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Cobalt(III) Complexes With 1,2-Propanediaminediacetic Acid

Paul John Magnell

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COBALT(III) COMPLEXES
WITH
1,2-PROPANEDIAMINEDIACETIC ACID

by

Paul John Magnell

A Thesis
Submitted to the
Faculty of the Graduate College
in partial fulfillment
of the
Degree of Master of Arts

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To Kath

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Paul John Magnell

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LIST OF ABBREVIATIONS

AEIDA.....	α -aminoethyliminodiacetate
ala.....	alanate
cd.....	circular dichroism
DEEDDA.....	N,N'-diethylethylenediamine-N,N'-diacetate
dien.....	diethylenetriamine
5,6-dimetrien.....	5,6-dimethyltriethyltetramine
DMEDDA.....	N,N'-dimethylethylenediamine-N,N'-diacetate
ECE.....	<u>trans</u> -N,N'-bis(β -aminoethyl)cyclohexane-1,2-diamine
EDDA.....	ethylenediamine-N,N'-diacetate
L,L-EDDP.....	ethylenediamine-N,N'-di-L- α -propionate
EDTA.....	ethylenediaminetetraacetate
eee.....	1,8-diamine-3,6-dithiaoctane
en.....	ethylenediamine
gly.....	glycinate
Hz.....	Hertz
IDA.....	iminodiacetate
5-metrien.....	5-methyltriethylenetetramine
MIDA.....	methyliminodiacetate
nmr.....	nuclear magnetic resonance
N ¹ ,N ¹ -DMPDDA.....	N ¹ ,N ¹ -diacetato-N ² ,N ² -dimethyl-1,2-propanediamine
N ² ,N ² -DMPDDA.....	N ² ,N ² -diacetato-N ¹ ,N ¹ -dimethyl-1,2-propanediamine
N ¹ ,N ² -PDDA.....	N ¹ ,N ² -diacetato-1,2-propanediamine

N ¹ ,N ¹ -PDDA.....	N ¹ ,N ¹ -diacetato-1,2-propanediamine
ord.....	optical rotatory dispersion
PDTA.....	1,2-propanediaminetetraacetate
pn.....	1,2-propanediamine
ppm.....	parts per million
s- <u>cis</u>	symmetrical <u>cis</u>
trien.....	triethylenetetramine
u- <u>cis</u>	unsymmetrical <u>cis</u>

INTRODUCTION

Aminocarboxylic acid cobalt(III) complexes have been of interest to inorganic chemists since 1909 when Ley and Winkler isolated violet and rose colored geometric isomers of tris amino acid complexes of glycine and alanine.¹ More recently, considerable interest has been shown in the study of the stereochemistry and optical activity arising from configurational and vicinal interactions of these complexes. Nuclear magnetic resonance of the methylene protons on the carboxylate portion of the coordinated ligand has also been studied.

Of immediate interest to this study is the stereochemistry of complexes containing flexible tetradentate ligands. A tetradentate ligand may be constructed such that the four coordination sites are arranged in a linear manner or in a branched or non-linear manner. In recent years, because of the variety of linear tetradentate ligands which are easily obtainable or readily synthesized, stereochemical studies of complexes containing these ligands have been considerably investigated while the non-linear ligands have not been extensively studied. Various donor atoms such as nitrogen, oxygen, sulphur, and phosphorous have been utilized. In addition, the lengths of the connecting alkyl chains have been varied and methyl substituents have

been placed at various sites along the tetradentate chain. The effect of these changes on the stereochemistry of the resulting complexes has been observed. An octahedral complex with a linear tetradentate ligand may assume three distinct geometrical arrangements as shown in Figure 1. (For simplicity, only the coordinated atoms are shown).

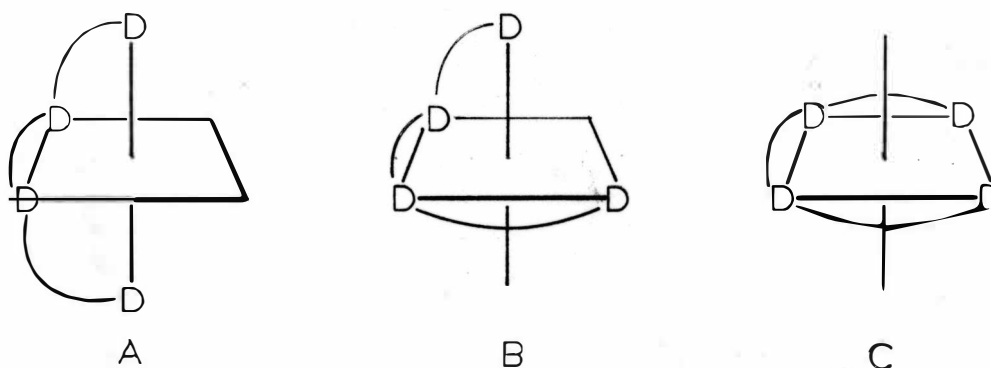


Figure 1. The three geometric isomers of a linear tetradentate ligand: (A) s-cis; (B) u-cis; (C) trans

As yet there has been no general agreement on the naming of complexes containing linear tetradentate ligands. Legg and co-workers² have recently suggested that the nomenclature introduced by Sargeson and Searle³ for the geometric isomers of $[\text{Co}(\text{trien})(\text{X})_2]^+$ should be used for all complexes containing linear tetradentate ligands. However, Busch and Worrell⁴ have recently introduced a more logical nomenclature for linear tetradentate ligands in their study of $[\text{Co}(\text{eee})-(\text{X})_2]^+$. In this system the isomers are identified according to the arrangement of the fifth and sixth groups and the overall symmetry of the complex. They are designated

symmetrical cis (s-cis), unsymmetrical cis (u-cis), and trans as shown in Figure 1. The two positions of the octahedra which are unoccupied in Figure 1 can be occupied by two monodentate ligands or by one bidentate ligand such as ethylenediamine. When a bidentate ligand is employed, only two geometric isomers are possible, namely, the s-cis and u-cis isomers.

The most extensively studied linear tetradentate ligand has been triethylenetetramine (trien) in which all four donor atoms are nitrogen. Basolo⁵ was the first to recognize that triethylenetetramine could be coordinated in three distinct ways and he was able to prepare the s-cis-[Co(trien)(Cl)₂]⁺ and u-cis-[Co(trien)(Cl)₂]⁺. He was not successful in preparing the trans-isomer which was later synthesized by Gillard and Wilkinson.⁶ Busch and Worrell⁴ prepared [Co(eee)(X)₂]⁺ where eee was 1,8-diamino-3,6-dithiaoctane and X was a monodentate ligand. Of the possible geometric isomers, only the s-cis isomer was found. The presence of the thioether donor atoms appears to induce an extreme geometric stereospecificity on this ligand.

Relating directly to the present work are cobalt(III) complexes with ethylenediamine-N,N'-diacetic acid (EDDA) and its nitrogen substituted analogs synthesized by Legg and Cooke.⁷ In their stereochemical study, they found that the s-cis-[Co(EDDA)(en)]⁺ was preferred over the u-cis

isomer and that no u-cis isomer was formed when the methyl substituted (DMEDDA) and ethyl substituted (DEEDDA) analogs were used in place of EDDA. The authors postulated that nonbonding interactions between the amine protons of the ethylenediamine and EDDA was responsible for the low yield of the u-cis isomer. This postulation later proved to be correct when high yields of the u-cis isomer were obtained when the ethylenediamine portion of the complex was replaced by oxalate and malonate.⁸ It was calculated with these complexes, in fact, that the u-cis isomer was 600 cal/mole more stable.²

In addition to geometric isomerism, linear tetradentate ligands may also exhibit optical isomerism. The principle factor in metal complexes resulting in this type of isomerism results from the arrangement of the chelate rings about the metal atom. This is generally referred to as the configurational effect. The four possible optical isomers are shown in Figure 2. (For convenience we will assume that the remaining two positions are taken by a bidentate ligand). Since the complexes discussed here have C_2 or pseudo- C_2 symmetry as do many cobalt(III) complexes, the absolute configurations are related to the configuration of $[\text{Co}(\text{en})_3]^{3+}$ and are designated Δ or Λ according to the chirality of the rings as viewed down a C_2 axis.⁹ It is seen that the s-cis isomers are dissymmetric (have some element of symmetry) and the u-cis isomers are asymmetric

(have no symmetry element except for a onefold axis of rotation). The s-cis isomer contains a two-fold axis of rotation passing through the bidentate ligand and the central chelate ring of the tetradentate ligand.

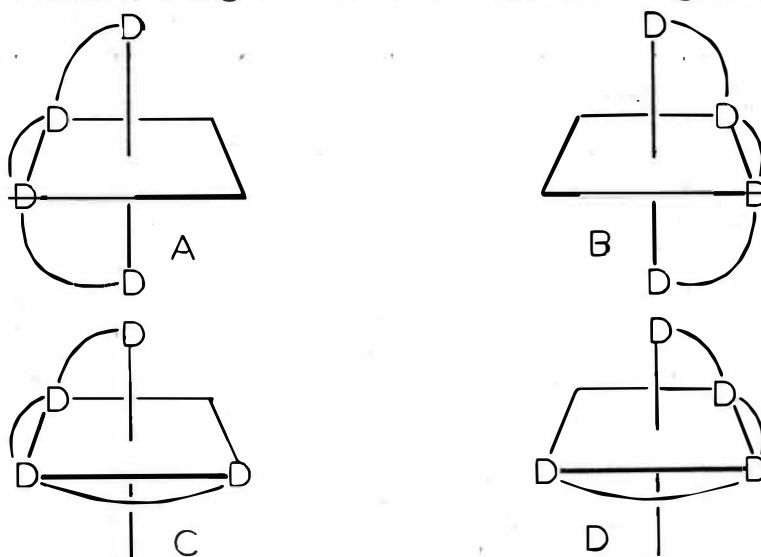


Figure 2. The four optical isomers of a linear tetradentate ligand: (A) Δ -s-cis; (B) Λ -s-cis; (C) Λ -u-cis; and (D) Δ -u-cis

If the optical isomers can be separated and isolated, it is of interest to determine the absolute configuration of a particular stereoisomer. Many methods for determining the absolute configuration of metal complexes have been developed. The most exact or definitive method is the x-ray technique developed by Bijvoet and co-workers¹⁰ which determines the absolute configuration directly. Other methods including least soluble diastereomer correlation,¹¹ "active racemates",¹² and even biological activity have been used.¹³

The most common method for determining the absolute

configuration of a complex is to compare its optical rotatory dispersion (ord) or circular dichroism (cd) spectra with those of a complex whose absolute configuration is known from x-ray analysis. A typical ord curve and cd curve are shown in Figure 3. Since these phenomena were first discovered by Cotton,¹⁴ each of the two phenomena or the combined effect is called the "Cotton" effect.

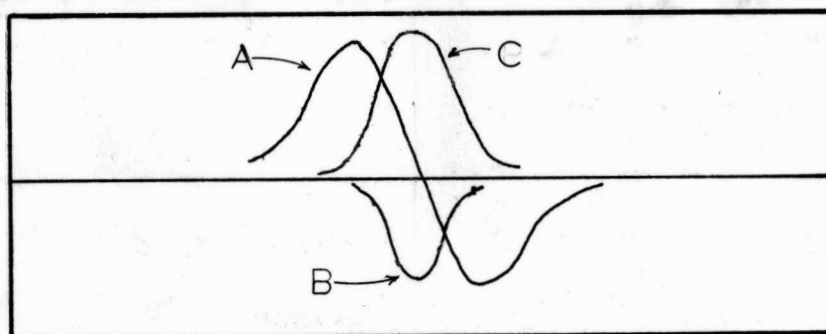


Figure 3. Typical plots of an (A) ord; (B) cd; and (C) absorption curve

Some attempts have been made to calculate the rotatory power of metals complexes theoretically,^{15,16,17} but as yet no theory has been found satisfactory. Several excellent review articles^{18,19,20} which deal with the use of rotatory dispersion and circular dichroism spectra in determining the absolute configuration of metal complexes have appeared.

Sargeson and Searle³ have succeeded in resolving several s-cis and u-cis isomers of $[\text{Co}(\text{trien})(\text{X})_2]^+$ and have assigned their absolute configuration by comparing their ord and cd spectra with those of $[\text{Co}(\text{en})_3]^{3+}$ and the related cis- $[\text{Co}(\text{en})_2(\text{X})_2]^+$ complexes.

Utilizing the same method, Legg, Cooke, and Douglas⁹ have assigned the absolute configuration for s-cis-[Co-(EDDA)(AA)]ⁿ⁺ complexes, where AA was en, R-pn, S-ala, and gly. These authors felt that these complexes were of particular interest since they form a link between the absolute configurations of [Co(EDTA)]⁻ and [Co(en)]³⁺.

Optical activity is also observed in complexes in which the symmetry arises due to arrangement of groups on an atom in a ligand such as R-1,2-propanediamine or S-alanine (R and S refer to the absolute configuration of the ligand). This effect is called the vicinal effect. In a metal complex, optical activity can arise from both configurational and vicinal interactions. The additivity of vicinal and configurational effects has been demonstrated by Douglas and co-workers^{21,22,23} by comparing an isomer containing an optically active ligand with one in which the asymmetric ligand has been replaced by an analogous optically inactive one.

Methyl substitution in the central chelate ring of a linear tetradentate ligand may often cause the ligand to be highly stereoselective. These stereochemical effects are almost certainly due to the fact that the central chelate ring is puckered. Corey and Bailar²⁴ showed that the preferred conformation of a five membered chelate ring is gauche and that a methyl substituent occupies an equatorial position.

Such stereoselectivity was observed by Goto and co-workers²⁵ in their studies of cobalt(III) complexes with R-5-methyltriethylenetetramine, S-5,6-dimethyltriethylenetetramine and R-trans-N,N'-bis(β -aminoethyl)cyclohexane-1,2-diamine. These workers found that these ligands gave only u-cis isomers and that the absolute configuration of the complex was determined by the absolute configuration of the ligand used. In another study, Worrell, MacDermott, and Busch²⁶ found that R-4-methyl-1,8-diamino-3,6-dithiaoctane gave only the Δ -s-cis isomer.

When the methyl substituent is on the end chelate ring, stereoselectivity may also be found. Liu and Asperger²⁷ found that L,L-2,9-diamino-4,7-diazadecane (L,L- α,α' -dimethyltrien) coordinated in two stereospecific forms, Δ -s-cis and Λ -u-cis. Again, the stereoselectivity can be accounted for on the basis of ring puckering. On the other hand, when the end chelate ring is a methyl substituted glycinate ring, as in ethylenediamine-N,N'-di-L-propionate(LL-EDDP), very little stereoselectivity is found, as shown by Schoenburg, Cooke, and Liu.²⁸ In their study, both the Δ -s-cis and Λ -s-cis isomers were found but only the Λ -u-cis isomer was isolated. The loss of stereoselectivity can be explained by the fact that a glycinate ring is more or less planar as compared to a five membered 1,2-propanediamine ring, and thus there is no preferred orientation for the methyl substituents.

Nonlinear tetradentate ligands have not been as extensively studied as linear tetradentate ligands although they also may show some interesting stereoisomerism. Chu, Cooke, and Liu²⁹ synthesized a cobalt(III) complex with β -aminoethyliminodiacetic acid (AEIDA) and ethylenediamine. They were able to isolate both the cis and trans(0)- $[\text{Co}(\text{AEIDA})(\text{en})]^+$ as shown in Figure 4. In these complexes, the cis isomer is asymmetric but the trans isomer is neither dissymmetric nor asymmetric if only the donor atoms are considered. When the puckered five membered ethylenediamine backbone chelate ring is considered, optical isomers can arise if one conformation is preferred over the other. Attempts to resolve this complex resulted in failure³⁰ presumably due to the rapid interchange between the two conformations.

