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Cobalt(III) Complexes of the Macrocycle *meso*-2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene[1]

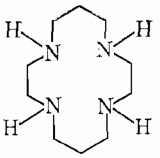
By Eiichiro Ochiai[2] and Daryle H. Busch[3]

Received October 18, 1968

Cobalt(III) complexes of a tetradentate macrocyclic ligand *meso*-CRH with the general formula $[Co(CRH)XY](ClO_4)_n$ have been prepared and characterized (XY = $(Cl^-)_2$, $(Br^-)_2$, (I^-Cl^-), $(H_2O)_2$, $(OH^-)_2$, $(N_3^-Cl^-)$, $(N_3^-)_2$, $(NCS^-)_2$, $(CN^-)_2$, $(NO_2^-)_2$, CO_3^{2-}, $C_2O_4^{2-}$, acac$^-$, and en). The cyclic ligand contains one pyridine nitrogen and three secondary amine nitrogens as its donor groups. The macrocycle can coordinate with all of its donor groups in one plane or in a folded form. This leads to the formation of geometrical (*cis–trans*) isomers. Both geometrical isomers can exist as configurational isomers because of the asymmetric tetrahedral nitrogens. In the case of the dichloro complexes two *trans*-configurational isomers (α and β) and one *cis* (β) isomer have been isolated, and their structures are tentatively assigned on the basis of theoretical considerations and chemical and physical studies. The conformations of saturated six-membered chelate rings are discussed in general terms.

Introduction

Although nickel(II) derivatives dominated early studies[4] with synthetic macrocyclic ligands, cobalt(III) complexes have recently attracted considerable interest.[5-9] Bosnich, Poon, and Tobe[5] obtained *trans*-diacido compounds of the general formula Co(cyclam)-X_2^+, where cyclam is 1,4,8,11-tetraazacyclotetradecane (I). Curtis and Whimp reported the *trans*-diacido complexes[6] of the formulas Co(*meso*-CTH)X_2^{n+} and Co(*dl*-CTH)X_2^{n+} and *cis* complexes[7] of the formula Co(*dl*-CTH)Y^{n+}, where *meso*-CTH and *dl*-CTH are the diastereoisomers of hexamethyl-1,4,8,11-tetraazacyclotetradecane (II), X is a monodentate ligand, and Y is a bidentate ligand. Sadasivan, Kernohan, and Endicott[8] also prepared some complexes of cobalt(III) with *meso*-CTH, *dl*-CTH, and hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,7-diene (1,7-CT, III). Collman and Schneider[9] reported the *cis*-diacido complexes of cobalt(III) with 1,4,7,10-tetraazacyclodecane (cyclen, IV). In the course of these studies, no one seems to have succeeded in obtaining both the *cis* and *trans* isomers of a single macrocyclic complex Co^{III}(macrocycle)X_2^{n+}, where X is a monodentate ligand. Further full advantage of these structures has not been taken in the study of chelate ring conformations. We report here the preparation and characterization of the complexes with the general formula $[Co(CRH)X_2](ClO_4)_n$, where CRH is *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (V) and X is a monodentate, or half of a bidentate, ligand. Both the *cis* and *trans* isomers (named with respect to locations of the monodentate groups) have been prepared. In addition, isomers arising from different configurations of the coordinated secondary amine nitrogens have been obtained. Recent studies[10-12] have shown the significance of the asymmetry of coordinated secondary amines in the stereochemistry of complexes.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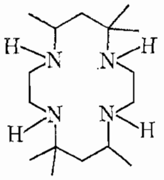
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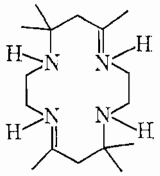
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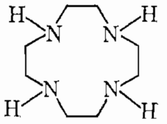
IV

Relatively few chelate systems containing polydentate ligands have been subjected to thorough stereochemical study. The detailed studies[13-16] reported on Co(trien)X_2^{n+}, where trien represents triethylenetetramine, illustrate the interplay between geometrical isomerism, enantiomorphism of the octahedron, optical activity of the donor atoms, and ring conformations. The present system provides a convenient vehicle for the further development of those stereochemical principles that determine the structures of chelate compounds.

The synthesis of a tetradentate macrocyclic complex of 2,12-dimethyl-3,7,11,17-tetraazabicylo[11.3.1]heptadeca-1(17),2,11,13,15-pentaenenickel(II), $Ni(CR)^{2+}$ (VII), results from the condensation of 2,6-diacetyl-

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[1] Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967.

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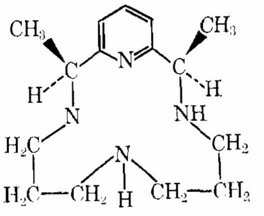
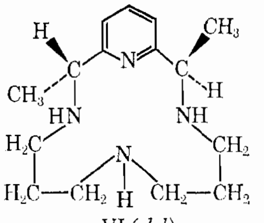
[16] A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 2172 (1967).

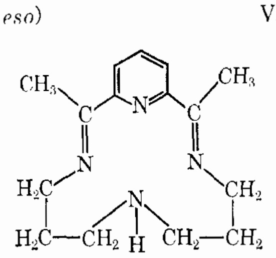
pyridine with bis(3-aminopropyl)imine in the presence of nickel ion.[17-19] Ni(CR)$^{2+}$ can be hydrogenated over PtO$_2$ catalyst,[17,19] producing Ni(CRH)$^{2+}$. This compound exists in two isomeric forms, depending on the configurations of the asymmetric carbon atoms in the ligand. These are *meso* (V) and racemic (VI), with the *meso* form predominating in the product of the above reaction.[18] The ligands CRH·H$_2$O can be liberated[19] from the complexes by adding an excess of sodium cyanide to an aqueous solution of Ni(CRH)$^{2+}$. This paper deals with synthesis and stereochemistry of the cobalt(III) complexes derived from the predominant *meso* isomer of CRH.



V (*meso*)



VI (*d,l*)



VII

Experimental Section

***meso*-2,12-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (CRH).**—The free ligand was prepared by the procedure of Karn.[19]

α-*trans*-[Co(CRH)Cl$_2$]ClO$_4$ and α-*trans*-[Co(CRH)Br$_2$]ClO$_4$.—An aqueous solution of cobalt(II) chloride hexahydrate, CoCl$_2$·6H$_2$O (3.0 g, 0.0126 mol), and CRH·H$_2$O (2.6 g, 0.01 mol) was heated for 10 min on the steam bath. Hydrochloric acid was added until the brown solution turned green and air was bubbled through the solution for 1 hr. Upon addition of a saturated aqueous solution of sodium perchlorate, green crystals formed (4.0 g, 80% yield). This crystalline product was a mixture of two forms, α(1) and α(2), with the α(1) form predominating. The pure α(2) form was obtained upon heating in hydrochloric acid or in methanol for a few hours. The pure α(1) form is obtained upon recrystallizing it from basic solution (methanol with 2,6-lutidine) followed by acidification with hydrochloric acid. α-*trans*-[Co(CRH)Br$_2$]ClO$_4$ was prepared by the same method by use of CoBr·6H$_2$O. This compound has only one form which is α(1), judged from the similarity of its ir spectrum to that of α(1)-*trans*-[Co(CRH)Cl$_2$]ClO$_4$.

α-*trans*-[Co(CRH)N$_3$Cl]ClO$_4$.—This compound was prepared by the reaction of cobalt(II) chloride, sodium azide (slightly in excess of a 2:1 molar ratio), CRH·H$_2$O, air, and sodium perchlorate in a slightly acidic medium (HClO$_4$). Upon reducing the volume of the reaction mixture *via* rotary evaporation and cooling, dark maroon crystals formed. The crystals were collected on a filter, washed with cold water, and recrystallized twice from hot methanol. The final product was obtained as dark maroon, cubic crystals. In the absence of perchloric acid, this reaction yielded α-*trans*-[Co(CRH)(N$_3$)$_2$]ClO$_4$. Attempts to prepare this compound (chloroazido) by adding 1 mol of sodium azide to the *trans*-dichloro complex in hot methanol were unsuccessful. A mixture of the diazido (predominating) and chloroazide complexes precipitated from the solution and it was difficult to separate them. This complex has been successfully prepared *via* a heterogeneous reaction by grinding a 1:1 mixture of the dichloro complex and sodium azide with a small amount of water. The infrared spectrum of the material thus prepared (KBr tablet and hexachlorobutadiene mull) was identical with that of the material obtained above.

α-*trans*-[Co(CRH)ICl]ClO$_4$, α-*trans*-[Co(CRH)(CN)$_2$]ClO$_4$, α-*trans*-[Co(CRH)(NO$_2$)$_2$]ClO$_4$, α-*trans*-[Co(CRH)(NCS)$_2$]ClO$_4$, and α-*trans*-[Co(CRH)(N$_3$)$_2$]ClO$_4$·0.5H$_2$O.—These complexes were prepared by essentially the same method. A slight excess over the required 2:1 molar ratio of the appropriate sodium salt was added to a hot methanolic solution of α(1)-*trans*-dichloro complex. The reaction solution rapidly turned from green to a characteristic color in each case and a precipitate or crystals formed upon cooling or slow evaporation. With the exception of the dicyano complex, all were recrystallized from hot methanol. α-*trans*-[Co(CRH)ICl]ClO$_4$ formed dark brown crystals; α-*trans*-[Co(CRH)(NCS)$_2$]ClO$_4$, red plates; α-*trans*-[Co(CRH)(NO$_2$)$_2$]ClO$_4$, fine orange crystals; and α-*trans*-[Co(CRH)(N$_3$)$_2$]ClO$_4$·0.5H$_2$O, dark red needles. α-*trans*-[Co(CRH)(CN)$_2$]ClO$_4$ was recrystallized from hot water as brown platelike crystals. α-*trans*-[Co(CRH)(N$_3$)$_2$]ClO$_4$·0.5H$_2$O has also been prepared directly from cobalt(II) chloride, sodium azide, and the free ligand CRH·H$_2$O followed by heating in methanol for a few hours. α-*trans*-[Co(CRH)(NO$_2$)$_2$]ClO$_4$ and α-*trans*-[Co(CRH)(N$_3$)$_2$]ClO$_4$·0.5H$_2$O prepared above were converted to α(2)-*trans*-[Co(CRH)Cl$_2$]ClO$_4$ upon treating them with concentrated hydrochloric acid at room temperature.

α-*cis*-[Co(CRH)CO$_3$]ClO$_4$·0.5H$_2$O.—A concentrated aqueous solution of *meso*-CRH·2HClO$_4$ (2.4 g) was added to a slurry of sodium tris(carbonato)cobaltate(III), Na$_3$[Co(CO$_3$)$_3$]·3H$_2$O (1.8 g). The solution was stirred and heated gently until effervescence ceased and the resulting solution turned bright red. The residue was removed by filtration and the filtrate was concentrated with a rotary evaporator. When the concentrate was allowed to evaporate slowly, red crystals formed. These were washed with a small amount of cold water and dried *in vacuo* (*ca.* 60% yield).

