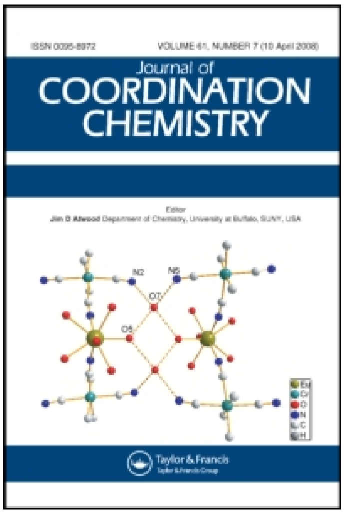

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SYNTHESIS AND CHARACTERIZATION OF COLBALT(III) COMPLEXES WITH A STEREOSPECIFIC LIGAND DERIVED FROM *S*-PROLINE

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SYNTHESIS AND CHARACTERIZATION OF COLBALT(III) COMPLEXES WITH A STEREOSPECIFIC LIGAND DERIVED FROM *S*-PROLINE

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This paper concerns the preparation, separation, and characerization of cobalt(III) complexes in which 2*S*, 2′*S*-1,1′-(ethane-1,2-diyl)*bis*(pyrrolidine-2-carboxylate), (pren), acts as etradentate ligand and the other two positions in the coordination sphere are occupied by monodentate or bidentate groups. The complex $[Co(pren)(H_2O)_2]^+$ exists only as the *cis*-α isomer, while in the case of $[Co(pren)en]^+$ complexes, substantial yields of both *cis*-α and *cis*-β isomers have been isolated through a series of chromatographic steps and fractional crystallizations. The geometrical and optical configurations are assigned on the basis of absorption, circular dichroism, and ^{13}C NMR spectra. In addition, the IR spectra of the complexes are discussed.

INTRODUCTION

The *tris* chelates $[Co(edda)X_2]$ of the tetradentate ligand ethylenediamine-*N,N′*-diacetate (edda) and its analogues can exist in three geometrical isomers (Fig. 1) of which the *trans* isomer could not be prepared. Because of the tetrahedral nature of the nitrogen the puckered chelate rings in the *cis*-β isomer are somewhat strained and slightly distored from the plane containing the nitrogen atoms so that this isomer might be expected to be less stable than the *cis*-α.[1,2]

Recently Woon and O'Connor reported[3] that synthesis of the $[Co(pren)CO_3]^-$, $[Co(pren)(H_2O)_2]^+$, and $[Co(pren)(H_2O)Cl]$ species in all cases gave only *cis*-α isomers. On the other hand, Garnett *et al*, found[4] that good yields of the *cis*-β-edda isomer could be obtained if the remaining two positions of the coordination sphere were occupied by carbonate, two chlorides, or two waters. In recent articles[5,6] we have found that the $[Co(ven)(H_2O)NO_3]$ complex existed only as the *cis*-α isomer, while in the case of $[Co(ven)(H_2O)_2]^+$ and $[Co(ven)en]^+$ complexes both *cis*-α and *cis*-β were found to exist (ven = ethylenediamine-*N,N′*-di-*S*-α-isovalerate).

To test above mentioned hypothesis concerning the relative stabilities of *cis*-α and *cis*-β isomers, cobalt(III) complexes of the optically active ligand pren have been prepared. Preliminary examination of molecular models indicated that the complexes should be formed stereospecifically because of the presence of the asymmetric carbon atom in the *S*-proline group.

EXPERIMENTAL

Preparation of 2S,2′S-1,1′-(Ethane-1,2-diyl)bis(pyrrolidine-2-carboxylic acid) Dihydrochloride, H_2pren.2HCl

In the previously reported studies[3,7] H_2pren.2HCl was prepared contaminated by unchanged *S*-proline and sodium chloride. However, the following method gives pure H_2pren.2HCl in a good yield.