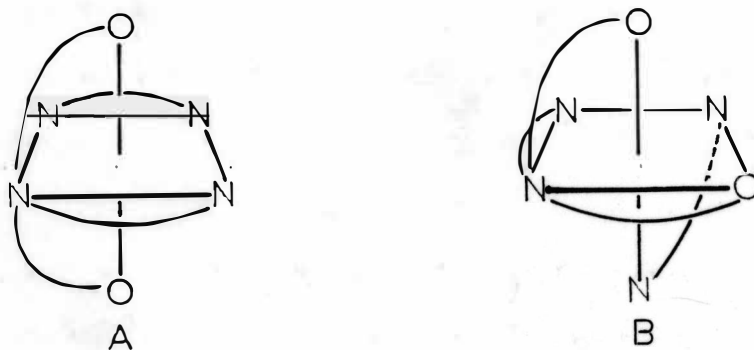


Figure 4. Isomers of $[\text{Co}(\text{en})(\text{AEIDA})]^+$: (A) trans(0); and (B) cis(0)

Other nonlinear tetradentate which have been studied include β , β' , β'' -triaminotriethylamine,^{31,32} nitrilotriacetic acid,^{33,34} and 4-diethylenetriamineacetic acid.³⁵

Nuclear magnetic resonance studies of aminocarboxylate chelates have been of interest in recent years. The nmr spectra of these chelates usually include overlapping AB patterns arising from various pairs of nonequivalent spin-coupled glycinate protons. Acid and base catalysed deuterium exchange of the α -H of the glycinate rings have been studied and the rates determined.^{36,37}

Legg and Cooke have found the nmr spectra very helpful in elucidating the stereochemistry of the cobalt(III) complexes of ethylenediamine-N,N'-diacetic acid and its nitrogen substituted analogs,⁷ and mixed cobalt(III) complexes of diethylenetriamine(dien) with iminodiacetic acid (IDA).³⁸ Cooke³⁹ also studied the bis complexes of cobalt(III) with iminodiacetic acid and methyliminodiacetic acid (MIDA).

Nuclear magnetic resonance spectroscopy has also been useful in elucidating the absolute configurations of metal complexes. Schoenburg, Cooke, and Liu²⁸ used nmr to determine the absolute configuration of cobalt(III) complexes with the ligand ethylenediamine-N,N'-di-L- α -proprionic acid in terms of the anisotropy of the C-N bond. More recently, Cooke and Dabrowiak⁴⁰ have utilized steric compression in the nmr to assign the absolute configuration of some cobalt(III) amino acid complexes.

It has been shown that linear tetradentate ligands which contain methyl substituents in the central diamine

chelate exhibit high stereoselectivity.^{25,26} The only studies of this nature to date have been ligands that contain a β -aminoethyl terminal chelate ring. In addition, no studies of similar non-linear tetradentate ligands have been carried out. It was the purpose of this study to make a linear tetradentate ligand with a methyl substituant in the central chelate ring and with an aminoacetate terminal chelate ring and study the stereochemistry of this ligand. In addition, a study was made to see if a non-linear tetradentate ligand with a methyl substituant on one of the chelate rings would also be stereoselective.

EXPERIMENTAL

A. Reagents and Physical Measurements

1. Electronic absorption spectra

The visible spectra were recorded at room temperature with a Cary 14 recording spectrophotometer in 1.0 cm cells using a weighed analytical sample diluted to a known volume. A baseline was run for each spectra and the absorbancies corrected.

2. Nuclear magnetic resonance spectra

The nuclear magnetic resonance (nmr) spectra were recorded using a Varian A-60 spectrometer or on a Varian 100 MHz nmr spectrometer (courtesy of the Upjohn Co., Kalamazoo, Mich.). All samples were run at ambient probe temperature (approximately 35°C). A typical sample consisted of 80 mg to 100 mg of the complex in about 0.5 ml D₂O. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal standard. All values reported are in ppm (δ) downfield from the reference. The proton exchange samples were prepared by dissolving 100 mg of sample in 0.4 ml of D₂O and adding a very small amount of 30% NaOD until the pH was about 10.

3. Optical rotary dispersion measurements

The optical rotary dispersion (ord) spectra were obtained with a Beckman-DU-2 spectrophotometer fitted with a Keston Model D Polarimeter attachment. The polarimeter attachment was manufactured by the Standard Polarimeter Co., Hackensack, New Jersey.

4. Elemental analysis

All elemental analyses were performed by either Gailbraith Laboratories, Knoxville, Tennessee or Midwest Microlabs Inc., Indianapolis, Indiana.

5. Reagents and chemicals

All chemicals used were reagent grade. The 98% ethylenediamine and 1,2-propanediamine were obtained from Matheson, Coleman, and Bell. The 1,2-propanediamine was resolved by the method of Dwyer, Garvan and Shulman.⁴⁴ The N²,N²-dimethyl-1,2-propanediamine was obtained from K and K Laboratories, Inc. The 30% sodium hydroxide-d was obtained from Fluka AG Chemische Fabrick, Buchs, Switzerland, and the DCl was obtained from Merck, Sharp, and Dohme, Montreal, Quebec.

B. Preparation of Ligands and Complexes

1. Preparation of the nitrogen substituted diacetic acid derivatives of 1,2-propanediamine

The various 1,2-propanediamine-diacetic acid ligands

were prepared by a method similar to that used by Dwyer and Garvan⁴¹ to prepare 1,2-propanediaminetetracetic acid. A potassium hydroxide solution, 13.5 g (0.24 mole) in 25.0 ml of cold water, was added dropwise to a constantly stirring monochloroacetic acid solution, 22.6 g (0.24 mole) in 25.0 ml of water, which was maintained in an ice bath so that the temperature of the reaction mixture did not rise above 10°C. After the addition of the potassium hydroxide, 7.2 g (0.1 mole) of racemic 1,2-propanediamine was added followed by another 13.5 g (0.24 mole) portion of potassium hydroxide dissolved in water (25.0 ml). The reaction mixture was allowed to warm to room temperature and stand for approximately five days. At the end of the five day period, the reaction mixture was acidified to pH 5 with concentrated hydrochloric acid. All attempts to isolate the desired ligands by the addition of ethanol or ether to the aqueous solution resulted in yellow oils which could not be induced to crystallize. The solution which contained the desired ligands was, therefore, used directly in the synthesis of the cobalt(III) complexes as has been done by other workers.^{42,43}

2. Preparation of N^2,N^2 -dimethyl- N^1,N^1 -diacetato-1,2-propanediamine

Ten and two tenths grams (0.1 mole) of N^2,N^2 -dimethyl-1,2-propanediamine was reacted with 18.8 g (0.2 mole)

of monochloroacetic acid in a manner identical to the procedure used in Part 1.

3. Preparation of the nitrogen substituted diacetic acid derivatives of R-1,2-propanediamine

A solution of 31.6 g (0.10 mole) of barium hydroxide octahydrate in 125.0 ml of water was added to 20.5 g (0.05 mole) of R-1,2-propanediamine-d-tartrate dihydrate in 125.0 ml water and filtered with suction to remove the precipitated barium tartrate. The filtrate which contained the desired R-1,2-propanediamine was added with stirring to an ice cold solution of 11.3 g (0.12 mole) monochloroacetic acid which had previously been neutralized with 13.7 g (0.24 mole) of potassium hydroxide in the manner described in Part 1. The reaction mixture was allowed to stand overnight and then heated at 55°C for one hour. Concentrated hydrochloric acid was added until the pH of the solution was 5, whereupon, the solution was rotary evaporated to a volume of 50.0 ml and filtered. This solution which contained the desired ligands was then used directly in the preparation of the cobalt(III) complexes.

4. Preparation and isolation of the isomers of N¹,N²-diacetato-1,2-propanediamine(ethylenediamine)cobalt(III) chloride and N¹,N¹-diacetato-1,2-propanediamine(ethylenediamine)cobalt(III)chloride

The procedure for the preparation of the cobalt(III)

complexes was adapted from that of Legg and Cooke⁷ for the preparation of the closely related complex $[\text{Co}(\text{EDDA})(\text{en})]\text{NO}_3$. The solution which contained the diacetato derivatives of 1,2-propanediamine prepared in Section B-1 was heated to 60°C and cobalt carbonate was added in one gram increments to the constantly stirring solution until the evolution of carbon dioxide was no longer apparent, 19.4 g (0.06 mole) were required. In this manner it was possible to approximate how much ligand is present in the crude reaction mixture. The reaction mixture was cooled in an ice bath and filtered through a "Celite" mat to remove any traces of unreacted cobalt carbonate. The pink filtrate was placed in an ice bath and cooled to about 15°C. Five grams of activated charcoal was added followed by 40.0 ml of 2N hydrochloric acid and 3.6 g (0.06 mole) of 98% ethylenediamine. The solution was oxidized to cobalt(III) by adding dropwise 6.5 g of 30% hydrogen peroxide. The reaction mixture was then stirred for about 30 minutes, removed from the ice bath and allowed to stir at room temperature for about three hours. A 5.0 ml aliquot was then drawn from the reaction mixture and filtered with suction to remove the charcoal. The dark red filtrate was placed on a small chromatography column (1 cm x 30 cm) containing about 25.0 ml of Dowex-50w-x8 ion-exchange resin in the H^+ form and eluted with 0.3N HCl. Two red bands moved down the column indicating that the desired complexes were present. A very small

brown band remained at the top of the column and was presumed to be impurities. The remaining reaction mixture was filtered with suction through a "Celite" mat to remove the charcoal.

The various isomers of the complexes were separated by ion-exchange chromatography. The filtered reaction mixture was rotary evaporated under reduced pressure at 40°C to a volume of about 200 ml. About 75.0 ml of the reaction mixture was placed on a chromatography column (5 cm x 1000 cm) containing approximately 1.5 l of Dowex 50W-x8 ion-exchange resin in the H⁺ form. The complexes formed a dark red band at the top of the column. The complexes were eluted with 0.3N HCl with flow rate adjusted to about 0.5 ml per minute. After about 5 days, separation of the various isomers became apparent as the large band which had formed at the top was now separating into distinct bands. After two weeks of elution, five bands had clearly separated and moved down the column indicating a +1 charged species. The large yellowish band which remained at the top of the column was presumed to be [Co(en)]³⁺ and other products. The portion of the resin containing the uppermost +1 band was removed by suction using a long glass tube attached with polyethylene tubing to a suction flask connected to a water aspirator. This resin was then placed in another chromatography column and the complex was eluted with 1.0N HCl. The resulting eluant was rotary evaporated under reduced

pressure at 40°C to dryness. About 200 ml water were then added and the solution rotary evaporated to dryness again. This was repeated four more times to assure removal of HCl. After the addition of the last portion of water, the volume of the solution was reduced to about 15-20 ml. About 200 ml absolute ethanol were added to this solution and allowed to stand overnight. By morning large crystals had formed which were filtered, washed with ethanol and acetone and air dried. This band was identified by its visible and nmr spectra as u-cis-[Co(N¹,N²-PDDA)(en)]Cl. The yield was about 0.6 g Anal. Calcd for [CoC₉H₂₀N₄O₄]Cl H₂O: C, 29.97; H, 6.15; N, 15.53. Found: C, 30.21; H, 6.33; N, 15.54. The next band was removed and treated in the same manner as the u-cis-oxygen isomer by its visible spectra and was thought to be cis(O)-[Co(N¹,N¹-PDDA)(en)]⁺. However, only a trace amount of this isomer was obtained and it was not characterized further, except for the ORD curve which will be discussed later. The remaining three bands were allowed to elute off the original column. The first band off the column was also a minor component. It consisted of two closely spaced bands which would not separate and because of their instability and small amount, these bands could also not be well characterized. They did appear to exhibit a trans spectrum and gave a positive Cotton effect in the ORD. The next bands which eluted from the column were identified

as trans(O)-[Co(N¹,N¹-PDDA)(en)]Cl and s-cis-[Co(N¹,N²-PDDA)(en)]⁺Cl by their visible and nmr spectra. The yields were 0.5 g and 0.4 g respectively. Anal. Calcd for trans(O)-[CoC₉H₂₀N₄O₄]Cl·1.5 H₂O: C, 29.24; H, 6.26; N, 15.15. Found: C, 29.58; H, 6.32; N, 15.39. Calcd for s-cis-[CoC₉H₂₀N₄O₄]Cl·1.5 H₂O: C, 30.73; H, 6.01; N, 15.93. Found: C, 31.00; H, 6.54; N, 15.79.

5. Preparation and isolation of the isomers of N¹,N²-diacetato-R-1,2-propanediamine(ethylenediamine)cobalt(III) chloride and N¹,N¹-diacetato-R-1,2-propanediamine(ethylenediamine)cobalt(III)chloride

The procedure for the preparation of these complexes was identical to that used in the preparation of the optically inactive complexes except that the amount of reagents used were one half those used in the previous procedure.

After the reaction mixture was filtered and evaporated to a volume of about 100 ml, a 50 ml portion was placed on a chromatography column (3 cm x 65 cm) filled with about 500 ml Dowex-50w-x8 cation exchange resin in the H⁺ form. The various complexes were separated by eluting with 0.1N HCl as in the previous section. Since the amount of complexes separated was very small, solid samples were not obtained. The complexes were simply eluted off the column and rotary evaporated several times to remove the HCl. The ord and cd spectra were then measured directly on these solutions and their concentrations measured spectrophotome-

trically using the Cary 14 spectrophotometer.

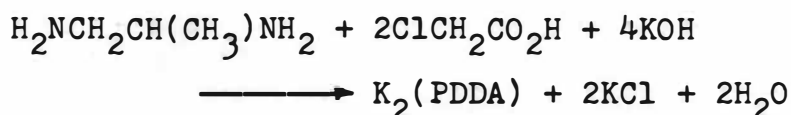
6. Preparation and isolation of N^1, N^1 -diacetato- N^2, N^2 -dimethyl-1,2-propanediamine(ethylenediamine)cobalt(III) chloride

The procedure for the preparation and isolation of this complex was the same as that used for the preparation and isolation of $[Co(N^1, N^2\text{-PDDA})(en)]Cl$. In this case, only one isomer was obtained, the trans(0) $[Co(N^1, N^1\text{-DMPDDA})(en)]Cl$. Since the chloride salt of this complex was too soluble to permit recrystallization, it was converted to the perchlorate salt by adding $AgClO_4$ and filtering the resulting $AgCl$. Recrystallization from water gave violet crystals. The yield was 3.0 g Anal. Calcd for $[CoC_{11}H_{24}N_4O_4]ClO_4$: C, 30.39; H, 5.56; N, 12.89. Found: C, 30.28; H, 5.73; N, 12.92.

RESULTS AND DISCUSSION

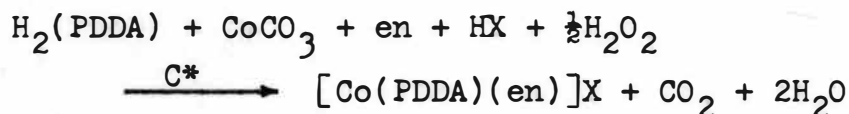
A. Synthesis of the Ligands and Complexes

The tetradentate ligands were prepared by means of reaction between monochloroacetic acid and 1,2-propanediamine as summarized in the following reaction.



Due to the unsymmetrical nature of the diamine used, three different PDDA products are possible. These are; $\text{HO}_2\text{CCH}_2\text{NHCH}_2\text{CH}(\text{CH}_3)\text{NHCH}_2\text{CO}_2\text{H}$ (N^1, N^2 -PDDA), $(\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ (N^1, N^1 -PDDA), and $\text{H}_2\text{NCH}_2\text{CH}(\text{CH}_3)\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ (N^2, N^2 -PDDA).

Since these ligands could not be isolated, the ligand reaction mixture was reacted directly with cobalt carbonate to produce the desired complexes. This reaction may be summarized as follows:



The complexes were separated by means of ion-exchange chromatography and characterized by their visible, nmr and ord spectra. Only the N^1, N^2 -PDDA and N^1, N^1 -PDDA complexes were found, indicating that either the N^2, N^2 -PDDA ligand is

produced in only small quantities or that the complex is unstable.

B. Separation of Isomers Using Ion-Exchange Chromatography

Since King and Walters⁴⁵ first separated the cis and trans isomers of $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]^+$ in 1952, use of ion-exchange chromatography has steadily increased among inorganic chemists. Although other chromatographic methods are slowly being utilized,^{46,47} ion-exchange chromatography will probably remain as the chief means of separating various isomers of cobalt(III) complexes.

Legg and Cooke⁷ used ion-exchange chromatography to separate complexes of the CoN_4O_2 type (s-cis and u-cis- $[\text{Co}(\text{EDDA})(\text{en})]^+$) and found that the order of elution was s-cis before u-cis. This is presumably due to the fact that the s-cis isomer has the two oxygens coordinated in trans position and has no net dipole moment as compared to the u-cis isomer in which the oxygens are cis. Thus, the cis isomer is more strongly adsorbed to the column substrate. Legg⁴⁸ has shown the ability of ion-exchange chromatography to separate diastereomeric complexes with only slightly differing polar characters when he separated all six possible isomers of $[\text{Co}(\text{EDDA})(\text{R-pn})]^+$.

