

FORMATION AND STABILITY OF HETEROMETAL COMPLEXES Co(III)-Ni(II) WITH AMINOALCOHOLS IN METHANOL SOLUTIONS AND THEIR USE AS PRECURSORS FOR PREPARATION OF ELECTROCATALYSTS

A.O. Zulfigarov*, A.V. Pidgornui, I.S. Kuzevanova, A.A. Andriiko

National Technical University of Ukraine "Igor Sikorskyi Kyiv Polytechnic Institute",
Kyiv, Ukraine

Abstract. The formation of heterometaltrinuclear 2Co(III)-Ni(II) complexes in methanol solutions with aminoalcohol ligands, monoaminoethanol $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$, HEtm (I), diminoethanol $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$, H_2Detm (II) and triaminoethanol $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, H_3Tetm (III) were studied by electron spectra method and their stability constants were calculated: $\beta_2 = (7.10 \pm 1.46) \cdot 10^4$ (I), $(11.30 \pm 0.37) \cdot 10^4$ (II), and $(6.65 \pm 0.72) \cdot 10^4$ (III). The binuclear complex Co-Ni was also detected in the system (III) with stability constant $\beta_1 = (1.79 \pm 0.29) \cdot 10^2$.

The complexes were absorbed from the solution on the surface of graphite powder, pyrolysed in pure argon at 500°C and the electrocatalytic properties of the samples thus obtained with regard to the reaction of Li intercalation were studied by galvanostatic cycling method. It was found that the catalytic effect is maximal for diaminoethanol complexes, intermediate for monoaminoethanol and minimal for triaminoethanol complexes, which correlates with the stability of the trinuclear 2Co-Ni complexes in the solutions.

Keywords: heterometal complexes, cobalt (III), nickel (II), aminoalcohol ligands, stability constants, electrochemical properties.

***Corresponding Author:** Artur Zulfigarov, National Technical University of Ukraine "Igor Sikorskyi Kyiv Polytechnic Institute", 37, Peremohy ave., Kyiv, Ukraine, 03056, Tel.: +38 (044) 454 98 83, e-mail: sars2007@ukr.net

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1. Introduction

Heterometalpolynuclear Co(III)-Ni(II) complex compounds with aminoalcohol ligands, such as monoaminoethanol $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$, HEtm, diminoethanol $\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$, H_2Detm and triaminoethanol $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, H_3Tetm , can be used as precursors for preparation of catalysts for various electrochemical processes. Up to date, four such processes were investigated using these electrocatalysts: 1) electroreduction of oxygen with possible applications in fuel cells and zinc-air batteries (Gupta *et al.*, 1989; Shi *et al.*, 1995; D'Souza *et al.*, 1997); 2) intercalation of Li into graphite (negative electrode of Li-ion batteries) (Reiter *et al.*, 2006; Andriiko *et al.*, 2008; Potaskalov *et al.*, 2010); 3) electrochemical synthesis of lithium fullerides (Zulfigarov *et al.*, 2013), and 4) discharge-ionization of hydrogen on carbon nanotube electrodes (hydrogen energy storage) (Andriiko *et al.*, 2013).

Preparation of the electrocatalysts consists of grafting the complexes onto the surface of carbon materials by adsorption from alcohol solutions. Subsequent pyrolysis in an inert atmosphere is required for the first three kinds of electrochemical reactions.

The precursor solutions are obtained in two steps. First, inner complex compounds of Co(III) are synthesized by the reactions (1a, 1b, 1c):



After separation of the potassium nitrate, nickel salt is added and the reactions (2) of the heterometal complexes take place:



where the symbol L denotes the inner complex compounds (ICC) with partly deprotonated molecules of the aminoalcohols, CoEtm_3 , $\text{Co}(\text{DetmHDetm})$ and $\text{Co}(\text{H}_2\text{TetmHTetm})$. Hence, the ICC are the specific kind of ligands with regard to the Ni^{2+} ions. According to the quantum chemical calculations (Zulfigarov *et al.*, 2016), the coordination knot of Ni in such complexes is the planar quadrangle with four bridge oxygen atoms (Fig.1). After the thermal decomposition, this structure forms solid spinel nanoparticles NiCo_2O_4 , which are catalytically active.