To a solution of *S*-proline (11.5 g, 0.1 mol) in 20 cm^3 water was added a solution of NaOH (4 g, 0.1 mol) in 20 cm^3 water with stirring and cooling. After 30 min at 40°, 5.3 g (50 mmol) of Na_2CO_3 and 8.7 g (50 mmol) of 1,2-dibromoethane were added in portions. The mixture was then heated at 60° for 30 hr and the pH was held at *ca* 11. After cooling and washing with petroleum ether, the reaction mixture was acidified to pH 2 with 17% HCl and evaporated to dryness. The residue was dried *in vacuo* at 44°. A sample free of *S*-proline but containing approximately 10% NaCl was obtained by precipitation of the product from an aqueous solution acidified to pH 2 with HCl by addition of ethanol-diethyl ether or acetone-diethyl ether mixtures. Pure H_2pren.2HCl was obtained by recrystallization from absolute methanol-acetone or absolute methanol. [*Yield:* 5 g (31%); MP 240°]. The product was characterized by elemental analysis, IR, and ^{13}C NMR spectroscopy. The latter indicated that there were no carbon-containing impurities. [*Anal.;* Calcd. for $C_{12}H_{22}N_2Cl_2O_4$: C, 44.01; H, 6.72; N, 8.65%. Found: C, 43.60; H, 6.29; N, 8.52%].

Synthesis of cis-α-Diaqua [2S,2'S-1,1'-(Ethane-1,2-diyl)bis(pyrrolidine-2-carboxylato)

Australian workers[3] have previously reported an alternative synthesis of this complex.

To a suspension of 1.1g (10 mmol) of freshly prepared $CoCO_3$ in 50 cm^3 water were added 3.3 g (10 mmol) of H_2pren.2HCl, 0.75 cm^3 65% HNO_3 diluted to 10 cm^3, and 0.2 g of activated carbon. The mixture was heated to 60°, and 1 cm^3 30% H_2O_2 diluted to 10 cm^3 was added dropwise; the system was held at this temperature for an additional 6 hr with vigorous stirring. After cooling, the reaction mixture was bubbled with air at room temperature overnight. The activated carbon and unreacted $CoCO_3$ was filtered off. The wine-red solution was admitted to a column packed with Dowex 50W-X8 cation excahnger (50–100 mesh) in the Na^+cycle. The mixture of products sorbed at the top of the column and pink impurities were eluted with water. Only one fraction was obtained by elution with 0.1 M $NaClO_4$ using a flow rate of about 1 cm^3 min^{-1}. The fraction was concentrated, freed from excess $NaClO_4$ by extraction into absolute ethanol, and the remaining $NaClO_4$ was removed by passing the sample through a small column of Sephadex G-10. The substance was then obtained by evaporating the solution to dryness on a water bath [*Yield* 1.7 g. Anal., Calcd. for $Co(C_{12}H_{22}N_2O_6)ClO_4$: C, 32.12; H, 4.94; N, 6.24%. Found: C, 31.86; H, 4.86; N, 6.17%].

Synthesis and Isolation of Ethylenediamine [2S,2'S-1,1'-(ethane-1,2-diyl)bis(pyrrolidine-2-carboxylato) (2-)] cobalt(III) Perchlorate Isomers, [Co(pren)en] ClO_4

The synthesis of the isomers was analogous to that used for the synthesis of the corresponding diaqua-complex except that 0.7 cm^3 (10 mmol) of ethylenediamine diluted to 15 cm^3 with water was used. Chromatography of the isomers was accomplished in a similar fashion. The mixture of complexes formed a compact band at the top of the column which was eluted with water to remove non-ionic species which inhibit crystallization of the desired products. The column was eluted with 0.1M $NaClO_4$. Two bands were collected. The first wine-red one was concentrated to near dryness with a rotary evaporator, and excess $NaClO_4$ was filtered off. After removing most of $NaClO_4$ by precipitation with absolute ethanol, final desalting was carried out by gel permeation chromatography on a column of Sephadex G-10. The solution was concentrated and after standing in a refrigerator overnight, purple needles of the *cis*-α isomer formed in the solution. The *cis*-α isomer was removed by filtration and washed with ethanol and then acetone. The yield was 2.4 g after air drying. The remaining solution was slowly evaporated whereupon the mauve *cis*-β isomer crystallized. The crystals were filtered and washed

