Δ-*Sym-cis* AND Δ-*unsym-cis*-CARBONATO-(2*S*,2′*S*)-2,2′-ETHYLENE--BIS(2-AMINO-3-METHYLBUTANOATO)COBALTATE(III) ISOMERS*

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Dedicated to Prof. B. Hájek on the occasion of his 60th birthday.

The tetradentate ligand (2*S*,2′*S*)-2,2′-ethylene-bis(2-amino-3-methylbutanoato) (eddval) is co-ordinated in the [Co(eddval)CO$_3$]$^-$ anion to give 88% of Δ-*sym-cis* and 12% of Δ-*unsym-cis* isomers. The stereospecific formation of the Δ-*sym-cis* isomer is explained by steric crowding in the Λ-*sym-cis* isomer. The predominance of the *sym-cis* isomer indicates that the synthesis is also influenced by kinetic effects. These are particularly pronounced in the case of the Δ-*unsym*--*cis* isomer which for steric reasons is thermodynamically less stable than the Λ-*unsym-cis* isomer. The secondary nitrogen atoms in the Δ-*sym-cis* isomer are of the *R* configuration whereas in the Δ-*unsym-cis* isomer they have configuration *R* and *S*. The absolute configuration of the isomers has been determined from their absorption, CD, ^{1}H and ^{13}C NMR spectra. Acid hydrolysis of Δ-*sym-cis*-[Co(eddval)CO$_3$]$^-$ proceeds with retention of configuration to give the Δ-[Co(eddval)(H$_2$O)$_2$]$^+$ isomer.

The carbonato-bis((*S*)-valinato)cobaltate(III) anion can exist in three diastereo-isomeric pairs: *trans*(N)–*cis*(O), C$_2$-*cis*(N), and C$_1$-*cis*(N). Of them, only Λ-C$_1$--*cis*(N) and Λ-*trans*(N)** have been hitherto prepared[2,3]. A synthesis starting by replacement of the carbonate group in [Co(CO$_3$)$_3$]$^{3-}$ by (*S*)-valine, afforded[3] a 70 : 30 mixture of Λ-C$_1$-*cis*(N) and Λ-*trans*(N) isomers. Their ratio was time--dependent[5], indicating kinetic control of the reaction. Spontaneous equilibration of the C$_1$-*cis*(N) and *trans*(N) isomers[5] at higher temperature led to the above--mentioned isomer ratio.

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** Since the difference in tetragonal splitting of the absorption band due to $^1A_{1g} \rightarrow {}^1T_{1g}$ transition between *cis*(N) and *trans*(N)-[Co(AB)$_2$CO$_3$]$^-$ (AB denotes an amino acid anion) is small, the first eluted isomer of [Co((*S*)-Val$_2$CO$_3$]$^-$ was incorrectly assigned[3] the C$_2$-*cis*(N) geometry. Investigation[4] of absorption spectra of complexes [Co(AB)$_2$BB]$^-$ with chelate rings AB and BB of different size (AB denotes α-alaninate, BB oxalate or malonate) has shown that the degree of tetragonal splitting depends on the difference in the ligand field induced by the ligands. We use the correct description *trans*(N) throughout this paper.

An analysis of interactions introduced by the valine isopropyl groups has shown steric crowding in the Δ-*trans*(N) and Λ-C_2-*cis*(N) isomers. On the other hand, no such interactions are present in the Λ-, Δ-C_1-*cis*(N), Δ-C_2-*cis*(N), and Λ-*trans*(N) isomers. Since the bis(bidentate) system such as $Co((S)$-$Val)_2$ has direct relation to octahedral complexes of tetradentate ligands, we may expect that the discriminating steric effects will also be decisive in the formation of $[Co(eddval)CO_3]^-$ isomers. The present paper concerns the preparation, properties, and acid decarboxylation of the $[Co(eddval)CO_3]^-$ isomers.