β-*cis*-[Co(CRH)(H$_2$O)$_2$](ClO$_4$)$_3$·2.5H$_2$O.—The *cis*-carbonato complex [Co(CRH)CO$_3$]ClO$_4$·0.5H$_2$O was dissolved in a small amount of water and filtered. Concentrated perchloric acid was added to the filtrate and the solution was concentrated by blowing air across it. Red crystals formed and were collected on a filter funnel, washed with a small amount of cold water, and dried *in vacuo* (*ca.* 60% yield).

β-*cis*-[Co(CRH)en](ClO$_4$)$_3$.—This compound was readily prepared by the addition of a weighed amount of ethylenediamine to a methanolic solution of the *cis*-diaquo complex. The reaction and precipitation of the product were immediate. It was obtained as orange crystals (yield 90%).

β-*cis*-[Co(CRH)(acac)](ClO$_4$)$_2$·0.5H$_2$O.—An aqueous solution of the *cis*-carbonato complex and 2,4-pentanedione was acidified with perchloric acid. The solution was allowed to evaporate slowly. In a few days red-orange crystals formed. These were collected on a filter funnel, washed with cold methanol, and air dried.

β-*trans*-[Co(CRH)(NCS)$_2$]ClO$_4$ and β-*trans*-[Co(CRH)(N$_3$)$_2$]ClO$_4$.—These compounds were prepared by the reaction of the β-*cis*-diaquo complex with the appropriate sodium salt in water. The crystals (red in the case of the thiocyanato complex and purple-red in the case of the azide complex) separated from the solution after a brief time (within 1–2 min). They were collected on a filter funnel, washed with a small amount of cold water, and air dried. The yields of both compounds were roughly 40%. No attempts were made to isolate the β-*cis* isomer or any other compounds which would remain in the mother liquor.

β-*trans*-[Co(CRH)Cl$_2$]ClO$_4$, β-*trans*-[Co(CRH)Cl$_2$]ClO$_4$·H$_2$O,

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[17] J. L. Karn and D. H. Busch, *Nature*, **211**, 160 (1966).

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[19] J. L. Karn and D. H. Busch, to be submitted for publication; J. L. Karn, Thesis, The Ohio State University, 1966.

and β-*cis*-[Co(CRH)Cl_2]ClO_4.—The addition of lithium chloride to an acidic methanolic solution of the *cis*-diaquo complex at room temperature gave rise to a green precipitate (*ca.* 60% yield), which was β-*trans*-[Co(CRH)Cl_2]ClO_4. The violet filtrate, from which the green β-*trans*-dichloro complex was separated, yielded violet crystals upon scratching the wall of the vessel (10% yield). This product was β-*cis*-[Co(CRH)Cl_2]ClO_4. Treatment of the *cis*-carbonato complex with hydrochloric acid at room temperature or the addition of sodium chloride to an aqueous solution of the *cis*-diaquo complex yielded a mixture of β-*trans*-[Co(CRH)Cl_2]ClO_4 and β-*trans*-[Co(CRH)Cl_2]$ClO_4 \cdot H_2O$. The latter compound was better obtained after reaction between sodium chloride and the *cis*-diaquo complex in a neutral aqueous solution by slow crystallization at low temperature (~5°). All of the crystalline products were washed with cold methanol and air dried.

β-*trans*-[Co(CRH)Br_2]ClO_4, β-*trans*-[Co(CRH)Br_2]$ClO_4 \cdot H_2O$, and β-*cis*-[Co(CRH)Br_2]ClO_4.—These were prepared by methods similar to those applicable to the dichloro complexes. The major product of the reaction of β-*cis*-Co(CRH)$(H_2O)_2^{3+}$ with sodium bromide in aqueous solution at room temperature is β-*cis*-[Co(CRH)Br_2]ClO_4 (40% yield). This product was obtained as relatively insoluble greenish brown crystals. The addition of sodium perchlorate to the filtrate and the slow evaporation of the resulting solution gave rise to green platelike crystals. These were β-*trans*-[Co(CRH)Br_2]$ClO_4 \cdot H_2O$ (*ca.* 15% yield). β-*trans*-[Co(CRH)Br_2]ClO_4 was prepared by the addition of sodium bromide to the methanol solution of the β-*cis*-diaquo complex (yield 70%). All crystals were washed with cold methanol and air dried.

β-*trans*-[Co(CRH)$(CN)_2$]ClO_4 and β-*trans*-[Co(CRH)$(CN)_2$]$ClO_4 \cdot H_2O$.—The addition of sodium cyanide to an aqueous solution of β-*cis*-Co(CRH)$(H_2O)_2^{3+}$ immediately produced yellow crystals which had the composition β-*trans*-[Co(CRH)$(CN)_2$]$ClO_4 \cdot H_2O$. If the yellow crystals were suspended in a small amount of water, they dissolved and formed brown crystals in a few days at room temperature (95% yield). The latter contained β-*trans*-[Co(CRH)$(CN)_2$]ClO_4. Both crystalline products were washed with small amounts of cold methanol and air dried.

β-*trans*-[Co(CRH)$(NO_2)_2$]ClO_4 and β-*cis*-[Co(CRH)$(NO_2)_2$]ClO_4.—The addition of sodium nitrite to an aqueous solution of β-*cis*-Co(CRH)$(H_2O)_2^{3+}$ produced yellow-light brown crystals (50% yield) after a few minutes at room temperature (β-*trans*-[Co(CRH)$(NO_2)_2$]ClO_4). The filtrate from which the β-*trans*-dinitro complex had been filtered yielded chocolate brown needlelike crystals upon scratching the walls of the vessel (*ca.* 10% yield). This product is the *cis* isomer β-*cis*-[Co(CRH)$(NO_2)_2$]ClO_4.

β-*cis*-[Co(CRH)(C_2O_4)]$ClO_4 \cdot 2H_2O$.—A slight excess of sodium oxalate in hot water was added to a boiling methanolic solution (0.5 g in 125 ml) of α(2)-*trans*-[Co(CRH)Cl_2]ClO_4 (H_2O:CH_3OH = 1:9). The solution changed from green to bright red within 10 min. The solution was cooled and the unreacted sodium oxalate was filtered off. Upon concentrating the red solution in a stream of air, a brown precipitate formed. Repeated concentrating and filtering of the brown precipitate continued to yield the brown solid from the clear, bright red solution through several cycles. To get red crystals of β-*cis*-[Co(CRH)(C_2O_4)]$ClO_4 \cdot 2H_2O$ from this solution, it was necessary to add a small crystalline sample of the material as seed. The addition of the seed was immediately followed by precipitation of red crystals.

The same reaction, when conducted in methanol–water solvent containing glacial acetic acid (CH_3OH:H_2O:HOAc = 90:5:5), gave rise to β-*cis*-[Co(CRH)(C_2O_4)]$ClO_4 \cdot 2H_2O$ in a different crystal form. In this reaction no brown precipitate was observed during the processes of concentration and crystallization. The reaction of β-*trans*-[Co(CRH)Cl_2]ClO_4 under the identical condition (CH_3OH:H_2O:HOAc = 90:5:5) produced the same compound, β-*cis*-[Co(CRH)(C_2O_4)]$ClO_4 \cdot 2H_2O$. β-*cis*-[Co(CRH)$(H_2O)_2$]$(ClO_4)_3 \cdot 2.5H_2O$ did not react with sodium oxalate in an acidic medium (with acetic acid), but the reaction did occur in a neutral or slightly basic medium, yielding β-*cis*-[Co(CRH)(C_2O_4)]$ClO_4 \cdot 2H_2O$.

Physical Measurements.—The electronic spectra of these complexes were recorded on a Cary Model 14 spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer, using Nujol and hexachlorobutadiene mulls and KBr tablets. Nmr spectra were obtained with Varian Model A-60 and A-60A spectrometers. Electrical conductivities were determined with an Industrial Instruments conductivity bridge. Elemental analyses were performed by Mr. P. Kovi of this department and by Galbraith Laboratories, Inc.

Results and Discussion

Preparation and Characterization of Compounds—2,6-Dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (CR) and the isomers of 2,6-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1-(17),13,15-triene (CRH) have structures VII, V, and VI, respectively. The investigations of concern here are restricted solely to the *meso* form of CRH.

This ligand can act as a tetradentate chelate in two ways, with all four nitrogen atoms in a single plane, forming *trans*-diacido compounds, and in *cis* forms with the folded CRH occupying four adjacent sites, leaving two *cis* sites for other ligands. The presence of two asymmetric secondary amine nitrogen atoms and a third symmetrically located secondary amine nitrogen atom complicates the stereochemistry and multiplies the possible configurations of the ligand in its complexes. This isomerism is detailed in a later section.

The general scheme for the preparation of the compounds is outlined in Figures 1 and 2. The elemental analyses for these compounds are reported in Table I. There are three main series of complexes—the α- and β-*trans* and the β-*cis*.

The key compound in the α-*trans* series is α-*trans*-[Co(CRH)Cl_2]ClO_4 which is prepared by the air oxidation of cobalt(II) chloride in the presence of the free ligand CRH·H_2O. The α-*trans*-dibromo, α-*trans*-diazido, and α-*trans*-chloroazido complexes are prepared by corresponding procedures. The other complexes of this series, α-*trans*-[Co(CRH)X_2]ClO_4, where X^- = 0.5(I^-Cl^-), N_3^-, NCS^-, NO_2^-, and CN^-, are prepared metathetically from α-*trans*-[Co(CRH)Cl_2]ClO_4. The α-*trans*-dichloro complex exists in two slightly different forms—α(1) and α(2). In fact, the direct oxidation of cobalt(II) in the presence of the free ligand CRH gives a mixture of α(1) and α(2) forms, the composition of which depends on the reaction conditions. Heating the mixture in an acidic medium (HCl) or in a neutral medium (CH_3OH) for a few hours gives the α(2) form. The reverse reaction α(2) → α(1) can be effected in a basic medium (2,6-dimethylpyridine in methanol) followed by acidification with hydrochloric acid at the end of the reaction. α(1)-*trans*-[Co(CRH)Cl_2]ClO_4 is also readily prepared by the action of sodium chloride on β-*cis*-Co(CRH)$(H_2O)_2^{3+}$ in a basic medium, followed by acidification with hydrochloric acid. The possibility that the α-*trans* complexes [Co(CRH)X_2]-

