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The Stereochemistry of Some Cobalt(III) Complexes with Ethylenediamine-N,N'-diacetic Acid and Some N-Substituted Analogs[1]

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A series of octahedral cobalt(III) complexes involving tetradentate diaminedicarboxylic acid chelating agents was prepared: $[Co(Am)(Lig)]^+$ where Am = ethylenediamine and Lig = ethylenediamine-N,N'-diacetate (EDDA), N,N'-dimethylethylenediamine-N,N'-diacetate (DMEDDA), and N,N'-diethylethylenediamine-N,N'-diacetate (DEEDDA); and where Lig = EDDA and Am = two ammonias. Red-violet *trans* (with respect to the oxygens) isomers were found for all the complexes, and red *cis* isomers were isolated for $[Co(en)(EDDA)]^+$ and $[Co(NH_3)_2(EDDA)]^+$ using ion-exchange chromatography. In the *trans* isomers the $^1A_1 \rightarrow {}^1T_1$ transition was split, and the principal band shifted to lower energies while exhibiting a shoulder isoenergetic to this transition in the parent hexaammine. This maximum was at lower energies for the bis-ammine complexes than for the corresponding ethylenediamine complexes and shifted to lower energies with increasing bulkiness of the N-alkyl substituent on the tetradentate ligand. In the *cis* isomers the band was only broadened and was shifted only half as much as in the *trans*. Characteristic p.m.r. spectra were observed for the various isomers. In the *trans* complexes the acetate ring protons exhibited AB spectra with chemical shifts in the region 3.5 to 4.3 p.p.m. (*vs.* NaTMS) while the ethylene ring protons exhibited A_2B_2 spectra with chemical shifts in the region 2.5 to 3.5 p.p.m. The *cis*-$[Co(en)(EDDA)]^+$ with acetate rings in two different environments gave two AB patterns. Bulky substitution on the EDDA nitrogen caused the ethylenediamine to become fixed and its single resonance peak collapsed into an A_2B_2 pattern. This substitution also caused slight changes in the proton chemical shifts which could be explained in terms of the magnetic anisotropy of the various C–N bonds. Protons located on the C–N axis were deshielded while those located perpendicular to the C–N bond were shielded. The p.m.r. spectrum of $[Co(EDTA^-)]$ is discussed.

Introduction

Tetradentate chelating agents can assume a variety of orientations in octahedral complexes which are dependent on the steric requirements of the ligands. In order to investigate the stereochemistry of such chelate systems a series of cobalt(III) complexes using the tetradentate ligands ethylenediamine-N,N'-diacetate (EDDA), N,N'-dimethylethylenediamine-N,N'-diacetate (DMEDDA), and N,N'-diethylethylenediamine-N,N'-diacetate (DEEDDA) were prepared. Mori and co-workers prepared the carbonato, diaquo, and dinitro cobalt(III) complexes of EDDA but isolated only one of the several geometric isomers which might be expected.[2] Liu has prepared the three geometric isomers of octahedral $[Pt(Cl)_2(EDDA)]$.[3]

The stereochemistry of the complexes prepared in this study was investigated through ion-exchange chromatography, electronic absorption spectroscopy, and proton nuclear magnetic resonance spectroscopy. The selectivity of ion-exchange resins has been used to distinguish between simple *cis* and *trans* isomers for complexes of many different metal ions.[4]

Wilkins and Williams[5] have summarized the use of electronic absorption spectroscopy to distinguish between *cis* and *trans* cobalt(III) isomers based on crystal field considerations as established by Ballhausen and Jørgensen,[6] Moffitt and Ballhausen,[7] and Yamatera.[8] It was of interest in the present work to learn to what extent these multidentate chelate systems followed the simple predictions of crystal field theory.

It was expected that coordination of the tetradentate chelating agents would result in a rigid orientation of the protons in different environments and that consequently characteristic resonance lines would be observed. Day and Reilley observed a complex spectrum for $[Co(EDTA)]^-$ and assigned part of the spectrum to the two kinds of acetate rings present.[9] Sawyer and coworkers were able to establish the structure of a Mo(VI)–EDTA complex by comparing its n.m.r. spectrum to that obtained for model compounds of methyliminodiacetic acid and nitrilotriacetic acid.[10] On the other hand, Powell and Sheppard observed a broad unresolved band for $[Co(en)_3]^{3+}$ in deuterium oxide,[11] and Gillard and Wilkinson observed similar spectra for Co(III) and Rh(III) triethylenetetramine complexes.[12] These workers suggested H–N–C–H spin–spin coupling, conformational exchange, and Co–H coupling as possible complicating factors.

Experimental

Preparation of the Ligands.—Ethylenediamine-N,N'-diacetic acid was commercially available (K and K Laboratories, Inc.) and was used without further purification.

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[1] (a) Abstracted from a thesis submitted by J. Ivan Legg to the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1965. (b) Presented in part to the Inorganic Division, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4–9, 1965.

[2] M. Mori, M. Shibata, E. Kuno, and F. Maruyama, *Bull. Chem. Soc. Japan*, **35**, 75 (1962).

[3] C. F. Liu, *Inorg. Chem.*, **3**, 680 (1964).

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

[5] R. G. Wilkins and M. J. G. Williams, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers Inc., New York, N. Y., 1960, pp. 187–191.

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

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

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

[9] R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964).

[10] S. I. Chan, R. J. Kula, and D. T. Sawyer, *J. Am. Chem. Soc.*, **86**, 377 (1964).

[11] D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 791 (1959).

[12] R. D. Gillard and G. Wilkinson, *ibid.*, 3193 (1963).

(a) **Preparation of Barium N,N′-Diethylethylenediamine-N,N′-diacetate.**—A cold solution of 41 g. (1.02 moles) of sodium hydroxide in 125 ml. of water was added to a cold stirred solution of 47.5 g. (0.5 mole) of monochloroacetic acid in 35 ml. of water at such a rate that the temperature did not rise above 10°. Upon neutralization the remaining base was added rapidly. To the stirred solution 29.5 g. (0.25 mole) of N,N′-diethylethylenediamine was added dropwise over a period of 90 min. The temperature was kept below 45° during the addition. After a 90-min. waiting period barium chloride dihydrate, 65 g. (0.26 mole), dissolved in 125 ml. of boiling water was added rapidly, and the solution was shaken. The cloudy suspension of Ba(DEEDDA) which formed was heated at 60° for 30 min. with occasional shaking, filtered from the hot solution, and washed. A second crop was obtained by evaporation. The combined wet yields were twice purified by stirring in 100 ml. of water at about 95° for 10 min. and filtered while hot. The salt was washed with acetone and dried for 2 hr. at 85°; yield 26 g. *Anal.* Calcd. for $Ba(C_8H_{18}N_2O_4)$: C, 32.66; H, 4.93; N, 7.62. Found: C, 32.39; H, 5.07; N, 7.55. On standing for several weeks Ba(DEEDDA) picks up 1 mole of water.

(b) **Preparation of Barium N,N′-Dimethylethylenediamine-N,N′-diacetate.**—The preparation is identical with that of Ba(DEEDDA) except that 22.0 g. of N,N′-dimethylethylenediamine was used and 20-ml. portions of water at 65° were used for the purification of Ba(DMEDDA). The salt was dried for 2.5 hr. at 110°; yield 22 g. *Anal.* Calcd. for $Ba(C_6H_{14}N_2O_4)$: C, 28.29; H, 4.15; N, 8.25. Found: C, 28.17; H, 4.26; N, 7.92.