EXPERIMENTAL

$(2S,2'S)$-2,2'-Ethylenebis(2-amino-3-methylbutanoate) (eddval) (*I*) was prepared according to Schoenberg *et al.*[6] from (S)-valine and 1,2-dibromoethane. The Δ-*sym-cis*- and Δ-*unsym-cis*- -$[Co(eddval)CO_3]^-$ isomers were obtained as described for preparation of $[Co(edda)CO_3]^-$ and separated by chromatography. Prior to the chromatography, the reaction mixture was desalted by evaporation *in vacuo* and extraction of the residue with methanol. Evaporation of the methanolic solution afforded a violet compound which was dissolved in water and applied on a column of Dowex 1X2 (Cl^- form, 100—200 mesh). Elution with 0·1M-NaCl gave two bands which were collected separately and cobalt content in the eluates was determined by atomic absorption. After evaporation, the residues were several times extracted with methanol. The methanolic extracts were concentrated, applied on a Sephadex G-10 column (Pharmacia, Uppsala, Sweden), eluted with 70% methanol and the solvent was evaporated. For $C_{13}H_{22}CoN_2NaO_7$ (400·2) calculated: 39·01% C, 5·53% H, 6·99% N; found for Δ-*sym-cis*: 39·09% C, 5·49% H, 6·39% N; found for Δ-*unsym-cis*: 38·97% C, 5·50% H, 6·40% N.

RESULTS AND DISCUSSION

According to steric requirements of the $Co((S)$-$Val)_2$ system, which is a part of the eddval ligand, the following four isomers should be preferred: Λ-, Δ-C_1-*cis*(N), Δ-C_2-*cis*(N), and Λ-*trans*(N). As shown previously[3], the substitution reaction (*A*)

$$[Co(CO_3)_3]^{3-} + (S)\text{-}Val \rightarrow [Co((S)\text{-}Val)_2CO_3]^- \tag{A}$$
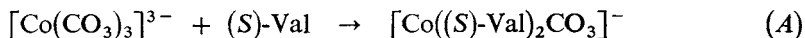
affords predominantly the Λ-C_1-*cis*(N) ismer. Thus, the geometry of this isomer should also be preserved in the $[Co(eddval)CO_3]$ anion. This complex was synthesized[3] by reaction of *I* with $K_3[Co(CO_3)_3]$. Chromatography of the product furnished two isomers which were identified using electronic absorption, ^{1}H and ^{13}C NMR, and CD spectra. The symmetrical absorption spectrum (positions and intensities of the bands are given in Table I) indicates the *cis*(N) geometry of both isomers. The same geometry was also derived from the NMR spectra (^{1}H NMR spectrum *sym-cis*: α-CH 2·86 ppm, *unsym-cis*: 2·85 and 3·14 ppm.; ^{13}C NMR spectrum *sym-cis*: α-C 75·0 ppm, *unsym-cis*: 71·0 and 77·3 ppm.

In the low-energy region of CD spectra both the isolated isomers exhibit two bands

of alternating signs (Fig. 1, Table I). These correspond to the components A and B of the $E(D_{4h})$ level. Since the $[Co(eddval)CO_3]^-$ anion has a C_2 symmetry (analogously to $[CoCl_2(en)_2]^+$) the absolute configuration can be determined using the Mason formalism. The low-energy $A(C_2)$ component (cis-N_2O_4 chromophore) retains[7] the sign of the component E_a $[Co(en)_3]^{3+}$. The E_a component is positive when the complex has configuration Λ and negative when its configuration is Δ (ref.[7]). On the basis of comparison of the components, the sym-cis isomer II (first eluted) has configuration $\Delta\Delta\Delta$ whereas the configuration of the $unsym$-cis isomer III
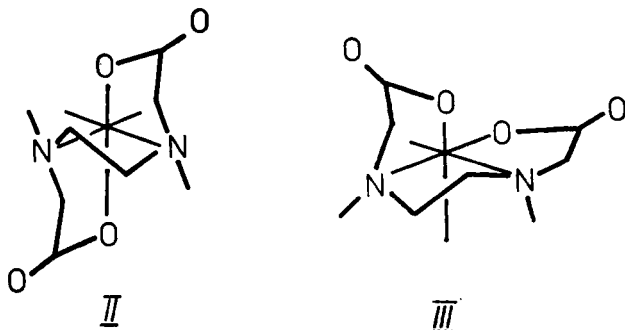
$\underline{II}$ $\underline{III}$

s $\Delta\Delta\Delta\Lambda$, or shortly $\Delta\Delta$. The observed difference in relative intensities of CD spectra of the isomers follows both from the different number of the chelate pairs of the Δ configuration in both isomers and from different contributions by the R and S nitrogen atoms. In the sym-cis isomer both the nitrogen atoms have configuration R whereas in the $unsym$-cis isomer their configuration is R and S. The N-vicinal contribution is positive for the R configuration and negative for the S configuration. Since the sign of N-vicinal contribution of the R nitrogen atoms in the sym-cis isomer are opposite to those of the configurational contribution, the rotational strength

