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The Stereochemistry of Mixed Cobalt(III) Complexes with Diethylenetriamine and Some Aminedicarboxylic Acids[1]

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Received August 9, 1965

A series of cobalt(III) complexes was prepared with the formula $[Co(dien)(L)]^+$ where dien is diethylenetriamine and L is iminodiacetate (IDA), methyliminodiacetate (MIDA), or pyridine-2,6-dicarboxylate (PDC). Three geometric isomers separated by ion exchange were found whose relative amounts depended on ligand steric requirements: a *trans* (related to oxygen) isomer with ligands spanning edges for all three L and two *cis* isomers (ligands span faces), an s-*cis* (secondary amines *trans*) with IDA and MIDA, and a u-*cis* (secondary amines *cis*) with IDA. From isomer distribution, IDA and MIDA favor the *cis* configuration (88% for IDA, 80% MIDA). Steric repulsions on the u-*cis*-IDA secondary amines make it less favored than the s-*cis* IDA (u-*cis* MIDA not observed). The ${}^1A_1 \rightarrow {}^1T_1$ electron transition was split and shifted to lower energies relative to $[Co(dien)_2]^{3+}$ in both *cis* and *trans* isomers (half as much in *cis*) except for u-*cis*-IDA where steric repulsions gave a large shift. *Dq*(acetate) followed the trend IDA > MIDA and *trans* ~ s-*cis* > u-*cis* in agreement with increased steric hindrance. Band intensities were greater when symmetry was lower: *trans* (where strain displaces end groups) > u-*cis* > s-*cis*. In the pmr spectra the acetate protons exhibited AB spectra at lower fields (3.3–4.3 ppm from NaTMS) than the dien protons (2.3–3.5 ppm). The s-*cis* isomers exhibited one AB acetate pattern but the u-*cis* and *trans* with each acetate in different environments gave two AB patterns. On changing from *cis* to *trans* the inner protons of one ligand arm were removed from the shielding environment of the other arm. These protons' signals moved to lower fields collapsing both acetate and dien patterns. In MIDA the N-methyl substitution gave shifts explainable in terms of the CN bond anisotropy.

Introduction

Although numerous examples of complexes formed between cobalt(III) and bidentate chelating agents are known, few complexes utilizing tridentates have been studied. Mann and Pope[2] prepared the bis complex of 1,2,3-triaminopropane and Mann[3] characterized the 2:1 complex of diethylenetriamine with cobalt(III). Mori and co-workers[4] and Tsuchida and coworkers[5] have made various bis complexes of cobalt(III) with iminodiacetic acid. No examples, however, are known of cobalt(III) complexes containing two different tridentate ligands. In this paper the preparation, separation, and visible and nmr spectral characterization of a series of cobalt(III) complexes of mixed tridentate ligands with the over-all formulation $[Co(amine)_4(carboxylic\ acid)_2]^+$ is described, in which diethylenetriamine is one of the ligands and various aminodicarboxylic acids act as the other ligand. The isomers were separated using the selectivity of ion-exchange resins for *cis* and *trans* isomers as observed by others.[6] The formation of mixed complexes utilizing two different tridentate ligands in some cases resulted in both ligands exhibiting geometries of attachment different from those found by Mann[3] and the Japanese workers.[4,5]

We have previously reported the visible and nmr spectral characterization of cobalt(III) complexes with the same over-all formulation as these complexes, utilizing the tetradentate ligand ethylenediamine-N,N′-diacetic acid and its N-substituted derivatives.[7] These complexes exhibited visible spectra which agreed with the crystal field considerations for *cis* and *trans* isomers as established by Ballhausen and Jørgensen,[8] Moffitt and Ballhausen,[9] and Yamatera.[10] In some of the complexes the stereochemistry of the ligand has resulted in steric strains which have altered the visible spectra somewhat from the predictions of simple crystal field theory.

In the nmr spectra of the tetradentate complexes[7] we have utilized the anisotropy of the C–N single bond, as suggested by Bothner-By and Naar-Colin,[11] to explain the shifts in the proton resonances found in the different geometric isomers. Similar arguments are applicable to the tridentate complexes. In some of them the slow rate of proton exchange on the secondary amine nitrogen along with the bond anisotropy has allowed the definite assignment of some of the proton resonances to specific protons.

Experimental Section

Preparation of Complexes.—The preparation of the complexes of iminodiacetate (IDA) and methyliminodiacetate (MIDA) is summarized in the equation

$$[Co(dien)Cl_3] + Ag_2L + AgNO_3 \xrightarrow[\text{[C]}]{\text{heat}} [Co(dien)(L)]NO_3 + 3AgCl$$

where L represents the tridentate chelating agents. The pyr-

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[1] Abstracted from a thesis submitted by J. Ivan Legg to The University of Michigan in partial fulfillment of the degree of Doctor of Philosophy, 1965.

[2] F. G. Mann and W. J. Pope, *Proc. Roy. Soc.* (London), **A107**, 80 (1925).

[3] F. G. Mann, *J. Chem. Soc.*, 461 (1934).

[4] M. Mori, M. Shibata, E. Kyuno, and F. Maryama, *Bull. Chem. Soc. Japan*, **35**, 75 (1962).

[5] J. Hidaka, Y. Shimura, and R. Tsuchida, *ibid.*, **35**, 567 (1962).

[6] See G. B. Kauffman, R. P. Pinnell, and L. T. T. Takahashi, *Inorg. Chem.*, **1**, 544 (1962), and references therein.

[7] J. I. Legg and D. W. Cooke, *ibid.*, **4**, 1576 (1965).

[8] C. J. Ballhausen, and C. K. Jørgensen, *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.*, **29**, 14 (1955).

[9] W. J. Moffitt and C. J. Ballhausen, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956).

[10] H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

[11] A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958).