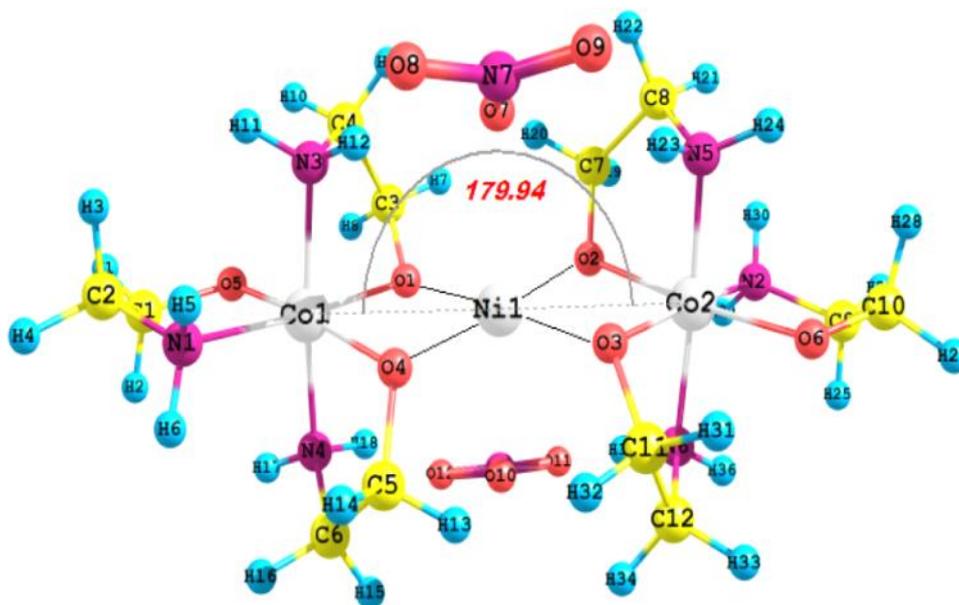


Figure1. Calculated structure of $[\text{Ni}(\text{CoEtm}_3)_2(\text{NO}_3)_2]$

In this work we have studied the formation of heterometal complexes in methanol solutions according to the equilibria (2) and estimated the stability constants for systems with mono-, di- and triaminoethanols. Obviously, such data are of importance for practical applications.

2. Experimental

The equilibria of Co(III)-Ni(II) heterometal complex methanol solutions were studied by electron absorption spectra (EAS) method on UV/VIS Specord 210

Plusspectrophotometer in wavelength from 250 to 750 nm in quartz cuvette with the thickness $l = 1\text{ cm}$.

The samples for electrochemical testing were prepared as follows. The powder of battery grade graphite Hohen (10-28) was contacted with the excess of methanol solution for 24 hours at room temperature. The liquid phase was filtered out, the powder was dried at 100°C and then thermally treated at 500°C in atmosphere of pure argon. The samples were tested in mockup coin cells of 2016 size vs. Li counter electrode: Li/electrolyte (Merck LP-30)/graphite sample on copper foil. The cells were assembled by standard technology in dry glove box.

3. Results and discussion

First, three series of EAS for isomolar solutions $\text{Ni}(\text{NO}_3)_2 - \text{ICC}$ were taken, where ICC – $\text{Co}(\text{Etm})_3$, $\text{Co}(\text{Detm})(\text{HDetm})$, $\text{Co}(\text{H}_2\text{Tetm})(\text{HTetm})$. Then, using Lambert-Beer's law, deviations of optical density from additivity were calculated by the equation (3)

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

where $D_{\text{exp.}}$ - experimental values of the optical density, c_1 and c_2 - concentrations of aminoalcohol cobalt complex and ions Ni^{2+} , ε_1 and ε_2 - molar extinction coefficients of the solution components. The sum $c_1 + c_2$ was equal to $0,01\text{ mol/l}$ for all systems. Figure 2 represents the obtained dependencies.

