

off and more perchloric acid was added to the resulting filtrate. By this method the complex was fractionally crystallized and the final fraction had the highest rotation. It was collected and washed as before; $[\alpha]_D -320^\circ$, 0.025% solution in water, 10-cm tube, $\alpha_D -0.08^\circ$. *Anal.* Calcd for $[\text{Ru}(\text{bipy})_2\text{phen}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ($\text{RuC}_{32}\text{H}_{28}\text{N}_6\text{O}_{10}\text{Cl}_2$): C, 46.3; H, 3.4; N, 10.1. Found: C, 46.7; H, 3.1; N, 10.4.

The diastereoisomer obtained from the $\text{Ru}(\text{bipy})_2\text{phen}^{2+}$ ion is much more soluble in water than that obtained from the $\text{Ru}(\text{phen})_2\text{bipy}^{2+}$ ion, and it is probable that, with larger amounts of the $[\text{Ru}(\text{bipy})_2\text{phen}]\text{Cl}_2$ salt and smaller volumes of water, the $(-)\text{-Ru}(\text{bipy})_2\text{phen}^{2+}$ ion could be obtained optically pure

in convenient amounts. However, the two (+) isomers used for the circular dichroism studies are probably optically pure.

The absorption spectra were measured using a Unicam SP-800-B (recording) spectrophotometer and the circular dichroism spectra were obtained using a Roussel-Jouan Dichrographe (sensitivity 1.5×10^{-4}).

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Nuclear Magnetic Resonance Determination of the Absolute Configuration of Complexes of Cobalt(III) with Asymmetric Tetradentate Ligands^{1a}

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The preparation, separation, and characterization of a series of cobalt(III) complexes containing the asymmetric tetradentate ligand ethylenediamine-*N,N'*-di-*L*- α -propionate (LL-EDDP) or -*D*- α -propionate (DD-EDDP) and ethylenediamine (en) or *l*-propylenediamine (*l*-pn) are reported. The absolute configurations of the complexes are assigned by considering the proton nmr spectra and the known configuration of the ligand. The *L-trans*-LL-EDDP isomer with the methyl group pointed toward the en exhibits a complicated en signal due to steric interaction. The acetate proton pattern confirms that the proton points toward the tetradentate backbone. In the *D-trans* isomer the methyl group points toward the backbone and a single en peak is observed plus an acetate proton pattern consistent with the proton pointing toward the en. Similar results were obtained for the other complexes. ORD and CD data confirm the nmr assignments.

Introduction

The study of the stereochemistry of the octahedral complexes of cobalt(III) has been the object of a large number of investigations during the past half-century.² In only a small minority of these cases, however, has an optically active ligand been utilized to influence the stereochemistry. Complexes containing optically active diamines and α -aminocarboxylic acids have been extensively studied.² However, few complexes with optically active multidentate chelating agents are known. The stereochemistry with optically active analogs of the tetradentate ligand triethylenetetramine has been studied. Asperger and Liu³ utilized optically active *L,L*-2,9-diamino-4,7-diazadecane and observed stereospecific formation of only the *D*- α -*cis* and *L*- β -*cis* optical isomers as determined by the ligand stereochemistry. Worrell and Busch⁴ prepared complexes from racemic 4-methyl-1,8-diamino-3,6-dithiaoctane and obtained the α -*cis* and β -*cis* complexes as racemates. Gill⁵ described the linear hexadentate ligand 3,10-bis-

(salicylideneamino)-5,8-dithiadodecane but did not investigate the isomerism of its metal complexes. Dwyer and MacDermott⁶ obtained only the isomers *D*-(-) and *L*-(+) upon the reaction of racemic 4-methyl-1,8-bis(salicylideneamino)-3,6-dithiaoctane although three apparently uncrowded and strain-free forms exist for each isomer of the base. Utilizing optically active ligand, 85% *D*-(-) and 15% *L*-(-) were obtained. Complexes prepared with optically active analogs of EDTA coordinate stereospecifically as found by Dwyer and Garvan⁷ with complexes of propylenediaminetetraacetic acid and *trans*-1,2-cyclohexanediaminetetraacetic acid. Legg and Cooke⁸ have shown that the steric requirements of *D*-(or *L*-)aspartate (aspart), functioning as a tridentate ligand, dictate the formation of both geometric and optical isomers in the complex $\text{Co}(\text{D- or L-aspart})(\text{dien})^+$.

The preparation, separation, and characterization of a series of cobalt(III) complexes containing the asymmetric tetradentate ligand ethylenediamine-*N,N'*-di-*L*- α -propionate (LL-EDDP) or -*D*- α -propionate (DD-EDDP) are reported in this paper. The ligands were prepared by allowing optically active alanine of known configuration to react with 1,2-dibromoethane. Complexes containing ethylenediamine or propylenedi-

(1) (a) Abstracted in part from the Ph.D. thesis of L. N. Schoenberg, The University of Michigan, 1966. (b) Author to whom correspondence should be addressed at the Department of Chemistry, Western Michigan University, Kalamazoo, Mich.

(2) See F. P. Dwyer and D. P. Mellor, "Chelating Agents and Metal Chelates," Academic Press, New York, N. Y., 1964, for references.

(3) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1395 (1965).

(4) J. H. Worrell and D. H. Busch, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, p 250.

(5) N. S. Gill, Ph.D. Thesis, University of Sydney, 1951, p 101.

(6) F. P. Dwyer and T. E. MacDermott, *J. Am. Chem. Soc.*, **85**, 2916 (1963).

(7) F. P. Dwyer and F. L. Garvan, *ibid.*, **83**, 2610 (1961).

(8) J. I. Legg and D. W. Cooke, *ibid.*, **89**, 6854 (1967).

amine in the fifth and sixth positions were prepared and separated into *cis* and *trans* isomers using the method of Legg and Cooke⁹ for the similar ethylenediamine-*N,N'*-diacetate complexes.

Experimental Section

Preparation of Ethylenediamine-*N,N'*-di-*L*- α -propionic Acid.—The general method of Bersworth¹⁰ was followed. Twenty grams (0.5 mol) of sodium hydroxide in 37.5 ml of water was added to 44.5 g (0.05 mol) of *L*-alanine. The solution was heated to reflux and 47 g (0.25 mol) of ethylene dibromide and 34.5 g (0.25 mol) of potassium carbonate were slowly added. The solution was stirred under reflux for 3 hr with some difficulty toward the end owing to undissolved potassium carbonate. Cooling and neutralization to a pH of 5 with concentrated hydrochloric acid resulted in the formation of the solid white product. This was washed well with water and air dried. The yield was 5.9 g or 11.6%. The melting point was 256–258°.