TABLE I
Spectral parameters of $[Co(eddval)CO_3]^-$ isomers

Parameter	Δ-sym-cis	Δ-$unsym$-cis
UV absorption, λ_{max}, nm	550	556
	377	377
CD, λ_{max}, nm, ($\Delta\varepsilon$)	595 ($-3\cdot80$)	587($-2\cdot39$)
	490 ($+0\cdot79$)	480 ($+0\cdot26$)
	420 ($-0\cdot28$)	420 ($-0\cdot15$)
	370 ($-0\cdot17$)	360 ($-0\cdot09$)

of this isomer[8] is somewhat lower than that of the $sym\text{-}cis$-$[Co(edda)CO_3]^-$ isomer. On the contrary, the intensity of the lowest-energy CD band is comparable with the intensity of the corresponding band for $\Delta\text{-}sym\text{-}cis$-$[Co(eddpa)(en)]^+$ (ref.[6]). This indicates that the isopropyl groups, in spite of their considerable steric bulk, do not influence the degree of puckering of the chelate rings and do not distort the coordination sphere. The chiral contributions of the R and S nitrogen atoms in the Δ-$unsym\text{-}cis$ isomer compensate each other without any effect on its rotational strength.

According to models, the optimum conformation of the ethylene bridge depends on the overall geomery of the coordination sphere. In the $sym\text{-}cis$ isomer the ethylene bridge adopts the δ-conformation whereas the $unsym\text{-}cis$ arrangement enforces the λ form. Both these conformations, forced in principle by the α-CH—COO$^{(-)}$ part of the ligand that is axially oriented relative to the ethylenediamine ring, contribute to the rotational strength in the opposite sense. The opposite conformations, $i.e.$ λ in II and δ in III, in which the —CH—COO$^{(-)}$ group is equatorial, are not probable because they lead to considerable deformation of the bond angles.

According to the coordination mode of the carboxyl group, the $[Co(eddval)CO_3]^-$ anion may exist as the $sym\text{-}cis$ and $unsym\text{-}cis$ isomer. The predominance of the $sym\text{-}cis$ isomer (non-equilibrium conditions, $sym\text{-}cis$: $unsym\text{-}cis$ 88 : 12), characteristic of complexes $[Co(edda)LL]^{n+}$ with monovalent ligands LL, follows from the smaller steric interactions between the ligands edda and LL (ref.[9]). These interactions are present neither in $[Co(eddval)CO_3]^-$ nor in $[Co((S)\text{-}Val)_2CO_3]^-$.

The mutual relation of the isopropyl groups represents a specific discriminating factor in the $[Co(eddval)CO_3]^-$ system determining, on the basis of steric requirements in the structural unit $Co((S)\text{-}Val)_2$, the existence (or selection) of the isomers $sym\text{-}cis$, $unsym\text{-}cis$, as well as the isomers Λ, Δ-C_1-$cis(N)$, Δ-C_2-$cis(N)$, and Λ-
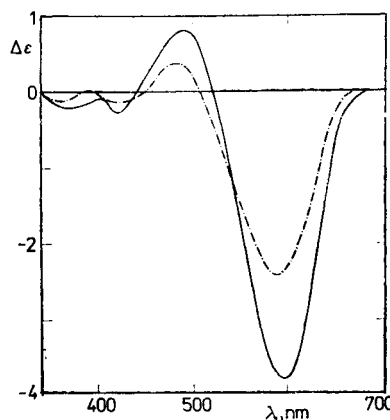
FIG. 1
Circular dichroism spectra of Δ-$sym\text{-}cis$
——— and Δ-$unsym\text{-}cis$ –·–·–·– isomers

