STEREOCHEMICAL CHANGES ACCOMPANYING ACID DECARBOXYLATION OF THE Λ-[Co((S)-VALINATO)₂CO₃]⁻ ISOMERS

František Jursík, Jana Ondráčková and Bohumil Hájek

Department of Inorganic Chemistry
Prague Institute of Chemical Technology, 166 28 Prague 6

Λ-*trans*(O)-[Co((S)-Val)₂CO₃]⁻ (Val = valine) reacts with 1M-HNO₃ (3 min, 28°C) to form 90% *trans*(O) and 10% *cis*(N)-[Co((S)-Val)₂(H₂O)₂]⁺. Addition of solid KHCO₃ to the reaction mixture containing diaquo species gives 96% (95% Λ) *trans*(O)- and 4% (56% Λ) C₁-*cis*(N)--[Co((S)-Val)₂CO₃]⁻ isomers indicating decarboxylation of *trans*(O) isomer proceeds without change in configuration. Acid decarboxylation of Λ-C₁-*cis*(N)-[Co((S)-Val)₂CO₃]⁻ leads to the mixture consisting from 65% of *cis*(N)- and 35% of *trans*(O)-[Co((S)-Val)₂(H₂O)₂]⁺. When this reaction mixture is treated with solid KHCO₃, 61% (92% Λ) of C₁-*cis*(N)- and 39% (95% Λ) of *trans*(O)-[Co((S)-Val)₂CO₃]⁻ isomers are formed. Results show that stereochemistry of acid decarboxylation products depends on the starting isomer geometry suggesting steric and electronic factors contribute to isomer proportions.
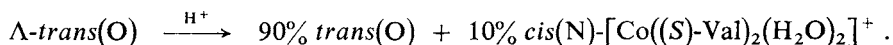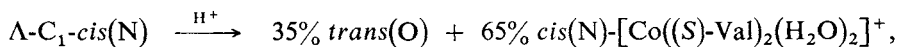
It is well established fact that hydrolysis (decarboxylation) of carbonato group in cobalt(III) complexes proceeds with the retention of configuration[1]. However, in contrast to these findings Gillard and Price[2] observed that the reaction of Λ-C₁--*cis*(N)-[Co((S)-Val)₂CO₃]⁻ (Val = valine) with HClO₄ gives Δ-[Co((S)-Val)₂.(H₂O)₂]⁺.

The study in the course of which the present data were obtained was undertaken in order to gain essential informations about the stereochemistry of intermediate ligand field cobalt(III) complexes and to reexamine the acid decarboxylation of [Co((S)-Val)₂CO₃]⁻ complexes in relation to the isomer geometry.

The complex Na[Co((S)-Val)₂CO₃] was prepared according to Shibata and co-workers[3] starting from K₃[Co(CO₃)₃]. The geometrical isomers (details concerning their characterization will be published[4]) were separated by ion exchange chromatography. Two distinct bands were separated on the column. The first compound eluted from the column was identified as *trans*(O)-*cis*(N) isomer while the second eluted compound was identified as *cis*(N)-*cis*(O) (C₁-*cis*(N)) isomer. All isomers were identified by their electronic absorption, circular dichroism and ¹H NMR spectra (Table I). Both ¹H NMR and electronic absorption spectra were consistent with the C₂ and C₁ symmetry of isomers obtained, while strong positive CD band observed under the ¹T₁g manifold, similarly as exert [Co(AB)₂ox]⁻ (AB = amino acid)

isomers[5,6], suggest that isomers have the Λ absolute configuration. The isomer ratio was *trans*(O) : C$_1$-*cis*(N) 30 : 70. Repeated experiments gave nearly the same isomer proportion indicating equilibrium in the preparative reaction.

