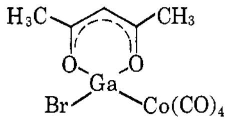
plexes such as $\mathrm{[Ga(dioxane)_2]Cl}$ from gallium dichloride in benzene suggests that species such as $\mathrm{ClGa(THF)_3}$ and $\mathrm{Cl_3Ga(THF)}$ may be present. Then one could visualize a reaction sequence such as

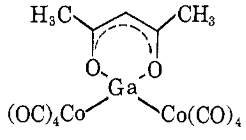
$$\mathrm{ClGa(THF)_3 + Co_2(CO)_8 \longrightarrow ClGa[Co(CO)_4]_2\cdot THF}$$

$$\mathrm{ClGa[Co(CO)_4]_2\cdot THF + Cl_3Ga\cdot THF \longrightarrow 2Cl_2GaCo(CO)_4\cdot THF}$$

The dichlorogallium derivative forms white needles which rapidly deliquesce in air, giving rise to the characteristic odor of cobalt carbonyl hydride. The dibromo derivative $\mathrm{Br_2GaCo(CO)_4\cdot THF}$ does not deliquesce, although both derivatives undergo rapid oxidation in air. Reaction of the latter with thallium(I) acetylacetonate affords compound III.



III



IV

Monohalogenogallium derivatives resulted from the reaction (X = Cl or Br)

$$\mathrm{X_2GaCo(CO)_4\cdot THF + NaCo(CO)_4 \longrightarrow XGa[Co(CO)_4]_2\cdot THF + NaX}$$

Again, the chloro derivative was deliquescent; the bromo derivative was less stable thermally. The acetylacetone derivative IV was prepared from $\mathrm{BrGa[Co(CO)_4]_2\cdot THF}$ and $\mathrm{TlC_5H_7O_2}$ or, rather unexpectedly, from $\mathrm{Br_2GaCo(CO)_4\cdot THF}$ and 2 moles of $\mathrm{TlC_5H_7O_2}$. A reaction sequence that would account for these products might involve the initial formation of III, followed by its reaction with a second mole of $\mathrm{TlC_5H_7O_2}$ to release $\mathrm{Co(CO)_4^-}$.

$$\mathrm{Br_2GaCo(CO)_4\cdot THF + TlC_5H_7O_2 \longrightarrow Br(acac)GaCo(CO)_4 + TlBr}$$

$$\mathrm{Br(acac)GaCo(CO)_4 + TlC_5H_7O_2 \longrightarrow [(acac)_2Ga]^+Co(CO)_4^- + TlBr}$$

$$\mathrm{Br(acac)GaCo(CO)_4 + Co(CO)_4^- \longrightarrow (acac)Ga[Co(CO)_4]_2 + Br^-}$$

By reaction of the gallium(III) halides with the stoichiometric quantity of $\mathrm{NaCo(CO)_4}$, one or two halide ions can be displaced. Excess $\mathrm{NaCo(CO)_4}$ does not displace the third halide group under our experimental conditions, and we did not obtain the tris(tetracarbonylcobalt)gallium compound.

Formally, the Tl(I)–Tl(III) system meets the requirements for insertion into $\mathrm{Co_2(CO)_8}$. Thallium(I) halides were too insoluble to react, and the moderately soluble thallium(I) acetylacetonate was investigated. However, the product of the reaction was $\mathrm{Tl[Co(CO)_4]_3}$ rather than the simple insertion product $\mathrm{(acac)Tl[Co(CO)_4]_2}$. A possible sequence of reactions is

$$\mathrm{Tl^+acac^- + Co_2(CO)_8 \longrightarrow (THF)_{\mathit{x}}Co(acac)_2 + TlCo(CO)_4 + CO}$$

$$\mathrm{TlCo(CO)_4 + Co_2(CO)_8 \longrightarrow Tl[Co(CO)_4]_3}$$

Thallium(III) chloride and excess $\mathrm{NaCo(CO)_4}$ gave the same product; in cyclohexane solution, this compound decomposed rather rapidly with formation of $\mathrm{Co_2(CO)_8}$.

