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Geometrical Isomerism Arising from Chelated (*R*)-1,2-Diaminopropane. Absolute Configuration of the Four Isomers of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$

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The unsymmetrical-cis isomers of [Co(EDDA)(L)] where L = ethylenediamine (en), (*R*)-1,2-diaminopropane (*R*-pn), and L-alanine (L-ala) have been synthesized, isolated, and characterized. The uncommon uns-cis geometry for the tetradentate ethylenediamine-*N,N'*-diacetate was produced by displacement of carbonate from *uns-cis*-[Co(EDDA)(CO$_3$)]$^-$, the preferred isomer for this complex. The *R*-pn and L-ala diastereoisomers were separated by chromatography while the en optical isomers were resolved using *d*-α-bromocamphor-π-sulfonate. The facial and meridional uns-cis isomers of [Co(EDDA)(L-ala)] were assigned on the basis of their visible absorption spectra. The methyl pmr resonances of these two distinctly different isomers were correlated with the corresponding resonances in the *R*-pn system and, in conjunction with circular dichroism spectra, were used to make tentative absolute configuration assignments to the four closely related *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ isomers. These assignments have been confirmed by a crystallographic study of one of the four isomers of the uns-cis *R*-pn series.

Introduction

The bidentate ligand 1,2-diaminopropane (propylenediamine, pn)[1] and its derivatives have served as key ligands in the determination of absolute configurations and in the study of conformational isomerism in metal chelates.[2] However, the geometrical isomerism arising from the two possible orientations of the unsymmetrical chelated *R*-pn molecule (Figure 1) has been given less attention.

R-pn is identical with the totally symmetrical bidentate ethylenediamine with respect to the chelating functional groups, differing only in the placement of a methyl group on the backbone. Due to the nearly symmetrical nature of *R*-pn, it would be expected that the two possible geometrical isomers would be nearly energetically equivalent and that both would be formed in reactions under equilibrium conditions. Chromatographic evidence suggests that this is the case for *trans*-[Co(*R*-pn)$_2$Cl$_2$]$^+$.[3] An earlier study established the existence of the more symmetrical (trans methyl) isomer.[4] Similar behavior is exhibited by the [Co(*R*-pn)$_3$]$^{3+}$ system. An X-ray structure determination of the easily crystallized fraction suggested that the cis isomer was the only product.[5] However, a chemical study[6] and recent nmr investigations[7,8] have produced evidence for the trans isomer as well. Unfortunately X-ray crystallography has not been successful in this case due to disorder in the crystals.[9] *R*-pn geometrical isomerism has also been suggested by chromatographic and pmr studies conducted on the [Co(2,3,2-tet)(*R*-pn)]$^{3+}$ [10] and [Co(*R*-pn)$_2$(NO$_2$)$_2$]$^+$ [11] complexes.

As none of these results have established conclusively geometrical isomerism for chelated *R*-pn, it was decided to synthesize a complex possessing only one *R*-pn molecule in order to facilitate the investigation of this type of isomerism. A preliminary chromatographic study of [Co(EDDA)(*R*-pn)]$^+$ suggested the presence of geometrical isomers arising from a change in the orientation of the pn molecule alone.[12] For this reason a more detailed examination of this system was attempted.

Geometric isomerism in [Co(EDDA)(L)]^n (L = bidentate) complexes has been studied extensively.[13] There are two geometries possible for the [Co(EDDA)(diamine)]$^+$ system, Figure 2. However, only with the uns-cis[14] geometry is additional isomerism possible when L is an unsymmetrical ligand such as pn. The thermodynamically favored *s-cis*-[Co(EDDA)(*R*-pn)]$^+$ isomers (Figure 2) were characterized in an earlier study,[15] but the uns-cis isomers were present in trace amounts only and were not characterized. We have now succeeded in synthesizing sufficient quantities of these isomers to permit a detailed stereochemical investigation.

The primary objective of the present study was to characterize the four *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ isomers shown in Figure 3. They consist of two sets, distinguished by the two possible modes of coordination of the pn molecule, the cis,cis(N-O) (the nitrogen next to the optically active carbon of *R*-pn is cis to both chelated EDDA oxygens) and the cis,trans(N-O) isomers (the same *R*-pn nitrogen is cis to one oxygen and trans to the other). Each set consists of diastereoisomeric pairs due to the presence of *R*-pn in both isomers.

In order to distinguish the closely related sets of isomers cis,cis(N-O) and cis,trans(N-O), the corresponding [Co(EDDA)(L-ala)] isomers were synthesized. L-Alanine is similar to *R*-pn with respect to the asymmetry generated by the methyl substituent. However, in contrast to the diamine, L-ala is also unsymmetrical with respect to the ligating atoms. It was thus anticipated that the distinctly different sets of isomers for this complex (facial and meridional, Figure 4) could be easily distinguished. Correlation of pmr and circular dichroism spectra between isomer sets could

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[1] Abbreviations used: *R*-pn, (*R*)-1,2-diaminopropane; en, ethylenediamine; EDDA, ethylenediamine-*N,N'*-diacetate; L-ala, L-alanine; 2,3,2-tet, 3,7-diaza-1,9-nonanediamine.

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[3] C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, 19, 1915 (1965).

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[7] J. L. Sudmeier, G. L. Blackmer, C. H. Bradley, and F. A. L. Anet, *J. Amer. Chem. Soc.*, 94, 757 (1972).

[8] K. L. Craighead, *J. Amer. Chem. Soc.*, 95, 4434 (1973); A. Johnson and G. W. Everett, Jr., *Inorg. Chem.*, 12, 2801 (1973).

