to the mark of a 10-ml volumetric flask with water to give a 0.033 *M* solution.

(1) **tren System.**—Procedure B was followed using 3 ml of 0.033 *M* trenCo^{III} species, 3 ml of 0.033 *M* glycylglycyl-L-phenylalanine, and 4 ml of 2,4,6-collidine buffer.

(2) **trien System.**—Procedure B was followed using 3 ml of 0.033 *M* trienCo^{III} species, 3 ml of glycylglycyl-L-phenylalanine, and 4 ml of 2,4,6-collidine buffer.

(3) **Blank.**—Procedure B was followed using 3 ml of 0.033 *M* glycylglycyl-L-phenylalanine and 3 ml of 2,4,6-collidine buffer and diluting to the mark in a 10-ml volumetric flask with water.

Reaction of Co(tren)Cl$_2$$^+$ with Glycylglycine.—Glycylglycine (300 mg) and [Co(tren)Cl$_2$]Cl (660 mg) were dissolved in 2 ml of hot water. After the solution turned pink, excess NaClO$_4$ was added and the whole mixture was allowed to stand at room temperature to crystallize the violet product. Addition of dilute HClO$_4$ to the filtrate increased the yield to a total of 500 mg. The analytical sample was recrystallized from water. *Anal.* Calcd for $[Co(C_6H_{18}N_4)(C_4H_8N_2O_3)Cl](ClO_4)_2 \cdot H_2O$: C, 20.42; H, 4.80; N, 14.13. Found: C, 20.18; H, 4.87; N, 14.14. The visible spectrum shows λ_{max} 503 nm (ϵ 102) and 358 nm (ϵ 93). The nmr spectrum contains CH$_2$ singlet (4.2 ppm), CH$_2$ singlet (4.0 ppm), and 12 H of the tren CH$_2$ as a broad multiplet. The infrared spectrum shows the amide carbonyl at 1695 cm^{-1} and the carboxylate at 1600 (b) and 1390 cm^{-1}.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ILLINOIS AT CHICAGO CIRCLE, CHICAGO, ILLINOIS

Isomers of the Bis(L-2,4-diaminobutyrato)cobalt(III) Ion and Conformation of the Chelate Rings

BY WADE A. FREEMAN AND CHUI FAN LIU

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The three optically active geometric isomers of the bis(L-2,4-diaminobutyrato)cobalt(III) ion were prepared, separated by ion-exchange chromatography, and identified. The identification of the three geometries is based upon the elution order of the complexes, the pmr spectra, the visible–ultraviolet spectra, the circular dichroism spectra, and comparison of these properties with those of an analogous series consisting of the three isomers of the bis(L-2,3-diaminopropionato)cobalt(III) ion. Pmr evidence indicates that the six-membered nitrogen–cobalt–nitrogen chelate rings in the bis(2,4-diaminobutyrato)cobalt(III) complexes are in rapid equilibrium between boat and chair conformations at room temperature. The effect of the flexible and flexing chelate ring system on the circular dichroism spectra of the complexes is discussed.

Introduction

In an effort to learn more about the contribution of ligand conformations to the circular dichroism of the d–d transitions in optically active metal ion complexes, the three possible geometrical isomers of bis(L-2,4-diaminobutyrato)cobalt(III) have been prepared and identified. These isomers are analogous to the three isomers of the bis(L-2,3-diaminopropionato)cobalt(III) ion which were prepared and identified in a previous report.[1,2] The bis(L-2,4-diaminobutyrato)cobalt(III) ion isomers, however, each contain two six-membered nitrogen–cobalt–nitrogen chelate rings. These rings are nonrigid and can assume either boat or chair conformations. This is in contrast to the case of the bis(L-2,3-diaminopropionato)cobalt(III) ions where the chelate ring systems are entirely rigid. It is this contrast that makes these new compounds of interest since identification of all the isomers of both series lends insight into the effects of ligand conformations on circular dichroism and other spectra. Like L-2,3-diaminopropionic acid, L-2,4-diaminobutyric acid is constrained to form facial isomers only when coordinated about cobalt(III). If, however, *rac*-2,4-diaminobutyric acid is coordinated to cobalt(III), five geometrical bis isomers are possible since the two ligands in the complex then may have opposite absolute configurations. These considerations have been explored for the 2,3-diaminopropionic case in an earlier paper.[1]

Experimental Section

Reagents.—Commercial reagent grade chemicals were used throughout, except where otherwise indicated.

