# STEREOCHEMISTRY OF [CARBONATO-BIS((*S*)-PROLINATO)]-COBALTATE(III) ANION

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The $\Lambda$-$C_1$-*cis*(N), $\Delta$-$C_1$-*cis*(N), $\Lambda$-$C_2$-*cis*(N) and $\Delta$-$C_2$-*cis*(N) isomers of the complex K[Co((S)-Pro)$_2$CO$_3$] were chromatographically separated and characterized by their electronic absorption spectra and CD spectra.

In metal complexes of the type $[Co(AB)_2CO_3]^-$ (where AB is an amino acid anion) the $CoN_2O_4$ chromophore determines the existence of three geometric isomers (Fig. 1) each of which, because of configurational chirality, represents a pair of $\Lambda$ and $\Delta$ diastereoisomers.

The aim of this work is stereochemical study of such complexes, since they belong to compounds which, similarly to $[Co\,en_2CO_3]^+$, are suitable starting material for investigation of a number of substitution reactions[1,2]. Complexes $[Co(AB)_2.CO_3]^-$, where AB = Gly, (S)-Val or (S)-Ala, as starting compounds for preparation of mixed complexes $[Co(AB)_2(A'B')]$, were studied by Shibata and coworkers[3]. Gillard and Price[4] described the course of acid hydrolysis of the $(+)_{589}$-*cis*(N)-*cis*(O)-[Co((S)-Val)$_2$CO$_3$]$^-$ isomer with change of absolute configuration. They prepared also carbonate complexes with other (S)-amino acids such as leucine, isoleucine, alanine and phenylalanine.

The specific feature of proline, *i.e.* the steric demands of the pyrrolidine rings and chirality of the nitrogen atom, led us to a more detailed study of the cobalt(III) complex K[Co((S)-Pro)$_2$CO$_3$].

## EXPERIMENTAL

### Chemicals and Apparatus

(S)-Proline ($[\alpha]_D$ −52 to 55° (0·5M-HCl)) was purchased from Reanal (Budapest, Hungary). Column chromatography was performed on Dowex 1X8AG, column 200/400 mesh, thin-layer chromatography (TLC) on Silufol plates (Kavalier, Sázava, Czechoslovakia). Electronic absorption spectra were taken on a Specord UV-VIS spectrometer (Carl Zeiss, G.D.R.) and CD spectra on a Roussel Jouan 185 instrument, Model II. Electrophoresis was carried out on a low-voltage electrophoresis apparatus (Carl Zeiss, G.D.R.).

Preparation of $K[Co((S)\text{-}Pro)_2CO_3]$

The title complex was prepared according to the method of Shibata and coworkers[3]. The salts (KCl, $KHCO_3$) present in the reaction mixture were precipitated by repeated addition of ethanol, filtered and the product-containing filtrate was taken down under reduced pressure. The dry residue obtained was dissolved in water and the solution passed through a column of an anion-exchanging resin ($HCO_3^-$ form). Water eluted $[Co((S)\text{-}Pro)_3]$ whereas elution with 0·05M-$KHCO_3$ gave two fractions, containing the isomers $P_1$ and $P_2$ of the composition $K[Co((S)\text{-}Pro)_2CO_3]$. Addition of an excess of ethanol to the concentrated eluates removed another portion of $KHCO_3$. Further concentration of the solutions afforded the crystalline geometric isomers. The purity of each eluate was checked by electrophoresis and thin-layer chromatography. The $R_F$ values (Silufol, ethanol–water 80 : 20) for the obtained compounds $P_1$ and $P_2$ are 0·25 and 0·38, respectively. For $P_1$ $K[Co((S)\text{-}Pro)_2CO_3].3\,H_2O.KHCO_3$ (534·4) calculated: 24·70% C, 4·30% H, 5·24% N; found: 24·50% C, 4·35% H, 5·30% N. For $P_2$ $K[Co((S)\text{-}Pro)_2CO_3].2\,H_2O.\,1{\cdot}3\,KHCO_3$ (552·4) calculated: 24·61% C, 3·85% H, 5·07% N; found: 24·42% C, 3·72% H, 5·10% N.

