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# MAGIC SQUARE. III. REVERSE ISOMERIZATION OF TRIS-CHELATE COMPLEXES OF COBALT (III) WITH NITROSONAPHTHOLS

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## ABSTRACT

Chromatographic behaviour of individual fac- and mer-isomer of Co(III) tris-chelate complexes with 1,2- and 2,1-nitrosouaphthols is studied. Chelating reagents in eluting mixtures with additives of carboxylic acids are retained more strongly than their complexes with cobalt. The method of magic square is used to study the process of fac  $\rightleftharpoons$  mer reverse isomerization under the influence of photoirradiation and temperature. The application of the magic square method for identification of stereochemical rigidity or nonrigidity of coordination compounds is shown to be possible.

INTRODUCTION

It was shown previously that under two-dimensional chromatography with the preliminary UV irradiation before each of them there forms a square of four spots of Z- and E- or syn- and anti-isomers at vertexes for the reverse-isomerizing organic compounds with multiple bonds /1,2/. Such a mode was called a magic square and it was used for identification of reverse-isomerizing compounds with  $-N=N-$ ,  $>C=N-$  and  $>C=C<$  bonds in mixtures with other organic compounds. Reverse isomerization is typical not only of the organic compounds with unsaturated bonds but also of their chelate complexes with metals /3/. In particular, octahedral complexes may be isomerized reversely both under the effect of temperature and of photoirradiation / 3,4 /.

The tris-chelate octahedral complexes of nitrosonaphthols with metals are characterized by sufficiently high stability and high light absorption in the visible spectrum region, that permits using them in the analysis of metal microquantities /5/. Besides, they are dissolved well in weak-polar extractants. In our opinion due to these qualities nitrosonaphthol chelate systems may be promising for separation and determination of metals by the method of liquid adsorption chromatography. The studies on behaviour of tris-chelate complexes of nitrosonaphthols with Co (III) in the thin layer have

shown that these coordinatively saturated compounds are chromatographed as two spots corresponding to two geometrical isomers / 6,7 /. The preparative separation by the method of thin-layer chromatography (TLC) and investigation of the complexes by the high resolution  $^1\text{H}$  and  $^{13}\text{C}$  NMR methods made it possible to identify unambiguously fac- and mer-configuration of these isomers / 7 /. When boiling the mixture of isomers of 1,2-nitrosonaphtholate Co (III) and 2,1-nitrosonaphtholate Co (III) in toluene the effect of thermal isomerization towards mer  $\rightarrow$  fac was observed in the work / 6 /. As it was mentioned in such cases the isomerization may occur under the effect of temperature, photoirradiation and other factors, and directions of the processes under the action of various factors may be different. Such effects, evidently, may lead to considerable changes in the ratio of isomers in the process of their separation and photometric detection and therefore to complexity of the procedure for determination of metals as chelates by means of liquid adsorption chromatography. This was the reason for investigation of reverse isomerization of tris-chelate complexes of Co (III) with nitrosonaphthols in solutions and in the adsorbed state under the effect of various factors. The magic square method was used for studies of the isomerization processes.

EXPERIMENTAL

The synthesis of the cobalt (III) complexes under study was realized according to the procedure / 6 /. The ethanol solution of 1-nitroso-2-naphthol (HL') (1 g, 3 mol-equiv in 100 cm<sup>3</sup>) was poured by drops during stirring to aqueous solution of sodium hexanitrocobaltate (III) (0.8 g, 1 mol-equiv in 100 cm<sup>3</sup>). After two-hour stirring in the magnetic mixer the obtained sediment was separated in the filter and dehydrated at 60°C / 1 mm Hg. The complex of cobalt (III) with 2-nitroso-1-naphthol (HL'') was obtained by the same way.

After synthesis the individual complexes were purified from nonreacted basic substances and by-products on the column ( $\emptyset = 3.4 \times 36$  cm) filled with aluminium oxide (L 40/250, neutral, Chemapol). Chloroform was used as an eluent. The ratio of complex-sorbent was 1 : 500. The results of C, H, N-elementary analysis correspond to the brutto-composition Co : ligand = 1 : 3.

The preparative separation of isomers was conducted on the ground glass plates of 200 x 200 mm size with the silicagel layer (LS 5/40, Chemapol) containing 13% gypsum. Silicagel together with gypsum as a binding agent was applied as aqueous suspension by means of a device for applying thin layers to plane plates. After drying the plates the layer thickness

was 0.8 mm. Before usage the plates were preliminary washed with acetone, dried and eluted with mobile phase.

After removal of the solvents vapours 2-3  $\mu$ l of the saturated solution of the complex in chloroform were applied as a strip to the plate by microsyringe. The distance of the band from the plate ends was 1 cm. After drying the plate was placed into the chromatographic tank preliminary saturated with vapours of the mobile phase and then it was subjected to chromatography in the mixture of benzene : hexane : isopropanol = 95 : 10 : 5. As a result of separation two bands were obtained. Then these bands were removed from the plates and individual isomers were extracted from the sorbent by chloroform. The extract was evaporated in the vacuum rotor evaporator RVO-64. By this method the individual isomers of tris(1,2-nitrosophthalate) Co(III) ( $\text{CoL}'_3$ ) were obtained. To separate isomers of tris(2,1-nitrosophthalate) Co(III) ( $\text{CoL}''_3$ ) the mentioned above column with aluminium oxide preliminary saturated with chloroform was used. After introduction of isomers into the column 200 ml of the mixture (heptane : chloroform : acetone = 7 : 2 : 1) were passed through the column with the subsequent elution of the individual isomers with benzene.

