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Synthesis and Characterization of Cobalt(III) Complexes with a Stereospecific Ligand Derived from (S)-Valine

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Complexes of the type $[CoLX_2]^+$ *and* $[CoLXY]$*, where L is the quadridentate ligand ethylenediamine-N,N'-di-(S)-α-isovalerate* (H_2ven) *and* $X = H_2O$ *or ethylenediamine (en) and* $Y = NO_3$ *have been prepared. Three geometrical isomers,* cis-α, cis-β, *and* trans *forms, may in principle be obtained. The complex* $[Co(ven)(NO_3)H_2O]$ *exists only as the* cis-α *geometrical isomer, while in the case of* $[Co(ven)(H_2O)_2]^+$ *and* $[Co(ven)en]^+$ *complexes both* cis-α *and* cis-β *are found to exist. The yields of the* cis-α *isomers exceeded considerably those of the* cis-β *isomers.* ^{13}C*-NMR and absorption spectral measurements confirm these arrangements. In addition, the IR spectra of the complexes are discussed.*

The compounds exhibit a strong negative CD bond under the $^1A_{1g} \rightarrow {}^1T_{1g}$ *cubic absorption band, which is due to the* $^1A_{1g} \rightarrow {}^1E_g$ *tetragonal component, consistent with the Δ absolute configuration imposed by the (S) configuration of the asymmetric carbon atom in the (S)-valine moiety.*

Introduction

The stereochemistry of cobalt(III) complexes with chiral amino acids is an attractive problem, and many studies have been directed toward the stereoselectivity or stereospecificity of those complexes. Recently, an attention has been focussed on the cobalt(III) complexes of stereospecific ligands derived from natural amino acids which are analogous to the quadridentate ligand $HOOCCH_2NHCH_2CH_2NHCH_2COOH$ (H_4edda) [1–3]. When the ligand is deprotonated it can coordinate to four of the octahedral sites around a cobalt(III) ion. The additional two positions may be occupied by two monodentate ligands or one bidentate ligand.

From Fig. 1 it is obvious that three geometrical isomers, *cis-α*, *cis-β* and *trans* forms, may in principle be obtained. To date, no *trans* isomers have been isolated. However, both *cis-α* and *cis-β* isomers containing the edda ligand and related molecules, where generally the coordination sphere is completed by a bidentate ligand such as ethylenediamine, have been extensively studied [4–6].

More recently we reported that a similar quadridentate ligand, H_2ven, may be prepared from the reaction of (S)-valine and 1,2-dibromoethane [3]. The present study involves the kinetically inert cobalt(III) complexes of the optically active ven ligand. Preliminary examination of the Dreiding models indicated that the complexes should be formed stereospecifically because of the presence of the asymmetric carbon atom in the (S)-valine moiety.

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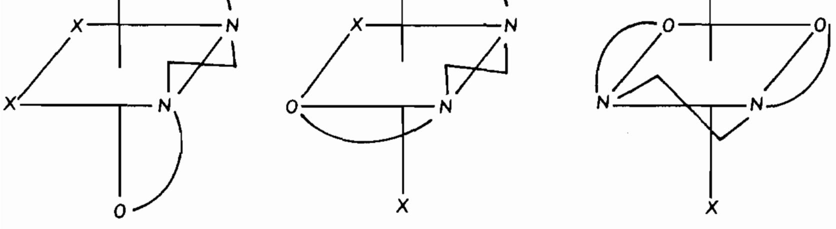


cis-α cis-β trans

Fig. 1. The possible geometrical isomers for octahedral $[Co(edda)X_2]$ complex.

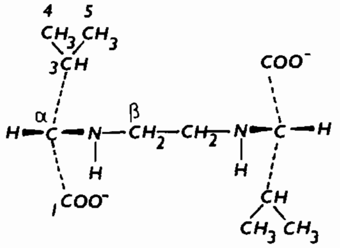


Fig. 2. A schematic drawing of the deprotonated ligand ven, showing the numbering system.