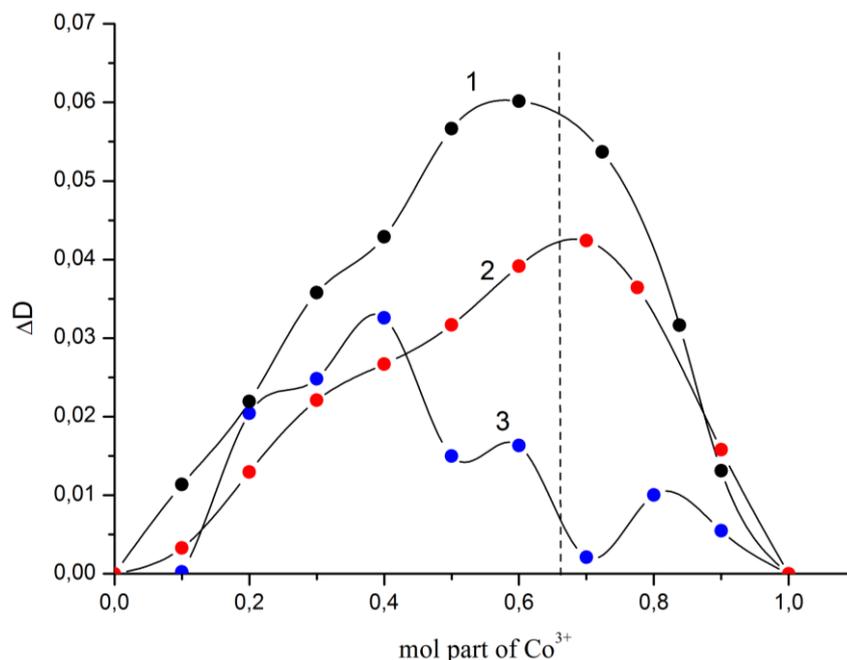


Figure 2. Deviation from additivity of the optical density in the isomolar series of solutions for the systems $\text{Ni}^{2+} - [\text{Co}(\text{Etm})_3]$ (1), $\text{Ni}^{2+} - [\text{Co}(\text{Detm})(\text{HDetm})]$ (2) and $\text{Ni}^{2+} - [\text{Co}(\text{H}_2\text{Tetm})(\text{HTetm})]$ (3); $C_{\text{Ni}^{2+}} + C_{\text{Co}} = 1 \cdot 10^{-2}\text{ mol/l}$; $\lambda = 450\text{ nm}$

In the simplest case when only one complex compound is formed, the dependency (3) should have a maximum at Co:Ni ratio which corresponds to the composition of the complex. Evidently, this is observed for mono- and diaminoethanol systems (Fig. 2,

curves 1,2) – the data indicate the formation of trinuclear complex $[\text{Ni}(\text{L})_2]$ in accordance with the reaction (2). The situation is more complicated in case of triaminoethanol system (Fig. 2, curve 3).

In order to establish the composition and stabilities of the heterometal complexes forming in the methanol solutions, we have calculated the concentrations of the free ligands from these spectra. The absorption bands in the range of 500 – 700 nm were used (Fig. 3). Since the absorption of pure Ni^{2+} compound is negligibly small in this region, the broad peak of the solutions consists of two overlapping bands related to the heterometal complex and ligand (ICC). Such bands were deconvoluted in two Gauss peaks (an example is shown in Fig. 4) and concentrations of free ligand were calculated.

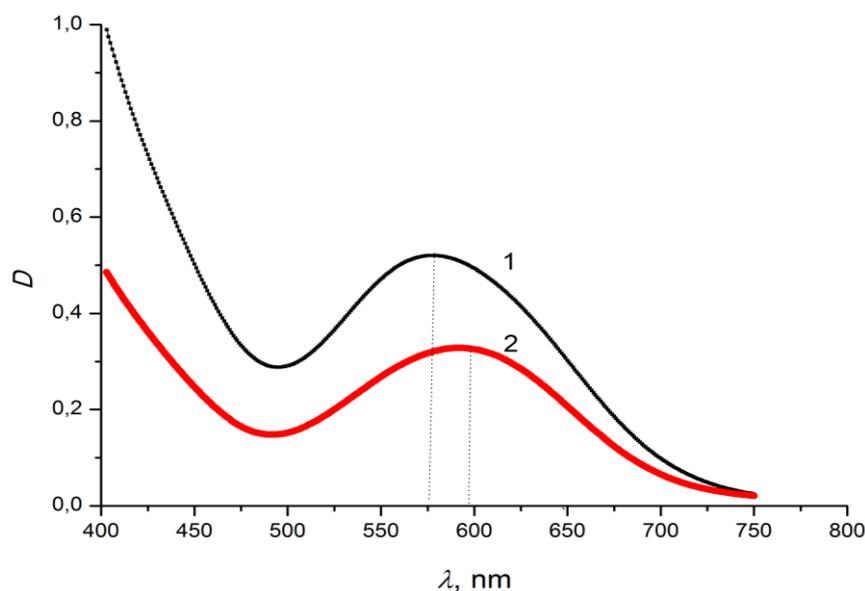


Figure 3. Absorption spectra of pure intracomplex compound $\text{Co}(\text{DetmHDetm})$ (1) and the solution with $\text{Co}:\text{Ni} = 1:1$ (2), $C_0 = C_{\text{Co}} + C_{\text{Ni}} = 1 \cdot 10^{-2} \text{mol/l}$