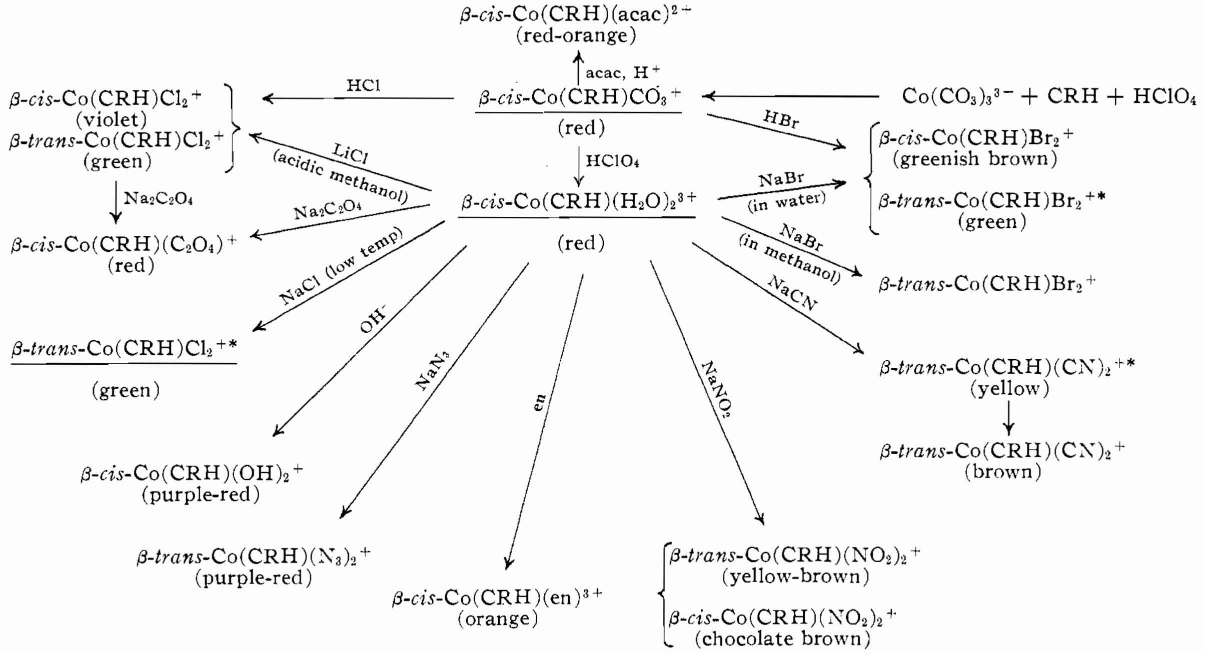

Figure 1.—Methods of preparation of β-*cis*-Co(CRH)XY^{n+} and β-*trans*-Co(CRH)XY^{n+} complexes. The complexes marked with asterisks are β-*trans*-[Co(CRH)X$_2$]ClO$_4$·H$_2$O.

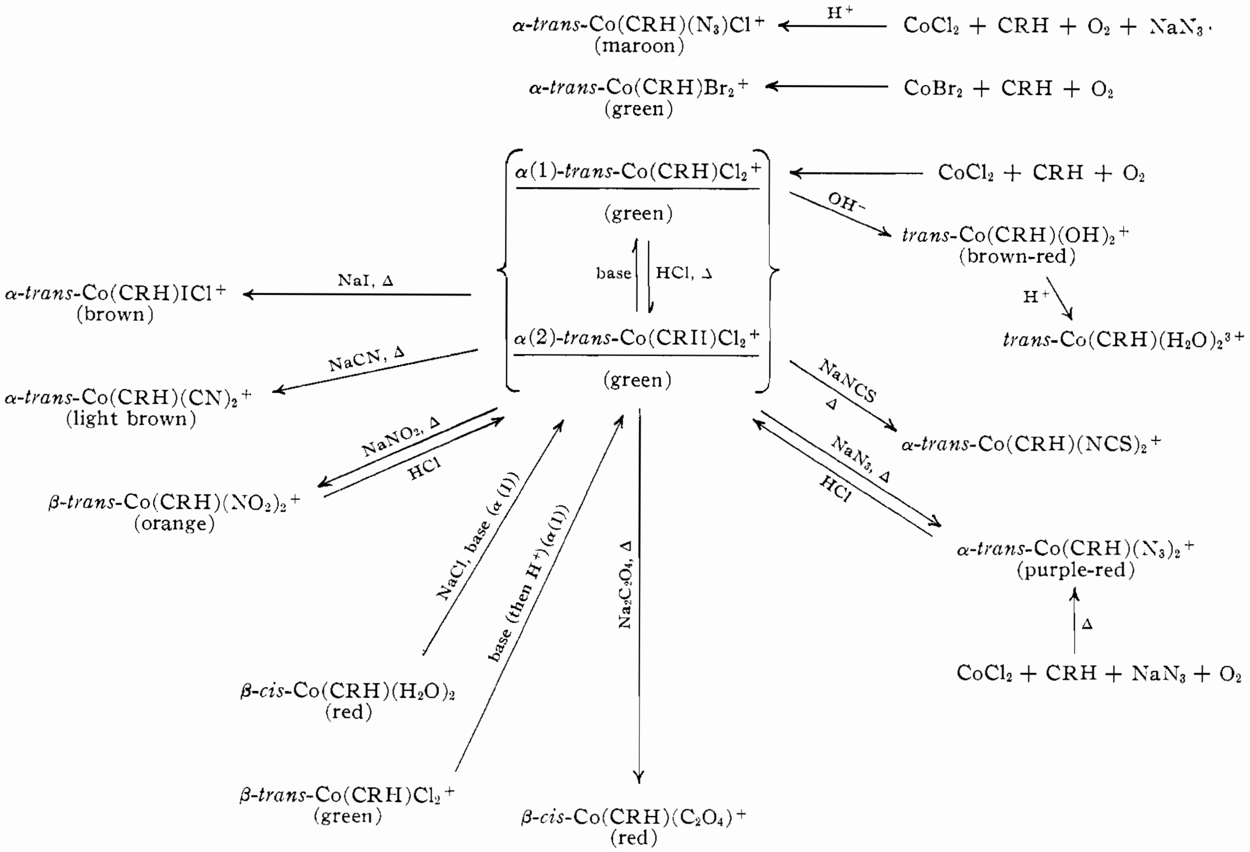

Figure 2.—Methods of preparation of α-*trans*-Co(CRH)XY^{n+} complexes.

ClO$_4$ with X other than chloride ion might exist in two or more forms has not yet been investigated in detail.

The second series of *trans* complexes, β-*trans*, is derived from β-*cis*-Co(CRH)(H$_2$O)$_2^{3+}$. This particular *cis* complex appears to be stable in solution, undergoing no *cis-trans* isomerization. However, when H$_2$O is replaced by another monodentate ligand X a mixture of isomers is produced. These reactions provide routes to β-*trans*-Co(CRH)X$_2^+$ in neutral or acidic media. β-*trans*-[Co(CRH)X$_2$]ClO$_4$ complexes with X = Cl, Br, N$_3$, NCS, NO$_2$, and CN have been prepared by this method. In the case of X = Cl, Br, and CN, crystals

TABLE I
ANALYTICAL DATA FOR THE NEW COMPLEXES $[Co^{III}(CRH)XY](ClO_4)_n$

Compound	Analyses, %: Found C	H	N	Calcd C	H	N
α(1)-*trans*-$[Co(CRH)Cl_2]ClO_4$	36.4	5.2	11.6	36.6	5.3	11.4
α(2)-*trans*-$[Co(CRH)Cl_2]ClO_4$	36.7	5.4	11.6	36.6	5.3	11.4
α-*trans*-$[Co(CRH)Br_2]ClO_4$	30.8	4.6	9.9	31.0	4.5	9.7
α-*trans*-$[Co(CRH)ICl]ClO_4$	31.9	4.7	9.8 (I, 21.6)	30.9	4.5	9.6 (I, 21.8)
α-*trans*-$[Co(CRH)N_3Cl]ClO_4$	36.2	5.3	19.4 (Cl, 14.5)	36.2	5.3	19.7 (Cl, 14.2)
α-*trans*-$[Co(CRH)(N_3)_2]ClO_4 \cdot 0.5H_2O$	35.4	5.4	27.6	35.1	5.3	27.3
α-*trans*-$[Co(CRH)(NCS)_2]ClO_4$	37.7	5.0	15.4	38.0	4.9	15.7
α-*trans*-$[Co(CRH)(NO_2)_2]ClO_4$	35.4	5.1	16.5	35.1	5.1	16.4
α-*trans*-$[Co(CRH)(CN)_2]ClO_4$	43.1	5.6	17.7	43.2	5.5	17.8
β-*trans*-$[Co(CRH)Cl_2]ClO_4$	36.4	5.4	11.6	36.6	5.3	11.4
β-*trans*-$[Co(CRH)Cl_2]ClO_4 \cdot H_2O$	35.6	5.4	11.1	35.4	5.5	11.0
β-*trans*-$[Co(CRH)Br_2]ClO_4$	30.9	4.5	9.5	31.0	4.5	9.7
β-*trans*-$[Co(CRH)Br_2]ClO_4 \cdot H_2O$	30.4	4.6	9.4	30.1	4.7	9.4
β-*trans*-$[Co(CRH)(N_3)_2]ClO_4$	36.0	5.0	27.7	35.7	5.2	27.8
β-*trans*-$[Co(CRH)(NCS)_2]ClO_4$	37.9	5.1	15.4	38.0	4.9	15.7
β-*trans*-$[Co(CRH)(NO_2)_2]ClO_4$	35.0	5.1	16.5	35.1	5.1	16.4
β-*trans*-$[Co(CRH)(CN)_2]ClO_4$	43.3	5.7	17.7	43.2	5.5	17.8
β-*trans*-$[Co(CRH)(CN)_2]ClO_4 \cdot H_2O$	41.5	5.7	17.5	41.6	5.8	17.1
β-*cis*-$[Co(CRH)Cl_2]ClO_4$	36.5	5.3	11.3	36.6	5.3	11.4
β-*cis*-$[Co(CRH)Br_2]ClO_4$	31.1	4.4	9.5	31.0	4.5	9.7
β-*cis*-$[Co(CRH)(NO_2)_2]ClO_4$	34.8	4.8	16.1	35.1	5.1	16.4
β-*cis*-$[Co(CRH)(H_2O)_2](ClO_4)_3 \cdot 2.5H_2O$	25.5	5.0	7.8	25.7	5.0	8.0
β-*cis*-$[Co(CRH)(CO_3)]ClO_4 \cdot 0.5H_2O$	39.4	5.8	11.3	39.2	5.6	11.4
β-*cis*-$[Co(CRH)(acac)](ClO_4)_2 \cdot 0.5H_2O$	38.2	6.0	8.7	38.2	5.5	8.9
β-*cis*-$[Co(CRH)(C_2O_4)]ClO_4 \cdot 2H_2O$	37.4	5.8	10.4	37.5	5.6	10.3
β-*cis*$[Co(CRH)(en)](ClO_4)_3$	30.3	5.0	12.2	30.4	5.0	12.4
$[(Co(CRH))_2C_2O_4](ClO_4)_2 \cdot 7H_2O$	30.6	4.9	8.8	30.6	5.3	8.9

with one molecule of water have also been obtained upon slow crystallization at lower temperature in a neutral aqueous medium (β-*trans*-$[Co(CRH)X_2]ClO_4 \cdot H_2O$).