Ligand.—L-2,4-Diaminobutyric acid–dihydrochloride was purchased from Mann Research Laboratories, Inc., New York, N. Y. This compound was listed as homogeneous upon paper chromatography. *Anal.* Calcd for $C_4H_{10}N_2O_2 \cdot 2HCl$: N, 14.66. Found: N, 14.7. $[\alpha]_D$ 14.3°. It was used as received.

Preparation of Complexes.—The mixture of the isomeric cobalt(III) complexes was prepared by the slow addition of a stoichiometric amount of freshly prepared sodium tris(carbonato)-cobaltate(III) trihydrate to 5.00 g of 2,4-diaminobutyric acid–dihydrochloride dissolved in 20 ml of warm water. This solution also contained a suspension of about 0.5 g of activated charcoal. The mixture was heated on the steam bath for 4 hr after the completion of the addition of the sodium tris(carbonato)cobaltate(III) trihydrate. It was then filtered hot from the charcoal and the charcoal was carefully washed with hot water. The washings and filtrate were combined and, after cooling, were immediately loaded on the ion-exchange column.

Separation of Isomers.—Separation was effected on a 5.0 ×

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(1) W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).
(2) C. F. Liu and J. A. Ibers, *ibid.*, **8**, 1911 (1969).

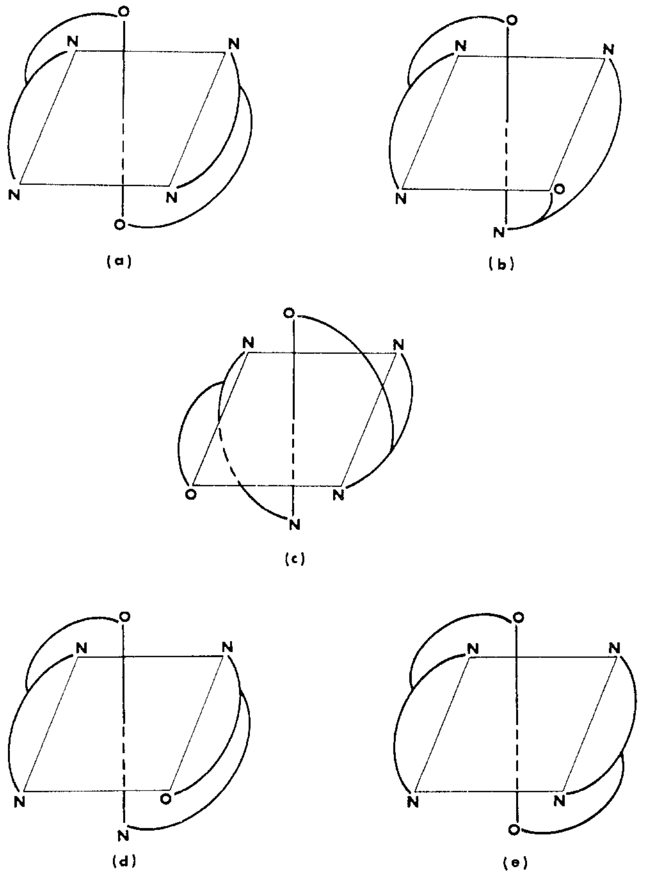

Figure 1.—a, b, and c: The three possible geometrical isomers of the bis(L-2,4-diaminobutyrato)cobalt(III) ion. These are, respectively, the *trans,cis,cis*, the *cis,cis,trans*, and the *cis,trans,cis* isomers. d and e: The *cis,cis,cis* and *trans,trans,trans* isomers which form only if *rac*-2,4-diaminobutyric acid is used.

50 cm column packed with 50–100 mesh Dowex 50W-X8 in the ammonium form. After the filtered and cooled reaction mixture was loaded onto the column and washed with about 2 l. of water, elution was allowed to proceed slowly (about 1 drop every 15 sec). The eluent was 0.25 *M* ammonium nitrate. Five distinct colored bands developed. The first three, which were much more fast moving than the others, were collected as they were eluted from the column. They were labeled α, β, and γ. These colored aqueous solutions were evaporated to dryness. The ammonium nitrate was removed by means of thorough washing with boiling absolute ethanol. The colored products α, β, and γ were each recrystallized from water and dried for 2 days in an oven at 110°. Their elemental analyses are given in Table I.