In the present work, the order of elution was that expected with the complex containing trans oxygens eluting before the corresponding cis isomers (as characterized by the

electronic absorption spectra). The ordering of the trans isomers as identified by the nmr spectra was trans(0)- $[\text{Co}(\text{N}^1, \text{N}^1\text{-PDDA})(\text{en})]^+$ followed by s-cis- $[\text{Co}(\text{N}^1, \text{N}^2\text{-PDDA})(\text{en})]^+$. This ordering is also expected since $\text{N}^1, \text{N}^1\text{-PDDA}$ is more symmetrical than $\text{N}^1, \text{N}^2\text{-PDDA}$. The ordering of the cis isomers was the same as the trans. All separations appeared to be complete in that no other isomers were detected.

C. Electronic Absorption Spectra

The visible absorption spectra of all the complexes synthesized in this study are shown in Figures 6 and 7 and are summarized in Table I together with data on analogous complexes. The wavelengths for the shoulders were obtained by subtracting a symmetrical trace of the major peak from the observed spectra.

In complexes of the CoN_4O_2 type, which can exist in both cis(0) and trans(0) configurations, there are spectral features which are diagnostic of the relative positions of the oxygen atoms. Simple crystal field theory^{49,50,51} shows that the visible absorption spectrum of an octahedral CoN_6 complex, for example, $[\text{Co}(\text{NH}_3)_6]^{3+}$, consists of two spin allowed bands arising from the excitation of an electron from the nondegenerate $^1\text{A}_{1g}$ ground state to two triply degenerate excited states ($^1\text{T}_{1g}$ and $^1\text{T}_{2g}$). When two of the six ligands are replaced by two different ones, as in a

CoN_4O_2 complex, the lowering of the octahedral symmetry will cause splitting of the two triply degenerate excited states (see Figure 5). Theory shows that the splitting of the T_{1g} state should be twice as large for the trans configuration as compared to the cis configuration. Yamada and Tsuchida⁵² have also shown theoretically that the cis isomers should have more intense spectra than the corresponding trans which was verified by Basolo and co-workers.⁵³

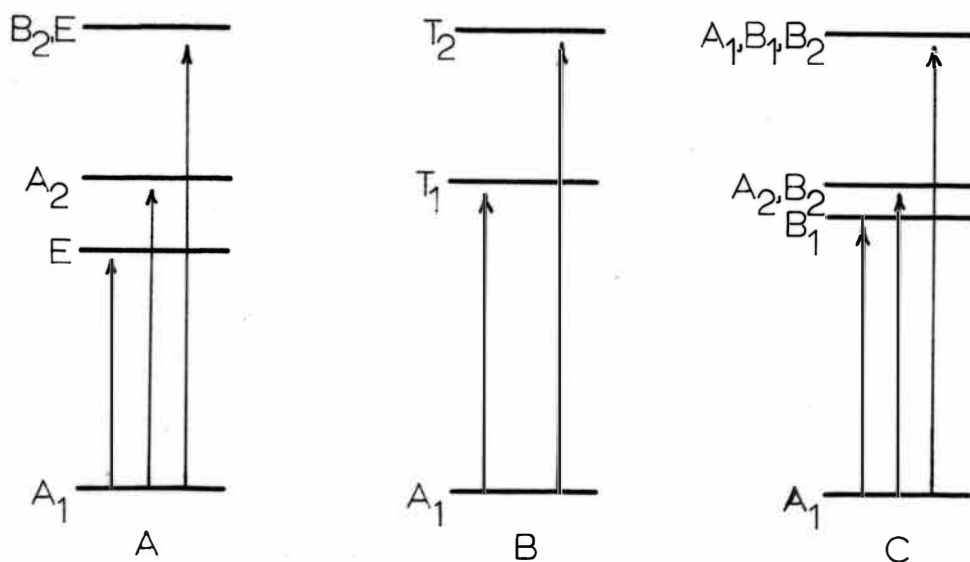


Figure 5. Diagrammatic representation of the energy levels in: (A) trans- CoN_4O_2 ; (B) CoN_6 ; (C) cis- CoN_4O_2

Legg and Cooke⁷ have discussed the visible spectra for s-cis and u-cis- $[\text{Co}(\text{EDDA})(\text{en})]^+$ and show that the observed spectra agree quite well with theory in that the complexes with trans(0) have an observable shoulder on the high energy side of the first absorption band while the corresponding band for the cis(0) complexes are only broadened. The analogous s-cis and u-cis- $[\text{Co}(\text{N}^1, \text{N}^2\text{-PDDA})(\text{en})]^+$

TABLE I

The Electronic Absorption Spectra of the Complexes
Prepared in this Investigation and Related Complexes

	Band I _a		Band I _b		Band II	
	$\bar{\nu}^a$	ϵ	$\bar{\nu}$	ϵ	$\bar{\nu}$	ϵ
s- <u>cis</u> -[Co(N ¹ ,N ² -PDDA)(en)]Cl	1.891	86.5	2.232	sh	2.763	110
s- <u>cis</u> -[Co(EDDA)(en)]NO ₃	1.890	87.3	2.232	sh	2.762	113
u- <u>cis</u> -[Co(N ¹ ,N ² -PDDA)(en)]Cl	1.819	sh ^d	2.027	162	2.783	160
u- <u>cis</u> -[Co(EDDA)(en)]Cl ^b	1.805	sh	2.020	169	2.778	168
<u>trans</u> (O)-[Co(N ¹ ,N ¹ -PDDA)(en)]Cl	1.896	161.8	2.222	sh	2.813	201
<u>trans</u> (O)-[Co(AEIDA)(en)]Cl ^c	1.894	144	2.237	sh	2.801	175
<u>cis</u> (O)-[Co(N ¹ ,N ¹ -PDDA)(en)]Cl ^e	1.820	sh	2.023		2.830	
<u>cis</u> (O)-[Co(AEIDA)(en)]Cl ^c	1.789	sh	2.008	107	2.801	117
<u>trans</u> (O)-[Co(N ¹ ,N ¹ -DMPDDA)(en)]ClO ₄	1.891	148	2.222	sh	2.702	161
s- <u>cis</u> -[Co(DEEDDA)(en)]NO ₃ ^b	1.869	77.7	2.162	sh	2.681	106

^aAll $\bar{\nu}$ in cm⁻¹ x 10⁻⁴. ^bSee ref. 7. ^cSee ref. 29. ^dsh=shoulder. ^enot isolated

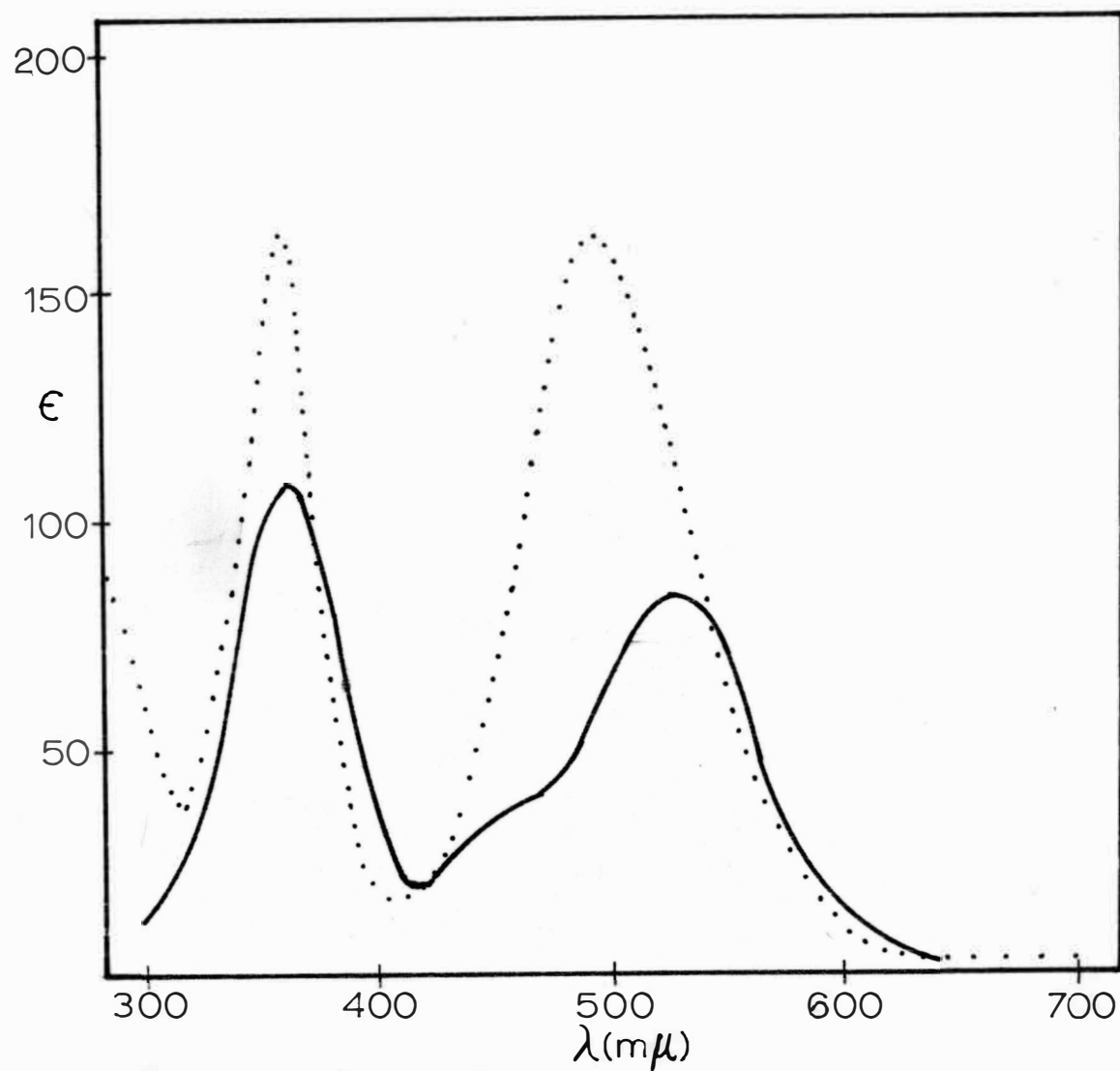


Figure 6. Visible spectra of $[\text{Co}(\text{N}^1, \text{N}^2\text{-PDDA})(\text{en})]^+$; s-cis(—), u-cis(···).

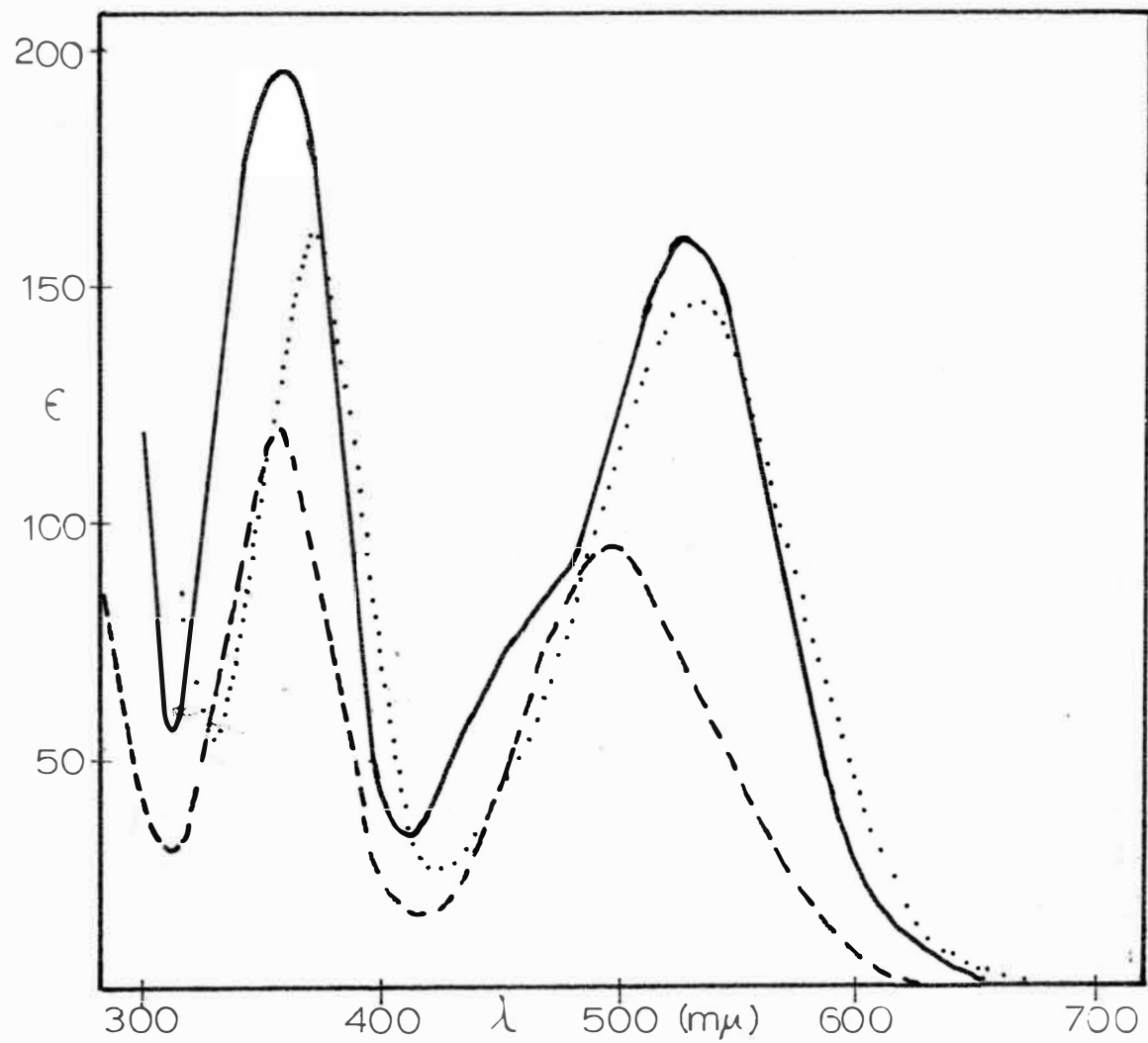


Figure 7. Visible spectra of trans(0)(—), cis(0)-[Co-(N¹, N¹-PPDA)(en)]⁺(--)(not quantitative), and trans(0)-[Co(N¹, N¹-DMPDDA)(en)]⁺(:..).

(see Figure 6) have almost identical visible spectra (see Table I) as would be expected.

The trans(O)-[Co(N¹,N¹-PDDA)(en)]⁺ complex also has a spectrum similar to the corresponding u-cis isomer (see Figure 7). However, the trans(O) isomer has more intense bands than the corresponding s-cis-[Co(N¹,N²-PDDA)(en)]⁺ isomer. This result agrees with the results found by Chu, Cooke and Liu²⁹ in their studies of the analogous cis(O) and trans(O)-[Co(AEIDA)(en)]⁺ complexes. In fact, they found that the intensity relationship between the cis and trans isomers is reversed from theory which predicts that cis should be more intense. These authors felt that the trans isomer gained intensity through the dissymmetry introduced by asymmetrical ligand vibrations.

The trans(O)-[Co(N¹,N¹-DMPDDA)(en)]⁺ complex (see Figure 7) has visible spectra which is shifted to lower energy from the analogous trans(O)-[Co(N¹,N¹-PDDA)(en)]⁺. An almost identical shift was also observed for s-cis-[Co(DEEDDA)(en)]⁺ by Legg and Cooke.⁷ This shift appears to be due to the fact that successive alkyl substitution at the coordinating nitrogens causes a lowering of the Dq value similar to that seen by Pavkovic and Meek⁵⁴ for a series of N-alkylated ethylenediamine nickel(II) complexes. These authors claim that steric factors may outweigh inductive factors for the contributions to Dq. Also, in the DMPDDA complex the shoulder on the high energy side of

the first band is not as pronounced as found in all the other trans(0) isomers. This is probably due to the low symmetry of the complex and the fact that the intensity of the second band is quite large.