The structure of the preparative isomers was established by analyzing the  $^{13}\text{C}$  -  $\{^1\text{H}\}$  and  $^1\text{H}$  NMR spe-

ctra. The  $^1\text{H}$  (200 MHz) and  $^{13}\text{C}$  (50, 33 MHz) NMR spectra of complexes in  $\text{CDCl}_3$  and  $(\text{CD}_3)_2\text{CO}$  were recorded on the CXP-200 pulse Fourier-spectrometer "Bruker". TMS was used as an internal standard. The concentration of the solutions was 1-3 weight %. Fig. 1 represents the NMR spectra of fac- and mer-isomers of  $\text{CoL}''_3$ . Since the fac-isomer due to the axis  $\text{C}_3$  has three equivalent chelate cycles with ten magnetically nonequivalent carbon atoms, then in the  $^{13}\text{C} - \{^1\text{H}\}$  NMR spectrum 10 lines should be expected, that in reality is observed for one of the isomers (Fig. 1b). In the spectrum of mer-isomer  $\text{CoL}''_3$  (the axis  $\text{C}_1$ ) 30 carbon (3 sets) signals may be expected theoretically due to different nature of three ligands. As it is seen from Fig. 1a the spectrum of this isomer consists of 30 lines. The same picture is characteristic of the  $^1\text{H}$  NMR spectra of  $\text{CoL}''_3$  isomers depicted in Fig. 2. The highly symmetric fac-isomer has a single set of lines which evidences for equivalency of three coordinated anions. In the case of low-symmetric mer-isomer a set of three signals of equal intensity, each responding to one of three ligands of the complex, is observed for isolated H3 and H8 protons. Thus, peculiarities of the considered  $^{13}\text{C} - \{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra permitted unambiguously identifying fac- and mer-structure of the individual isomers.

Isomerization of the synthetic mixture and of individual isomers in the thin layer was conducted under

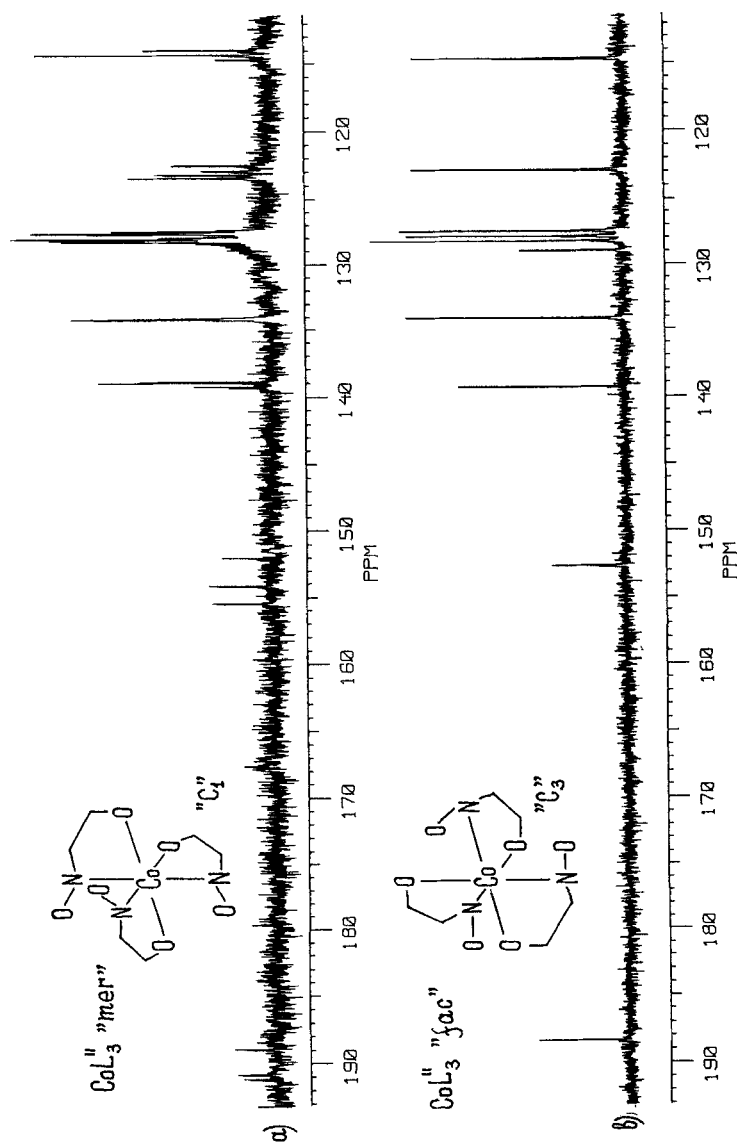


Figure 1. The  $^{13}\text{C}$  -  $\{^1\text{H}\}$  NMR spectra of  $\text{CoL}_3$  in  $\text{CDCl}_3$ :

a) mer-isomer; b) fac-isomer (HL"-2-nitroso-

-I-naphthol)