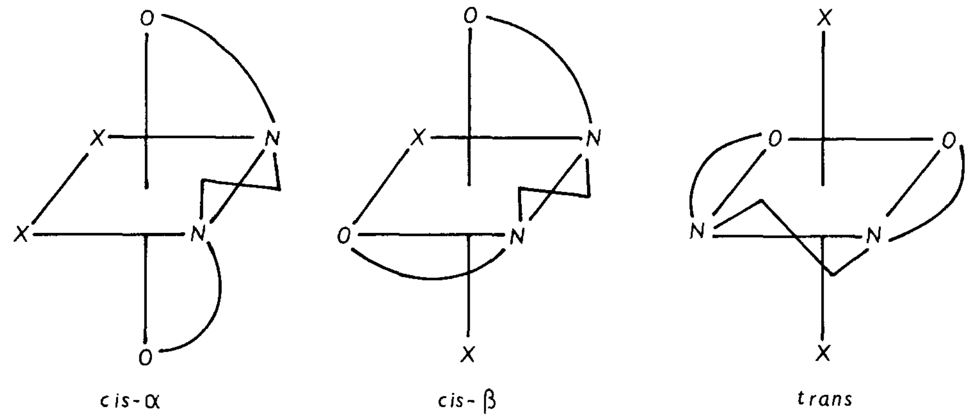

FIGURE 1 The possible geometrical isomers for octahedral [Co(edda)X_2] complexes.

with acetone and diethyl ether. The air-dried yield was 0.3 g. Further evaporation produced an additional 0.4 g of the *cis*-β isomer. The both isomers may be recrystallized without change from water. [*Anal.*, Calcd. for $Co(C_{14}H_{26}N_4O_4)ClO_4$: C, 35.57; H, 5.54; N, 11.85% and for $Co(C_{14}H_{26}N_4O_4)ClO_4.2H_2O$: C, 33.05; H, 5.94; N, 11.08%. Found; *cis*-α: C, 33.16; H, 5.87; N, 10.98%; *cis*-β: C, 35.71; H, 5.48; N, 11.81%].

The second pink band remaining at the top of the column was assumed to be a hydrolysis product, and was not further investigated.

Physical Measurements

To verify the purity and charge of the individual complexes paper electrophoresis was used. All elemental analyses were obtained using a Carlo Erba M 1102 instrument. Electronic absorption spectra were measured on a Carl Zeiss Specord UV VIS spectrophotometer. 10^{-3} M solutions were prepared and 1 cm cells were used. Circular dichroism spectra were recorded on a CNRS-Roussel Joun Dichrograph III in the region 200 - 700 nm. The concentration of the aqueous solutions used was of the order of 10^{-4} M in 5 mm cells. A Jeol FX-100 FT-NMR spectrometer with a working frequency 35.3 kHz was used to record the ^{13}C spectra of the compounds in D_2O solution. Dioxan was used as an internal reference and all spectra are referenced to tetramethylsilane, 0 ppm. All spectra were broad-band decoupled. Well-resolved spectra were normally obtained after 3000 pulses. Generally solutions were 10% w/w. The infrared spectra were run on a Perkin-Elmer 337 spectrophotometer using the KBr disk technique. All spectra were recorded at room temperature.

RESULTS AND DISCUSSION

Separation and Distribution of Isomers

The tetradentate ligand used in this work was prepared from optically active proline of known configuration. The configuration of the ligand is as shown in Fig. 2. The carbon atom C_α is asymmetric and, because the reaction to form the ligand does not involve this atom, it must therefore have the *S* absolute configuration as it does in *S*-proline. The syn-

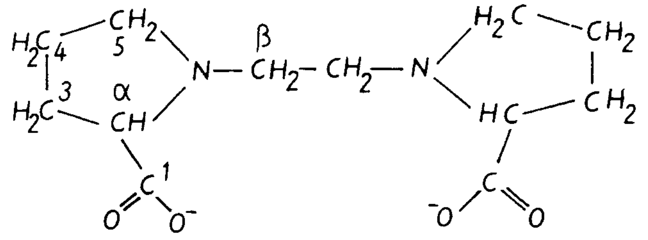

FIGURE 2 A schematic drawing of the deprotonated ligand pren, showing the numbering system.

thesised complexes are optically active analogues of octahedral [Co(edda)X_2] complexes, and in the systems so far reported[2,3,6] the *cis*-α isomer appears to form almost exclusively. In the case of the [Co(pren)en]$^+$isomers the number of possible geometrical isomers (Fig. 1) is reduced to two, because ethylenediamine is unable to span the *trans* position. Both *cis* isomers are capable of existence in optical forms.