[9] P. F. Crossing and M. R. Snow, *J. Chem. Soc., Dalton Trans.*, 295 (1972).

[10] R. H. Lewis and M. D. Alexander, *Inorg. Chim. Acta*, 5, 86 (1971).

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[12] J. I. Legg, *Chem. Commun.*, 675 (1967).

[13] G. R. Brubaker, D. P. Schaefer, J. H. Worrell, and J. I. Legg, *Coord. Chem. Rev.*, 7, 161 (1971).

[14] There are several nomenclatures used to describe the isomers of a linear tetradentate chelate. The one used here has been used before for EDDA chelates by W. T. Jordan and B. E. Douglas, *Inorg. Chem.*, 12, 403 (1973). It is based on the arrangement of positions on the octahedron not occupied by the tetradentate.

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

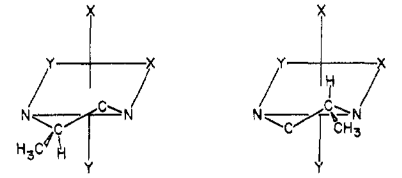
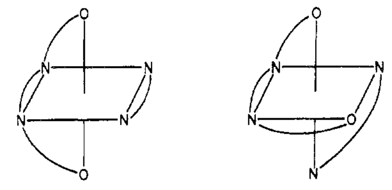
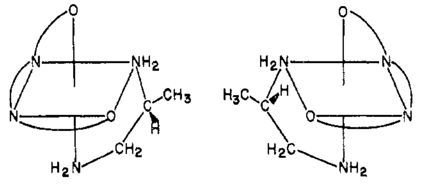


Figure 1. Possible orientations of the chelated (*R*)-1,2-diaminopropane molecule. The existence of geometric isomerism is dependent on the overall geometry of the complex.

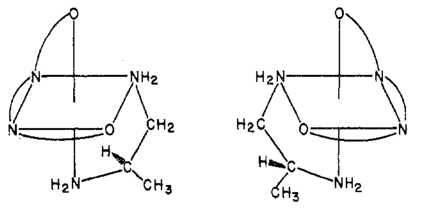


s-cis uns-cis

Figure 2. Possible ligand configurations in an EDDA–diamine complex.



Δ-cis,cis(N-O) Λ-cis,cis(N-O)



Δ-cis,trans(N-O) Λ-cis,trans(N-O)

Figure 3. Isomers of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$.

then be used to assign the stereochemistry of the four closely related *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ isomers. This paper reports the isolation and characterization of these isomers as well as the resolution and characterization of the analogous [Co(EDDA)(en)]$^+$ isomers.

Experimental Section

Synthesis of Sodium Ethylenediamine-*N,N'*-diacetato(carbonato)-cobaltate(III). To a slurry of 25.9 g (0.0715 mol) of freshly prepared $Na_3[Co(CO_3)_3]\cdot 3H_2O$[16] in 70 ml of water was added 12.65 g (0.0715 mol) of ethylenediamine-*N,N'*-diacetic acid. The mixture was stirred until visible reaction ceased and then 10.0 ml of concentrated HCl diluted to 30 ml was added. The solution was stirred for several hours at room temperature until the color had changed from dark green to purple and then was filtered to remove a solid residue. The filtrate was concentrated by evaporation under an airstream to *ca.* 75 ml. The solution was diluted to 120 ml with 95% ethanol and cooled in a refrigerator for several days. A dark purple solid was filtered, washed with ethanol-water and 95% ethanol, and air-dried to yield 16.1 g. The filtrate and washings (approximate volume 150 ml) were again refrigerated. The procedure above was repeated to give a second yield of 3.7 g. The total yield was 80.6% based on cobalt. A sample of the complex was recrystallized from ethanol-water before analysis. *Anal.* Calcd for $Na[CoC_7H_{10}N_2O_7]\cdot 1.5H_2O$: C, 24.50; H, 3.82; N, 8.16. Found: C, 24.64; H, 3.79; N, 8.17. From subsequent reactions it was shown that the complex was predominantly the uns-cis isomer.

Synthesis and Separation of the Isomers of Ethylenediamine-*N,N'*-diacetato(ethylenediamine)cobalt(III) Chloride. Solid ethylenediamine dihydrochloride (3.32 g, 0.025 mol) was added to a solution of 7.9 g (0.023 mol) of $Na[Co(EDDA)(CO_3)]\cdot 1.5H_2O$ in 50 ml water. The solution was stirred for 12 hr at room temperature. Part of the uns-cis product, 1.34 g, was present as a solid and was removed by filtration. The rest of the uns-cis complex was separated from the s-cis isomer by using a very short (4.5-cm diameter, 3.0-cm length) column of Dowex 50W-X8, 50–100 mesh, Na^+ form. The reaction solution was loaded on the column in fractions and eluted with 0.5 *M* NaCl. The second band was collected, combined with the other second band fractions, and evaporated under an airstream until solid NaCl collected. Ethanol was added to precipitate additional salt and the mixture was filtered. The process was repeated on the filtrate until treatment with ethanol caused a red powder to precipitate. At this point the solution was evaporated to a small volume to remove ethanol and final desalting was accomplished by gel permeation chromatography on Sephadex G-10. The solid $[Co(EDDA)(en)]Cl\cdot 3H_2O$ was isolated by evaporation of the resulting solution. The isomer was recrystallized from ethanol-water. The combined yield was 3.10 g of *uns-cis*-$[Co(EDDA)(en)]Cl\cdot 3H_2O$.