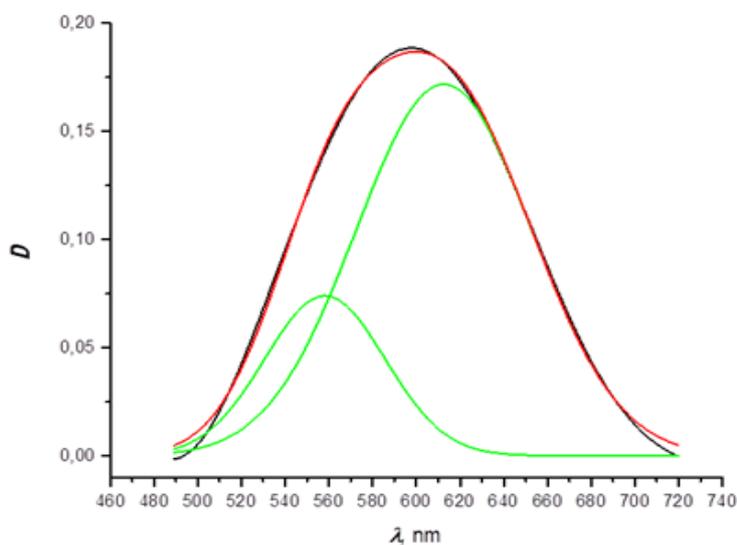


Figure 4. Deconvolution of peak 2 (Figure 3). The left peak correspond to free ligand (ICC)

After that, the average coordination number (Bjerrum function) was calculated for each of the three systems (4):

$$\bar{n} = \frac{c_{Co-L}}{c_{Ni}} \quad (4)$$

These functions are plotted in Fig. 5.

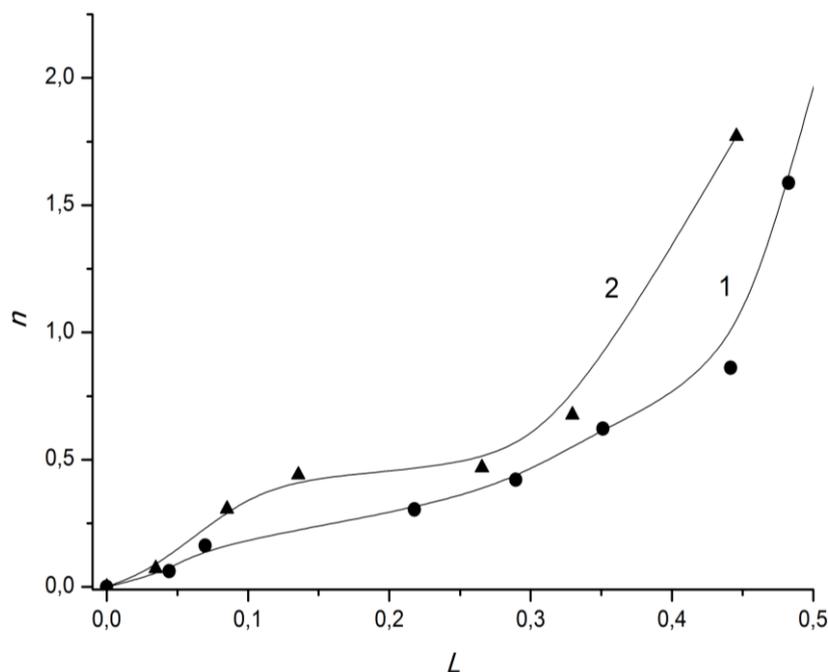


Figure 5. Bjerrum functions for mono- (1) and triaminoethanol (2) Co-Ni complexes in methanol solutions

Stability constants, in principle, can be calculated by classic Bjerrum method using half-integer values of the average coordination numbers. However, such method is not much reliable and requires repeated recalculations. Thus, we applied other calculation method, which is as follows.

