CHROM. 3482

Thin-layer chromatographic separation of *cis–trans* isomers of trisglycinatocobalt (III)

In the course of our studies of metal amino acid complexes we observed that an aqueous solution of bisglycinatocobalt(II) in the presence of glycine is slowly oxidized by air and trisglycinatocobalt(III) is formed[1]. Starting from the fact that cobalt(III) complexes of monoaminomonocarboxylic acids generally exist in four isomeric forms, the problem arose of the separation of possible isomers formed by the reaction mentioned and the analysis of the reaction mixture, which also contained bisglycinatocobalt(II).

Trisglycinatocobalt(III) exists in the two geometrical isomers which are racemates and differ from each other in solubility and symmetry. Considering the nature of the compounds to be separated, a suitable solvent system and stationary phase had to be used. By employing buffered cellulose layers, separation of bisglycinatocobalt(II) and *cis–trans* isomers of trisglycinatocobalt(III) on the same chromatogram was

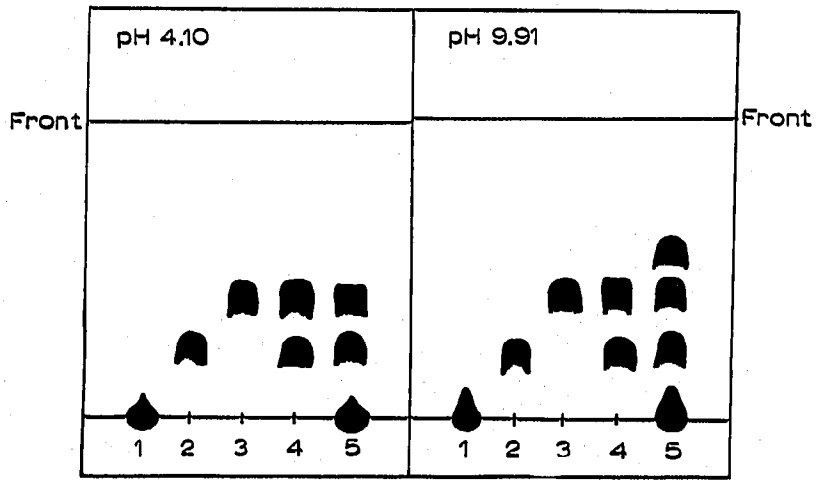

Fig. 1. Cellulose thin-layer chromatograms of bisglycinatocobalt (II) (1), *cis* trisglycinatocobalt(III) (2), *trans* trisglycinatocobalt(III) (3), a mixture of *cis–trans* isomers of trisglycinatocobalt(III) (4), and a reaction mixture of bisglycinatocobalt(II) after oxidation by air (5).

possible. As may be noted from the data presented in Table I (and in Fig. 1), bisglycinatocobalt(II) has an R_F value of zero. This is due to its low stability in an aqueous solution (formation of Co(II)-insoluble products). The *cis* isomer is practically insoluble in any solvent with the exception of electrolyte solutions and hence it must be concluded that the decrease in R_F value with the increasing ionic strength of the buffer used (see Table II) is a result of its increased solubility in the polar stationary phase (isopropanol–water system). The R_F values of the *trans* isomer were not affected by the ionic strength of the buffer. On the other hand, separation did not occur at lower ionic strength in the ethanol–water system. The independence of the R_F values on the distance from the start as well as of the load shows that the successful separation of isomers must be considered to be a result of partition. Isomers were separated following their expected dipole moments in accordance with observations of other authors on simple *cis* and

TABLE I

R_F VALUES OF Co(GLYCINATE)$_2$ AND *cis–trans* ISOMERS OF Co(GLYCINATE)$_3$ AT DIFFERENT pH

pH	*4.10*	*6.09*	*7.96*	*8.95*	*9.91*
Ionic strength	*1.93*	*1.74*	*1.17*	*1.08*	*0.99*
Solvent:	60% ethanol				
Co(glycinate)$_2$			0	0	0
Cis isomer	0.25	0.19	0.19	0.19	0.24
Trans isomer	0.42	0.38	0.41	0.42	0.42
Unidentified spot			0.48	0.50	0.57
Solvent:	60% isopropanol				
Co(glycinate)$_2$			0	0	0
Cis isomer			0.16	0.15	0.15
Trans isomer			0.32	0.40	0.39

trans complexes[2]. In all cases the *trans* isomer with low dipole moment had higher R_F values than the *cis* isomer.

Chromatography of the reaction mixture containing bisglycinatocobalt(II) and glycine, after oxidation by air, showed the presence of three compounds, the R_F values of which correspond to bisglycinatocobalt(II) (R_F value zero) and the *cis* and *trans* isomers of trisglycinatocobalt(III). The latter two were present in an equilibrium mixture, which may be due to the catalytic effect of the kinetically labile cobalt(II) complex. Moreover from pH 7.96 to 9.91, four spots were observed on the chromatogram, *e.g.*, bisglycinatocobalt(II), a pair of isomers of trisglycinatocobalt(III) and one unidentified spot. The R_F value of the latter increased with increasing pH suggesting that this compound had an anionic nature. With regard to the possible mechanism of formation of cobalt(III) complexes, it is probably by way of a polynuclear intermediate.

TABLE II

EFFECT OF IONIC STRENGTH OF THE BUFFERS ON THE R_F VALUES OF *cis–trans* ISOMERS OF Co(GLYCINATE)$_3$

Solvent: 60% isopropanol.

pH	*7.96*		*8.95*		*9.91*	
Ionic strength	*1.17*	*0.117*	*1.08*	*0.108*	*0.99*	*0.099*
Cis isomer	0.16	0.24	0.15	0.25	0.15	0.24
Trans isomer	0.32	0.39	0.40	0.40	0.39	0.39

Experimental

The mobile solvents used were both ethanol–water and isopropanol–water, 60:40 (v/v). The spots were visualized with Na_2S. All chromatograms were run on glass plates (10 × 20 cm) coated with a well-stirred suspension of cellulose (Bělá p. Bezděz,

Č.S.S.R.) in an appropriate buffer. The buffers used here were universal Britton-Robinson buffers, the pH of which was checked. The coated plates were air-dried. The solvents were allowed to travel 10 cm from the application point. From the $1 \cdot 10^{-3}$ *M* solution containing a mixture of both isomers in the proper buffer, 10-μl samples were applied at the starting line which was 2 cm from the lower edge of the plates.

Cis and *trans* isomers of trisglycinatocobalt(III) were prepared by the method of LEY AND WINKLER[3], while bisglycinatocobalt(II) was prepared according to the procedure of PETRŮ AND JURSÍK[1]. The identity of the synthesized products was established by means of electronic spectra and infrared spectroscopy.

Oxidation of bisglycinatocobalt(II)

10 ml of a $1 \cdot 10^{-2}$ *M* solution of bisglycinatocobalt(II) containing $1 \cdot 10^{-4}$ mole of glycine was saturated by passing a stream of air through it (at room temperature) for about 2 h. After this time 5-μl aliquots were applied at the starting line.

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Received March 4th, 1968

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