TABLE I

CHEMICAL ANALYSES OBTAINED FOR THE VARIOUS SALTS OF THE ISOMERS PREPARED

Isomer	% C		% H		% N	
	Calcd	Found	Calcd	Found	Calcd	Found
trans-IDA, $[CoC_8H_{18}N_4O_4]Cl \cdot H_2O$	27.71	27.55	5.82	5.74	16.16	16.14
s-*cis*-IDA, $[CoC_8H_{18}N_4O_4]ClO_4 \cdot {}^1/_2H_2O$	23.92	24.09	4.77	4.88	13.95	14.14
s-*cis*-IDA, $[CoC_8H_{18}N_4O_4]Cl$	29.23	28.31	5.52	5.67	17.05	17.39
u-*cis*-IDA, $[CoC_8H_{18}N_4O_4]ClO_4$	24.46	24.55	4.62	4.54	14.27	13.86
u-*cis*-IDA, $[CoC_8H_{18}N_4O_4]Cl \cdot 2H_2O$	26.34	26.49	6.08	5.66	15.37	15.54
trans-MIDA, $[CoC_9H_{20}N_4O_4]ClO_4 \cdot {}^1/_2H_2O$	24.92	24.97	5.34	4.93	12.92	12.65
s-*cis*-MIDA, $[CoC_9H_{20}N_4O_4]NO_3$	29.27	28.92	5.46	5.15	18.97	19.14
trans-PDC, $[CoC_{11}H_{16}N_4O_4]NO_3 \cdot H_2O$	32.44	32.61	4.45	4.24	17.20	17.29

idine-2,6-dicarboxylate (PDC) complex was prepared as summarized in the equation

$$[Co(dien)Cl_3] + Na_2PDC + 3AgNO_3 \longrightarrow [Co(dien)(PDC)]NO_3 + 3AgCl$$

Starting Materials.—$[Co(dien)Cl_3]$ was prepared by the method of Crayton and Mattern.[12] *Anal.* Calcd for $[Co(C_4H_{13}N_3Cl_3)]$: C, 17.89; H, 4.87; N, 15.65; Cl, 39.62. Found: C, 17.95; H, 4.84; N, 15.41; Cl, 39.66 ± 0.12. Different preparations gave the same analysis but the visible absorption spectra of the solutions on reaching equilibrium varied slightly.

Silver Salts of Aminodicarboxylic Acid Ligands.—To 13.3 g (0.10 mole) of iminodiacetic acid suspended in 50 ml of water, 8 g of sodium hydroxide in 50 ml of water was added until a pH of 10 was reached. To the stirred solution at 40°, 34.0 g (0.20 mole) of silver nitrate in 50 ml of water was added dropwise. After cooling to room temperature the precipitate was filtered, washed four times with 40-ml portions water and acetone, and air-dried; yield 31.0 g. (89%). *Anal.* Calcd for $Ag_2(C_4H_5NO_4)$: Ag, 62.2. Found: Ag, 61.97, 61.82.

The synthesis of A_2MIDA is the same except that 14.7 g of methyliminodiacetic acid is used; yield 23.7 g (66%). *Anal.* Calcd for $Ag_2(C_5H_7NO_4)$: Ag, 59.78. Found: Ag, 60.02, 59.57.

Isomers of Iminodiacetato(diethylenetriamine)cobalt(III).—To 5.38 g (0.020 mole) of $[Co(dien)Cl_3]$ dissolved in 100 ml of water kept at 50° and constantly stirred was added 2 g of decolorizing charcoal. After 15 min solid Ag_2IDA (6.98 g, 0.020 mole) was added in small portions over a period of 5–10 min. After 10 min a solution of 3.54 g (0.0204 mole) of silver nitrate in 20 ml of water was added dropwise over a period of 5 min. After 10–15 min of additional stirring the mixture was cooled for about 1 hr, and the silver chloride and charcoal were removed by filtration. The isomers were separated using a cation-exchange column with 0.5 *N* $NaClO_4$ eluting agent in a manner described earlier.[7] A small violet band eluted with the water wash. The 22-day elution yielded first a *trans* isomer and then *cis* isomers, first s-*cis* and then u-*cis*. Individual fractions were checked for purity by their visible spectra. A very small brown band was not moved by the eluent. The very insoluble *trans* isomer precipitated from the solutions, but quantities of $NaClO_4$ had to be extracted from the *cis* isomers with absolute ethanol. The salts thus isolated were further washed with ethanol and acetone and air-dried. The yields were 0.82 g of *trans*, 3.48 g of s-*cis*, 1.53 g of u-*cis*, and a mixture of *cis* isomers (0.61 g). The more dilute fractions from the end of each band were concentrated, and quantitative visible spectra were obtained. From this information and the amounts of each isomer isolated, it was possible to estimate the quantity of each isomer present in the original equilibrium as summarized in Table II.

Purification was accomplished by dissolving 1 g of s-*cis*-$[Co(dien)(IDA)]ClO_4$ in 10 ml of hot (50–60°) water, filtering, and precipitating the salt from the hot solution by slow addition of 90 ml of ethanol. The u-*cis* isomer was dissolved in a minimum amount of water at 50°, and the solution was evaporated to induce crystallization. The *trans* isomer was converted to the chloride without further purification. The chemical analyses obtained for these isomers are given in Table I.

The soluble chloride salts were obtained by passing solutions of the perchlorate through strong-base anion-exchange resin columns in a manner similar to that described earlier.[7]

Reaction of Silver Iminodiacetate with Trichloro(diethylenetriamine)cobalt(III) in the Absence of Carbon.—When the synthesis was performed without carbon, evaporation of the solution yielded a red oil which was converted to a hard glaze by repeated treatment with ethanol. Refluxing of this product with methanol yielded a dilute solution which upon evaporation gave a red powder analyzing as $[Co(dien)(IDA)]Cl$. *Anal.* Calcd for $[CoC_8H_{18}N_4O_4]Cl$: C, 29.23; H, 5.52; N, 17.05. Found: C, 29.49; H, 5.78; N, 16.76. Chromatography of this solution as previously described revealed a large violet water-soluble band and a red-brown band not moved by 0.5 *M* $NaClO_4$ as well as the three bands corresponding to the isomers of $[Co(dien)(IDA)]^+$.

Isomers of Methyliminodiacetato(diethylenetriamine)cobalt(III).—The isomers of $[Co(dien)(MIDA)]^+$ were prepared as the IDA isomers except that the temperature was kept at 65° and 7.22 g (0.020 mole) of Ag_2MIDA was used. Evaporation of the solution in air yielded red crystals of pure s-*cis*-$[Co(dien)(MIDA)]NO_3$ which were washed with 75% ethanol, ethanol, and acetone and air-dried.