Preparation of the Complexes. (a) **Preparation of *trans*-N,N′-Diethylethylenediamine-N,N′-diacetato(ethylenediamine)cobalt(III) Nitrate.**—To a rapidly stirred suspension of 3.68 g. (0.01 mole) of Ba(DEEDDA) dissolved in 20 ml. of water at about 50°, 2.81 g. (0.01 mole) of cobaltous sulfate heptahydrate dissolved in 20 ml. of water was added over a period of 20 min. After heating at 60° for 30 min., the solution was filtered through a layer of Fuller's earth. The precipitate was washed with 15 ml. of hot water. To the combined filtrate and washings were added successively 5 ml. of 2 *N* nitric acid, 1 g. of activated charcoal, and 0.61 g. (0.01 mole) of 98% ethylenediamine in 4 ml. of water. Air was bubbled through the mixture for 8 hr. and the charcoal removed by filtration. (The oxidation may also be carried out by the dropwise addition of 1.1 g. of 30% H_2O_2 in 15 ml. of H_2O to the stirred solution.) The solution was evaporated almost to dryness on a steam bath, and the red precipitate was taken up in 170 ml. of 90% ethanol at 5°. After filtration to remove a trace of yellow substance, the solution was evaporated in air. The red crystals of *trans*-[Co(en)(DEEDDA)]-NO_3 which formed were washed with ethanol and acetone and dried for 4 hr. at 105°; yield 3.7 g. *Anal.* Calcd. for $[CoC_{12}H_{26}N_4O_4]NO_3$: C, 35.04; H, 6.37; N, 17.03. Found: C, 35.20; H, 6.17; N, 17.14.

(b) **Preparation of *trans*-N,N′-Dimethylethylenediamine-N,N′-diacetato(ethylenediamine)cobalt(III) Nitrate.**—The preparation is identical with that of [Co(en)(DEEDDA)]NO_3 except that 3.40 g. of Ba(DMEDDA) was used. Upon slow evaporation of a saturated solution, large, flat, hexagonal crystals formed. These were washed with 95% ethanol, absolute ethanol, and acetone and air dried. *Anal.* Calcd. for $[CoC_{10}H_{22}N_4O_4]NO_3\cdot 1.5H_2O$: C, 29.26; H, 6.14; N, 17.07. Found: C, 29.34; H, 6.17; N, 17.41.

(c) **Preparation of *trans*-Ethylenediamine-N,N′-diacetato(ethylenediamine)cobalt(III) Nitrate.**—A suspension of 13.1 g. of cobaltous carbonate and 17.6 g. (0.1 mole) of ethylenediamine-N,N′-diacetic acid in 250 ml. of water was heated at 60° with occasional stirring until the carbon dioxide evolution ceased (about 20 min.). The pink solution was filtered through a medium fritted glass filter and treated as described for the preparation of *trans*-[Co(en)(DEEDDA)]NO_3 using ten times the quantities of reagents. After the oxidation and removal of the charcoal, evaporation of the solution on a steam bath to about 50 ml. yielded red-violet crystals which were filtered, washed with three 10-ml. portions of water, 50% ethanol, ethanol, and acetone, and air-dried; yield of *trans*-[Co(en)(EDDA)]-$NO_3\cdot H_2O$ 24 g. *Anal.* Calcd. for $[CoC_6H_{16}N_4O_4]NO_3\cdot H_2O$: C, 25.74; H, 5.40; N, 18.77. Found: C, 25.86; H, 5.63; N, 18.60. More product was obtained by evaporation of the combined filtrate and washings. The oxidation could also be carried out with 11 g. of 30% hydrogen peroxide as described for the preparation of *trans*-Co(en)(DMEDDA)]NO_3.

(d) **Preparation of *cis*-Ethylenediamine-N,N′-diacetato(ethylenediamine)cobalt(III) Perchlorate.**—A solution containing 0.10 mole of cobalt(II) EDDA was prepared as described for the *trans* isomer except that it was heated over 1 hr. before removing the excess cobaltous carbonate and instead of nitric acid 14.4 g. of 70% perchloric acid in 40 ml. water was used. The oxidation was carried out using 11 g. of 30% hydrogen peroxide. The *trans*-[Co(en)(EDDA)]ClO_4 which had precipitated during the oxidation and the charcoal was removed, and the solution was evaporated on a steam bath to about 50 ml. and further evaporated to a paste with air. The mixture was cooled in an ice bath and the *cis* isomer removed by washing the precipitate with three 20-ml. portions of 50% ethanol. (The *trans*-[Co(en)(EDDA)]-ClO_4 which remained was recrystallized from hot water, washed with ethanol and acetone, and air-dried. Its electronic absorption spectrum was identical with that of the nitrate salt.)

The combined extractions were diluted to 1500 ml. with water and added at a rate of 1.5 ml./min. to a column (diameter 4.5 cm.) containing 280 cc. of strong-acid cation-exchange resin (Dowex 50W-X8, 50–100 mesh) in the sodium form prepared as described by Dow.[13] Water was passed through the column (2 ml./min.), eluting a large volume of purplish solution. The remainder of the layer was eluted with 0.5 *M* sodium perchlorate over a period of 4 days at about 0.4 ml./min. During this time the layer separated into three bands. Evaporation of a portion of the first eluted band yielded red crystals whose electronic absorption was identical with that of *trans*-[Co(en)(EDDA)]ClO_4 previously isolated. The second band was the *cis* complex and the third dark brown band which remained at the top of the column was presumably some +2 or +3 decomposition product.

The combined fractions from the second band were evaporated to a solid mass in a rotary evaporator. The sodium perchlorate was filtered off using two 15-ml. portions of ethanol to rinse the crystals free of red solution. Twice the volume of ethanol was added to the filtrate, and the evaporation and filtration steps were repeated. This process was repeated until addition of ethanol to the filtrate just produced cloudiness which cleared on swirling. The clear solution was placed in a stoppered flask, whereupon red crystals of *cis*-[Co(en)(EDDA)]ClO_4 formed, usually within a day. (If no crystals formed, the process of evaporation and filtration was repeated.) The crystals were filtered, stirred with ethanol to remove any sodium perchlorate which may have formed, refiltered, washed with acetone, and air-dried; yield 2.5 g. A portion of this was recrystallized from water at 60°. *Anal.* Calcd. for $[CoC_6H_{16}N_4O_4]ClO_4\cdot H_2O$: C, 23.40; H, 4.91; N, 13.64. Found: C, 23.66; H, 5.09; N, 13.59.

(e) **Preparation of *cis*-Ethylenediamine-N,N′-diacetato(ethylenediamine)cobalt(III) Chloride.**—About 1.5 g. of *cis*-[Co(en)-(EDDA)]ClO_4 (not recrystallized) dissolved in 50 ml. of water was passed through a column of strong-base anion-exchange resin (Dowex 2-X8, 50–100 mesh) in the chloride form at a rate of about 0.7 ml./min. After evaporation of the eluent to 25 ml., *cis*-[Co(en)(EDDA)]Cl was precipitated by adding 200 ml. of ethanol dropwise, filtered, washed with ethanol and acetone, and air-dried; yield 0.4 g. *Anal.* Calcd. for $[CoC_6H_{16}N_4O_4]Cl\cdot 3H_2O$: C, 25.10; H, 6.32; N, 14.64. Found: C, 25.10; H, 6.17; N, 14.80.