D. Nuclear Magnetic Resonance Spectra

1. General considerations

The nmr technique has been extensively utilized in studies of the stereochemistry and reactions of aminocarboxylate chelates of cobalt(III) complexes.^{7,8,28,29,36,37} The nmr spectra of these complexes usually consist of overlapping AB spectra due to spin-spin coupled methylene glycinate protons and more complicated resonances due to methylene protons of the diamine backbone.⁷ (For simplicity, this discussion will be limited to only those aminocarboxylate ligands which contain nitrogen substituted diamines, such as EDDA or PDTA). The spectra can be quite simple to interpret as in s-cis-[Co(EDDA)(en)]⁺⁷ or very complex as in [Co(PDTA)]⁻.⁵⁵

Legg and co-workers⁸ have divided the possible types of glycinate chelate rings into four categories depending on the conformation of the glycinate ring with respect to the diamine backbone. These categories consist of: two types of out-of-plane acetates, one which is attached to a secondary amine, R₁, and one which is attached to a ter-

tiary amine having an additional chelated glycinate attached, R_2 ; and two types of in-plane glycinate, G_1 and G_2 , classified in the same manner as the R rings. (The in-plane and out-of-plane refer to the plane of the diamine backbone).

In cobalt(III) complexes containing these ligands there are several mechanisms by which the electronic environment and, thus, the chemical shift of a particular proton can be affected. These include inductive effects, bond anisotropy effects and steric compressions. The inductive effects account for the shift of the glycinate proton signals to lower field than those of the methylene protons associated with the diamine portion of the ligand.^{7,56,57} The glycinate protons are subjected to the combined deshielding effects of the carboxylate and amine groups, whereas, the methylene protons of the diamine backbone experience only the inductive effects of the adjacent amine groups. Legg and Cooke^{7,38} have discussed the differences in chemical shifts of the glycinate ring protons in terms of C-N bond anisotropy. In *s-cis* and *u-cis*-[Co(EDDA)(en)]⁺ a proton lying directly over a C-N bond is shielded relative to one that lies along the bond axis. Similar shifts were found for the mixed complexes of IDA and MIDA with dien.³⁹ Cooke and Dabrowiak⁴⁰ have recently invoked steric compression arguments to explain the variance of proton chemical shifts in bis(amino acid) complexes. This effect is produced when a hydrogen atom is forced into proximity of

some other atom in the molecule. The proton involved in the compression is found to resonate at lower field than when the compression is absent.

Also helpful in assigning a particular pair of resonances in an AB quartet to a particular glycinate proton is H-N-C-H spin-spin coupling observed by Sudmeier and Occupati³⁷ in cobalt(III) complexes with EDDA. They invoked the Karplus relationship⁵⁸ which shows that the proton-proton coupling varies with dihedral angle, and were able to assign the glycinate protons, designated H_a and H_b (see Figure 22), to particular resonances. Their assignment agreed with that made earlier by Legg and Cooke.⁷ Cooke³⁹ has also observed H-N-C-H spin coupling in the bis complexes of cobalt(III) with IDA and MIDA.

It has also been demonstrated that the methylene protons adjacent to a coordinated carboxylate in certain chelate systems are susceptible to deuterium substitution.^{36,59} Sudmeier and Occupati³⁷ demonstrated that the less sterically hindered proton in *s-cis*-[Co(EDDA)(en)]⁺, H_a in Figure 22, exchanges with deuterium in D₂O approximately 10 times faster than H_b . The exchange is catalyzed by both acid and base. Thus observing which proton exchanges with deuterium is helpful in assigning the various glycinate protons.

2. The nmr spectrum of s-cis-N¹,N²-diacetato-1,2-panediamine(ethylenediamine)cobalt(III)

The nmr spectra associated with the second trans band are shown in Figures 8 and 9 and the chemical shifts are tabulated in Table II. This complex is identified as $s\text{-cis-}[\text{Co}(\text{N}^1, \text{N}^2\text{-PDDA})(\text{en})]^+$. In the spectrum of the undeuterated complex, two broad resonances characteristic of amine protons are seen (Figure 9). The signal at 5.46 ppm corresponds to 4 protons and is assigned to the amine protons on ethylenediamine. The low field protons at 7.25 ppm corresponding to 2 protons are in a region characteristic of secondary amine protons. Sudmeier³⁷ observed resonances in this region for $[\text{Co}(\text{EDDA})(\text{en})]^+$ which were assigned to the secondary amine protons on EDDA. The presence of these secondary amines requires that the complex contains $\text{N}^1, \text{N}^2\text{-PDDA}$.

The $s\text{-cis-}[\text{Co}(\text{N}^1, \text{N}^2\text{-PDDA})(\text{en})]^+$ ion can exist in two diastereomeric forms. However, the single sharp methyl doublet centered at 1.45 ppm and the presence of only two sharp AB quartets in the region characteristic of glycine protons suggests that only one of the diastereomers exists in significant quantities. Stereochemical considerations to be discussed in Section F indicate that the most stable isomer for $s\text{-cis-}[\text{Co}(\text{N}^1, \text{N}^2\text{-PDDA})(\text{en})]^+$ is Δ if the PDDA is in the R configuration and Λ if the PDDA is S. A representation of this complex is shown in Figure 22.

The nmr spectrum of this complex is most easily understood when it is interpreted in conjunction with the

TABLE II

Proton Chemical Shifts^a of the Complexes
Synthesized in this Study and Related Complexes

	R ₁ -ring		R ₂ -ring		G ₁ -ring		
	H _a	H _b	H _a	H _b	H _a	H _b	N-CH ₃
<u>s-cis</u> -[Co(N ¹ ,N ² -PDDA)(en)] ⁺	4.24	3.42					
	3.86	3.58					
<u>s-cis</u> -[Co(EDDA)(en)] ⁺ b	4.22	3.38					
<u>u-cis</u> -[Co(N ¹ ,N ² -PDDA)(en)] ⁺	4.01	3.14			3.70		
<u>u-cis</u> -[Co(EDDA)(en)] ⁺ c	4.02	3.15			3.71		
<u>trans</u> (O)-[Co(N ¹ ,N ¹ -PDDA)(en)] ⁺			4.60	4.05			
			4.28	4.05			
<u>trans</u> (O)-[Co(N ¹ ,N ¹ -DMPDDA)(en)] ⁺			4.58	4.11			
			4.15	4.03			2.17
<u>trans</u> (O)-[Co(AEIDA)(en)] ⁺ d			4.43	4.06			

Table II (Cont.)

	en	pn	R-CH ₃	R-NH ₂	R ₂ NH
<u>s-cis</u> -[Co(N ¹ ,N ² -PDDA)(en)] ⁺	2.9		1.43	5.45	7.25
<u>s-cis</u> -[Co(EDDA)(en)] ⁺	2.83			5.46	7.30
<u>u-cis</u> -[Co(N ¹ ,N ² -PDDA)(en)] ⁺	3.2—2.25		1.47	5.34	7.10
<u>u-cis</u> -[Co(EDDA)(en)] ⁺					
<u>trans</u> (O)-[Co(N ¹ ,N ¹ -PDDA)(en)] ⁺	2.8—3.6		1.38	5.2	5.70
<u>trans</u> (O)-[Co(N ¹ ,N ¹ -DMPDDA)(en)] ⁺	2.5—3.5		1.22	6.1	
<u>trans</u> (O)-[Co(AEIDA)(en)] ⁺					

^appm from DSS. ^bSee Ref. 7. ^cSee Ref. 8. ^dSee Ref. 29.

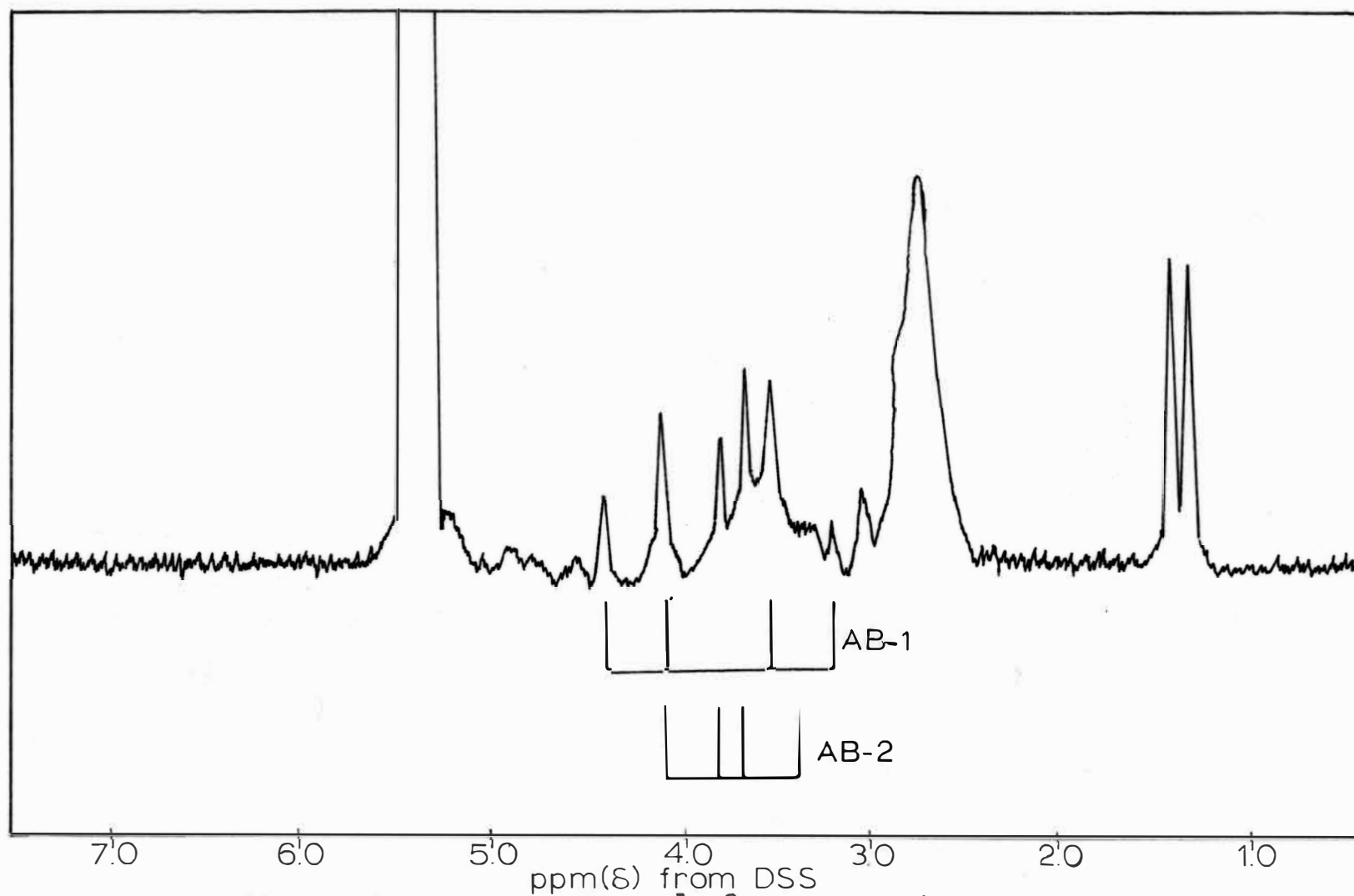


Figure 8. The nmr spectrum of *s-cis*-[Co(N¹,N²-PDDA)(en)]⁺. (Amine protons exchanged).

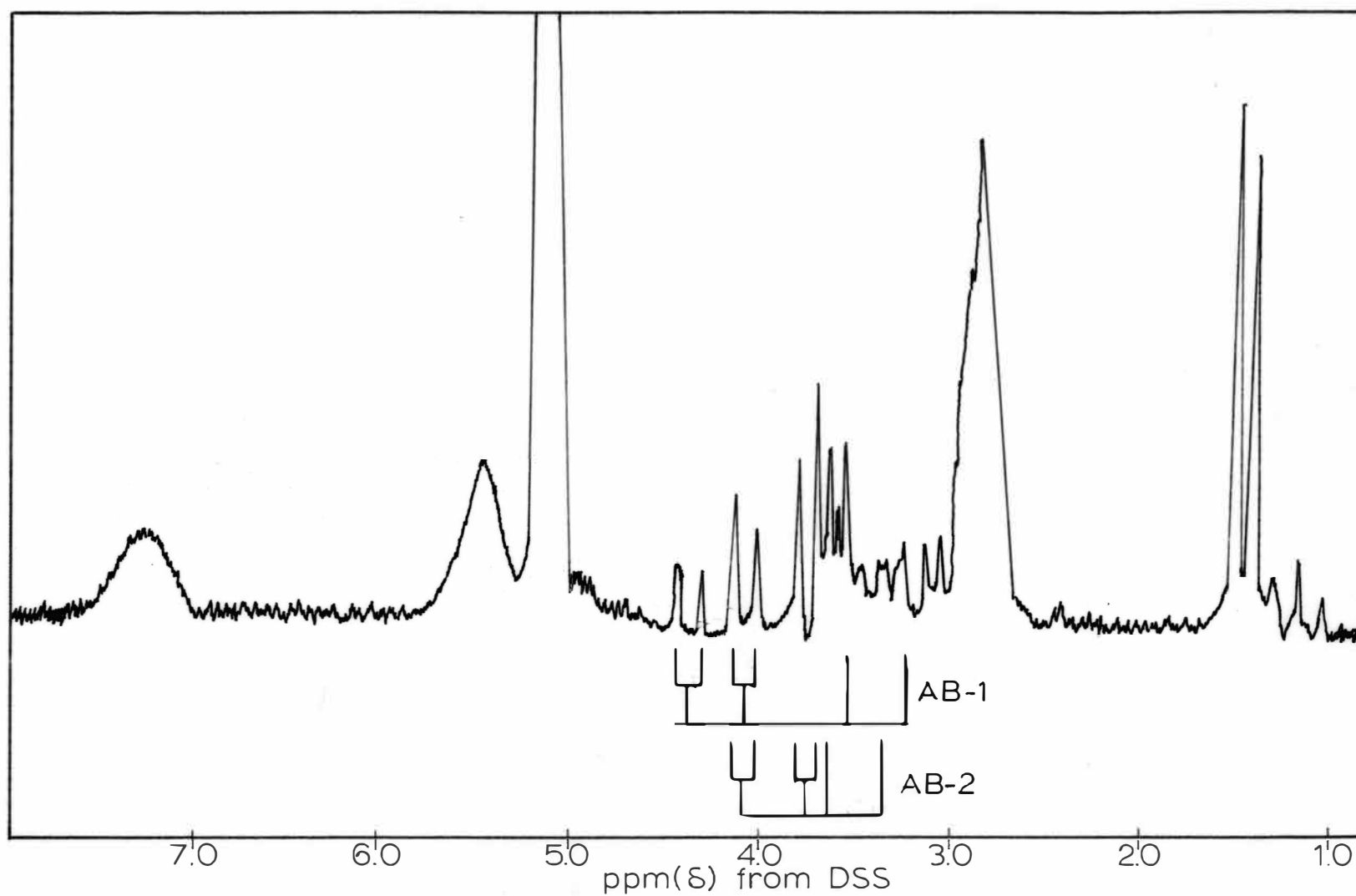


Figure 9. The nmr spectrum of *s-cis*-[Co(N¹,N²-PDDA)(en)]⁺ before amine proton exchange.