A solution containing 20 mmoles of complex was chromatographed as described for $[Co(dien)(IDA)]^+$. A small violet band was eluted with water and a small red-brown band was not moved by the 0.5 *M* $NaClO_4$. The two bands (*trans*-$[Co(dien)(MIDA)]^+$ and s-*cis*-$[Co(dien)(MIDA)]^+$) eluted over a period of 8 days in that order as confirmed by visible spectra of the fractions. The distribution of the isomers on the column was estimated visually and is summarized in Table II.

A small amount of *trans*-$[Co(dien)(MIDA)]ClO_4$ was isolated by repeated concentration and extraction of solid $NaClO_4$ as described earlier for the isolation of *cis*-$[Co(en)(EDDA)]ClO_4$.[7] The salt was dissolved in water and the solution was filtered and evaporated almost to dryness. The product was filtered and washed with a small amount of ice-cold 50% ethanol, ethanol, and acetone and air-dried.

The *trans* and u-*cis* salts were converted to the chlorides as described for the IDA isomers. The analyses are given in Table I.

Pyridine-2,6-dicarboxylato(diethylenetriamine)cobalt(III) Nitrate.—Silver nitrate (1.94 g, 0.030 mole) dissolved in 25 ml of water and acidified with 3 drops of concentrated HNO_3 was added slowly (5 min) to a stirred solution of 2.69 g (0.010 mole) of $[Co(dien)Cl_3]$ in 50 ml of water at 40°. The mixture was stirred 15 min at 40° and cooled to room temperature. The silver chloride was removed using water acidified with concentrated HNO_3 to wash and transfer. A solution of sodium pyridine-2,6-dicarboxylate (Na_2PDC) prepared by adding sodium hydroxide solution (0.82 g dissolved in 5 ml of water) to 1.67 g of H_2PDC suspended in 30 ml of water was added dropwise (5 min) to the stirred filtrate (about 150 ml) at 40°. The mixture was set aside for 1 hr to cool, and the dark crimson $[Co(dien)(PDC)]NO_3$ was filtered with difficulty, washed with 50% ethanol, ethanol, acetone, and air-dried; yield 3.5 g.

The complex was dissolved in 100 ml of water at 90°, and the

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[12] P. H. Crayton and J. A. Mattern, *J. Inorg. Nucl. Chem.*, **13**, 248 (1960); *Inorg. Syn.*, **7**, 207 (1963).

solution was filtered rapidly and cooled slowly to 0°. (Slow cooling leads to a more filterable product.) The oily crimson plates which formed were then filtered, washed as before, and air-dried; yield 2.7 g. The analysis is given in Table I.

Electronic Absorption Spectra.—Spectra were recorded at room temperature using a Cary Model 11 spectrophotometer for 10^{-2} *M* solutions in 1-cm cells.

Proton Magnetic Resonance Spectra.—The chloride salts of the isomers were sufficiently soluble to render a good signal-to-noise ratio. Spectra were recorded on a Varian A-60 spectrometer (60 Mc/sec) at about 35°, the internal temperature of the instrument. Deuterium oxide solutions were prepared by dissolving with gentle heating as much of the sample as necessary to obtain a good spectrum (minimum sample size 0.45 ml). The addition of a fraction of a drop of concentrated HCl shifts the HDO peak downfield 0.3–0.5 ppm, facilitating the integration of adjacent sample peaks. A granule of NaTMS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) was added to serve as an internal reference. All resonances occurred to the low-field side of NaTMS and are arbitrarily made positive. When dissolved in deuteriochloroform TMS resonates +0.05 ppm from NaTMS in D_2O.

Analyses.—The C, H, and N analyses were done by the Spang Microanalytical Laboratory, Ann Arbor, Mich. The silver analyses were performed by the Volhard method[13] and chloride content was determined gravimetrically.[14]

Discussion of the Results

Isolation and Distribution of Geometric Isomers.—The six different isomers which were found are shown in Figure 1. (The designation *cis* or *trans* defines the position of the coordinated oxygens around the cobalt(III) octahedra.) Although certain of the isomers could be precipitated from aqueous solution the initial separation were carried out using ion exchange. The different isomers were eluted following their expected dipole moments in accordance with observations of others on simple *cis* and *trans* complexes.[6] The *trans* complexes with very low dipole moments were first eluted followed by two closely spaced bands of the s-*cis* (symmetrical) and then the u-*cis* (unsymmetrical) isomer which should have the most unsymmetrical distribution of charge.

The possible geometric isomers depended upon the stereochemistry of the chelating agents. In the complexes with diethylenetriamine and IDA the three donor sites on each ligand are capable of coordinating along either an edge (meridional configuration) or a face (facial configuration) of an octahedron and three different isomers are found. This separation of the two facial isomers as well as the meridional isomer of [Co(dien)(IDA)]$^+$ is the first known case where an octahedral complex consisting of two tridentate chelating agents has been shown to exist in its three isomeric forms. The ligand PDC should only span an edge and only the *trans* isomer is found. Both *trans*- and s-*cis*-[Co(dien)(MIDA)] were obtained but the u-*cis* was not found. The absence of this isomer is due to steric repulsions which will be discussed later.

The distribution of the geometric isomers is compared to the calculated statistical distribution in Table II. Although some eluted fractions were too dilute to warrant workup and in some cases neighboring bands overlapped, the figures can be considered semiquantitative in nature.

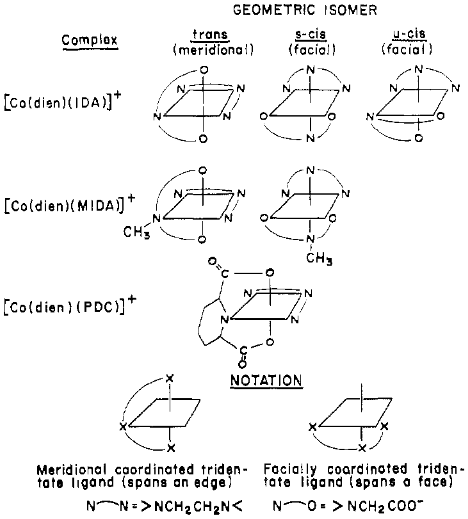

Figure 1.—The geometric isomers of the tridentate chelate complexes which were prepared and characterized.

