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Cobalt(III) Complexes Derived from 1,8-Diamino-3,6-dithiaoctane. I. Preparation and Reactions

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The flexible quadridentate ligand 1,8-diamino-3,6-dithiaoctane (eee), having the donor atom sequence nitrogen–sulfur–sulfur–nitrogen, forms monomeric octahedral complexes with cobalt(III). The following complex cations have been prepared and characterized: $Co(eee)Cl_2^+$, $Co(eee)Br_2^+$, $Co(eee)CO_3^+$, $Co(eee)(NO_2)_2^+$, and $Co(eee)(NH_2CH_2COO)^{2+}$. Although three geometric isomers are theoretically possible, the presence of thioether donors appears to induce an extreme geometric specificity and we have succeeded in characterizing only the symmetrical *cis* isomer in which the primary amine groups are coordinated *trans* to each other. Methods of preparation, chemical interconversions, electronic adsorption spectra, infrared spectra, and nuclear magnetic resonance data are presented and discussed.

Introduction

In the past few years stereochemical studies of metal chelates derived from flexible linear quadridentate ligands have enjoyed a period of active investigation. To date, the more complete researches have dealt strictly with the donor atom arrangement

$$\mathrm{N\frown N\frown N\frown N}$$

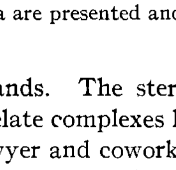
in which the connecting alkyl chains have been varied in length[1-4] or contain selectively placed methyl groups.[5] In addition, metal chelates derived from the hetero donor atom sequences

$$\mathrm{O\frown N\frown N\frown O}^{6} \qquad \mathrm{P\frown S\frown S\frown P}^{7}$$

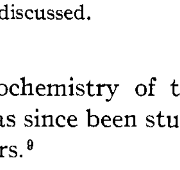
have also been reported.

In 1947 Dwyer and Lions[8] first prepared α,ω-dithiamines with the general formula $NH_2(CH_2)_xS(CH_2)_yS(CH_2)_zNH_2$ (where x, y, and z = 2 or 3) as organic intermediates in the synthesis of sexadentate ligands. The stereochemistry of the resulting metal chelate complexes has since been studied extensively by Dwyer and coworkers.[9]

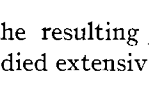
We now wish to report the preparation and stereochemistries for a series of new cobalt(III) complexes derived from the flexible linear quadridentate 1,8-diamino-3,6-dithiaoctane (abbreviated eee) and which has the skeletal arrangement of $NH_2CH_2CH_2$–S–CH_2–CH_2–S–$CH_2CH_2NH_2$. In principle metal complexes derived from 1,8-diamino-3,6-dithiaoctane can exist in three distinct geometrically isomeric forms. On the basis of symmetry these can be designated symmetrical *cis* and unsymmetrical *cis* and *trans*. The nitrogen atoms are *trans* to each other in the symmetrical *cis* arrangement (I) and *cis* to each other in the unsymmetrical *cis* configuration (II), while the two monodentate groups are mutually *cis* in both structures. In the *trans* geometry, all four donor atoms of the fused chelate ring system lie in the same plane (III).



s-cis
I



uns-cis
II



trans
III

The objectives of this investigation were to prepare the diacidocobalt(III) complexes, identify geometric

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[1] G. H. Searle, Ph.D. Thesis, Australian National University, 1963.

[2] (a) A. M. Sargeson and G. H. Searle, *Nature*, **200**, 356 (1963); (b) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

[3] (a) E. Kyuno, L. Boucher, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **87**, 4458 (1965); (b) E. Kyuno and J. C. Bailar, Jr., *ibid.*, **88**, 1120, 1125, 5447 (1966); (c) D. House and C. Garner, *ibid.*, **88**, 2156 (1966).

[4] H. Hamilton, Jr., and M. D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).

[5] (a) R. G. Asperger and C. F. Liu, *ibid.*, **4**, 1395 (1965); *J. Am. Chem. Soc.*, **89**, 708, 1533 (1967); (b) S. Yoshikawa, T. Sekihara, and M. Goto, *Inorg. Chem.*, **6**, 169 (1967).

[6] (a) C. F. Liu, *ibid.*, **3**, 680 (1964); (b) J. I. Legg, Ph.D. Thesis, The University of Michigan, 1965; (c) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965); (d) L. Schoenberg, D. W. Cooke, and C. F. Liu, paper presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[7] G. Degischer and G. Schwarzenbach, *Helv. Chim. Acta*, **49**, 1927 (1966).

[8] F. P. Dwyer and F. Lions, *J. Am. Chem. Soc.*, **69**, 2017 (1947).

[9] (a) F. P. Dwyer and F. Lions, *ibid.*, **72**, 1545, 5037 (1950); (b) F. P. Dwyer, N. S. Gill, E. Gyarfas, and F. Lions, *ibid.*, **74**, 4188 (1952).

isomers, separate optical isomers,[10] and assign the absolute stereochemistries of these new complexes using visible, infrared, nuclear magnetic resonance, circular dichroism,[10] and optical rotatory dispersion spectra[10] in conjunction with chemical interconversion methods.

Experimental Section

Preparation of Ligand.—1,8-Diamino-3,6-dithiaoctane was prepared from 1,2-ethanedithiol (Aldrich Chemical Co.) and N-β-bromoethylphthalimide (K & K Laboratories, Inc.) as described by Dwyer and Lions.[8] *Anal.* Calcd for the dihydrochloride $C_6H_{18}N_2S_2Cl_2$: C, 28.48; H, 7.12; N, 11.07; S, 25.31. Found: C, 28.63; H, 6.94; N, 11.07; S, 25.25.

Preparation of Complexes. (a) ***s-cis*-Dinitro(1,8-diamino-3,6-dithiaoctane)cobalt(III) Chloride.**—Cobalt(II) chloride hexahydrate (7.9 g, 0.0332 mol) was placed in a 500-ml round-bottom flask and 250 ml of absolute methanol was added. The solution was warmed to 50° and stirred continuously. Solid 1,8-diamino-3,6-dithiaoctane (6.00 g, 0.0332 mol) and 2.80 ml of 12 *N* hydrochloric acid were mixed in 150 ml of absolute methanol and then were added to the cobalt(II) chloride solution. A vigorous stream of air was drawn through the brown mixture. Solid sodium nitrite (3.0 g, 0.043 mol) was added and the solution was warmed to 50°, stirred, and aerated for 1 additional hr. More sodium nitrite (2.0 g, 0.028 mol) dissolved in 20 ml of water was added to the rust-colored mixture. Air oxidation and warming were continued for 20 min; then 2.0 ml of 12 *N* hydrochloric acid was added. Thirty minutes later, the mixture was filtered rapidly at 50°. The orange product was washed with ethanol, acetone, and ether and air dried; yield, 12.0 g, 98%.