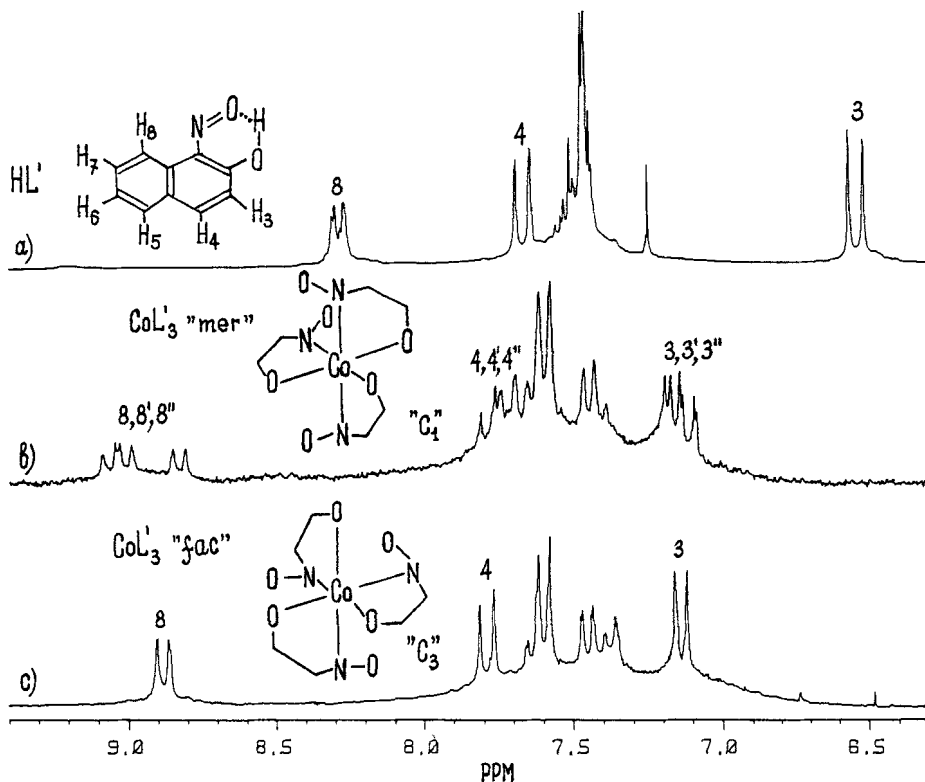


Figure 2. The  $^1\text{H}$  NMR spectra (200 MHz) in  $\text{CDCl}_3$ :  
 a) I-nitroso-2-naphthol; b) mer-isomer;  
 c) fac-isomer

the effect of photoirradiation and temperature on "Merck" N5721 (BDR) plates of 100x100 and 200x200 mm size and on Silufol-UV 254 (ČSSR) plates (150x150 mm). Photoisomerization of the complexes in solutions was performed by irradiating solutions of individual isomers in toluene with the concentration of 0.05 mg/ml.

The plates and quartz cells with solutions were irradiated by visible light using the illuminator with fibrous light guide OVS-1 and lamp KGM 9-70 (the distance from the light source of the object was 1-2 cm) and also with UV light from lamp SVD-120A (the distance to the object - 10-15 cm). Thermoisomerization on plates was performed in the vacuum drying cabinet LP-404/2 at the pressure of  $10^{-1}$  mm Hg and temperature up to  $200^{\circ}\text{C}$ . After the effect of temperature the plate was allowed to stand in the fume hood for 5-6 hr before elution. Chromatography was conducted in the rectangular tank with saturation and 150 ml eluent. After chromatography the plates were thoroughly dried.

Densitograms and electronic spectra of diffuse reflection (DRES) were recorded on spectrodensitometer KM-3 (Opton, BDR). The slit of 0.2-0.2x3.5-14.0 mm size (depending on the chosen spectrum range) was used for the scanning of plates. The recorder scale was 0.5 V, sensitivity of the amplifier - 1 : 1. The analytical wavelengths for scanning were chosen from electronic spectra of diffuse reflection received from spots of fac- and mer-isomers of  $\text{CoL}'_3$  and  $\text{CoL}''_3$  and also of HL' and HL''. For these purposes the substances in the quantity of  $0.5\ \mu\text{g}$  were applied by a microsyringe to the plate "Merck" and then they were eluted in the toluene-formic acid system. After drying the entire spectra of DRES were recorded. The view of the entire

