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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrochemical Synthesis of Complex Compounds of Transition Elements with Carboxyl- and Carbonyl-containing Ligands

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Abstract—Complex compounds of *d*- and *f*-elements with carboxyl- and carbonyl-containing ligands were synthesized by the electrochemical method. The influence exerted by a number of factors on the process course was studied. The dependence of the electrosynthesis parameters on the composition of the forming compounds was established. The composition of these compounds was determined. A new method for anodic synthesis of these compounds was developed.

The electrochemical method simplifies synthesis of known compounds [1–5] and makes it possible to synthesize compounds that cannot be obtained otherwise [6]. Moreover, the advantage of the anodic synthesis is in that the process can be controlled and performed in mild conditions with a high yield and purity of the final products [7].

Despite that the electrosynthesis is one of the oldest methods for synthesis of coordination compounds [8], the analysis of the anodic synthesis methods in [1–7, 9–13] shows that many problems concerning the theory and practical application of the method have not been studied.

Transition-metal carboxylates of composition $M(O_2CR)_n$ (M = Cr; R = C_2H_5 or C_6H_5; $n = 3$; M = Mn, Fe, or Ni; R = CH_3, C_2H_5, C_6H_5, or n-C_7H_{15}; $n = 2$) have been prepared [14] by electrochemical oxidation of the corresponding metals in solutions of carboxylic acids RCOOH in acetonitrile. In [15–17], monocarboxylic acids containing one to four atoms in the carbon chain were successfully used to synthesize $M(O_2CR)_2$ salts. Oxalate complexes of iron and copper were synthesized by the electrochemical method in [18]. On the whole, publications devoted to carboxylate complexes are scarce and analyze a rather small number of the ligands.

The goal of this study was to develop new original methods that would enable application of the electrochemical synthesis in a wider range and to a larger number of objects and make it possible to perform directed syntheses in which the composition of the forming products is controlled by varying the process conditions (ligand concentration, temperature, solvent, and electrode potential), and also to compare the properties of compounds synthesized by electrochemical methods with those produced by chemical methods. Acetylacetonates of rare-earth elements (REE) were synthesized to confirm the suggestion that substances exhibiting a tendency toward sublimation, which could not be synthesized previously by other methods [19, 20], can be obtained by electrochemical synthesis.

EXPERIMENTAL

The installation for anodic synthesis (Fig. 1) comprised a three-electrode cell, PI-50-1 potentiostat,

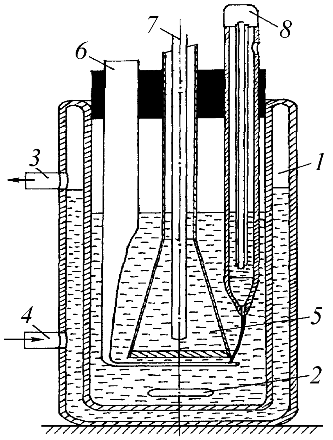


Fig. 1. Schematic of a three-electrode cell for electrochemical anodic synthesis (*1*) Thermostating jacket, (*2*) stirrer, (*3*) outlet, (*4*) inlet, (*5*) separator, (*6*) working electrode, (*7*) auxiliary electrode, and (*8*) reference electrode.