The pivotal compound for the series of β-*cis* complexes is β-*cis*-$[Co(CRH)(H_2O)_2](ClO_4)_3 \cdot 2.5H_2O$, which is prepared by the action of perchloric acid on β-*cis*-$[Co(CRH)(CO_3)]ClO_4 \cdot 0.5H_2O$. The carbonate complex is, in turn, prepared by the replacement of two carbonate groups of sodium tris(carbonato)cobaltate(III) with the free ligand CRH. The action of bidentate ligands such as ethylenediamine, 2,4-pentanedione, and sodium oxalate on either the diaquo or the carbonato complex leads directly to the corresponding *cis* complexes.

The addition of sodium chloride, bromide, or nitrite to a solution of the β-*cis*-diaquo complex in either water or methanol gives a mixture, as stated above, of β-*trans* and β-*cis* complexes. They can be separated by fractional crystallization because of their different solubilities and readiness of crystallization. In the case of the dichloro complexes, the β-*trans* complex is less soluble and more easily crystallized (from acidic methanol) than the β-*cis* complex. The β-*cis*-dibromo complex is much less soluble and more readily isolable (from water) then the corresponding β-*trans*-$[Co(CRH)Br_2]ClO_4 \cdot H_2O$. The behavior of the dinitro complexes in water is almost the same as that of the dichloro complexes.

The transformation of a *trans* complex into a *cis* complex has only been accomplished by the bidentate ligand, oxalate. The reaction of either α(2)- or β-*trans*-$Co(CRH)Cl_2^+$ with sodium oxalate gives rise to β-*cis*-$[Co(CRH)(C_2O_4)]ClO_4 \cdot 2H_2O$. Attempts have been made in vain to prepare *cis* complexes by the reaction between *trans*-$Co(CRH)Cl_2^+$ and such bidentate ligands as ethylenediamine, sodium carbonate, or 2,4-pentanedione.

Molar conductance data for some of the $[Co(CRH)X_2](ClO_4)_n$ complexes are reported in Table II. As expected, the complexes with monodentate anionic groups are 1:1 electrolytes in methanol.[20] *trans*-

TABLE II
MOLAR CONDUCTIVITIES OF $[Co(CRH)X_2](ClO_4)_n$ COMPLEXES [(0.5–1.5) × 10^{-3} *M*]

Complex	Solvent	Molar conductivity
α-*trans*-$[Co(CRH)Cl_2]ClO_4$	H_2O	345
α-*trans*-$[Co(CRH)Cl_2]ClO_4$	CH_3OH	91.5
β-*trans*-$[Co(CRH)Cl_2]ClO_4$	H_2O	322
α-*trans*-$[Co(CRH)Br_2]ClO_4$	H_2O	430
α-*trans*-$[Co(CRH)Br_2]ClO_4$	CH_3OH	108
α-*trans*-$[Co(CRH)ICl]ClO_4$	H_2O	355
α-*trans*-$[Co(CRH)ICl]ClO_4$	CH_3OH	90.3
α-*trans*-$[Co(CRH)(NCS)_2]ClO_4$	CH_3OH	90.0
α-*trans*-$[Co(CRH)(N_3)_2]ClO_4 \cdot 0.5H_2O$	CH_3OH	101
α-*trans*-$[Co(CRH)(N_3)Cl]ClO_4$	CH_3OH	98.9
α-*trans*-$[Co(CRH)(NO_2)_2]ClO_4$	CH_3OH	94.9
β-*trans*-$[Co(CRH)(NO_2)_2]ClO_4$	CH_3OH	103
β-*trans*-$[Co(CRH)(CN)_2]ClO_4 \cdot H_2O$	CH_3OH	95.3
β-*cis*-$[Co(CRH)(C_2O_4)]ClO_4 \cdot 2H_2O$	H_2O	100
β-*cis*-$[Co(CRH)(acac)](ClO_4)_2 \cdot 0.5H_2O$	H_2O	212
β-*cis*-$[Co(CRH)(en)](ClO_4)_3$	H_2O	318

[20] E. C. Evers and A. G. Knox, *J. Am. Chem. Soc.*, **73**, 1739 (1951); R. E. Jervis, D. R. Muir, J. P. Butler, and A. R. Gordon, *ibid.*, **75**, 2855 (1953).

TABLE III

ELECTRONIC SPECTRA OF *trans*-[Co^{III}(CRH)X_2](ClO_4)]$_n$

X_2	Solvent	$^1E_g{}^a \leftarrow {}^1A_{1g}$		$^1A_{2g} \leftarrow {}^1A_{1g}$		$^1B_{2g} \leftarrow {}^1A_{1g}$ + $^1E_g{}^b \leftarrow {}^1A_{1g}$ or charge transfer	
		ν_{max}, kK	ϵ(molar), M^{-1} cm^{-1}	ν_{max}, kK	ϵ(molar), M^{-1} cm^{-1}	ν_{max}, kK	ϵ(molar), M^{-1} cm^{-1}
α(1)-*trans*-(Cl^-)$_2$	CH_3OH	16.2	44	21.2	181	25.9	148
α(2)-*trans*-(Cl^-)$_2$	CH_3OH	16.1	43	21.2	178	25.4	135
β-*trans*-(Cl^-)$_2$	CH_3OH	16.4	41	21.5	166	25.5	148
β-*trans*-(Cl^-)$_2{}^a$	CH_3OH	16.4	43	21.6	165	25.6	135
α-*trans*-(Br^-)$_2$	CH_3OH	15.2	60	20.8	183	26.5	2,860
β-*trans*-(Br^-)$_2$	CH_3OH	15.7	59	20.8	189	26.8	2,960
α-*trans*-(I^-Cl^-)	CH_3OH	15.1	79	20.6	1100	26.5	2,030
α-*trans*-($N_3{}^-Cl^-$)	CH_3OH	18.1	301	20.9	235	29.5	5,850
α-*trans*-(H_2O)$_2$	H_2O	17.3	29	22.1	245		
α-*trans*-(OH^-)$_2$	H_2O	17.0	29	20.1	152	{25.9	103
						{29.2	183
α-*trans*-($N_3{}^-$)$_2$	H_2O	18.3	736	...		29.3	11,600
β-*trans*-($N_3{}^-$)$_2$	H_2O	18.5	776	...		29.6	9,960
α-*trans*-(NCS^-)$_2$	H_2O	19.3	393	21.0	364	31.3	3,290
β-*trans*-(NCS^-)$_2$	H_2O	19.8	428	...		31.5	4,780
α-*trans*-($NO_2{}^-$)$_2$	CH_3OH	22.0	...	...	314	28.1	3,790
β-*trans*-($NO_2{}^-$)$_2$	CH_3OH	22.1	...	...	291	28.0	3,670
α-*trans*-(CN^-)$_2$	CH_3OH	25.0	84	21.5	151	32.7	315
β-*trans*-(CN^-)$_2$	H_2O	26.2		21.8		32.3	
β-*trans*-(CN^-)$_2{}^b$	H_2O	25.2	82	21.7	158	32.3	275

[a] β-*trans*-[Co(CRH)Cl_2]$ClO_4 \cdot H_2O$. [b] β-*trans*-[Co(CRH)$(CN)_2$]$ClO_4 \cdot H_2O$.

[Co(CRH)X_2]ClO_4, where X_2 = Cl_2, Br_2, and ICl, aquates readily in water and shows the conductance of a 3:1 electrolyte. β-*cis*-[Co(CRH)(C_2O_4)]$ClO_4 \cdot 2H_2O$, β-*cis*-[Co(CRH)(acac)]$(ClO_4)_2 \cdot 0.5H_2O$, and β-*cis*-[Co(CRH)en]$(ClO_4)_3$ are, as expected, 1:1, 2:1, and 3:1 electrolytes, respectively.

Electronic spectra (Tables III and IV) provide a good criterion to distinguish between *trans* (idealized D_{4h} symmetry) and *cis* (idealized C_{2v}) forms in the case of cobalt(III) complexes. The spectra are consistent with expectation and the first band is split into two distinct absorption peaks in the cases of *trans*-Co(CRH)-$X_2{}^+$, where X = Cl, Br, 0.5(ICl), OH, and H_2O, while it is not split in the cases of the corresponding *cis* forms. Spectral assignments and derived parameters are discussed below.

TABLE IV

ELECTRONIC SPECTRA OF *cis*-[Co^{III}(CRH)X_2](ClO_4)$_n$

X_2	Solvent	$^1E_1 \leftarrow {}^1A_1$ + $^1A_2 \leftarrow {}^1A_1$		$^1B_2 \leftarrow {}^1A_1$ + $^1E_1 \leftarrow {}^1A_1$ or charge transfer	
		ν_{max}, kK	ϵ(molar), M^{-1} cm^{-1}	ν_{max}, kK	ϵ(molar), M^{-1} cm^{-1}
(H_2O)$_2$	H_2O	20.2	208	26.6	280
(OH^-)$_2$	H_2O	21.1	121	{25.7	81
				{28.5	115
(Cl^-)$_2$	DMSO	18.2	160	23.9	191
(Br^-)$_2$	DMSO	17.3	144	22.1	641
($NO_2{}^-$)$_2$	DMSO	21.1	330	29.1	4770
$CO_3{}^{2-}$	H_2O	19.3	292	27.0	339
$C_2O_4{}^{2-}$	CH_3OH	19.5	271	26.7	329
acac$^-$	H_2O	19.7	301	26.4	280
en	H_2O	20.7	250	29.0	256

Table V shows the infrared spectral bands assignable to the ligands (or ligand) XY in the complexes [Co(CRH)XY]$(ClO_4)_n$. These data show that the reported formulations of the complexes are correct. The bidentate ligands coordinate in the usual[21] ways. The best criterion indicating the mode of coordination of thiocyanate, M–NCS *vs.* M–SCN, is the position of the C–S stretching mode which appears around 840 cm^{-1} in the case of M–NCS but around 700 cm^{-1} in the case of M–SCN.[22] The data shown in Table V indicate that NCS coordinates through nitrogen in these complexes. NO_2 gives three peaks around 1400 cm^{-1} (vs) ($\nu_{as}(NO_2)$), 1310 cm^{-1} (vs) ($\nu_s(NO_2)$), and 820 cm^{-1} (δ(ONO)) in the case of Co^{III}–NO_2 complexes, but in the case of Co^{III}–ONO complexes, the $\nu_s(NO_2)$ peak characteristically appears around 1060 cm^{-1} instead of 1310 cm^{-1}.[23] The complexes reported in Table V have the intense $\nu_s(NO_2)$ band at 1310 cm^{-1}, indicating that they are nitro complexes. β-*cis*-[Co(CRH)$(NO_2)_2$]ClO_4 has a more complex pattern of NO_2 peaks (Figure 3) than the *trans* isomers do. This is consistent with the lower symmetry of the *cis* form. With regard to the *cis–trans* isomerism, one useful band occurs in the C–H stretching region. For β-*cis*-[Co(CRH)X_2]ClO_4, where X^- is a monodentate ligand, such as Cl^-, Br^-, $NO_2{}^-$ (and H_2O), this unique band occurs at 2817 cm^{-1} (Figure 3). No *trans* complex has this band.