Table I

Analyses (%) of Isomers of Bis(2,4-diaminobutyrato)cobalt(III) Nitrate

	Calcd for $CoC_8H_{18}N_5O_7$	Found Isomer α	β	γ
C	27.05	26.96	26.92	26.95
H	5.11	5.24	5.08	5.12
N	19.72	19.37	19.80	19.75

The slow-moving bands were also removed from the column. They were separated from the contaminating ammonium nitrate in the same way. Evaporation of aqueous solutions of the colored residues gave powders.

Conductance Measurements.—Conductances were measured on all of the species using a Serfass Model RCM 15B1 conductivity bridge and a Sargeant conductivity cell with platinized electrodes. The cell constant was determined on solutions of potassium chloride. Conductivities of all of the products from the column separation were measured on solutions containing on the close order of 1 g of material/l. of solution.

Proton Magnetic Resonance Spectra.—The α and β isomers were converted from their nitrates to their fluorides to gain the maximum solubility. These conversions were effected using an anion-exchange column packed with Dowex 2X-8 in the correct anionic form. The isomer γ was converted to its bromide. Spectra were measured in saturated 99.77% deuterium oxide solutions *vs*. *t*-butyl alcohol (δ 1.22 ppm) as an internal standard. A Varian A-60A spectrometer was used.

Electronic Absorption Spectra.—Spectra were recorded at room temperature using a JASCO ORD/CD/UV-5 spectrophotometer.

Circular Dichroism.—These curves were recorded at room temperature using the same instrument.

Analyses.—Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Results and Discussion

Coordination of L-2,4-diaminobutyric acid as a tridentate ligand to cobalt(III) can result in three bis complex ions of +1 charge and different geometries. Since the ligand is asymmetric, all three of these isomers are dissymmetric. The isomers are named by considering first the spatial relationship of the two donor oxygens, then of the two α nitrogens, and finally of the two γ nitrogens (Figure 1). The three isomers—the *trans,cis,cis*, the *cis,trans,cis*, and the *cis,cis,trans*—can be regarded as generated at 120° intervals by an imaginary twist of one coordinated ligand relative to the other about an axis passing through the two ligand-occupied triangular faces of the cobalt(III) coordination octahedron. The same kind of relationship exists for the facial isomers of the bis(diethylenetriamine)-cobalt(III) ion and the facial isomers of the bis(imidoacetato)cobaltate(III) ion. In these latter two cases, the imaginary twist gives, at 120° intervals, the symmetrical facial and the enantiomeric unsymmetrical facial isomers.

Reasoning that this change in absolute configuration between two of the three isomers occurs generally whenever such an imaginary "twist" relationship holds, it would be expected that when two L-2,4-diaminobutyric acid anions are coordinated as tridentate ligands, two of the three geometrical isomers would have opposite absolute configurations. The third however would not be "symmetrical" as in the two examples cited because of the dissymmetry of the ligands. Still, this third isomer's optical activity may be considered the result of the vicinal effects of the two optically active ligands and not the result of configurational effects.[3] The same result, that two of the three isomers have opposite absolute configurations and that the third represents the ligand vicinal effect, comes from an application of the ring-pairing method proposed by Legg and Douglas.[4] The only difference is that no attempt is made to assign any label to the absolute configurations. Exactly the same kind of "twist" relationship in absolute configuration can be set forth for the three isomers of the bis(L-2,3-diaminopropionato)-

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[3] B. E. Douglas, "Proceedings of the John C. Bailar, Jr., Symposium on Coordination Chemistry, June 1969," Plenum Press, New York, N. Y., 1969, p 29.

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

cobalt(III) ion. Since the absolute configurations of these analogous three are definitely known,[2] there is little doubt about the above comments.[5]

Separation of the expected three ions was accomplished on a cation-exchange resin column. In this experiment, five colored species were isolated from the column. These fell into two groups, a much faster moving group containing the three species labeled α, β, and γ, alphabetically in order of elution, and a slower moving group containing the δ and the ϵ species. The gram-conductances of the first three in order of elution were 0.2274, 0.2241, and 0.2227 mho cm^2/g. In contrast, the gram-conductances of the members of the slower moving group were both greater than 0.5 mho cm^2/g. Since geometrical isomers should have similar gram-conductances, this establishes that the species in the slower moving group were certainly not isomers of those in the first group. Their greater affinity for the column suggests that they are species of greater than +1 charge. The molar conductances of the first three species off the column, using the molecular weight of the nitrate salt, were, respectively, 80.75, 79.57, and 79.10 mho cm^2/mol indicating the three are 1:1 electrolytes.[6] Together with the elemental analyses, this establishes the α, β, and γ species as the three isomeric bis(L-2,4-diaminobutyrato)cobalt(III) ions.