Table II

The Equilibrium Distribution (%) Found for the Geometric Isomers of the Tridentate Chelate Complexes Compared to Calculated Statistical Distributions

	Bis complexes		Mixed ligand complexes		
	[CoA$_2$]$^{+a}$	[CoL$_2$]$^{-b}$	*trans*	s-*cis*	u-*cis*
Statistical	25	25	17	11	22
Statistical if only mixed found	0	0	33	22	45
Found for IDA	Trace	Trace	12	59	29
Found for MIDA	Trace	Trace	20	80	0

[a] A = dien. [b] L = IDA, MIDA.

The isomer distribution is of interest. When the syntheses were performed with carbon only, trace amounts of [Co(dien)$_2$]$^+$ and [Co(L)$_2$]$^-$ were found. However, when carbon was not used larger quantities of these complexes were observed. The use of carbon as a catalyst has been discussed by others[15] and two different mechanisms have been put forth concerning the catalysis. The mechanism is felt to be either electron transfer between a cobalt(III) complex and labile cobalt(II) or the formation of a spin-free activated state for the cobalt(III) on the catalyst surface. Because of the small amount of [Co(dien)$_2$]$^{3+}$ formed, it is tempting to assume that the carbon forms the spin-free activated state with [Co(dien)Cl$_3$] which leads to the easy removal of the chloride ions without removing the dien. The addition of the other tridentate ligand should then result in the formation of an equilibrium mixture of the mixed isomers.

To explain the observed distribution of complexes, Table II, it is necessary to consider the stereochemistry of the chelate rings. The work of Crayton and Mattern[12] suggests that diethylenetriamine prefers a meridional configuration in [Co(dien)(NO$_2$)$_3$] even though models show that both configurations are possible.

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[13] W. J. Blaedel and V. W. Meloche, "Elementary Quantitative Analysis," Row, Peterson and Co., Evanston, Ill., 1957, p 292.

[14] Reference 13, p 214.

[15] See, for example, F. P. Dwyer, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., p 28.

TABLE III

THE ELECTRONIC ABSORPTION SPECTRA OF THE TRIDENTATE CHELATE COMPLEXES

	Spectral bands ($\bar{\nu}$)				*Dt*, cm^{-1}	*Dq*(OAc$^-$), cm^{-1}
	Ia	Ib	II	III		
trans-[Co(dien)(IDA)]$^{+c}$	1.961[a] (174)[b]	2.247 sh[i]	2.777 (189)	4.444 (208)[d]	206	2169
s-*cis*-[Co(dien)(IDA)]$^+$	1.842 sh[i]	2.058 (72)	2.857 (85)	4.587 (246)[d]	190	2197
u-*cis*-[Co(dien)(IDA)]$^+$	1.953 (105)	. . .	2.801 (124)	4.608 (213)[d]	430	1777
trans-[Co(dien)(MIDA)]$^{+c}$	1.953 (129)	2.198 sh[i]	2.725 (173)	*e*	215	2154
s-*cis*-[Co(dien)(MIDA)]$^+$	1.825 sh[i]	2.032 (67)	2.842 (72)	4.608 (270)[d]	247	2098
trans-[Co(dien)]PDC]$^+$	1.931 (220)	2.299 (146)	3.450[f]	*g*	240	2110
						Dq (dien)
Co(dien)$_2{}^{3+h}$	2.141		2.933			2530

[a] All $\bar{\nu}$ in cm^{-1} × 10^{-4}. [b] Extinction coefficients (ϵ) in parentheses. [c] Concentration 0.688 × 10^{-2} *M*, all other concentrations 1.375 × 10^{-2} *M*. [d] ϵ × 10^{-2}. [e] Spectrum not taken. [f] Shoulder, obscured by strong ultraviolet absorption. [g] Steady increase in ϵ with decreasing λ. [h] F. Brigando, *Bull. Soc. Chim. France*, 211 (1957). [i] The wavelengths for the shoulders are determined assuming a symmetrically shaped curve for the main peaks.

However, they were not able to show this configuration conclusively for [Co(dien)$_2$]$^{3+}$ and [Co(dien)Cl$_3$]. The investigations in this work on the preparation and spectra of [Co(dien)Cl$_3$] suggest that this complex may exist in several isomeric forms.

Although diethylenetriamine could exist in either configuration, models show that IDA is very strained when in a meridional configuration. Tsuchida and coworkers[5] suggested that IDA in *trans*-[Co(IDA)$_2$]$^-$ which they had prepared was in the less strained facial configuration. Work to be reported elsewhere on the nmr spectra of [Co(IDA)$_2$]$^-$ and [Co(MIDA)$_2$]$^-$ verifies the facial configuration. The preference of IDA for a facial configuration explains why only 12% rather than the statistical 33% of *trans*-[Co(dien)(IDA)]$^+$ is formed. If diethylenetriamine is meridionally oriented in the starting material, the carbon must be capable of loosening or lengthening the N–Co^{III} bonds, permitting rearrangement to a facial configuration to account for the formation of the *cis* isomers of the mixed complex.

Molecular models suggest that in the u-*cis* isomer there are steric repulsions between the amine substituent of the dicarboxylic acid and the –CH$_2$– protons of diethylenetriamine. These repulsions should follow the trend MIDA > IDA. This accounts for the observations that no u-*cis* isomer forms with MIDA and that the s-*cis* isomer in IDA (where there are no such steric interactions) predominates over the statistically favored u-*cis* isomers. Preliminary results indicate that when the tridentate ligand aspartic acid is used (where steric interactions are minor), a nearly statistical distribution is obtained of s-*cis* and u-*cis* isomers. The ratios of *trans* to s-*cis* isomers in the IDA and MIDA complexes are comparable, suggesting that the steric interactions involving MIDA in both of these isomers must be similar.