The crude product (12.0 g) was dissolved in 150 ml of hot water and filtered rapidly; then 150 ml of boiling ethanol was added slowly with stirring. The clear orange solution was allowed to cool slowly in the refrigerator for several hours. The first crop of deep orange crystals (6.8 g) was collected by filtration, washed with ethanol and acetone, and air dried. Careful fractionation of the filtrate yielded an additional 3.5 g of complex; yield, 85%. *Anal.* Calcd for $[Co(C_6H_{16}N_2S_2)(NO_2)_2]Cl \cdot H_2O$: C, 18.73; H, 4.68; N, 14.57; Cl, 9.21. Found: C, 18.90; H, 4.74; N, 14.53; Cl, 9.35.

(b) ***s-cis*-Dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) Chloride.**—Twice recrystallized *s-cis*-$[Co(eee)(NO_2)_2]Cl \cdot H_2O$ (10.0 g, 0.026 mol) was dissolved in 90 ml of 12 *N* hydrochloric acid and warmed to 40° with frequent stirring for 1–2 hr. When the conversion was complete, the solution appeared to be deep blue and evolution of nitrogen oxides ceased. The solution was filtered warm and 200 ml of hot absolute ethanol was added slowly with stirring. The clear blue solution was placed in the refrigerator and allowed to cool to 0° for several hours. The deep blue crystalline product was collected by filtration, washed with cold absolute methanol, acetone, and ether, and air dried; yield, 8.2 g 92%. The product was recrystallized from 12 *N* hydrochloric acid (10 ml/g) and hot absolute ethanol (10 ml/g). *Anal.* Calcd for $[Co(C_6H_{16}N_2S_2)Cl_2]Cl$: C, 20.87; H, 4.64; N, 8.11; Cl, 30.78. Found: C, 20.85; H, 4.68; N, 8.02; Cl, 30.59.

(c) ***s-cis*-Dibromo(1,8-diamino-3,6-dithiaoctane)cobalt(III) Bromide.**—Cobalt(II) bromide hexahydrate (18.1 g, 0.055 mol) was dissolved in 100 ml of absolute methanol at 40°. To this solution was added 250 ml of absolute methanol containing 9.38 g of 48% hydrobromic acid and 1,8-diamino-3,6-dithiaoctane (10.0 g, 0.055 mol). A vigorous stream of air was drawn through the mixture and it was warmed to 40° for several hours. The desired green product began to form in about 30 min. The solution was filtered, yielding 16 g (60%) of crude green product which was washed with methanol and acetone and air dried. The product was recrystallized from hot $HBr–C_2H_5OH$ solution. *Anal.* Calcd for $[Co(C_6H_{16}N_2S_2)Br_2]Br$: C, 15.05; H, 3.35; N, 5.85; Br, 50.00. Found: C, 15.22; H, 3.50; N, 5.82; Br, 50.24.

(d) ***s-cis*-Carbonato(1,8-diamino-3,6-dithiaoctane)cobalt(III) Chloride.**—Once recrystallized *s-cis*-$[Co(eee)Cl_2]Cl$ (2.4 g, 0.0069 mol) was stirred in 20 ml of water at 50°. To this stirred solution was added lithium carbonate (0.74 g, 0.01 mol) and the solution was warmed until it became deep red (about 10 min). The hot (50°) basic solution was quickly filtered and poured into 600 ml of ice-cold absolute ethanol. The flocculent pink precipitate was collected by filtration, washed with methanol, acetone, and ether, and air dried; yield, 2.15 g, 93%. This complex was very soluble in water and very difficult to recrystallize except as the perchlorate salt. *Anal.* Calcd for $[Co(C_6H_{16}N_2S_2)CO_3]Cl$: C, 25.13; H, 4.79; N, 8.38; Cl, 10.59. Found: C, 25.22; H, 4.68; N, 8.49; Cl, 10.41.

(e) ***s-cis*-Glycinato(1,8-diamino-3,6-dithiaoctane)cobalt(III) Bromide Monohydrate.**—Once-recrystallized dibromo(1,8-diamino-3,6-dithiaoctane)cobalt(III) bromide (1.0 g, 0.0028 mol), glycine methyl ester hydrobromide (0.352 g, 0.0028 mol), and 20.6 ml of 0.1 *N* sodium hydroxide were ground together in a mortar. The original green color quickly changed to orange-red upon warming to 40°. The solution was filtered and the crude product was caused to precipitate from the filtrate by the addition of ethanol and ether. The product was recrystallized from methanol–water; yield, 0.60 g, 50%. *Anal.* Calcd for $[Co(C_6H_{16}N_2S_2)(C_2H_2NO_2)]Br_2 \cdot H_2O$: C, 19.56; H, 4.48; N, 8.56; Br, 32.61. Found: C, 19.71; H, 4.35; N, 8.45; Br, 32.80.

Nuclear Magnetic Resonance Spectra.—Saturated D_2O solutions of the complexes were prepared and syringed into nmr tubes. Spectra were obtained using a Varian A-60 Instrument. The nmr spectrum of *s-cis*-$[Co(eee)(NO_2)_2]Cl$ was obtained using a Varian HA-100 spectrometer at Argonne National Laboratory. Hexamethylsiloxane was the internal standard.

Infrared Spectra.—High-resolution infrared spectra were obtained using a Beckman IR-9 double-beam, prism-grating instrument. Absorptions listed are accurate to ± 1 cm^{-1}. Both potassium bromide pellet and Nujol mull techniques were employed with all compounds.

Electronic Absorption Spectra.—Electronic spectra were recorded at 25° by a Cary Model 14 recording spectrophotometer using aqueous solutions of the complexes in 1.0-cm matched cells.

Analyses.—Nitrogen analyses were obtained in these laboratories using a Coleman nitrogen analyzer. All other microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Results and Discussion

Ligand Synthesis.—The ligand preparation initially developed by Dwyer and Lions,[8] although costly, provides the most efficient means of obtaining reasonable quantities of 1,8-diamino-3,6-dithiaoctane. This preparative method utilizes a reaction sequence in which 1 equiv of 1,2-ethanedithiol is condensed with 2 equiv of N-β-bromethylphthalimide in sodium ethoxide solution. When the resultant bisphthalimido compound (*ca.* 90% yield; mp 146–147°) is treated with hydrazine and concentrated hydrochloric acid, the dithiadiamine dihydrochloride is produced. The solution containing the ligand is treated with solid sodium hydroxide whereupon the free dithiadiamine separates as an oil which is subsequently extracted into ether. The pure ligand is a white waxlike solid which melts at about 35°.

The elegance of this method can be appreciated when one considers that a multitude of interesting ligands can be synthesized with various connecting carbon chains between donor atoms, simply by selecting the appro-

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[10] Part II of this series reports the optical resolutions and assignments of absolute configurations: J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1572 (1969).

priate alkyldithiol and/or N-β-bromalkylphthalide reactants.