Infrared data are listed in Table II and representative spectra are shown in Figures 1–4. In those cases where the molecular symmetry can be inferred, assuming trigonal-pyramidal $\mathrm{Co(CO)_4}$ groups, the observed number of strong carbonyl stretching bands is in accord with group theoretical predictions.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NEW MEXICO STATE UNIVERSITY,
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Some Cobalt(III) Complexes of Glycine

BY M. DALE ALEXANDER[1] AND DARYLE H. BUSCH

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Two new cobalt(III) complexes containing monodentate glycine, *cis*-chloro(N-glycine)- and *cis*-chloro(N-glycinato)bis(ethylenediamine)cobalt(III) chloride, have been prepared and characterized *via* elemental analyses, conductivity measurements, and visible and infrared spectral data. The latter of these is isomeric with the well-known complex glycinatobis(ethylenediamine)cobalt(III) chloride and readily isomerizes to this complex in aqueous solution. The other new complex is an acid having a strength comparable to that of glycine hydrochloride.

Introduction

The complex glycinatobis(ethylenediamine)cobalt(III) chloride, $\mathrm{[Co(en)_2(NH_2CH_2CO_2)]Cl_2}$, was prepared by Meisenheimer a number of years ago by the reaction of glycinate ion, $\mathrm{NH_2CH_2CO_2^-}$, with *trans*-$\mathrm{[Co(en)_2Cl_2]Cl}$ in aqueous solution.[2] After characterizing the complex by means of elemental analysis and resolu-

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(2) J. Meisenheimer, *Ann.*, **438**, 217 (1924).

tion into optical antipodes, this author proposed the presently accepted structure for the complex in which two ethylenediamines and a glycinate ion are chelated to the metal ion.

We have now prepared a monodentate glycine complex, *cis*-chloro(N-glycine)bis(ethylenediamine)cobalt(III) chloride, and its conjugate base, *cis*-chloro(N-glycinato)bis(ethylenediamine)cobalt(III) chloride, the latter of which is a novel isomer of the chelated glycinato complex. Herein, these two new complexes are described and various properties of the isomeric glycinato complexes are compared.

Experimental Section

Preparation of Glycinatobis(ethylenediamine)cobalt(III) Chloride.—A new method of preparing this complex was developed. Twenty grams of *trans*-$[Co(en)_2Cl_2]Cl$ was suspended in 40 ml of water and to this was added 8.1 g of silver oxide. Using a mortar and pestle, this mixture was ground periodically over a period of 1 hr. Silver chloride was removed by filtration and washed with hot water until the combined filtrate and washings totaled about 80 ml. In this solution was dissolved 6.9 g of glycine. The solution, which was red in color, was evaporated on a steam bath under a stream of air to a syrup. On cooling and standing at room temperature, extensive crystallization occurred; orange crystals of the crude product were filtered, washed with a little cold water, and recrystallized from water. The complex was dried *in vacuo* overnight over $Mg(ClO_4)_2$ at 25°. *Anal.* Calcd for $Co(C_6H_{20}N_5O_2)Cl_2 \cdot H_2O$: C, 21.1; H, 6.5; N, 20.5; Cl, 20.7. Found: C, 21.8; H, 6.5; N, 20.4; Cl, 20.6.

Preparation of *cis*-Chloro(N-glycine)bis(ethylenediamine)cobalt(III) Chloride.—Eight grams of the glycine methyl ester complex, *cis*-$[Co(en)_2(NH_2CH_2CO_2CH_3)Cl]Cl_2$, prepared as described by Alexander and Busch,[3] was shaken with 100 ml of 4 *M* hydrochloric acid for 24 hr. Isopropyl alcohol, 200 ml, was added to this mixture, and after cooling in ice for several hours, the red crystalline product was removed by filtration. The product was taken up in a minimum of water and recrystallized by adding saturated sodium chloride solution. This recrystallized product was filtered and washed successively with methanol, ethanol, and ether and dried *in vacuo* overnight over P_4O_{10} at 50°. *Anal.* Calcd for $Co(C_6H_{21}N_5O_2Cl)Cl_2$: C, 20.0; H, 5.9; N, 19.4. Found: C, 19.7; H, 5.9; N, 19.3.