When several NiL_i complexes are formed, the Bjerrum function can be represented as (5):

$$\bar{n} = \frac{\sum_{i=1}^N i\beta_i L^i}{1 + \sum_{i=1}^N \beta_i L^i} \quad (5)$$

The polynom (6) in denominator of the equation (5):

$$F = 1 + \sum_{i=1}^N \beta_i L^i \quad (6)$$

is known as Froneus function. Evidently, the average coordination number is a logarithmic derivative of this function (7):

$$\bar{n} = \frac{d \ln F}{d \ln L} \quad (7)$$

The function F is more convenient for the calculations of stability constants. It was calculated (8) by integration of the equation (7):

$$\ln F = \int \bar{n} d \ln L = \int \frac{\bar{n}}{L} dL + const \quad (8)$$

The integration constant is provided by the condition $F=1, L=0$.

Thus obtained, the dependency $F(L)$ was approximated by polynomial function and the available complexes and their stability constants were calculated from the polynomial coefficients. Such approximations are shown in Fig. 6.

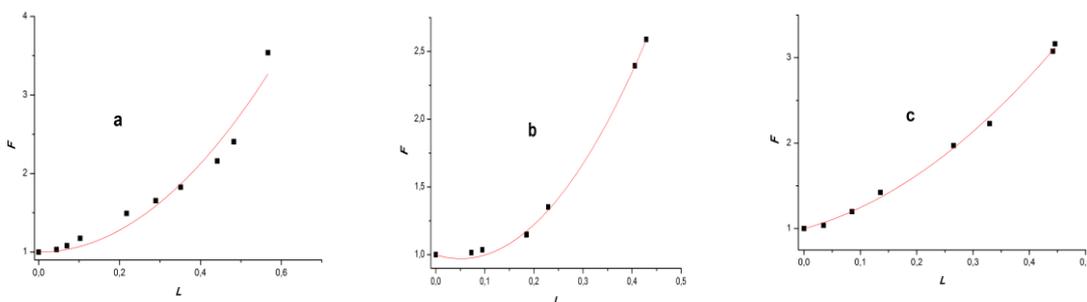


Figure 6. Approximation by polynomial function $F(L) = 1 + aL + bL^2$: (a) - Ni^{2+} - $[\text{Co}(\text{Etm})_3]$; (b) - Ni^{2+} - $[\text{Co}(\text{DetmHDetm})]$ and (c) - Ni^{2+} - $[\text{Co}(\text{H}_2\text{TetmHTetm})]$. The coefficients a of the polynomial function are insignificant for systems (a) and (b)

The stability constants are presented in Table 1.

Table 1. Formation constants of heterometal complexes NiL (β_1) and NiL_2 (β_2)

Ligands	$\beta_1 \cdot 10^{-2}$	$\beta_2 \cdot 10^{-4}$
HEtm	-	7.10 ± 1.46
H ₂ Detm	-	11.30 ± 0.37
H ₃ Tetm	1.79 ± 0.29	6.65 ± 0.72

As follows from the data, binuclear compound NiL can be detected only in triaminoethanol system. The trinuclear compounds form in all three systems. Most stable NiL_2 complex is formed in case of diaminoethanol ligands. Using the values of constants in Table 1, the distributions of species in methanol solutions at $C_{\text{Co}} + C_{\text{Ni}} = 1 \cdot 10^{-2} \text{ mol/l}$ were calculated. They are plotted in Figures 7-9 for all three systems.

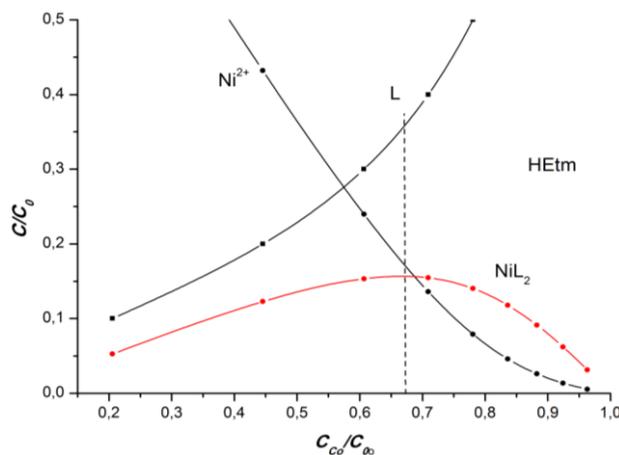


Figure 7. Distribution of the species in methanol solutions of the system Ni^{2+} - $[\text{Co}(\text{Etm})_3]$