The Electronic Absorption Spectra.—Table II summarizes the spectra of the complexes which are shown in Figure 2 for the IDA and PDC complexes. The MIDA complexes are similar to those of IDA. We have discussed[7] the spectra for isomers of cobalt(III) having the general formulation [Co(amine)$_4$(carboxylic acid)$_2$]$^+$. On the high-energy side of band Ia the *trans* isomers exhibit a shoulder (band Ib) which is of comparable energy to band I in the parent compound [Co(dien)$_2$]$^{3+}$. Band Ia is shifted to lower energy as acetate is a weaker ligand than ammonia.[16] The *cis* isomers are split less than the *trans* isomers (theoretically only half as much[10]) and are shifted approximately half as much as the *trans* isomers. The major exception is u-*cis*-[Co(dien)(IDA)]$^+$, whose much larger shift will be rationalized later in terms of steric considerations.

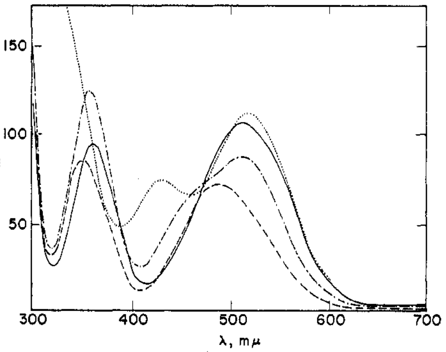

Figure 2.—The electronic absorption of s-*cis*-[Co(dien)(IDA)]$^+$ (– – – –), u-*cis*-[Co(dien)(IDA)]$^+$ (———), *trans*-[Co(dien)-(IDA)]$^+$ (– · –), and *trans*-[Co(dien)(PDC)]$^+$ (· · · ·). (For the *trans* isomers the ordinate values should be increased by a factor of 2.)

The values of *Dt′*, the tetragonal splitting parameter, have been calculated using the method of Wentworth and Piper,[17] were *Dt′* is given by the equation

$$Dt'\ (trans) = {}^4/_{35}(\text{band I (dien)} - \text{band Ia})$$
$$Dt'\ (cis) = {}^8/_{35}(\text{band I (dien)} - \text{band Ib})$$

From the values of *Dt′* a *Dq* for acetate was calculated using the Wentworth and Piper formula

$$Dt' = {}^4/_7(Dq(\text{dien}) - Dq(\text{acetate}))$$

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[16] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 311 (1956).

[17] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

The values for *Dq*(acetate) do not vary appreciably from one tridentate ligand to another in this series but are in general somewhat higher than the value of 2020 cm^{-1} found for tetradentate diaminediacetic acid ligands.[7]

The trends in *Dq*(acetate) are explainable on steric grounds. (Note: No data on N-substituted dien were available, requiring that values for dien be used in all calculations. Thus many of the differences observed in *Dq*(acetate) actually reflect a change in *Dq*(amine).) The values of *Dq*(acetate) for similar isomers follow the trend IDA > MIDA in all cases. This is a reflection of the steric interactions due to the methyl substitution in MIDA as discussed in the isomer distributions and found with the tetradentate complexes.[7] This effect results in a lengthening of the metal–ligand bond to decrease the interaction and would give a lower *Dq* in MIDA. The increased steric repulsions expected for both of the u-*cis* isomers are seen by the shift to lower energy in u-*cis*-[Co(dien)(IDA)]$^+$ which is much larger than expected. The similarities in the *Dq* values in *trans*- and s-*cis*-IDA suggest that the steric factors involved in these isomers are similar.

Simple crystal field theory predicts[18] that monodentate *cis* isomers which lack a center of symmetry should have a more intense spectra than the *trans* isomers which have this center. However, caution must be taken concerning the relative intensities. As pointed out by Dunn[19] and Ballhausen[20] these d–d transitions gain intensity through the dissymmetry introduced by asymmetrical ligand vibrations. The vibrational motions in our chelate systems should be more complex than in the monodentate complexes upon which the intensity predictions are based. This factor causes a reversal of the behavior of the *cis* and *trans* isomers of IDA and MIDA. As was pointed out previously, IDA and MIDA are strained in the *trans* (meridional) configuration, as supported by the low amounts of the *trans* isomers found (Table II). This strain could displace the carboxyl oxygens from the normal octahedral positions on the *z* axis and remove the the effective center of symmetry from the complex. Also the puckered nature of the dien rings removes the plane of symmetry besecting the O–N–O plane in IDA and MIDA. (This fact was demonstrated by the pmr measurements.) The removal of these elements of symmetry, particularly the center of symmetry, results in the *trans* isomers exhibiting more intense spectra than the *cis* isomers. Similarly the spectrum of the u-*cis* isomer of IDA is more intense than that of the s-*cis* isomers, which has plane of symmetry.

The large splitting of the first band of [Co(dien)(PDC)]$^+$ agrees with equilibrium studies of Anderegg.[21] He found that +2 transition metal ions formed stronger complexes with IDA than with PDC. Because there is little flexibility of the C–N–C angle of the pyridine ring the carboxyl oxygens in the pyridine ligand are displaced from the *z* axis and the metal ion–oxygen distance is greater than with IDA. Thus, the pyridine ligand would form weaker complexes. This weaker oxygen–metal ion electrostatic interaction causes a greater difference in the dipole moment contributions along the *x* and *z* axes which results in a greater tetragonal splitting of band I. Pyridine is similar to NH_3 in the spectrochemical series,[16] but it may be that cobalt(III) exhibits greater metal–ligand interaction through the conjugated π system of PDC than with NH_3. Thus the parent compound should be one with higher *Dq* than $[Co(dien)_2]^{3+}$, resulting in the general shift to higher energies observed for bands Ia and II in this complex. If pyridine is indeed somewhat stronger in these complexes a rhombic distortion should result. This distortion together with the oxygen displacement which removes the effective center of symmetry would cause an increase in intensity. The spectrum of this complex shows the greatest intensity of all the complexes observed.