An alternate preparative method was investigated. It is possible to obtain 1,8-diamino-3,6-dithiaoctane by condensing 2 equiv of β-mercaptoethylamine with 1 equiv of 1,2-dibromoethane in sodium ethoxide solution. The free ligand can be isolated as in the alternate procedure.[8] Despite the apparent simplicity of this second method, it is inferior. The desired compound can be obtained in yields of 20–50%; however, purity of the product is always in question because this second method yields a product which invariably decomposes slowly over a period of several weeks. Ligand prepared by the method of Dwyer and Lions can be stored indefinitely without decomposition.

Synthesis of Complexes.—A very general synthetic route to the cobalt(III) complexes of 1,8-diamino-3,6-dithiaoctane involves the air oxidation of an appropriate cobalt(II) salt and ligand monohydrohalide in methanol and/or methanol–water mixtures. Octahedral complexes of the general type $Co(eee)L_2^{n+}$, where monodentate L is Cl^-, Br^-, or NO_2^-, and bidentate L_2 is CO_3^{2-} or $NH_2CH_2COO^-$, can be prepared by metathetical interaction of *s-cis*-$[Co(eee)Cl_2]Cl$ with the appropriate salt NaX or Na_2X. The complex most easily obtained in excellent yield (80–95%) is *s-cis*-$[Co(eee)(NO_2)_2]Cl$. It is prepared in warm methanol by air oxidation of cobalt(II) chloride hexahydrate in the presence of 1,8-diamino-3,6-dithiaoctane monohydrochloride and excess sodium nitrite. It may also be synthesized by treating the corresponding *s-cis*-$[Co(eee)Cl_2]Cl$ with sodium nitrite in a 50:50 methanol–water slurry. The *s-cis*-$[Co(eee)(NO_2)_2]Cl$ prepared by both methods was exhaustively recrystallized from hot 1:1 methanol–water solutions and the high-resolution infrared spectrum of every fraction was compared, looking for relative intensity or frequency differences. No differences were found from fraction to fraction. Accordingly, the visible and ultraviolet electronic absorption spectra for the various fractions were identical regardless of the preparative method employed. The purity of *s-cis*-$[Co(eee)(NO_2)_2]Cl$ was established by elemental analyses and chromatographic techniques. It was chromatographed separately on paper, cellulose, and Dowex 50-X2 resin using several solvents. The compound was eluted as a single spot using water, water–methanol (50:50 and 10:90), water–ethanol (50:50), and methanol–0.01 *N* hydrochloric acid (90:10). A mixture of 40% 1-butanol, 30% water, 20% pyridine, and 10% glacial acetic acid also failed to give evidence for the presence of two or more geometrical isomers. This latter solvent mixture was employed successfully to separate *s-cis*-$[Co(trien)(NO_2)_2]Cl$ and *uns-cis*-$[Co(trien)(NO_2)_2]Cl$ geometric isomers.[11,12]

By warming *s-cis*-$[Co(eee)(NO_2)_2]Cl$ in concentrated hydrochloric acid, it is converted quantitatively to the deep blue *s-cis*-$[Co(eee)Cl_2]Cl$. Again extensive fractional crystallization followed by individual infrared and visible electronic spectra for each fraction failed to provide any evidence suggesting the presence of geometric isomers. Air oxidation of cobalt(II) chloride hexahydrate and ligand monohydrochloride in water, methanol, or ethanol–water mixtures failed to produce crystalline *s-cis*-$[Co(eee)Cl_2]Cl$. Amorphous intractable materials were usually obtained.

A striking contrast to this behavior is observed in the preparation of *s-cis*-$[Co(eee)Br_2]Br$. Air oxidation of aqueous or alcoholic solutions of ligand monohydrobromide and cobalt(II) bromide hexahydrate results in the almost immediate precipitation of green crystalline *s-cis*-$[Co(eee)Br_2]Br$. Yields are always 50–75%. Addition of concentrated hydrobromic acid to the first filtrate with subsequent cooling results in an additional 20% increase in yield over the quantity of complex first collected by filtration. Additional methods of synthesizing *s-cis*-$[Co(eee)Br_2]Br$ include treatment of *s-cis*-$[Co(eee)(NO_2)_2]Br$ with concentrated hydrobromic acid in hot ethanol solution or treating solid *s-cis*-$[Co(eee)CO_3]Br$ with dry HBr gas in ethanol. Infrared and electronic absorption spectra for various fractions of *s-cis*-$[Co(eee)Br_2]Br$, prepared by both methods, again failed to demonstrate the presence of isomeric forms.

Both sodium bicarbonate and lithium carbonate react with *s-cis*-$Co(eee)L_2^{n+}$ (where L = Cl^-, Br^-, H_2O) to produce red *s-cis*-$Co(eee)CO_3^+$. It can be isolated as the chloride or bromide salts; however, it is most easily crystallized when the precipitating anion is perchlorate. A sample of *s-cis*-$[Co(eee)CO_3]Cl$, prepared by each of three separate methods, was converted into *s-cis*-$[Co(eee)(NO_2)_2]Cl$, *s-cis*-$[Co(eee)Cl_2]Cl$, and *s-cis*-$[Co(eee)Br_2]Br$. Infrared spectra and visible absorption spectra clearly demonstrated that these three derivatives were exactly the same as obtained previously.

The synthesis of the four compounds—*s-cis*-$[Co(eee)(NO_2)_2]Cl$, *s-cis*-$[Co(eee)Cl_2]Cl$, *s-cis*-$[Co(eee)Br_2]Br$, and *s-cis*-$[Co(eee)CO_3]Cl$—followed by the complete conversion of each into the other three without the production of additional geometrical isomers, as evidenced by high-resolution infrared spectra over the range 400–4000 cm^{-1} and visible absorption spectra, strongly suggests that all four compounds have a common configuration. The chemical interconversions are summarized in Figure 1.

Geometrical Isomers.—The preceding compounds have been resolved into their optical isomers.[10] The optical resolutions have established the *cis* configuration for these complexes. It is now appropriate to present evidence in support of the symmetrical *cis* arrangement (I) as opposed to the unsymmetrical *cis* geometry (II). Each of the physical measurements employed—nuclear magnetic resonance, high-resolution infrared, and visible absorption spectra—has, in the past, provided a means for identifying and assigning geometry to inorganic coordination compounds.