Individual carbonato isomers undergo instantly H$^+$ induced aquation with opening of a chelated carbonate. However, regardless of whether the starting complex was either one of the two isomers a mixture of diaquo products is yielded which can be separated into two fractions on a column of cation exchange resin:

$$\Lambda\text{-C}_1\text{-}cis(\text{N}) \xrightarrow{\text{H}^+} 35\% \ trans(\text{O}) + 65\% \ cis(\text{N})\text{-}[\text{Co}((S)\text{-Val})_2(\text{H}_2\text{O})_2]^+,$$

$$\Lambda\text{-}trans(\text{O}) \xrightarrow{\text{H}^+} 90\% \ trans(\text{O}) + 10\% \ cis(\text{N})\text{-}[\text{Co}((S)\text{-Val})_2(\text{H}_2\text{O})_2]^+.$$

The hydrolysis products were not isolated, but they were characterized in solution by their absorption and circular dichroism spectra (Fig. 1, 2, Table I). As can be expected the coordination of two valine molecules gives rise to two *cis*(N) isomers. It should be pointed out, however, that it is difficult to discriminate between C$_1$- and C$_2$-*cis*(N) isomers solely on the basis of the visible absorption spectra. Electronic spectra obtained together with chromatographic behaviour[7] confirm thus only *cis*(N) and *trans*(O) configuration of the aquo forms, while ^{1}H NMR spectroscopy assigned[2] C_2 symmetry to *cis*(N) isomer. Furthermore, connection of the negative sign of the circular dichroism band in the $^1T_{1g}$ spectral region with absolute configuration suggests that diaquo species produced here, similarly as found Gillard and Price[2], should have the Δ configuration. It must be stressed, however, that the circular dichroism spectra recorded correspond to species which can be converted only partially back to Λ-[Co((S)-Val)$_2$CO$_3$]$^-$ due to the isomerization
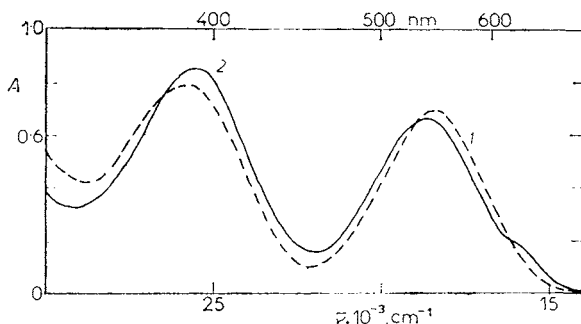

FIG. 1

The electronic absorption spectra of [Co((S)-Val)$_2$(H$_2$O)$_2$]$^+$ isomers. *1 cis*(N), *2 trans*(O)

TABLE I

Electronic absorption (nm), circular dichroism and ^{1}H NMR chemical shifts (ppm) of $[Co((S)$-$Val)_2XX]^{\pm}$ isomers

Isomer	$\lambda_{max}(\varepsilon)$	δ_{CH_3}	$CD_{max}(\Delta\varepsilon)$
	$[Co((S)$-$Val)_2CO_3]^-$		
Λ-$trans$(O)	$550^a(87\cdot1)$, $394(115\cdot6)$	$1\cdot35$ d, $0\cdot95$ d	$548(+4\cdot50)$
Λ-C_1-cis(N)	552 $(83\cdot8)$, $398(106\cdot0)$	$1\cdot20$ q, $0\cdot94$ q	$558(+3\cdot48)$
	$[Co((S)$-$Val)_2(H_2O)_2]^+$		
$trans$(O)^b	$538^c(82\cdot1)$, $390(98\cdot8)$	—	$523(-1\cdot75)$ $385(+0\cdot30)$
cis(N)^b	540 $(86\cdot9)$, $387(94\cdot1)$	—	$532(-0\cdot48)$ $400(+0\cdot12)$
$trans$(O)^d	$537^c(82\cdot0)$, $390(89\cdot0)$	—	$522(-1\cdot71)$ $390(+0\cdot50)$
cis(N)^d	541 $(87\cdot0)$, $295(94\cdot8)$	—	$530(-0\cdot54)$ $400(+0\cdot10)$

^{a} Shoulder approx. at 616 nm; ^{b} product of decarboxylation of Λ-$trans$(O)-$[Co((S)$-$Val)_2CO_3]^-$; ^{c} shoulder approx. at 625 nm; ^{d} product of decarboxylation of Λ-C_1-cis(N)-$[Co((S)$-$Val_2)CO_3]^-$; ^{e} shoulder approx. at 625 nm.
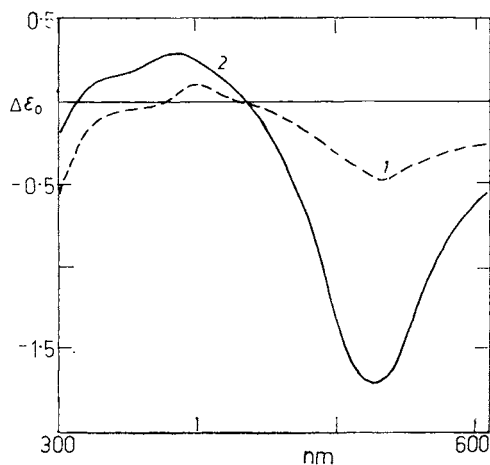
FIG. 2