Electronic Spectra.—The electronic spectra measured over the visible range for the complexes [Co(CRH)-XY]$(ClO_4)_n$ are summarized in Tables III and IV. The spectra of some of the complexes are reproduced in Figure 4. The electronic energy level diagrams for cobalt(III) d^6 in strong octahedral and tetragonal

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(21) See, *e.g.*, K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

(22) C. Pecile, *Inorg. Chem.*, **5**, 210 (1966); A. Sabatini and I. Bertini, *ibid.*, **4**, 1665 (1965).

(23) P. B. Penland, F. J. Lane, and J. V. Quagliano, *J. Am. Chem. Soc.*, **78**, 887 (1956); D. M. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **5**, 1303 (1966).

TABLE V

SELECTED INFRARED SPECTRAL BANDS[a] FOR $[Co(CRH)XY](ClO_4)_n$

Complex	XY ligand bands, cm^{-1}	Assignment
α-*trans*-$[Co(CRH)N_3Cl]ClO_4$ (N)	2020 vs 1946 w, sh	$\nu(NN)$
	1285 m	
α-*trans*-$[Co(CRH)(N_3)_2]ClO_4 \cdot 0.5H_2O$ (N)	2033 vs 2004 s	$\nu(NN)$
	1297 m	
	1280 s	
β-*trans*-$[Co(CRH)(N_3)_2]ClO_4$ (N)	2025 vs	$\nu(NN)$
	1286 s	
α-*trans*-$[Co(CRH)(NCS)_2]ClO_4$ (N)	2096 vs, sh 2062 vs	$\nu(NC)$
	844	$\nu(CS)$
β-*trans*-$[Co(CRH)(NCS)_2]ClO_4$ (N)	2092 vs 2032 m, sh	$\nu(NC)$
	837	$\nu(CS)$
α-*trans*-$[Co(CRH)(CN)_2]ClO_4$ (K)	2128 s	$\nu(CN)$
β-*trans*-$[Co(CRH)(CN)_2]ClO_4$ (K)	2141 2123 m	$\nu(CN)$
β-*trans*-$[Co(CRH)(CN)_2]ClO_4 \cdot H_2O$ (K)	2132 s	$\nu(CN)$
α-*trans*-$[Co(CRH)(NO_2)_3]ClO_4$ (K)	1406 vs	$\nu_{as}(NO_2)$
	1314 vs	$\nu_s(NO_2)$
	829 m	$\delta(ONO)$
β-*trans*-$[Co(CRH)(NO_2)_2]ClO_4$ (K)	1412 vs	$\nu_{as}(NO_2)$
	1310 vs	$\nu_s(NO_2)$
	827 m	$\delta(ONO)$
β-*cis*-$[Co(CRH)(NO_2)_2]ClO_4$ (K)	1403 1393 ms	$\nu_{as}(NO_2)$
	1333 1316 ms 1309	$\nu_s(NO_2)$
	829 824 m	$\delta(ONO)$
β-*cis*$[Co(CRH)CO_3]ClO_4 \cdot 0.5H_2O$ (K)	1664 1631 vs	$\nu(C{=}O)$
	1233 m	
	806 m	
	757 m	
β-*cis*$[Co(CRH)en]ClO_4$ (K)	3077 vs	$\nu(NH_2)$
	1567 m	$\delta(NH_2)$
α-*cis*-$[Co(CRH)(acac)](ClO_4)_2 \cdot 0.5H_2O$ (K)	1563 vs	$\nu(C\overset{\cdots}{-}O)$
	1531 vs	$\nu(C\overset{\cdots}{-}O)$
	1431 m	$\nu(C\overset{\cdots}{-}C) + \delta(CH)$
	1354 s	$\delta_s(CH_3)$
	1287 m	$\nu(C\overset{\cdots}{-}C) + \nu(CCH_3)$
β-*cis*-$[Co(CRH)(C_2O_4)]ClO_4 \cdot 2H_2O$ (N)	1689 vs	$\nu_{as}(C{=}O)$
	1672 vs	$\nu_s(C{=}O)$
	1397 s[b]	$\nu_s(C{-}O) + \nu(C{-}C)$
	1259 m	$\nu_s(C{-}O) + \delta(O{-}C{=}O)$
	819 802 m	$\delta(O{-}C{=}O) + \nu(Co{-}O)$
cis-$[(Co(CRH)_2)C_2O_4](ClO_4)_4 \cdot 7H_2O$ (K)	1638 vs	$\nu(C{=}O)$
	1381 m	$\nu_s(C{-}O) + \nu(C{-}C)$
	1260 m	$\nu_s(C{-}O) + \delta(O{-}C{=}O)$
	805 m	$\delta(O{-}C{=}O) + \nu(Co{-}O)$

[a] K, KBr tablet method; N, Nujol mull method. The spectra taken by different methods (KBr, Nujol, or hexachlorobutadiene mull) are almost identical. [b] Measured in aqueous solution.

fields are well known.[24] The first band due to the transition $^1T_1 \leftarrow {}^1A_1$ in an octahedral environment (O_h) splits into two bands, $^1E^a \leftarrow {}^1A_1$ and $^1A_2 \leftarrow {}^1A_1$, in a tetragonal environment (D_{4h}), *i.e.*, *trans*-CoX_4Z_2. The splitting between these two bands is $^{35}/_4Dt$, where Dt is denoted as the tetragonal splitting parameter. A positive value of Dt indicates that $Dq^{xy} > Dq^z$. In the *cis* form (C_{2v}), a corresponding splitting is expected, but the magnitude of the interval is approximately half that expected for the D_{4h} case. In the *cis* isomer (C_{2v}), the interval between the two bands derived from $^1T_1 \leftarrow {}^1A_1$ is usually so small that only a single envelope is observed. If Dt is small, *i.e.*, if the axial field is of about the same strength as the in-plane field, the splitting in the first band would not be observed even in the spectrum of a *trans* isomer. In such a circumstance the assignment is rendered some-

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(24) A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

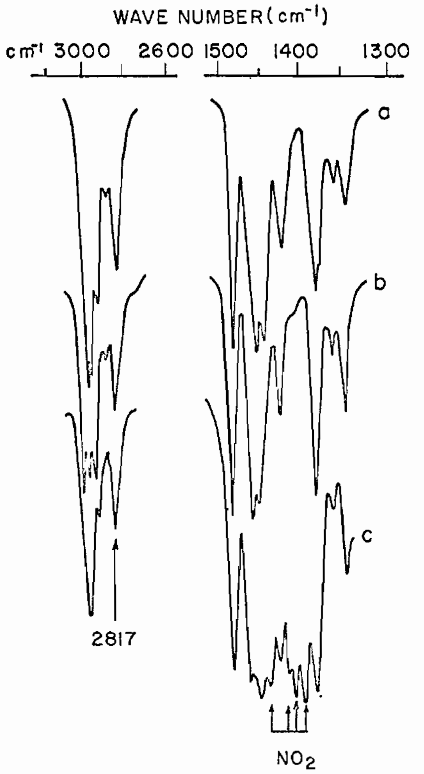

Figure 3.—The unique band at 2817 cm^{-1} observed in the infrared spectra of the complexes β-*cis*-[Co(CRH)X$_2$]ClO$_4$ (X$^-$: a, Cl$^-$; b, Br$^-$; c, NO$_2^-$) and the similarity of the patterns of C–H deformation bands (1470–1300 cm^{-1}) of these complexes.

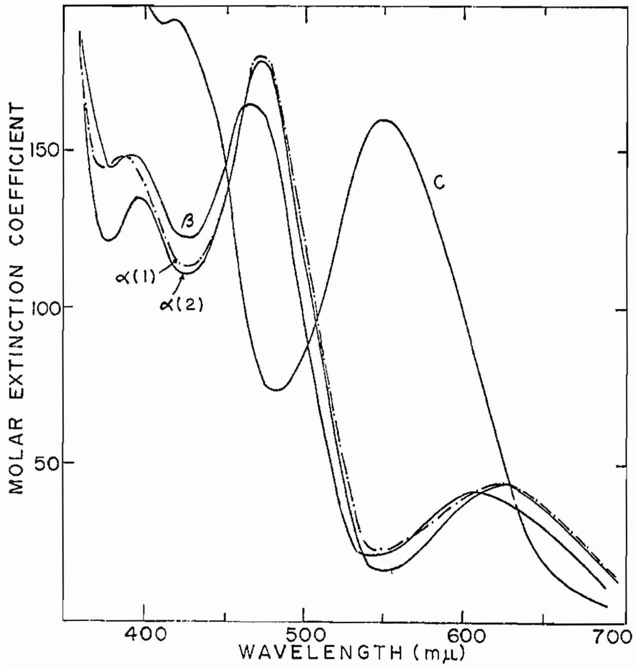

Figure 4.—The electronic spectra of the [Co(CRH)Cl$_2$]ClO$_4$ complexes: α(1) = α(1)-*trans*-[Co(CRH)Cl$_2$]ClO$_4$; α(2) = α(2)-*trans*-[Co(CRH)Cl$_2$]ClO$_4$; β = β-*trans*-[Co(CRH)Cl$_2$]ClO$_4$; c = β-*cis*-[Co(CRH)Cl$_2$]ClO$_4$.

what ambiguous by questions concerning the relative intensities of the two overlapping absorption bands. Well-split first bands are observed in *trans*-[Co(CRH)X$_2$](ClO$_4$)$_n$ complexes where X$_2$ = Cl$_2$, Br$_2$, ICl, N$_3$-Cl, (H$_2$O)$_2$, (OH)$_2$, (NCS)$_2$, and (CN)$_2$, as shown by Tables III and IV and Figure 4. The dinitro complexes exemplify the ambiguous case, and the assignment of their absorption bands requires more information. The diazido complexes usually have a single intense band in the first region and exhibit no evidence of a second band even in the *trans* form.[5] Although it must be considered tentative, the observed band in the diazido complex is assigned to the transition $^1E^a \leftarrow {}^1A_1$.