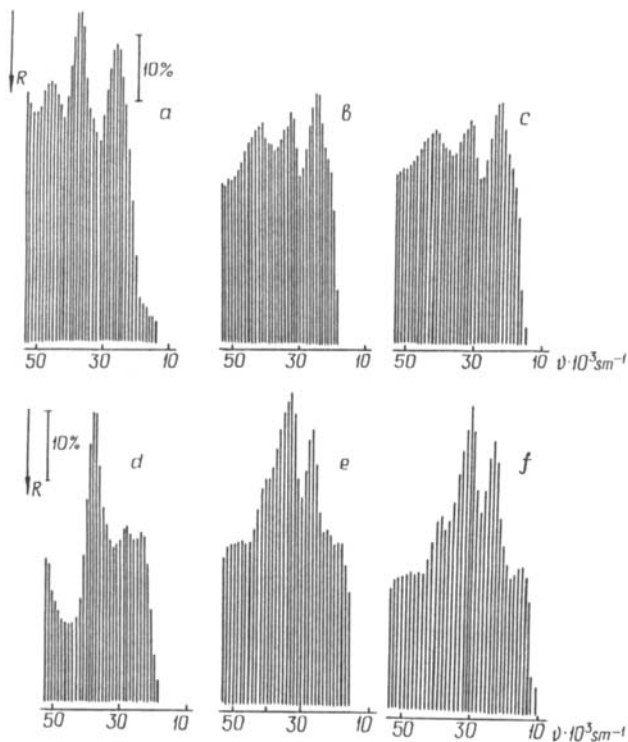


Figure 3. Electronic spectra of diffuse reflection:

- a)  $HL'$ ; b)  $fCoL'_3$ ; c)  $mCoL'_3$ ; d)  $HL''$ ;  
 e)  $fCoL''_3$ ; f)  $mCoL''_3$

spectra recorded with a step of  $1000\text{ cm}^{-1}$  is given in Fig. 3. The absorption bands for the scanning of plates were chosen from the spectra recorded with a  $200\text{ cm}^{-1}$  step. Their values are given in Table 1.

### RESULTS AND DISCUSSION

As it was shown in introduction the nitrosonaphthol chelate systems may be rather promising for the

TABLE 1  
 Position of Bands in Electronic Spectra of Diffuse Reflection  
 of Chelating Reagents and Chelate Complexes of Co (III)

Compound	Position of absorption band, nm		
I-nitroso-2-naphthol	212	255	352 410 -
I-nitroso-2-naphtholate of Co (III)	219	242.5	312 424 -
2-nitroso-I-naphthol	-	256	345 400 550
2-nitroso-I-naphtholate of Co (III)	216	250	303 370 525

analysis of metal mixtures as their chelate complexes by the method of liquid adsorption chromatography. At present this method is intensely developed for other chelate systems / 8, 9 / . The existence of geometrical isomers for tris-chelate complexes of different metals and in particular of fac- and mer-isomers of  $\text{CoL}'_3$  and  $\text{CoL}''_3$  noticeably complicates the process of the liquid adsorption-chromatographic separation and determination of metals in the thin layer. The mentioned fact resulted in necessity of detailed investigations of chromatographic properties of individual isomers and the effect of isomerization on analytical behaviour of  $\text{CoL}'_3$  and  $\text{CoL}''_3$ .

In the first place the  $R_f$  values were determined on "Merck" plates for individual isomers of  $\text{fCoL}'_3$ ,  $\text{mCoL}'_3$ ,  $\text{fCoL}''_3$  and  $\text{mCoL}''_3$  separated by the method of the preparative thin-layer chromatography and for basic chelate-forming reagents  $\text{HL}'$  and  $\text{HL}''$ . The elution was performed in individual solvents following the series described in / 10 / as well as in binary mixtures with the use of a background solvent and polar additives to it in the quantity of 3-20% in such a way that the  $R_f$  values should be within 0.1-0.9. The results obtained are given in Tables 2 and 3. The analysis of the data on chromatographic mobility in one-component eluents (Table 2) permits concluding that the chelate-

TABLE 2

Chromatographic Mobility of Chelating Reagents and Individual Isomers of Co (III) Chelates in Euototropic Series

Eluent	Parameter $\epsilon$ according to Snyder	$R_f$ value					
		HL'	fCol' <sub>3</sub>	mCol' <sub>3</sub>	HL''	fCol'' <sub>3</sub>	mCol'' <sub>3</sub>
Hexane	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Tetrachloromethane	-	0.00	0.00	0.00	0.00	0.00	0.00
Toluene	0.29	0.24	0.04	0.10	0.06	0.24	0.24
Diethyl ether	0.38	0.89	0.73	0.81	0.87	0.83	0.83
Dichloromethane	0.42	0.24	0.18	0.30	0.05	0.35	0.40
1,2-Dichloroethane	0.44	0.47	0.41	0.61	0.095	0.71	0.71

TABLE 3  
 Chromatographic Mobility of Chelating Reagents  
 and Individual Isomers of Co (III) Chelates  
 in the Binary Eluting Systems

Eluent	Volume ratio	Parameter $\epsilon^0$ of polar additive according to Snyder	$R_f$ value					
			HL'	fCOL' <sub>3</sub>	mCOL' <sub>3</sub>	HL''	fCOL'' <sub>3</sub>	mCOL'' <sub>3</sub>
Toluene-diethyl ether	9 : 1	0.38	0.56	0.34	0.55	0.18	0.75	0.75
Toluene-dichloroethane	1 : 4	0.42	0.37	0.23	0.37	0.25	0.43	0.51
Toluene-methyl-ethylketone	90 : 3	0.51	0.46	0.22	0.36	0.17	0.59	0.59
Toluene-acetone	97 : 3	0.56	0.52	0.33	0.46	0.19	0.64	0.64