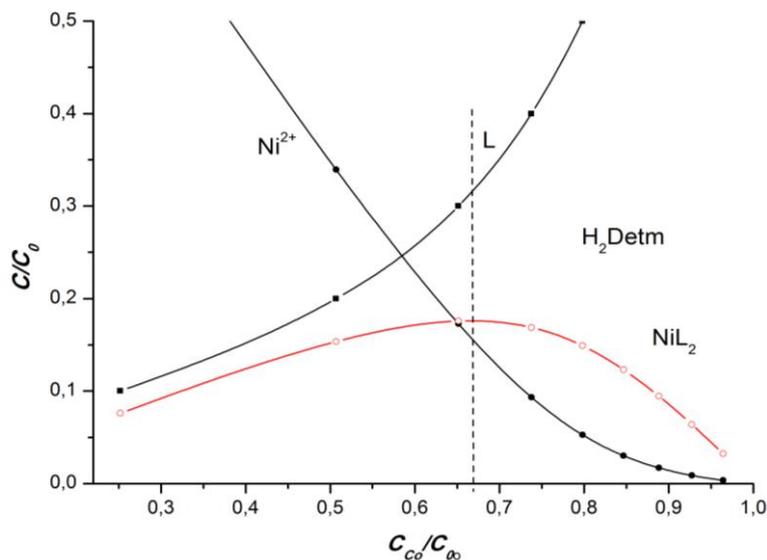


Figure 8. Distribution of the species in methanol solutions of the system Ni^{2+} - $[\text{Co}(\text{DetmHDetm})]$

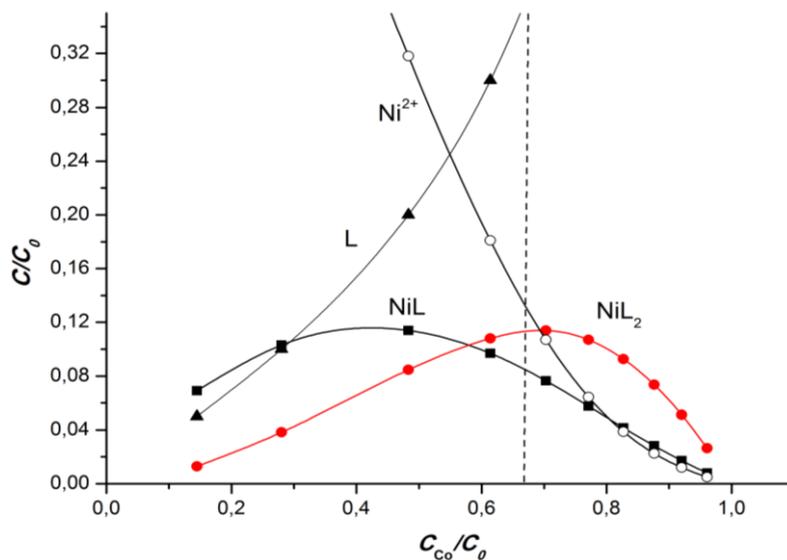


Figure 9. Distribution of the species in methanol solutions of the system Ni^{2+} - $[\text{Co}(\text{H}_2\text{TetmHTetm})]$

Thus, the trinuclear complexes are in equilibrium with free intra-complex compounds of $\text{Co}(\text{III})$ and Ni^{2+} compounds. Their relative contents at $C_0 = C_{\text{Co}} + C_{\text{Ni}} = 1 \cdot 10^{-2} \text{ mol/l}$ and stoichiometric ratio $\text{Co}:\text{Ni} = 2:1$ are given in Table 2. Naturally, concentrations of the complexes will be higher at higher total concentration C_0 .