Experimental

Preparation of Compounds

The optically active ligand, H_2ven, as well as [Co(ven)$(H_2O)_2$] ClO_4 isomers were prepared by the method previously reported [3].

cis*-α-Ethylenediamine-N,N'-di-(S)-α-isovalerate(nitro)aquo cobaltate(III)([Co(ven)(NO$_3$)H$_2$O])*

To a suspension of 0.65 g (2.5 mmol) of H_2ven in 3.5 ml of water were added a suspension of 0.3 g (2.5 mmol) of freshly prepared $CoCO_3$ in 20 ml of water and 0.1 g of charcoal and 0.2 ml of 65% HNO_3. The mixture was heated to 60 °C, and 0.3 ml of 30% H_2O_2 was added dropwise; the system was held at this temperature for an additional 7 hr with vigorous stirring. After cooling, the charcoal and unreacted $CoCO_3$ were filtered off. The wine-red solution was subjected to chromatographic treatment on a column packed with Dowex 50-WX8 resin in the H^+ form that had previously been equilibrated in distilled water. The column was eluted with distilled water at a flow rate of 1 cm^3 min^{-1}. Only one fraction gave 0.6 g of the required product. The violet compound is sparingly soluble in water and may be recrystallized without change. *Anal.* For [Co($C_{12}H_{26}N_3O_8$)] calculated: 36.10%, C; 6.56%, H; 10.52%, N. Found: 36.20%, C; 6.55%, H; 10.36%, N.

Ethylenediamine-N,N'-di-(S)-α-isovalerate(ethylenediamine)cobalt(III) Perchlorate ([Co(ven)en]-ClO$_4$)

To a suspension of 1.3 g (5 mmol) of H_2ven in 5 ml of water were added a suspension of 0.6 g (5 mmol) of freshly prepared $CoCO_3$ in 40 ml of water, 0.5 ml of 65% HNO_3 diluted to 5 ml, 0.1 g of activated charcoal (to facilitate the formation of the equilibrium isomer mixture), and 0.35 ml (5 mmol) of ethylenediamine diluted to 15 ml. The mixture was heated on a steam bath to about 60 °C, and 1 ml of 30% H_2O_2 was added dropwise. Heating was continued with vigorous stirring for 6 hr. The resulting wine-red solution was filtered away from the charcoal and a trace of unreacted cobalt carbonate. It was then added to a large ion-exchange column full of 50–100 mesh Dowex 50-WX8 cation-exchange resin in the sodium form. The mixture of complexes formed a compact band at the top. Washing with water removed a purplish material that was not absorbed on the column. Elution with 0.2 *M* $NaClO_4$ at a rate of about 1 cm^3 min^{-1} caused a splitting into two bands. The fractions were concentrated, freed from $NaClO_4$ by extraction into absolute ethanol, and the remaining sodium perchlorate was removed by passing through a small column of Sephadex G-10. Solid, bright violet, crystalline products were obtained from the two bands by slow evaporation. The yields were 1.2 g of *cis-α* isomer from band I and 0.01 g of *cis-β* isomer from band II. *Anal.* For [$CoC_{14}H_{30}N_4O_4$]-ClO_4 calculated: 35.27%, C; 6.34%, H; 11.75%, N; 7.44%, Cl. Found: *cis-α*: 35.34%, C; 6.16%, H; 11.64%, N; 7.64%, Cl. *cis-β*: 35.41%, C, 6.31%, H; 11.61%, N; 7.50%, Cl.

Measurements

Electrophoresis without the glass vessels (with platinum electrodes) [7] was used in order to verify the purity, as well as the magnitude of charge of the individual complexes. All elemental analyses were done by Elemental Analyzer M 1102 (Carlo Erba). Electronic absorption spectra were measured on a Specord UV VIS (Carl Zeiss) spectrophotometer at room temperature. 10^{-3} *M* solutions were prepared and 1 cm cells were used. Circular dichroism spectra were recorded on a CNRS Roussel Juan dichrograph in the region 200–700 nm. The concentration of the aqueous solutions was of the order of 10^{-4} *M* in 5 mm cells.

A Jeol FX-60 pulse FT-NMR spectrometer with the working frequency 35.3 KHz/4000 Hz was used to record ^{13}C spectra of the compounds in D_2O solution. Dioxan was used as an internal reference (all spectra were referenced to tetramethylsilane, 0 ppm). All spectra are broad-band noise-decoupled. Well-resolved spectra were normally obtained after 3000 pulses. Generally solutions were 10% w/w where possible.

The infrared spectra were run on a Perkin-Elmer 337 spectrophotometer using the KBr disk technique.