Identification of Isomers.—It is necessary to know both the geometrical isomerism of the three species and the absolute configuration of the three. Fortunately, knowledge of the former automatically gives knowledge of the latter because the absolute configuration of the ligand is known. Chemical correlation of L-2,4-diaminobutyric acid with L-glutamic acid[7] has established the absolute configuration of the ligand that was used. Thus, the problem reduces to the identification of the geometrical isomers.

Proton magnetic resonance spectra for the three isomers of the bis(L-2,4-diaminobutyrato)cobalt(III) ion in D_2O solution are given in Figure 2. Only the resonances of the five carbon-bound protons are shown. Since all three of the isomers possess C_2 symmetry, the two chelate ring systems in each complex ion are equivalent. Furthermore, the individual chelate ring system formed by the coordination of one ligand is stereochemically the same in all three of the isomers. Because of the identity of the chelate ring systems, the coupling constant scheme among the five protons in each ligands's ring system may well be similar in the three cases. The geometrical isomerism would then manifest itself mostly in different chemical shifts for the five carbon-bound protons in each of the three isomers and result in the different spectra observed for the three. Since all of the spectra were taken under conditions where the nitrogen protons exchange rapidly with the solvent, D_2O, there are no contributions to the spectra attributable to coupling involving nitrogen protons, and there are no nitrogen-bound proton resonances in the region of δ 4–8 ppm. The lowest field resonance multiplets in the three spectra can definitely be attributed to the protons on the 2 carbons in the three cases. This assignment is based both on the relative deshielding expected for a proton bound to a carbon bearing both amine and carboxylate electron-withdrawing functions and on the integrated intensity data which show that the intensities of the lowest field multiplet in the three spectra are one-fourth those of the rest of the spectrum in all three of the cases. The observed differences in the chemical shift of the 2-carbon proton in the three isomers can serve as a basis for the identification of the geometries of the three. The pmr spectra of the analogous and definitely identified series of three isomeric bis(2,3-diaminopropionato)cobalt(III) ions[8] reveal that the 2-carbon proton signal lies at higher field in the *cis,cis,trans* isomer than in the *cis,trans,cis* or *trans,cis,cis* isomer. This difference in chemical shifts is the result of different ligand–ligand interactions in the different geometries and would not be expected to differ too significantly between the two series of isomers. The 2-carbon proton resonances in the bis(L-2,4-diaminobutyrato)cobalt(III) ions lies at higher field in the γ isomer than in the α and β isomers. Among the three, therefore, γ is tentatively assigned the *cis,cis,trans* geometry. This identification of the γ isomer, which is borne out by other evidences cited below, is that given in Figure 2.

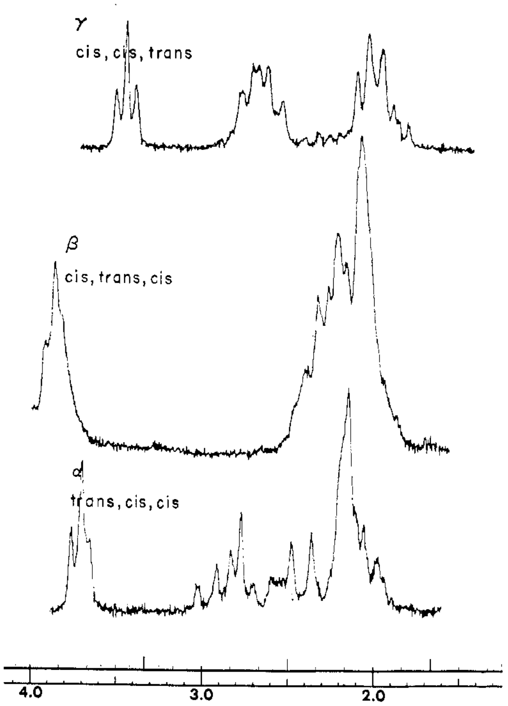

Figure 2.—Pmr spectra of the three isomers of the bis(L-2,4-diaminobutyrato)cobalt(III) ion.