Anal. Calcd for $C_5H_{10}N_2O_4$: C, 46.90; H, 7.89; N, 13.70. Found: C, 46.81; H, 7.65; N, 13.71. The procedure for making ethylenediamine-*N,N'*-di-*D*- α -propionic acid was identical except that *D*-alanine was used.

Preparation and Isolation of the Isomers of Ethylenediamine-*N,N'*-di-*L*- α -propionato(ethylenediamine)cobalt(III) Perchlorate.—The method of Legg and Cooke for the related ethylenediamine-diacetic acid complexes was followed.⁹ To a suspension of 4.32 g (0.036 mol) of cobalt carbonate in 350 ml of water were added 7.32 g (0.036 mol) of ethylenediamine-*N,N'*-di-*L*- α -propionic acid, 3.24 g (0.036 mol) of concentrated nitric acid diluted to 50 ml, 1 g of activated charcoal, and 2.36 ml (0.036 mol) of 98% ethylenediamine diluted to 50 ml. The charcoal was added to favor the formation of an equilibrium mixture of isomers. The mixture was heated on the steam bath to about 60° and 4.08 g (0.036 mol) of 30% hydrogen peroxide diluted to 50 ml was added dropwise. The ethylenediamine-*N,N'*-di-*L*- α -propionic acid and cobalt carbonate soon dissolved. Heating was continued with occasional stirring for 4 hr. The resulting deep red solution was filtered away from the charcoal and a trace of unreacted cobalt carbonate. It was then added to a large (2000-ml) ion-exchange column about 75% full of 50–100 mesh Dowex 50-WX8 cation-exchange resin in the sodium form. The mixture of complexes formed a compact band at the top. Washing with water removed a purplish material that was not absorbed on the column. Elution with 0.35 *M* sodium perchlorate at the rate of about 1 ml a minute caused a splitting into three bands. A solid, bright red, crystalline product was obtained from each of the first two eluted bands by slow evaporation. A red oil was obtained from the third band. This was dissolved in water and converted to the chloride salt by passing it through a small column of 50–100 mesh Dowex 2-X8 anion-exchange resin. Red crystalline plates were obtained. The yields were 2.3 g of *L-trans* isomer from band I, 2.2 g of *D-trans* isomer from band II, and 0.6 g of *L-cis* isomer from band III.

Anal. Calcd for $[CoC_{10}H_{22}N_4O_4]ClO_4$: C, 28.55; H, 5.27; N, 13.32; Cl, 8.43. Calcd for $[CoC_{10}H_{22}N_4O_4]ClO_4 \cdot H_2O$: C, 27.38; H, 5.51; N, 12.77; Cl, 8.08. Found: *L-trans*: C, 28.36; H, 5.21; N, 13.20; Cl, 8.52; *D-trans*: C, 27.38; H, 5.37; N, 12.70; Cl, 8.04. The *L-cis* isomer proved to be contaminated with sodium chloride. However, the relative amounts of carbon, hydrogen, and nitrogen corresponded well with the formula $[CoC_{10}H_{22}N_4O_4]Cl \cdot 2H_2O$.

Preparation and Isolation of the Isomers of Ethylenediamine-*N,N'*-di-*L*- α -propionato(*l*-propylenediamine)cobalt(III) Perchlorate.—A solution of 22.7 g (0.072 mol) of barium hydroxide octahydrate in 100 ml of water was added to 14.77 g (0.036 mol) of *l*-propylenediamine-*d*-tartrate dihydrate¹¹ in 100 ml of water. The resulting aqueous solution of *l*-propylenediamine was used

in the reaction after removal of the precipitated barium tartrate. The preparation was identical with that of the ethylenediamine complexes except that 5.2 g (0.036 mol) of 70% perchloric acid was used instead of nitric acid. A pink precipitate formed upon slow evaporation of the reaction solution. The yield was 4.0 g of *L-trans* isomer.

After removal of this isomer, the solution was diluted to 400 ml and placed on a large ion-exchange column. After removal of some purple nonabsorbed material by washing with water, elution with 0.5 *M* sodium perchlorate produced two bands. The red crystalline product was obtained from the first band by successive evaporation, removal of sodium perchlorate, addition of ethyl alcohol, and further evaporation until product formed. The yield was 0.4 g of *D-trans* isomer.

In the same way, a very small amount of red *L-cis* isomer was obtained from the second band.

Anal. Calcd for $[CoC_{11}H_{24}N_4O_4]ClO_4$: C, 30.39; H, 5.57; N, 12.89; Cl, 8.16. Found: *L-trans*: C, 30.35; H, 5.62; N, 12.98; Cl, 8.11; *D-trans*: C, 30.27; H, 5.68; N, 12.74; Cl, 8.07.

Preparation and Isolation of the Isomers of Ethylenediamine-*N,N'*-di-*D*- α -propionato(*l*-propylenediamine)cobalt(III) Perchlorate.—The preparation of a solution of the three isomers was identical with the procedure using ethylenediamine-*N,N'*-di-*L*- α -propionic acid except that 0.008-mol quantities of the reagents were used. A pink precipitate was formed upon slow evaporation of the solution. The yield was 0.7 g of *L-trans* isomer. After removal of this isomer, the solution was placed on a small ion-exchange column. After removal of some purple nonabsorbed material by washing with water, elution with 0.5 *M* sodium perchlorate produced a separation into two bands. The pink, powdery *D-trans* isomer was obtained from the first band by successive evaporation, removal of sodium perchlorate, addition of ethyl alcohol, and further evaporation until product formed. The yield was 0.2 g. No solid material was obtained from the second band; however, visible spectra and optical rotatory dispersion curves were obtained from the solution. No elemental analyses were obtained from the last two bands. However, the absorption spectra and the ORD curves showed that they are the isomers indicated here.

Anal. Calcd for $CoC_{11}H_{24}N_4O_4$: C, 30.39; H, 5.57; N, 12.89; Cl, 8.16. Found: *L-trans*: C, 30.28; H, 5.59; N, 13.09; Cl, 8.31.

Electronic Absorption Spectra.—Spectra were recorded at room temperature with a Cary Model 11 spectrophotometer using 10^{-3} *M* solutions in 1-cm cells.