Results and Discussion

Separation and Distribution of Isomers

The quadridentate ligand used in this work was prepared from optically-active valine of known configuration. The absolute 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)-valine [3]. The complexes synthesized by us are optically-active analogues of octahedral [Co(edda)X_2] complexes, and construction of Dreiding molecular models shows that the isomers depicted in Fig. 1 are possible for the octahedral [Co(ven)X_2] species. The amount of bond-angle strain appears to be in the order *cis*-α > *cis*-β > *trans* when X is a monodentate ligand. So far, however, no *trans* isomer has been isolated. In the case of the [Co(ven)en]ClO_4 isomers the number of possible geometrical isomers is reduced to two, because ethylenediamine is unable to span the *trans* position. The *cis* isomer could gain dissymetry [8] through (i) the distribution of chelate rings about the Co(III) ion, (ii) the conformations of the chelate rings, (iii) the distribution of H_2O and NO_3 about the Co(III) ion, and (iv) the coordination of the optically active ven, so that two additional diastereoisomers can be attributed to them.

Geometrical isomers are nowadays usually separated by ion exchange chromatography. Much less work has been carried out on the separation of optical isomers. The order of elution of complexes followed the expected order in that the *cis*-α isomers, with smaller dipole moments, were eluted before the *cis*-β isomers.

cis-β-[Co(ven)(NO_3)H_2O] isomer was not detected. It is not immediately apparent from molecular models why this should be so. In each case there was a much greater yield of *cis*-α isomers than of *cis*-β ones. The tendency of a quadridentate ligand of the type used here to prefer a *cis*-α orientation has been noted previously [1].

Identification and Characterization of the Isomers

NMR Spectra

The geometrical isomers were identified by employing ^{13}C NMR spectroscopy. The ^{13}C NMR chemical shifts relative to tetramethylsilane for the ligand and other compounds are shown in Fig. 3 and in Table I. The spectra are well resolved and a typical example, that of [Co(ven)en]ClO_4 in D_2O solution, is shown in Fig. 4.

From inspection of Table I it is obvious that the chelation of ven to cobalt(III) ion brings about downfield changes in ^{13}C NMR chemical shifts of its carboxyl-carbons (C_1) and α-carbons (C_α). Chelation causes an decrease of the electron density on the C_1 and C_α carbon atoms. In determining carbon chemical shifts at least three factors are important. These are the diamagnetic term (σ_d), the paramagnetic term

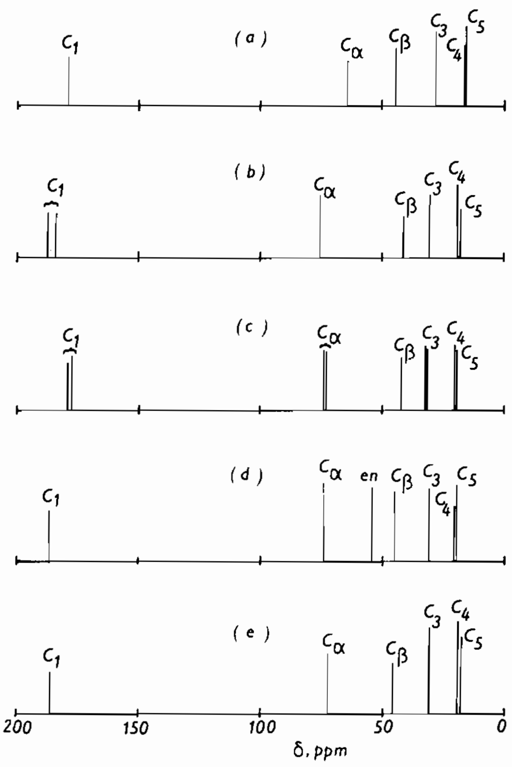


Fig. 3. A schematic representation of the ^{13}C NMR spectra for D_2O solutions: (a) H_2ven, (b) Δ-*cis*-α-[Co(ven)(H_2O)$_2$]ClO_4, (c) Δ-*cis*-β-[Co(ven)(H_2O)$_2$]ClO_4, (d) Δ-*cis*-α-[Co(ven)en]ClO_4, (e) Δ-*cis*-α-[Co(ven)(NO_3)H_2O].

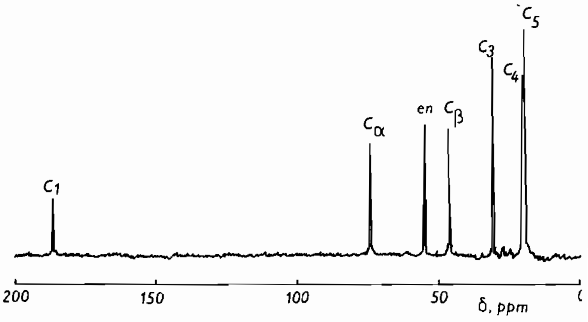


Fig. 4. The ^{13}C NMR spectrum of Δ-*cis*-α-[Co(ven)en]ClO_4 in D_2O.