Nuclear Magnetic Resonance Spectra.—The nmr

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[11] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

[12] trien = $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$

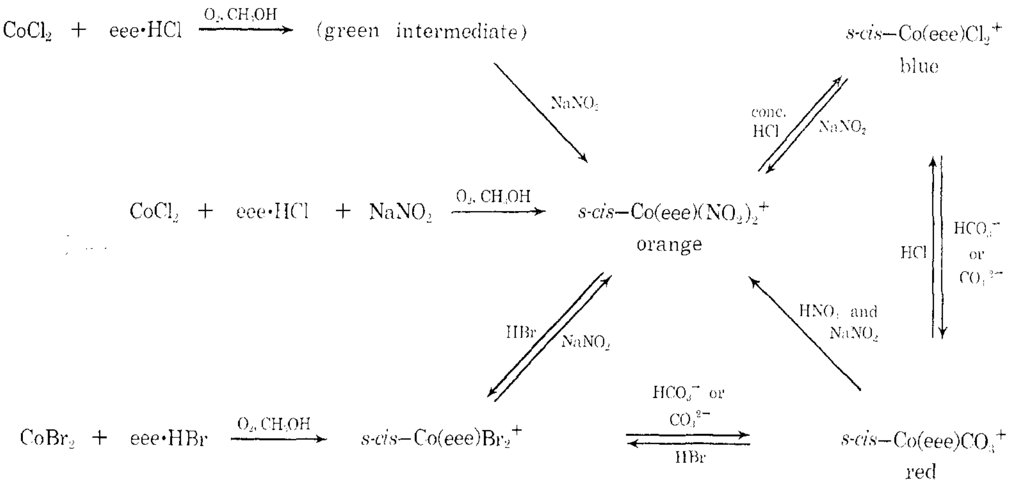
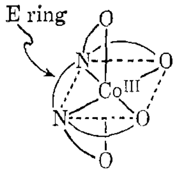
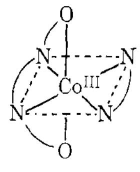


Figure 1.—Chemical interconversions for several Co(eee)L_2^+ complexes.

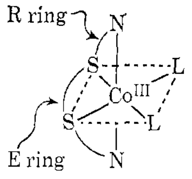
researches of Williams[13] and Day and Reilley[14] for the Co(EDTA)$^-$ system in conjunction with the observations of Legg and Cooke[15] for the *s-cis* and *uns-cis* isomers of Co(EDDA)en$^+$ are particularly helpful in the identification and assignment of geometries in the present work. Williams[13] first observed a characteristic A_2B_2 quartet pattern for the backbone ethylene linkage in Co(EDTA-d_8)$^-$ in which all of the protons of EDTA except the E ring (IV) were replaced by deuterium atoms. Legg and Cooke[15] also observed this distinctive quartet in *s-cis*-Co(EDDA)en$^+$ complexes and it was unequivocally assigned to the backbone E ring (V). For the *uns-cis* geometry (II), the asymmetry introduced by having three different chelate rings on the same molecule results in a complex ABCD pattern for the E-ring protons.[15]



IV



V



VI

The HA-100 high-resolution proton magnetic resonance spectrum of *s-cis*-[Co(eee)$(NO_2)_2$]Cl taken in D_2O is illustrated in Figure 2. Here the distinctive quartet resonance is clearly discernible with a center at 3.77 ppm downfield from hexamethylsiloxane (HMS). The HMS resonance is taken as zero and is experimentally equivalent to that of tetramethylsilane (TMS). If the E ring was changing its conformation from k to k′, this quartet pattern would be reduced to a single sharp resonance.[13,15] That this is not observed is indicative of having the E ring frozen in place, thus causing each H_A and H_B proton set to become distinguishable and giving rise to the observed A_2B_2 spectrum. The complex overlay of resonance patterns from 3.68 to 2.87 ppm is due to the R-ring protons and cannot be definitely assigned at this time. It should be noted that the E-ring resonances for Co(EDTA)$^-$ and Co(EDDA)en$^+$ occur as quartets centered at 3.10 and 3.61 ppm, respectively.[15] In accord with the deshielding influence of the adjacent sulfur donor atoms, the E-ring resonance for *s-cis*-Co(eee)$(NO_2)_2^+$ is centered at 3.77 ppm. This A_2B_2 pattern for the backbone chelate ring clearly establishes the symmetrical *cis* arrangement (VI) for this complex.[16] It is possible to assign the *s-cis* configuration to other complexes of this series on a similar basis.[17] Furthermore, the circular dichroism spectra for all compounds in this series clearly support the *s-cis* geometry.[10]

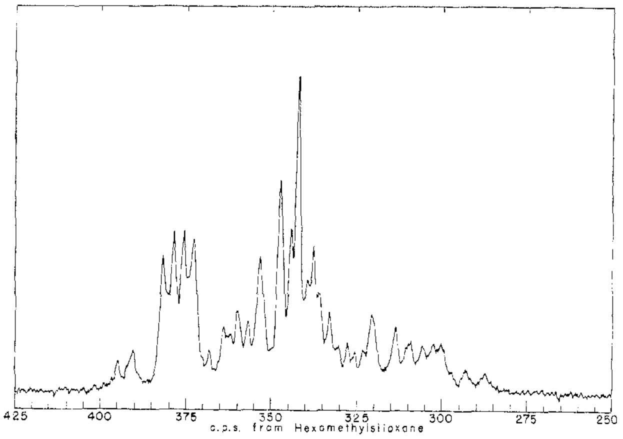


Figure 2.—The HA-100 pmr spectrum of *s-cis*-[Co(eee)$(NO_2)_2$]Cl in D_2O.

High-Resolution Infrared Spectra.—It was initially believed that high-resolution infrared spectra could be used to distinguish successfully between the *s-cis*, *uns-cis*, and *trans* geometries. Complexes which possess the *s-cis* or *trans* geometry have two equivalently bonded NH_2 groups while the *uns-cis* configuration exhibits two nonequivalently positioned NH_2 groups. One, therefore, could rationally expect complexes of the

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(13) D. H. Williams, Ph.D. Thesis, The Ohio State University, 1964.

(14) R. J. Day and C. H. Reilley, *Anal. Chem.*, **36**, 1073 (1964).

(15) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

(16) Substitution of a methyl group for one of the protons on the E ring in *s-cis*-Co(eee)$(NO_2)_2^+$ causes the quartet resonance to collapse, resulting in numerous weaker absorptions.

(17) It was observed that the position of the E-ring quartet resonance is a complex function of the monodentate groups present in the complex. A more detailed paper on the nmr characteristics for this metal–ligand system will be reported.