Table 2. Relative concentrations of species in Ni^{2+} L systems at $C_0 = C_{\text{Co}} + C_{\text{Ni}} = 1 \cdot 10^{-2} \text{ mol/l}$ and $\text{Co}:\text{Ni} = 2:1$

Ligands	$[\text{Ni}^{2+}] \cdot 10^2$	$[\text{L}] \cdot 10^2$	$[\text{NiL}] \cdot 10^2$	$[\text{NiL}_2] \cdot 10^2$
HEtm	0.157	0.360	-	0.154
H ₂ Detm	0,152	0.315	-	0.177
H ₃ Tetm	0.128	0.360	0.084	0.113

Figure 10 shows the results of electrochemical testing of the graphite samples modified with the methanol solution of 2Co-Ni complexes.

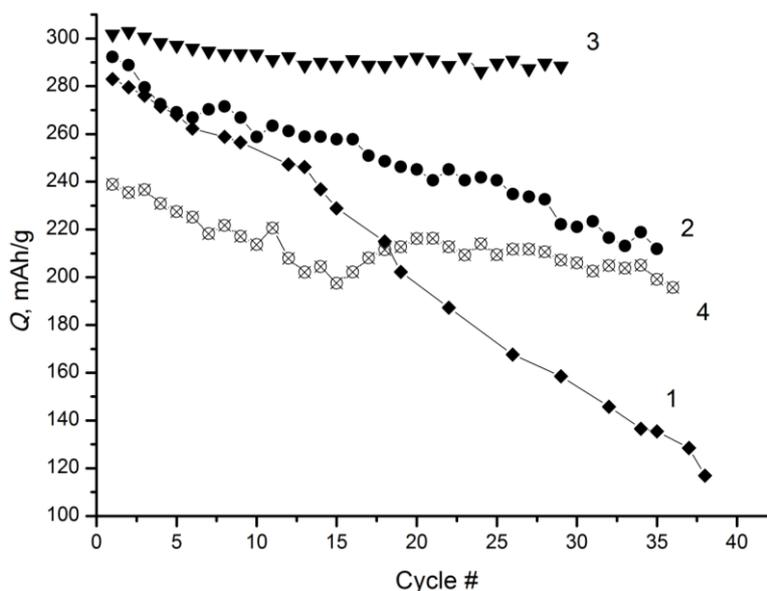


Figure 10. Variation of the specific capacity vs. cycle number of the graphite samples in the reaction of electrochemical intercalation of Li: 1 – pristine graphite Hohen (10-28); the same graphite modified with 2Co-Ni complexes with mono- (2), di- (3) and triaminoethanol (4) ligands. Galvanostatic cycling in voltage range 0.02 – 1.5 V vs. Li, current load 20 mA/g

As follows from the Fig. 10, all three types of complexes improve the electrochemical behavior of graphite in the reaction of reversible Li intercalation. However, the effect is maximal for diaminoethanol complexes, intermediate for monoaminoethanol and minimal for triaminoethanol complexes. Evidently, it correlates with the stability of the trinuclear 2Co-Ni complexes in the solutions used for grafting them onto the surface of graphite.

4. Conclusions

It was established that the stability of heterometaltrinuclear 2Co(III)-Ni(II) complexes depends on the nature of aminoalcohol ligands. The complex with diaminoethanol, $\text{Ni}[\text{Co}(\text{Detm})(\text{HDetm})]_2^{2+}$ is most stable ($\beta_2 \cdot 10^{-4} = 11.30 \pm 0.37$). The triaminoethanol complex, $\text{Ni}[\text{Co}(\text{H}_2\text{Tetm})(\text{HTetm})]_2^{2+}$ is the less stable ($\beta_2 \cdot 10^{-4} = 6.65 \pm 0.72$), and monoaminoethanol complex, $\text{Ni}[\text{Co}(\text{Etm})_3]_2^{2+}$ is of intermediate stability ($\beta_2 \cdot 10^{-4} = 7.10 \pm 1.46$). Besides, the binuclear complex $\text{Ni}[\text{Co}(\text{H}_2\text{Tetm})(\text{HTetm})]_2^{2+}$ is formed in case of triaminoethanol ligands ($\beta_1 \cdot 10^{-2} = 1.79 \pm 0.29$). The higher is the stability of 2Co(III)-Ni(II) complexes, the larger is the equilibrium concentration of these complexes in the solution, and the better electrocatalytic performance of the modified graphite is expected when using these solutions as precursors for the modification. This conclusion is verified experimentally with regard to the electrochemical reaction of reversible Li insertion into the modified graphite materials.

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