Proton Nuclear Magnetic Resonance Spectra.—The pmr spectra of IDA and MIDA complexes are tabulated in Table IV and several of the spectra are shown in Figures 3–6. The spectra are similar to those for the tetradentate complexes discussed earlier.[7] Except for the broad N–H resonances, the spectra are observed to be quite sharp due to the fixed chelate rings and exhibit no coupling with the ^{59}Co nucleus. The methylene protons on the acetate rings occur at lower fields (3.3–4.3 ppm) than the ethylene protons on diethylenetriamine (2.3–3.5 ppm) owing to the combined deshielding effect on the acetate protons from both the carboxylate and the amine groups and observed in similar complexes.[22]

Drawings of IDA with the proton orientations in *cis* and *trans* configurations are shown in Figure 7. Because complexation in these configurations fixes the acetate protons in different environments, symmetrical AB quartets due to two spin-coupled protons[23] are observed in the acetate region as found in similar complexes.[7,22] The dien molecule in either a facial or a meridional configuration is puckered, influencing the acetate ring chemical environment. The number of AB patterns expected for the acetate ring protons in the two *cis* and *trans* configurations was an unequivocal method for assigning isomer geometries. The s-*cis* isomers exhibit one AB quartet as both acetate rings are in the same environment. The *trans* and u-*cis* isomers exhibit two overlapping AB quartets as the acetate rings are in slightly different environments. The chemical shifts and coupling constants for the acetate ring protons calculated according to Jackman[23] are summarized in Table V.

Although both halves of the dien molecule are mirror

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(18) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 405 (1955).

(19) T. M. Dunn, private communication.

(20) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 186.

(21) G. Anderegg, *Helv. Chim. Acta*, **43**, 414 (1960).

(22) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Am. Chem. Soc.*, **85**, 2930 (1963); R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964); J. L. Sudmeier and C. N. Reilley, *ibid.*, **36**, 1698 (1964).

(23) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 89.

TABLE IV

RESONANCE FREQUENCY ASSIGNMENTS AND INTEGRATION VALUES FROM THE PMR SPECTRA OF THE TRIDENTATE CHELATES[a]

Part I—Isomers with Facial Acetate Rings

	s-*cis*-[Co(dien)-(IDA)]$^+$		s-*cis*-[Co(dien)-(MIDA)]$^+$		u-*cis*-[Co(dien)(IDA)]$^+$		
Assignment	Res freq, ppm	No. of H's[b]	Res freq, ppm	No. of H's[c]	Res freq, ppm	Res freq, ppm	No. of H's[e]
$-NH_2$, $>NH$	4.6		4.9		7.0	6.6	
						5.7	
					4.62^{j}	4.55^{j}	
	4.47	0.68	4.37	0.39		(4.49)	1.1^{g}
$>NCH_2COO^-$	4.17	1.3	4.09	1.6	$(4.38)^{i}$		1.2
	3.57		3.79	1.5	4.32	4.25	
	3.27		3.51			(4.19)	
					3.59	3.54	1.1^{g}
					3.28	3.23	0.94
		3.9		2.0			
	3.50		3.63		3.17		
	↓		↓		↓		7.7
NCH_2CH_2N	3.13		3.24		2.60		
	3.02		3.11				
	↓	6.0	↓	6.3			
	2.64		2 65				
$N-CH_3$			2.99	3.4			

Part II—Isomers with Meridional Acetate Rings

	trans-[Co(dien)(IDA)]$^+$			*trans*-[Co(dien)(MIDA)]$^+$		
Assignment	Res freq, ppm	Res freq, ppm	No. of H's[d]	Res freq, ppm	Res freq, ppm	No. of H's[b]
$-NH_2$, $>NH$	4.9					
$>NCH_2COO^-$	4.37^{j}	4.32^{j}		4.43^{j}	4.55^{j}	
	4.07	4.06	3.8^{h}	4.15	4.27	4.08^{h}
		3.99		4.04	4.07	
	3.78	3.72		3.77	3.79	
					3.12	4.72
$>NCH_2CH_2NH_2$		3.14^{f}	8.2		3.03	3.18
$>N-CH_3$					2.90	3.02

[a] All frequencies on low-field side of NaTMS (NaTMS = 0). [b] Represents an average of three values. [c] Represents an average of two values. [d] Only one integration performed. [e] Integration performed with planimeter. [f] Peak broad. [g] Integration of first column is top value. [h] Integration value for both columns. [i] Numbers in parentheses are part of spectrum of A rings resulting from H–N–C–H coupling. [j] Where two overlapping patterns exist they are presented in different columns.

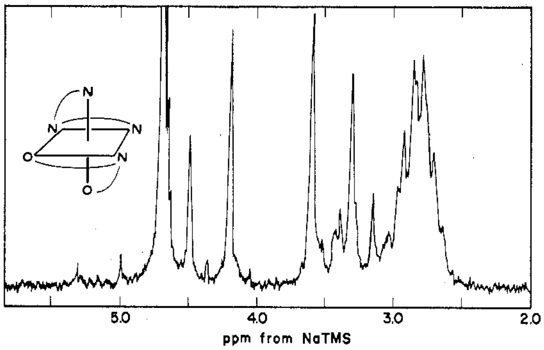

Figure 3.—The pmr spectrum of s-*cis*-[Co(dien)(IDA)]$^+$ (trace of HCl present).

images of each other, an ABCD spectrum is observed since the four protons in each arm are not equivalent. The approximate centers of the ABCD spectra are given in Table V.

The changes observed in the chemical shifts can be explained in terms of the magnetic anisotropy of the various bonds as discussed with the tetradentate com-

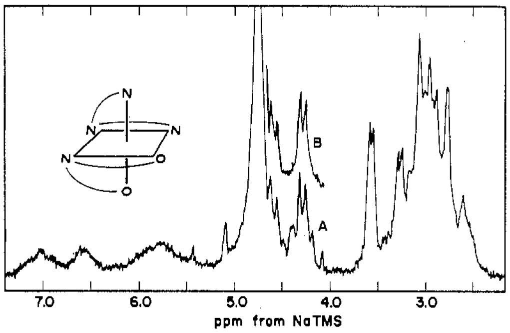

Figure 4.—The pmr spectrum of u-*cis*-[Co(dien)(IDA)]$^+$ (trace of HCl present): A, spectrum before amine proton exchange; B, spectrum after amine proton exchange.

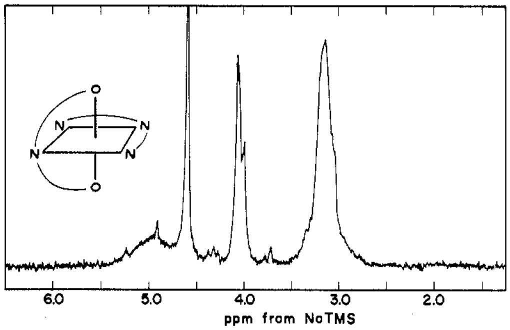

Figure 5.—The pmr spectrum of *trans*-[Co(dien)(IDA)]$^+$.