Nuclear Magnetic Resonance Spectra.—Spectra were recorded on a Varian A-60 spectrometer (60 Mc/sec) at about 35°, the internal temperature of the probe. Some of the spectra were re-run on a Varian HA-100 (100 Mc/sec). A reference standard of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (NaTMS) was used. When dissolved in deuteriochloroform, TMS resonates +0.05 ppm from NaTMS in deuterium oxide. All spectra were run in deuterium oxide or a 1:1 volume solution of deuterium oxide and deuteriosulfuric acid. All of the perchlorate salts were converted to the chloride form before the spectra were run in order to obtain sufficient solubility.

Optical Rotatory Dispersion Measurements.—The ORD curves were measured at 50-Å intervals over the range of 6750–3850 Å on a Keston Model D polarimeter attachment for a Beckman DU spectrophotometer. The attachment was manufactured by the Standard Polarimeter Co., Hackensack, N. J., and was calibrated over the working range using freshly prepared sucrose solutions.

Circular Dichroism Measurements.—Circular dichroism spectra were recorded on a Model ORD/W-5 spectrometer manufactured by Japan Spectroscopic Co., Ltd., Tokyo, Japan. Dr. Hans Brintzinger of the University of Michigan cooperated in the use of this instrument.

Elemental Analyses.—All elemental analyses were done by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Reagents.—The *L*- and *D*-alanine were purchased from Nutri-

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

(10) F. C. Bersworth, British Patent 723,316 (1955).

(11) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

tional Biochemical Corp., Cleveland, Ohio. All of the other chemicals used were commercial reagent grade.

Discussion of Results

Separation and Distribution of Isomers.—The tetradentate ligands used in this work were prepared from optically active alanine of known configuration. The absolute configurations of the ligands are as shown in Figure 1. Because the reaction does not involve the optically active carbon center, it is assumed that no isomerization occurred during the preparation. The four possible isomers of $\text{Co}(\text{LL-EDDP})\text{en}^+$ are depicted in Figure 2. The *trans* and *cis* designations refer to the oxygen atoms of the tetradentate ligand. D and L refer to the chirality of the rings around the atom and are in agreement with the choice of nomenclature of Sargeson and Searle,¹² who studied a series of triethylenetetramine complexes. The isomers in this paper are designated by their absolute configurations which are assigned by nmr data.

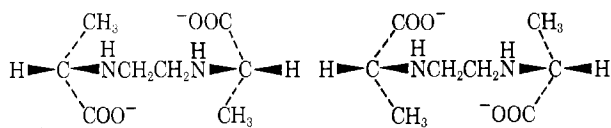


Figure 1.—The configurations of LL-EDDP (left) and DD-EDDP (right).

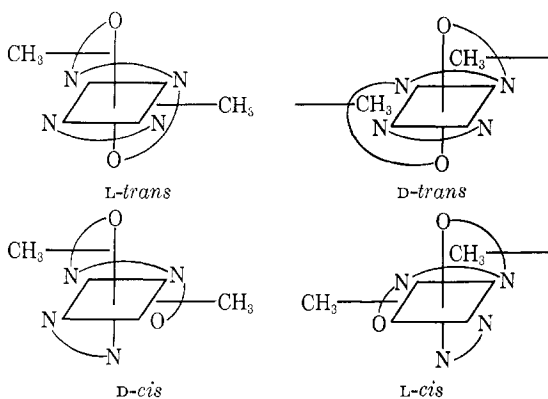


Figure 2.—The four possible isomers of $\text{Co}(\text{LL-EDDP})\text{en}^+$.

The two propionate arms are equivalent in the *trans* isomers. In the *L-trans* isomer both methyl groups point away from the en backbone while in the *D-trans* isomer both point toward the en backbone. The arms are nonequivalent in the *cis* isomers. The propionate arm that is in the plane formed by the cobalt atom and the backbone chelate ring of the tetradentate ligand is designated the meridional arm. The propionate arm that is not in the aforementioned plane is designated the facial arm.

Ion-Exchange Chromatography and Separation of the Isomers.—Ion-exchange chromatography has been in use for the separation of geometric isomers of coordination compounds for about 15 years. Much less work has been carried out on the separation of optical isomers. The present work is one of the first instances of dia-

stereoisomers being separated *via* this procedure on a nonoptically active absorbent.

Denning and Piper¹³ separated the *cis* and *trans* isomers of $\text{Co}(\text{aa})_3$, where aa = the anion of L-leucine or L-proline, on an alumina column. They were able further to separate *trans-Co(L-leu)*₃ into its (+) and (−) components. The remaining optical isomers were separated by crystallization procedures.

The order of elution of complexes in the present work followed the expected order in that the *trans* isomers, with small dipole moments, were eluted before the *cis* isomers. The ordering of the *trans* isomers depended on the absolute configuration of the tetradentate ligand relative to that of the complex. In the complexes with LL-EDDP the *L-trans* isomers eluted before the *D* isomers and with DD-EDDP the *D-trans* isomer eluted first regardless of whether en or *l-pn* was the other ligand. In the complexes eluted first, the methyl groups are pointed away from the en backbone and the complexes are possibly held less strongly owing to the steric interactions of these methyl groups with the resin.

By contrast the relative solubilities appear to depend on the bidentate ligand. With en as a ligand the *L-trans* isomer is more soluble but with *l-pn* both of the *trans* isomers are more soluble than their *L-trans* counterparts.

D-cis-Co(en)(LL-EDDP)⁺ and *L-cis-Co(en)(DD-EDDP)*⁺ were not detected. It is not immediately apparent from molecular models why this should be so. The problem is complicated by the various possible configurations around the nitrogens.¹⁴

In each case there was a much greater yield of *trans* isomers than of *cis* isomer. The tendency of a tetradentate ligand of the type used here to prefer a *trans* orientation has been noted previously.⁹

Electronic Absorption Spectra.—The visible spectra of the LL-EDDP-en complexes are shown in Figure 3, and all of the spectra are summarized in Table I. The wavelengths for the shoulders were obtained by subtracting a symmetrical trace of the major peak from the observed spectra. The assignments of the spectra are consistent with those made by Legg and Cooke⁹ for analogous complexes.

It can be noted that for both *trans* pairs containing LL-EDDP the *D-trans* isomer has slightly more intense bands. The difference is greater in the *l-propylenediamine* pair than in the ethylenediamine pair. Furthermore, the peaks in the *D-trans* isomers are at slightly higher energy than the corresponding peaks in the *L-trans* isomers. By contrast in the *trans* pair containing DD-EDDP the peaks of the *L-trans* isomer are at slightly higher energy. The frequency of the first band is equal to $10Dq - C$,¹⁵ where *C* is a Racah parameter.¹⁶ Since $10Dq$ is a measure of the strength of the crystal field, an

(13) R. G. Denning and T. S. Piper, *ibid.*, **5**, 1065 (1966).