-*trans*(N)-$[Co((S)\text{-Val})_2 CO_3]^-$. In addition to these interactions, one has also to consider interactions between the isopropyl groups and the —CH_2— groups of the ethylenediamine part of the ligand. This interaction, most important in the Λ-*sym-cis* isomer, may be the reason why this isomer does not appear in the reaction mixture. A similar steric crowding may also occur in the Δ-*unsym-cis* isomer but in this case it can be avoided by a small conformational distortion of the ethylene-diamine ring. On the other hand, the Λ-*unsym-cis* isomer, without any interaction of the isopropyl group with the —CH_2— group of the ethylene bridge, was not identified among the products. One, but not the sole, reason may be the unfavourable envelope conformation of ethylenediamine ring in the Λ-*unsym-cis* configuration. We also cannot exclude a kinetically controlled inversion Λ-*unsym-cis* → Δ-*sym-cis*, observed[10] in the case of $[Co(edda)CO_3]^-$.

If the formation of the $[Co(eddval)CO_3]^-$ isomers is thermodynamically con-trolled, the *unsym-cis* isomer should predominate among the products because it is much more stable than the *sym-cis* isomer[9]. However, since the synthesis of $[Co(eddval)CO_3]^-$ leads to an 88 : 12 ratio of the *sym-cis* to *unsym-cis* isomers, we may justifiably assume that the synthesis is controlled rather by kinetic effects, such as the mentioned inversion-isomerization and the destabilizing effect of the carbonate group. The latter is suppressed, but not completely eliminated, by the ethylene bridge. The ethylene bridge also represents the only structural difference between octahedral complexes of bidentate and tetradentate ligands containing $Co((S)\text{-Val})_2$ as the structural unit. It is therefore clear that the presence of the bridge affects the isomer population in the reaction mixture and determines their chirality: the synthesis of $[Co((S)\text{-Val})_2 CO_3]^-$ leads[3] to Λ isomers of C_1 and C_2 symmetry in the ratio 70 : 30 (the isomers C_2 and C_1 correspond to the respective isomers *sym-cis* and *unsym-cis*-$[Co(eddval)CO_3]^-$) whereas in the synthesis of $[Co(eddval)CO_3]^-$ only Δ isomers are formed.

The acid-catalyzed decarboxylation of $[Co(eddval)CO_3]^-$ (Eq. *B*) proceeds with retention of configuration, as follows from comparison of the

$$\Delta\text{-}sym\text{-}cis\text{-}[Co(eddval)CO_3]^- \xrightarrow{\text{H}^+} \Delta\text{-}[Co(eddval)(H_2O)_2]^+ \qquad (B)$$
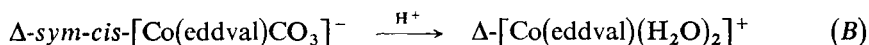
published[11] chiroptical data of the diaqua complexes (Eq. *B*, $\Delta\varepsilon_{550} = -1.30$, $\Delta\varepsilon_{470} = +0.39$, $\Delta\varepsilon_{385} = -0.24$).

REFERENCES

1. Abdel-Moez S., Jursík F.: *Proc. 10th Conf. Coord. Chem., Smolenice 1985*, p. 1.
2. Shibata M., Nishikawa H., Nishida Y.: Inorg. Chem. *7*, 9 (1968).
3. Jursík F., Ondráčková J., Hájek B.: This Journal *50*, 1582 (1985).
4. Jursík F.: unpublished results.
5. Jursík F., Hájek B.: Sb. Vys. Sk. Chem.-Technol. Praze, Anorg. Chem., Chem. Technol. B *31*, 5 (1986).
6. Schoenberg L. N., Cooke D. W., Liu C. F.: Inorg. Chem. *7*, 2386 (1986).
7. McCaffery A. J., Mason S. F., Norman B. J.: J. Chem. Soc. *1985*, 5094.
8. Van Saun C. W., Douglas B. E.: Inorg. Chem. *8*, 115 (1969).
9. Garnett P. J., Watts D. W., Legg J. I.: Inorg. Chem. *8*, 2534 (1969).
10. Cox M. A., Griffiths R. H., Williams P. A., Vagg R. S.: Inorg. Chim. Acta *103*, 155 (1985).
11. Strašák M., Bachratý F., Majer J.: This Journal *47*, 210 (1982).

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