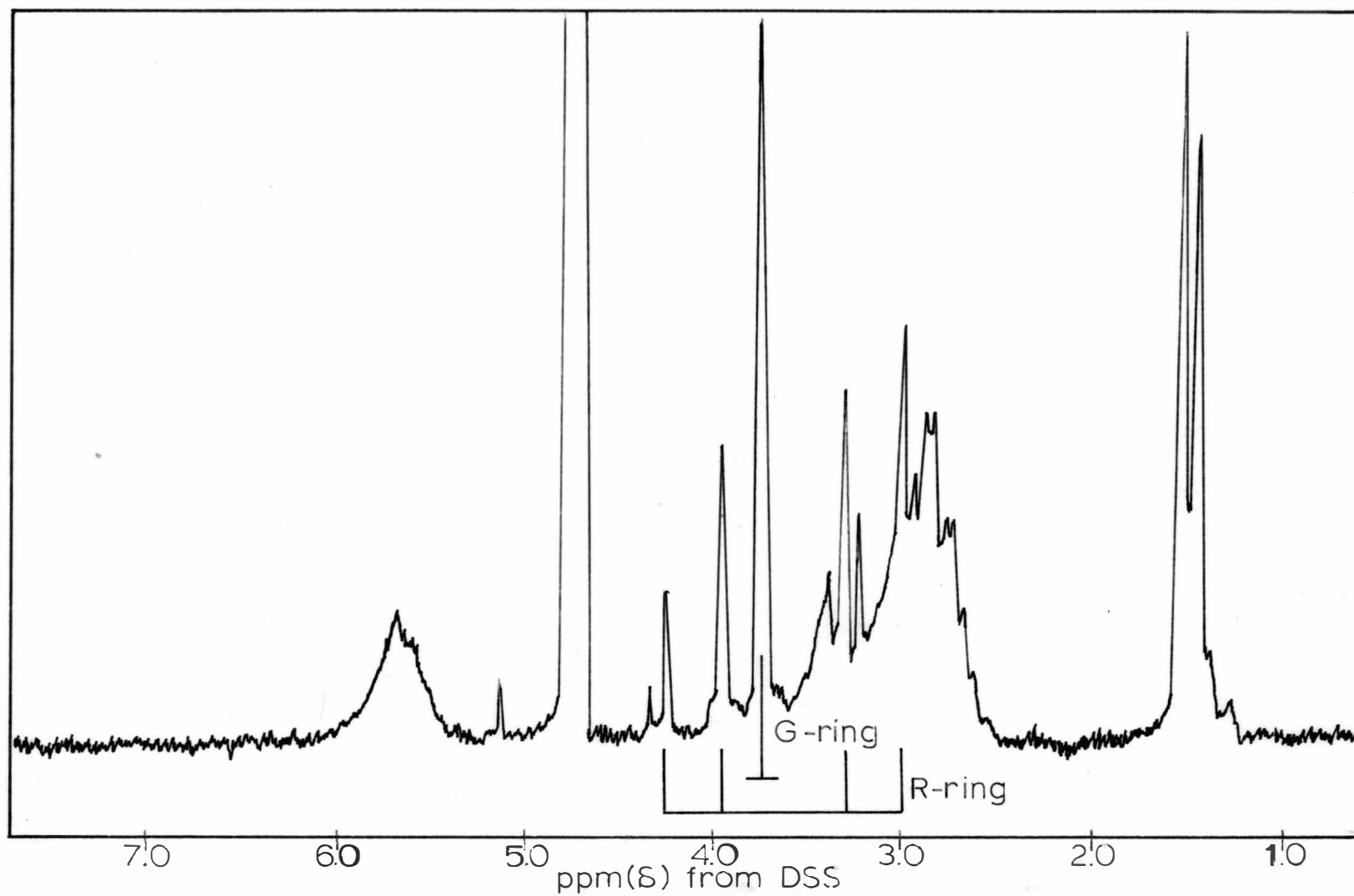


Figure 10. The nmr spectrum of $u\text{-cis-}[\text{Co}(\text{N}^1, \text{N}^2\text{-PDDA})(\text{en})]^+$. (Amine protons exchanged).

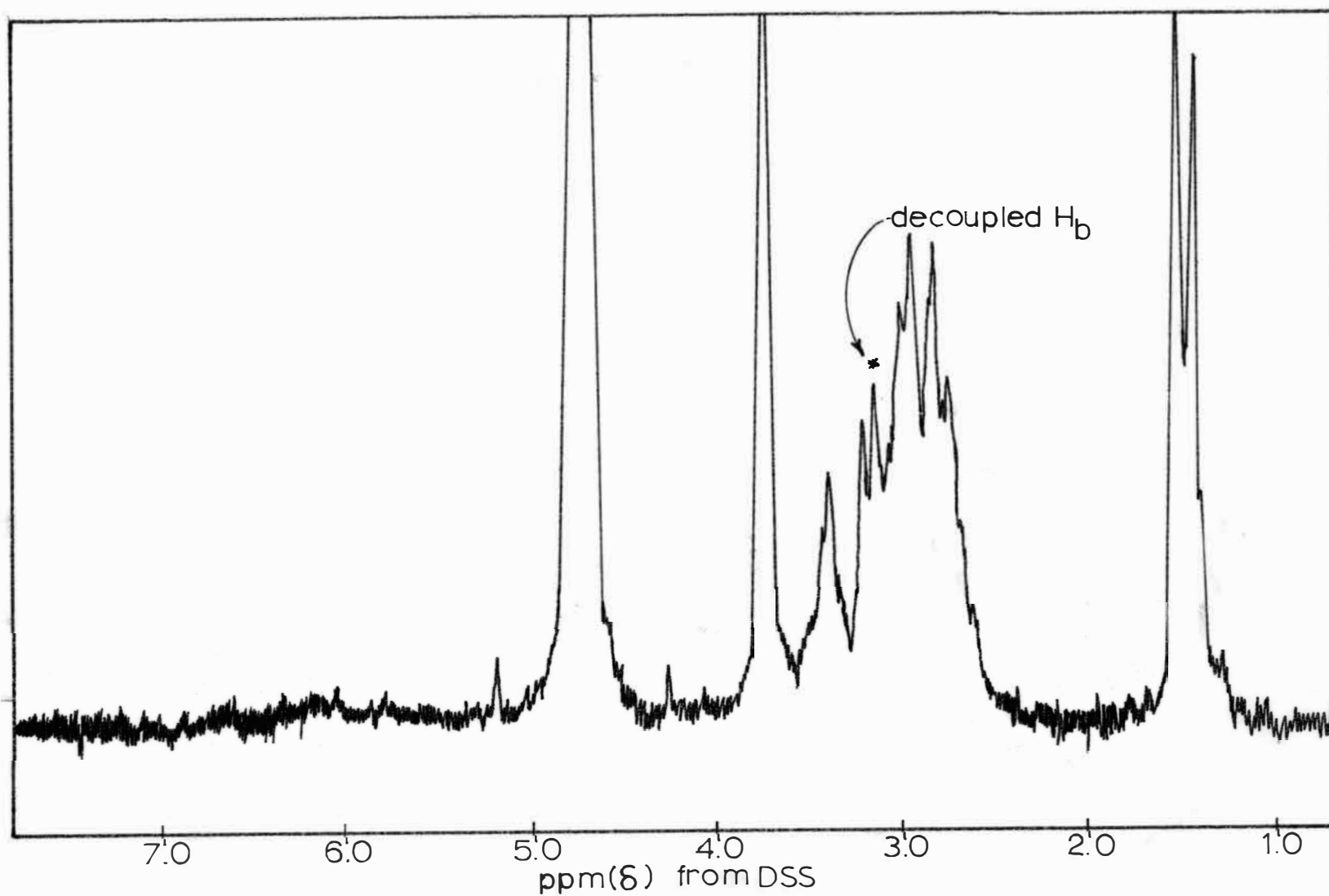


Figure 11. The nmr of u-cis-[Co(N¹,N²-PDDA)(en)]⁺ in basic D₂O.

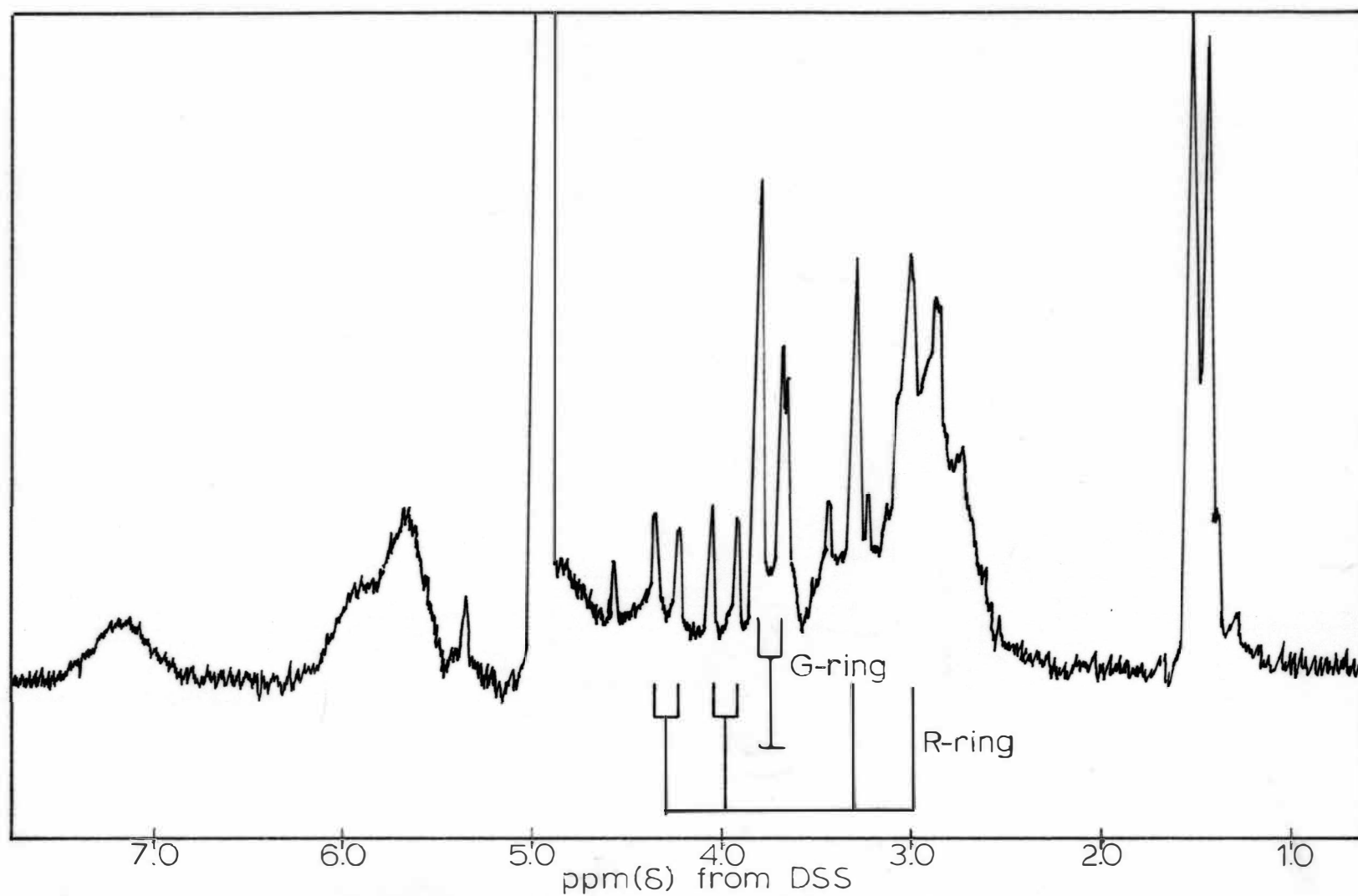


Figure 12. The nmr of $u\text{-cis-}[\text{Co}(\text{N}^1, \text{N}^2\text{-PDDA})(\text{en})]^+$ before amine proton exchange.

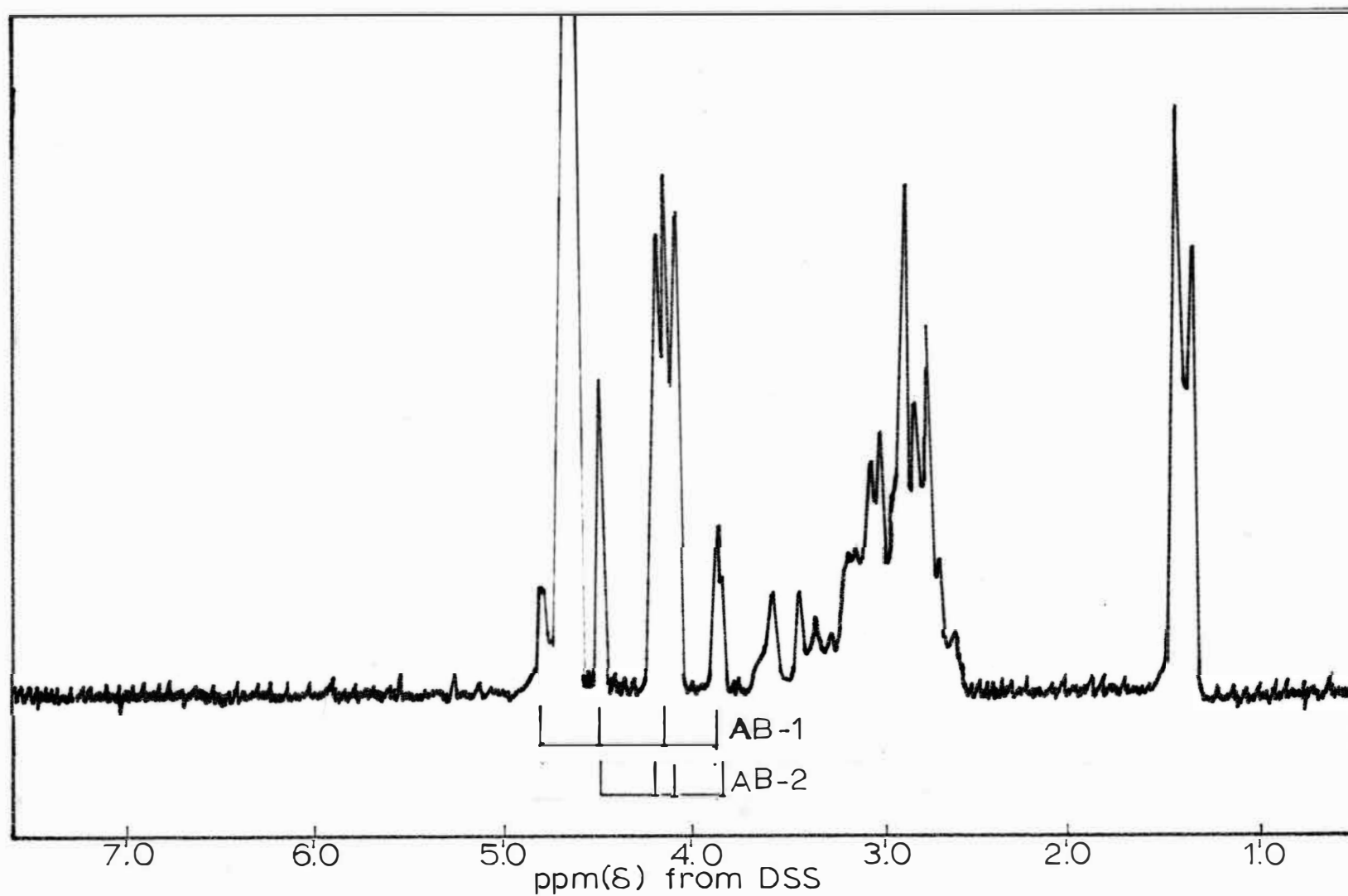


Figure 13. The nmr spectrum of trans(0)-[Co(N¹,N¹-PDDA)(en)]⁺.

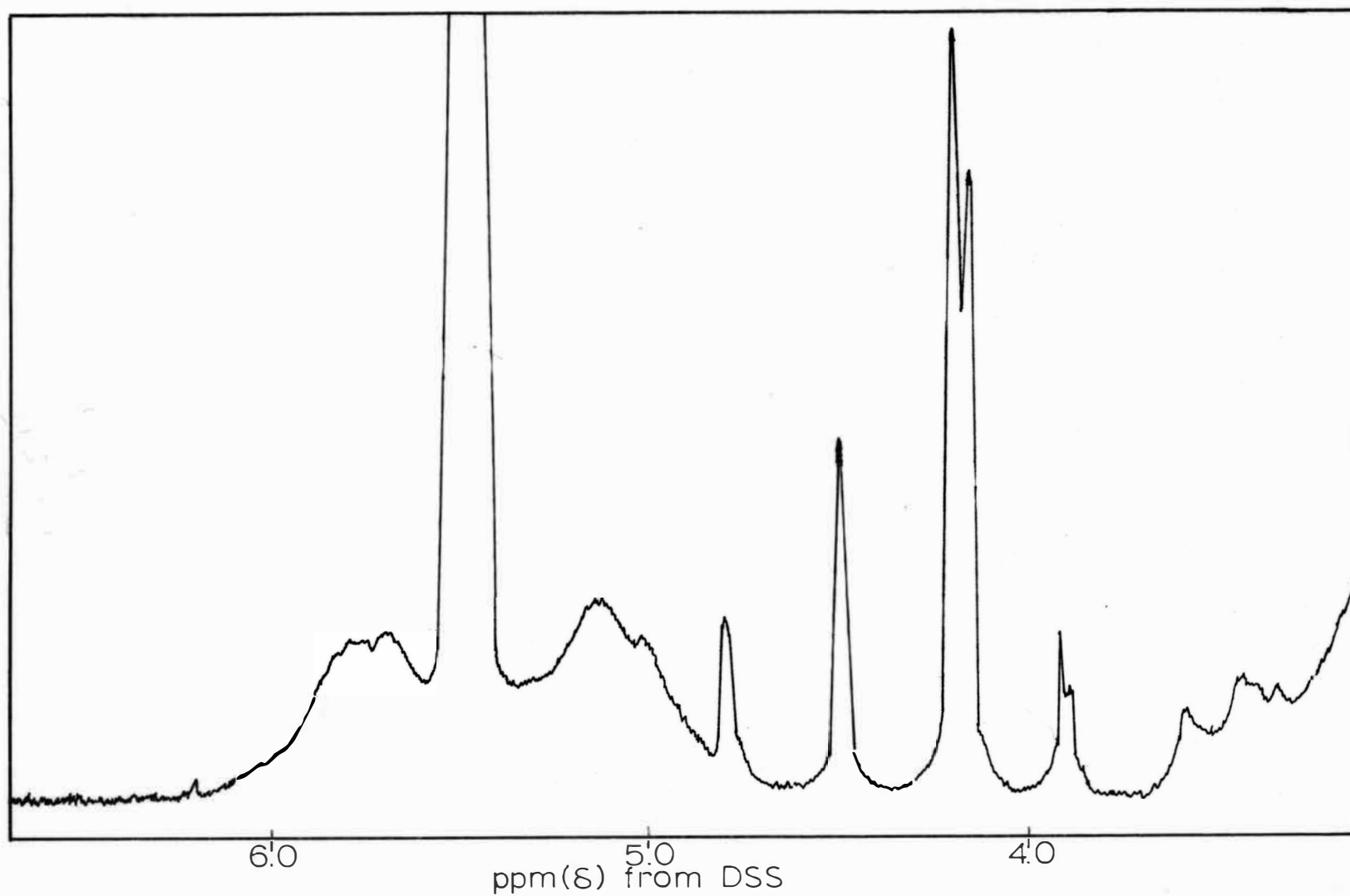


Figure 14. The nmr of trans(0)-[Co(N¹,N¹-PDDA)(en)]⁺ before amine proton exchange.