Resolution of *uns-cis*-Ethylenediamine-*N,N'*-diacetato(ethylenediamine)cobalt(III) Chloride. *uns-cis*-$[Co(EDDA)(en)]Cl\cdot 3H_2O$, 1.79 g (0.0047 mol), was dissolved in 40 ml of water by heating to 60°. Silver *d*-α-bromocamphor-π-sulfonate monohydrate (prepared by fractional crystallization of a solution of ammonium bromocamphorsulfonate (NH_4BCS) and $AgNO_3$), 2.04 g (0.0047 mol), was added and then further excess portions were added until the solution gave no test for chloride ion. The solution was maintained at 60° for 0.5 hr to coagulate the silver chloride and then was filtered. The silver chloride was washed with several portions of water until the washings were colorless. The filtrate and washings were fractionally crystallized by evaporation under an airstream followed by refrigeration. A series of fractions was collected, and those with similar CD spectra were combined and recrystallized to constant $\Delta\epsilon$ values. The $\Delta\epsilon$ values were calculated assuming anhydrous salts. The yields were 1.124 g of $(-)_{485}$-*uns-cis*-[Co(EDDA)(en)]BCS ($\Delta\epsilon_{485} = -1.85$) and 0.751 g of $(+)_{485}$-*uns-cis*-[Co(EDDA)(en)]BCS ($\Delta\epsilon_{485} = +2.05$).

Chloride salts of the optical isomers were prepared by removing the resolving agent with ion-exchange resin. A 0.47-g sample of $(-)_{485}$-*uns-cis*-[Co(EDDA)(en)]BCS was dissolved in 10 ml of water and 4.0 g of washed Dowex 1-X8, 100–200 mesh, Cl^- form, was added. The mixture was allowed to sit with periodic stirring for several hours. The resin was filtered off and washed until the washings were colorless. Another 4-g batch of resin was added and the above procedure repeated. The filtrate and washings were concentrated under an airstream to 10 ml. The solution was heated to dissolve the solid that had formed and, while the solution was still hot, 5 ml of absolute ethanol was added. The mixture was cooled in a refrigerator and filtered, and the product was washed with ethanol-water and absolute ethanol to yield 0.215 g of thin red platelets. The other optical isomer was recovered in the same way—0.324 g of diastereoisomer gave 0.184 g of the chloride salt. *Anal.* Calcd for $[CoC_8H_{18}N_4O_4]Cl\cdot 3H_2O$: C, 25.11; H, 6.32; N, 14.64. Found for (+) isomer: C, 25.06; H, 5.90; N, 14.69. Found for (−) isomer: C, 25.08; H, 6.04; N, 14.75.

Preparation and Separation of the Isomers of Ethylenediamine-*N,N'*-diacetato((*R*)-1,2-diaminopropane)cobalt(III) Chloride. A solution of 4.0 g (0.0117 mol) of $Na[Co(EDDA)(CO_3)]\cdot 1.5H_2O$ and 1.87 g (0.0127 mol) of (*R*)-1,2-diaminopropane dihydrochloride[17] in 10 ml of water was prepared. The solution was heated on a steam bath until the color changed from purple to red-orange (*ca.* 0.5 hr). The reaction solution was diluted to 0.75 l. and loaded on a column (4.5 × 50 cm) of Dowex 50W-X8, 200–400 mesh, Na^+ form. The column was washed with several liters of water to remove a nonadsorbed brown material and then eluted with 0.2 *M* NaH_2PO_4–Na_2HPO_4 buffer (pH 6.8). The adsorbed complex rapidly separated into several bands, two rapidly moving, red s-cis bands and the more tightly adhering uns-cis band. The former were eluted after 1 week. After several weeks the uns-cis fraction split into three well-resolved bands, the first containing two overlapping isomers. This band was collected in multiple 20-ml fractions. Fractions with similar CD spectra were combined. The latter two completely separated bands were collected in fractions of approximately 500 ml and treated as above. Phosphate salts could not be removed by gel chromatography; therefore, as much phosphate as possible was removed by evaporation to a small volume and filtration of the resulting solid phosphate salts.

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(16) H. F. Bauer and W. C. Drinkard, *Inorg. Syn.*, 8, 202 (1966).

(17) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, 81, 290 (1959); J. C. Bailar, Jr., H. B. Jonassen, and A. D. Gott, *ibid.*, 74, 3131 (1952).

The complex was then adsorbed on a small amount of cation-exchange resin (Dowex 50W-X8, 100–200 mesh, Na^+ form) which was washed to remove the remaining phosphates. The resin was added to a column, and the complex was removed by elution with 0.5 *M* NaCl solution. The resulting solution was desalted and the solid isomers were isolated as described for the corresponding ethylenediamine isomers. The four isomers were recrystallized from ethanol–water solution before analysis. *Anal.* Calcd for $[CoC_9H_{20}N_4O_4]Cl\cdot H_2O$: C, 29.97; H, 6.15; N, 15.53. Found for isomer 1: C, 29.99; H, 6.04; N, 15.18. Found for isomer 3: C, 29.88; H, 5.80; N, 15.68. Calcd for $[CoC_9H_{20}N_4O_4]Cl\cdot 3H_2O$: C, 27.25; H, 6.61; N, 14.12. Found for isomer 2: C, 27.10; H, 6.52; N, 14.23. Calcd for $[CoC_9H_{20}N_4O_4]Cl\cdot 2H_2O$: C, 28.55; H, 6.39; N, 14.79. Found for isomer 4: C, 28.38; H, 6.37; N, 14.82.