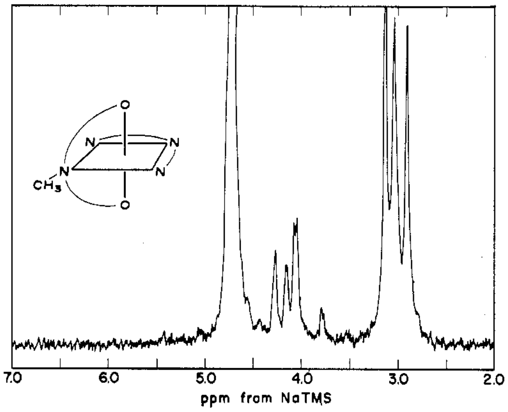

Figure 6.—The pmr spectrum of *trans*-[Co(dien)(MIDA)]$^+$ (trace of HCl present).

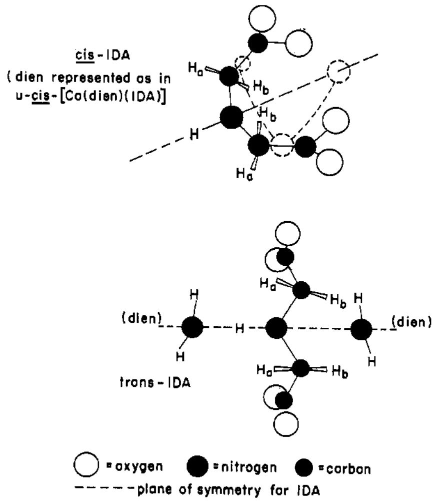

Figure 7.—Orientation of IDA in *cis* and *trans* configuration.

TABLE V

CHEMICAL SHIFTS OF THE DIETHYLENETRIAMINE AND ACETATE RING PROTONS OF THE TRIDENTATE COMPLEXES[a,b]

Complex	dien ring[g]	Meridional[c] ring δ_a	Meridional[c] ring δ_b	Facial[c] ring δ_a	Facial[c] ring δ_b
s-*cis*-[Co(dien)(IDA)]$^+$	2.8[e]			4.29	3.45
				(0.84)[d]	
s-*cis*-[Co(dien)(MIDA)]$^+$	2.8[e]			4.19	3.69
	2.99[f]			(0.50)	
u-*cis*-[Co(dien)(IDA)]$^+$	2.9[e]			4.45	3.47
				(0.98)	
				4.35	3.41
				(0.94)	
trans-[Co(dien)(IDA)]$^+$	3.1	4.12	3.92		
		(0.20)			
		4.11	4.03		
		(0.08)			
trans-[Co(dien)(MIDA)]$^+$	3.1	3.96	4.23		
	2.90[f]	(−0.27)			
		3.98	4.36		
		(−0.38)			

[a] Calculated according to Jackman.[23] [b] Values in ppm. [c] Proton coupling constants (J_{AB}) vary from 16 to 18 cps. [d] $\delta_a - \delta_b$. [e] Approximate center of an unsymmetrical series of peaks. [f] Chemical shift of N-methyl protons. [g] Mean chemical shift.

plexes.[7] Bothner-By and Naar-Colin[24] found that anisitropic shielding occurred with C–C single bonds and suggested that other single bands may exhibit similar behavior. A proton located along the bond axis is deshielded; one perpendicular to the bond axis is shielded.

(a) **The s-*cis* Complexes.**—The plane of symmetry in s-*cis*-[Co(dien)(IDA)]$^+$ and s-*cis*-[Co(dien)(MIDA)]$^+$ results in only one AB pattern. An integration value of 2.0 for the low-field doublet is obtained. (The high-field doublet overlaps the dien proton absorptions.) The b protons are assigned the high-field chemical shift in each isomer as they are located in a shielded region of the C–N bond associated with the other b proton. A similar conclusion is reached if the weaker C–H bond anisotropy is considered. The chemical shifts in IDA are comparable with those of 4.19 and 3.37 ppm found in the tetradentate series.[7] In the tetradentates, models indicate that both a and b protons are in somewhat more shielded environments than in IDA.

In the MIDA complex the N-CH_3 bond anisotropy places H_a in a more shielded environment and H_b in a less shielded environment. The decrease of H_a by 0.10 ppm and increase of H_b by 0.24 ppm compare with the corresponding values of 0.08 and 0.32 ppm in the tetradentate series.[7]

The $>NCH_3$ gives a sharp absorption at 2.99 ppm in the spectrum of s-*cis*-[Co(dien)(MIDA)]$^+$ which is downfield from the $>NCH_3$ absorption at 2.67 ppm[7] in *trans*-[Co(en)(DMEDDA)]$^+$. This is possibly due to a greater diamagnetic deshielding of the $>N-CH_3$ protons in the former complex. The tridentate chelate complexes exhibited higher *Dq* values than the tetradentate chelate complexes, suggesting that the electron density on the MIDA C–N bond would be lower than on the substituted tetradentate nitrogens.

The dien protons in both complexes gave an unsymmetrical ABCD spectra with center at about 2.8 ppm.

(b) **u-*cis*-[Co(dien)(IDA)]**.—In u-*cis*-IDA the plane of symmetry is removed, and the two acetate rings are in slightly different chemical environments with respect to the dien, Figure 7. Two superimposed AB spectra similar to the s-*cis* pattern are observed. The b proton chemical shifts are similar to those of s-*cis*-IDA. The a protons are at somewhat slightly lower fields than in s-*cis*-IDA. This deshielding may be due to a change in the C–N–C bond angle in IDA due to the greater steric crowding in the u-*cis* isomer compared to the s-*cis* isomer or due to anisotropy related to the amine on dien.