Following the work of Wentworth and Piper[24] ligand field splitting parameters can be assigned to the macrocycle (Dq^{xy}) and to the axial ligands (Dq^z) in the case of *trans* isomers. The following equations apply: $\nu_A = 10Dq^{xy} - C$, $Dt'(\text{exptl}) = {}^4/_{35}[10Dq^{xy} - \nu_E]$, and $Dq^z = Dq^{xy} - {}^7/_4Dt'$. Table VI summarizes these estimated values, assuming Dq^{xy}(CRH) = 2500 cm^{-1} (estimated from the average value of ν_A) and assuming the Racah parameter C = 3800 cm^{-1}.[24] The value of Dq^{xy}(CRH) is intermediate between those of ammonia (2490 cm^{-1}) and ethylenediamine (2530 cm^{-1}).[24] The Dq^z values thus estimated fall in the usual range found for other tetragonal cobalt(III) complexes,[8,24] except that the Dq^z for NO$_2^-$ appears to be a little lower than usual. Although the Dq^z value of NO$_2^-$ is a little low, it does not necessarily mean that it coordinates as a nitrito ligand though that possibility does merit consideration in view of the known Dq value for that ligand.[25] The infrared spectra discussed above are most consistent with N coordination. In the *trans*-dicyano complexes, Dq^z is so great that the ν_E and ν_A peaks are reversed in position and Dt is inverted in sign. ν_A occurs at 21.5 kK and ν_E at 25.0 kK. This assignment results in reasonable values for Dt' and Dq^z.

TABLE VI

SPECTRAL PARAMETERS FOR THE TETRAGONAL COMPLEXES[a] *trans*-Co^{III}(CRH)X$_2$$^{n+}$

X$_2$	Dt', cm^{-1}	Dq^z, cm^{-1}
α-*trans*-(I$^-$Cl$^-$)	700	1020 (I$^-$)
α-*trans*-(Br$^-$)$_2$	690	1300
α(1)-*trans*-(Cl$^-$)$_2$[b]	570	1500
α(2)-*trans*-(Cl$^-$)$_2$[b]	580	1480
β-*trans*-(Cl$^-$)$_2$[c]	550	1540
(OH$^-$)$_2$	480	1660
(H$_2$O)$_2$	450	1720
α-*trans*-(N$_3^-$Cl$^-$)	350	1880
α-*trans*-(N$_3^-$)$_2$	330	1920
α-*trans*-(NCS$^-$)$_2$	220	2120
α-*trans*-(NO$_2^-$)$_2$	−183	2820
(CN$^-$)$_2$	−440	3260

[a] Dq^{xy}(CRH) = 2500 cm^{-1}. [b] Dq^{xy} values for α(1) and α(2) isomers are assumed to be equal. [c] If Dq^{xy}(β-CRH) is equal to Dq^{xy}(α-CRH), Dt' = 550 cm^{-1} and Dq^z = 1540 cm^{-1} in the β complex. If Dq^z(Cl$^-$) is identical in both α and β isomers, Dq^{xy}·(β-CRH) = 2460 cm^{-1}.

Stereochemistry.—The possible isomers for planar coordination of the CRH ring are depicted in Figure 5, following the scheme of Bosnich, *et al.*[4] Among those six configurations shown in Figure 5, VIII and XII,

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(25) J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers, New York, N. Y., 1960.

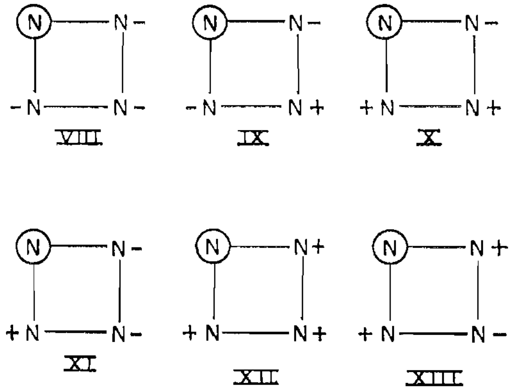

Figure 5.—Possible configurational isomers of planar, coordinated *meso*-CRH; the methyl groups are below the plane. Ⓝ represents the pyridine nitrogen and + and − indicate whether the H of N-H is above (+) or below (−) the plane.

IX and XIII, and X and XI may seem pairwise equivalent, but they are not because the orientations of the two methyl groups distinguish between the regions above and below the plane of chelation. For the present discussion the two methyl groups are presumed to be below the plane. Taking bond angle strain and steric repulsion into consideration,[26] the order of stability of these six isomers most probably is VIII $>$ IX $>$ X $\approx$ XI $>$ XII $>$ XIII. The conclusion that both VIII and IX are more stable than XIII seems secure because the bulk of the chelate ring atoms are crowded onto the same side of the plane as the methyl groups in the latter two cases. This obviously maximizes nonbonded repulsion. The intermediate structures (X and XI) presumably respond to the same relationships and therefore enjoy intermediate stabilities. The choice between structures VIII and IX as the most stable isomer is not clear-cut. It may be concluded on the basis of apparent strain and nonbonded repulsions (Dreiding models) that VIII is probably the more stable.

The six-membered chelate rings in coordinated CRH will adopt conformations approximating the chair and boat forms of cyclohexane and the possibility that the barrier to conformer interconversion may be large substantially expands the number of thinkable isomers. A given structure such as VIII could exist in four forms —two *meso* (chair–chair and boat–boat) and two enantiomeric (chair–boat). These are shown for structure VIII in Figure 6. The existence of these two conformers for a six-membered chelate ring in a planar tetradentate macrocycle requires the two NH's of the ring to have their H atoms on the same side of the plane of coordination. The rings flanked by one NH above and one below the plane can exhibit only a single conformation in these structures. Consequently structure IX should not yield conformational isomers. The chelate ring conformations in such structures might best be called *twist* forms. Each such ring is dissymmetric and structure IX would actually be *meso* with respect to ring conformation, as well as to asymmetric carbons and nitrogens. When these considerations are all assessed, it is apparent that structure VIII should be the more stable because it can exist in a *meso* conformation having two six-membered chelate rings of chair form. Conformational isomers such as racemic VIII and *meso* VIII may be thermally interconvertible, especially in solution; however, the conversion must require some energy of activation although the barrier has not been estimated for chelate rings.

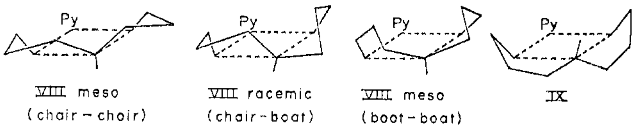

Figure 6.—Conformations of the six-membered chelate rings in some of the planar coordinated forms of CRH.

Of the six isomeric forms shown in Figure 5, four can be folded to yield *cis* isomers as shown in Figure 7.

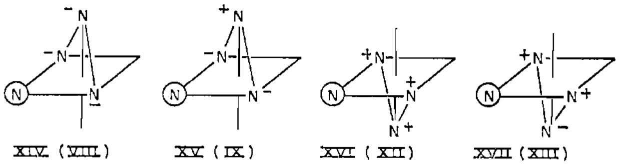

Figure 7.—Configurational isomers of folded, octahedrally coordinated *meso*-CRH. The meanings of the symbols are the same as those in Figure 5. The number of the structure given in parentheses is that of the corresponding planar structure.

It should be noted that only those forms which are *meso* with respect to the asymmetric nitrogens—VIII, IX, XII, and XIII—can fold; *i.e.*, folding of the *dl* isomers X and XI would require inversion of a nitrogen atom. The latter two *cis* forms, XVI and XVII, which would be formed from XII and XIII, respectively, exhibit such large steric hindrance between the two methyl groups and the hydrogens of the six-membered chelate rings that their existence is unlikely. The two remaining forms, XIV and XV, however, are not equally probable, because XIV should exhibit a large steric repulsion between the electron cloud of the pyridine ring and the hydrogen atoms of the three carbon rings. Further, in structure XV, both of the two six-membered rings could take the more stable chair form. Thus, XV is expected to be more stable than XIV (Figure 8).

In a neutral or an acidic solution, two sets of *cis–trans* isomers, VIII $\rightleftarrows$ XIV and IX $\rightleftarrows$ XV, would be interconvertible through a single edge displacement process (stereochemically speaking); these represent the most favorable isomerization processes. Other *cis–trans* isomerizations such as VIII $\rightleftarrows$ XV and X $\rightleftarrows$ XV and isomerizations between different *trans*-configurational isomers, for example, VIII $\rightleftarrows$ IX, require the inversion of the configuration of at least one secondary amine nitrogen. Such reactions may occur readily in an alkaline solution.[10–12] These considerations reveal that there are several conceivable *trans* isomers and two possible *cis* isomers in the case of [Co^{III}(*meso*-CRH)X$_2$]Y complexes.

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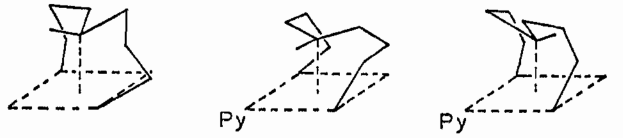
[26] For discussion of these factors, see, *e.g.*, B. Bosnich, R. O. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc., A*, 1331 (1966).



XIV (chair-chair) XIV (boat-twisted) XV

Figure 8.—Conformations of the six-membered chelate rings in some of the folded octahedrally coordinated forms of CRH.

Experimental Findings.—In this study, three different *trans* isomers and a *cis* isomer have been obtained. Of the three *trans* forms, two isomers, α(1) and α(2), are very similar in character, but the remaining β isomer is distinctly different from the α forms. Although there are two conceivable *cis* isomers, only one has been found and this is designated as the *β-cis* form (XV). Discussion will first be directed toward the *β-cis* form and then the *trans* isomers will be considered.

The full intricacy of the system is not revealed by the mention of the few well-characterized isomers as outlined above. Indeed, some of the salts appear to have dimorphic or even polymorphic solid phases. Further, a number of them exhibit different degrees of hydration in accompaniment with the formation of distinct solid forms.

Two useful practices have led to the understanding presented in the pages to follow. First, we have relied heavily on differences in solution properties (nmr, ir, and R_f values) in distinguishing between isomers and in establishing the very existence of the isomerization phenomenon. Such differences can definitely be attributed to differences in molecular structure, whereas substances differing only in solid-state properties may contain isomerically identical complex ions in different crystal forms, states of purity, degrees of hydration, etc. The second practice has involved constant appeal to the principles of structure implied by the stereochemical model presented a few paragraphs earlier.

As indicated above, the series of *cis*-diacido complexes is derived from *cis*-$Co(CRH)CO_3^+$, which is prepared from $Co(CO_3)_3^{3-}$ by a substitution reaction. The only other route to *cis* isomers involves the action of oxalate ion to cause the *trans* → *cis* conversion

$$\alpha(2)\text{- or }\beta\text{-}trans\text{-}[Co(CRH)Cl_2]ClO_4 + C_2O_4^{2-} \longrightarrow \beta\text{-}cis\text{-}Co(CRH)C_2O_4^+$$

The *β-cis* complex formed in this way from either the α(2)-*trans* or the *β-trans* reactant is identical with that prepared from *β-cis*-$[Co(CRH)(H_2O)_2](ClO_4)_3 \cdot 2.5H_2O$ (the latter is derived from *β-cis*-$Co(CRH)CO_3^+$). The fact that the same exclusive product can be obtained by three paths each beginning with a different reactant justifies the view that the *β-cis* complex must exist in the most stable configuration. This conclusion provides ample basis for assigning structure XV to the *β-cis* isomer for, as explained above, this structure should be much more stable than any of the others involving folded forms of CRH.