(14) See D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *ibid.*, **6**, 1032 (1967), for a discussion of the stereochemistry of coordinated secondary NH groups.

(15) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961, p 236.

(16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, p 595.

(12) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

TABLE I
 THE ELECTRONIC ABSORPTION SPECTRA AND OPTICAL SPECTRA OF THE COMPLEXES PREPARED IN THIS INVESTIGATION

	Band I _a		Band I _b		Band II		ORD [M] ₅₈₉	CD _{max}		
	$\bar{\nu}^a$	ϵ	$\bar{\nu}$	ϵ	$\bar{\nu}$	ϵ		I _a ($\Delta\epsilon$)	I _b ($\Delta\epsilon$)	
L- <i>trans</i> -[Co(en)(LL-EDDP)]ClO ₄	1.876	97.0	2.227	sh	2.725	115.9	-6408	1.88 (-3.54)	2.22 (1.15)	
D- <i>trans</i> -[Co(en)(LL-EDDP)]ClO ₄ ·H ₂ O	1.905	97.6	2.242	sh	2.762	122.7	+6026	1.89 (4.01)	2.24 (-1.41)	
L- <i>cis</i> -[Co(en)(LL-EDDP)]Cl·2H ₂ O	1.815	sh ^b	2.024	177.4 ^d	2.786	175.7 ^d	-1076 ^d	2.13 (-4.01) ^d	2.41 (-0.41) ^d	
L- <i>trans</i> -[Co(<i>l</i> -pn)(LL-EDDP)]ClO ₄	1.876	73.1	2.188	sh	2.725	92.9	-6305	1.87 (-3.69)	2.22 (1.16)	
D- <i>trans</i> -[Co(<i>l</i> -pn)(LL-EDDP)]ClO ₄	1.901	84.1	2.227	sh	2.755	113.0	+6487	1.89 (4.02)	2.23 (-1.36)	
L- <i>cis</i> -[Co(<i>l</i> -pn)(LL-EDDP)]ClO ₄	1.845	sh	2.037	125.8 ^d	2.778	146.2 ^d	-981	
L- <i>trans</i> -[Co(<i>l</i> -pn)(DD-EDDP)]ClO ₄	1.898	95.6	2.227	sh	2.747	111.4	-6403	1.89 (-3.85)	2.24 (1.42)	
D- <i>trans</i> -[Co(<i>l</i> -pn)(DD-EDDP)]ClO ₄	1.873	...	2.169	sh	2.725	
D- <i>cis</i> -[Co(<i>l</i> -pn)(DD-EDDP)]ClO ₄	1.842	sh	2.033	...	2.778	
	Band I									
[Co(en)] ₃ ³⁺ ^c			2.105	...	2.950	...				

^a All $\bar{\nu}$ in cm⁻¹ × 10⁻⁴. ^b sh = shoulder. ^c F. Brigardo, *Bull. Soc. Chim. France*, 211 (1957). ^d Estimated value.

 TABLE II
 RESONANCE FREQUENCY ASSIGNMENTS OF THE *trans* ISOMERS^a

	α proton		Methyl		NH
	δ_B	δ_A	EDDP	<i>l</i> -pn	
<i>trans</i> -Co(en)(EDDA) ^{+b}	3.37	4.19			
L- <i>trans</i> -Co(en)(LL-EDDP) ⁺	3.53		1.55		7.0
D- <i>trans</i> -Co(en)(LL-EDDP) ⁺		3.99	1.45		7.15
L- <i>trans</i> -Co(<i>l</i> -pn)(LL-EDDP) ⁺	3.51		1.53	1.42	6.85
D- <i>trans</i> -Co(<i>l</i> -pn)(LL-EDDP) ⁺		4.15 4.08	1.45	1.38	7.2
L- <i>trans</i> -Co(<i>l</i> -pn)(DD-EDDP) ⁺		3.93	1.47	1.42	7.0
D- <i>trans</i> -Co(<i>l</i> -pn)(DD-EDDP) ⁺	3.54		1.61	1.33	7.13

^a All frequencies in ppm relative to NaTMS. ^b Reference 9. ^c Broad unresolved peak.

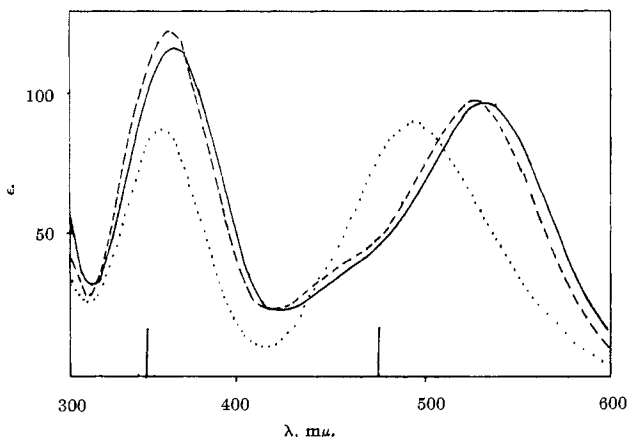


Figure 3.—The electronic absorption spectra of L-*trans*-Co(en)(LL-EDDP)⁺ (—), D-*trans*-Co(en)(LL-EDDP)⁺ (---), and L-*cis*-Co(en)(LL-EDDP)⁺ (···). (For L-*cis*-Co(en)(LL-EDDP)⁺ ordinate values should be increased by a factor of 2.) Vertical lines indicate absorption maxima of Co(en)₃³⁺.

increase in the frequency of the first band might be an indication of increasing stability. Because of the small differences involved, however, a conclusion as to the relative stability of the D-*trans* and L-*trans* isomer pairs would be tenuous at best.

Nuclear Magnetic Resonance

The resonance frequency assignments are given in Tables II and III.