(f) **Preparation of *trans*-Ethylenediamine-N,N′-diacetato(diammine)cobalt(III) Nitrate.**—To a solution containing 0.01 mole of cobalt(II) EDDA prepared as described in the synthesis of

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[13] "Dowex-Ion Exchange," The Dow Chemical Co., Midland, Mich., 1958.

trans-[Co(en)(EDDA])NO_3, 16.0 g. of ammonium nitrate and 10 g. of charcoal were added. Air was bubbled through this mixture for 8 hr., and 24 ml. of concentrated ammonia was added dropwise to the stirred mixture. The solution stood 2 days, and the charcoal was removed. Evaporation in a stream of air on a steam bath yielded red-violet crystals of *trans*-$[Co(NH_3)_2(EDDA)]NO_3$ which were filtered, washed with a small amount of water, 50% ethanol, ethanol, and acetone, and air-dried; yield 7 g. *Anal.* Calcd. for $[CoC_6H_{16}N_4O_4]NO_3$: C, 21.89; H, 4.89; N, 21.28. Found: C, 22.08; H, 4.75; N, 21.25.

Ion-Exchange Chromatography.—Three mmoles of each of the complexes was diluted to 100 ml. and added to a 100-ml. buret containing 90 cc. of Dowex 50W-X8 (50–100 mesh). After sweeping the column with water the adsorbed band was eluted with 0.5 *M* $NaClO_4$ at 0.1 to 0.5 ml./min. The *cis* and *trans* isomers of $[Co(en)(EDDA)]^+$ were cleanly separated. No corresponding *cis* band was found for either the DMEDDA or DEEDDA complexes. Although $[Co(NH_3)_2(EDDA)]^+$ could not be prepared in good yields it exhibited two bands on elution which behaved like those of $[Co(en)(EDDA)]^+$. The spectrum of the last eluted band was very similar to that of *cis*-$[Co(en)(EDDA)]^+$. When the syntheses were performed without charcoal lower yields were obtained but no evidence for the *cis* isomers of the DMEDDA and DEEDDA complexes was found when the solutions were chromatographed.

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.—Spectra were recorded on a Varian A-60 spectrometer (60 Mc./sec.) at about 35°, the internal temperature of the probe. Deuterium oxide solutions were prepared by dissolving with gentle heating as much of the finely powdered sample as necessary to obtain a good spectrum (minimum sample size 0.45 ml.). The addition of a fraction of a drop of concentrated hydrochloric acid was found to shift the HDO peak downfield about 0.3 to 0.5 p.p.m., 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. When dissolved in deuteriochloroform TMS resonates +0.05 p.p.m. from NaTMS in deuterium oxide. The nitrate salts of the *trans* isomers were sufficiently soluble to obtain good p.m.r. spectra. *cis*-$[Co(en)(EDDA)]ClO_4$ had to be converted to the more soluble chloride.

Analyses.—The C, H, and N analyses were done by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Discussion of Results

Separation of Isomers.—The isomers which were prepared in this study are shown in Figure 1. The order of column elution of the EDDA isomers of first *trans* and then *cis* agrees with the greater effective dipole moment expected for the *cis* isomer[14] and is consistent with the work of Mori and co-workers[15] and Kyuno[16] on *cis* and *trans* cobalt(III) complexes.

It was expected that using a charcoal catalyst would result in equilibrium.[17] The fact that no *cis* isomers were found for the DMEDDA and DEEDDA complexes and only traces of the *cis* isomers for the EDDA complexes can be explained from steric considerations and will be discussed with the n.m.r. spectra of these complexes.

Electronic Absorption Spectra.—The spectra of the complexes are shown in Figure 2 and summarized in Table I.

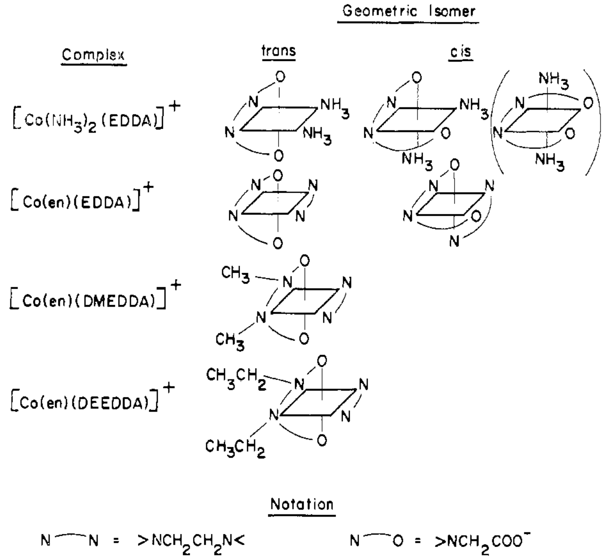

Figure 1.—The geometric isomers of the tetradentate chelate complexes which were synthesized and characterized.

Band I for the *trans* complexes consists of a weak shoulder superimposed upon a symmetrical main peak. The wave lengths for the shoulder were obtained by subtracting a symmetrical trace of the major peak from the observed spectrum. It is assumed that the same situation applies for the *cis* complexes. If we utilize the alternate assumption that the *cis* band I is the center of two peaks of equal intensity the calculated values of *Dq* (acetate) are much too high.

Ballhausen[6,7] and Yamatera[8] have discussed theoretically the expected shifts and splittings in the absorption peaks which are shown in Figure 3. The complexes agree with this theory. Band Ia in the *trans* complexes has shifted to lower energies but a low intensity shoulder (band Ib) with energy comparable to band I in the parent $Co(en)_3{}^{+3}$ is found on the high-energy side of band Ia. (In the absence of data on tetradentate polyamines the values for $Co(NH_3)_6{}^{+3}$ and $Co(en)_3{}^{+3}$ are used. For the NH_3 complexes the value of band I was taken to be two-thirds of band I for $Co(en)_3{}^{+3}$ and one-third of band I for $Co(NH_3)_6{}^{+3}$). In the *cis* isomer the major first band (band Ib) is only broadened and is shifted only half as much from the parent compound as in the *trans* isomer (1290 $cm.^{-1}$ *vs.* 2630 $cm.^{-1}$ for the NH_3 compounds and 1270 $cm.^{-1}$ *vs.* 2570 $cm.^{-1}$ for the en compounds). Band I in the *cis* compounds has greater area than the corresponding band in the *trans* compounds, in conformity with crystal field predictions[18] and as verified experimentally.[19] It should be pointed out, though, that since neither the *trans* nor the *cis* isomer has a center of symmetry, the intensity (area) relationship might not necessarily apply in this instance.[19]

The absorption maxima of band I of both the *cis*

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[14] E. L. King and R. R. Walters, *J. Am. Chem. Soc.*, **74**, 4471 (1952).

[15] M. Mori, M. Shibata, and J. Azami, *J. Chem. Soc. Japan*, **76**, 1003 (1955); M. Mori, M. Shibata, and N. Nanasawa, *Bull. Chem. Soc. Japan*, **29**, 947 (1956); M. Mori, M. Shibata, and K. Hori, *ibid.*, **34**, 1809 (1961).