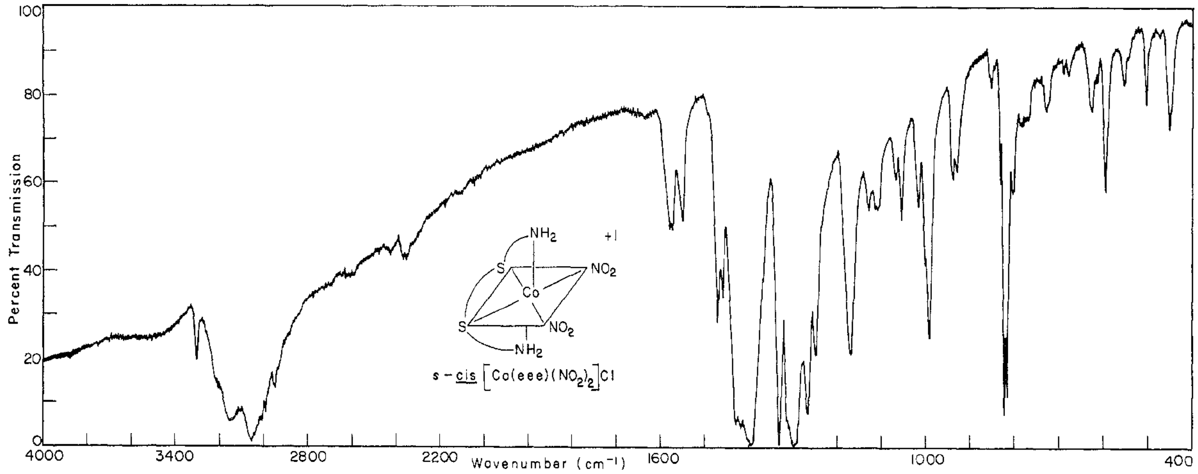

Figure 3.—Infrared spectrum of *s-cis*-[Co(eee)$(NO_2)_2$]Cl.

uns-cis configuration to produce infrared spectra with more complex N–H stretching and NH_2 deformation regions than complexes with the *s-cis* or *trans* geometries. Accordingly, Buckingham and Jones[18] have used infrared spectra to distinguish between the *s-cis*- and *uns-cis*-diacido(triethylenetetramine)cobalt(III) complexes. The *s-cis* isomers invariably exhibited three or four strong bands in the N–H stretching region and the NH_2 deformation band occurred as a sharp singlet absorption. The *uns-cis* isomers always had four or five major N–H stretching bands and the NH_2 deformation was observed to be a distinct doublet.

Figure 3 illustrates the infrared spectrum taken in KBr for *s-cis*-[Co(eee)$(NO_2)_2$]Cl. Aside from the Nujol absorption, an identical spectrum is obtained when taken in Nujol. The *s-cis*-[Co(eee)$(NO_2)_2$]Cl has three strong absorptions in the N–H stretching region at 3055, 3155, and 3212 cm^{-1} and a fourth very sharp, intense band at 3306 cm^{-1}. The corresponding NH_2 deformation region is a composite of three bands of medium intensity positioned at 1552, 1572, and 1578 cm^{-1}.

The infrared spectra reported by Buckingham and Jones and their structure assignments based on the number of N–H stretching and NH_2 deformation bands for the very similar *s-cis*- and *uns-cis*-[Co(trien)L_2]L complexes would suggest that the *cis*-[Co(eee)$(NO_2)_2$]Cl complex examined here is of the unsymmetrical *cis* geometry. That this structure assignment is in direct opposition to the previous nmr data, which unequivocally established the *s-cis* geometry for this complex, strongly suggests that one should *not* casually infer geometry from ir data alone. Further, one would expect the N–H stretching region of eee complexes to exhibit simpler absorption patterns than the corresponding trien complexes because the present chelate system containing sulfur donor atoms does not possess the proton of the secondary nitrogen atoms as do trien derivatives.

In metal–amine compounds, the four principal regions of amine absorptions are ~3200, ~1600, ~1300, and ~800 cm^{-1}. These have been assigned to N–H stretching, asymmetric deformation, symmetric deformation, and rocking modes, respectively.[19] In general, bands in the regions 3000–3310, 1560–1600, 1250–1302, 1110–1160, 930–1055, and 730–855 cm^{-1} showed isotopic shifts upon deuteration of *s-cis*-[Co(eee)L_2]L complexes. Table I lists the frequencies of the infrared absorptions which disappear on deuteration, as well as the new absorptions exhibited by the deuterated complex *s-cis*-[Co(eee-d_4)$(NO_2)_2$]Cl. Strong absorptions due to the $-NO_2$ group, in addition to the complexity of the spectra in the region 990–1165 cm^{-1}, do not allow confident assignments to be made for the other vibrations of the NH_2 group aside from the N–H stretching and NH_2 deformation bands.

TABLE I[a]

INFRARED ABSORPTIONS DUE TO THE COORDINATED NH_2 GROUP IN *s-cis*-[Co(eee)$(NO_2)_2$]Cl (cm^{-1})

Disappear on deuteration	Appear on deuteration
3306 s	2459 s
3212 m	2388 m
3155 s	2338 m
3055 s	2262 s
	1350 w
1578 m	1212 w
1575 m	1205 w
1552 m	
1260 s	1032 m
1170 s	862 s
1130 w	
1055 m	
1000 sh	
730 m	
555 w	

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

The *s-cis*-[Co(eee)$(NO_2)_2$]Cl complex exhibits an N–O asymmetric stretch at 1395 cm^{-1} and a symmetric N–O stretch at 1331 cm^{-1}, while the O–N–O deformation is a multiplet at 814 and 822 cm^{-1}.

Variation in the nature of the anion results in major

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(19) F. A. Cotton, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, pp 362–365.

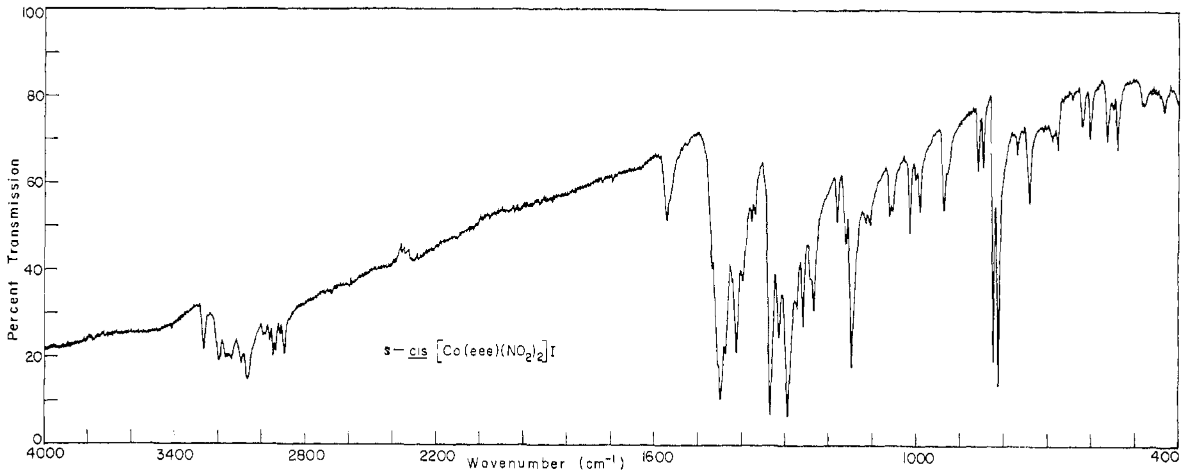

Figure 4.—Infrared spectrum of *s-cis*-[Co(eee)$(NO_2)_2$]I.