Toluene- methyl- acetate	95 : 5	-	0.49	0.29	0.44	0.15	0.63	0.63
Toluene- ethylace- tate	95 : 5	0.58	0.47	0.27	0.42	0.14	0.61	0.61
Toluene- acetonit- rile	95 : 5	0.65	0.59	0.33	0.53	0.18	0.74	0.74
Toluene- butanol-2	95 : 5	0.70	0.28	0.25	0.31	0.19	0.46	0.58
Toluene- formic acid	97 : 3	-	0.41	0.38	0.45	0.21	0.51	0.61
Toluene- formic acid	94 : 6	-	0.26	0.46	0.53	0.17	0.53	0.59



forming reagents HL' and HL'' as well as their complexes  $\text{CoL}'_3$  and  $\text{CoL}''_3$  are related to compounds of the average polarity. They are eluted by a group of solvents with the Snyder polarity criterion  $\epsilon^\circ$  equalled 0.3-0.5. It ought to note that such an eluent as dichloromethane completely separates between themselves fac- and mer-isomers of  $\text{CoL}'_3$  and  $\text{CoL}''_3$ . Disadvantage of dichloromethane as an eluent is its instability in time to different transformations. In this case more polar components are accumulated and an increase in the chromatographic mobility of spots as well as a decrease in a degree of isomer separation are observed. Besides, in dichloromethane and also in 1,2-dichloroethane 1-nitroso-2-naphthol is eluted between fac- and mer-isomers of its chelate with Co (III). The spot of HL' with the washed-out front overlaps partially the zone of fac-isomer of  $\text{CoL}'_3$ . Thus, all individual eluents presented in Table 2 do not permit separating completely the six-component mixture ( $\text{CoL}'_3 + \text{CoL}''_3 + \text{HL}' + \text{HL}''$ ). In order to obtain satisfactory separation of this mixture a search for binary eluting mixtures was made. Toluene was chosen as a background solvent and then ketones, acetates and other polar solvents were added to it. The results of selection of such systems are given in Table 3.

It should be noted that according to the chromatographic properties the ternary mixture  $\text{HL}' + \text{fCoL}'_3 +$

+  $mCoL'_3$  differs considerably from that of  $HL'' + fCoL''_3 + mCoL''_3$ . As it was indicated in discussion of the data from Table 2  $HL'$  and one of the isomers ( $fCoL'_3$  or  $mCoL'_3$ ) are a critical pair in the six-component system. In this connection separation of  $HL'$  and isomers of its complex with Co (III) would be considered more in detail. As it is seen from the Table an increase in polarity of the additive in the binary mixture as compared with elution in pure toluene leads to a gradual decrease in mobility of  $HL'$  relative to its mer-isomer. In this case conditions are achieved when  $HL'$  is eluted between fac- and mer-isomers of  $CoL'_3$ , for instance, in the mixture of toluene :  $HCOOH = 97 : 3$ . A subsequent increase in the formic acid content in this mixture lowers mobility to a greater extent. In the mixture of toluene :  $HCOOH = 94 : 6$  the  $R_f$  value for  $HL'$  is already much lower than that for fac- and mer-isomers of  $CoL'_3$ . As to  $HL''$  and fac- and mer-isomers of  $CoL''_3$  the  $HL''$  separation from isomers of  $CoL''_3$  is reached in any of the studied binary mixtures. However, in this case the effective separation between fac- and mer-isomers may be obtained only in mixtures with H-acids (dichloromethane), alcohols (butanol-2) and carboxylic acids ( $HCOOH$ ).

Thus, the toluene- $HCOOH$  mixture in the volume ratio of 94 : 6 is the most effective system which permits not only separating all constituents of the six-

component system but also retaining strongly HL' and HL'' as compared to  $\text{CoL}'_3$  and  $\text{CoL}''_3$ . Densitogram of the test mixture separation in the found eluent is presented in Fig. 4a. Here the value of resolution,  $R_g$ , for  $\text{fCoL}'_3$  and  $\text{mCoL}'_3$  is 0.68, while for  $\text{fCoL}''_3$  and  $\text{mCoL}''_3$  - 1.23. Densitogram of the six-component mixture separation in dichloromethane is also presented in the same figure. The  $R_g$  value was calculated from densitograms according to / 11 /. As it has been indicated a satisfactory separation of the six-component mixture may be also obtained in dichloromethane but as distinct from the toluene : HCOOH mixture HL' is eluted in it between fac- and mer-isomers, thus making the analysis of chelates with the reagent excess difficult. However, to separate the mixtures of  $\text{CoL}'_3$  and  $\text{CoL}''_3$  isomers in the absence of HL' it is more convenient to use the purified dichloromethane because the elution rate in it is higher as against to the toluene : HCOOH eluent and it is easier to remove it from the plates. Due to it we have used dichloromethane for studies on reverse isomerization of complexes.

Using the data of Tables 2 and 3 it is possible to conclude that the chromatographic behaviour of chelates differs considerably from that of the chelating reagents. As it is known chromatographic mobility of substances in the eluotropic series should increase /10/.