Each of the geometric isomers ($P_1$ and $P_2$) was further chromatographed on a column of Dowex ($HCO_3^-$ form) with 0·05M-$KHCO_3$ as eluting agent, collecting 5 ml fractions whose optical rotation was measured. In both cases the optical isomers were separated, the $(+)_{589}$ isomer being eluted first. On the basis of colour intensity of the chromatographic bands the ratio of the obtained isomers was estimated to be roughly $P_1(+)_{589} : P_1(-)_{589} : P_2(+)_{589} : P_2(-)_{589} = 1 : 2 : 1 : 20$.

## RESULTS AND DISCUSSION

Of the three theoretically possible geometric isomers with the chromophore $CoN_2O_4$ only two were obtained in the case of the complex $K[Co((S)\text{-}Pro)_2CO_3]$. The electronic absorption spectra (Fig. 2) of solutions of both isomers $P_1$ and $P_2$, obtained chromatographically, exclude the presence of the *trans*(N)-*cis*(O) isomer, since no splitting of the first absorption band corresponding to the magnetic dipole allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition[5] was observed. Absorption spectra of both the obtained *cis*(N)-isomers are very similar and, like the complexes $[Co(AB)_2ox]^-$ (AB =

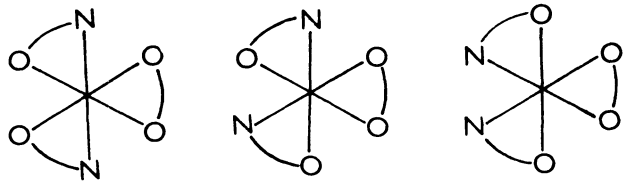


FIG. 1

Geometric isomers of $[Co((S)\text{-}Pro)_2CO_3]^-$; *a* *trans*(N)-*cis*(O), *b* *cis*(N)-*cis*(O), *c* *cis*(N)-*trans*(O)

= (S)-Ala, (S)-Ser,Gly; chromophore $CoN_2O_4$), the isomers $C_2$-*cis*(N) and $C_1$-*cis*(N) differ in position of the second absorption band[6]. The band of the $C_2$-*cis*(N) isomer ($P_1$) is shifted towards higher energies (360 nm) as compared with the $C_1$-*cis*(N) isomer ($P_2$; 410 nm).

Both the *cis*(N) isomers were separated into the diastereoisomers the CD spectra of which are depicted in Fig. 3. In addition to the configurational chirality and the C-vicinal effect, also the chirality of the nitrogen donor atom contributes to the chiroptical properties. The course of the CD spectra corresponds to those of complexes with the $CoN_2O_4$ chromophore and *cis*(N) arrangement of the donor atoms. The absolute configuration of all the isomers can be determined from the sign of the principal CD band in the first absorption region[7], *i.e.* $P_1(+)_{589}\Lambda$, $P_1(-)_{589}\Delta$, $P_2(+)_{589}\Lambda$, $P_2(-)_{589}\Delta$.

The absolute configuration can be also deduced from the $^1H$ NMR spectra in which the mutual position of the rigid (S)-proline rings manifests itself by the characteristic change of the signal multiplicities[8] due to the dipole–dipole interaction between protons of the pyrrolidine rings.

The difference in the CD spectra of the isomers $C_1$-*cis*(N) and $C_2$-*cis*(N) is apparent in the region of the second absorption band, particularly when the absolute

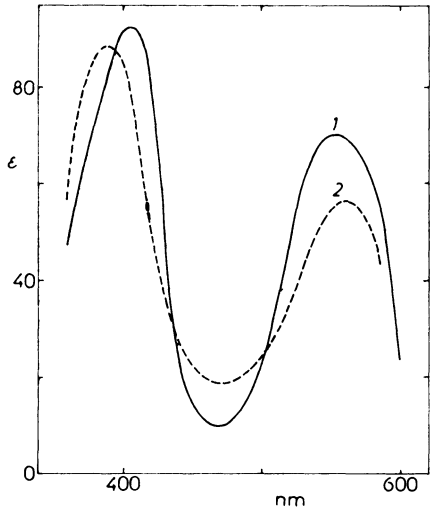


FIG. 2

Electronic absorption spectra of the isomers of K[Co((S)-Pro)$_2$CO$_3$]; *1* $C_1$-*cis*(N), *2* $C_2$-*cis*(N)