The circular dichroism spectra of $[Co((S)$-$Val)_2(H_2O)_2]^+$ isomers. *1* cis(N), *2* $trans$(O)

and dimerization as noted Gillard and Price[2] and thus any conclusion concerning the absolute configuration of diaquo complexes is dubious.

In order to detect any change in configuration, in a separate experiment acid hydrolysis was quenched by the addition of solid KHCO$_3$ which rapidly and quantitatively converts $[Co((S)\text{-Val})_2(H_2O)_2]^+$ to $[Co((S)\text{-Val})_2CO_3]^-$ (as demonstrated Dwyer and coworkers[8], $\Lambda\text{-}cis\text{-}[Co(en)_2(H_2O)_2]^{3+}$ reacts with KHCO$_3$ under retention of configuration to give $\Lambda\text{-}[Co(en)_2CO_3]^+$). After chromatographic separation on a column of anion exchange resin two products irrespective to geometry of isomer used were obtained and their chiroptical properties were compared with those of pure $\Lambda\text{-}C_1\text{-}cis(N)\text{-}$ and $\Lambda\text{-}trans(O)\text{-}[Co((S)\text{-Val})_2CO_3]^-$ isomers. The reaction sequences of the decarboxylation and regeneration are summarized in the Scheme 1. As follows from the Scheme 1 the interconversion

$$[Co((S)\text{-Val})_2CO_3]^- \xrightarrow{\text{H}^+} [Co((S)\text{-Val})_2(H_2O)_2]^+ \xrightarrow{\text{HCO}_3^-}$$
$$\longrightarrow [Co((S)\text{-Val})_2\text{-}CO_3]^-$$
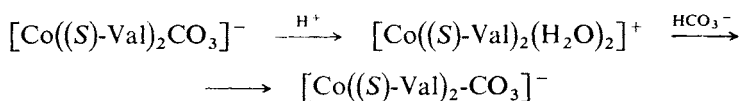
proceeds with the formation of a mixture composition of which is (within the experimental errors) very close to those obtained in the decarboxylation step demonstrating retention in the regeneration of carbonato complex.

$\Lambda\text{-}C_1\text{-}cis(N)\text{-}[Co((S)\text{-Val})_2CO_3]^-$, $[M]_D = +3\,743°$

$\text{H}^+/\text{HCO}_3^-$

39% $\Lambda\text{-}trans(O)$
$(\varepsilon_{392} = 116.2, \varepsilon_{551} = 88.0$
$[M]_D = +3\,727°)$

61% $\Lambda\text{-}C_1\text{-}cis(N)$
$(\varepsilon_{398} = 107.7, \varepsilon_{552} = 84.5$
$[M]_D = +3\,443°)$

$\Lambda\text{-}trans(O)\text{-}[Co((S)\text{-Val})_2CO_3]^-$, $[M]_D = +3\,912°$

$\text{H}^+/\text{HCO}_3^-$

96% $\Lambda\text{-}trans(O)$
$(\varepsilon_{396} = 115.0, \varepsilon_{550} = 88.5,$
$[M]_D = +3\,718°)$