TABLE I. Carbon-13 Chemical Shifts for the Compounds.

Compound	δ (ppm from $SiMe_4$)
H_2ven	179.33, 63.93, 44.18, 28.20, 16.24, 15.85
Δ-*cis*-α-[Co(ven)(H_2O)$_2$]ClO_4	187.65, 183.75, 72.06, 41.43, 30.93, 19.43, 17.74
Δ-*cis*-β-[Co(ven)(H_2O)$_2$]ClO_4	178.81, 176.79, 74.07, 73.03, 42.23, 31.64^s, 20.27, 19.49
Δ-*cis*-α-[Co(ven)en]ClO_4	186.41, 74.00, 54.45, 46.00, 30.86, 20.21, 19.43
Δ-*cis*-α-[Co(ven)(NO_3)H_2O]	186.15, 72.10, 47.11, 30.99, 19.20, 17.41

^{s}splitting

(σ_p), and the anisotropy of neighbouring atom (σ_{ani}) [9]. The chemical shifts of cobalt(III) complexes are affected by the anisotropic effect of cobalt(III) [10]. This could be equal for studied complexes and, therefore, σ_p term makes major contribution to carbon chemical shifts. Similar down-field chemical shifts of carbon atoms of ethylenediamine were observed for [Co(ven)en]ClO_4 complex.

The metal complex with the *cis*-α structure has approximately a C_2 symmetry while there is no symmetry for the *cis*-β isomer. The ^{13}C signal for a particular carbon atom should theoretically occur as a single peak for a *cis*-α isomer and as a doubled signal for the corresponding carbon atom in the *cis*-β isomer. Thus, complexes in the cases (b), (d) and (e) in Table I may be unambiguously assigned as the *cis*-α isomers. The ^{13}C NMR spectrum shows only one signal for each carbon in the chelated ligand.

Electronic Absorption Spectra

Further support for distinguishing geometrical isomers comes from electronic absorption spectroscopy. The visible spectra, together with CD spectra of some complexes, are shown in Fig. 5 and all of the spectra are summarized in Table II.

It can be noted that both *cis*-β isomers have less intense bands. Furthermore, the peaks of the first band are at slightly higher energies than the corresponding peaks in the *cis*-α isomers. The frequency of the first band is equal to 10Dq-C, where C is a Racah parameter [11]. Since 10Dq is a measure of the strength of the ligand field, an increase in frequency of the first band might be an indication of increasing stability. Because of the small differences involved, however, a conclusion as to the relative stability of the *cis*-α and *cis*-β isomers would be tenuous at best.

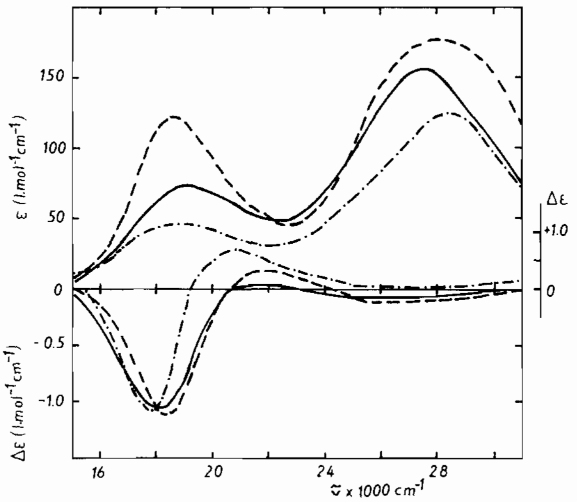


Fig. 5. Absorption (ε) and circular dichroism (Δε) spectra of aqueous solutions of Δ-*cis*-α-[Co(ven)(NO_3)H_2O] (——), Δ-*cis*-α-[Co(ven)en]ClO_4 (– – –), and Δ-*cis*-β-[Co(ven)en]ClO_4 (– · – ·).

