

## SYNTESIS ROUTE FOR PREPARATION OF PRECURSOR SOLUTIONS

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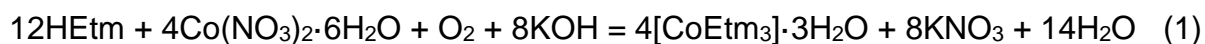
A method of surface modification of carbon materials (including their nanoforms such as fullerenes and nanotubes) for electrochemical applications has been developed. The core idea of the method is preparation of the precursor methanol solutions containing heteronuclear coordination compounds with aminoalcohols followed by the adsorption of these compounds on the surface and, if necessary, the subsequent pyrolysis in controlled conditions. Thus, the isolation of the complexes, as it was in the early versions of the method, is not required, which simplifies the procedure and permits to avoid the losses of the product at the intermediate stages of crystallization.

The formation of trinuclear 2Co-Ni complexes with aminoalcohols, e.g.  $[\text{Ni}(\text{CoEtm}_3)_2](\text{NO}_3)_2$  (Etm is the deprotonated form of monoaminoethanol  $\text{H}_2\text{NC}_2\text{H}_4\text{OH}$ ), was proved by IR and electron absorption spectra.

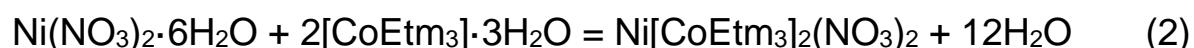
It is known that the most of the practically important electrochemical reactions (evolution of hydrogen, reduction of oxygen, intercalation of Li into carbons etc.) requires catalysts in order to increase the operating currents and decrease the polarization of the electrode. The heterometal polynuclear aminoalcohol complexes of Co(III) with other 3d-metal ions are of particular interest due to its low cost, environmentally friendliness and effectiveness. It was found earlier that such complexes, especially 2Co(III)-Ni(II), and/or their pyrolysis products grafted on the surface of carbon materials can be used in the electrochemical reduction of oxygen in fuel cell's electrodes [1,2], reversible intercalation of Li into graphites [1,3-5], discharge-ionization of hydrogen on carbon nanotubes in aqueous electrolytes [6], electrochemical synthesis of lithium fullerenes [7].

The trinuclear complexes 2Co(III)-Ni(II) with mono-, di- and triaminoethanol ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ , Hetm;  $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$ ,  $\text{H}_2\text{detm}$ ;  $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ ,  $\text{H}_3\text{tetm}$  accordingly) have been known for a long time [8,9]. Commonly, their preparation includes two steps with isolation of the intermediate and final products from the reaction media. The first one is

the synthesis of inner complex compound, which, in the case of monoaminoethanol ligands, proceeds in alcohol (methanol) solutions in the presence of atmospheric oxygen according to equation (1)



Further on, the deposit of potassium nitrate is filtered out and the inner complex compound is crystallized from the methanol solution at room temperature for several days. Then the crystals of  $\text{CoEtm}_3$  are filtered, dried and dissolved in the methanol again. After that, nickel nitrate is added to the solution and synthesis of the trinuclear compound is performed according to equation (2)



The final compound,  $\text{Ni}[\text{CoEtm}_3]_2(\text{NO}_3)_2$ , is crystallized for at least 3 days and stored. For the preparation of the electrocatalysts, this compound is dissolved in methanol again and the complex is grafted onto the surface of a carbon material and, if necessary, pyrolysed in an inert atmosphere.

One can see that such synthesis requires rather long time and inevitably brings about significant losses of the complexes. That is why the development of one-pot method of preparation of the precursor solutions of the trinuclear 2Co(III)-Ni(II) complexes with monoaminoethanol ligands, without the intermediate steps of isolation of the solid compounds, was the purpose of the present work.

To achieve this goal, the complex formation in the methanol solutions must be studied in order to obtain the final precursor solution containing the trinuclear  $\text{Ni}[\text{CoEtm}_3]_2(\text{NO}_3)_2$  compound with no other admixtures. This was done by means of the methods of IR and electron absorption spectra.