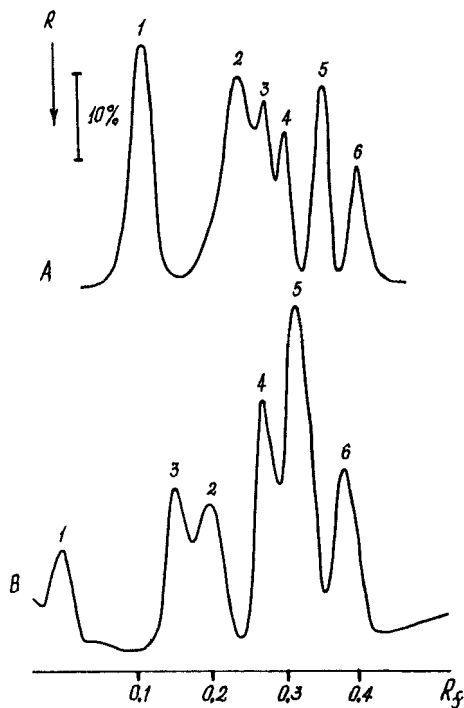
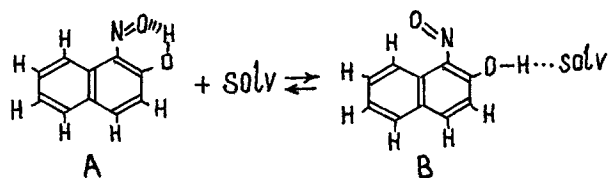


Figure 4. Densitograms of the six-component mixture of HL' (1); HL'' (2); fCoL'<sub>3</sub> (3); mCoL'<sub>3</sub> (4); fCoL''<sub>3</sub> (5); mCoL''<sub>3</sub> (6) in eluents:  
 A) toluene : HCOOH = 94 : 6;  
 B) dichloromethane

This regularity is kept for the CoL'<sub>3</sub> and CoL''<sub>3</sub> complexes in the eluents used. However, mobility of HL' and HL'' ligands is not subjected to such a regularity. Thus, when  $\epsilon^\circ$  increases the  $R_f$  values for HL' and HL'' at first also become higher and further they are maximal

in diethyl ether. Then an insignificant rise of  $\xi^{\circ}(\text{H-acids})$  leads to sharp changes in chromatographic mobility. This effect is more considerable for HL'' ( $R_f$  drops from 0.9 to 0.1) than for HL' ( $R_f$  drops from 0.9 to 0.5). The explanation to such an anomalous behaviour of HL' and HL'' mobility will be, probably, find in properties of their chelate ring, i.e. in properties of intramolecular (IHB) and intermolecular (IMHB) hydrogen bond formed by NO and OH groups.

The existence of rotameric equilibrium between conformers with IHB and IMHB is observed for solutions of HL' in the work / 12 / :



The use of solvents, being strong acceptors of hydrogen bond, leads to a destruction of IHB of 1,2-nitrosonaphthol, to an increase in the transformation rate of  $A \rightleftharpoons B$  as well as to changes in the population of conformers. Conformer B having no IHB during solvation by these solvents is stabilized more strongly and its content relative to that in nonsolvating media grows considerably. The same equilibrium is observed in solutions of 2,1-nitrosonaphthol as well, the only difference is that the moiety of conformer without IHB is much higher here. The HL' and HL'' molecules on the hydroxy-

lated surface of silicagel consisting of nonpolar eluents are adsorbed in a form of A with IHB producing, evidently,  $\pi$ -complexes with silanol groups. With an increase in eluent polarity IHB breaks with the production of stronger complexes at the expense of the formation of IMHB with silanol groups of the surface. This leads to a stronger retaining of chelating reagents. Thus, instead of the expected rise of the  $R_f$  value with an increase in the solvent polarity the  $R_f$  values for HL' and HL'' decrease. The similar behaviour of naphthoquinones hydroxy-derivatives was described in / 13 /. The authors consider that the abnormal changes in mobility in the elutropic series is a diagnostic test for chelating and nonchelating hydroxyl groups.

As to chromatographic behaviour of complexes no abnormalities connected with the dependence of the  $R_f$  values on the eluting ability of solvents are observed for them. However, the process of chromatography of the chelate complexes becomes more complicated, that is associated to a considerable extent with the possibility of reverse isomerization of the fac  $\rightleftharpoons$  mer type. The effect of isomerization on the chromatographic behaviour of the chelate complexes of  $CoL'_3$  and  $CoL''_3$  is studied by the magic square method. For this purpose solutions of the both complexes were applied to one point and chromatographed in dichloromethane. Then they were ac-

