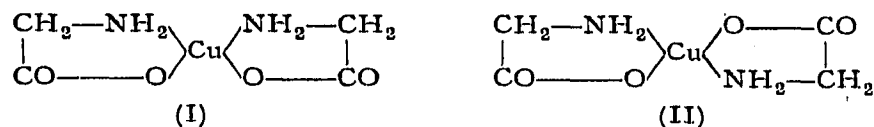


## Paper chromatographic behaviour of *cis* and *trans* isomers of copper bis(glycinate)\*

The existence of two different crystalline modifications of copper bis(glycinate) has been known for a long time<sup>1,2</sup>. On the basis of infrared spectroscopy TOMITA<sup>3</sup> found that these crystalline forms were *cis* (I) and *trans* (II) isomers:



Owing to the fact that this is the only case so far known of *cis-trans* isomerism of copper amino acid chelates, we were interested in the chromatographic differentiation of both isomers.

### Experimental

Both isomers were prepared according to references<sup>1,4</sup> and identified using infrared spectroscopy<sup>3</sup> (UR-10 C. Zeiss-Jena apparatus, KBr-method in the region 400–2000  $\text{cm}^{-1}$ ). Infrared spectra are given in Fig. 1.

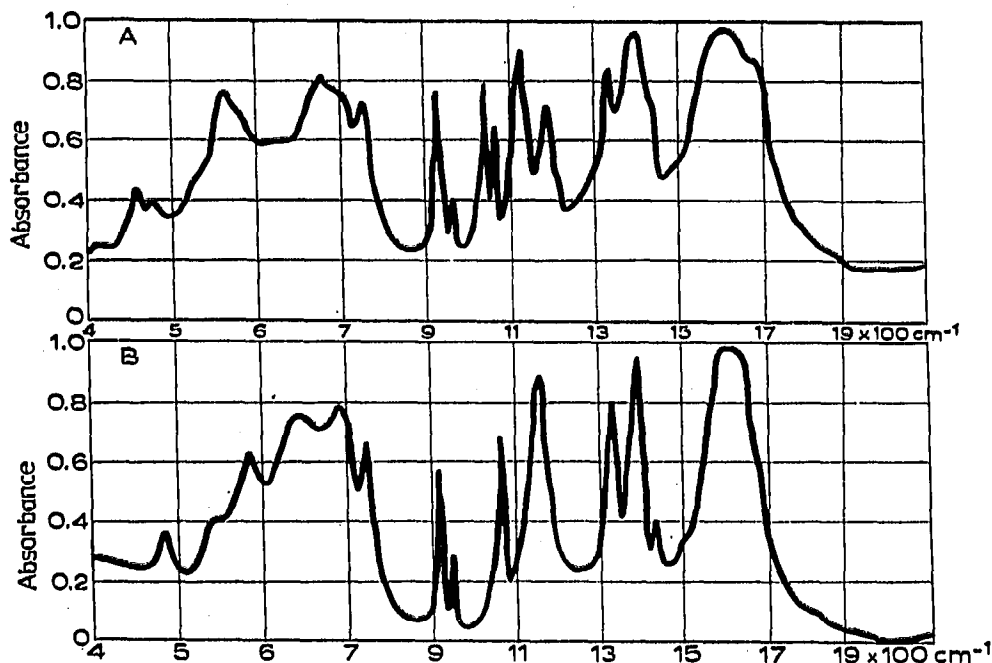


Fig. 1. Infrared spectra of *cis* (A) and *trans* (B) stereoisomers of copper bis(glycinate).

Whatman No. 3 paper and the ascending strip method was used. In each case 0.01 ml of an 0.01 *M* solution of both isomers was spotted. The aqueous solution of both isomers was prepared a short time before chromatography. The spotting was made within one minute. Both isomers were detected with a 5% solution of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .  $R_F$  values were measured as the centre of the distance between the front and the end of the spot as recommended by LACOURT *et al.*<sup>5</sup>.

\* Dedicated to Professor ST. ŠKRAMOVSKÝ for his 65th birthday.

### Results and discussion

It can be seen from Table I that the  $R_F$  values of the *cis* isomer are somewhat higher than those of the *trans* form, with the exception of the methanol-water solvent system. These results agree with those of STEFANOVIĆ AND JANJIĆ<sup>6,7</sup>, who found for the *cis* isomer of some cobalt(III) complexes higher  $R_F$  values than for the *trans* isomer.

TABLE I  
 $R_F$  VALUES OF *cis* AND *trans* ISOMERS OF COPPER BIS(GLYCINATE)

Isomer	Water content in the solvent used (%)							
	20	30	40	50	60	70	80	90
	<i>Methanol</i>							
<i>Cis</i>	0.36	0.48	0.60	0.67	0.75	0.81	0.85	0.90
<i>Trans</i>	0.33	0.47	0.62	0.67	0.75	0.82	0.84	0.88
	<i>Ethanol</i>							
<i>Cis</i>	0.22	0.39	0.50	0.60	0.73	0.79	0.86	0.91
<i>Trans</i>	0.15	0.28	0.41	0.53	0.65	0.75	0.84	0.90
	<i>n-Propanol</i>							
<i>Cis</i>	0.12	0.29	0.39	0.52	0.62	0.72	0.81	0.87
<i>Trans</i>	0.05	0.15	0.29	0.43	0.54	0.69	0.78	0.87
	<i>Acetone</i>							
<i>Cis</i>	0.06	0.26	0.42	0.58	0.71	0.74	0.75	0.79
<i>Trans</i>	0.03	0.18	0.36	0.55	0.68	0.75	0.77	0.80
	<i>Dioxane</i>							
<i>Cis</i>	0.06	0.32	0.49	0.60	0.69	0.76	0.79	0.86
<i>Trans</i>	0.03	0.24	0.45	0.59	0.70	0.75	0.80	0.85

There is a relationship between the separability of both isomers and solvent composition. Thus  $R_F$  values of both isomers increase with increasing water content in the solvent used and decrease in the following order of solvents: methanol > ethanol > *n*-propanol > acetone > dioxane. The differences between the  $R_F$  values of both stereoisomers increase with decreasing  $R_F$  value and decrease further with increasing number of carbon atoms in the molecule of alcohol used. These results indicated the polar character of both isomers and showed further that the *trans* isomer has a more hydrophilic character. The chromatographic behaviour of the two stereoisomers is not connected with their dipole moments, because in the symmetric *trans* form a zero dipole moment would be expected and a higher  $R_F$  value would be obtained<sup>8</sup>.

Furthermore, the  $R_F$  values of the two stereoisomers are not related to their stability. In the aqueous solution the *trans* isomer is more stable than *cis*<sup>9</sup>.  $R_F$  values of amino acid chelates are rather related to the ionic radii of the central atom<sup>10</sup>. Since in the case of copper bis(glycinate) isomers both central atom and ligand are the same, the differences in  $R_F$  values may be due to the steric hindrance or to different adsorptivity of both stereoisomers, which increase (similarly as other amino acid chelate of some transition metals) with decreasing water content in the solvent used<sup>11</sup>.

It is unlikely that isomerisation occurs during chromatography. The isomerisation *cis* → *trans* begins in aqueous solution after eight days and is accelerated by the presence of mother liquor<sup>9</sup>. In aqueous organic solutions the p*K* value of chelates increases as the water content decreases<sup>12</sup> and the isomerisation decreases to a minimum.

With more than 60 % water in the solvents, the formation of tails was observed. The presence of KCl or LiCl decreased diffusion of spots.

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