Preparation of *cis*-Chloro(N-glycinato)bis(ethylenediamine)cobalt(III) Chloride.—An aqueous solution containing 2.8 g (0.0068 mole) of *cis*-$[Co(en)_2(NH_2CH_2CO_2H)Cl]Cl_2$, prepared as described above, in 17.5 ml of water was mixed rapidly with a solution containing 7.5 ml of water, 2.5 ml of ethanol (95%), and 1.05 ml of triethylamine (0.0068 mole). The resulting solution was immediately mixed with 350 ml of ethanol (95%) causing extensive precipitation. After cooling the mixture in ice, the ruby-red crystalline precipitate was filtered, washed with ethanol, and dried *in vacuo* overnight over P_4O_{10} at 50°.

Infrared Spectra.—Infrared spectra were obtained using Perkin-Elmer Models 21 and 137 infrared spectrophotometers both of which were equipped with sodium chloride optics. Nujol mulls and deuterium oxide solutions were employed. For measurements with D_2O solutions, the cell used consisted of two calcium fluoride plates separated by an aluminum spacer (0.003-in. thickness) coated with silicone grease to protect it from acid. Concentrations of D_2O solutions were 0.150 g of complex/1.0 ml of D_2O. Some measurements were made with acidified D_2O solutions. To acidify a solution, 0.05 ml of 70% perchloric acid was added to 1.0 ml of solution.

Determination of pK_a of *cis*-$[Co(en)_2(NH_2CH_2CO_2H)Cl]Cl_2$.—The pK_a of the complex was determined from measurements of pH of solutions containing both *cis*-$[Co(en)_2(NH_2CH_2CO_2H)Cl]^{2+}$ and *cis*-$[Co(en)_2(NH_2CH_2CO_2)Cl]^+$. A solution 0.010 *M* in *cis*-$[Co(en)_2(NH_2CH_2CO_2H)Cl]Cl_2$ and 0.005 *M* in NaOH was prepared by dissolving 0.213 g of complex in 25 ml of water, rapidly mixing this solution with 3.74 ml of 0.067 *M* NaOH, and adjusting the total volume to 50 ml. A solution 0.010 *M* in *cis*-$[Co(en)_2(NH_2CH_2CO_2)Cl]Cl$ and 0.005 *M* in HCl was prepared in a similar manner except that 0.195 g of this complex and 2.51 ml of 0.098 *M* HCl were used. The pH values of the two solutions, measured with a Beckman expanded-scale pH meter at 25°, were 2.75 and 2.67, respectively. Assuming activity coefficients of unity, the approximate pK_a calculated from the above pH measurements was found to be 2.1.

Visible Spectra.—Visible spectra were obtained using a Cary Model 14 recording spectrophotometer and a Beckman Model DB spectrophotometer equipped with a recorder. One-centimeter silica cells were employed. Measurements were made on aqueous solutions (0.0200 g of complex/10.00 ml of water). For the visible spectrum of *cis*-$[Co(en)_2(NH_2CH_2CO_2H)Cl]Cl_2$, 0.1 *M* HCl was used instead of water in order to suppress the ionization of the acid function.

Conductivity Measurements.—Measurements were made at 25°, using an Industrial Instruments conductivity bridge, upon aqueous solutions of the complexes (0.0010 *M*). Molar conductivities for $[Co(en)_2(NH_2CH_2CO_2)]Cl_2$, $[Co(en)_2(NH_2CH_2CO_2H)Cl]Cl_2$, and $[Co(en)_2(NH_2CH_2CO_2)Cl]Cl$ were 252, 402, and 104 $ohm^{-1}\ cm^2$, respectively.

Isomerization of *cis*-Chloro(N-glycinato)bis(ethylenediamine)cobalt(III) Chloride to Glycinatobis(ethylenediamine)cobalt(III) Chloride.—The solution of *cis*-$[Co(en)_2(NH_2CH_2CO_2)Cl]Cl$, prepared for determining the visible spectrum of the complex, was observed to change from red to orange on standing for a period of 2 weeks. The visible spectrum of the resulting solution was found to be indistinguishable from that of the chelated glycinato complex (maxima at 346 and 487 mμ with molar extinction coefficients of 107 and 98, respectively). The infrared spectrum of a deuterium oxide solution of the complex after standing for a similar period was found to contain an intense band at 1640 cm^{-1}, the position of the CO-stretching band in the chelated glycinato complex. Evaporation of the solution to dryness yielded the glycinato complex identified *via* its infrared spectrum.