Complex compounds obtained by electrochemical synthesis

Compound	Formula	Ligand concentration, $c \times 10^2$, M	Supporting electrolyte and solvent	Anode	Cathode	Anode potential, V	Current density, A dm^{-2}		T, °C	Current efficiency, %
							anode	cathode		
I	$CuSuc \cdot 5H_2O$	10	H_2O	Cu	Cu	0.5	5	5	25	85.3
II	$CuSuc \cdot 5H_2O$	10	H_2O	Cu	Cu	0.5	5	5	60	80.6
III	$CuSuc \cdot 5H_2O$	10	H_2O–alcohol	Cu	Cu	0.05	5	5	25	53.2
IV	$ZnSuc \cdot 2H_2O$	10	H_2O	Zn	Zn	0.8	5	5	25	98.6
V	$ZnSuc \cdot 2H_2O$	10	H_2O	Zn	Zn	0.8	5	5	60	99
VI	$Cu(ButOH)_2 \cdot 2H_2O$	0.5	H_2O	Cu	Cu	0.5	5–10	5–10	25	78.7
VII	$Cu(ButOH)_2 \cdot 2H_2O$	0.5	H_2O	Cu	Cu	0.5	5–10	5–10	60	81.5
VIII	$Ni(ButOH)_2 \cdot 2H_2O$	5	H_2O	Ni	Ni	0.5	5–10	5–10	60	83.2
IX	$CuLac_2 \cdot 5H_2O$	5–10	H_2O	Cu	Cu	0.5–1	10–50	10–30	25	98.5
X	$CuLac_2$		LiCl, HLac	Cu	Cu	1–1.5	0.1–0.2	0.1–0.2	25–80	64.2
XI	$ZnLac_2 \cdot 2H_2O$	0.5	H_2O	Zn	Zn	0.8	5–10	5–10	60	87.8
XII	$CuMal \cdot 5H_2O$	1	H_2O	Cu	Cu	0.3	10–20	10–20	25	97.6
XIII	CuMal		LiCl, H_2Mal	Cu	Cu	1–1.5	0.1–0.2	0.1–0.2	135	45.9
XIV	$ZnMal \cdot 2H_2O$	1	H_2O	Zn	Zn	0.8	5–8	10–15	25	80.3
XV	$CuHCit \cdot 5H_2O$	0.5–1	H_2O	Cu	Cu	0.3–0.5	10–15	10–20	25	96.4
XVI	CuHCit	LiCl,	H_3Cit	Cu	Cu	1–1.5	0.1–0.2	0.1–0.2	165	35.6
XVII	$ZnHCit \cdot 2H_2O$	1	H_2O	Zn	Zn	0.8	3–10	10–15	25	87.8
XVIII	$CuArg_2 \cdot 5H_2O$	5–10	H_2O	Cu	Cu	0.15–0.3	10–15	10–20	25	89.6
XIX	$ZnArg_2 \cdot 2H_2O$	0.5–1	H_2O	Zn	Zn	0.5	5–8	10–20	25	81.5
XX	$NiArg_2 \cdot 3H_2O$	0.5	H_2O	Ni	Ni	0.5	1–5	5	25	78.9
XXI	$CuVal_2 \cdot 5H_2O$	5	H_2O	Cu	Cu	0.25	10–15	10–20	25	95.3
XXII	$ZnVal_2 \cdot 2H_2O$	1	H_2O	Zn	Zn	0.25	10–15	15–20	25	76.8
XXIII	$NiVal_2 \cdot 3H_2O$	0.5	H_2O	Ni	Ni	0.5	3–5	5–15	25	56.8
XXIV	$CuMet_2 \cdot 5H_2O$	10	H_2O	Cu	Cu	0.3	5–15	10–25	25	92.7
XXV	$ZnMet_2 \cdot 2H_2O$	1	H_2O	Zn	Zn	0.25	5–10	5–15	25	85.2
XXVI	$NiMet_2 \cdot 3H_2O$	50	H_2O	Ni	Ni	0.8	1–3	1–5	25	65.4
XXVII	$NdLac_3 \cdot 6DMF$	50	LiCl, DMF	Nd	Pt	0.5	1–3	1–5	25	
XXVIII	$TbLac_3 \cdot 8DMF$	50	LiCl, DMF	Tb	Pt	0.3–0.5	1–3	1–5	25	
XXIX	$GdLac_3 \cdot 8MDF$	50	LiCl, DMF	Gd	Pt	0.3–0.5	1–5	1–5	25	
XXX	$Nd_2Mal_3 \cdot 6MDF$	50	LiCl, DMF	Nd	Pt	0.5	1–5	1–5	25	
XXXI	$Tb_2Mal_3 \cdot 8DMF$	50	LiCl, DMF	Tb	Pt	0.5	1–3	1–5	25	
XXXII	$Er_2Mal_3 \cdot 10MDF$	50	LiCl, DMF	Er	Pt	0.5	1–5	1–5	25	
XXXIII	$NdLac_3$	50	LiCl, Acn	Nd	Pt	0.5	1–3	1–5	25	
XXXIV	$TbLac_3$	50	LiCl, Acn	Tb	Pt	0.3–0.5	1–3	1–5	25	
XXXV	$GdLac_3$	50	LiCl, Acn	Gd	Pt	0.3–0.5	1–5	1–5	25	
XXXVI	Nd_2Mal_3	50	LiCl, Acn	Nd	Pt	0.5	1–5	1–5	25	
XXXVII	Tb_2Mal_3	50	LiCl, Acn	Tb	Pt	0.5	1–3	1–5	25	
XXXVIII	Er_2Mal_3	50	LiCl, Acn	Er	Pt	0.5	1–5	1–5	25	
XXXIX	$NdAcac_3$	50	LiCl, Acn	Nd	Pt	0.5	10–15	10–15	25	
XL	$TbAcac_3$	50	LiCl, Acn	Tb	Pt	0.5	10–15	10–15	25	