The complexes were prepared by oxidation of cobalt(II) in the presence of the desired ligand using carbon as a catalyst which may result in equilibrium being established. The geometrical isomers could be isolated either by chromatography on ion-exchange resin or by fractional crystallization. The higher yield of the *cis*-α isomer in spite of using carbon as catalyst supported the observation from molecular models that the nonbonding interactions of the amine protons of the en ligand with pren are significantly greater in the *cis*-β isomer (Fig. 3). The *cis*-β-[Co(pren)(H_2O)$_2$]$^+$isomer was not detected. However, this may be fortuitous. Experimental isomer distribution in cobalt(III) complexes is known to be highly dependent on synthetic conditions.[8,9]

Identification and Characterization of the Isomers

NMR spectra

The ^{1}H NMR spectra of all the compounds were of little use for stereochemical assignment because of the overlap of the proton signals due to the *S*-proline group and because

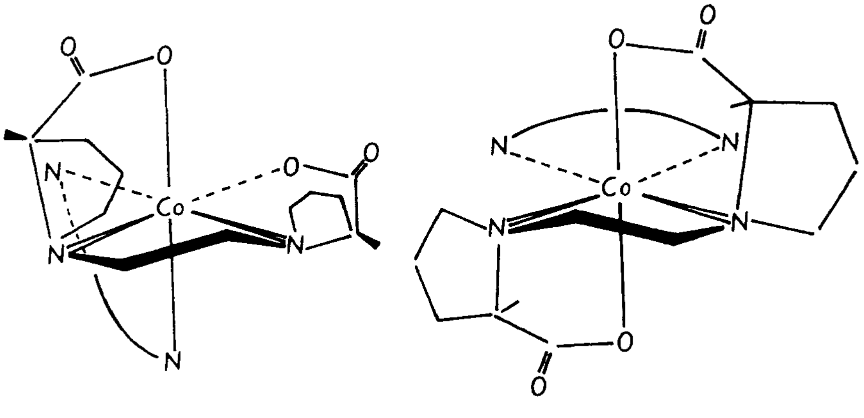

FIGURE 3 Two geometrical isomers of [Co(pren)en]$^+$.

TABLE I
Carbon-13 chemical shifts.

Compound	δ (ppm from TMS)
H_2pren.2HCl	172.93, 70.67, 56.81, 52.24, 30.66, 24.86
Δ-*cis*-α-[Co(pren)(H_2O)$_2$]ClO_4	187.34, 76.88, 64.59, 62.47, 30.21, 24.91
Δ-*cis*-α-[Co(pren)en]ClO_4.$2H_2O$	187.25, 75.11, 64.19, 62.38, 45.42, 30.15, 24.82
Δ-*cis*-β-[Co(pren)en]ClO_4	165.62, 162.36, 70.12, 68.84, 54.17, 52.53, 41.15, 39.84, 29.46, 23.50

of signal broadening which may be due to spin-spin coupling with ^{59}Co. Therefore the geometrical isomers were identified by employing ^{13}C NMR spectroscopy. The ^{13}C NMR chemical shifts relative to TMS for the ligand and compounds are shown in Table I.

From inspection of Table I it is obvious that the chelation of pren to cobalt(III) ion brings about down-field changes in ^{13}C NMR chemical shifts of its carboxyl-carbon (C_1) and α-carbon (C_α) atoms. Chelation causes a decrease of the electron density on the C_1 and C_α carbon atoms. Chemical shifts in cobalt(III) complexes are influenced by the anisotropic effects of cobalt(III) and by the *trans*-influence of the coordinating atoms.[10,11] Considering the chemical shifts of the both C_1 and C_α glycinate carbon atoms we conclude that they are primarily effected by the ligand in the *trans* position (Fig. 3). If in *trans*-position the ligator is an oxygen atom (*cis*-α isomer), the C_1 and C_α chemical shifts are displaced to lower fields than when the ligator is nitrogen (*cis*-β). This conclusion is supported by data published elsewhere.[12]

The Co(III) complexes with the *cis*-α structure have a C_2 rotation axis while there is no such symmetry for the *cis*-β isomers. Therefore, complexes which shows only one signal for each kind of carbon atom in the chelated ligand in the ^{13}C NMR spectrum may be unambiguously assigned as *cis*-α isomers.

Electronic absorption spectra

Further examination of molecular models of both geometrical isomers shows that the species can exist only as the dissymmetric forms shown in Fig. 3. Their enantiomers are precluded because of the necessity for C_α to have the *S* configuration. The compounds therefore have the Δ absolute configuration and are formed stereospecifically. The coordinated nitrogen atoms also necessarily have fixed configurations. Stereospecificity associated with an asymmetric nitrogen atom in cobalt(III) complexes has been observed recently.[3,6]

Confirmation that these compounds have the configuration assigned by ^{13}C NMR spectroscopy is given by the absorption and circular dichroism spectral data shown in Table II and Fig. 4. From Table II it is obvious that the first and second absorption maxima are shifted to higher energy for [Co(pren)en]$^+$ compared with the [Co(pren)(H_2O)$_2$]$^+$ complexes. The first band for the *cis*-β isomer consists of a shoulder superimposed upon a symmetrical main peak. The wavelengths for the shoulder were obtained by subtracting a symmetrical trace of the major peak from the observed spectrum.