[16] E. Kyuno, *J. Chem. Soc. Japan*, **80**, 981 (1959); *ibid.*, **81**, 724 (1960).

[17] C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 405 (1955).

[18] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **26**, 15 (1953).

[19] F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

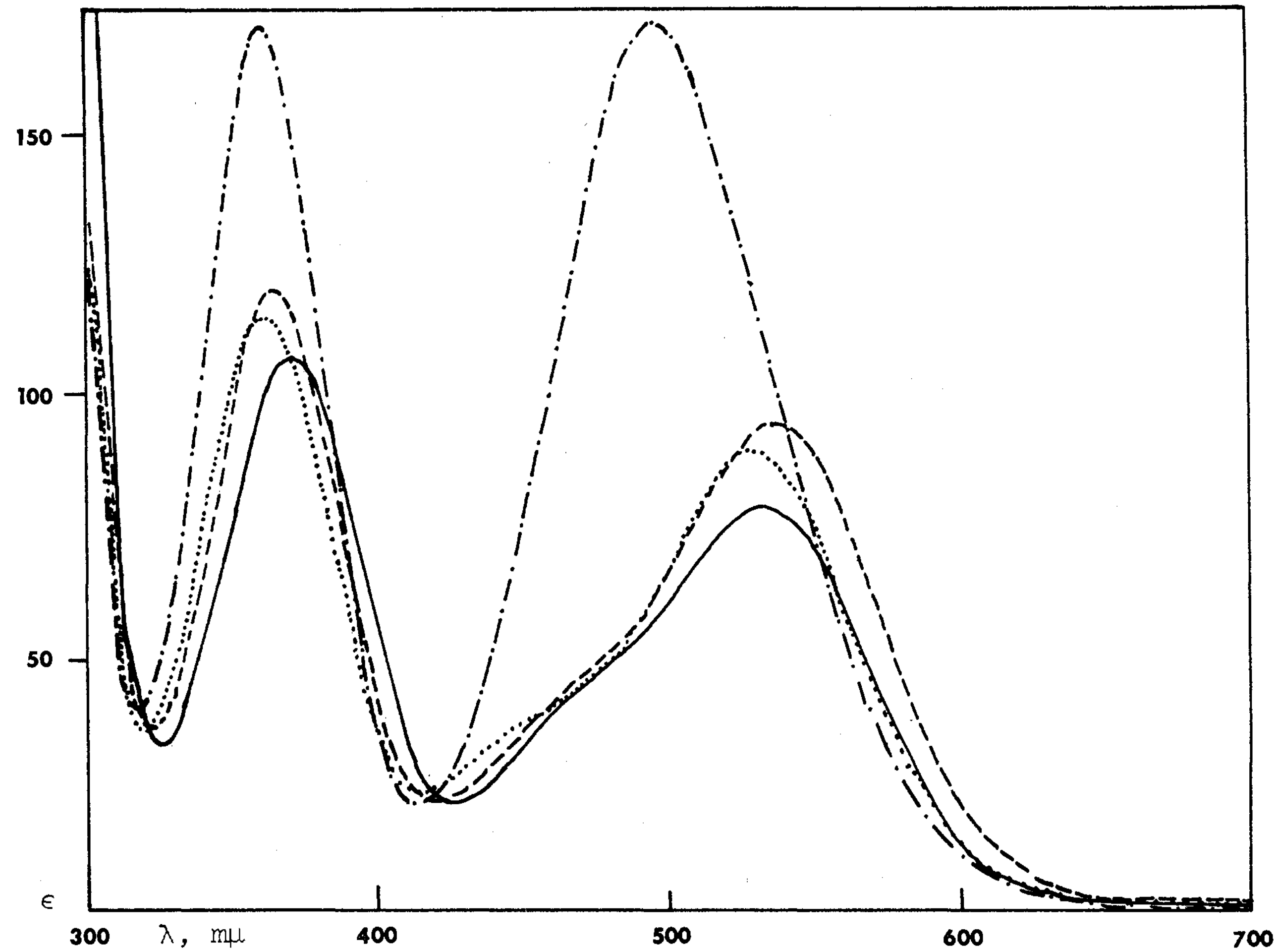

Figure 2.—The electronic absorption spectra of *trans*-$[Co(NH_3)_2(EDDA)]^+$ (– – –), *trans*-$[Co(en)(EDDA)]^+$ (· ·), *trans*-$[Co(en)(DEEDDA)]^+$ (———), *cis*-$[Co(en)(EDDA)]^+$ (— · —).

TABLE I

THE ELECTRONIC ABSORPTION SPECTRA OF THE TETRADENTATE CHELATE COMPLEXES

	Band Ia			Band Ib		Band II		Band III		Dt', cm.$^{-1}$	Dq (acetate), cm.$^{-1}$
	$\bar{\nu}^a$	ϵ		$\bar{\nu}$	ϵ	$\bar{\nu}$	ϵ	$\bar{\nu}$	$\epsilon \times 10^{-4}$		
trans-$[Co(NH_3)_2(EDDA)]NO_3$[b]	1.866	92.6		2.169	sh	2.747	118	(4.762)[c]	(2.48)	301	1993
cis-$[Co(NH_3)_2(EDDA)]ClO_4$[d]				2.000		2.793		[e]		295	2004
trans-$[Co(en)(EDDA)]NO_3 \cdot H_2O$	1.890	87.3		2.232	sh	2.762	113	(4.717)	(2.62)	287	2027
cis-$[Co(en)(EDDA)]Cl \cdot 3H_2O$	1.805	sh		2.020	169	2.778	168	4.484	2.18	276	2047
trans-$[Co(en)(DMEDDA)]NO_3 \cdot 1.5H_2O$	1.880	77.7		2.174	sh	2.710	110	4.608	2.42	298	2008
trans-$[Co(en)(DEEDDA)]NO_3$	1.869	77.7		2.162	sh	2.681	106	4.651	2.18	311	1986
											Dq (amine)
$Co(NH_3)_6^{+3}$[f]			2.105			2.941					2490
$Co(en)_3^{+3}$[f]			2.141			2.950					2530
$Co(dien)_2^{+3}$[f]			2.141			2.933					2530

[a] All $\bar{\nu}$ in cm.$^{-1}$ × 10^{-4}. [b] All concentrations 1.375 × 10^{-2} *M*. [c] Values in parentheses not certain. [d] Nonquantitative. [e] Spectrum not taken. [f] F. Brigando, *Bull. soc. chim. France*, 211 (1957).

and *trans* isomers of $[Co(en)(EDDA)]^+$ occur at higher energy than for the corresponding diammine isomers. This is in keeping with the expected greater stability due to the chelate effect of ethylenediamine when compared to two ammonias.[20] Table I also shows a shift of band Ia to lower energy as the hydrogens on the nitrogens of EDDA are progressively substituted by methyl (DMEDDA) and then ethyl (DEEDDA). This shift is probably due to the lengthening of metal–ligand bonds to accommodate the N-substituted alkyl groups. Steric interaction between DEEDDA and ethylenediamine was demonstrated by the n.m.r. studies, *vide infra*. A decrease in stability with N-alkyl substitution in a series of amine +2 metal complexes was also observed by Leussing.[21]

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(20) See, for example, R. W. Parry, "The Chemistry of the Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, Chapter 5 and references therein.

(21) D. L. Leussing, *Inorg. Chem.*, **2**, 77 (1963).

