of the dichloro-, diazido-, and chloroazido perchlorates. The blue solid was suspended in boiling water (75 ml.), and the hot solution was filtered and cooled as soon as possible. Most of the insoluble dichloro perchlorate was thereby removed and the cooled solution deposited the diazido perchlorate and the last traces of the dichloro complex. Further quantities of the diazido complex were precipitated from the mother liquor by adding excess sodium perchlorate until there was no further precipitation. The now blue mother liquor was then treated with a large amount of ethanol and ether to precipitate the blue *trans*-chloroazido perchlorate, which was recrystallized by dissolving it in the minimum amount of cold water and adding excess sodium perchlorate; yield 0.05 g. The poor yield is the consequence of the need to obtain an analytically pure sample. Much higher yields can be obtained with 10–15% contamination by the diazido complex.

Anal. Calcd. for [Co(C₁₀H₂₄N₄)N₃Cl]ClO₄: C, 27.5; H, 5.5; total N, 22.5; N₃⁻, 9.6; total Cl, 16.3; coordinated Cl, 8.1; Co, 13.5. Found: C, 27.5; H, 5.7; total N, 22.4; N₃⁻, 10.1; total Cl, 16.0; coordinated Cl, 8.1; Co, 13.4.

trans-**Chloroisothiocyanato(1,4,8,11-tetraazacyclotetradecane)-cobalt(III) Perchlorate.**—*trans*-[Co(cyclam)Cl₂]NO₂ (0.25 g.) was dissolved in water (50 ml.) and the insoluble thiocyanate was precipitated by adding a concentrated aqueous solution of sodium thiocyanate. The pale green solid was filtered off, washed, and suspended in water (20 ml.) and the mixture digested on a steam bath for 15 min., after which time the bright red solution was filtered, cooled, and treated with excess sodium perchlorate. Violet-blue crystals separated and were filtered off and washed with a little ice-cold water; yield 0.2 g.

Anal. Calcd. for [Co(C₁₀H₂₄N₄)NCSCl]ClO₄: C, 29.2; H, 5.35; N, 15.5; Cl, 15.7. Found: C, 29.1; H, 5.5; N, 14.6; Cl, 15.95.