ted upon by temperature or irradiation with visible or UV light and rechromatographed in the direction perpendicular to the previous one. The results obtained are given in Figs 5B and 5C. Here in Fig. 5A the result of two-dimensional chromatography without an additional action before the second elution is presented. As it is seen (Fig. 5A) the spots are arranged on a diagonal of the square chromatographic plate. In the case depicted in Fig. 5B one can observe two spots for each of the complexes after the first chromatography. Rechromatography after photoirradiation shows that under the effect of visible light each spot corresponding to individual isomer divides into two spots. Thus, photoisomerization causes the formation of a figure with four spots at vertexes. Evidently, fac-isomers were partially isomerized into mer- and mer- partially passed into fac-isomers. In order to prove the authenticity of this fact we have conducted not only identification on coincidence of the  $R_F$  values but also measurements of DRES of substances which were obtained due to isomerization. Coincidence of DRES and the  $R_F$  values with the spectra and the  $R_F$  values of  $CoL'_3$  and  $CoL''_3$  of fac- and mer-isomers will unambiguously evidence for identity of these compounds /14,15/. DRES of individual isomers (Fig. 3) were obtained from the plate presented in Fig. 5A. Spectra of the compounds corresponding to spots

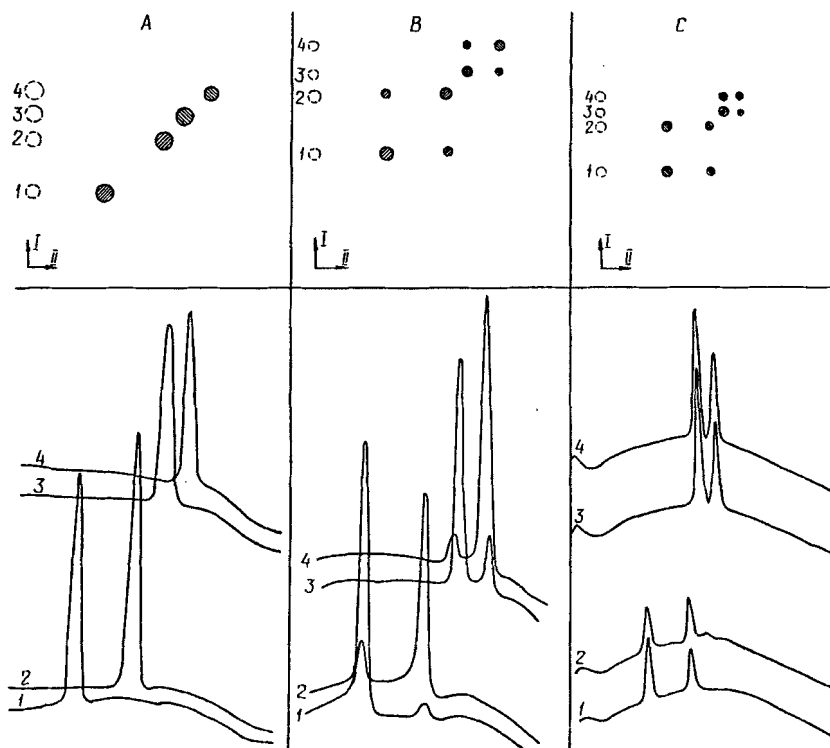


Figure 5. Two-dimensional chromatograms and their densitograms for  $\text{CoL}'_3$  and  $\text{CoL}''_3$ :

A) without the effect;

B) with visible light irradiation;

C) temperature effect.

Numeration on densitograms corresponds to numbers of scanning tracks



with  $R_F$  equalled the  $R_F$  values of fac- and mer-isomers completely coincided by the location of the absorption band maxima and the ratio of intensities with the spectra presented in Fig. 3.

The reverse isomerization of tris-chelate complexes of  $\text{CoL}'_3$  and  $\text{CoL}''_3$  was observed not only under the effect of visible light but also due to UV irradiation. The effect after the first elution of UV light for 1 h on plates with isomers leads to the appearance of a distinctly visible square after the second elution in the perpendicular direction. It is impossible to prolong more than for 1 h the irradiation effect in the UV region since most of chelate complexes are not eluted after the irradiation.

Besides, we have studied the possibility of isomerization for  $\text{CoL}'_3$  and  $\text{CoL}''_3$  complexes in solutions with the use of irradiating the individual isomer solutions in chloroform by visible light and in toluene - by UV light. After one-dimensional chromatography of spots applied to the plate of the irradiated solutions the appearance of the second spot was observed for basic fac- and mer-isomers. The  $R_F$  values and DRES of spots made it possible to identify them as mer-isomers in the case of basic fac- and as fac-isomers in the case of the basic mer-.

Thus, due to the studies conducted we have revealed the phenomenon of reverse isomerization of

Co (III) tris-chelate complexes with 1,2- and 2,1-nitrosonaphthols in solutions and on hydroxyl surface of chromatographic plates with the silicagel layer under the effect of both visible and UV light.