It is convenient at this point to illustrate the tantalizing character of some of these isomer systems since the reaction of α(2)-*trans*-$[Co(CRH)Cl_2]ClO_4$ with sodium oxalate seemed to produce different isomers, depending on the acidity of the reaction medium. In fact, the product from an acidic medium (acidified with acetic acid) and that from a neutral medium have different solid-state infrared spectra (ν_s(C–O + C–C) occurs at 1397 cm^{-1} for the former and at 1371 cm^{-1} for the latter in the Nujol spectra). The other physical data for the products as measured in solution (nmr, R_f value, and infrared spectra) are, however, exactly the same. Recrystallization of the compound prepared in neutral media from an acidic solution gives the same compound as prepared in acidic media. The reverse is also true. This shows that they are different only in the solid state.

Two different *trans* isomers, designated as α- and *β-trans*-$[Co(CRH)X_2]ClO_4$, have been prepared with X = Cl, Br, NO_2, N_3, NCS, and CN. The *trans* structures of these compounds have been confirmed by their electronic spectra as discussed above. Several kinds of data which distinguish between the α- and *β-trans*-$[Co(CRH)Cl_2]ClO_4$ have been obtained. They are summarized in Table VII. (See also Figures 9 and 10.) Although these data alone do not permit the assignment of isomeric structures, they do show that the two isomers are distinctly different in their molecular structures. The differences in infrared spectra obtained on solid samples provide the most obvious and greatest distinction but such differences may be attributed to extraneous sources. In contrast, the differences in nmr, solution ir, and chromatographic R_f values definitely require the existence of a true isomerism.

The observation that the β isomers isomerize to the α forms (α(1)) in the presence of base indicates that the distinction between the isomers is attributable to different configurations of one or more secondary amine nitrogens.[9–11] The α form, however, does not isomerize to the β form even in basic media. This clearly indicates that the *α-trans* isomer is the more stable.

The ready conversion of *β-cis* compounds to *β-trans* compounds in acidic media provides a key connection between these isomers. Since no N–H inversion should occur under these conditions, this leads to the assignment of the structure IX to the *β-trans* isomer. Proceeding from this assignment it is logical to assign structure VIII to the *α-trans* isomer, since VIII is expected to represent the most stable configuration and the *α-trans* isomer is the most stable product. It should be noted that the inversion of only a single N–H is required in order to convert the *β-trans* (IX) to the *α-trans* (VIII). These assignments are also in accord with the expectation that the most stable *trans* isomer (α, VII) should be obtained from the reaction between Co(II) and free CRH ligand followed by air oxidation.

The fact that the *β-cis* isomer is obtained from the *α-trans* compound upon treatment with oxalate implies that the inversion of the N–H *trans* to the pyridine ring occurs in the reaction of α(2)-*trans*-$[Co(CRH)Cl_2]ClO_4$

TABLE VII

DISTINGUISHING PROPERTIES OF THE CONFIGURATIONAL ISOMERS OF *trans*-$[Co(CRH)Cl_2]ClO_4$

Property	$\alpha(2)$-*trans*-$[Co(CRH)Cl_2]ClO_4$[a]	β-*trans*-$[Co(CRH)Cl_2]ClO_4$[b]
Preparation	$CoCl_2 + CRH + O_2$	β-*cis*-$Co(CRH)(H_2O)_2^{3+} + H^+ + Cl^-$
Interconversion	Does not isomerize to β form $\alpha(2) \rightarrow \alpha(1)$ in basic media $\alpha(1) \xrightarrow{\Delta} \alpha(2)$ in acidic media	$\beta \rightarrow \alpha(1)$ in basic media
Visible spectra	Figure 4, Table III	
Ir in solid	Figure 9	
Ir in DMSO-d_6 solution	Figure 10	
R_f value[c]	0.51 ($\alpha(2)$), 0.50 ($\alpha(1)$)	0.66
Nmr spectra[d] in DMSO-d_6	8.12 (d, 6) CH_3	8.34 (d)
	7.92 (b, 4) CH_2 (β to secondary N)	7.65
	7.20 7.02 (b, 8) CH_2 (α to secondary N)	7.12 6.97
	5.32 (t, 2) CH	4.77
	4.06 (b, 2) NH (β from pyridine)	3.82
	3.94 (b, 1) NH (*trans* to pyridine)	2.82
	2.56 (d, 2) 1.96 (t, 1) pyridine	~2.5 ~1.9

[a] The form $\alpha(1)$ differs from $\alpha(2)$ in solid ir spectrum and solution ir spectrum (small differences). The nmr spectrum of $\alpha(1)$ is very similar to that of $\alpha(2)$, though the peaks of the former are less well resolved and broader than those of the latter at 10°. At 45° the nmr spectrum of $\alpha(1)$ becomes essentially identical with that of $\alpha(2)$. [b] β-*trans*-$[Co(CRH)Cl_2]ClO_4 \cdot H_2O$ is indistinguishable from this compound by the methods listed here, except for solid ir spectrum. [c] Paper chromatography, eluting with n-C_4H_9OH–DMSO–H_2O–HCl (7:1:1:1) at room temperatuie (~23°). [d] Internal TMS standard: d, doublet; t, triplet, b, broad. The number in parentheses indicates the relative intensity of the peak. In fact, the spectrum of β-*trans*-$[Co(CRH)Cl_2]ClO_4$ in DMSO shows the presence of both α and β isomers. The latter part of the spectrum diminishes in intensity with time, while the peaks of the α isomers intensify.

with sodium oxalate, even in slightly acidic (5% $HC_2H_3O_2$) media. The same trend has also been observed in the system of $NiCRH^{2+}$ complexes.[27] Experiments have been designed to determine the role of oxalate in effecting the exchange of the hydrogens on the amine nitrogens for deuterium, during the course of this reaction. Heating $\alpha(2)$-*trans*-$[Co(CRH)Cl_2]ClO_4$ in CH_3OH–D_2O (2:1)–HOAc (10%) for 15 min leads to only rather limited hydrogen–deuterium exchange (~8%). The reaction of $\alpha(2)$-*trans*-$[Co(CRH)Cl_2]ClO_4$ with $Na_2C_2O_4$ (slightly excess over 1:1 molar ratio) in a medium of the same composition as above (time 15 min) gives a more greatly deuterated (~30%) β-*cis*-$Co(CRH)C_2O_4^+$ complex. Since only a single N–H need be exchanged to convert from α-*trans* to β-*cis*, the theoretical percentage is only 33. This means that $C_2O_4^{2-}$ acts to remove the protons from the amine nitrogens even in this slightly acidic medium. These observations are reconcilable with the stereochemistry of the system and the present state of knowledge concerning substitution reactions of cobalt(III) complexes.[28] A model is shown in Figure 11. The same deprotonated intermediate might be formed as a result of proton transfer to the oxalate ion regardless of whether the original reactant had the α-*trans* or the β-*trans* configuration. This intermediate eventually leads to the formation of the most stable β-*cis*-oxalato complex.

The differences in physical properties between $\alpha(1)$ and $\alpha(2)$ forms are small, except for those of the solid infrared spectra (Figure 9). There are, however, a few chemical differences. The $\alpha(1)$-*trans*-$[Co(CRH)Cl_2]ClO_4$ isomerizes to the $\alpha(2)$ form upon heating in concentrated hydrochloric acid or methanol for a few hours. The reverse conversion is effected by treatment in basic media followed by acidification with hydrochloric acid. Another chemical difference is observed in their reaction with sodium oxalate to form oxalato complexes. The reaction takes place readily with the $\alpha(2)$ form in boiling methanol–water (10%) to give one product, the monomeric β-*cis*-oxalato complex. The reaction with the $\alpha(1)$ form, however, is much slower under the same conditions and gives two products, the dimeric bridged oxalato complex $Co_2(CRH)_2C_2O_4^+$ in addition to the monomeric complex. It is not surprising that a dimeric bridged oxalato complex has been obtained for cobalt, because only such dimeric oxalato complexes have so far been obtained in the case of $Ni(CRH)^{2+}$ complexes.[19] These phenomena (including the physical data) suggest two possibilities. One is that $\alpha(1)$ and $\alpha(2)$ differ in the conformations of their six-membered chelate rings, but that they are the same in the configurations of their secondary amine nitrogens, as illustrated in Figure 6. An alternate possibility is that $\alpha(1)$ is the same compound as $\alpha(2)$ but in a different crystal form and contaminated with a very small amount of a cobalt(II) species. The second explanation is consistent with the nmr data, the visible spectral data, and the known fact that a cobalt(III) species tends to be reduced to cobalt(II) in basic media. It is, however, difficult to apply this idea to the explanation of the difference in chemical reactivity ($\alpha(1)$ should react faster for it would contain catalytic amounts of cobalt(II)) and the great difference in the solid infrared spectra, although it is possible that a small amount of impurity might greatly change the crystal habit. The other interpretation

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(27) E. Ochiai and D. H. Busch, to be submitted for publication.

(28) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

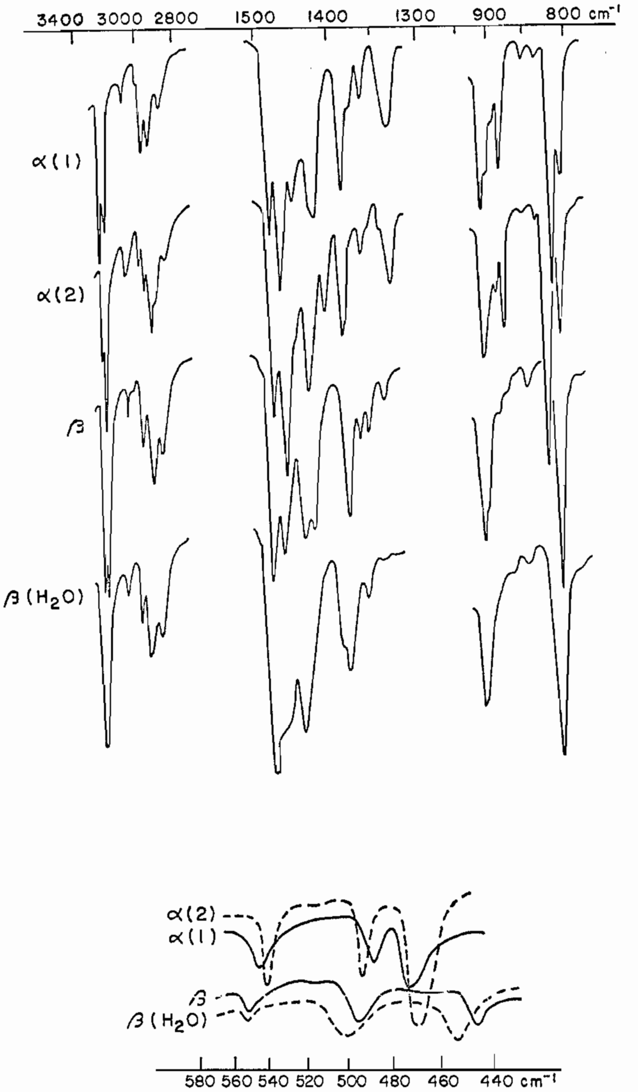

Figure 9.—Solid-state infrared spectra (KBr pellet) of the different isomers of *trans*-Co(CRH)Cl_2^+: α(1) = α(1)-*trans*-[Co(CRH)Cl_2]ClO_4; α(2) = α(2)-*trans*-[Co(CRH)Cl_2]ClO_4; β = β-*trans*-[Co(CRH)Cl_2]ClO_4; β(H_2O) = β-*trans*-[Co(CRH)Cl_2]$ClO_4 \cdot H_2O$.