Fine structure is seen flanking the low-field components of the AB spectra, and three amine absorptions are found below the HDO peak. The spectrum was retaken after the solution had stood several months, and the amine absorption at 7.0 ppm and the fine structure had disappeared. The simultaneous disappearance of these peaks suggest that the fine structure is due to H–N–C–H coupling with the secondary amine of IDA which is confirmed to be the peak at 7.0 ppm. The slow amine proton exchange on IDA is in agreement with the steric hindrance observed at that proton. This slow exchange was not found in s-*cis*- or *trans*-IDA because much less steric hindrance at the amine proton is expected.

Clifton and Pratt studied acido pentaammine- and bis(ethylenediamine)cobalt(III) complexes and found that amine protons *trans* to acido species resonated at higher fields than those *cis* to acido species.[25] Since the N–H group in IDA is *cis* to both acido groups, its resonance should occur downfield from the dien NH resonance, further confirming the assignment.

The amine proton is seen to couple only with the low-field protons. Karplus has shown that the coupling constants between two protons on adjacent carbon atoms depends on the dihedral angle between the protons.[26] Models indicate that this angle is approximately zero for N–C–H_a and near 100° for N–C–H_b. If coupling through a tetrahedrally bonded nitrogen is similar to that through carbon, then the a and b protons should exhibit coupling constants of 8 cps and less than 1 cps, respectively. A coupling constant of 7.8 cps is observed for the low-field protons, which then must be the H_a protons. This assignment of H–N–C–H coupling to H_a confirms the earlier assignment made from a consideration of the magnetic anisotropy of the C–N bonds.

The amino proton should split each resonance line into a doublet[27] as shown in Figure 8. Deuterium, however, would not be expected to couple with H_a due to its quadrupolar relaxation. When the spectrum was recorded, the secondary amine had been partially deuterated and the spectrum of the protonated complex is superimposed on that of the deuterated complex. This

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(24) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958).

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

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

(27) See ref 23, p 20.

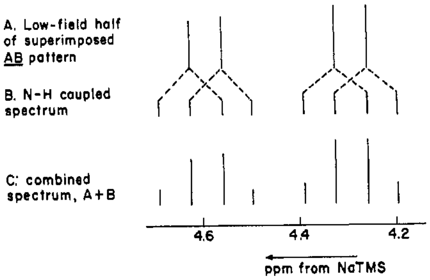

Figure 8.—Explanation of fine structure observed for low-field half of superimposed AB spectra found for u-*cis*-[Co(dien)(IDA)]$^+$.

assumes[27] that the two AB spectra observed are close to first-order spectra in which the intensities of components should be of comparable magnitude and $J_{ab}/(\delta_a - \delta_b)$ should be less than 0.33. This is justified since $J_{ab}/(\delta_a - \delta_b) = 0.32$ and the intensities are comparable.

(c) **The *trans* Isomers.**—When the configuration of the IDA is changed to *trans* the chemical shifts of both the acetate and dien protons change. This configuration change brings the protons into more nearly identical chemical environments. In the strained *trans* configuration the C–N–C bond angle in IDA probably is greater than 109°, similar to the G rings[28] in [Co(EDTA)]$^-$. This strain causes H_a and H_b to be more symmetrically placed with respect to the opposite C–N bond as well as their orientation to the C═O bond and H_a is more shielded and H_b less shielded than in the *cis* cases. The dien protons in the *trans* isomer are displaced from the shielding environment of the other arm resulting in an over-all deshielding from 2.8 to approximately 3.1 for the two *trans* complexes. The dien spectrum becomes more symmetrical, indicating the chemical environments of the dien protons are quite comparable. Models also show that the dien molecule is not symmetrical about the nitrogen plane. Thus, the two acetate rings are in slightly different environments with respect to the dien, and two superimposed AB spectra are seen representing the two acetate groups. In IDA the peaks and satellites at 4.0 ppm are resolvable into two AB spectra. In each pattern H_a is in the same chemical environment but one H_b is 0.11 ppm upfield from the other owing to some shielding environment.

The replacement of the IDA amine proton with $-CH_3$ in MIDA should have little influence on the dien spectra, but the added C–N anisotropy will influence the spectra of the acetate rings. If the C–N anisotropy change is similar to that observed for the s-*cis* complexes the shifts should be −0.10 ppm for H_a and +0.24 for H_b. The actual shifts are shown in Table VI and are consistent with each other. The slight differences in agreement can probably be related to the geometry changes in the strained *trans* ring.

TABLE VI

COMPARISON OF ACETATE PROTON CHEMICAL SHIFTS FOR THE *trans* ISOMERS

	δ_a	δ_b	δ_a	δ_b
trans-[Co(dien)(IDA)]$^+$	4.12	3.92	4.11	4.03
trans-[Co(dien)(MIDA)]$^+$	3.96	4.26	3.98	4.36
Shift on N-substitution	−0.16	+0.31	−0.13	+0.33

The sharp peak at 2.90 ppm with an integration value of 3.02 protons is assigned to the $N-CH_3$ protons on MIDA. This assignment is tentative because one of the other nearly sharp peaks may be a combination of the $N-CH_3$ protons plus a portion of the dien protons. It is expected that the opening up of the C–N–C bond in the *trans*-MIDA configuration would place the $N-CH_3$ protons in a more shielded environment than in the *cis*-MIDA configuration. The shift of the $N-CH_3$ from *cis*- to *trans*-MIDA of 2.99 to 2.90 ppm agrees with this effect.

The broad absorption at 4.9 ppm is assigned to some or all of the amine protons on the dien. After the solution had stood for several months, this peak had disappeared and the dien peak at 3.1 had sharpened somewhat. This confirms the assignment of the dien amine protons.

Summary of Pmr Spectra.—The chemical shifts are readily explained in terms of the magnetic anisotropy of the different single bonds. When both IDA and MIDA are in a facial configuration, the protons (H_b protons) pointing toward the opposite ring are in general in the shielding environment of the single bonds of that ring. This places the signal due to these protons at higher fields. The change from facial to meridional partially removes these H_b protons from the shielding environment and places them in a chemical environment more nearly like that of the protons (H_a protons) pointing away from the opposite arm. Although the dien proton resonances cannot be assigned definitely, a similar over-all deshielding is observed for the resonances on ring opening. With methyl substitution on the IDA nitrogen the anisotropy of the C–N bond shields H_a by 0.10–0.14 ppm and deshields H_b by 0.24–0.32 ppm.

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(28) H. A. Weakhem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).