Esterification of Glycinatobis(ethylendiamine)cobalt(III) Chloride.—$[Co(en)_2(NH_2CH_2CO_2)]Cl_2$ (0.5 g) was finely powdered and suspended in 200 ml of ethanolic hydrogen chloride (approximately 1 *M* in HCl). The mixture was refluxed for 6 hr and then filtered, while hot, to remove a small amount of unreacted glycinato complex. On cooling overnight in a refrigerator, red needles of the glycine ethyl ester complex, *cis*-$[Co(en)_2(NH_2CH_2CO_2C_2H_5)Cl]Cl_2$, crystallized out of the solution. The complex was identified *via* comparison of its infrared spectrum to that of the complex prepared by other means.[3]

Results and Discussion

Alexander and Busch have prepared a series of glycine ester complexes of cobalt(III) having the formulation *cis*-$[Co(en)_2(NH_2CH_2CO_2R)Cl]Cl_2$, in which the ester functions as a monodentate ligand coordinating through the amine group.[3] If the methyl ester complex is allowed to stand in strongly acidic aqueous solution for several hours, a ruby-red crystalline material can be isolated from solution which is not the methyl ester complex.

Elemental analysis indicates that the material is a complex of the formulation $Co(en)_2(NH_2CH_2CO_2H)Cl_3$, which in turn indicates hydrolysis of the dangling ester function has occurred. If the only change which occurs is ester hydrolysis, then structure I is expected for the complex. A number of observations confirm this structure.

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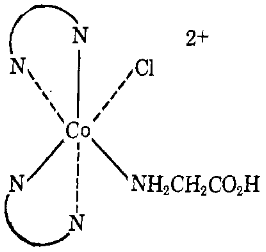
(3) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, **5**, 602 (1966).



I

In the infrared spectrum of the complex, a sharp and intense band occurs at 1735 cm^{-1}. Since this is in the region where CO-stretching bands of α-amino acid hydrochlorides are found,[4] the presence of the acid function is indicated.

The pK_a of the acid function was found to be approximately 2.1, which is very low for alkylcarboxylic acids but quite similar to that of glycine hydrochloride ($pK_a = 2.34$.)[5] Since the low pK_a for glycine hydrochloride is due to the presence of the positive charge of the ammonium function, the pK_a of the complex is consistent with the proposed structure.

The visible spectrum of the complex, which consists of two bands, is indistinguishable from the spectra of the glycine ester complexes, *cis*-$[Co(en)_2(NH_2CH_2CO_2R)Cl]Cl_2$, and is very similar to that of *cis*-$[Co(en)_2NH_3Cl]Cl_2$ (Table I). This not only substantiates the chloro(amine)bis(ethylenediamine)cobalt(III) formulation but also indicates the *cis* configuration. The bands in the spectrum would be expected to be significantly less intense if the configuration were *trans*.[3,6]

Table I

Visible Spectral Data

Compd	$\lambda_{max} \pm 2$, $m\mu$	$\epsilon_{max} \pm 2$, $M^{-1}\ cm^{-1}$
cis-$[Co(en)_2(NH_2CH_2CO_2H)Cl]Cl_2$	525	79
	365	83
cis-$[Co(en)_2(NH_2CH_2CO_2R)Cl]Cl_2{}^a$	526	77
	366	82
cis-$[Co(en)_2(NH_3)Cl]Cl_2$	525^b	73^b
	365^b	77^b
cis-$[Co(en)_2(NH_2CH_2CO_2)Cl]Cl$	525	80
	365	83
$[Co(en)_2(NH_2CH_2CO_2)]Cl_2$	487	98
	346	107

[a] $R = CH_3, C_2H_5, i\text{-}C_3H_7$. [b] R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).

Further verification of the *cis* assignment is obtained from infrared data. In the region around 890 cm^{-1}, bands occur assigned to CH_2-rocking modes in ethylenediamine chelate rings. In the case of bis(ethylenediamine)cobalt(III) complexes, a single CH_2-rocking band occurs for *trans* isomers while the band is split into at least two components for *cis* isomers.[7] This splitting is observed in the particular case of *cis*-$[Co(en)_2(NH_2R)Cl]Cl_2$ complexes.[8] In the spectrum of the glycine complex, the CH_2-rocking band is indeed split (bands occur at 890 and 880 cm^{-1}).