### **Research methodology**

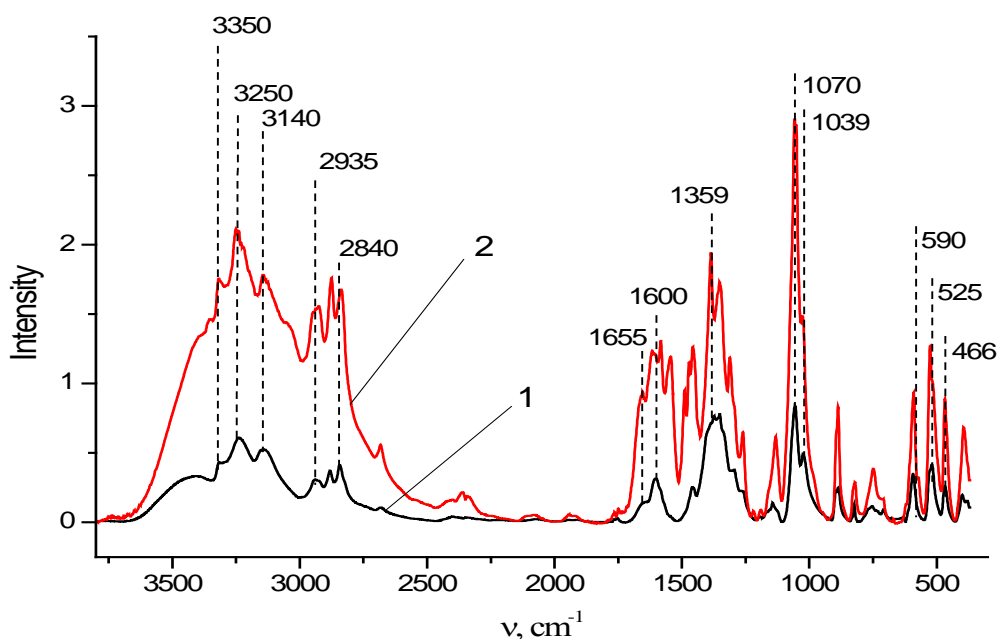
The intermediate methanol solution of the inner complex compound  $\text{CoEtm}_3$  was obtained according to equation (1) followed by filtering out the deposit of potassium nitrate, which is poorly soluble in methanol. Part of this solution was investigated by IR and electron spectra, the other part was used for the preparation of the trinuclear complex according to equation (2).

IR-spectra were taken with FTIR spectrometer Specord 751R in the region  $450\text{cm}^{-1} - 4000\text{cm}^{-1}$ . Electron spectra in visible and UV regions were obtained with a spectrophotometer UV/VIS Specord 210 Plus in quartz vessels of 1cm thickness.

## Results and discussion

Preliminary information on the complex formation in methanol solutions was obtained from IR spectra. Fig.1 shows the IR spectra of the inner complex compound (product of the reaction 1) and heteronuclear complex 2Co(III)-Ni(II) with monoaminoethanol ligands.

The spectra were described using the reference literature [10]. The high-frequency region of the absorption spectra contains the vibration bands at 3350, 3250 and 3140  $\text{cm}^{-1}$ , which can be attributed to valence vibration of OH group, asymmetric and symmetric vibrations of N-H bonds. Besides, the vibrations at 2935, 2840, 1655, 1600, 1359, 1070 и 1039  $\text{cm}^{-1}$  are observed, which corresponds, accordingly, to the valence asymmetric and symmetric vibrations of  $\text{CH}_2$ , space deformation vibrations of OH and NH, stretching deformation vibrations of OH and frequency vibrations  $\nu(\text{C-O})$  and  $\nu(\text{CN})$ . The absorption band  $\nu(\text{CO})$  at 1070 - 1010  $\text{cm}^{-1}$  may be the evidence for the coordination of the ligands via oxygen atoms. Besides, the vibration bands in the region of 450 – 590  $\text{cm}^{-1}$  can be attributed to the valence vibrations of M-O bonds.



