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Photosubstitution of Cl^- Ions in Λ-*Cis*-$[CoCl_2(en)_2]^+$ with Carbonate or Hydroxamate Anions Facilitated by Solid State Adsorption on Silicagel

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Owing to the low photosensitivity in the 1st and 2nd ligand region (L_1 and L_2) photosubstitution reactions of cobalt(III) complexes represent a generally difficult problem. The photoaquation observed as a result of excitation in the charge transfer region [1] cannot be considered as a primary photosubstitution process because it is a consequence of bond homolysis.

In this paper we describe the photosubstitution reaction of Λ-*cis*-$[CoCl_2(en)_2]^+$ with carbonate or hydroxamates (RCONHOK, R = C_6H_5, C_2H_5, CH_3) proceeding in an adsorbed state on the silicagel surface with the aim of studying the labilisation effect facilitating these reactions which under other conditions do not occur. Specific character of the reactions discussed below, which so far as we know have not yet been described in the literature, is determined by the following factors: no solvent effect (usually taking place in solution), no thermodynamic limitations by crystal lattice (which, beside diffusion, controls the reaction proceeding in solid state), specific influence of nucleophilic OH groups acting on the silicagel layer.

Photosubstitution reactions between Λ-*cis*-$[CoCl_2(en)_2]^+$ and carbonate or hydroxamates ions were studied in the following manner. Aqueous solutions of the starting complex and ligand were applied on the silicagel thin layer. After drying, layers were irradiated by radiation excluding charge transfer excitation (spectral region included only d–d transitions). It was found that after irradiation of Λ-*cis*-$[CoCl_2(en)_2]^+$ in the presence of ligand photosubstitution reaction takes place resulting in only one reaction product in a high yield:

$$\Lambda\text{-}cis\text{-}[CoCl_2(en)_2]^+ \xrightarrow[K_2CO_3]{h\nu(LF)} rac\text{-}[CoCO_3(en)_2]^+ + trans\text{-}[CoCl_2(en)_2]^+ \qquad (1)$$

$$\Lambda\text{-}cis\text{-}[CoCl_2(en)_2]^+ \xrightarrow[RCONHO]{h\nu(LF)} rac\text{-}[CoRCONHO(en)_2]^{2+} \qquad (2)$$

In case of (1) photosubstitution is accompanied by a simultaneous isomerisation of the starting complex. However, in the absence of the incoming ligand, photoisomerisation of the starting complex was not observed. In both cases (*e.g.* reactions 1,2) a racemic product was obtained. Owing to the fact that under the experimental conditions used there is no racemisation of both starting complex and reaction product, the racemisation proceeds as a consequence of the photosubstitution of chloride ions.

To explain the results obtained we suppose that chemisorption causes a specific activation of the complex under investigation, during which the nucleophilic character of silicagel OH groups very probably plays an important role (Table I).

Experimental

Chemicals

Potassium acetohydroxamate, propionohydroxamate and benzohydroxamate were prepared according to reference [2]. For the preparation of starting complex the standard method was used [3].

Photochemical Study

An aqueous solution (0.5 N) of the proper potassium hydroxamate or carbonate was applied on the silicagel thin layer plate (0.2 mm) (Silufol, Kavalier-Sázava, Č SSR) and the spots obtained were dried *in vacuo.* On the adsorbed hydroxamate or carbonate

TABLE I. Analysis and Spectral Data.

		C	H	N	λ_{max}(nm)	$\epsilon_{max}(M^{-1}\ cm^{-1})$
$[CoC_6H_5CONHO(en)_2]Cl_2$	calcd. %	34.21	5.74	18.14	524	125
	found %	34.53	5.27	18.26	275	1.0×10^4
$[CoC_2H_5CONHO(en)_2]Cl_2$	calcd. %	24.86	6.56	20.71	516	105
	found %	24.50	6.73	20.65	264	0.9×10^4
$[CoCH_3CONHO(en)_2]Cl_2$	calcd. %	22.23	6.22	21.61	508	100
	found %	22.20	6.25	21.18	243	1.1×10^4
$[CoCO_3(en)_2]Cl$	calcd. %	21.87	5.87	20.41		
	found %	21.93	5.95	20.25		

on the start line an aqueous solution of Λ-*cis*-[$CoCl_2$-$(en)_2$] Cl was also applied and dried. After drying, the sample on the start line was irradiated. For this purpose a mercury lamp RVL 400W (Tesla, ČSSR) with a monochromatisation of irradiation (520–580 nm) through a glass filter was used. Exposition time in all cases was 3–10 s. After irradiation samples were directly chromatographed in the isopropylalcohol–water (75:25 w/w) system. The spots separated were mechanically removed and dissolved in methanol. Electronic absorption spectra of these solutions were found to be identical with those prepared independently [4]. Methanolic solutions were evaporated to dryness at room temperature and after recrystalisation from water were analysed.

References

1 A. Vogler, A. W. Adamson, *J. Phys. Chem., 74,* 67 (1970).

2 C. R. Hanser, W. B. Renfrow, *Org. Syn., 1,* 67 (1941).

3 J. C. Bailar, *Inrog. Syn., 2,* 222 (1946).

4 B. Hájek, F. Benda, *Proc. XVth ICCC, 2,* 258, Moscow, 1973.