Synthesis and Separation of the Isomers of Ethylenediamine-*N,N′*-diacetato(L-alaninato)cobalt(III). To a solution of 5.52 g (0.0161 mol) of $Na[Co(EDDA)(CO_3)]\cdot 1.5H_2O$ in 30 ml of water was added 1.56 g (0.0175 mol) of L-alanine. The solution was heated to 50° and 1.4 ml of concentrated HCl, diluted to 10 ml, was added dropwise. The heating was continued for 5 hr. At the end of this time the solution was filtered to remove the insoluble s-cis isomers that had formed. The filtrate was placed on an anion-exchange column (Dowex 1-X8, 50–100 mesh, Cl^- form) and eluted with water to remove any residual starting material or anionic products. The eluate was evaporated under an airstream to 30 ml and again filtered to remove insoluble isomers. The filtrate was placed on a cation-exchange column (Dowex 50W-X4, 200–400 mesh, Na^+ form, 4.5 × 55 cm) and washed through with water. The colored materials separated into two bands, a purple band and a slower moving red band. The uns-cis meridional isomers were fractionally crystallized from the purple band as minor constituents. (The major portion of the band consisted of s-cis isomers.) Attempts to separate the diastereoisomers by fractional crystallization and chromatography were unsuccessful. *Anal.* Calcd for mixed meridional isomers $[CoC_9H_{16}N_3O_6]\cdot H_2O$: C, 31.87; H, 5.35; N, 12.39. Found: C, 31.58; H, 5.15; N, 12.20.

The red solution was fractionally crystallized in an attempt to isolate both diastereoisomers of the uns-cis facial configuration. However, one of the isomers was apparently very soluble and could not be isolated. The isolated isomer was recrystallized from ethanol–water solution. *Anal.* Calcd for $[CoC_9H_{16}N_3O_6]\cdot 5H_2O$: C, 26.29; H, 6.37; N, 10.22. Found: C, 26.39; H, 6.00; N, 10.24.

Physical Measurements. Visible absorption spectra were recorded on a Cary Model 14 spectrophotometer. Circular dichroism spectra were obtained on a JASCO ORD/UV5 with CD attachment. The CD instrument was calibrated with recrystallized *d*-10-camphorsulfonic acid ($\Delta\epsilon = +2.34$ at 290 nm).[18]

Proton magnetic resonance spectra were recorded on a Varian A-60 nmr spectrometer. All pmr spectra were run in deuterium oxide with sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal standard. For deuteration studies a few granules of anhydrous Na_2CO_3 were added to the sample and deuteration occurred at the internal temperature of the probe (*ca.* 37°).

Analyses were performed by the Materials Science Division of Washington State University.

Results and Discussion

Synthesis and Separation of Isomers. The uns-cis isomers of the diamine and amino acid complexes were synthesized in appreciable yields by displacement of carbonate from the *uns-cis*-$[Co(EDDA)(CO_3)]^-$ complex in the absence of a catalyst at 50°. Garnett found that the carbonato complex is present as an equilibrium mixture of 30% s-cis and 70% uns-cis isomers.[19] Previous syntheses of the diamine and amino acid complexes, under conditions which favor the equilibrium distribution of products (oxidation in the presence of charcoal), yielded largely the s-cis isomers.[15,20] However, under the controlled reaction conditions used in the present syntheses, the kinetic inertness of the Co^{III}EDDA chelate inhibits the rapid isomerization of the complex even when the carbonate is displaced and leads to partial retention of configuration on going from the carbonato to diamine or amino acid complexes. Approximately equal amounts of the s- and uns-cis isomers are obtained. In contrast, the addition of charcoal to the reaction mixture results in rapid isomerization and gives predominantly the s-cis isomer.

Ion-exchange chromatography was an indispensable aid in the separation of the *uns-cis*-$[Co(EDDA)(R\text{-pn})]^+$ isomers. Attempted fractional crystallization of the mixed isomers resulted in noncrystalline glasses. However, once separated by chromatography, the isomers crystallized easily as chloride salts. Sodium chloride was first used as an eluent but it was later found that buffered phosphate was more efficient for isomer separation.[21] The four uns-cis *R*-pn isomers were eluted in two groups of closely spaced bands, the first two bands still overlapping. These two groups were identified as the diastereoisomeric pairs of cis,cis(N–O) and cis,trans(N–O) isomers. The two cis,cis(N–O) isomers were eluted somewhat overlapping followed by the closely spaced cis,trans isomers. It was recently discovered that elution with 0.3 *M* sodium iodide solution gives visible separation of the two cis,cis(N–O) isomers. The complexes also crystallize readily as iodide salts.

Surprisingly, a cation-exchange column could be employed to separate the facial and meridional isomers of the neutral [Co(EDDA)(L-ala)] complex (Figure 4). The meridional isomers, consisting of the s- and uns-cis meridional forms, were cleanly separated from the uns-cis facial isomers by elution with water. The uns-cis facial diastereoisomers were retained more effectively by the resin than the meridional isomers and one diastereoisomer was later isolated by fractional crystallization. The uns-cis meridional isomers could be isolated from the more insoluble s-cis meridional isomers by fractional crystallization. However, complete separation of the two uns-cis meridional diastereoisomers from each other was not achieved. The s-cis isomers have been previously characterized.[15]

In contrast to the *uns-cis*-$[Co(EDDA)(R\text{-pn})]^+$ isomers, a significant amount of *uns-cis*-$[Co(EDDA)(en)]^+$ present in a reaction solution could be isolated by fractional crystallization. Both the racemic mixture and the resolved isomers crystallized easily as chloride salts. The *uns-cis*-$[Co(EDDA)(en)]^+$ isomers were resolved by diastereoisomer formation with *d*-α-bromocamphor-π-sulfonate. Fractional crystallization separated the diastereoisomers which exhibited quite different crystal habits; the (−)-diastereoisomer gave massive, rectangular crystals while the (+)-diastereoisomer gave needlelike crystals.

