BRIEF COMMUNICATIONS

TEMPLATE ELECTROSYNTHESIS OF COMPLEXES OF NICKEL WITH SCHIFF BASES

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A suitable method is proposed for the electrosynthesis of complexes of nickel with Schiff bases containing a hydroxyl group (homogeneous catalysts of chemical and electrochemical reactions) in a single stage with a high material yield.

Keywords: Electrosynthesis, template synthesis, nickel complex.

Intensive research into catalysis by metal complexes have consistently led to the discovery of new catalytic reactions and to extension of the range of metal-complex catalysts. This trend has prompted the search for new effective methods of synthesis, distinguished by simplicity in execution and ecological cleanliness. In a number of cases electrosynthesis has advantages compared with traditional chemical methods in the production of complexes with a metal ion in lower degrees of oxidation. Frequently this advantage lies in the purity of the product, the selectivity of the process, and the possibility of controlling the reaction. Published data on the electrosynthesis of complexes usually concerned with the cathodic reduction of solutions of a previously prepared ligand in a cell with a dissolving anode. The exhaustive reduction of complex ligands usually requires low current densities and this leads to low productivity. Thiolate [1], phenylselenolate [2], and 2,2'-dipyridylamine complexes [3], ferrocene [4], Cu(II) alkoxides [5], cyclopentadienyl complexes [6], and complexes with Schiff bases [7, 8] have been obtained in this way.

Our version of the synthesis of nickel(II) complexes with Schiff bases is also based on the anodic dissolution of a metallic anode, but the complex is formed directly during electrolysis as a result, probably, of a template synthesis. The anodically generated Ni(II) ion here acts as matrix around which the aldehyde and amine components are coordinated in a single complex. The detailed mechanism of formation of the product is unknown. It can be supposed that the nickel ions are combined both with the hydroxyl-containing form of the initial reagent and with the Schiff base (ligand). It is known that the formation of the ligand in the absence of Ni²⁺ requires more rigorous conditions (boiling with a reflux condenser at 80-100°C) and sometimes baking at 300°C (the reaction of salicylamide with o-aminophenol) [9]. Thus, the role of the nickel ions lies in promotion of the reaction of the aldehyde and amine forms with the formation of a single complex of nickel under mild conditions. The complex is most likely formed at the nickel-ion matrix as a result of a template synthesis [10], in which the Ni²⁺, aldehyde, and amine react simultaneously.

The protons released during the reaction combine with the cathodically generated base (the alkoxide ion). In nonpartitioned electrolysis with nickel electrodes the initial aldehyde and amine (Table 1) dissolve in the alcohol medium in a molar ratio of 1:1. The concentration of the supporting electrolyte NaBr of $10^{-3} M$ was sufficient to attain high electric conductivity and satisfactory current densities (up to 10 mA/cm²). The anodic process was the dissolution of nickel: Ni⁰ - 2e⁻ \rightarrow Ni²⁺. The cathodic process was reduction of the alcohol with the release of hydrogen, which maintains an inert atmosphere during electrolysis and prevents oxidation of the components of the solution:

$2EtOH-2e^{-}\rightarrow 2EtO^{-}+H_{2}^{\dagger}$.

The formation of the complexes can be described by the reaction:



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Aldehyde	Amine	Complex	Yield, % material
Salicylaldehyde	1-Aminoanthra- cene	-CH=N-R, R=	88
	1-Aminonaphthal- ene	» R =	85
Benzaldehyde	o-Aminophenol	R- $CH=N-$, $R=H$	80
n-Propoxybenzaide- hyde	*	$ \begin{cases} 2NNI=0' \\ N & R = PrO \end{cases} $	81
Salicylamide Furfural	» Hydroxylamine		80
			82
		$ \begin{array}{c c} 0 & CH = N \\ 2 \\ Ni \longrightarrow 0 \end{array} $	

TABLE 1. Yields of the Complexes of Nickel with Schiff Bases

The process takes place similarly in the case of other aldehydes and amines. The electrolysis products and their yields are given in Table 1.

The described process makes it possible in principle to use any aldehyde and amine reagents and various anode materials for the synthesis of the complexes. The proposed methods of synthesis have a series of advantages over already known methods; they are single-stage processes, avoid the preliminary operations often requiring harsh conditions in the synthesis of the ligands, make it possible to use high current densities, and make it possible to isolate the required complex without complications – about half the product has already separated during electrolysis, and the process takes place under mild conditions at ~20°C. The complexes are obtained with sufficiently high purity so that they can then be used as effective catalysts of electrochemical reactions. The structure and physical characteristics of the complexes correspond to those described in the literature [9,10].

EXPERIMENTAL

The preparative electrolyses were conducted by means of a P-5848 potentiostat at a cathodic current density of 10 mA/cm² in a 150-ml cell without partitioning of the anode and cathode compartments with nickel electrodes. The solvent was ethanol, and the supporting salt was tetraethylammonium bromide $(10^{-3} M)$. The amount of electricity passed through the electrolyte was 2F/mole of aldehyde, and the aldehyde and amine were in a molar ratio of 1:1 $(5 \cdot 10^{-2} \text{ mole})$. At the end of the electrolysis most of the solvent was evaporated from the electrolyte, the nickel complex was filtered off, and the product was washed with chloroform and dried under vacuum.

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