If chelate rings are ignored, the effective crystal field symmetry of the complexes is *cis*-CoN_4O_2 and *cis*-CoN_2O_4, respectively. By the electrostatic model for treating crystal field potentials, these complexes (ignoring chelate rings) have tetragonal symmetry. Under tetragonal symmetry the $T_{1g}(O_h)$ level, which is the first excited state for low-spin Co(III), is split into levels with A_2 and E symmetry. Whether the E state lies lower than the A_2 state or higher depends upon the arrangement of the ligands and their relative crystal strengths. It is predicted that the E level will lie lower than the A_2 level for these complexes.[13] Such a splitting of the first absorption band is seen clearly for *cis*-β-[Co(pren)en] ClO_4 in aqueous solution (Fig. 4).

Circular dichroism measurements

The CD of the d-d transitions of the central cobalt(III) ion constitues a sensitive probe of the ligand environment. The optically active *cis* isomers could gain dissymmetry[14] through configurational dissymmetry due to the chirality of the chelate system, conformational dissymmetry due to the indivudual chelate ring conformations, and the vicinal dissymmetry due to asymmetric C_α and donor atoms of the pren ligand. Thus, the absolute configurations of all the isomers were assigned form the sign of major CD band in the region of the first absorption band.

Under an octahedral ligand field, both the T_{1g} and T_{2g} spin-allowed transitions are electric-dipole-forbidden. Therefore, the d-d transitions gain electric-dipole intensity through a vibronic mechanism. The T_{1g}, but not the T_{2g}, transitions are magnetic-dipole-allowed; therefore the rotational strengths of the $T_{1g}(O_h)$ transitions are of a higher order of magnitude than those from $T_{2g}(O_h)$. As seen in Fig. 4 and Table II the CD spectra of the optically active complexes have a large and negative peak of an E_g (D_{4h}) component in the longer wavelength region and a small peak of an $A_{2g}(D_{4h})$ component in the shorter wavelength region. The latter is negative for *cis*-α-[Co(pren)$(H_2O)_2$] ClO_4 but

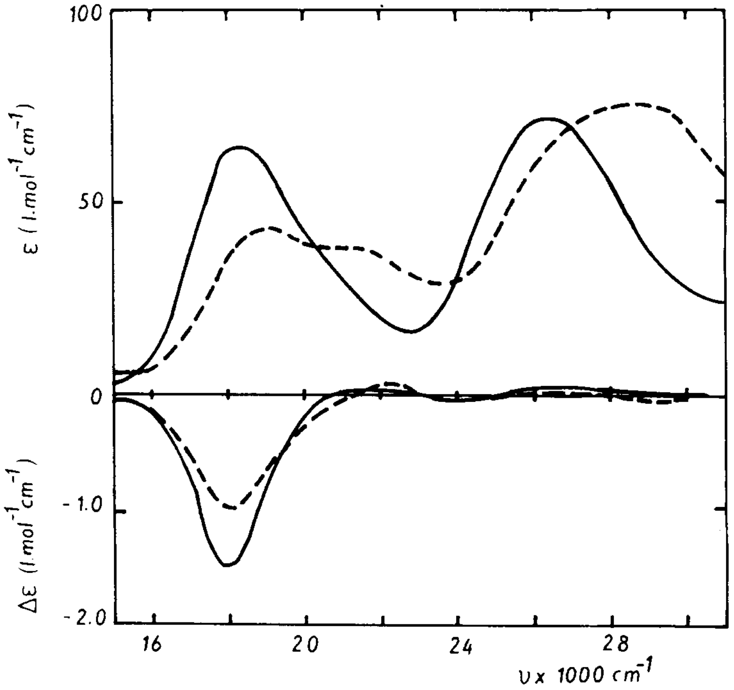

FIGURE 4 Absorption (ε) and circular dichroism (Δε) spectra of aqueous solutions of Δ-*cis*-α-[Co(pren)en] $ClO_4 . 2H_2O$ (——), and Δ-*cis*-β-[Co(pren)en] ClO_4 (---).

TABLE II
Electronic spectral data for aqueous solutions of the cobalt(III) complexes[a].