Visible Absorption Spectra. Assignment of the [Co(EDDA)(L-ala)] Isomers. The visible absorption spectra, Table I, of the *uns-cis*-$[Co(EDDA)(R\text{-pn})]^+$ isomers are not helpful in configuration assignment. All four isomers are *cis*-N_4O_2 systems with differences too subtle to be interpreted from the electronic absorption spectra. However, the uns-cis isomers are easily distinguished from the s-cis isomers on the basis of their absorption spectra.[20]

It is only in the case of the [Co(EDDA)(L-ala)] system that visible spectra are useful in differentiating between uns-cis isomers. The possible geometrical isomers of the complex are shown in Figure 4. In the uns-cis facial isomer, the holohedrized symmetry of the ligand field is cubic, the aver-

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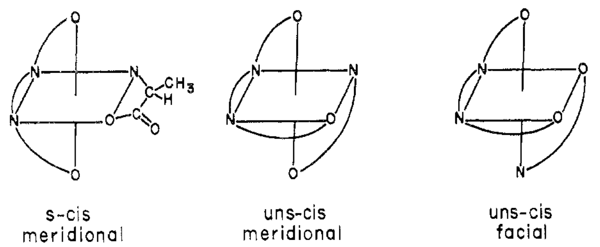
[18] W. C. Krueger and L. M. Pschigoda, *Anal. Chem.*, 43, 675 (1971). *d*-10-Camphorsulfonic acid appears to be one of the most suitable standards for CD calibration since it is readily purified and gives a sharp CD maximum in the near-uv region. However, there is not, at this time, agreement as to the absolute circular dichroism of this compound. Therefore, the value used to calibrate the instrument is given here to facilitate accurate comparison of CD data.

[19] P. J. Garnett, Ph.D. Thesis, University of Western Australia, 1972; P. J. Garnett and D. W. Watts, *Inorg. Chim. Acta*, 8, 293 (1974).

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

[21] We are grateful to Dr. David Buckingham for this suggestion.



s-cis meridional uns-cis meridional uns-cis facial

Figure 4. Configurational isomers of [Co(EDDA)(L-ala)].

Table I. Visible Absorption Spectra

Complex	Absorption maxima, nm (ϵ, M cm^{-1})
uns-cis-[Co(EDDA)(en)]$^+$	493 (170), 359 (169)
s-cis-[Co(EDDA)(en)]$^+$ [20]	528 (87.3), 449 sh, 364 (113)
uns-cis-[Co(EDDA)(*R*-pn)]$^+$	
Isomer 1	494 (167), 358 (170)
Isomer 2	493 (171), 358 (170)
Isomer 3	494 (167), 358 (172)
Isomer 4	495 (178), 358 (177)
s-cis-[Co(EDDA)(*R*-pn)]$^+$ [15]	529 (94.5), 451 sh
uns-cis-[Co(EDDA)(L-ala)]	
Meridional	580 sh, 493 (163), 370 (189)
Facial	520 (250), 374 (184)
s-cis-[Co(EDDA)(L-ala)][15]	544 (95), 466 sh

age contribution along all three axes is approximately the same. However, in the uns-cis meridional isomer, the holohedrized symmetry is rhombic, with the average contribution being different along all three axes. This loss of symmetry from facial to meridional is expected to cause a splitting or at least a broadening of the lowest energy absorption band.[22] This has been observed previously in other CoN_3O_3 systems possessing facial and meridional isomers.[23] A definite shoulder is found for the low-energy absorption band of (meridional) *s-cis*-[Co(EDDA)(L-ala)].[15] The spectra obtained for the two *uns-cis*-[Co(EDDA)(L-ala)] isomers are shown in Figure 5. The purple uns-cis isomer clearly shows this splitting and was assigned the meridional geometry; the red isomer exhibits a symmetrical band and was assigned the facial geometry.

Proton Magnetic Resonance Spectra. Assignment of the cis,cis(N–O) and cis,trans(N–O) Geometrical Isomers of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$. The pmr spectra of various uns-cis EDDA complexes have been analyzed by Legg and coworkers[24] and more recently by Garnett and Watts.[19] It was found in the current investigation that the spectra of the *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ isomers were very similar to the ethylenediamine complex spectrum as expected. A spectrum typical of the four isomers is illustrated in Figure 6. The resonances have been assigned by reference to the analogous *uns-cis*-[Co(EDDA)(en)]$^+$ complex and by selective deuteration studies as previously described for similar isomers.[24] The distinct upfield doublet was assigned to the methyl group of *R*-pn. Downfield from the methyl doublet is a complex group of resonances from the ethylene protons on the EDDA and *R*-pn backbones. Superimposed on this are two sharp peaks which were shown by deuteration studies[24] to be the upfield half of an AB pattern generated by the out-of-plane acetate protons. The other half of the pattern is downfield, next to the HOD peak as indicated. Between these resonances is the singlet of the in-plane (G-ring) acetate protons of the EDDA. This agrees with the results found for the uns-cis ethylenediamine, oxalate, and malonate isomers,[24] the singlet indicating very similar magnetic environments for the two in-plane acetate protons. A slight splitting into an AB spectrum has been observed for the *uns-cis*-[Co(EDDA)(CO_3)]$^-$ and *uns-cis*-[Co(EDDA)(H_2O)$_2$]$^+$ complexes, as reported by Garnett.[19]