The molar conductance of the complex is 402 $ohm^{-1}\ cm^2$. This is much too high for a di-univalent electrolyte (normal range for 0.001 *M*, 225–270 $ohm^{-1}\ cm^2$)[9] but is not inconsistent with the proposed structure since the acid function, at 0.001 *M* concentration, is approximately 90% dissociated (the molar conductance of 0.001 *M* HCl is 432 $ohm^{-1}\ cm^2$).

It is possible to isolate the conjugate base of the acid complex after reaction of the acid complex with an equimolar amount of triethylamine in aqueous solution. The conjugate base would be expected to have a structure analogous to that of the acid complex with a glycinate ion functioning as a monodentate ligand. This structure is verified by the following data. (1) The visible spectrum of the complex is indistinguishable from that of the conjugate acid, Table I. (2) Its molar conductance is 104 $ohm^{-1}\ cm^2$, which is in the range for uni-univalent electrolytes (96–115 $ohm^{-1}\ cm^2$).[9] (3) Its infrared spectrum has an intense band at 1600 cm^{-1}, where carboxylate ions absorb, and a pair of bands in the CH_2-rocking region (895 and 880 cm^{-1}).

This complex is isomeric with the chelated glycinato complex, $[Co(en)_2(NH_2CH_2CO_2)]Cl_2$, and can be considered as being derived from the chelated complex by opening the glycinato chelate ring at the carboxylate group and placing chloride in the vacated coordination site.

In the visible spectrum of the chelated glycinato complex, bands occur at 346 and 487 $m\mu$, which result from d–d transitions. These bands are higher in frequency than the two bands in the spectrum of the monodentate complex (Table I), which reflects the relative positions of carboxylate and chloride in the spectrochemical series.[10]

An intense CO-stretching band occurs at 1640 cm^{-1} in the infrared spectrum of the chelated complex, while for the monodentate complex the CO-stretching band is at 1600 cm^{-1}. The higher frequency for the coordinated carboxylate is expected.[11] In the spectra of the complexes dissolved in deuterium oxide, the positions of the CO bands are unchanged with respect to the solid-state spectra. If their solutions are made strongly acidic, the band in the chelated case changes very little, <10 cm^{-1}, while in the monodentate case, the band shifts to 1735 cm^{-1}, the position of the CO band in the acid complex. These observations further confirm the chelated and monodentate structures for the respective complexes.

On the basis of the chelate effect,[12] the chelated structure would expectedly be more stable than the monodentate structure. This is borne out experimentally, for the monodentate complex readily isom-

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(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 242.

(5) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943.

(6) T. Yasui and Y. Shimura, *Bull. Chem. Soc. Japan*, **36**, 1286 (1963).

(7) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).

(8) S. C. Chan and F. Leh, *ibid.*, A129 (1966).

(9) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 254.

(10) W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956).

(11) F. A. Cotton, "Modern Coordination Chemistry," Interscience Publishers, New York, N. Y., 1960, Chapter 5.

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erizes to the chelated glycinato complex in aqueous solution.

Attempts to open the glycinato chelate ring by heating the complex in concentrated hydrochloric acid were unsuccessful. This method has been used to open one of the chelate rings (an NRR'CH$_2$CO$_2^-$ chelate ring) in ethylenediaminetetraacetatocobaltate-(III) ion to yield chloro(ethylenediaminetriacetatoacetic acid)cobaltate(III) ion.[13]

The chelate ring can be opened, however, if the glycinato complex is refluxed in ethanolic HCl for several hours. In this case esterification of the glycine occurs without rupture of any amine–cobalt(III) bonds to yield the glycine ester complex, *cis*-[Co(en)$_2$(NH$_2$CH$_2$CO$_2$C$_2$H$_5$)Cl]Cl$_2$.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[13] F. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **80**, 4480 (1958).