The trend observed in the chemical shifts of the 2-carbon resonances is obviously due to differences in geometry. In the *trans,cis,cis* and *cis,trans,cis* isomers of both the bis(L-2,3-diaminopropionato)cobalt(III) series and the bis(2,4-diaminobutyrato)cobalt(III) ser-

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[5] For a discussion of a similar isomer relationship also involving optically active amino acids as tridentate ligands, see J. I. Legg and D. W. Cooke, *J. Am. Chem. Soc.*, **89**, 6854 (1967).

[6] A. Werner and A. Miolate, *Z. Physik. Chem.*, **14**, 506 (1894).

[7] D. W. Adamson, *J. Chem. Soc.*, 1564 (1939).

[8] W. A. Freeman and C. F. Liu, unpublished observations.

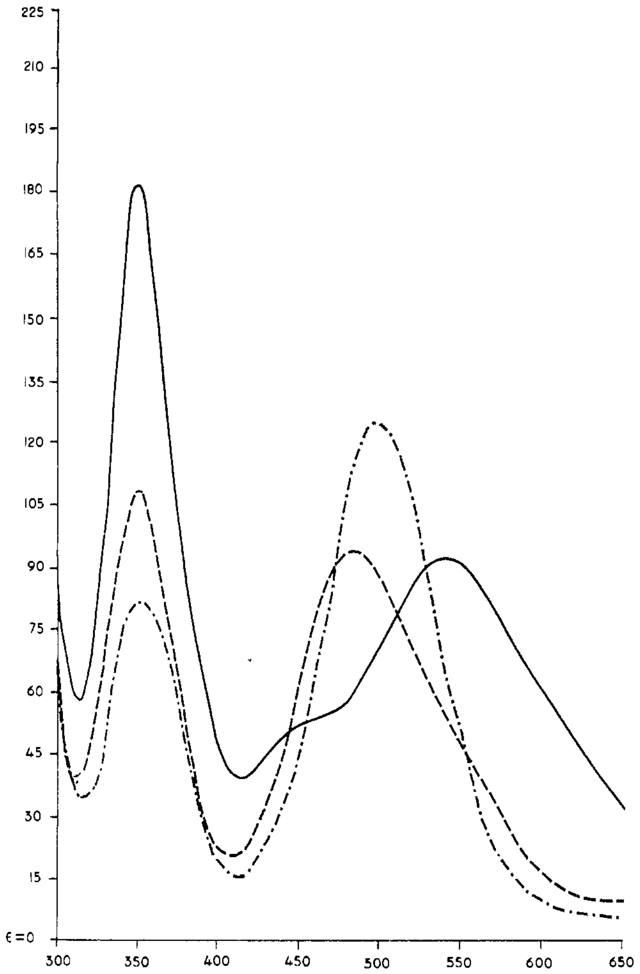

Figure 3.—Visible–ultraviolet spectra of the three isomers of the bis(L-2,4-diaminobutyrato)cobalt(III) ion: ———, α isomer; – – – –, β isomer; – · – · –, γ isomer *vs.* wavelength in millimicrons.

ies the 2-carbon proton of each ligand is *cis* to the carboxylate donor of the other ligand. In the *cis,cis,trans* isomers of the two ions, there are fewer carboxylate donors *cis* to the 2-carbon proton since in this geometry the 2-carbon proton of each ligand is *trans* to the carboxylate donor of the other ligand. It is in the pmr spectra of these latter, the *cis,cis,trans* isomers of the two series, that the highest field 2-carbon proton resonances occur. This observation corresponds to that made by Cooke[9] on the *cis* and *trans* isomers of the bis(imidodiacetato)cobaltate(III) ion. The *cis* isomer of this complex has the resonance of its 2-carbon protons at higher field than the *trans*. And it is in the *cis* isomer that there are fewer carboxylate groups *cis* to the 2 carbons.

Cooke pointed out that this relative shielding of the 2-carbon proton resonance when there are fewer carboxylate donors *cis* to the 2-carbon proton is similar to the results of Clifton and Pratt[10] involving the relatively shielded resonance of amine protons when fewer acido donors are *cis* to the amine.

