

Substitution of Cl^- Ligands in Λ -*cis*- $[\text{CoCl}_2(\text{en})_2]^+$ with Benzohydroxamate Anion. Inversion of the Configuration

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In our previous paper the proper reaction conditions for the preparation of benzohydroxamato-bis(ethylenediamine)cobalt(III) chloride, $[\text{Co}(\text{en})_2\text{C}_6\text{H}_5\text{CONHO}]\text{Cl}_2$, were studied [1]. Utilizing results obtained we concentrated in this paper our further effort to the study of some problems concerning stereochemistry of substitution reaction of optically active *cis*- $[\text{CoCl}_2(\text{en})_2]^+$ with potassium benzohydroxamate, $\text{C}_6\text{H}_5\text{CONHOK}$. Substitution reaction was studied either in diluted water solution or in paste. Owing to the character of electronic spectra (see ref. 1) and analogy with the conclusions described in the literature [2, 3] it was possible to consider that both starting complexes and reaction products which are dextro-rotatory at the Na_D line have the same configuration. As a starting point of relative configuration identification $[\text{Co}(\text{en})_2\text{C}_6\text{H}_5\text{CONHO}]\text{Cl}_2$ was prepared by the independent method [1] and resolved using Λ - $\text{Na}[\text{Coen}(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ analogously as described in the case $[\text{Co}(\text{en})_2\text{CO}_3]^+$ [4]. The mentioned method gave the $(+)_D$ - $[\text{Co}(\text{en})_2\text{C}_6\text{H}_5\text{CONHO}]^{2+}$ enantiomer, which was isolated as iodide ($[\alpha]_D = 1050^\circ$). The starting complex, Λ -*cis*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$, was prepared according to literature [5] and resolved using Λ - $\text{Na}[\text{Coen}(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ similarly as hydroxamato complex. By this procedure $(+)_D$ -*cis*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ was obtained ($[\alpha]_D = 734^\circ$).

Reactions between $(+)_D$ -*cis*- $[\text{CoCl}_2(\text{en})_2]^+$ and hydroxamate anion in water solution were modified so that to the 0.1–0.6 M solution of starting complex solid potassium benzohydroxamate in molar ratio ranging from 1:1 up to 1:6 was added. Reaction mixture was stirred and heated during 2–3 min. Then the reaction mixture was cooled to 5 °C and separated on the cation exchange resin as described previously [1]. Under the mentioned reaction conditions $(+)_D$ - $[\text{Co}(\text{en})_2\text{C}_6\text{H}_5\text{CONHO}]^{2+}$ is formed as a main product which does not undergo racemization.

Reaction path up to ratio 1:6 is not dependent on the ratio of reactants.

Reaction in paste was made as follows. To a mixture of pulverized solid $(+)_D$ -*cis*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ and $\text{C}_6\text{H}_5\text{CONHOK}$ in the molar ratio 1:3 was made wet with water, heated to 60 °C and the paste formed was heated with continuous stirring to 40 °C. After 1–2 min the paste was rapidly cooled to 0 °C and $[\text{Co}(\text{en})_2\text{C}_6\text{H}_5\text{CONHO}]\text{Cl}_2$ formed, dissolved and the less soluble Λ -*cis*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}_2$ isomer remaining in the reaction mixture was filtered off. Under these conditions from the reaction mixture $(-)_D$ - $[\text{Co}(\text{en})_2\text{C}_6\text{H}_5\text{CONHO}]\text{I}_2$ ($[\alpha]_D = 980^\circ$) was isolated.

Utilizing above mentioned rules and results of resolution of $[\text{Co}(\text{en})_2\text{C}_6\text{H}_5\text{CONHO}]\text{Cl}_2$ prepared independently it is possible to consider that while the reaction in water solution proceeds with the retention of configuration, in paste the formation of product with inverted configuration is observed. Thus it is possible to assume the analogy with the substitution reaction between $(+)_D$ -*cis*- $[\text{CoCl}_2(\text{en})_2]^+$ and carbonato anion, described by Bailar *et al.* [6], which proceeds with the inversion of configuration. In the case of large excess of $\text{C}_6\text{H}_5\text{CONHOK}$ and high concentration of the reaction mixture inversion of configuration occurs due to the basic hydrolysis which is followed in the second step by the substitution reaction with $\text{C}_6\text{H}_5\text{CONHO}^-$ anion. This presumption was supported by the reaction of $(-)_D$ -*cis*- $[\text{Co}(\text{OH})_2(\text{en})_2]^+$ (prepared *in situ*) with $\text{C}_6\text{H}_5\text{CONHOK}$ which proceeds with the retention of configuration giving $(-)_D$ - $[\text{Co}(\text{en})_2\text{C}_6\text{H}_5\text{CONHO}]^{2+}$.

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