Compound	Absorption				Circular Dichroism		Transition
	$^1A_{1g} \longrightarrow {}^1T_{1g}$		$^1A_{1g} \longrightarrow {}^1T_{2g}$				
	ν	ϵ	ν	ϵ	ν	$\Delta\epsilon$	
Δ-*cis*-α-[Co(pren)($H_2O)_2$]ClO_4	18000	110	25440	75	18520	− 1.84	E_g
					22990	− 0.13	A_{2g}
					25640	+ 0.06	$E(T_{2g})$
Δ-*cis*-α-[Co(pren)en]ClO_4.$2H_2O$	18150	68	26100	79	17990	− 1.49	E_g
					21740	+ 0.06	A_{2g}
					24160	− 0.05	$E(T_{2g})$
					26525	+ 0.09	B_{2g}
Δ-*cis*-β-[Co(pren)en]ClO_4	18690	43	28330	75	18020	− 1.02	E_g
	21600	sh			22220	+ 0.03	A_{2g}
					24330	− 0.05	$E(T_{2g})$
					28490	− 0.05	B_{2g}

[a] v is the position of a maximum in the absorption spectrum, or a maximum or minimum in the CD spectrum in cm^{-1}; ϵ is the molar absorptivity and is given, together with $\Delta\epsilon$, in units of $l\ mol^{-1}\ cm^{-1}$.

positive for both *cis*-α- and *cis*-β-[Co(pren)en] ClO_4 complexes. This fact is in accord with the prediction[15] that the Cotton sign of $R(A_{2g})$ in CoN_2O_4 complexes is opposite that in CoN_4O_2 complexes.

In each case the dominant peak appears to be related to the dominant peak in the spectrum of corresponding eddp[16] and ven[6] complexes. The absolute configurations are, therefore, assigned in the same manner as for the ven complexes[6]; a negative dominant peak indicated a Δ configuration. Such a result is in agreement with the stereospecific formation of the Δ enantiomer predicted from model studies.

Infrared spectroscopy

Although IR spectroscopy is not the most reliable method of differentiation between diastereomers, it can give valuable information about the order of strength of the coordinate bonds by comparing the magnitudes of the band shifts. A carboxylate ion is of such a low symmetry (C_{2v}) that its all vibrational modes are IR active, and therefore no great decrease in symmetry is to be expected on complex formation. The antisymmetric OCO (ν_{as}OCO) and the symmetric OCO (ν_sOCO) vibrations are expected to be more sensitive to coordination and the frequencies due to them could be shifted on complexation. The magnitude of separation (Δv) between the frequencies due to ν_{as}OCO and ν_sOCO in different amino acids has been found helpful in distinguishing all the main types of carboxylate binding.[6] Thus, in the case of H_2pren.2HCl, both the CO bonds are equivalent, and the antisymmetric and symmetric OCO stretching bands appear at 1625 and 1447 cm^{-1} respectively (Table III). From the data in Table III it may be observed that in all of the complexes the directions of the shifts in the frequencies due to ν_{as}OCO and ν_sOCO are higher and lower respectively relative to those for H_2pren.2HCl. Unidentate coordination removes the equivalence of the two oxygen atoms and the two C-O bond orders are appreciably altered giving rise to a pseudo-ester type arrangement.[17] The separation of the two CO bands may be proportional to the strength of the Co-O bond and it is in order Δ-*cis*-α-[Co(pren)en] ClO_4.$2H_2O$ > Δ-*cis*-β-[Co(pren)en] ClO_4 > Δ-*cis*-α-[Co(pren)

TABLE III
The OCO stretching frequencies of the cobalt(III) complexes (in cm^{-1}).

Compound	ν_{as}OCO	ν_sOCO	$\Delta\nu$
H_2pren.2HCl	1625	1441	184
Δ-*cis*-α-[Co(pren)$(H_2O)_2$]ClO_4	1620	1427	193
Δ-*cis*-α-[Co(pren)en]ClO_4.$2H_2O$	1636	1354	282
Δ-*cis*-β-[Co(pren)en]ClO_4	1625	1362	263

$(H_2O)_2$]ClO_4. This is in keeping with the expected greater stability due to the chelate effect of en.

Finally it is evident that the *cis*-α-en isomer is formed in a greater amount. However, diastereoselectivity is apparently smaller than is the case with [Co(ven)en]ClO_4 complexes[6] where the Δ-*cis*-α diastereomer is formed stereoselectively.

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