A similar train of reasoning, based however on the trends of the 4-carbon protons' resonance in the three isomers, leads to a similar identification. It would be expected that in all three of the geometries under consideration the two protons on the 4 carbon of the ligand would resonate at lower field than the two on the 3-carbon because of the deshielding effect of the electron-withdrawing amine function on the 4 carbon. Analysis of the pmr spectrum of the γ isomer (see Table III) confirms that the 4-carbon protons indeed resonate on intermediate field strength. In the case of the γ isomer, this difference in chemical shift is clear-cut—there are three regions of resonance of integrated intensity ratio 1:2:2 corresponding to the 2-carbon proton, the 4-carbon protons, and the 3-carbon protons. In the β isomer, on the other hand, the chemical shifts of the 3- and 4-carbon protons are more nearly the same and the result is the observed complex signal of integrated intensity 4 times that of the 2-carbon proton. Apparently in the α isomer the chemical shifts of the 4-carbon protons are more widely separated from those of the 3-carbon protons than in the β isomer, but less widely separated than in the γ isomer (Figure 2). The *cis,trans,cis* geometry has fewer carboxylate donors *cis* to the 4 carbon than the other two geometries. This follows because in the *cis,trans,cis* geometry, the carboxylate of the other ligand is *trans* to the 4 carbon. On the basis of the correlation used earlier then, the resonances of the 4-carbon protons in the *cis,trans,cis* isomer should lie toward higher field than in the other two isomers. This tends to assign the β isomer to the *cis,trans,cis* geometry. A similar relation is obtained for the 3-carbon protons in the bis(L-2,3-diaminopropionato)cobalt(III) complexes.[8] Thus, a complete tentative identification of the geometries is made on the basis of the chemical shift differences.

Another means of identification of the bis(2,4-diaminobutyrato)cobalt(III) ion isomers lies with the visible–ultraviolet spectra which are given in Figure 3. These spectra agree with the predictions from crystal-field theory for complexes of the donor type bis(carboxylate)(tetraammine)cobalt(III).[11] The α isomer shows a shoulder on the high-energy side of the long-wavelength absorption band. Close inspection of the spectra of the other two isomers, β and γ, reveals slight shoulders on the low-energy sides of their long-wavelength absorption bands. The shoulder is especially noticeable in the case of the β isomer. The observations indicate that the α isomer has *trans* oxygens and that the β isomer and the γ isomer have *cis* oxygens. Because only the *trans,cis,cis* geometry has *trans* oxygens, the α isomer is again identified as the *trans,cis,cis* isomer. The spectra of these three bis(L-2,4-diaminobutyrato)cobalt(III) ions are similar to those of the three bis(L-2,3-diaminopropionato)cobalt(III) ions. It is seen in Table II that the energy of the long-wavelength absorption increases in the bis(L-2,3-diaminopropionato)cobalt(III) series in the order *trans,cis,cis*, *cis,cis,trans*, and *cis,trans,cis*. In the bis(L-2,4-diamino-

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(9) D. W. Cooke, *Inorg. Chem.*, **5**, 114 (1966).

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

(11) C. J. Ballhausen, *J. Inorg. Nucl. Chem.*, **2**, 178 (1956).

TABLE II

COMPARISON OF ULTRAVIOLET–VISIBLE AND CIRCULAR DICHROISM SPECTRA OF ISOMERS OF BIS(L-2,3-DIAMINOPROPIONATO)COBALT(III) AND BIS(L-2,4-DIAMINOBUTYRATO)COBALT(III) IONS

Bands in elution	Geometry assigned	Absorption, $10^{-4}\bar{\nu}$ (ϵ)			Circular dichroism, $10^{-4}\bar{\nu}$ ($\Delta\epsilon$)	
		Ia	Ib	II	Ia	Ib
		Bis(L-2,4-diaminobutyrato)cobalt(III) Ions				
α	*trans,cis,cis*	1.85 (93.7)	2.17 sh	2.82 (183)	1.74 (+2.23)	1.94 (−3.30)
β	*cis,trans,cis*	2.07 (93.7)	...	2.85 (108.7)	1.83 (+2.18)	2.10 (−0.60)
γ	*cis,cis,trans*	2.00 (124.5)	...	2.82 (81.7)		1.98 (−1.00)
		Bis(L-2,3-diaminopropionato)cobalt(III) Ions[a]				
1	*trans,cis,cis*	1.90 (57.0)	2.22 sh	2.85 (123.7)	1.79 (+2.82)	2.00 (−2.78)
2	*cis,trans,cis*	2.03 (106.5)	...	2.83 (71.5)	1.84 (+5.00)	2.10 (−2.68)
3	*cis,cis,trans*	2.00 (114.7)	...	2.83 (71.5)	1.82 (−0.64)	2.08 (+0.82)

[a] W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7,** 764 (1968).

butyrato)cobalt(III) series, the corresponding order is α, γ, and β. This tends again to identify the α isomer as *trans,cis,cis*, the β as *cis,trans,cis*, and the γ as *cis,cis,trans*—the same identification that was made above on the basis of the chemical shifts of the pmr spectra.