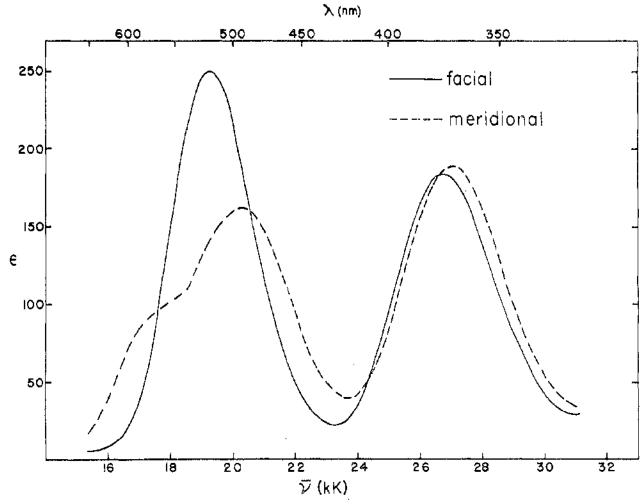


Figure 5. Visible absorption spectra of the *uns-cis*-[Co(EDDA)(L-ala)] isomers.

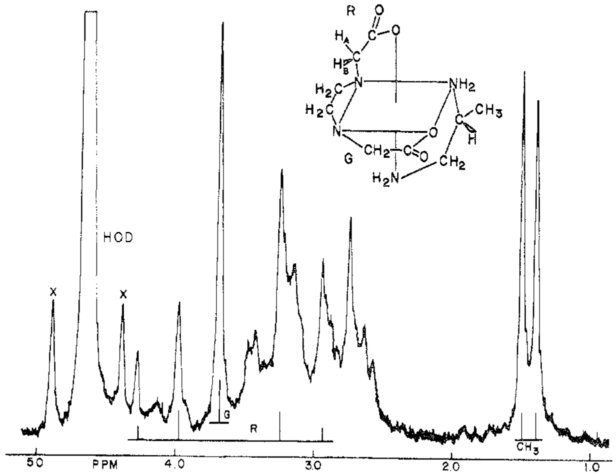


Figure 6. Proton magnetic resonance spectrum of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ (isomer 1 in neutral D_2O).

Table II summarizes the pmr spectra obtained for all the uns-cis complexes examined in this study. Figure 7 shows the relationship between the *R*-pn and L-ala systems. The L-ala isomer with the same relative methyl group position as the cis,cis(N–O) *R*-pn isomers is, necessarily, the meridional isomer. The L-ala isomer corresponding to the cis,trans(N–O) *R*-pn isomers is the facial isomer. As was discussed, these two *uns-cis*-[Co(EDDA)(L-ala)] geometries can be readily distinguished by visible absorption spectroscopy.

The meridional and facial L-ala isomers as well as the *R*-pn isomers exhibit a significant difference in the methyl group resonance (Table II). The meridional L-ala isomers are shifted downfield relative to the facial isomers. Assuming that the major environmental factor contributing to this shift is the relative position of the methyl group in the complex, isomers 1 and 2 of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ which have downfield methyl resonances are assigned as cis,cis(N-

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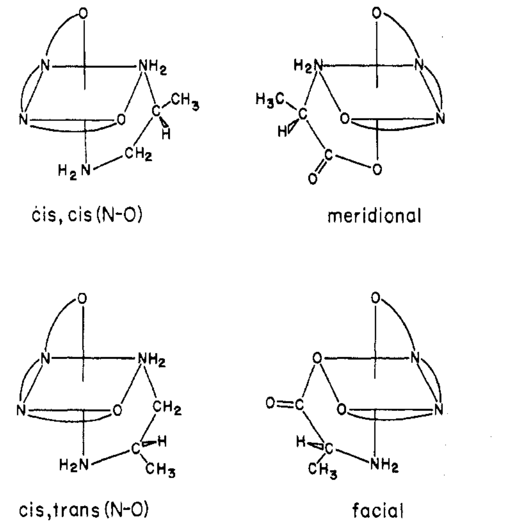

Figure 7. Comparison between the uns-cis isomers of [Co(EDDA)-(*R*-pn)]$^+$ and [Co(EDDA)(L-ala)].

Table II. Pmr Spectra

Complex	Methyl[a]	R ring[b] H_A	R ring[b] H_B	G ring
uns-cis-[Co(EDDA)(en)]$^+$		4.02	3.15	3.71
(+)-*s-cis*-[Co(EDDA)(*R*-pn)]$^+$	1.44	4.26 4.23	3.36	
(−)-*s-cis*-[Co(EDDA)(*R*-pn)]$^+$	1.44	4.16	3.34	
uns-cis-[Co(EDDA)(*R*-pn)]$^+$				
Isomer 1	1.45	4.11	3.12	3.69
Isomer 2	1.44	4.07	3.11	3.68
Isomer 3	1.30	4.03	3.11	3.68
Isomer 4	1.31	4.05	3.11	3.68
(+)-*s-cis*-[Co[EDDA)(L-ala)]	1.52	c		
(−)-*s-cis*-[Co(EDDA)(L-ala)]	1.53	c		
uns-cis-[Co(EDDA)(L-ala)]				
Meridional (mixed)	1.57	4.02	3.07	3.70
Facial	1.43	3.92	3.12	3.52

[a] $J = 5$–7 Hz. [b] $J_{AB} = 17$–18 Hz. [c] These compounds were very insoluble and detailed spectra were not obtained.