PR-8 programmer, copper coulometer, instruments for external monitoring of the current and voltage (potential), magnetic or mechanic stirrer, and thermostat.

The working electrode was made of the metal subjected to anodic dissolution. Auxiliary electrodes were made of inert materials or of the same materials as working electrodes, depending on the objective. A standard silver chloride electrode served as a reference. In nonaqueous solvents, an electrolytic bridge was also used to prevent contamination of the solvent with water.

The cell includes a thermostated jacket for performing syntheses at elevated temperatures. In addition, the cathodic and the anodic compartments of the cell are separated with a porous glass separator. The electrochemical measurements can be performed using a magnetic stirrer. The PR-8 programmer makes it possible to apply to the potentiostat a potential that can be varied by an arbitrary program, including linear or stepwise parts. The circuit includes a copper coulometer for determining the current efficiency.

The table lists the conditions in which complex compounds of zinc, copper, nickel, and a number of REEs (Nd, Tb, Pr, Gd, Er) with lactic (HLac), malic (H_2Mal), citric (H_3Cit), succinic (H_2Suc), and γ-oxybutyric (HButOH) acids, arginine (HArg), valine (HVal), methionine (HMet), and acetylacetone (HAcac) were synthesized. The presence of the compounds as individual phase was confirmed by elemental and thermogravimetric (TG) analyses and by IR spectroscopy.

The content of metals was determined by complexometric titration [21] and that of carbon, hydrogen, and nitrogen, by elemental gas-volumetric analysis.

The IR spectra were measured on a Perkin–Elmer 180 spectrophotometer in the range 4000–400 cm^{-1} in a Vaseline oil suspension. The IR spectra of the carboxylic acid compounds synthesized were mainly analyzed for the position of the absorption bands associated with the carboxylic group and carboxylate ion, which is consistent for the compounds studied with published data [20, 22–25] for compounds with similar structure and composition.

The thermogravimetric curves were measured at 20–1000°C on an MOM derivatograph (Hungary). We used platinum crucibles, a platinum–platinum-rhodium thermocouple, and aluminum oxide as reference. The weighed portions were 50 mg, and the heating rate, 10 deg min^{-1}. As objects of analysis of the thermogravimetric data served DTA, DTG, and TG curves. In those cases when the composition of the final phase formed by the thermolysis can be predicted rather reliably (e.g., formation of CuO as the final product for complex copper compounds), we performed a quantitative analysis for the content of the ligand. The results of such an analysis were always in an agreement with the data obtained by chemical analysis.

The synthesis was performed in water and in nonaqueous solvents: acetonitrile (Acn) and dimethylformamide (DMF). In aqueous solutions, the synthesis was carried out without a supporting electrolyte, with the electric conduction provided by ions formed upon the dissociation of the ligands (H^+, L^{n-}). The decrease in the electrical conductivity, which is due to the fact that these substances are weak electrolytes, is compensated for by the absence of foreign ions in the solution, and, consequently, by the formation of simpler complex compounds. The ions formed upon dissociation migrate toward the electrodes and enter into the electrode reactions [4, 12].