CONTRIBUTION FROM THE W. A. NOYES LABORATORY,
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Optical Activity and Electronic Spectra. Pseudo-tetragonal *l*-Cyclohexanediamine Complexes of Cobalt(III)

BY R. S. TREPTOW[1]

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A series of pseudo-tetragonal complexes of *l-trans*-1,2-diaminocyclohexane (*l*-chn) have been prepared. The ions studied are *trans*-[Co(*l*-chn)$_2$X$_2$]$^+$ (where X$^-$ = F$^-$, Cl$^-$, Br$^-$, and NO$_2^-$), *trans*-[Co(*l*-chn)$_2$(NH$_3$)$_2$]$^{3+}$, and *trans*-[Co(*l*-chn)$_2$(NH$_3$)Cl]$^{2+}$. Absorption, circular dichroism, and optical rotatory dispersion spectra are reported in the region 220–700 mμ. Assignments of the ligand field and charge-transfer transitions are made using selection rules applicable to circular dichroism curves. Rotational strengths and absorption intensities are discussed.

Introduction

The correlation of circular dichroism, optical rotatory dispersion, and electronic absorption spectra of optically active coordination compounds provides a valuable tool in the study of electronic and molecular structure. This is largely due to the unique selection rules and resolving power of circular dichroism. Two recent reviews underline the principles involved.[2,3]

Most of the complexes investigated to date have been of trigonal symmetry, such as tris(ethylenediamine)cobalt(III) of the D$_3$ point group. Another optically active geometry, that of D$_2$ symmetry, presents a new opportunity for investigation. These "digonal dihedral" compounds have been considered in a recent theoretical treatment by Liehr.[4] Experimental results have been reported on *trans*-diacidobis(*l*-propylenediamine)cobalt(III) complexes, which approximate D$_2$ symmetry.[5]

We now report some complex ions of exact D$_2$ or C$_2$ symmetry. They are *trans*-[Co(*l*-chn)$_2$X$_2$]$^+$ (where X$^-$ = F$^-$, Cl$^-$Br$^-$, and NO$_2^-$), *trans*-[Co(*l*-chn)$_2$(NH$_3$)$_2$]$^{3+}$, and *trans*-[Co(*l*-chn)$_2$NH$_3$Cl]$^{2+}$. The optically active chelate *l*-chn (*l-trans*-1,2-diaminocyclohexane) was first synthesized and resolved by Jaeger and co-workers.[6] Only *trans*-[Co(*l*-chn)$_2$Cl$_2$]$^+$ has been previously reported.[5b,6c,7] A series of various X ligands has been used in the present work to provide a more extensive study. They were chosen to represent a variety of bonding types and positions in the spectrochemical series. Another purpose in changing the *trans* ligands was to determine their influence on optical activity.

Experimental Section

Resolution of the Ligand.—*trans*-1,2-Diaminocyclohexane sulfate, purchased from Aldrich Chemical Co., was dissolved in boiling water with the calculated amount of Ba(OH)$_2\cdot$8H$_2$O. After cooling, the thick BaSO$_4$ precipitate was removed by centrifugation. Resolution[6b] was accomplished by precipitation as the *d*-tartrate salt from hot aqueous solution. The less soluble diastereoisomer, *l*-chn *d*-tartrate, was recrystallized to a constant optical rotation, $[\alpha]_D$ +12.0° (lit.[6b] +11°). *Anal.* Calcd for C$_{10}$H$_{20}$N$_2$O$_6$: C, 45.44; H, 7.63; N, 10.60. Found: C, 45.54; H, 7.68; N, 10.61.

For preparative purposes a stock solution of *l*-chn was conveniently made by addition of the calculated amount of Ba(OH)$_2\cdot$8H$_2$O to a hot suspension of *l*-chn *d*-tartrate. After cooling overnight in an ice bath, the precipitated barium tartrate was removed.

Preparation of the Coordination Compounds.—The syntheses described here are generally modifications of those used to prepare the well-known ethylenediamine analogs. The chemical properties and spectra of complexes formed by the two chelates are very similar. This fact facilitated the characterization of

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[1] This research was begun under the direction of the late Professor T. S. Piper. Because of his untimely death, the results and discussions are entirely those of R. S. Treptow. Address correspondence to Miami Valley Laboratories, Procter and Gamble Company, Cincinnati, Ohio.

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