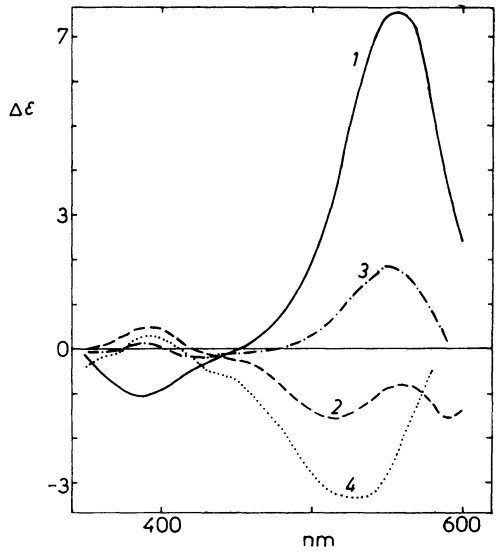


FIG. 3

CD Spectra of the isomers of K[Co((S)-Pro)$_2$.CO$_3$]; *1* $\Lambda$-$C_2$-*cis*(N), *2* $\Delta$-$C_2$-*cis*(N), *3* $\Lambda$-$C_1$-*cis*(N), *4* $\Delta$-$C_1$-*cis*(N)

configuration is *Λ*. In the spectrum of the *Λ*-$C_1$-*cis*(N) isomer ($P_2(+)_{589}$) the band is split into three components (−, +, −) whereas the spectrum of the *Λ*-$C_2$-*cis*(N) isomer ($P_1(+)_{589}$) exhibits only one negative component. The same difference in the CD spectra was observed[6,7] with $C_1$-*cis* and $C_2$-*cis* isomers of the complexes $[Co(AB)_2ox]^-$ and $[Co(AB)_2en]^+$. The signs of the three components in the higher energy region, observed with the *Λ*-$C_1$-*cis* isomers (+, −, +), are opposite to those for the *Λ*-$C_1$-*cis*(N) isomer of $K[Co((S)\text{-Pro})_2CO_3]$. This, as well as some other differences, observed particularly for the CD curves of the *Δ*-*cis*(N) isomers (Fig. 3), and the high positive $\Delta\varepsilon$ value of the dominant CD band of the *Λ*-$C_2$-*cis*(N) isomer, is ascribed to the effect of the chiral nitrogen atom in the coordinated (S)-proline. The position of this atom in the rigid five-membered ring forces its (*S*)-configuration. Due to the direct Co—N bond, its vicinal contribution is more effective[9] than that of chiral α-carbon atom.

Dreiding molecular models show that in the studied complex there are non-bonding interactions between the rigid five-membered rings of the coordinated (S)-proline molecules. Most important are the interactions between the 4-$CH_2$ groups of both pyrrolidine rings in the *Δ*-$C_2$-*cis*(N) and *Λ*-$C_1$-*cis*(N) isomers whereas interactions in the remaining two isomers are very weak. The preparation of the complex $K[Co((S)\text{-Pro})_2CO_3]$ gives predominantly the *Δ*-$C_1$-*cis*(N) isomer (see Experimental), *i.e.* the isomer with minimal non-bonding interactions. The preferential formation of this isomer (as compared with the *Λ*-$C_2$-*cis*(N) isomer) proves that for metal complexes with $CoN_2O_4$ chromophore the $C_1$-*cis* structure is more stable than the $C_2$-*cis* one, analogously as found[10] for complexes with the $CoN_4O_2$ chromophore.

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REFERENCES

1. Keyes W. E., Legg J. I.: J. Amer. Chem. Soc. *98*, 4970 (1976).
2. Chan S. C., Poon C. K.: J. Chem. Soc. (A) *146* (1966).
3. Shibata M., Nishikawa H., Nishida Y.: Inorg. Chem. *7*, 9 (1968).
4. Gillard R. D., Price M. G.: J. Chem. Soc. (A) *2271* (1971).
5. Yamatera H.: Bull. Chem. Soc. Jap. *31*, 95 (1958).
6. Matsuoka N., Hidaka J., Shimura Y.: Bull. Chem. Soc. Jap. *48*, 458 (1975).
7. Matsuoka N., Hidaka J., Shimura Y.: Inorg. Chem. *9*, 719 (1970).
8. Hájek B., Šrank Z., Sýkorová D.: Inorg. Chim. Acta L *76* (1983).
9. Yasui T.: Bull. Chem. Soc. Jap. *38*, 1746 (1965).
10. Matsuoka N., Hidaka J., Shimura Y.: Bull. Chem. Soc. Jap. *45*, 2491 (1972).

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