1. The Nmr Spectra of the *trans* Isomers of Ethylenediamine-N,N'-di-L- α -propionato(ethylenediamine)-cobalt(III).—Figure 4 shows portions of the nmr spectra of the two *trans* isomers and of *trans*-Co(en)(EDDA)⁺⁹ as well as schematic representations of the molecules. The ethylenediamine ligand is indicated by

TABLE III

 RESONANCE FREQUENCY ASSIGNMENTS OF THE *cis* ISOMERS^a

	α proton	Methyl	NH
<i>cis</i> -Co(en)(EDDA) ^{+b}	3.62 4.02		
	3.71 3.71		
L- <i>cis</i> -Co(en)(LL-EDDP) ⁺	3.72	1.38	6.9 ^c
	3.95	1.52	6.0
			5.5
L- <i>cis</i> -Co(<i>l</i> -pn)(LL-EDDP) ⁺	3.66	1.37	...
	4.00	1.41	
		1.51	

^a All frequencies in ppm relative to NaTMS. ^b Reference 9. ^c Backbone.

two nitrogens and a connecting dashed line. There is a C₂ symmetry axis passing through the ethylenediamine, the cobalt atom, and the N-C-C-N backbone of the tetradentate which makes the two acetate or propionate arms equivalent.

The chelate arms of the tetradentate ligand are rigidly oriented and thus magnetic anisotropy should be exhibited by the axially symmetric groups of electrons in the C—C, C—N, and C=O bonds.¹⁷ In particular, the different chemical shifts of the α protons of the EDDA (labeled a and b) can be explained in terms of the magnetic anisotropy of the C—N bond.⁹

If ϕ is the angle between a line connecting a proton with the electrical center of gravity of the C—N bond and the C—N bond axis and r is the length of the proton connecting line, then the shielding constant, σ , for this proton is approximated by the expression

$$\sigma = \frac{(3 \cos^2 \phi - 1)\chi}{3r^3}$$

(17) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1964, p 112.

where χ is a measure of the magnetic anisotropy of the C-N bond.¹⁵ The sign of χ has been assumed to be negative.⁹ Thus the shielding will be negative when ϕ is $<55^\circ$ and positive if ϕ is $>55^\circ$. For a given value of r , the shielding will be the most negative when the proton is on the C-N bond axis directly over the electrical center of gravity. It should be noted that shielding of this type falls off rapidly with distance owing to the inverse dependence on r^3 .

The b protons are located almost directly above the C-N bond axis and are shielded by it. The a protons are relatively unaffected by this bond and as a result resonate at lower fields than the b protons. The signals of the a and b protons are indicated in the top spectrum of Figure 4.

The middle spectrum of Figure 4 exhibits only an a proton signal indicating the methyl groups must have replaced the b protons in the isomer giving this spectrum. It is assumed that replacing a proton by a methyl group has little effect on the remaining proton. Knowing the absolute configuration of the tetradentate ligand enables a D absolute configuration to be assigned to this isomer. As shown in the schematic drawing, it is in the D isomer that the methyl groups are in toward the backbone of the tetradentate ligand replacing the b protons.

The bottom spectrum of Figure 4 exhibits only a b proton signal indicating that methyl groups must have replaced the a protons. The isomer giving this spectrum was assigned an L absolute configuration. As shown in the schematic drawing, it is in the L isomer that the methyl groups are pointed away from the backbone of the tetradentate replacing the a protons.

The methyl group signals are not shown but the values of their chemical shifts are given in Table II. The methyl groups of the D isomer which are directly

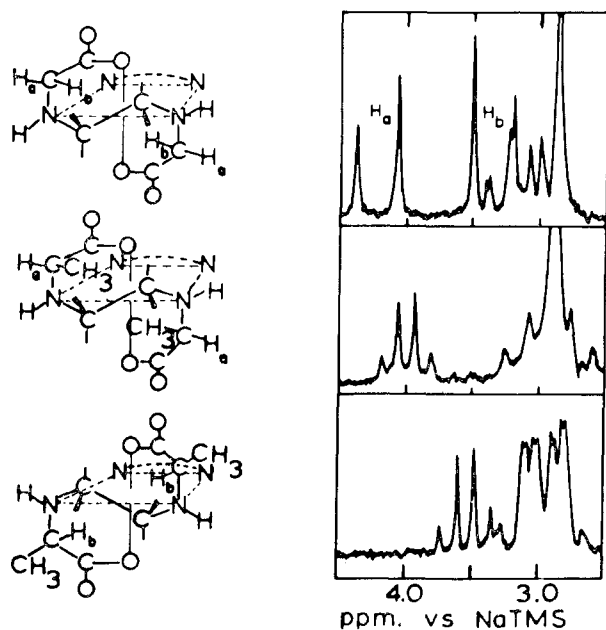


Figure 4.—Representations of *trans*-Co(en)(EDDA)⁺ (top), *D-trans*-Co(en)(LL-EDDP)⁺ (middle), and *L-trans*-Co(en)(LL-EDDP)⁺ (bottom) and portions of their nmr spectra.

over the C-N bond resonate at higher field than the methyl groups of the L isomer which are away from the C-N bond.

The remaining parts of the spectra shown in Figure 4 are a superimposition of the signals due to the methylene protons of the ethylenediamine and of the tetradentate backbone. In the *D-trans* isomer the ethylenediamine is free of interference from the methyl groups and can oscillate back and forth between its two possible conformations. The result is one intense peak since the chemical environments of all four protons are equivalent. Interference from the methyl groups causes the ethylenediamine of the L isomer to adopt a particular conformation and the result is a more complicated pattern.

Also of interest is the spectrum of the D isomer that was obtained before the amine hydrogens had exchanged with the deuterium oxide solvent. A portion of this spectrum is shown in Figure 5 along with the same portion after exchange had occurred.

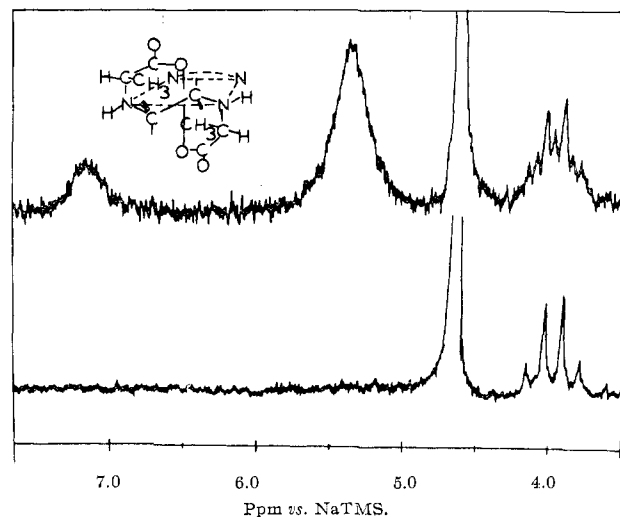


Figure 5.—The nmr spectrum of *D-trans*-Co(en)(LL-EDDP)⁺ before (top) and after (bottom) amine-proton exchange.