The visible spectra of the complexes are related with those of the corresponding *cis*-[Co(edda)X_2] species [12]. Compounds of this type have been treated as *cis*-CoN_4O_2 species, the chelate rings being

TABLE II. Electronic Spectral Data for the Aqueous Solutions of the Cobalt(III) Complexes.[a]

Compound	Absorption				Circular Dichroism		Transition
	$^1A_{1g} \rightarrow {}^1E_g$		$^1A_{1g} \rightarrow {}^1T_{2g}$		$\tilde{\nu}$	Δε	
	$\tilde{\nu}$	ε	$\tilde{\nu}$	ε			
Δ-*cis*-α-[Co(ven)(H_2O)$_2$]ClO_4	19278	130	30248	189	18083	−1.41	E_g
					21367	+0.33	A_{2g}
					25974	−0.27	T_{2g}
Δ-*cis*-β-[Co(ven)(H_2O)$_2$]ClO_4	21536	71	29360	126	18416	−1.36	E_g
					22727	+0.09	A_{2g}
					28170	−0.27	T_{2g}
Δ-*cis*-α-[Co(ven)en]ClO_4	18471	122	28070	176	18298	−1.13	E_g
					21910	+0.34	A_{2g}
					25955	−0.12	T_{2g}
Δ-*cis*-β-[Co(ven)en]ClO_4	18955	46	28554	124	17720	−1.08	E_g
					20858	+0.70	A_{2g}
Δ-*cis*-α-[Co(ven)(NO_3)H_2O]	19200	73	27480	157	17865	−1.09	E_g
					21410	+0.09	A_{2g}
					26320	−0.08	T_{2g}

[a] $\tilde{\nu}$(the position of a maximum in the absorption spectrum, or a maximum or minimum in the CD spectrum) in cm^{-1}; ε (the molar absorptivity) and Δε in l mol^{-1} cm^{-1}.

ignored. Under tetragonal symmetry the degeneracy of the triplet states is removed and $^1T_{1g}(O_h)$ level, which is the first excited state for a cobalt(III) d^6 low-spin complex, is split into ^1E_g and $^1A_{2g}$ levels. Although the entire term diagram of Co^{3+} is not known in detail, transitions from the $^1A_{1g}$ ground state, $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$, are expected in the lower-energy band in the visible region of the absorption spectrum. It is also predicted that the ^1E_g level will be at a lower energy than the $^1A_{2g}$ level [5]. The *cis-α* and *cis-β* geometrical isomers were assigned on the argument that the *cis-α* isomer is more like the octahedral complex and should have a more symmetric absorption band, while the *cis-β* isomer should have a broad absorption band at lower energy and a lower molar extinction coefficient. The electronic absorption spectra measured (Fig. 5, Table II) are consistent with the expected behaviour.

Circular Dichroism

The spin-allowed transitions of d^6 configurations have T_{1g} and T_{2g} symmetries. Under octahedral ligand field, both these transitions are electric-dipole-forbidden and this holds true even when the molecular symmetry of an octahedral complex is much lower than O_h. Therefore, the d–d transitions gain electric-dipole intensity through a vibronic mechanism. The T_{1g}, but not the T_{2g}, transition is magnetic-dipole-allowed; therefore the rotational strengths of the transitions derived from $T_{1g}(O_h)$ are of a higher order of magnitude than those from T_{2g}.

As seen in Fig. 5 and Table II the complexes described here show two Cotton effects in the region of the $^1A_{1g} \rightarrow {}^1T_{1g}$ band, one strong and negative at the longer wavelength, and the other weak and positive at the shorter wavelength. The compounds have actual or approximate C_2 symmetry and the ^1E level should split further into two non-degenerate levels. In all previously studied systems, this splitting appears to be very small and does not need to be considered when the following correlation is made. Compounds of the *cis-α*-$[Co(edda)X_2]$ type, when X_2 is chelated ethylenediamine, having the Λ absolute configuration, exhibit a positive CD band at lower energy which arises from the $A_1 \rightarrow E$ transition [5]. Such a correlation holds for the present complexes, which all have a corresponding strong negative CD band at lowest energy, and is as expected for *cis-α*-$[Co(ven)X_2]$ complexes having the Δ absolute configuration. Such a result is in agreement with the stereospecific formation of the Δ enantiomer. In these complexes there are contributions to the optical activity from the spiral configuration of the complex as a whole and from the vicinal effect of the optically active ligand ven. The small difference in the behaviour of CD curves can be explained by supposing that the intramolecular interactions between the isopropyl groups and the other atoms are different in the individual complexes. The difference in the type of interaction may result in non-planar chelate rings with different conformations, which will be related to the rotational strength.