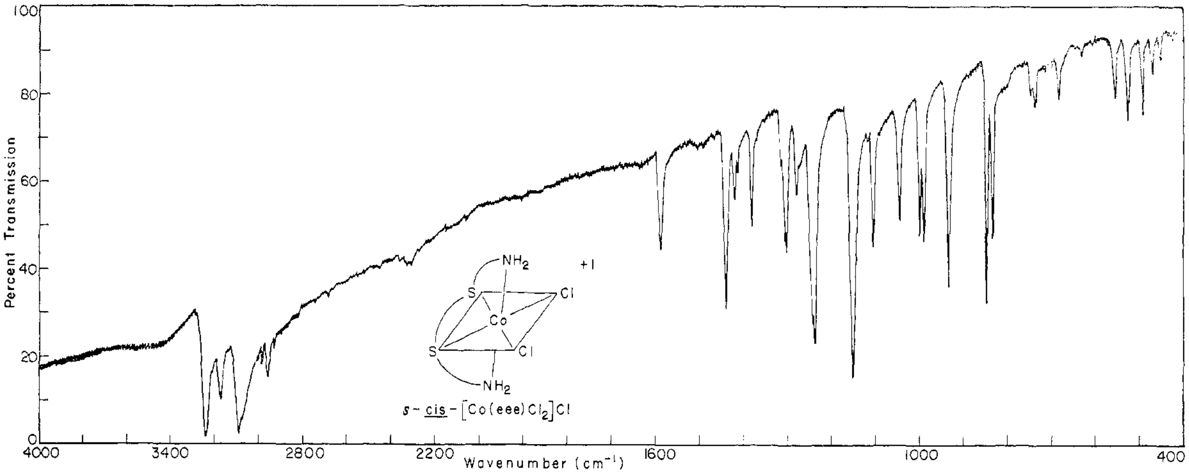

Figure 5.—Infrared spectrum of *s-cis*-[Co(eee)Cl_2]Cl.

alterations in the infrared spectra, especially in the N–H stretching and NH_2 deformation regions. The high-resolution infrared spectra of *s-cis*-[Co(eee)-$(NO_2)_2$]L, where $L^- = Cl^-$, Br^-, I^-, NO_3^-, or ClO_4^-, were examined in detail and the results are listed in Table II for the NH_2 deformation and N–H stretching regions.

TABLE II[a]

ANION EFFECT WITH *s-cis*-[Co(eee)$(NO_2)_2$]L, FOR THE N–H STRETCHING AND DEFORMATION MODES (CM^{-1})

		L^-		
ClO_4^-	NO_3^-	I^-	Br^-	Cl^-
3275 s	3289 s	3265 s	3261 s	3306 s
3265 s	3265 s	3195 s	3195 s	3213 m
3225 s	3190 s	3160 m	3160 s	3155 s
3140 b	3070 b	3140 m	3100 m	3055 s
3080 s	3000 b	3095 s	3055 s	
			3025 sh	
1578 m	1578 m	1570 m	1581 m	1578 m
			1568 m	1575 m
				1552 m

[a] Abbreviations: s, strong; m, medium; b, broad; sh, shoulder.

A trend exhibiting a greater number of bands at higher energies appears to occur in the sequence $ClO_4^- > NO_3^- > I^- > Br^- > Cl^-$. Also, as one systematically varies the anion, in the same series, the splitting or broadening observed for the NH_2 deformation band decreases in the order $Cl^- > Br^- > I^- > NO_3^- \sim ClO_4^-$. The over-all infrared spectra for *s-cis*-[Co(eee)-$(NO_2)_2$]L, where $L^- = Br^-$, I^-, or NO_3^-, are quite similar. The infrared spectrum of *s-cis*-[Co(eee)-$(NO_2)_2$]I is illustrated in Figure 4, allowing a direct comparison to be made with the spectrum of the quite different chloride salt given in Figure 3.

The infrared spectra of *s-cis*-[Co(eee)Cl_2]Cl taken in Nujol and KBr were the same. The spectrum taken in KBr is illustrated in Figure 5. This complex exhibits three strong absorptions at 3090, 3170, and 3240 cm^{-1} in the N–H stretching range and a single, sharp NH_2 deformation band at 1588 cm^{-1}. This is the type of spectrum one might expect for the *s-cis* geometry.

The green *s-cis*-[Co(eee)Br_2]Br exhibits an infrared spectrum identical with that observed for the *s-cis*[Co-(eee)Cl_2]Cl except for minor shifts in the N–H stretching region, there being three strong absorptions at 3080, 3160, and 3230 cm^{-1}, and the NH_2 deformation band, being of medium intensity at 1583 cm^{-1}. This strongly supports the premise that these two complexes are of the same geometry.

Figure 6 presents the infrared spectrum of *s-cis*-

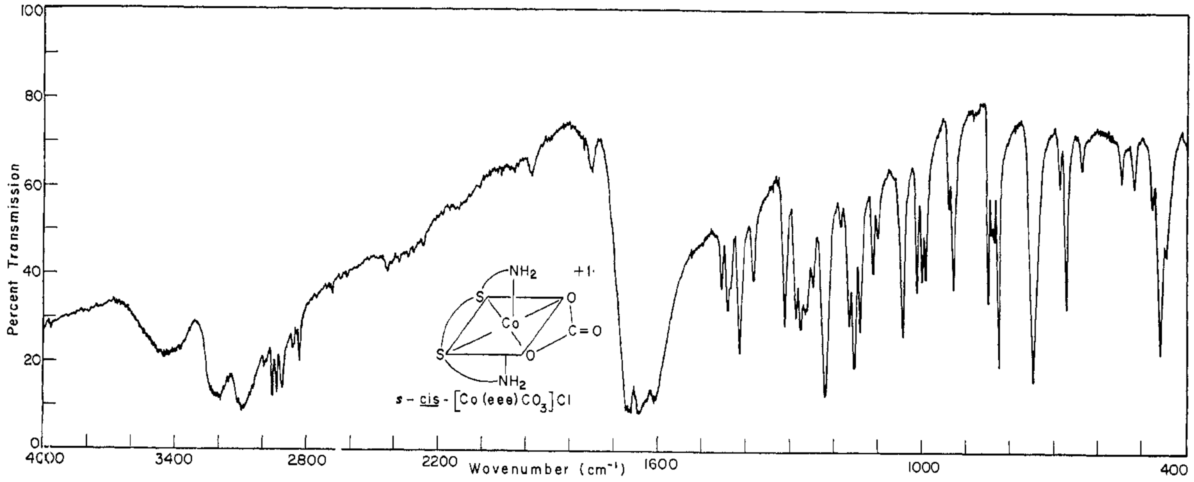

Figure 6.—Infrared spectrum of *s-cis*-[Co(eee)CO_3]Cl.