Table II

Resonance Frequency Assignments and Integration Values from the P.m.r. Spectra of the *trans*-Tetradentate Chelate Complexes

Assignment	$[Co(NH_3)_2(EDDA)]^+$ Res. freq., p.p.m.[a]	$[Co(NH_3)_2(EDDA)]^+$ No. of H's[b]	$[Co(en)(EDDA)]^+$ Res. freq., p.p.m.	$[Co(en)(EDDA)]^+$ No. of H's	$[Co(en)(DMEDDA)]^+$ Res. freq., p.p.m.	$[Co(en)(DMEDDA)]^+$ No. of H's	$[Co(en)(DEEDDA)]^+$ Res. freq., p.p.m.	$[Co(en)(DEEDDA)]^+$ No. of H's
NH_3	~4.4	1.6+[c]						
	4.40	1.2−[c]	4.37	0.87	4.32	0.40	4.30	0.48
$>NCH_2CO_2^-$	4.09	3.6−[c]	4.07	1.4	4.01	1.6	3.99	1.5
(R ring)	3.51	1.8	3.49	1.4	3.80	1.4	3.72	1.4
	3.19		3.20		3.49	0.47	3.42	0.7
	3.46		3.41					
	3.44		3.38					
$>NCH_2CH_2N<$	3.37	5.8[e]		4.4[e]				
(E ring)	3.28		3.23		2.89		2.84	
	3.15		3.13		2.86	3.8	2.81	4.5[d]
	3.09		3.08		2.80		2.76	
	2.97		2.99		2.78		2.74	
	2.87							
	2.81						2.60	
	2.78						2.56	
$>NCH_3$							3.26	
					2.67	5.8	3.13	
							3.00	
$>N\mathit{CH}_2CH_3$							2.88	7.4[d]
							3.32	
$D_2NCH_2CH_2ND_2$			2.87	4.1	3.09	4.2	3.28	
$>NCH_2\mathit{CH}_3$							1.50	1.9
							1.38	3.0
							1.26	1.1

[a] All frequencies on low-field side of NaTMS (NaTMS = 0). [b] Represents an average of two values. [c] NH_3 absorption located in same region as low-field R ring AB doublet absorption. [d] Band at 2.88 p.p.m. integrated with ethylenic protons belonging to DEEDDA. [e] High-field peak of R ring integrated with E ring protons.

Table III

Resonance Frequency Assignments and Integration Values from the P.m.r. Spectra of *cis*-$[Co(en)(EDDA)]^+$ and $[Co(EDTA)]^-$

Assignments	$[Co(EDTA)]^-$ Res. freq., p.p.m.[a]	$[Co(EDTA)]^-$ No. of H's[b]	*cis*-$[Co(en)(EDDA)]^+$ Res. freq., p.p.m.	*cis*-$[Co(en)(EDDA)]^+$ No. of H's[c]
	4.09		4.22	0.28
	3.83		3.92	0.68
	3.67		3.71	2.1
	3.40		3.43[d]	0.48
$>NCH_2COO^-$ (G and R rings)		6.8[f]		
	4.23			
	3.92[e]		3.71	2.1
	3.91[e]			
	?			
	3.72			
$>NCH_2CH_2N<$	3.64[g]		3.40[d]	
	3.58	5.2[f]	↓	6.0
	3.50		2.50[d]	
	3.33[d]			
$D_2NCH_2CH_2ND_2$			2.94	2.4

[a] All frequencies are on low-field side of NaTMS (NaTMS = 0). [b] Represents an average of four values. [c] Integration performed once. [d] Peaks not well-defined. [e] Peaks coalesced into single peak. [f] Peaks at 3.67 and 3.40 included in integration of $>NCH_2CH_2N<$. [g] Shoulder.

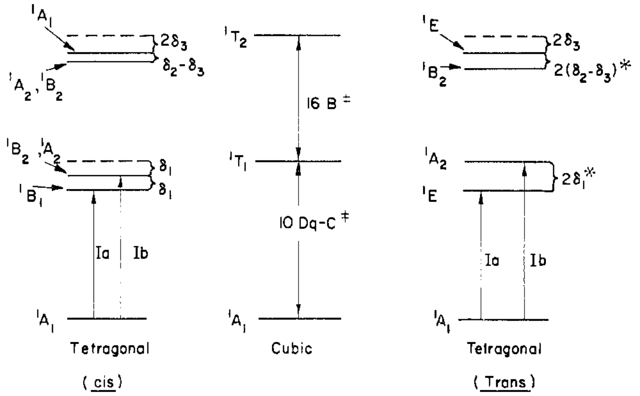

Figure 3.—The expected shifts and splittings in tetragonal complexes of Cobalt(III). *Note:* Although the energy of the ground state $^1A_1$ varies on changes of symmetry from cubic to tetragonal we are interested only in the energies of the transitions between states and have arbitrarily shown no change in the energy of the ground state.

* In terms of the notation of Ballhausen $2\delta_1 = {}^{35}/_4Dt$ and $2(\delta_2 - \delta_3) = 6Ds - {}^5/_4Dt$.

‡ *B* and *C* are the Racah Parameters and *Dq* depends only on the field strength of the in-plane amine ligands.

Wentworth and Piper[22] have discussed the calculation of *Dt'*, an approximation to *Dt*, in which off-diagonal matrix elements are neglected. This parameter is given by the equation

$$Dt' = {}^4/_{35}[(10Dq - C) - W]$$

where *W* is the energy of major peak of band I in the *trans* complexes. Using the theory developed by Yamatera[8] a similar formula for the *cis* complexes is obtained in which ${}^8/_{35}$ is substituted for ${}^4/_{35}$. Wentworth and Piper observed that the value of *C* for several different cobalt(III) complexes is approximately con-

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

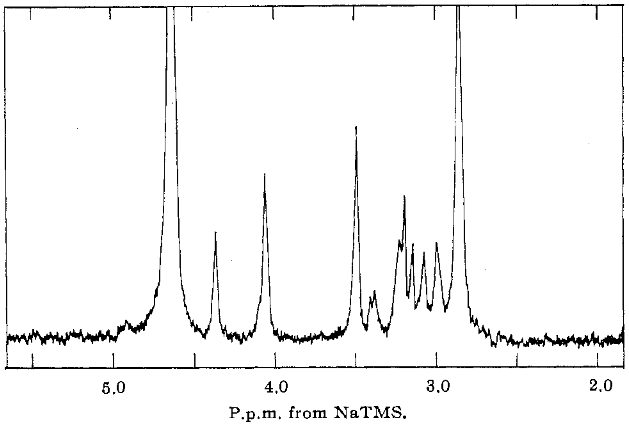

Figure 4.—The p.m.r. spectrum of *trans*-[Co(en)(EDDA)]$^+$.