A further identification of the isomers can be made on the basis of a comparison of the circular dichroism spectra of the two series. The CD spectra of the three bis(L-2,4-diaminobutyrato)cobalt(III) ions are given in Figure 4. The comparison is set forth in Table II. The α isomer of the bis(L-2,4-diaminobutyrato)cobalt(III) series was firmly identified above on the basis of the visible spectrum as the *trans,cis,cis* isomer. The circular dichroism of this complex ion is similar to the CD of the *trans,cis,cis*-bis(L-2,3-diaminopropionato)cobalt(III) ion. Since the two complexes have the same symmetry and the same disposition of the chelate rings, the observed differences in the CD spectra are effects of the replacement of six-membered for five-membered nitrogen–cobalt–nitrogen chelate rings. This replacement does not lead to any profound changes in the CD at room temperature in this geometry. It is then reasonable to think that the difference in ring size will not effect major changes in the CD in the other geometries. Thus, the CD spectrum of the β-bis(L-2,4-diaminobutyrato)cobalt(III) ion is more nearly like that of the *cis,trans,cis*-bis(2,3-diaminopropionato)cobalt(III) ion. The CD spectrum of the γ-bis(2,4-diaminobutyrato)cobalt(III) ion on the other hand is of the same sign and general magnitude as that of the *cis,cis,trans,*-bis(2,3-diaminopropionato)cobalt(III) ion. These comparisons lead again to the identification of the β isomer as the *cis,trans,cis* geometry and the γ isomer as the *cis,cis,trans* geometry.

Finally, there is the cation-exchange column elution order of the isomers as a basis for identification. The bis(2,3-diaminopropionato)cobalt(III) ions eluted in the order *trans,cis,cis*, *cis,trans,cis*, and *cis,cis,trans*. Under the same conditions, the bis(2,4-diaminobutyrato)cobalt(III) ions eluted in the order α, β, and γ. If the elution order in the two series can be expected to be the same, then the α isomer is *trans,cis,cis*, the γ isomer is *cis,trans,cis*, and the γ isomer is *cis,cis,trans*. This again is the same identification as that made by other means above.

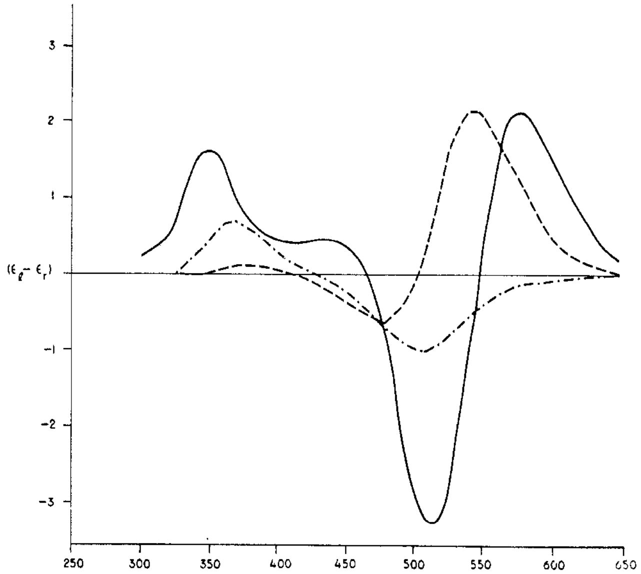

Figure 4.—Circular dichroism spectra of the three isomers of the bis(L-2,4-diaminobutyrato)cobalt(III) ion: ———, α isomer; – – – –, β isomer; – · – · –, γ isomer *vs.* wavelength in millimicrons.