O) isomers while isomers 3 and 4 with upfield resonances are assigned as cis,trans(N–O) isomers.

These effects could be reasonably ascribed to differences in intramolecular nonbonding interactions rather than to the influence of ligating atoms. In the uns-cis facial L-ala and the corresponding cis,trans(N–O) *R*-pn isomers, models show close, nonbonding proton–proton interactions which would tend to change the conformation of the bidentate chelate ring and distort the methyl group position away from equatorial. The interactions are minimized in the other geometrical isomers, the uns-cis meridional L-ala and cis,cis(N–O) *R*-pn isomers. However, in a series of mixed en–*R*-pn Co(III) isomers which exhibit a systematic and defined change in relative ring conformations,[2,25] the chemical shift differences were not greater than 0.06 ppm[26] compared to the 0.13-ppm shift between cis,cis(N–O) and cis,trans(N–O) isomers. It is not likely, then, that the large chemical shifts observed in this study can be attributed solely to steric and conformational differences between isomers.

A more likely explanation for the observed methyl group shifts is the effect of the electronic environment on the *R*-pn ring, specifically the arrangement of ligating atoms in the other four coordination sites. In both Δ- and Λ-*s-cis*-[Co(EDDA)(*R*-pn)]$^+$ isomers (cis,cis(N–O) isomers), the methyl resonance is nearly the same as the position observed in the cis,cis(N–O) uns-cis isomers (Table II). It is only in the cis,trans(N–O) uns-cis isomers that the methyl resonance is shifted. This relationship is also followed in the *s*- and *uns-cis*-[Co(EDDA)(L-ala)] isomers (Table II).

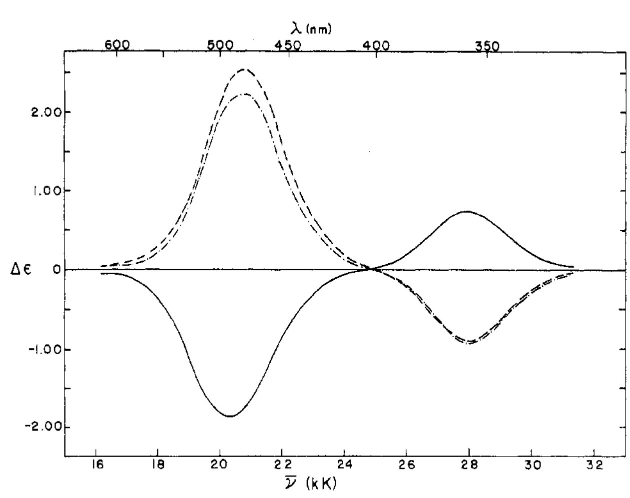

Figure 8. Representative circular dichroism spectra for the *uns-cis*-[Co(EDDA)(diamine)]$^+$ complexes: Δ-*cis,cis(N–O)-uns-cis*-[Co(EDDA)(*R*-pn)]$^+$, ——; Λ-*cis,cis(N–O)-uns-cis*-[Co(EDDA)(*R*-pn)]$^+$, - - - -; Λ-*uns-cis*-[Co(EDDA)(en)]$^+$, · - · - ·.

Table III. Circular Dichroism Spectra

Complex	λ_{max}, nm	$\Delta\epsilon$
(−)-*uns-cis*-[Co(EDDA)(en)]$^+$	484	−2.24
	357	+0.89
uns-cis-[Co(EDDA)(*R*-pn)]$^+$		
Isomer 1	492	−1.90
	357	+0.74
Isomer 2	481	+2.56
	359	−0.91
Isomer 3	493	−1.70
	358	+0.77
Isomer 4	482	+2.40
	359	−0.90
(+)-*uns-cis*-[Co(EDDA)(L-ala)] (facial)	526	+1.22
	370	−0.83

Circular Dichroism Spectra. Absolute Configuration Assignments of the *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ Diastereoisomers and *uns-cis*-[Co(EDDA)(en)]$^+$ Optical Isomers. Having assigned the cis,cis- and cis,trans(N–O) geometrical isomers by pmr, CD was utilized to make the final absolute configuration assignment to each of the *R*-pn diastereoisomers. Correlation of absolute configurations of multidentate chelates with the simpler bis and tris bidentates of known absolute configurations can be achieved using the ring-pairing scheme.[27] By this method the chirality of the four *R*-pn isomers can be assigned. The sign of the dominant peak in the lower energy T_{1g} transition region of the circular dichroism spectrum can be related to the net chirality of the complex.[27,28] A Δ configuration of chelate rings is expected to produce a negative dominant peak in the T_{1g} region while a Λ configuration would produce a positive dominant peak.[28]

The CD spectra of isomers 1 and 2 of *uns-cis*-[Co(EDDA)-(*R*-pn)]$^+$ are presented in Figure 8 and data for the very simi-

