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### Thin-layer chromatographic separation of $\Delta$ -fac(N) and $\Delta$ -mer(N) isomers of tris(S-(+)- $\alpha$ -alaninato)cobalt (III)

$\alpha$ -Amino acids, which are bidentate ligands, coordinate around  $\text{Co}^{3+}$  in either  $\Delta(\text{C}_3)$  or  $\Lambda(\text{C}_3)$  absolute configuration (PIPER's notation<sup>1</sup>), while the unsymmetrical character of these ligands leads to geometrical isomerism. Many of the stereochemical questions are connected with both the rapid and the efficient separation of possible isomers. In the case of S-(+)- $\alpha$ -alanine, four isomers are known<sup>2,3</sup>:  $\Delta, \Delta$ -fac(N) and  $\Delta, \Delta$ -mer(N). From these, the  $\Delta$ -fac(N) isomer is quite insoluble in water and the  $\Delta$ -mer(N) one is only sparingly soluble. In the present note we describe the separation of geometrical isomers of  $\Delta$  configuration with the axial disposition of  $\text{CH}_3$  groups ( $k'k'k'$  arrangement of chelate rings, ob conformation with the C-C chelate axes oblique to the  $\text{C}_3$  axis of rotation<sup>4</sup>) (Fig. 1).

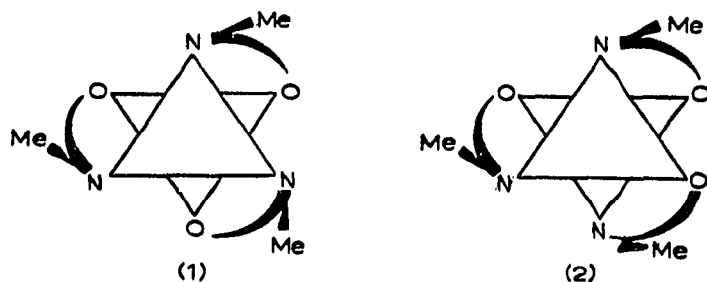


Fig. 1.  $\Delta$ -Fac(N) (1) and  $\Delta$ -mer(N) (2) isomers of  $\text{Co}(\text{S-(+)-}\alpha\text{-alaninate})_3$ . Projection around  $\text{C}_3$  axis of rotation.

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### Results

From the data given in Table I the following conclusions can be drawn. The best separation was achieved when the water content varied from 30 to 40%. The  $R_F$  values of the fac(N) isomer decrease with the decreasing polarity of the solvent systems used. Even though the polarity of isopropanol (based on dielectric constants<sup>5</sup>)

TABLE I

$R_F$  VALUES OF  $\Delta$ -fac(N) AND  $\Delta$ -mer(N) ISOMERS OF Co(S-(+)- $\alpha$ -ALANINATE)<sub>3</sub>

Isomer	Water content in the alcohol used (%)	
	30	40
	<i>Ethanol</i>	
fac(N)	0.55	0.70
mer(N)	0.71	0.75
	<i>n-Propanol</i>	
fac(N)	0.38	0.57
mer(N)	0.57	0.73
	<i>Isopropanol</i>	
fac(N)	0.43	0.56
mer(N)	0.67	0.81

is lower than that of *n*-propanol, higher  $R_F$  values were obtained in the former case and thus steric factors must be taken into account. Differences in solvation of CH<sub>3</sub> groups cannot be considered, because both isomers have their alkyl groups in the axial position. As in other octahedral cobalt(III) complexes, the mer(N) isomer (usually called *trans* or  $\alpha$ ) has higher  $R_F$  values than the fac(N) one<sup>6,7</sup>. Because both isomers differ only in their symmetry, we assume that separation occurs on account of the difference in dipole moments. Actually it was observed that in the systems with the more polar stationary phase, for the compounds with the lower dipole moment higher  $R_F$  values were obtained<sup>8</sup>. Dipole moment differences further lead to different adsorbability, which would be greater for fac(N) isomers. This was demonstrated by chromatography on different adsorbents, where  $R_F$  values of fac(N) isomers decreased in the order cellulose > silica gel > alumina, while  $R_F$  values of mer(N) isomers were almost constant (see Table II).

TABLE II

$R_F$  VALUES OF  $\Delta$ -fac(N) AND  $\Delta$ -mer(N) ISOMERS OF Co(S-(+)- $\alpha$ -ALANINATE)<sub>3</sub> ON DIFFERENT SORBENTS

Solvent system: *n*-propanol-*n*-butanol-water (4:3:3).

Isomer	Cellulose <sup>a</sup>	Silica gel <sup>b</sup>	Alumina <sup>c</sup>
fac(N)	0.35	0.29	0.20
mer(N)	0.49	0.49	0.44

<sup>a</sup> Bělá p. Bezděz, Č.S.S.R.

<sup>b</sup> MN-G, Macherey, Nagel & Co.

<sup>c</sup> Reanal, Hungary.

Using 70% isopropanol as solvent, we found that  $\Delta$ -fac(N) and  $\Delta$ -mer(N) isomers are formed initially (detectable after less than 5 min) in the reaction of  $\text{Co}(\text{OH})_3$  with S-(+)-, or RS- $\alpha$ -alanine, respectively. The same isomers were also detected in the reaction of  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  with the same ligands, although according to the literature<sup>2,9</sup> this method would give only insoluble  $\Delta$ -fac(N)-Co(S-, or RS- $\alpha$ -alaninate)<sub>3</sub>. These results, which will be published in more detail elsewhere, are supported by the fact that in  $\text{Co}(\alpha\text{-amino-acidate})_3$  complexes little stereospecificity occurs.

### Experimental

Geometrical isomers of  $\text{Co}(\text{S-(+)-}\alpha\text{-alaninate})_3$  were prepared according to DENNING AND PIPER<sup>3</sup> and characterized on the basis of elemental analysis, electron absorption spectra ( $\Delta$ -fac(N):  $\lambda_{\text{max}} = 375$  and  $520 \mu\text{m}$ ,  $\epsilon = 150$  and  $188$ ;  $\Delta$ -mer(N):  $\lambda_{\text{max}} = 375$  and  $535 \mu\text{m}$ ,  $\epsilon = 95$  and  $60$ ), and specific rotation ( $\Delta$ -fac(N):  $[\alpha]_{\text{D}} = -986^\circ$ ;  $\Delta$ -mer(N):  $[\alpha]_{\text{D}} = -655^\circ$ ).

Chromatography was carried out on silica gel coated (MN-G, Macherey, Nagel & Co.) glass plates (10 × 20 cm). Ten microlitres of an approximately  $1 \cdot 10^{-4} M$  solution of isomers were applied on the starting line (1 cm from the lower edge of the plates). The plates were developed to a height of 10 cm. Detection was made with  $\text{Na}_2\text{S}$ .

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