Conformation.—The nonrigid six-membered nitrogen–cobalt–nitrogen chelate rings in each of the three isomeric complexes can have either a boat conformation or a chair conformation or be in rapid equilibrium between the two extremes. In Table III are compiled the results of analysis of the pmr spectrum of the *cis,cis,trans* isomer of the bis(L-2,4-diaminobutyrato)cobalt(III) ion.[12] In this table assignments of protons 2 and 3 and of protons 4 and 5 can be reversed. Examination of a molecular model of the boat conformation and the application of the approximate theoretical results of Karplus[13] regarding the dependence on the dihedral angle formed by the $H_1C_aC_b$ and $H_2C_aC_b$ planes of the contact coupling constant between vicinal protons suggest that the coupling constant J_{12} in the boat conformation would be about 1.5 cps and J_{13} would be about 6.8 cps. Further, in the boat conformation, the coupling constant J_{24} would be *ca.* 2 cps and J_{25} *ca.* 9 cps. Also J_{34} and J_{35} in the boat conformation would both be

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(12) J. D. Swalen and C. A. Reilly, "Nuclear Magnetic Resonance Iteration Program," Program 33, Quantum Chemistry Program Exchange, Indiana University, 1968.

(13) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2870 (1963).

TABLE III

CHEMICAL SHIFTS AND COUPLING CONSTANTS FROM ANALYSIS OF THE PMR SPECTRUM OF THE *cis,cis,trans*-BIS(L-2,4-DIAMINOBUTYRATO)COBALT(III) ION AND AN APPROXIMATE THEORETICAL PREDICTION FOR TWO EXTREME CONFORMATIONS

	Coupling constants, cps		
	Obsd	Boat	Chair
J_{12}	3.41	1.5	3.5
J_{13}	4.15	6.8	1
J_{14}	0.02	0	0
J_{15}	−0.02	0	0
J_{23}	11.61	...	...
J_{24}	7.08	2	3
J_{25}	3.27	9	2
J_{34}	6.19	2	9
J_{35}	4.73	2	2
H_{45}	12.66	...	...

		Chem shifts, ppm[a]
2-Carbon proton	δ_1	3.46
3-Carbon protons	δ_2	1.92
	δ_3	2.10
4-Carbon protons	δ_4	2.56
	δ_5	2.75

[a] *Vs.* TMS.

approximately 2 cps. None of these predicted constants is in even rough correspondence with these observed values. On the other hand, when models of the ligand system in the chair conformation are examined and the approximate theoretical result of Karplus applied, J_{12} is predicted to be *ca.* 3.5 cps, J_{13} *ca.* 1 cps, J_{24} about 3 cps, J_{25} about 2 cps, J_{35} about 9 cps, and J_{45} about 2 cps. None of the constants (with the exception of J_{12}) is in agreement with this set of chair-conformation based coupling constants. Even if the assignments of the protons 2 and 3 and protons 4 and 5 are reversed, the observed coupling constants fit neither the boat- nor the chair-derived theoretical scheme even approximately. Rapid equilibrium between the two conformations is however consistent with the observed coupling constant scheme. In such a case, the 2-carbon proton for example would see on the average the two nonequivalent 3-carbon protons with the coupling constants being the weighted means of the values for the two extreme conformations.

To sum up, in theory both the boat and chair conformations lead to one large (~9 cps) and three small (~2 cps) coupling constants among J_{24}, J_{35}, J_{34}, and J_{35}. The observation of four varyingly medium-sized (~3–7 cps) coupling constants points toward the intermediate situation of rapid equilibrium.

The pmr spectra of the other two isomers, the *trans,-cis,cis* and *cis,trans,cis*, have not been analyzed. However, on the basis of the close similarity of the 2-carbon proton resonance among the three spectra, it can be reasonably concluded that the same kind of conformational equilibrium exists in all three cases.

A further and interesting consideration tends to rule out the boat conformation. When the six-membered nitrogen–cobalt–nitrogen chelate ring is in the boat conformation, it has definite chirality (in these cases where L ligand is coordinated, it is λ). The presence of two such definite chiral rings in the ligand system of each complex might be expected to exert considerable influence on the circular dichroism spectra of the complexes.[14,15] On the other hand, the rings when in their chair conformations have no chirality. As pointed out above in the comparison of the CD spectra of the bis(L-2,3-diaminopropionato)cobalt(III) and bis(L-2,4-diaminobutyrato)cobalt(III) series, the introduction of the six-membered in place of the five-membered ring did not result in any profound changes in the CD spectra. This tends to rule out the boat conformation, although a rapid equilibrium between the two conformations with a small equilibrium concentration of the boat conformation certainly remains possible. Of course, it might be that neither ligand conformation contributes much to the ligand vicinal effect and thus to the CD in these cases despite the suggestion[14] that ring conformation makes an important contribution to optical activity in chelate complexes.

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