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lar isomers 3 and 4 as well as the other complexes studied are tabulated in Table III. There is only one peak in the T_{1g} region of the spectrum, and absolute configuration assignments are easily made. Isomers 1 and 3 of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ which have negative peaks are assigned as net Δ isomers[27] (Δ, Δ, Δ, Λ)[29] and isomers 2 and 4 with positive peaks are assigned as net Λ isomers (Λ, Λ, Λ, Δ). Comparison of the *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ CD spectrum with those obtained for the closely related optical isomers of *uns-cis*-[Co(EDDA)(en)]$^+$, Figure 8, permits the assignment of absolute configuration to these isomers. Table IV presents the complete assignments for the *uns-cis*-[Co(EDDA)(en)]$^+$ and *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$ isomers. These assignments have been recently confirmed by a crystal and molecular structure determination of the Δ-cis,trans(N-O) isomer of *uns-cis*-[Co(EDDA)(*R*-pn)]$^+$.[30]

Table IV. Summary of Assignments of *uns-cis*-[Co(EDDA)(en)]$^+$ and [Co(EDDA)(*R*-pn)]$^+$ Isomers

Isomer	Methyl position in pmr	Geometrical isomer	Absolute confign
(+)-[Co(EDDA)(en)]$^+$			Λ
(−)-[Co(EDDA)(en)]$^+$			Δ
[Co(EDDA)(*R*-pn)]$^+$			
1[a]	Downfield	Cis,cis(N–O)	Δ
2	Downfield	Cis,cis(N–O)	Λ
3	Upfield	Cis,trans(N–O)	Δ
4	Upfield	Cis,trans(N–O)	Λ

[a] Order of elution from Dowex 50W-X8 cation-exchange column.

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Registry No. Na[Co(EDDA)(CO$_3$)], 50306-68-8; (−)-*uns-cis*-[Co(EDDA)(en)]BCS, 51921-55-2; (+)-*uns-cis*-[Co(EDDA)(en)]BCS, 51920-86-6; (−)-*uns-cis*-[Co(EDDA)(en)]Cl, 51897-56-4; (+)-*uns-cis*-[Co(EDDA)(en)]Cl, 51897-57-5; Δ-*cis,cis*(N–O)-[Co(EDDA)(*R*-pn)]Cl, 51920-87-7; Λ-*cis,cis*(N–O)-[Co(EDDA)(*R*-pn)]Cl, 51920-88-8; Δ-*cis,trans*(N–O)-[Co(EDDA)(*R*-pn)]Cl, 51920-89-9; Λ-*cis,trans*(N–O)-[Co(EDDA)(*R*-pn)]Cl, 51922-19-1; meridional *uns-cis*-[Co(EDDA)(L-ala)], 51922-20-4; facial *uns-cis*-[Co(EDDA)(L-ala)], 51920-90-2.

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Rotation of Coordinated Cyanoolefins in Their Adducts with Some Rhodium(I) Isocyanide Complexes

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The three types of rhodium(I) isocyanide complexes [Rh(RNC)$_4$]X, [Rh(RNC)$_2$(PPh$_3$)$_2$]X, and Rh(RNC)(PPh$_3$)$_2$Cl react with tetracyanoethylene (TCNE) and fumaronitrile (FN) to give the complexes [Rh(RNC)$_4$(TCNE)]X (X = BPh$_4$, R = CH$_3$; X = ClO$_4$, R = *p*-CH$_3$OC$_6$H$_4$, *o*- and *p*-CH$_3$C$_6$H$_4$, *p*-ClC$_6$H$_4$), Rh(RNC)$_2$(PPh$_3$)(olefin)I and [Rh(RNC)$_2$(PPh$_3$)$_2$(olefin)]ClO$_4$ (R = CH$_3$, *p*-CH$_3$OC$_6$H$_4$, olefin = TCNE, FN), and Rh(*p*-CH$_3$OC$_6$H$_4$NC)(PPh$_3$)$_2$(TCNE)Cl. Their ir and pmr spectra suggest configurations of these complexes in solution. The TCNE adducts except [Rh(RNC)$_4$(TCNE)]X show little temperature dependence in their pmr spectra and may have the TCNE coordinated rigidly perhaps in a trigonal-bipyramidal configuration. On the other hand, [Rh(RNC)$_4$(TCNE)]X and each of the FN adducts give temperature-dependent pmr spectra, which may be interpreted in terms of the cyanoolefin rotation in time-averaged square-pyramidal configurations. The difference in the bonding is discussed qualitatively in terms of the basicity of the metal substrates and the acidity of the cyanoolefins.

Introduction

The coordination compounds formed between basic transition metal complexes and various π acids have been extensively investigated in recent years.[1] This can be attributed to the profound relation of these compounds to homogeneous catalysis,[2] as well as to the still controversial aspects of the chemical bonding involved in the system,[3] although the problem seems to be settled qualitatively.[4] Most studies have dealt with the combination of phosphine and/or carbonyl complexes of Rh(I), Ir(I), Ni(0), and Pt(0) and activated olefins and acetylenes. Especially, cyanoolefins are widely used as π acids,[5] and the adducts isolated generally contain the cyanoolefins coordinated rigidly to the metal atoms.[1]

It is anticipated that if the transition metal basicity[6] of a certain square-planar complex is only moderate or weak, then its interaction with cyanoolefins will be different from those of other complexes described so far, possibly leading to some novel type of bonding. Isocyanides are known to be moderate σ donors and are probably intermediate in π-acceptor capacity between tertiary phosphines and carbon monoxide.[7] In this respect it is of interest to examine the behavior of some square-planar isocyanide complexes of Rh(I) toward various cyanoolefins.

Here we report the preparative and ir and variable-temperature pmr spectral studies on the reactions of tetracyanoethylene (TCNE) and fumaronitrile (FN) with the following

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