[Co(eee)CO_3]Cl. The N–H stretching region consists of two prominent bands, one at approximately 3100 cm^{-1} and the second at about 3200 cm^{-1}. The band at 3200 cm^{-1} is broad and appears to consist of two components positioned at 3197 and at 3130 cm^{-1}. Absorptions due to the carbonate group completely obscure the NH_2 deformation range.

The bidentate carbonate group gives rise to absorptions positioned at 460, 672, 749, 828, 1220, 1278, 1605, 1645, and 1670 cm^{-1} in the *s-cis*-[Co(eee)CO_3]Cl complex. Absorptions occurring at these frequencies are fairly intense and are absent in the corresponding dichloro- and dibromo(1,8-diamino-3,6-dithiaoctane)cobalt(III) complexes.

From this infrared investigation, the most obvious conclusion is that geometric structure cannot simply be assigned on the basis of infrared spectra alone, especially if the major criterion for distinguishing *s-cis* from *uns-cis* geometries is to be differences noted in the N–H stretching and NH_2 deformation regions. The observed splittings appear to be a strong function of the anion.

Visible Absorption Spectra.—It should be possible to assign the *s-cis* or *uns-cis* geometric configuration to the Co(eee)L_2^{n+} complexes on the basis of electronic spectra. For convenience, the states are labeled on the basis of the parent octahedron. For the symmetrical *cis* arrangement, characteristic tetragonal splitting of the $^1T_{1g}$ state is expected. This will occur because the average in-plane (*xy*) ligand field will not be the same as the axial field along the *z* axis. In contrast to this, the $^1T_{1g}$ band would *not* be expected to split in the unsymmetrical *cis* structure because then the donor atoms of the quadridentate ligand and two acido groups are positioned so as to result in three unique axial fields of comparable magnitude.

In support of this premise, no splitting is observed for the $^1T_{1g}$ band in *uns-cis*-Co(trien)L_2^+ or *uns-cis*-Co(EDDA)en$^+$ type of complexes.[15] Splitting of the $^1T_{1g}$ band is observed, however, for the corresponding *s-cis* isomers.

Typical electronic spectra for various diacido(1,8-diamino-3,6-dithiaoctane)cobalt(III) complexes are illustrated in Figure 7 and are summarized in Table III.

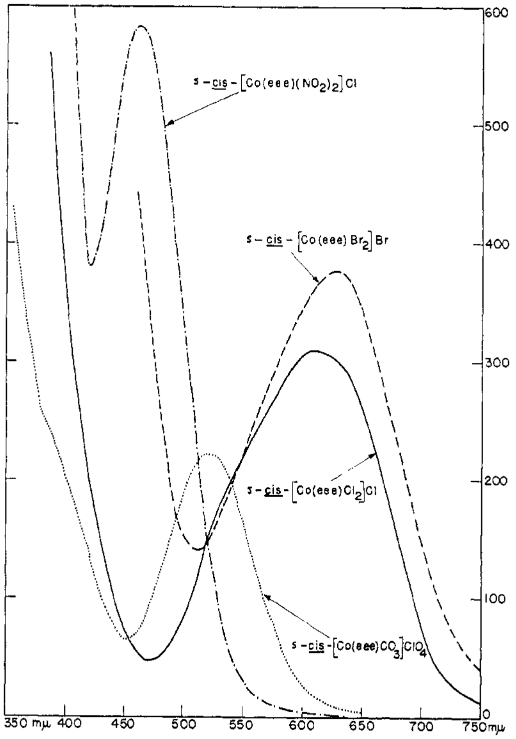

Figure 7.—Visible absorption spectra for diacido(1,8-diamino-3,6-dithiaoctane)cobalt(III) complexes.

The *s-cis*-Co(eee)Cl_2^+ and *s-cis*-Co(eee)Br_2^+ ions exhibit spectra in which a definite splitting of the low-energy $^1T_{1g}$ band is observed. The wavelength of maximum absorption for the principal band of *s-cis*-[Co(eee)Cl_2]Cl is 610 mμ (16,393 cm^{-1}) with a molar extinction coefficient of 308 ± 4. A shoulder occurs on the high-energy side of this principal band at approximately 550 mμ (18,181 cm^{-1}) and appears to be less intense than the major band. It is assumed that the axially positioned NH_2 groups provide a considerably stronger ligand field than do the in-plane chloride and thioether atoms. The intense low-energy component

Table III[a]

Wavelengths of Maximum Absorption and Molar Extinction Coefficients for Various Diacido(1,8-diamino-3,6-dithiaoctane)cobalt(III) Complexes

s-cis compound	λ_{max}, mμ	ϵ_{molar}, M^{-1} cm^{-1}
$[Co(eee)(NO_2)_2]Cl$	463	588 ± 4
	347	11,900
	273	14,600
	235	11,500
$[Co(eee)Cl_2]Cl$	610	308 ± 4
	545 sh	
	282	13,400
	224	13,800
$[Co(eee)Cl_2]ClO_4$	610	309 ± 4
	550 sh	
	288	12,300
	223	13,400
$[Co(eee)Br_2]Br$	628	375 ± 5
	575 sh	
$[Co(eee)CO_3]Cl$	520	215 ± 5
	390 sh	
	303	12,000
	238	9,150

[a] sh = shoulder.

is therefore assigned to the ${}^1A_1 \rightarrow {}^1A_2$ (${}^1T_1$) transition and the higher energy, although less intense, shoulder component is assigned to the ${}^1A_1 \rightarrow E_a$ (${}^1T_1$) transition. Comparable assignments can be made for the other complexes. The results are entirely consistent with the structures assigned.

It is interesting to note that these cobalt(III) complexes have but a single composite absorption at very low energy with molar extinction coefficients from 215 to 588. The tail of an intense charge-transfer band at about 400 mμ (25,000 cm^{-1}) completely obscures the second d–d transition. Thus, the in-plane thioether donor atoms produce spectral effects that provide a contrast to the multidentate ligands containing nitrogen and/or oxygen donor atoms.

Attempted Preparation of *uns-cis* and *trans* Isomers. —The experimental conditions under which the carbonato(triethylenetetramine)cobalt(III) ion is generated determines the resultant geometry of the complex. By treating *s-cis*-dichloro(triethylenetetramine)cobalt(III) chloride with an equivalent quantity of sodium bicarbonate in aqueous solution, the *s-cis*-carbonato compound is produced in better than 90% yield. If instead, excess lithium carbonate is used and the solution is allowed to become alkaline, the resultant species is exclusively of the *uns-cis* geometry. The *uns-cis*-$[Co(trien)CO_3]Cl$ prepared in this way provided the *only* source from which *all* other *uns-cis* complexes could be prepared.[2,11]

Naively, one might expect the corresponding cobalt(III) complex with the quadridentate ligand eee to undergo a similar rearrangement in alkaline solution since it also has two terminal NH_2 groups, and it is simply the movement of one of these groups from the z axis, in the *s-cis* arrangement, to a position on the xy plane that results in the formation of *uns-cis* isomers.