Karplus¹⁸ has shown that the coupling constant between two protons on adjacent carbon atoms depends on the dihedral angle between the protons. The theoretical value of the constant varies in a smooth curve from 8.2 cps for a zero dihedral angle to -0.3 cps at 90° and 9.2 cps at 180° . Legg and Cooke¹⁹ have postulated that these values may be used for tetrahedrally bonded nitrogen as well as carbon.

Molecular models indicate that the H-N-C-H_a angle in the D isomers is about 10° . Thus significant coupling would be expected and is observed as shown in the top spectrum of Figure 5. The H-N-C-H angle in the L isomer is about 110° . Little coupling would be expected and none is found.

2. The Nmr Spectrum of *cis*-Ethylenediamine-N,N'-di-L- α -propionato(ethylenediamine)cobalt(III).—The nmr spectrum and a representation of this isomer are shown in Figure 6. It is assumed that the configu-

(18) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(19) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

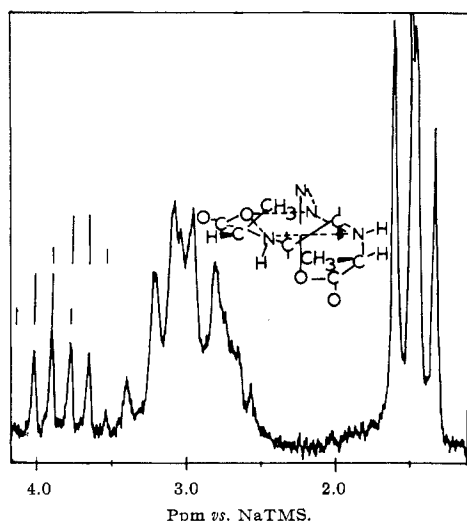


Figure 6.—The nmr spectrum of *L-cis*-Co(en)(LL-EDDP)⁺. The positions of the α -proton quartets are indicated by vertical lines.

ration around the tetradentate ligand nitrogens is the one, as shown by molecular models, that would minimize the steric interaction between the methyl groups and the remainder of the molecule. This is only one of many possibilities.¹⁴ Significant data are given in Table IV. The propionate arms are not equivalent so there are two overlapping α -proton quartets and three methyl doublets. The α protons are no longer of a or b character so an assignment of absolute configuration in the same manner as for the *trans* isomers is no longer possible. However, various other evidence enables an L absolute configuration to be assigned.

TABLE IV
RESONANCE FREQUENCY ASSIGNMENTS (PPM)
OF THE ISOMERS OF Co(en)(LL-EDDP)⁺

Complex	Backbone NH (splitting)	α proton	CH ₃ (splitting)
<i>L-trans</i>	7.0	3.53 (CH ₃ out)	1.55 (7.8 cps)
<i>D-trans</i>	7.15 (7 cps)	3.99 (CH ₃ in)	1.45 (7.0 cps)
<i>L-cis</i>	6.0 (7 cps)	3.95 (facial)	1.38 (7.0 cps)
	6.9	3.72 (meridional)	1.52 (7.2 cps)

Two amine-proton resonances due to the backbone of the tetradentate ligand were observed at 6.9 and 6.0 ppm. By comparison to work of Clifton and Pratt²⁰ the 6.0-ppm signal can be assigned to the NH *trans* to an oxygen and the 6.9 ppm signal is close to that of the *trans*-Co(en)(LL-EDDP)⁺ isomers (7.0 and 7.15 ppm) which have both of the NH groups of the tetradentate *trans* to a nitrogen.

Before the amine hydrogens exchanged, coupling was observed between the NH *trans* to an oxygen and the α proton resonating at 3.95 ppm. These protons are in the facial arm and molecular models with the configurational assumption discussed above indicate that the dihedral angle between them in the *L-cis* isomer is such that coupling should occur. No coupling was observed between the CH and NH in the meridional arm. The dihedral angle between them in the *L-cis* isomer is about

55° and the value of the coupling constant should be small. In the *D-cis* isomer, models indicate that coupling would occur in the meridional arm and not in the facial arm. Thus the *cis* isomer could be assigned an L absolute configuration.

A further piece of evidence was obtained from the chemical shift value of the α proton of the facial arm. The *L-cis* isomer is related to the *D-trans* isomer by a shift in position of one of the arms. Thus the facial arm of the *L-cis* isomer has an α -proton resonance of 3.53 ppm. The *D-cis* isomer resonance should be close to this value.

Furthermore, the magnitude of the splitting of the methyl doublets of the *cis* isomer agrees more closely with the methyl doublet splitting in the *D-trans* isomer than with the same splitting in the *L-trans* isomer. This might indicate²¹ that the amount of strain in the arms of the *cis* isomer is about the same as the strain in the arms of the *D-trans* isomer. Since the facial arm of the *L-cis* isomer is related to the *D-trans* isomer, this evidence also agrees with an L configurational assignment to the *cis* isomer.

3. The Nmr Spectra of the *trans* Isomers of Ethylenediamine-*N,N'*-di-*L*- α -propionato(*l*-propylenediamine)cobalt(III).—The significant portions of the nmr spectra of these compounds are shown in Figures 7 and 8. Absolute configurations were assigned to these isomers by the same arguments that were applied to the analogous ethylenediamine complexes. The methyl group signals of the *D-trans* isomer as shown on the right side of Figure 8 consist of two doublets. The more intense doublet is assigned to the two EDDP methyl groups which should exhibit a signal twice as intense as that due to the single *l*-propylenediamine methyl group. In the *L-trans* isomer spectrum on the left side of Figure 8, the two doublets coincide. The EDDP methyl groups of the *D-trans* isomer which, as a result of the configuration of the ligand, are over the C-N bond, resonate at higher fields than the backbone methyl groups of the *L-trans* isomer which are away from the C-N bond. Similarly, as shown in Figure 7, the α protons of the *L-trans* isomers, which are directly over the C-N bond, resonate at higher field than do their *D-trans* counterparts.

The *D-trans* isomer shows two overlapping α -proton quartets, although, from symmetry considerations, only one would be expected. Further discussion of the point is postponed until section 5.

The *l*-propylenediamine adopts a fixed conformation in both isomers owing to the requirement that the methyl group be in a pseudo-equatorial position.²² The result is the complicated nmr pattern for this portion of the molecule that is shown in Figure 7.