4% $\Lambda\text{-}C_1\text{-}cis(N)$
$(\varepsilon_{398} = 106.4, \varepsilon_{555} = 82.9,$
$[M]_D = +2\,096°)$
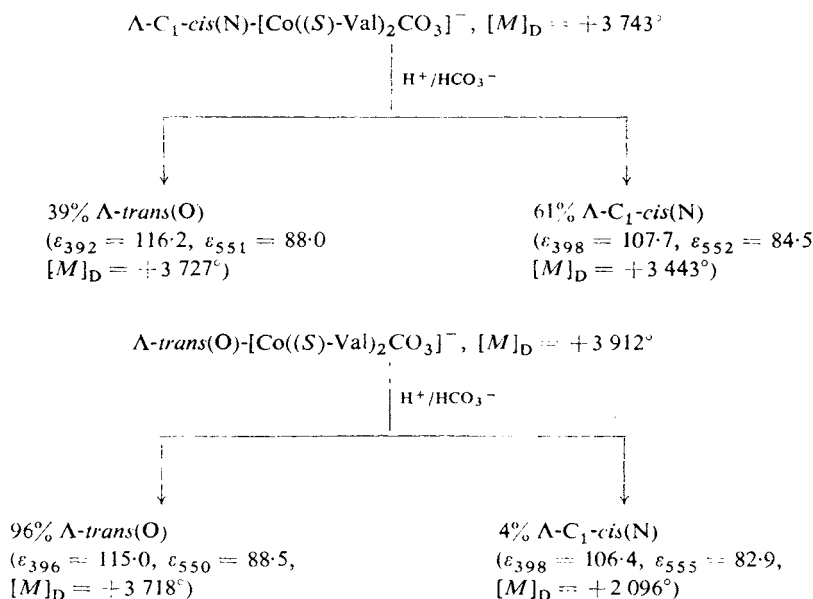
SCHEME 1

Results obtained show that both Λ-*trans*(O)- and Λ-C_1-*cis*(N)-$[Co((S)\text{-Val})_2CO_3]^-$ isomers give a mixture of the same products but not in the same ratio suggesting that decarboxylation is to some extent kinetically controlled: Λ-*trans*(O) isomer does not isomerize (98% retention) and remains essentially fully active (85%). On the other hand Λ-C_1-*cis*(N)-$[Co((S)\text{-Val})_2CO_3]^-$ isomer decarboxylates with stereochange to give 39% (95% Λ) *trans*(O)- and 61% (92% Λ) C_1-*cis*(N)-$[Co((S)\text{-Val})_2$.$.CO_3]^-$. At the same time activity of C_1-*cis*(N) isomer depends on whether it is a product of isomerization or not, indicating some racemization of the more labile isomer in the course of protonation or isomerization occurred. It is obvious from the results obtained that the stereochemistry of the reaction products of $[Co((S)\text{-Val})_2$.$.CO_3]^-$ decarboxylation depends markedly on the starting isomer geometry which suggests steric and electronic factors may also contribute to isomer proportions. We are aware that knowledge of the products distribution for the reactions of $[Co((S)\text{-Val})_2CO_3]^-$ isomers does not necessarily lead to an unequivocal assignment of mechanism of acid decarboxylation. However, in the light of results[9] concerning aquation of $[Co(en)_2XY]^{n+}$ complexes, it may be that both protonation of $[Co((S)$-$.Val)_2CO_3]^-$ and isomerization of $[Co((S)\text{-Val})_2(H_2O)_2]^+$ proceeds *via* five-coordinated trigonal bipyramidal intermediate, even in the case of *trans*(O) isomer which decarboxylates with the retention of configuration.

Acid decarboxylation of Λ-C_1-*cis*(N)-$[Co((S)\text{-Val})_2CO_3]^-$ isomer proceeds as mentioned with some stereochange. Optical activity measurements excluded the predominance of Δ isomer suggesting that the decarboxylation does not go with the inversion at the cobalt center. Any amount of the Δ isomer in the regenerated carbonato complex can be ascribed to the isomerization and racemization of the diaquo complex which is a common feature of these species. The inversion which could be imposed for example by the relief of appropriate steric crowding in one diastereoisomer need not to be considered because steric interactions between two isopropyl groups as a main source of the steric strain are, as follows from molecular models, just missing in Λ isomers, although some differences between Δ-*trans*(O) and Δ-C_1-$.cis$(N) isomers from the view of steric requirements can be observed. Lower degree of nonbonding interactions in Δ-C_1-*cis*(N) isomer may cause that this isomer can occur in the reaction mixture in greater proportion than the sterically less favoured Δ-*trans*(O) one. Furthermore, the fact that Λ-*trans*(O) and Λ-C_1-*cis*(N) isomers, both free of nonbonding interactions, give different product ratios supports our opinion that the relief of steric strain cannot be the principal factor in the steric course, although it may be important in discrimination of the reaction intermediates. However, as showed the acid decarboxylation of the C_1-*cis*(N)-$[Co(Gly)_2CO_3]^-$ (Gly = glycine) isomer, product distribution (10% *cis*(N)-*trans*(H$_2$O), 40% *trans*(N) and 50% *cis*(N)-$[Co(Gly)_2(H_2O_2]^+$) markedly depends on the steric bulkiness of the substituent protruding from the α-carbon atom of the amino acid.