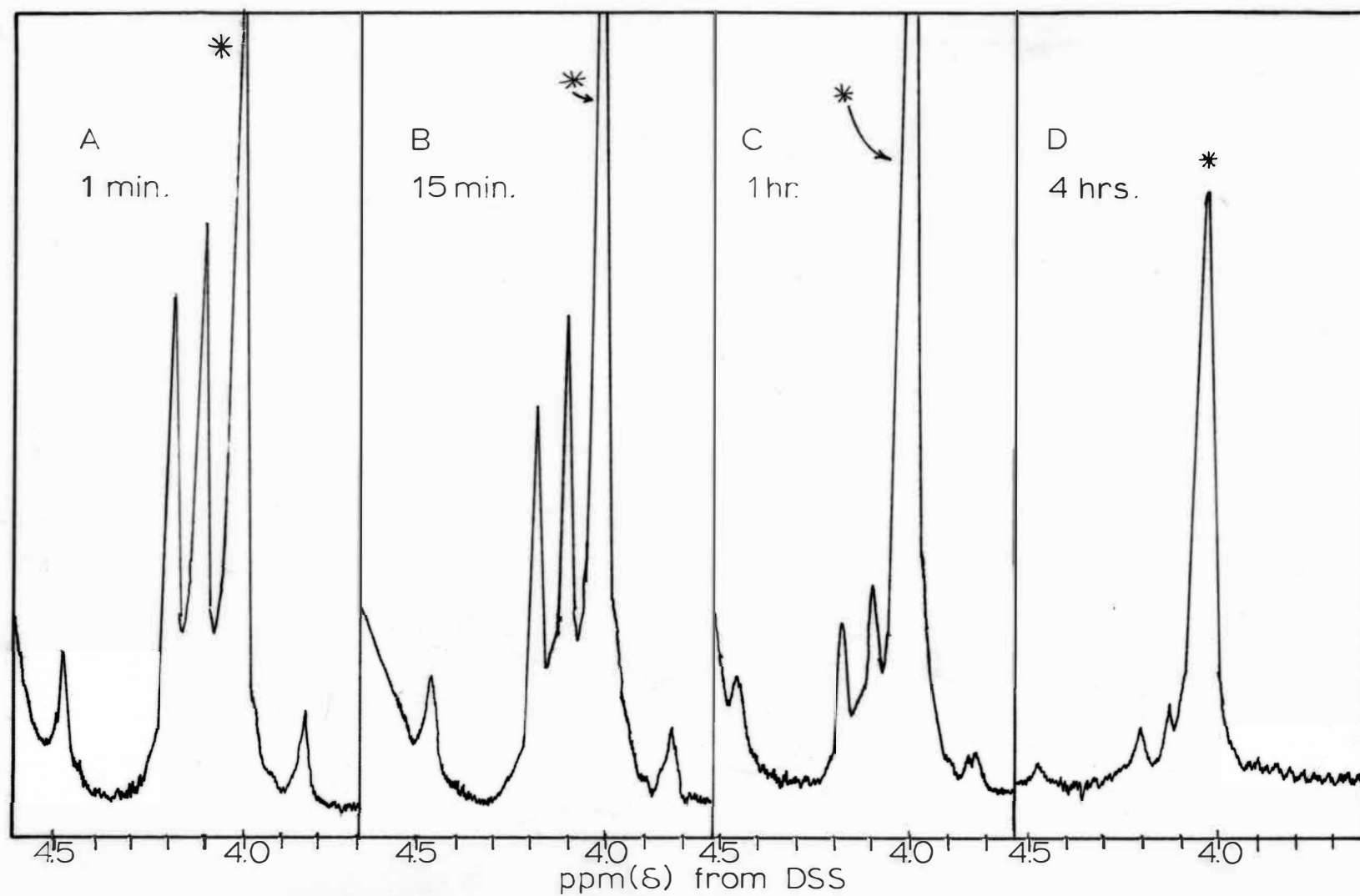


Figure 15. The nmr of trans(O)-[Co(N¹,N¹-PDDA)(en)] in basic D₂O.

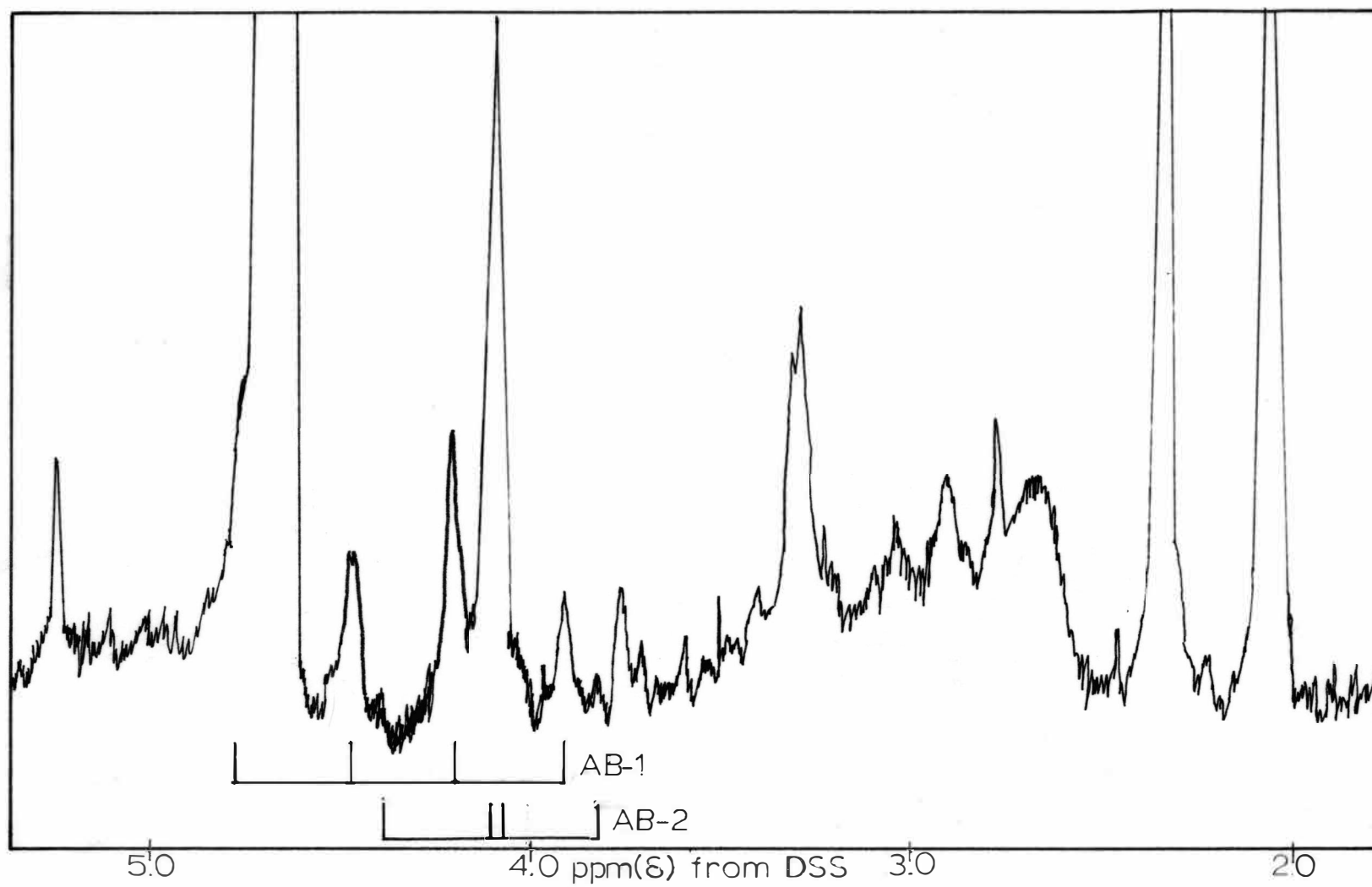


Figure 16. The nmr spectrum of trans(0)-[Co(N¹,N¹-DMPDDA)(en)]⁺.

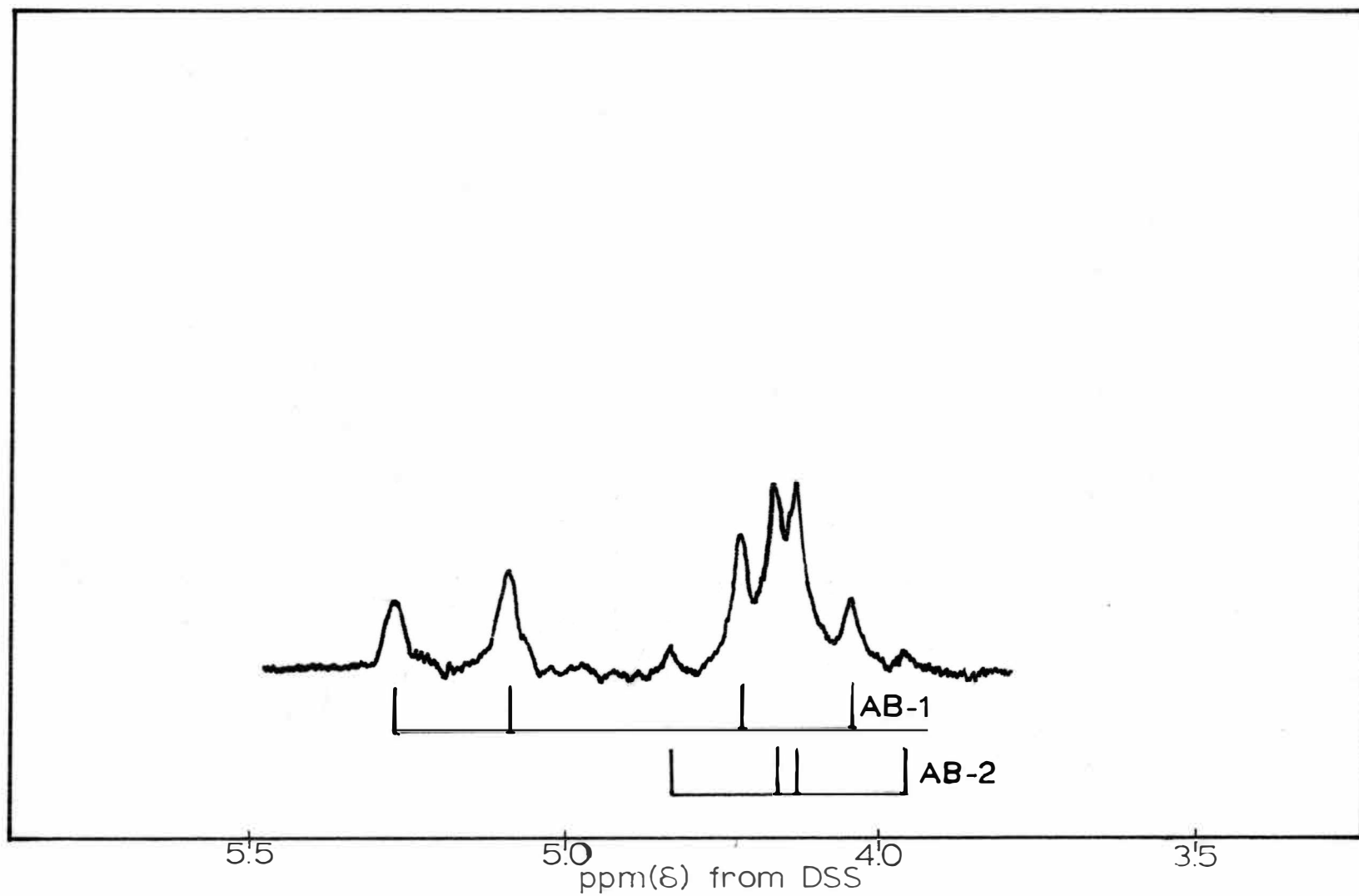


Figure 17. The 100 MHz spectrum of trans(0)-[Co(N¹,N¹-DMPDDA)(en)]⁺.

parent *s-cis*-[Co(EDDA)(en)]⁺ discussed by Legg and Cooke.⁷ The *s-cis*-EDDA complex possesses a C₂ axis of symmetry, thus, the glycinate chelate rings are equivalent and only one glycinate AB pattern is observed. When the ethylenediamine backbone is replaced by 1,2-propanediamine, this center of symmetry is destroyed, the glycinate rings are no longer chemically equivalent, and two overlapping AB patterns are observed (see Figure 8).

The AB pattern with resonances at 264.6, 246.5, 213.3, and 195.4 Hz is designated AB 1 and that with resonances at 245.1, 226.9, 220.0, and 201.8 Hz is designated AB 2. These assignments were confirmed by studying the 100 MH spectrum.

The chemical shifts for AB 1 are calculated⁶⁰ to be 4.24 and 3.42 ppm with a J value of 18.0 Hz and are very similar to those found for the EDDA complex which had chemical shifts of 4.19 and 3.37 ppm. Thus, AB 1 can be assigned to the glycinate ring which is in an environment most similar to that in the EDDA complex, that is, the ring furthest removed from the methyl substituent. Cooke and Legg⁷ assigned the upfield resonance to the proton which extends over the central ethylenediamine backbone (designated H_b in Figure 22) and the downfield portion to the proton which extends away from the diamine backbone (designated H_a in Figure 22). Their assignment was based on the anisotropy of the C-N bonds in the vicinity of these protons. H_b extends directly over a C-N bond in a region of shielding

while H_a does not.

This same assignment for the N^1, N^2 -PDDA complex is confirmed by H-N-C-H spin coupling. A spectrum of the PDDA complex was obtained before the amine hydrogens had exchanged and is shown in Figure 9. The splitting of the downfield glycinate resonances is pronounced but no splitting of the upfield portion of the spectrum is evident. This difference in coupling may be found in the differences in the dihedral angles between H-N-C- H_a and H-N-C- H_b . Examination of molecular models shows that the angles are about 10° and 110° respectively. Using the Karplus relationship⁵⁸ the coupling constants should be about 8 Hz for H-N-C- H_a and 1 Hz for H-N-C- H_b . The observed coupling constants were 8 Hz for the downfield resonances and no splittings were observed for the upfield resonances. Similar coupling was observed by Sudmeier and Occupati³⁷ for the EDDA complexes.

The chemical shifts of AB 2 are calculated to be 3.86 and 3.58 ppm with $J=18.2$ Hz, and on the basis of H-C-N-H couplings, (see Figure 9) the downfield portion of the AB pattern may be assigned to H_a , and the upfield portion to H_b , (see Figure 22).