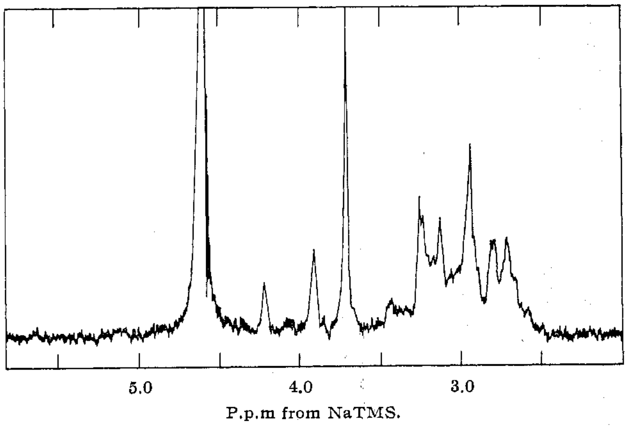

Figure 5.—The p.m.r. spectrum of *cis*-[Co(en)(EDDA)]$^+$.

stant (at about 3800 cm.$^{-1}$) and have used the value of $10Dq - C$ from the parent compound (in this case $Co(en)_3^{+3}$) in the calculations. Calculations of Dt' are tabulated in Table I. They also express the values of Dt' in terms of the Dq values of amine and acetate as follows

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

The calculated values of Dq (acetate) (Table I) are in good agreement with a Dq of about 2000 cm.$^{-1}$ calculated by Piper and Carlin[23] for $Co(C_2O_4)_3^{-3}$.

Proton Nuclear Magnetic Resonance Spectra.—The resonance line assignments for the complexes are given in Tables II and III and typical spectra are shown in Figures 4 and 5. Several features are apparent. The protons associated with the $>NCH_2COO^-$ rings and subjected to the combined deshielding effects of the carboxylate and amine groups are found at lower fields (3.5 to 4.3 p.p.m.) than those associated with the $>NCH_2CH_2N<$ rings (2.5 to 3.5 p.p.m.) which are influenced only by the inductive effect of the amine groups. These observations are consistent with data on similar complexes.[9,24]

In these inert complexes the conformation of the acetate ring is fixed, resulting in a symmetrical AB quartet due to two spin–spin coupled protons in different chemical environments.[25] This type of spectrum has been observed for compounds with similar acetate rings.[10,24]

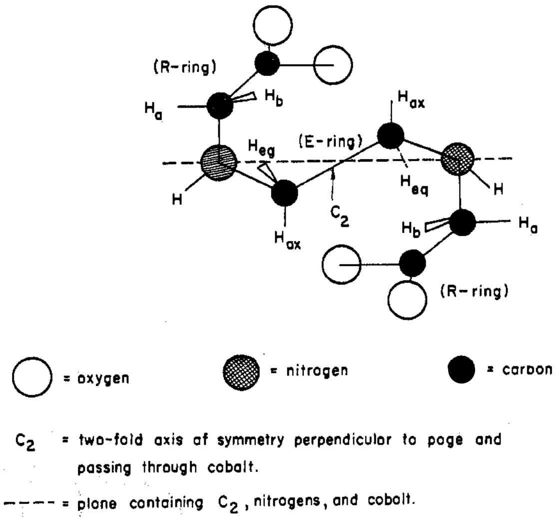

Figure 6.—Orientation of carbon hydrogen in a *trans*-coordinated EDDA-type chelating agent.

A perspective drawing of the *trans*-coordinated EDDA molecule showing the relative orientations of the protons is shown in Figure 6. The two sets of acetate ring protons are in identical chemical environments, and only one AB pattern, determined by the relative environments of H_a and H_b, with an integrated value equivalent to four protons (Table II) is seen, confirming this configuration for the *trans* EDDA molecule.

In the *cis* isomer the asymmetry introduced by changing one of the R acetate rings[26] (oxygen above the plane containing Co and EDDA nitrogens) to a G ring (oxygen in Co–EDDA nitrogen plane) should result in two different acetate ring patterns. The *cis* isomer exhibits a more complex spectrum in the acetate region where a single intense peak is observed at 3.71 p.p.m. superimposed on the same type of AB quartet found in the *trans* complexes. These peaks integrate to a total value of four, accounting for all the acetate protons. As pointed out by Jackman,[25] if the chemical shifts of the two protons are not too different, the AB quartet collapses into a strong center peak with weak side peaks separated from the center by the value of J_{AB}, the spin–spin coupling constant. Very weak side peaks are detectable in the *cis* spectrum. X-Ray data on [Co(EDTA)]$^-$ by Weakliem and Hoard[26] indicate that the bond angle between the G and E rings is opened up to 116°, making the chemical environments of the protons more alike.

Although the possibility exists that this single peak may be due to a labile G ring, evidence that we have obtained on similar systems suggests that this is not the case. We have prepared the mixed complexes of cobalt

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[23] T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **35**, 1809 (1961).

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

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

[26] The letter designations for the various rings are those used for [Co(EDTA)]$^-$ by H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

with diethylenetriamine and iminodiacetic acid (IDA) and find that when the IDA oxygens are *trans* (with orientation analogous to the *cis* G ring in EDDA) a single acetate peak with minor side bands exists. When a CH_3 group is placed on the IDA nitrogen resulting in a different environment for each proton the single peak splits into a normal AB pattern. It would be expected that the N-substituted IDA would be comparable in lability to the IDA and *cis*-EDDA. Thus the single peak is due to the protons in similar chemical environments. These results will be reported elsewhere.[27]

The E ring of the *trans* complexes has two equivalent proton sets, each set having an equatorial (eq) and axial (ax) proton, Figure 6. These protons exhibit a symmetrical A_2B_2 pattern, which theoretically can have from 14 to 24 lines depending on the chemical shifts and the coupling constants between the ax and eq protons[28] and is easily assigned in *trans*-$[Co(NH_3)_2(EDDA)]^+$ and *trans*-$[Co(en)(EDDA)]^+$ to the peaks with centers at 3.12 and 3.10 p.p.m., respectively. The *trans*-$[Co(en)(DMEDDA)]^+$ shows four closely spaced lines (integrating to 3.8 protons) centered at 2.83 p.p.m. which can be unequivocally assigned to the E ring of DMEDDA since the remainder of the spectrum can be assigned to the other functional groups. The E ring in *trans*-$[Co(en)(DEEDDA)]^+$ is in a similar environment, and the four lines at 2.78 p.p.m. are assigned to its protons. (This assignment is confirmed when the magnetic anisotropy of the C–N bonds is considered.)

The only N–H resonance observed was a broad peak in *trans*-$[Co(NH_3)(EDDA)]^+$, at 4.4 p.p.m.; it is assigned to the ammonia protons. The amine protons of complexes with ethylenediamine and EDDA apparently exchange rapidly with the solvent and are effectively decoupled from the remaining protons on the ligands.

In *trans*-$[Co(en)(EDDA)]^+$ the single strong resonance absorption at 2.87 p.p.m. with an integration value of 4.1 is due to the four ethylene protons on the ethylenediamine. The sharpness of the peak shows unequivocally that the ring is rapidly changing conformation. In *trans*-$[Co(en)(DMEDDA)]^+$ the ethylenediamine peak shifts to 3.09 p.p.m. Its integration value of 4.2 protons differentiates it from the $>NCH_3$ peak at 2.67 p.p.m. integrating to 5.8 protons.

In *trans*-$[Co(en)(DEEDDA)]^+$, apparently due to increased steric crowding brought on by the introduction of two N-ethyl substituents into the structure of the tetradentate ligand, the conformation of the ethylenediamine has become fixed, for what was formerly a single sharp resonance has collapsed. The resonance lines must be located under the $-CH_2-$ spectrum of $>NCH_2CH_3$ centered at 3.06 p.p.m. which is split into a quartet by the $-CH_3$. This quartet is identified from the coupling constant determined from the $-CH_3$ triplet (split by $-CH_2-$) centered at 1.38 p.p.m. The location of the ethylenediamine protons at about 3.05 p.p.m. is also in agreement with the location of this group at 3.09 p.p.m. for the DMEDDA isomer.