Infrared Spectroscopy

Although infrared spectroscopy is not the most reliable method of differentiation between *cis-α* and *cis-β* isomers, it brings valuable informations about the order of strength of the coordinate bonds by comparing the magnitudes of the band shifts. In a series of metal complexes having the same structure, the magnitude of these band shifts becomes larger as the coordinate bond becomes stronger. Investigations on complexes of amino acids showed that the NH stretching vibration decreases with an increase in complex stability [13]. From Table III it is seen that for all investigated complexes the NH stretching vibration decreases in the range 100–300 cm^{-1}. However, such results must be interpreted with caution because the hydrogen of the amino groups may form inter- and intra-molecular hydrogen bonds in these complexes, and this gives rise to greater changes in the NH vibrations than do variations in the strength of the cobalt–nitrogen bond. Nevertheless, these results verified the strong covalent character of this bond.

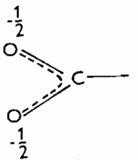
Interpretation of these changes produced by complex formation on the vibrations of the carboxyl groups is also a difficult task. The oxygen atoms of the carboxyl groups can be coordinated to the cobalt atom, or they may be linked by hydrogen bonds to

TABLE III. The N–H and COO Stretching Frequencies of the Cobalt(III) Complexes.[a]

Compound	$\bar{\nu}_{NH}$	$\bar{\nu}_{asCOO}$	$\bar{\nu}_{sCOO}$	$\Delta\bar{\nu} = (\bar{\nu}_{as} - \bar{\nu}_s)$
H_2ven	3400	1590	1395	195
Δ-*cis-α*-$[Co(ven)(H_2O)_2]ClO_4$	3200	1635	1380	255
Δ-*cis-β*-$[Co(ven)(H_2O)_2]ClO_4$	3100	1624	1389	235
Δ-*cis-α*-$[Co(ven)(NO_3)H_2O]$	3220	1637	1370	267
Δ-*cis-α*-$[Co(ven)en]ClO_4$	3250	1640	1374	266
Δ-*cis-β*-$[Co(ven)en]ClO_4$	3290	1627	1382	245

[a] Values in cm^{-1}.

the amino group of a neighbouring complex molecule. In addition, the direction of the band shifts depends on the structure of the metal complex formed, on the nature of the normal vibration and the effect of coordination on it [14]. In the case of a carboxylate ion the two types of coordination shown in II and III are known to exist. The free ion



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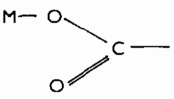

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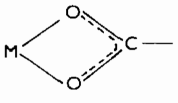
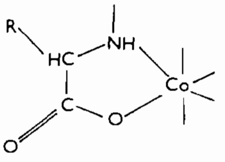


III

(structure I) has low symmetry (C_{2v}), and therefore no great decrease in symmetry is to be expected on complex formation. Thus, in the case of H_2ven, both the CO bonds are equivalent, and the antisymmetric and symmetric COO stretching bands appear at 1590 and 1395 cm^{-1} respectively (Table III). The formation of complexes of different types causes different changes in the structure of the carboxyl group. If coordination occurs symmetrically (structure III), both the COO stretching bands may be shifted in the same direction, since the bond orders of both CO bonds may be changed by the same amount. If coordination occurs as shown in structure II, the antisymmetric and symmetric COO stretching bands will be shifted to higher and lower frequencies respectively. In the series of investigated complexes having similar structure the symmetry of complexes is approximately identical, and therefore it can be assumed that the hydrogen bonds affecting the vibrations of the carboxyl groups are the same in number and character. Thus, the separation of the two CO bands may be proportional to the strength of the cobalt–oxygen bond. The chelation of H_2ven should be of type as structure IV, where R is the isopropyl group.



IV

From inspection of Table III, and on the basis of the above discussion, we may predict the order of stability of the investigated complexes as Δ-*cis*-α-[Co(ven)(NO_3)H_2O] ≈ Δ-*cis*-α-[Co(ven)en] ClO_4 > Δ-*cis*-α-[Co(ven)(H_2O)$_2$]ClO_4 > Δ-*cis*-β-[Co(ven)en]-ClO_4 > Δ-*cis*-β-[Co(ven)(H_2O)$_2$]ClO_4. The higher stability of 'en' complexes should be explained by chelate effect of the present en.

Acknowledgments

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