The downfield shift of H_b , relative to H_b (3.58 ppm vs. 3.42 ppm) can only be attributed to the interaction of this proton with the methyl group on the diamine backbone. Molecular models indicate that in the R-1,2-propanediamine

complex with the Δ absolute configuration, this interaction is severe and thus H_b , would experience a steric compression as discussed by Dabrowiak and Cooke.⁴⁰ H_a , exhibits an up-field shift relative to H_a (3.86 ppm vs. 4.24 ppm). In the cobalt(III) complex with 1,2-propanediaminetetraacetic acid, the corresponding H_a , exhibits a similar shift when compared to $[CoEDTA]^-$ (3.39 ppm vs. 3.76 ppm).⁵⁵ A possible explanation for this shift is that the steric interaction between the methyl group and H_b , is so great that the glycinate chelate ring puckers to relieve some of the repulsions. Space filling molecular models indicates that this is possible and that the resulting arrangement is less crowded. The effect on H_a , would be to move it away from the amine protons of the ethylenediamine chelate ring and thus into a region of higher shielding (less steric compression).

The remaining nmr resonances can be attributed to the methylene protons associated with the ethylenediamine (2.85 ppm) and the protons of the propanediamine backbone which are spread over the region from 2.6 ppm to 3.0 ppm.

3. The nmr spectrum of u-cis-N¹,N²-diacetato-1,2-propanediamine(ethylenediamine)cobalt(III)

The nmr spectrum of the complex from the second cis band are shown in Figures 10, 11, and 12 and the chemical shifts are given in Table II. The presence of secondary amine resonances in the undeuterated spectrum indicates

that the complex contains N^1, N^2 -PDDA and the sharpness of the methyl and glycine proton signals suggest it contains only one diastereomer. Figure 22 shows a representation of this complex.

It is also very helpful to discuss the spectra of this complex in conjunction with the corresponding EDDA complex which has been thoroughly discussed by Legg and co-workers.⁸ The spectrum of this complex in the glycine proton region consists of one AB pattern assigned to the out-of-plane R_1 ring and one sharp singlet for the in-plane G_1 -ring. (See Figure 10).

Because the positions of the upfield signals for the AB pattern overlapped the region containing the propylene-diamine and ethylenediamine protons, the assignment of these upfield signals were made with the help of deuterium exchange. As stated previously, it has been shown³⁷ that the H_a protons of R_1 rings exchange about 10 times faster than the more sterically hindered H_b protons. Figure 11 shows the spectrum of the u-cis- N^1, N^2 -PDDA complex after the addition of one drop of 30% NaOD. Examination of the spectrum shows that H_a has been completely exchanged and that H_b has undergone a redistribution of intensity resulting from the 6.5 times smaller (the ratio of proton to deuterium gyromagnetic ratios) deuterium proton geminal coupling constants.⁵⁵ In effect, a new peak appears to grow in at a frequency corresponding to the chemical shift of H_b . This

new signal is marked by an asterisk and is located at 188 Hz (3.14 ppm). This is a very quick and easy method of assigning proton chemical shifts of out-of-plane acetate rings.

The AB pattern consists of resonances at 252.0, 234.0, 196.0, and 178.0 Hz with calculated chemical shifts of 4.01 ppm and 3.14 ppm, $J=18.0$ Hz. These shifts are almost identical to those found for the EDDA complex which has chemical shifts of 4.02 and 3.14 ppm. The assignment of H_a and H_b is again made on the basis of H-N-C-H spin coupling with H_a being the signal furthest downfield (see Figure 12).

The sharp singlet located at 3.7 ppm is assigned to the in-plane G_1 ring. The corresponding signal in the EDDA complex is a 3.71 ppm and was assigned by Legg and co-workers⁸ on the basis of deuterium exchange studies. It has been shown that in-plane acetate rings are relatively insensitive to acid⁵⁹ or base³⁷ catalysed deuterium exchange. Figure 11 shows that this signal is unaffected in basic D_2O solution. Perhaps the most conclusive support to this assignment is H-N-C-H coupling. Figure 12 shows that this signal is split when the amine protons are unexchanged, indicating that it is indeed the out-of-plane acetate ring.

It is important to note that the spectrum of the u-cis- N^1, N^2 -PDDA complex is identical to that of the u-cis-EDDA complex. This similarity lends itself to only one explanation; that the methyl group must occupy a position

in the molecule such that it does not affect the acetate protons. Thus, the R_1 ring must be associated with the N^1 nitrogen (an R ring on the N^2 nitrogen would give a pattern similar to AB 2 on the s-cis- N^1, N^2 -PDDA complex). Inspection of molecular models indicates that only one structure fits this criteria, namely the Λ -RS-u-cis isomer (assuming an R-configuration for the propanediamine backbone). Legg and co-workers,⁸ however, observed that u-cis-[Co(EDDA) C_2O_4]⁻ adopted the RR or SS configuration about the asymmetric nitrogens. This difference in conformation may be due to the different stereochemical requirements of $C_2O_4^{2-}$ compared to en.

From the results of the s and u-cis isomers, it is seen that the linear tetradentate ligand N^1, N^2 -PDDA is a highly stereoselective ligand. Reasons for this stereoselectivity will be discussed in a later section.

4. The nmr spectrum of trans(0)- N^1, N^1 -diacetato-1,2-propanediamine(ethylenediamine)cobalt(III)

The nmr spectra of the complex from the first trans band may be seen in Figures 13, 14, and 15 and the chemical shifts are tabulated in Table II.

As can be seen in Figure 13, this complex gives two overlapping AB quartets. Due to the synthetic method used to produce this complex, some confusion was caused by its spectrum. At first it was thought that this complex was the

diastereomer of the corresponding s-cis-N¹,N²-PDDA complex. This idea was quickly dispelled when a spectrum was taken in a H₂SO₄·D₂O solution (the complex had been converted to the more soluble sulfate salt to permit a better spectrum) shown in Figure 14. It should be noted that in the spectrum of the undeuterated complex, some of the signals are shifted, causing the overlapping of some signals. (Shifting of signals with a change of pH was also observed in the u-cis-PDDA complex). It is obvious that no H-N-C-H coupling is present and no resonance is observed where secondary amine proton signals have previously been noted (ca. 7.0-7.5 ppm). Thus, it was concluded that this complex was the result of dicondensation of chloroacetic acid at only one end of the 1,2-propanediamine. Evidence for dicondensation at the N¹ end is seen when this spectrum is compared to the N¹,N¹-DMPDDA analog. Only small differences in the nmr spectrum of the DMPDDA complex from that of the PDDA complex are observed, thus confirming the structure of the PDDA complex. (See Part 5 of this section). Further evidence came from an attempted preparation of the complex with N²,N²-DMPDDA. When this complex was eluted from an ion exchange column, it decomposed on concentration of the solution and could not be isolated. This complex would be expected to be unstable as would the N²,N²-PDDA complex because of steric interaction. A representation of the N¹,N¹-PDDA complex may be seen in Figure 23.

Since the two AB spectra were so closely spaced, it was difficult deciding which pair of upfield resonances belonged to the corresponding downfield resonances. This difficulty was overcome with the help of selective base catalysed deuteration. The pD of an nmr sample was adjusted to about 10 using a 10% NaOD solution and the subsequent deuterium exchange was followed over a four hour period. The acetate portions of these spectra are shown in Figure 15 at about 1.0 min. (A), 15 min. (B), 60 min. (C), and 4 hours (D) respectively. It is observed in (A) that one of the acetate rings exchanges much more rapidly than the other since the signal at 269.5 Hz has drastically decreased in intensity and the signal at 250 Hz has disappeared entirely. The signal furthest downfield (287.0 Hz) is obscured by the "HOD" peak. Also, a new signal has appeared at about 242 Hz (4.03 ppm) (marked by an asterisk) due to a redistribution of intensity of the downfield resonances. In (B) and (C) the signals 269.5, 252.5, 247.7, and 230.5 Hz are all decreasing at the same rate and the signal at 242 Hz is increasing at approximately the same rate (B,C), although later the rate of increase of the signal at 242 Hz slowed and finally started to decrease (D) due to exchange of these protons. Thus, on the basis of this information, we can assign the signals at 287.0, 269.5, 250.0, and 232.2 Hz to one AB pattern (AB 1) and the ones at 269.5, 252.5, 247.7, and 230.5 Hz to the other (AB 2).

The calculated chemical shifts for AB 1 are 4.60 ppm and 4.05 ppm ($J=17.5$ Hz) and for AB 2, 4.28 ppm and 4.05 ppm ($J=17.1$ Hz).

The comparison of the spectrum of this complex with the parent compound trans-(O)-[Co(AEIDA)(en)]⁺ raises some questions. In this parent compound, Chu, Cooke, and Liu²⁹ found only one AB pattern with chemical shifts of 4.43 and 4.06 ppm. Using studies with methyliminodiacetic acid as a basis, the signal at 4.06 ppm was assigned by these workers to the protons over the ethylenediamine backbone (the H_b protons). In the PDDA complex, the upfield chemical shifts are substantially changed (4.6 and 4.28 vs. 4.43 ppm). Inspection of molecular models suggest that if the diamine backbone conformation is fixed as it is in the PDDA complex, only the H_b protons should be affected. This effect would not be observed in the AEIDA complex where the conformation of the backbone is not fixed (see Introduction page 9) since an interchange of conformations averages out any proton-proton interactions. It is interesting to observe that the average of the downfield chemical shifts in the PDDA complex is 4.44 ppm, almost the exact position of the chemical shift of the downfield protons in the AEIDA complex (4.43). The conclusion that these observations suggest is that the low field protons are H_b rather than H_a.

However, the deuteration studies seem to contradict this argument. The protons most readily exchanged were

the downfield protons, and previous studies have shown that the protons away from the backbone (H_a protons) are those which exchange unless the preferential deuteration is also reversed. This matter needs further clarification.

5. The nmr spectrum of trans(O)-N¹,N¹-diacetato-N²,N²-dimethyl-1,2-propanediamine

The spectra of this complex are shown in Figures 16 and 17. The chemical shifts are tabulated in Table II.

This particular complex was synthesized to confirm the nature of the N¹,N¹-PDDA complex discussed in Part 4. The spectrum of this complex is very similar to that of the N¹,N¹-PDDA complex with only small differences in the chemical shift values. The shifts obtained were 4.58 and 4.11 ppm for AB 1 and 4.15 and 4.03 ppm for AB 2. The assignments of the particular AB patterns were confirmed by obtaining the spectra of a 100 MHz instrument. This spectra is shown in Figure 17.

The small difference in the spectra when compared to that of the N¹,N¹-PDDA complex may be attributed to the N-methyl substituents which would cause the propanediamine backbone to take up a slightly different conformation. Also, interactions between these methyl substituents and the amine protons on the en ring would cause that ring to change somewhat. It is interesting to note that the average of the

downfield shifts (4.37 ppm) is also very similar to that of the parent AEIDA complex (4.43). The upfield shifts also average out to give very close agreement (4.07 vs. 4.06). This again suggests a crossover of the H_a and H_b protons.

E. Optical Rotatory Dispersion Spectra

1. General considerations

The ord spectra of the PDDA complexes derived from R-pn are shown in Figures 18 and 19. As stated in the introduction, the most common method for determining the absolute configuration of a complex is to compare its ord or cd spectra with that of a complex whose absolute configuration is known. The complexes with which the comparison will be made in this study are those with the ligand ethylenediamine- N,N^1 -di-L- α -propionic acid (LL-EDDP), studied by Schoenburg, Cooke, and Liu.²⁸ The absolute configurations of these complexes were determined both by nmr and ord methods. Since they are CoN_4O_2 complexes, a comparison is probably quite valid. The optically active complexes used in this study were obtained by using the optically active ligand R-pn and separating the complexes by ion-exchange chromatography (see Experimental section).

2. The ord spectra and absolute configurations of s-cis and u-cis-[Co(N^1, N^2 -PDDA)(en)]⁺

The ORD spectra of these complexes are shown in Figure 18. The s-cis isomer has a positive Cotton effect and when compared to the analogous LL-EDDP complex, we find that this corresponds to a Δ absolute configuration. The molar rotation at $589.0\text{ m}\mu$ was $+3853^\circ$ which is low when it is compared to the EDDP complex (approximately $+6000^\circ$) and the analogous EDDA complex ($+5770^\circ$). This is perhaps an indication that optical purity was not obtained and some of the Λ diastereomer was present. Another explanation could be that N^2,N^2 -PDDA complex was present and was not separated on the ion-exchange column. However, the amount of optical activity indicates that this ligand is highly stereospecific.

The u-cis isomer has a negative Cotton effect and comparison with the corresponding EDDP isomer shows that it has Λ configuration. The molar rotation $[(M)_{589} = -1200^\circ]$ of this isomer indicates that it is optically pure as the corresponding EDDP isomer gives similar rotations $[(M)_{589} = -1100^\circ]$.

3. The ORD spectra of trans(O) and cis(O)-[Co(N^1,N^1 -PDDA)(en)]

These spectra are shown in Figure 19. The trans(O) isomer does not show any Cotton effect but gives a positive curve with two maxima in it. Since this complex has no net chirality, the only activity possible is the vicinal effect for the R-1,2-propanediamine and from the λ conformation of

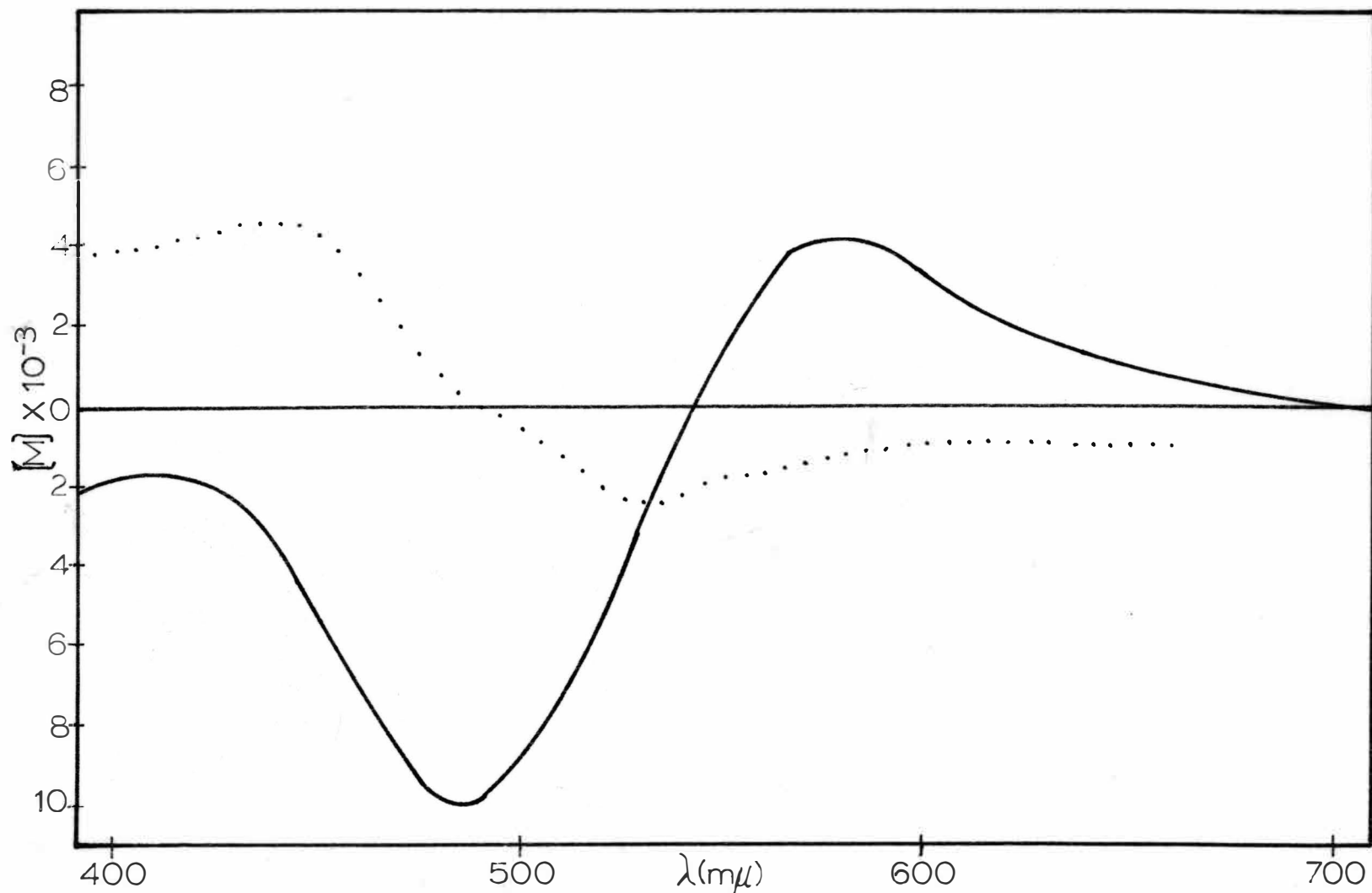


Figure 18. The ord curves of Δ -cis-[Co(N¹,N²-R-PDDA)(en)]⁺(—) and Λ -u-cis-[Co(N¹,N²-PDDA)(en)]⁺ (···).