All attempts to produce an *s-cis* isomerization in the preparation of $[Co(eee)CO_3]Cl$ were unsuccessful. Both sodium bicarbonate and lithium carbonate react with the *s-cis*-$[Co(eee)Cl_2]Cl$ to produce the same $[Co(eee)CO_3]Cl$ complex regardless of the temperature, the solvent, or how alkaline the reaction solution is. Prolonged contact with strong base, regardless of temperature, results in a slow decomposition of the complex as evidenced by a change in the color of the solution from red to orange then to brown. The decomposition is accompanied by the generation of a rank odor which is due to the presence of a free-sulfur compound.

That the carbonato complexes produced by these various methods were the same was evidenced by high-resolution infrared spectra in conjunction with chemical interconversion methods. The *s-cis*-$[Co(eee)CO_3]Cl$ complexes were *each* converted to the corresponding dichloro, dibromo, and dinitro derivatives. The infrared spectra of these derivatives were in exact agreement with the infrared spectra obtained for the previously described *s-cis*-$[Co(eee)Cl_2]Cl$, *s-cis*-$[Co(eee)Br_2]Br$, and *s-cis*-$[Co(eee)(NO_2)_2]Br$ complexes which were, in turn, prepared by an independent method. Figure 8 illustrates the lengthy chemical interconversions performed. It is these results which establish the unique geometric stereospecificity with which eee chelates. This, of course, contrasts sharply with the behavior of trien. The interconversions in Figure 8 strongly support the premise that the carbonato complexes are of the *s-cis* geometry.

Attempts to prepare *trans*-$[Co(eee)Br_2]Br$ and *trans*-$[Co(eee)Cl_2]Cl$ were not successful. The methods used included attempted isomerization by heating these compounds in the solid state, water, ethanol, and methanol mixtures. Prolonged heating of *s-cis*-$[Co(eee)Cl_2]Cl$ at 50–70° in methanolic hydrochloric acid followed by evaporation to dryness gave a "green" solid which analyzed correctly for carbon, hydrogen, and nitrogen based on the formulation $[Co(eee)Cl_2]Cl \cdot H_2O$. This material could not be recrystallized from aqueous or alcoholic solvents. Dissolution of this green material immediately imparted a red-brown coloration to the solvent and the compound could not be recovered from solution. Without additional evidence, this compound cannot be considered as a *trans* isomer of $[Co(eee)Cl_2]Cl$.

Further, treatment of *s-cis*-$[Co(eee)Cl_2]Cl$ with hot concentrated hydrobromic acid followed by evaporation at 25° did not yield the *trans* isomer but yielded instead *s-cis*-$[Co(eee)ClBr]Br$. This compound occurs as deep green rhombic plates and its formulation is consistent with analyses and its reactivity toward mercury(II) ion in acid solution. The *s-cis*-$Co(eee)Br_2^+$ ion reacts immediately with Hg(II) to give the diaquo complex. The *s-cis*-$Co(eee)Cl_2^+$ ion reacts much more slowly, the first chloride ion being removed in about 2 min giving the aquochloro complex. Formation of the diaquo species then required an additional reaction time of several hours. The above $Co(eee)ClBr^+$ ion reacted immediately to give the $Co(eee)ClH_2O^{2+}$ ion which

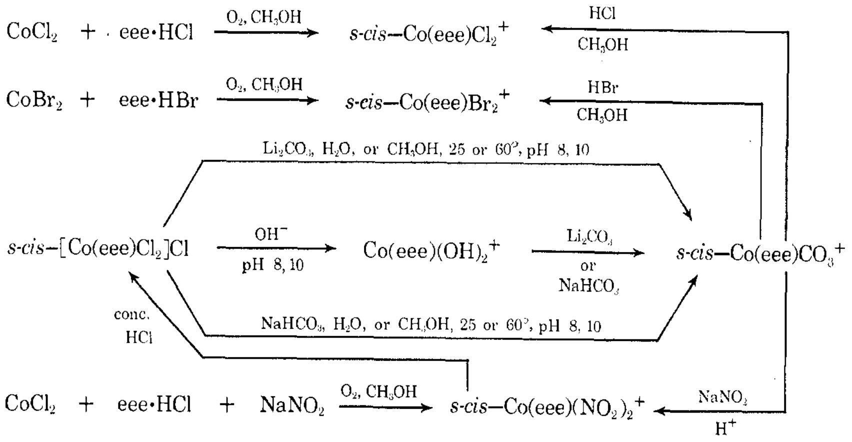

Figure 8.—Chemical interconversion methods used to characterize *s-cis*-Co(eee)CO_3^+.

slowly aquated to the diaquo compound in the presence of Hg(II).

From the foregoing work, it is concluded that the methods reported for the preparation of *trans*-[Co(trien)L_2]L by Selbin and Bailar[20] do not give *trans*-[Co(eee)L_2]L compounds. It should be noted that Buckingham[18] and Searle[1] reported that the *trans* derivatives of *trien* can only be prepared from the corresponding *uns-cis* isomers.

In the present work, even after detrmined efforts, no evidence could be found suggesting the existence of either the *trans* or the unsymmetrical *cis* geometry.

Hydrolysis of Polypeptides.—Of particular significance is the cobalt(III)-promoted selective N-terminal hydrolysis of polypeptides and related compounds. It was found that *s-cis*-Co(eee)Cl_2^+ and *s-cis*-Co(eee)Br_2^+ react at room temperature with glycine, glycine esters, and glycylglycine to give the corresponding glycinato complex [Co(eee)NH_2CH_2COO]L_2 (where $L^- = Cl^-$, Br^-, ClO_4^-). Exploratory attempts to isolate the chloroglycinato methyl and ethyl ester complexes [Co(eee)(NH_2CH_2COOR)Cl]Cl were unsuccessful, the totally hydrolyzed glycinato chelate always being the final isolatable cystalline product. The infrared spectra taken in KBr of the bromide and perchlorate salts exhibit broad N–H stretching ranges with major components at 3065 and 3160 cm^{-1}. The NH_2 deformation bond is a singlet position at 1593 cm^{-1}. The coordinated carbonyl group has an intense band at 1648 cm^{-1} as compared to the free carbonyl having a C–O stretch at about 1700 cm^{-1}. Work in this area is continuing.

Acknowledgments.—We are greatful to the National Science Foundation for support of this work. J. H. W. wishes to thank Dr. Tom MacDermott for bringing to his attention the fact that the chelate chemistry of dithia-α,ω-diamines had not previously been investigated.

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