The integration values found are in agreement with the above assignments. The peaks at 3.32 and 3.28 p.p.m. belonging to ethylenediamine and the peaks at 3.26, 3.13, and 3.00 p.p.m. belonging to the first three components of the 1:3:3:1 quartet of the $>NCH_2-$ group, which also include the major portion of the ethylenediamine, integrate to 7.4 protons. The calculated value would be 3.5 protons from the quartet and almost 4 protons from the ethylenediamine or a total of almost 7.5 protons. The peak at 2.88, the upfield component of the $>N\mathit{CH_2}CH_3$ quartet, and the peaks at 2.84, 2.81, 2.76, 2.74, 2.60, and 2.56 p.p.m. assigned to the E ring, integrate to 4.5 protons. The calculated value would be 0.5 proton for the upfield component of the $>N\mathit{CH_2}CH_3$ group and a little less than 4 for the $>NCH_2CH_2N<$ or a total of almost 4.5 protons.

As would be expected, due to lack of symmetry in *cis*-$[Co(en)(EDDA)]^+$, an unsymmetrical ABCD spectrum for the E ring and the ethylenediamine protons is observed, Figure 5. Thus, it is difficult to assign the individual absorptions to either ethylenediamine or the E ring. The peak at 2.94 p.p.m. has been tentatively assigned to ethylenediamine since it has a comparable chemical shift to that found in the *trans* isomer, 2.87 p.p.m. However, its integration value, 2.4, is low (expected value 4); the peak is not sharp and may be due to the coincidence of two peaks from the ethylenediamine and/or the E ring. Molecular models indicate that there is more steric interaction between the ligands than was found in the *trans* isomer. This would result in a collapsing of the single ethylenediamine peak. Further support comes from the absence of *cis* isomers of the N-alkyl-substituted chelates where the steric interactions would be greater.

Magnetic Anisotropy of C–N Bonds.—The simplicity of an AB spectrum allows the calculation of the chemical shifts and coupling constant for the two acetate ring protons[25] which is summarized in Table IV. On the other hand, due to the complicated nature of an A_2B_2 spectrum, the chemical shifts of the individual protons cannot be readily determined, but since the spectrum is symmetric the mean chemical shift is easily located as summarized in Table IV.

The chemical shifts can be explained in terms of the magnetic anisotropy of the C–N bonds. Bothner-By and Naar-Colin investigated the anisotropic shielding by C–C bonds of protons in cyclohexane systems[29] and suggested that other single bonds may exhibit similar shielding behavior.[30] The anisotropic shielding expected for a C–N bond is illustrated in Figure 7. According to this interpretation, a proton located over the bond axis in the positive region will be the most shielded,

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[27] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, submitted for publication.

[28] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 142.

[29] A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958).

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

TABLE IV

CHEMICAL SHIFTS OF ETHYLENE AND METHYLENE PROTONS OF COMPLEXES INVESTIGATED[a,b]

	E ring (mean chemical shift)	R ring[c]			G ring[c]		
		δ_a		δ_b	δ_a		δ_b
trans-[Co(NH$_3$)$_2$(EDDA)]$^+$	3.12	4.22		3.38			
			(0.84)[d]				
trans-[Co(en)(EDDA)]$^+$	3.10	4.19		3.37			
			(0.82)				
trans-Co(en)(DMEDDA)]$^+$	2.83	4.11		3.69			
			(0.42)				
trans-[Co(en)(DEEDDA)]$^+$	2.78	4.10		3.62			
			(0.48)				
cis-[Co(en)(EDDA)]$^+$	*f*	4.02		3.62	3.71		3.71[e]
			(0.40)			(0.00)	
[Co(EDTA)]$^-$	3.61	3.96		3.88	3.59		3.91
			(0.08)			(0.32)	

[a] Calculated according to Jackman (ref. 25). [b] Values in p.p.m. from NaTMS. [c] Proton coupling constants (J_{ab}) vary from 16 to 19 c.p.s. [d] ($\delta_a - \delta_b$). [e] Splitting of central peaks and outer peaks not discernible. [f] Not well-defined.

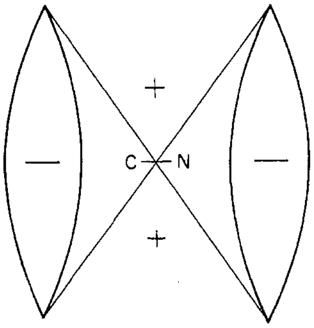

Figure 7.—Anisotropic shielding expected for a C–N bond.

and one located in the axis (along the center of the negative cone) will be the most deshielded. Thus, a proton situated on the edge of the cone, approximately 55° to the axis, will not be effected by the anisotropy of the bond.

Without an X-ray determination of the structure, it is impossible to tell the exact orientation of the protons with respect to the C–N bonds and, thus, to discuss quantitatively the magnitude of the shielding and deshielding due to the C–N bond. However, with the use of molecular models it is possible to discuss qualitatively the trends in the orientation of the protons.

For the *trans*-EDDA complexes where the nitrogen is unsubstituted, the following observations can be made. H_{eq} and H_{ax} (Figure 6) of the E ring are symmetric with respect to the C–N bond in this ring and will be shielded equally by that bond. However, the approximate bond angles that the E ring protons make with the C–N bond in the R ring are different (about 80° for H_{eq} and 40° for H_{ax}), resulting in shielding of H_{eq} and deshielding of H_{ax}. Thus the two sets of protons exhibit an A_2B_2 spectrum with a center of symmetry at 3.12 p.p.m. for *trans*-[Co(NH$_3$)(EDDA)]$^+$ and 3.10 p.p.m. for the ethylenediamine analog.

Alkyl substitution on the nitrogen adds an additional anisotropic C–N bond which would be expected to influence H_{eq} and H_{ax}. The angles these protons make with this additional C–N bond are about 65 and 85°, respectively. Both of these are in the positive region, indicating shielding, and the center of the A_2B_2 spectrum is seen to shift to higher fields (2.83 p.p.m. in *trans*-[Co(en)(DMEDDA)]$^+$ and 2.78 p.p.m. in the DEEDDA analog), confirming this increased shielding.

In *cis*-[Co(en)(EDDA)]$^+$ the angles that the E ring –CH$_2$– protons make with the G ring are somewhat smaller than those made with the R ring, and it would be expected that the E ring protons would be somewhat less shielded. Unfortunately, due to the lack of symmetry in the E ring in the *cis* isomer, the chemical shift of the two protons cannot be determined.

Using the observations of the E ring protons to confirm the sign of the shielding in the C–N bond it is possible to study the effects of these bonds on the R ring protons.

The proton which is on the same side of the ring as the amine proton or alkyl substituent will be designated H_a and the proton on the other side of the ring will be designated H_b as shown in Figure 6. These two protons are symmetric with respect to the C–N bond in the R ring and will be shielded equally by this bond, but H_b is situated over the C–N bond in the E ring whereas H_a is situated about 40° above the C–N symmetry axis. Thus, H_b should be shielded relative to H_a. The *trans*-EDDA complexes are examples of this situation (see Table IV).