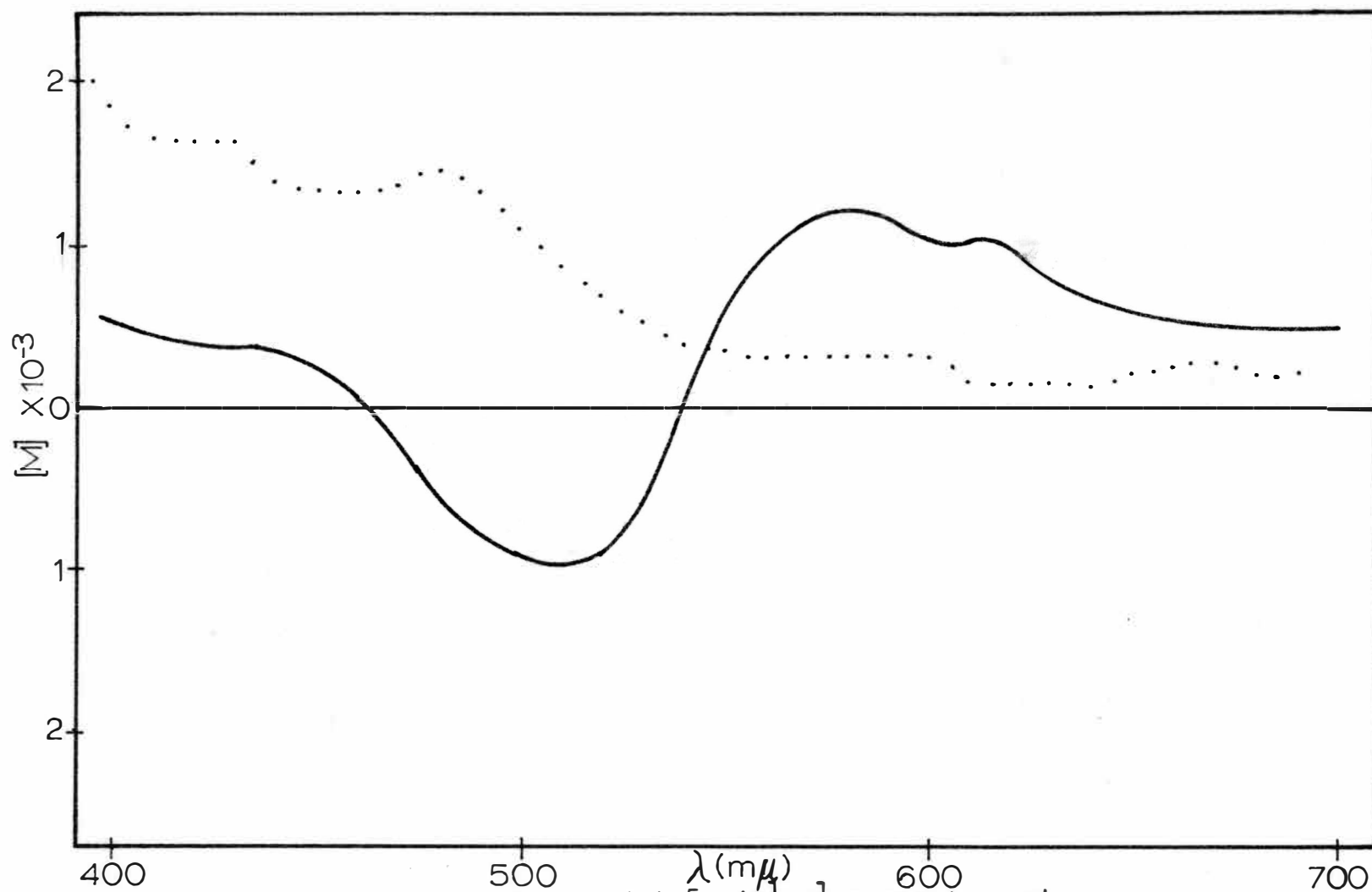


Figure 19. The ord curves of trans(0)-[Co(N¹,N¹-R-PDDA)(en)]⁺ (...) and cis(0)-[Co(N¹,N¹-R-PDDA)(en)]⁺ (—) (not quantitative).

the diamine chelate ring caused by the equatorial methyl group. This is the reason for the small rotations of this complex.

The complex which was suspected of being the cis(O)-N¹,N¹-PDDA isomer on the basis of its visible spectra has the ord curve shown in Figure 19. This complex shows a small negative Cotton effect but because of the small amount of sample available, quantitative measurements were impossible. No designation of Δ or Λ is possible since this complex has no net chirality. When this complex is related to $[\text{Co}(\text{en})_3]^+$ by the "ring pairing" method of Legg and Douglas,⁶¹ the result is one ring pair with $\Delta(\text{C}_2)$ configuration and another of $\Lambda(\text{C}_2)$ giving a net chirality of zero. Thus, the optical activity arises from inherent "asymmetry" due to the different rings (glycine vs. ethylenediamine) rather than from "chirality". A more thorough study of this complex is in order.

F. Stereochemistry

1. General considerations

As stated in the introduction, methyl substitution in the central chelate ring of a linear tetradentate ligand may often cause the ligand to be highly stereospecific. The fact that a five membered chelate ring is gauche²⁴ can account for these effects. Kobayashi⁶² was the first to suggest

the non-planarity of the ethylenediamine ring in Δ -[Co(en)₃]³⁺ from ord evidence and later Corey and Bailar²⁴ in a classic paper performed a conformational analysis of the chelate ring formed by ethylenediamine. Their calculations showed that the preferred conformation of a five membered chelate ring is gauche, and were confirmed by x-ray analysis.^{63,64} A five membered chelate ring in the gauche conformation may possess mirror images designated δ and λ and are illustrated in Figure 20.

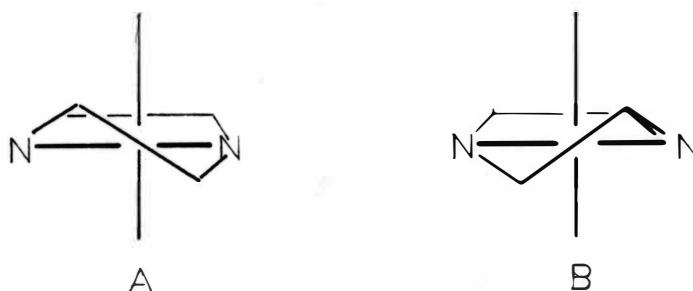


Figure 20. Mirror image conformations of a diamine chelate: (A) δ ; (B) λ

When ethylenediamine is replaced by R-1,2-propanediamine, we find that the λ conformation is preferred to the δ conformation. This preference is due to the steric requirement of the methyl group which prefers to be in an equatorial as opposed to a more sterically hindered axial position. The energy difference between a conformation in which a methyl group is axial vs. the equatorial arrangement has been assessed at greater than 2 kal/mole in favor

of the equatorial form for the propylenediamine chelate.⁶⁵ Thus, if a tetradentate ligand has R-1,2-propanediamine or another such similar optically active five membered ring as the central chelate ring, one could expect that the ligand could show stereoselectivity.

Such stereoselectivity was observed by Goto and co-workers²⁵ who studied the cobalt(III) complexes with methyl substituted triethylenetetramine at the central chelate bridge. It was found that R-5-metrien and R-ECE formed only the Δ -u-cis complex and S-5,6-dimetrien formed only the Λ -u-cis. The preferred conformations of the central chelate rings for each of these ligands should be λ , λ , and δ respectively. Therefore, the absolute configurations of the cobalt(III) complexes with the trien analogs are determined by the conformations of the central diamine rings. In this study, these authors distinguished the two possible bonding directions of the nitrogen atoms of the ethylenediamine chelate when fixed in a λ conformation, as shown in Figure 21. The bonding direction which is pseudo-axial is denoted A and that which is pseudo-equatorial is denoted B. This scheme will be used when the ligands synthesized in this study are discussed.

Another stereospecific linear tetradentate ligand, RS-4-methyl-1,8-diamino-3,6-dithiaoctane, was studied by Worrell, MacDermott, and Busch.²⁶ They found that only the Δ -s-cis isomer was formed by the ligand with R absolute

configuration and only the Δ -cis isomer was formed by the enantiomeric ligand. Again, this stereospecificity can be accounted for by the conformation of the central diamine backbone.

2. The stereochemistry of N^1, N^2 -diacetato-R-1,2-propane-diamine

This ligand is very similar to those studied by Goto and co-workers²⁵ except that the end β -aminoethyl chelate rings are replaced by acetate groups. Thus, we may consider the stereochemistry of this ligand in terms of the possible bonding directions of nitrogen atoms in the central diamine chelate ring fixed in a λ conformation as shown in Figure 21.

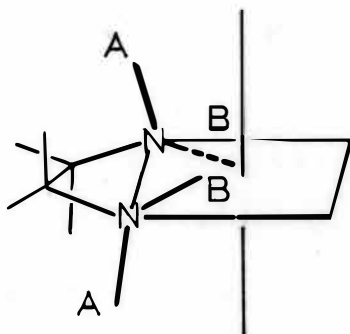


Figure 21. The bonding directions of the nitrogen atoms of the coordinated diamine having the λ conformation

Molecular models show that only three isomers are possible when the central diamine ring is fixed in the λ conformation. These are the Δ -s-cis, which corresponds

to the AA bonding directions, $SS-\Delta$ -u-cis which requires BB bonding (SS refers to the configurations about the secondary nitrogen atoms), and $RS-\Lambda$ -u-cis with AB bonding directions.

For s -cis- $[Co(N^1, N^2-R-PDDA)(en)]^+$ the prediction of Δ absolute configuration is shown to be correct by the ord curve exhibited by this complex and is further substantiated by the nmr spectrum which exhibits only two sharp AB quartets and one methyl doublet. A somewhat low molar rotation (see ord section) indicates that this ligand may not be 100% stereoselective. A representation of this complex is given in Figure 22.

For u -cis- $[Co(N^1, N^2-R-PDDA)(en)]^+$, ord evidence suggests that only the Λ isomer is formed in significant amounts. Examination of molecular models shows that the Δ configuration is more strained, and requires that the glycine rings be more puckered than those found in the Λ configuration. The x-ray evidence of Weakleim and Hoard⁶⁶ shows that glycinate chelate rings are more or less planar, therefore, the Δ configuration would be less favored. In addition, for the Λ - RS -u-cis complex, two more isomers arising from the difference of the position of the substituted methyl group are possible. The nmr of the complex isolated suggests that the only positional isomer obtained in significant amounts is the one with the methyl group adjacent to the in-plane G-ring. (See the discussion of this complex

in Section D). Figure 22 shows a representation of this complex. A similar result was suggested for 5-metrien by Goto and co-workers.²⁵

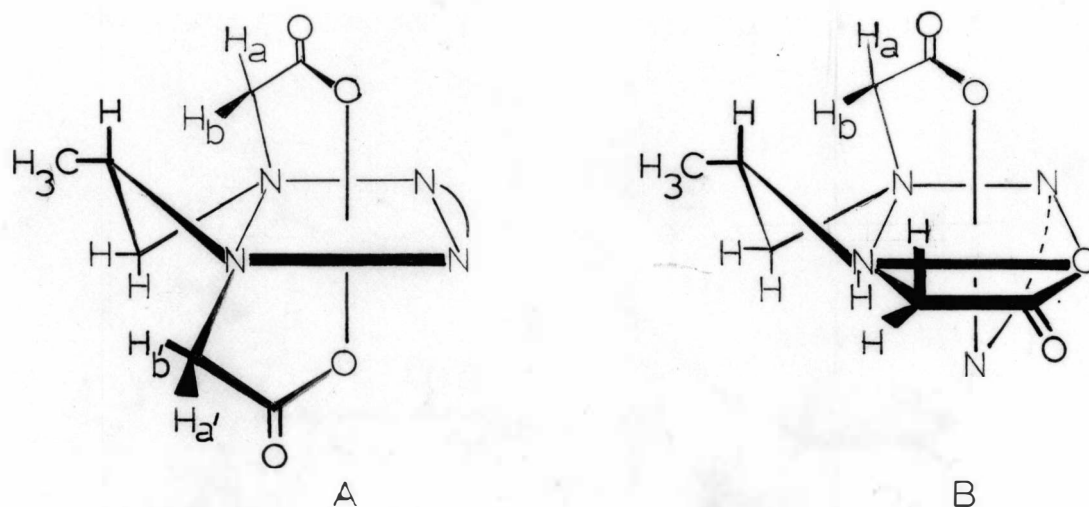


Figure 22. The two isomers of N^1, N^2 -R-PDDA: (A) Δ -s-cis-[Co(N^1, N^2 -R-PDDA)(en)]⁺; (B) Λ -RS-u-cis-[Co(N^1, N^2 -R-PDDA)(en)]⁺

3. The stereochemistry of N^1, N^1 -diacetato-R-1,2-propanediamine

No cobalt(III) complexes containing a branched chain tetradentate ligand in which one of the chelate rings contains an asymmetric methylated carbon atom have been thoroughly characterized. This ligand may exist in two geometric isomers; trans(0) and cis(0) shown in Figure 23. The stereochemistry of the trans(0) isomer is not dependent on the conformation of the diamine chelate ring since this molecule is symmetric (it has a mirror plane passing through

the plane of the two diamine chelate rings, ignoring the puckering of these rings). However, the stereochemistry of the cis(0) isomer is dictated by the conformation of the diamine ring and using arguments presented previously, the configuration of this complex must be as shown in Figure 23.

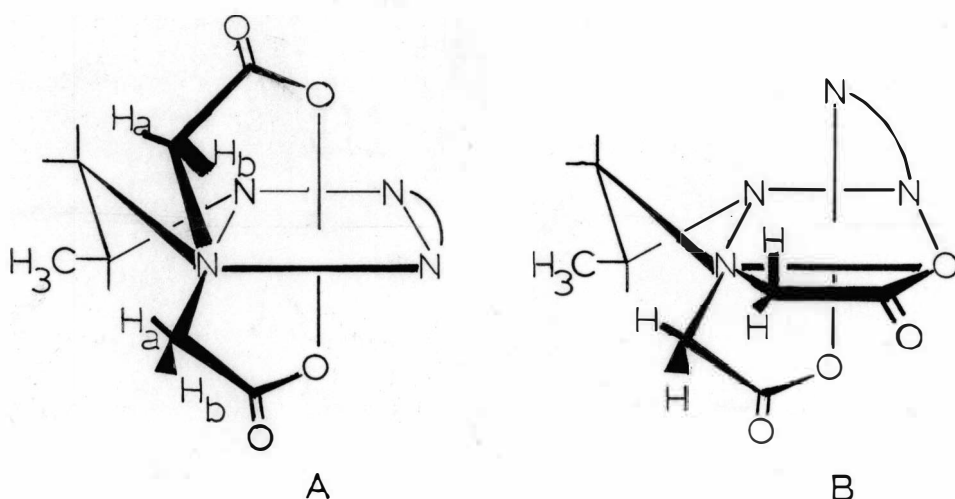


Figure 23. The two isomers of N^1,N^1 -R-PDDA: (A) trans(0)- $[\text{Co}(N^1,N^1\text{-R-PDDA})(\text{en})]^+$; (B) cis(0)- $[\text{Co}(N^1,N^1\text{-R-PDDA})(\text{en})]^+$.

CONCLUSION

In conclusion, it has been shown that the new linear tetradentate ligand, N^1, N^2 -diacetato-1,2-propanediamine is highly stereoselective. It was found that when this ligand has an R absolute configuration, only the Δ -s-cis and Λ -u-cis isomers are formed in significant amounts. The stereoselectivity may be explained by the methyl substituent in the central diamine chelate which causes the central ring to have a fixed conformation. The amount of stereoselectivity was not as great as that found by other workers for 5-metrien²⁵ and epe.²⁶ This result may be attributed to the different stereochemical requirements of glycinate rings. Also, it has been shown that a non-linear tetradentate ligand with a fixed diamine chelate ring conformation may exhibit stereoselectivity.

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