4. The Nmr Spectrum of *cis*-Ethylenediamine-*N,N'*-di-*L*- α -propionato(*l*-propylenediamine)cobalt(III).—The nmr spectrum and a representation of this isomer are shown in Figure 9. The two overlapping α proton quartets and three methyl doublets are better seen in

(20) P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

(21) R. S. Day and C. N. Reilly, *Anal. Chem.*, **37**, 1326 (1965).

(22) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

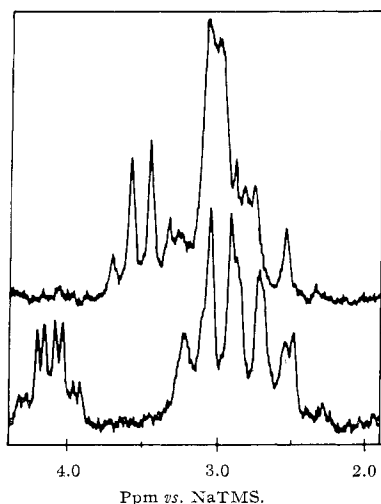


Figure 7.—The nmr spectra of *L-trans*-Co(*l-pn*)(LL-EDDP)⁺ (top) and *D-trans*-Co(*l-pn*)(LL-EDDP)⁺ (bottom).

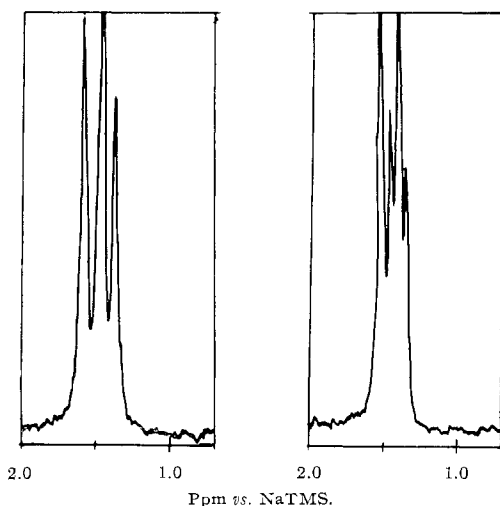


Figure 8.—The methyl regions of the nmr spectra of *L-trans*-Co(*l-pn*)(LL-EDDP)⁺ (left) and *D-trans*-Co(*l-pn*)(LL-EDDP)⁺ (right).

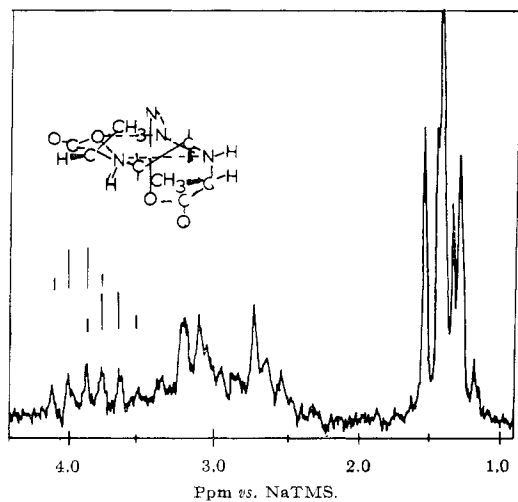


Figure 9.—A representation and the nmr spectrum of *L-cis*-Co(*l-pn*)(LL-EDDP)⁺. The positions of the α -proton quartets are indicated by vertical lines.

the portions of the 100-Mc spectrum shown in Figure 10. A change in the field strength of the spectrometer results in a proportionate change in the chemical shift values but has no effect on the magnitude of the coupling constants.

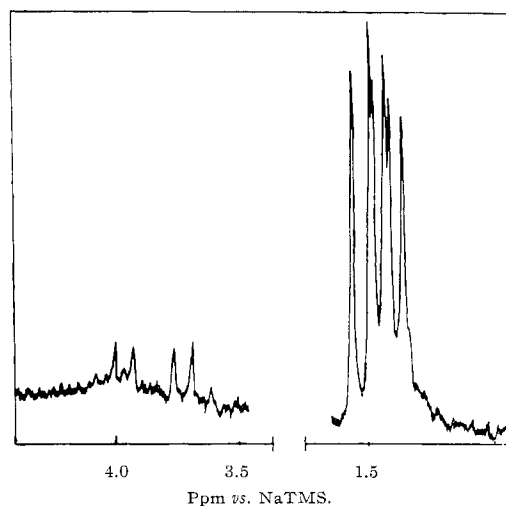
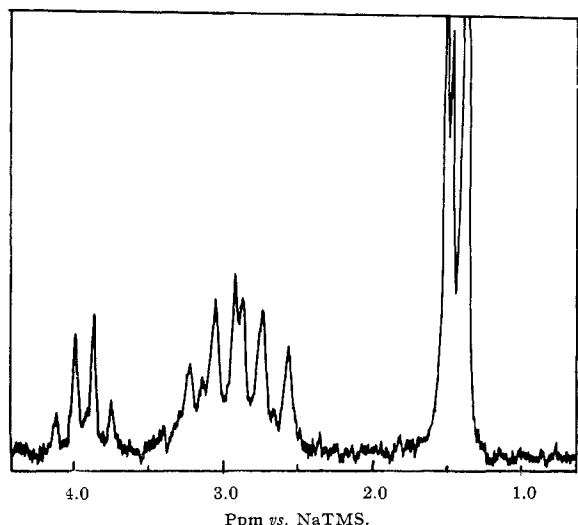
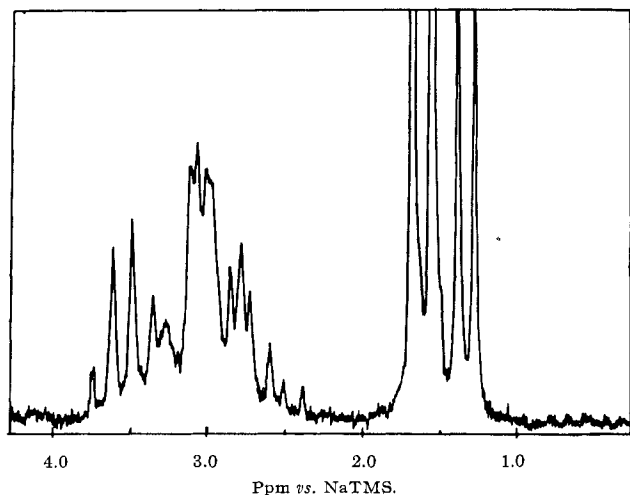


Figure 10.—The 100-Mc nmr spectrum of *L-cis*-Co(*l-pn*)(LL-EDDP)⁺.