When the proton on the nitrogen is replaced by an alkyl group, the protons on the R ring are situated differently with respect to the C–N bond of the alkyl substituent. H_a is at right angles to the bond axis, and H_b is about 35° out of the bond axis. This should lead to a shielding of H_a and a deshielding of H_b and is precisely what is found, Table IV. H_a shifts upfield from values of 4.22 and 4.19 p.p.m. in the EDDA complexes to 4.11 and 4.10 p.p.m. in the DMEDDA and DEEDDA complexes, and H_b shifts downfield from values of 3.38 and 3.37 p.p.m. to 3.69 and 3.62 p.p.m. We have observed similar chemical shifts showing the influence of C–N magnetic anisotropy in tridentate chelates utilizing the ligands iminodiacetic acid and methyliminodiacetic acid.[27]

In *cis*-[Co(en)(EDDA)]$^+$ with two different AB patterns, that pattern with the large chemical shift between H_a and H_b must be due to the R ring analogous to the similar R rings in the *trans* complexes because models indicate that the R ring protons in the *cis* complexes still are in different environments. In the case of the G ring of *cis*-[Co(en)(EDDA)]$^+$, there is a change in its orientation of both the G ring and E ring in order to accommodate the three coordination sites in the same plane. It is clear that this change in orientation of the E ring is of primary importance in determining the chemical shift changes in the R ring when going from *trans* to *cis* complex. In the G ring besides changing the orientation of the –CH$_2$– groups with respect to the N–C bonds, models indicate that the positions of H_a and H_b are altered relative to the carbonyl bond which is also magnetically anisotropic. These factors apparently combine to give comparable shielding to the two protons on the G ring. In the R rings, H_a and H_b appear to be symmetrically oriented with respect to the carbonyl, and no net effect of this group on the protons would be expected.

The [Co(EDTA)]⁻ Spectrum.—Day and Reilley[9] studied the n.m.r. spectrum of $[Co(EDTA)]^-$ which is summarized in Table IV.[31] They assigned the AB spectrum with only a small chemical shift to the R ring and the spectrum with a larger chemical shift to the G ring. This same assignment would be anticipated in terms of the anisotropy of the C–N bonds. It is interesting to compare differences between $[Co(EDTA)]^-$ and *cis*-$[Co(en)(EDDA)]^-$ to the differences between *trans*-$[Co(en)(EDDA)]^+$ and *trans*-$[Co(en)(DEEDDA)]^+$. In the latter case H_a is shifted upfield by 0.09 p.p.m. and H_b is shifted downfield by 0.25 p.p.m. on the addition of alkyl substitution. The spectra of *cis*-$[Co(en)(EDDA)]^+$ and $[Co(EDTA)]^-$ appear to be similarly related as summarized in Table V. This interesting correlation tends to confirm the assignments of *cis*-$[Co(en)(EDDA)]^+$ and $[Co(EDTA)]^-$ and suggests that the anisotropic effects for these various complexes are similar.

TABLE V

COMPARISON OF CHEMICAL SHIFTS OF *cis*-[Co(en)(EDDA)] AND [Co(EDTA)]⁺

	R ring		G ring	
	δ_a	δ_b	δ_a	δ_b
cis-$[Co(en)(EDDA)]^+$	4.02	3.62	3.71	3.71
Obsd. $[Co(EDTA)]^-$ spectrum	3.96	3.88	3.59	3.91
Shift on alkyl substitution	−0.06	+0.26	−0.12	+0.20

Finally, by analogy with the n.m.r. spectra of the *trans* isomers the E ring of $[Co(EDTA)]^-$ should exhibit an A_2B_2 spectrum. Examination of the spectrum reveals a symmetrical set of lines superimposed on the two AB spectra of $[Co(EDTA)]^-$. The integration values are in good agreement with the assignments, Table III. The average chemical shift of 3.61 p.p.m. is less shielded than the 3.10 p.p.m. found for the corresponding E ring in *trans*-$[Co(en)(EDDA)]^+$. This indicates that the opening up of the C–N–C bond on coordination of the G acetate group results in a positioning of the E ring protons in a region of deshielding.

[31] The spectrum that we list is the compilation of several measurements on our instrument over several months time using different samples of complex and standard. A comparable spectrum was obtained on the 60-Mc. instrument at the University of Pittsburgh using their sample and standard for which we thank Miss M. Gordon. Although Day and Reilley list no tabulation of numbers, our spectrum appears to be uniformly displaced 0.30 p.p.m. upfield from theirs, although we presumably are using the same standard. Although we are unable to explain this displacement in the spectra, the numbers that we obtain for $[Co(EDTA)]^-$ and our complexes are consistent within themselves.

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β-Diketone Complexes of Cobalt(III). I. Synthesis and Spectroscopy of Bis(acetylacetonato)diaminecobalt(III) Salts[1]

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The first known *cis*-$[Co^{III}(acac)_2L_2]^{x\pm}$ complexes have been prepared and studied by proton n.m.r., infrared, visible, and ultraviolet spectroscopy. The proton n.m.r. spectra of these stable complexes amplify the caution necessary in assigning coordination compound configurations based on chemical shifts—the $[Co(acac)_2(en)]^+$ ion, necessarily of *cis* configuration, exhibits only one sharp methyl resonance peak even though two are predicted. Salts of the ethylenediamine complex, of $[Co(acac)_2(bipy)]^+$, of $[Co(acac)_2(py)_2]^+$, and of *cis*- and *trans*-$[Co(acac)_2(NH_3)_2]^+$ have been synthesized using carbon as a catalyst.

Introduction

Whereas most cobalt(III) complexes that have been studied undergo substitution reactions with a predominant retention of configuration, the D*-*cis*-dichlorobis(ethylenediamine)cobalt(III) ion reacts with ammonia[2] and hydroxide ion[3] to give mainly *trans* and L* products, where D* and L* indicate relative configurations.[2] Fragmentary studies with the corresponding chlorobromo and dibromo complexes[2,4] suggest that these species behave in a manner similar to the dichloro ion. These dihalo ions possess weaker ligand fields than any other complexes of the bis(ethylenediamine) series. Since members of the bis(β-diketone) series should have lower ligand field strengths than the corresponding ethylenediamine complexes,[5] and since the β-diketone

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[1] Amine is used herein to indicate any nitrogen electron-pair donor, whereas ammine is reserved for coordinated ammonia. Abbreviations used include: acac = anion of the enol form of 2,4-pentanedione (*i.e.*, acetylacetonate); bipy = 2,2′-bipyridine; en = ethylenediamine; py = pyridine; L = a unidentate ligand or one-half of a bidentate ligand; and x = the charge on the complex species.

[2] R. D. Archer, Proceedings of the Eighth International Conference on Coordination Chemistry, Vienna, 1964, pp. 111–114; R. D. Archer and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **83**, 812 (1961).

[3] L. J. Boucher, E. Kyuno, and J. C. Bailar, Jr., *ibid.*, **86**, 3656 (1964).

[4] J. C. Bailar, Jr., and D. F. Peppard, *ibid.*, **62**, 820 (1940); S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).

[5] The $^1T_{1g}$ energy level of $[Co(acac)_3]$ lies about 17,000 cm.⁻¹ above the $^1A_{1g}$ ground state compared to about 21,000 cm.⁻¹ for the $[Co(en)_3]^{3+}$ ion: C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, and references cited therein.