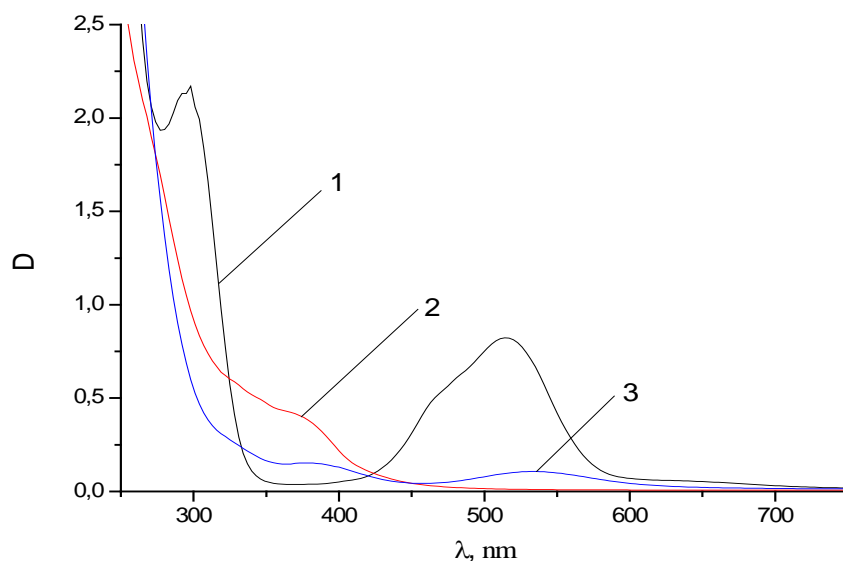
**Fig.1.** IR absorption spectra of the inner complex compound Co(III) with monoaminoethanol (1) and trinuclear complex 2Co-Ni (2)

More information on the complex formation in methanol solutions follows from electron absorption spectra.

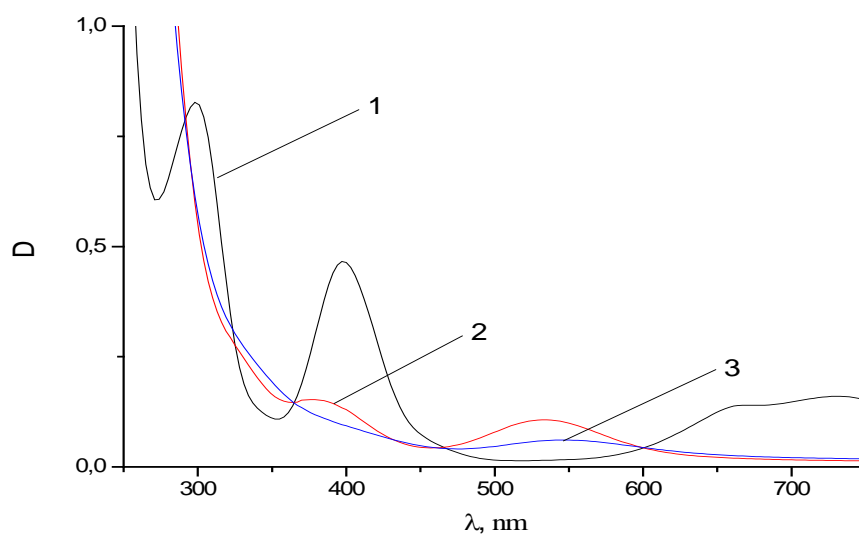
The spectrum of methanol solution after the reaction (1) is presented in Fig.2 in comparison with the spectra of the initial reactants.

As follows from the spectra, the bands corresponding to the absorption of pure Co nitrate and ligand are not observed in the spectrum of the reaction product, which proves the reaction (1) of complex formation in the solution.

The spectrum of the solution after the reaction (2) is shown in Fig.3 together with the spectra of  $\text{Co}(\text{Etm})_3$  and nickel nitrate.