The revealed effects of photoisomerization in solutions and on the surface evidence for the possibility of isomerization under the influence of temperature which proceeds not only in solutions as it was previously established in / 6 / but also on the surface. The magic square obtained due to thermal isomerization is given in Fig. 5C. In order to prevent oxidation and decomposition of chelates we have conducted thermoisomerization on plates in vacuum at the pressure of  $10^{-1}$  mm Hg. A comparison of peaks of fac- and mer-isomers on densitograms of Figs 5B and 5C shows that for the same time of action (4 hs) a greater degree of transformations is observed in case of thermal isomerization than in case of photoisomerization. This is valid only for the temperature above  $150^{\circ}\text{C}$ . At lower temperatures the products of isomerization are not observed on the surface for the same time. Evidently, the reverse-isomerization rate is rather low at temperatures below  $100^{\circ}\text{C}$ . A low rate of isomerization under these conditions is typical of the solutions as well. In NMR experiments of  $^1\text{H}$  and  $^{13}\text{C}$  no signs of shifts of the fac  $\rightleftharpoons$  mer equilibrium or changes in its

rate were observed when the temperature of the equilibrium mixture in  $\text{CDCl}_3$  and  $(\text{CD}_3)_2\text{CO}$  rose up to  $60^\circ\text{C}$ .

Thus, our studies have revealed reverse isomerization of the fac  $\rightleftharpoons$  mer type for tris-chelate complexes of  $\text{CoL}'_3$  and  $\text{CoL}''_3$  in solutions and in the adsorbed state on the hydroxyl surface of silicagel both under the effect of photoirradiation and temperature. Application to the plate of individual isomer and subsequent two-dimensional chromatography with photoirradiation or thermal effect either in the vacuum or in the inert medium before each elution results in the origin of magic square. For the isomer mixture formed during synthesis the magic square arises under the single action on spots only before the second elution. If there is no photo- or thermal effect the spots of  $\text{CoL}'_3$  and  $\text{CoL}''_3$  isomers are arranged on the square diagonal.

At first the magic square method was suggested to identify the reverse-isomerizing substances in mixtures of organic compounds. As follows from the results of this paper such a procedure may be used for identification of stereochemical rigidity (or nonrigidity) of chelate complexes of organic compounds with metals which are able to be isomerized. The studied chelates of  $\text{CoL}'_3$  and  $\text{CoL}''_3$  should be considered as stereochemically rigid in the chromatography scale

since they are chromatographed as compact spots and are arranged on the square diagonal (Fig. 5A). According to / 14 / these compounds should be attributed to the so-called "slow complexes" since reverse isomerization  $\text{fac} \rightleftharpoons \text{mer}$  under ordinary conditions occurs slowly that it is possible to isolate and study the individual isomers.

Thus, the magic square method without additional actions before chromatography may be successfully used as a rather simple and visual technique to determine stereochemical rigidity (nonrigidity) of coordination compounds. In the case when the square is not formed after the second elution, i.e. when the isomer spots are arranged on the plate diagonal we have reasons to state that isomers are stereochemically rigid in the chromatographic scale, and therefore, under these conditions (temperature, illumination) they may exist as individual ones for a long time. If we observe the existence of the magic square after the second elution in the perpendicular direction, then the complexes are stereochemically nonrigid and under these conditions cannot be obtained as individual isomers.

Besides, the magic square method in combination with spectrodensitometry may be used for qualitative and quantitative studies on the reverse isomerization processes of coordination compounds in the thin-layer

and in solutions both under the effect of temperature and irradiation by visible and UV light. To characterize relative stability of isomers in the fac  $\rightleftharpoons$  mer equilibrium mixture the value of isomerization constant,  $K_i$ , is used as a rule:

$$K_i = \frac{[\text{mer CoL}_3]}{[\text{fac CoL}_3]} = \frac{k_{\text{fac} \rightarrow \text{mer}}}{k_{\text{mer} \rightarrow \text{fac}}}$$

If the complete energies of fac- and mer-isomers are equal, then  $K_i = 3$ , since under statistical distribution of populations three complexes of mer-structure fall on one complex of fac-structure. According to spectrodensitometry  $K_i = 1.27$  and  $0.82$  for  $\text{CoL}'_3$  and  $\text{CoL}''_3$ , respectively. Consequently, fac-isomers of these complexes are more stable.

The magic square method permits investigating the temperature dependence of  $K_i$ . In this case it is necessary to obtain the equilibrium state which should be achieved only by long exposition of plates at the chosen temperature. However, the studied system of complexes may be obtained easily in the experiment in the state far from being equilibrium and it is possible to calculate the rates of  $k_{\text{fac} \rightarrow \text{mer}}$  and  $k_{\text{mer} \rightarrow \text{fac}}$  processes and then to determine  $K_i$  as well.

As follows from Figs 5B and 5C the square of four spots appears under photo and thermal isomerization after the second elution. This evidences for the ef-

fective process of photo- and thermal isomerization of individual isomers both in the forward and back directions. In other words, the effect of light and temperature increases the rate of both the forward and back reaction and, on the whole, mobility of ligands in the  $\text{CoL}'_3$  and  $\text{CoL}''_3$  complexes rises considerably. This is typical of isomerization both in the thin layer and in solutions. The absence of differences in the direction of thermal and photoisomerization of complexes indicates the same type of potential energy surfaces for the ground and excited states.

The revealed reverse transitions of tris-chelate complexes of Co (III) with 1,2- and 2,1-nitrosonaphthols under the effect of visible and UV light and also of temperature should be taken into account in purification, analysis and chromatographic separation of the complexes. These effects should be taken into consideration and used when developing extraction-and-thin layer chromatographic methods for determining cobalt and other metals in aqueous media as their nitrosonaphtholate chelates.

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