Because only a very small amount of sample was available, no studies of the NH-CH coupling were made. The α proton of the facial ring resonates at 3.90 ppm and the splitting of the methyl doublets is 7.0 cps. Both figures are in better agreement with *D-trans*-Co(*l-pn*)(LL-EDDP)⁺ than with *L-trans*-Co(*l-pn*)(LL-EDDP)⁺. Since it is the *L-cis* isomer that is related to the *D-trans* isomer, this evidence favors an *L* configurational assignment. The resonance positions are also in agreement with those of *L-cis*-Co(en)(LL-EDDP)⁺. The ORD spectrum, discussed later, further confirms the *L* assignment.

5. The Nmr Spectra of the *trans* Isomers of Ethylenediamine-*N,N'*-di- α -propionato(*l*-propylenediamine)cobalt(III).—The nmr spectra of these compounds are shown in Figures 11 and 12 and the pertinent chemical shift values are summarized in Table III. Because of the opposite configuration of the tetradentate ligand, there is a correspondence with regard to the orientation of the methyl groups between *L-trans*-Co(*l-pn*)(LL-EDDP)⁺ and *D-trans*-Co(*l-pn*)(DD-EDDP)⁺ and between *D-trans*-Co(*l-pn*)(LL-EDDP)⁺ and *L-trans*-Co(*l-pn*)(DD-EDDP)⁺. Absolute configurations can be assigned to the DD-EDDP complexes in the same manner as for the related LL-EDDP complexes. The α protons of *D-trans*-Co(*l-pn*)(DD-EDDP)⁺ which are directly over the C-N bond resonate at higher field than the corresponding protons of *L-trans*-Co(*l-pn*)(DD-EDDP)⁺ which are away from the C-N bond. This may be compared with the LL-EDDP case in which the *L-trans* α protons resonate at higher field than the *D-trans*. Similarly the methyl resonance of the backbone of *L-trans*-Co(*l-pn*)(DD-EDDP)⁺ is at higher field than the *D-trans* isomer counterpart and the opposite ordering occurs in the LL-EDDP isomers.

Figure 11.—The nmr spectrum of *L-trans*-Co(*l-pn*)(DD-EDDP)⁺.Figure 12.—The nmr spectrum of *D-trans*-Co(*l-pn*)(DD-EDDP)⁺.

The backbone amine-proton resonances of *L-trans*-Co(*l-pn*)(DD-EDDP)⁺ are in almost the same place as those of *D-trans*-Co(*l-pn*)(LL-EDDP)⁺. The NH-CH dihedral angle is correct for coupling to occur before the NH has exchanged and indeed coupling was observed. No coupling was observed in *D-trans*-Co(*l-pn*)(DD-EDDP)⁺ and the dihedral angle is such that the expected coupling is at a minimum.

The methyl group signal due to the tetradentate portion of *D-trans*-Co(*l-pn*)(DD-EDDP)⁺ is not a simple doublet. As mentioned earlier, the α -proton signal of *D-trans*-Co(*l-pn*)(LL-EDDP)⁺ is not a simple quartet. The nmr of the latter compound was rerun on a 100-Mc spectrometer. The two quartets moved further apart establishing that the two α protons are in different chemical environments rather than being coupled with a neighboring group. The two tetradentate methyl groups of the former compound must likewise be in different chemical environments.

Similar behavior has been noted in *D*- and *L*-Co(*l-pn*)(EDDA)⁺²³ and it has been postulated that

(23) J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, **6**, 700 (1967).

in the *L* absolute configuration, the α proton is situated between the two amine protons of *l*-propylenediamine while in the *D* absolute configuration the α proton is directly opposed to one amine proton of *l*-propylenediamine.

Optical Activity Measurements

The spectroscopic data are contained in Table I. We shall consider first the *trans* isomer. *D*-Co(en)₃³⁺ has a positive Cotton effect. The *trans*-EDDP-diamine complex can be figuratively related to Co(en)₃³⁺ by removing the backbone of the EDDP and replacing the *trans* oxygens by nitrogens. If Co(III), as has been postulated,²¹ retains effective C₂ symmetry when coordinated to an EDDP type of molecule, the *D-trans* isomers would be expected to have a positive Cotton effect, and the *L-trans* isomers, a negative Cotton effect. As may be seen in Table I, this is indeed the case. The *trans* isomers, whose absolute configurations were all determined unequivocally *via* nmr, have Cotton effects whose signs are in accord with the isomer of Co(en)₃³⁺ to which they are related by the reasoning given above. The values of the molar rotation of a given *D,L* pair are not equal and opposite since the *D* and *L* compounds are diastereoisomers rather than enantiomorphs.

The frequencies of the absorption maxima and the CD maxima coincide almost precisely. The dominant low-energy CD band can be related to the dominant A₁ → E_a transition of Co(en)₃³⁺ which is positive in the *D* isomer and negative in the *L* isomer.

It is more difficult to figuratively relate the *cis* isomers to a structure of known absolute configuration. A ring-pairing method has been proposed²⁴ for relating absolute configurations of octahedral chelate complexes of different symmetries based on the net chirality of all possible ring combinations that form a helical set. The *cis* isomer of Co(en)(LL-EDDP)⁺, whose *L* configuration we have ascertained *via* nmr, would be predicted by this method to have a negative Cotton effect and a negative long-wavelength CD component. This is indeed the case. Since the ORD spectrum of *cis*-Co(*l-pn*)(LL-EDDP)⁺ is almost identical, it too may be assigned an *L* structure confirming, in the absence of coupling data, the conclusion reached from nmr.

The correspondence of CD, ORD, and nmr data means that the former methods may be used with confidence to assign absolute configurations to similar complexes that are less suited to nmr techniques.

A case in point is *cis*-Co(*l-pn*)(DD-EDDP)⁺ for which no nmr data were available. Since its ORD curve is almost the mirror image of the curves of *L-cis*-Co(en)(LL-EDDP)⁺ and *L-cis*-Co(*l-pn*)(LL-EDDP)⁺, it may be assigned a *D* absolute configuration.

Acknowledgment.—Financial support by the National Science Foundation is gratefully acknowledged. L. N. S. also wishes to thank the Minnesota Mining and Manufacturing Co., Stauffer Chemical Co., and the Union Carbide Chemical Co. for their support.

(24) J. I. Legg and B. E. Douglas, *J. Am. Chem. Soc.*, **88**, 2697 (1966).