**Fig.2.** Electron absorption spectra of methanol solutions in visible region:  
 1 –cobalt(II) nitrate,  $C_{\text{Co(II)}} = 1 \cdot 10^{-2}$  mol/l; 2 – monoaminoethanol,  $C_{\text{HEtm}} = 2 \cdot 10^{-2}$  mol/l;  
 3 -  $\text{Co}(\text{Etm})_3$ ,  $C_{\text{Co(III)}} = 1.5 \cdot 10^{-2}$  mol/l



**Fig.3.** Electron absorption spectra of methanol solutions:  
 1 –  $\text{Ni}(\text{NO}_3)_2$ ,  $C_{\text{Ni(II)}} = 5 \cdot 10^{-3}$  mol/l; 2 -  $\text{Co}(\text{Etm})_3$ ,  $C_{\text{Co(III)}} = 1.5 \cdot 10^{-2}$  mol/l;  
 3 - product of the reaction (2),  $C_{\text{Co(III)}} = 1 \cdot 10^{-2}$  mol/l,  $C_{\text{Ni(II)}} = 5 \cdot 10^{-3}$  mol/l

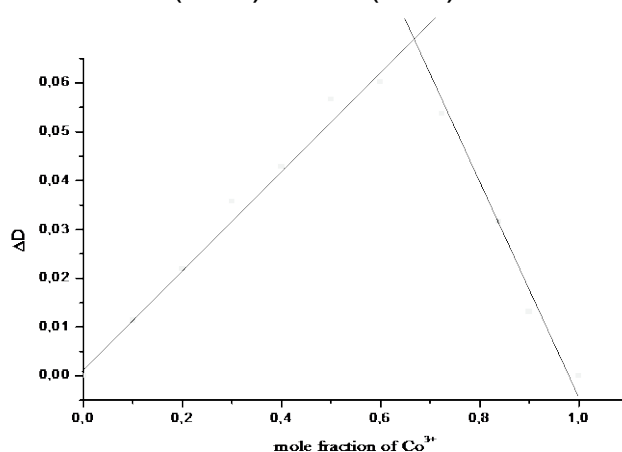
According to Fig.3, the spectrum of the reaction product (curve 3) does not contain the d-d bands at 298 nm and 397 nm, which are characteristics of pure nickel nitrate spectrum. The band at 357 nm of the inner complex compound (curve 2) vanishes and maximum at 535 nm shifts to 547 nm.

The above spectral data confirm the formation of heterometal complex containing both cobalt and nickel. The exact composition of this complex in methanol solution was established by measuring the electron spectra of isomolar solution series [11]. In this method, the optical densities for the series of solutions with equal sum of  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Co}(\text{Etm})_3$  concentration and different Ni to Co molar ratios are determined and deviations from additivity are calculated by the formula(3)

$$\Delta D = D_{\text{exp.}} - (\varepsilon_1 c_1 l + \varepsilon_2 c_2 l), \quad (3)$$

where  $D_{\text{exp}}$  is the experimental optical density,  $c_1$  and  $c_2$  – concentrations of the above components,  $\varepsilon_1$  and  $\varepsilon_2$  = the absorption coefficients of the components. The sum  $c_1 + c_2$  in our experiments was equal to 0.01 mol/l, the thickness of the absorptive layer  $l=1$  cm.

Fig.4 represents the deviation from additivity of absorption density in the isomolar solution series  $\text{Ni}(\text{NO}_3)_2 - \text{Co}(\text{Etm})_3$



**Fig.4.** Deviations from additivity of the optical density ( $\lambda=450$  nm) the isomolar series of solutions containing  $\text{Ni}^{2+}$  and  $[\text{Co}(\text{Etm})_3]$ . The sum of the components concentrations is  $1 \cdot 10^{-2}$  mol/l

One can see that the dependence in Fig.4 has the maximum at the ratio  $\text{Ni}/\text{Co}=1/2$ . This confirms the existence of trinuclear complex  $\text{Ni}[\text{Co}(\text{Etm})_3](\text{NO}_3)_2$  in the methanol solutions, which can be used as precursors for preparation of the electrocatalysts.

## Conclusions

The spectral studies confirm the possibility of simplified one-pot synthesis of the methanol solutions of trinuclear 2Co(III)-Ni(II) complex compound. These solutions can be applied directly for the preparation of catalysts on the surface of carbon materials for various electrochemical applications avoiding the laborious intermediate stages, and thus, diminishing the losses of the d-metal compounds.

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