EXPERIMENTAL

Electronic absorption spectra were recorded on a Specord UV VIS spectrophotometer (C. Zeiss, Jena). Optical rotations were obtained on a Perkin–Elmer 241 spectropolarimeter. A Roussel Jouan 185 Model II Dichrograph was used to record the circular dichroism spectra.

Λ-C$_1$-*cis*(N), Λ-*trans*(O)-Na[Co((S)-Val)$_2$CO$_3$] and C$_1$-*cis*(N)-Na[Co(Gly)$_2$CO$_3$] isomers were obtained according to literature[3,4]. For Λ-C$_1$-*cis*(N)-Na[Co((S)-Val)$_2$CO$_3$].3 H$_2$O (428·2) calculated: 30·86% C, 6·12% H, 6·54% N; found: 30·61% C, 5·71% H, 6·21% N. For Λ-*trans*(O)--Na[Co((S)-Val)$_2$CO$_3$].2·5 H$_2$O.NaCl (477·6) calculated: 27·66% C, 5·28% H, 5·87% N; found: 27·49% C, 5·77% H, 6·15% N. For C$_1$-*cis*(N)-Na[Co(Gly)$_2$CO$_3$].2·5 H$_2$O (335·1) calculated: 17·92% C, 3·91% H, 8·36% N; found: 18·22% C, 4·03% H, 8·25% N.

Acid decarboxylation: 0·2 g of appropriate isomer was allowed to react with 10 ml of 1M-HNO$_3$ in a thermostat at 28°C for 3 min. The mixture was diluted to 100 ml and adsorbed on a Dowex 50WX8 (100—200 mesh, Na$^+$ cycle) ion exchange column. The band adsorbed on the top was washed with water and then eluted with 0·1M-NaClO$_4$ acidified with HClO$_4$ to pH 4—5. Two distinct bands were separated. The [Co] in the eluates of the known volume was determined by atomic absorption. Both eluates were characterized by electronic and circular dichroism spectra.

Regeneration of carbonato complexes: 0·2 g of either Λ-*trans*(O) or Λ-C$_1$-*cis*(N)-Na[Co((S)--Val)$_2$CO$_3$]$^-$ isomer was dissolved in 5 ml of 1M-HNO$_3$ at 28°C in a thermostat. After 3 min excess of solid KHCO$_3$ was added. When the colour of the mixture changed from red-violet to violet, solution was evaporated *in vacuo* at 30°C. The solid obtained was dissolved in methanol, insoluble material was filtered off and filtrate after dilution with water was applied on the Dowex 1X8 (100—200 mesh, Cl$^-$ cycle) ion exchange column. After the column was swept with water, two bands were eluted with 0·05M-NaClO$_4$. The [Co] in the eluates of the known volume was determined by atomic absorption and eluates were further characterized by electronic absorption spectra, circular dichroism spectra and by optical rotations.

REFERENCES

1. Basolo F., Pearson R. G.: *Mechanism of Inorganic Reactions*, p. 137. Wiley, New York 1958.
2. Gillard R. D., Price G. G.: J. Chem. Soc. (A) *1971*, 2271.
3. Shibata G., Nishikawa H., Nishida Y.: Inorg. Chem. *7*, 9 (1968).
4. Jursík F., Ondráčková J., Hájek B.: Unpublished results.
5. Matsuoka N., Hidaka J., Shimura Y.: Bull. Chem. Soc. Jap. *40*, 1868 (1967).
6. Matsuoka N., Hidaka J., Shimura Y.: Inorg. Chem. *9*, 719 (1970).
7. Jursík F. in the book: *Liquid Column Chromatography. A Survey of Modern Techniques and Applications* (Z. Deyl, K. Macek, J. Janák, Eds), J. Chrom. Library, p. 1087. Elsevier, Amsterdam 1975.
8. Dwyer F. P., Sargeson A. G., Reid I. K.: J. Amer. Chem. Soc. *85*, 1215 (1963).
9. Chan S. C., Tobe G. L.: J. Chem. Soc. *1963*, 5700.

Translated by the author (F. J.).