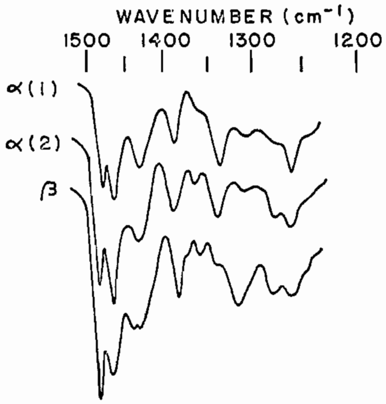

Figure 10.—Solution infrared spectra (in DMSO-d_6) of the different isomers of *trans*-Co(CRH)Cl_2^+ in the C–H deformation region.

(conformational isomers) can also be reconciled with the nmr results, the visible spectral data, and the chemical reactivity data. In one of the conformational isomers shown in Figure 6, the six-membered chelate rings may be more flexible than those in the other isomers; this might produce the broadening in the nmr spectrum at lower temperatures. The conversion between such conformers may require considerable thermal energy, for the energy barrier between the conformations might be substantial. In basic media, all of the protons of the secondary amine nitrogens are supposed to exchange so that the whole CRH ligand is free to assume the most stable form *via* N–H inversion mechanism. This may represent the conversion α(2) → α(1). Despite

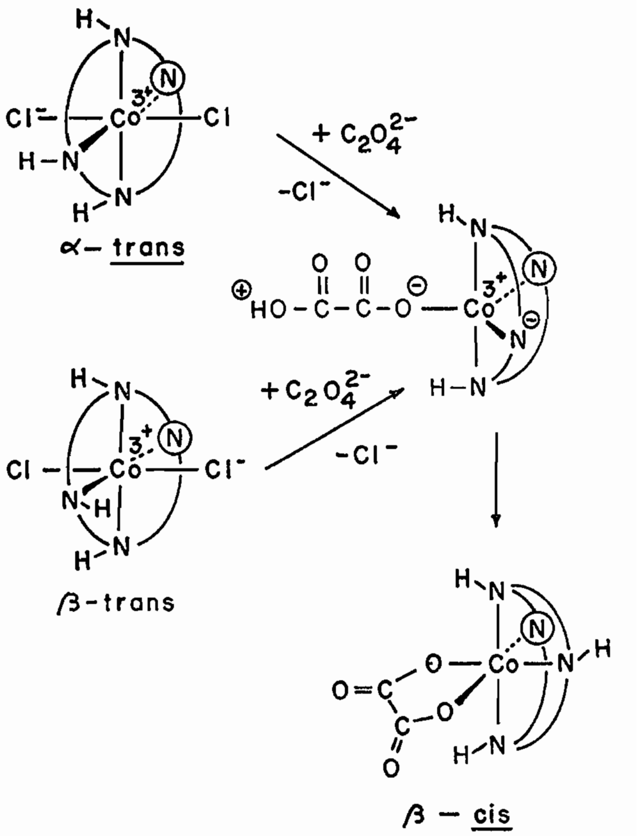

Figure 11.—A mechanism for the reaction: α- or β-*trans*-Co(CRH)Cl_2^+ + $C_2O_4^{2-}$ $\xrightarrow{H^+}$ β-*cis*-Co(CRH)(C_2O_4)$^+$ + $2Cl^-$.

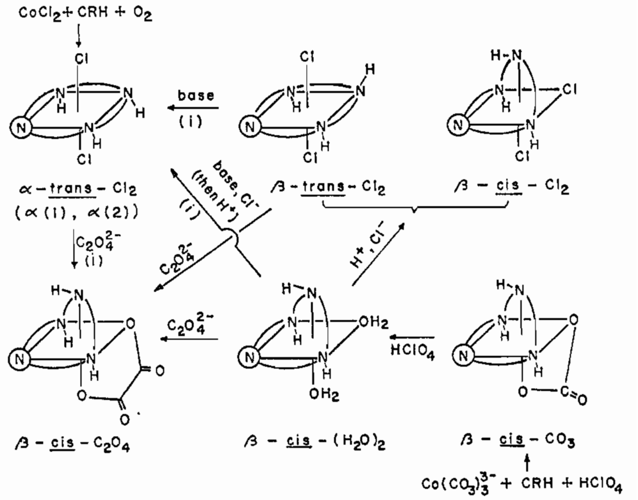

Figure 12.—A summary of this multiform system. (i) means that the process requires the inversion of a secondary amine nitrogen.

these considerations and much intense experimental effort, no unequivocal conclusions can be drawn with regard to the structural difference between the $\alpha(1)$ and $\alpha(2)$ isomers at the present time. We recognize the possibility of other sources for the isomerism; *e.g.*, different modes of oxalate coordination, etc.

The stereochemical relationships in the multiform system $[\mathrm{Co^{III}(CRH)X_2}](\mathrm{ClO_4})]$ are summarized in Figure 12.

Acknowledgment.—This program has been supported in part by the National Science Foundation and by the National Institute of General Medical Science of the United States Public Health Service (GM-10040).

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Kinetics of the Reactions between 1,2-Diaminocyclohexanetetraacetatocobaltate(II) Ion and Cyanide Ion

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Received January 24, 1969

Cyanide ion reacts very rapidly with cobalt(II)–CyDTA to form a 1:1 mixed complex. The formation rate, studied from 5 to 25° by the temperature-jump relaxation technique, is first order in cobalt–CyDTA and first order in cyanide ion with a rate constant of $k_1 = 1.8 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ at 25°. The activation energy, 0.8 kcal/mol, and the fact that k_1 is about 5000 times larger than expected from the characteristic water-exchange value of Co(II), suggest that cobalt–CyDTA–cyanide is a seven-coordinate complex. The stability constant of $\mathrm{CoCyCN^{3-}}$ at 25° is 39 M^{-1} as determined by both temperature-jump and spectrophotometric techniques. The rate of complete replacement of CyDTA by cyanide to give $\mathrm{Co(CN)_5^{3-}}$ (and its oxidized products) is slow. The reaction is first order in $\mathrm{CoCyCN^{3-}}$ and second order in $\mathrm{CN^-}$ with a rate constant equal to $9.5 \times 10^{-3}\ M^{-2}\ \mathrm{sec}^{-1}$. The mechanism for the replacement of CyDTA from cobalt by cyanide ion is the same as that observed for the reactions of cyanide ion with $\mathrm{NiEDTA^{2-}}$ and $\mathrm{CoEDTA^{2-}}$, which also involve three cyanide ions. The cyanide ion displacement of CyDTA from cobalt(II) is 1.2×10^5 times slower than the corresponding displacement of EDTA.

Introduction

There is a rapid reaction between *trans*-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetatocobaltate(II) ion, $\mathrm{CoCy^{2-}}$, and cyanide ion to form a 1:1 mixed complex

$$\mathrm{CoCy^{2-} + CN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoCyCN^{3-}} \qquad (1)$$

The reaction is sufficiently fast that it was necessary to use the temperature-jump relaxation method to study it. The rate was more than 1000 times that predicted from the characteristic water-exchange rate constant for the aquocobalt(II) ion after correction for outer-sphere repulsion.

With a large excess of cyanide ion a second much slower reaction occurs with the displacement of the CyDTA and the formation of $\mathrm{Co(CN)_5^{3-}}$ and its air-oxidized products.

$$\mathrm{CoCyCN^{3-} + 2CN^- \xrightarrow[\text{rate-detn}]{k_2} (intermediate\ species)} \qquad (2)$$

$$\mathrm{(intermediate\ species) + 2CN^- + H^+ \xrightarrow{fast} Co(CN)_5^{3-} + HCy^{3-}} \qquad (3)$$

$$\mathrm{Co(CN)_5^{3-} \xrightarrow{O_2} [Co(CN)_5]_2O_2^{6-},\ Co(CN)_5(H_2O)^{2-},\ etc.} \qquad (4)$$

The kinetic dependence is given by eq 2; a total of only three cyanide ions, including the one in eq 1, is needed in the rate-determining step. The nature of the intermediate species is not known and might be $\mathrm{Co(CN)_3Cy^{5-}}$ or $(\mathrm{Co(CN)_3^- + Cy^{4-}})$, but the cobalt species is a kinetic intermediate without appreciable concentration and it reacts rapidly with additional cyanide ion. The rate of release of $\mathrm{HCy^{3-}}$ in eq 3 equals the rate of disappearance of $\mathrm{CoCyCN^{3-} + CoCy^{2-}}$. A mixture of products is formed after the rapid reaction of $\mathrm{O_2}$ with $\mathrm{Co(CN)_5^{3-}}$.

Experimental Section

The acid form of CyDTA was obtained from LaMont Laboratories and was purified by recrystallization from water.

Standard solutions of cobalt–CyDTA, 0.018–0.054 M, were prepared by adding an excess of cobalt(II) perchlorate to a standard CyDTA solution and removing the excess cobalt by hydroxide precipitation at pH 10.

Sodium cyanide solutions were standardized before use by titration with silver nitrate in the presence of iodide ion.

Absorption spectra were recorded on a Cary 14 spectrophotometer. The spectrum of $\mathrm{CoCy^{2-}}$ had absorption maxima at 608, 510, and 460 mμ with extinction coefficients of 1, 7, and 8 $M^{-1}\ \mathrm{cm}^{-1}$, respectively. Air oxidation of $\mathrm{CoCy^{2-}}$ to give the Co(III)–CyDTA complex is extremely slow and could not be detected spectrophotometrically over a period of several months. The Co(III) complex, obtained by $\mathrm{H_2O_2}$ oxidation, has absorption maxima at 550 and 380 mμ. The mixed Co(II)–CyDTA–cyanide complex, with an absorption maximum at 487 mμ (ϵ 72.5 $M^{-1}\ \mathrm{cm}^{-1}$) and a shoulder at 510 mμ, also was stable to air oxidation.

Kinetic Measurements Using Temperature-Jump Relaxation.—The apparatus used was described earlier.[2] The temperature-

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[1] Correspondence to be addressed to this author.

[2] D. W. Margerum and H. M. Rosen, *J. Am. Chem. Soc.*, **89**, 1088 (1967).