$$\text{C: } 2H^+ + 2e \rightarrow H_2 \quad (H_nL + ne \rightarrow L^{n-} + n/2H_2),$$

$$\text{A: } mL^{n-} + nM - (nm)e \rightarrow M_nL_m.$$

In the electrochemical systems Cu/HLac, Cu/H_2Mal, and Cu/H_3Cit, the synthesis was performed using a liquid (molten) ligand as a solvent. The working temperature of the synthesis (see table) was higher than the melting point of the ligand and lower than its decomposition point. Inorganic chlorides were added to the molten ligand, and the supporting electrolyte was formed directly by the reaction

$$nLiCl + H_nL \rightleftarrows Li_nL + nHCl\uparrow.$$

The synthesis in a liquid ligand was performed with a preliminary dehydration of the ligands to a water content of 1–10 mmol l^{-1}. The compounds obtained contained a large amount of water, but their degree of hydration was considerably lower than that for compounds obtained from solution and subjected to dehydration. Therefore, the synthesis in a melt can be recommended for obtaining substances with the minimum content of water or compounds hardly hydrated by the conventional methods. However, the process rate is low in this case.

To choose the optimal range of ligand concentrations for the anodic synthesis, we studied how the potential of the metal electrodes varies with the ligand concentration in the solution at a constant ionic strength (1 M LiCl).

The dependences of the electrode potentials on the ligand concentration in solution are shown in Fig. 2 for three typical systems. For the system constituted by copper and amino acid (curves *1*), extrema are observed in the ligand concentration range studied (0.005 M). In those cases when a complex compound has a low stability constant, the equilibrium potential of the electrode is mainly determined by the concentration of the metal aqua complexes. If the complex compound forms a sparingly soluble phase on the electrode surface and(or) a very stable complex compound is formed, then the electrode potential is also dependent on the concentration of the anionic form of the ligand in solution. This predetermines the complicated character of the dependences presented.

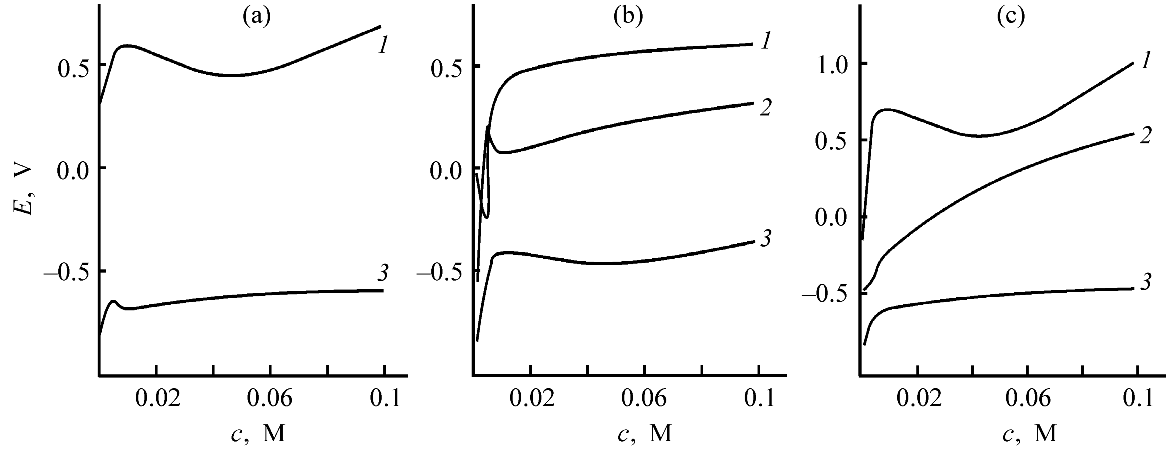


Fig. 2. Potential *E* of (*1*) copper, (*2*) nickel, and (*3*) zinc vs. the concentration *c* of (a) malic acid, (b) valine, and (c) arginine.

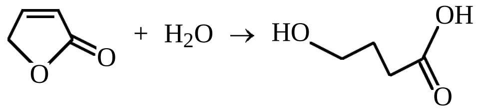
At low concentrations of the ligand (0.005 M and less), the electrode is frequently passivated. In the absence of a supporting electrolyte, such concentrations also lead to a low electrical conductivity of the solution. In these cases, it is suggested to perform electrolysis at high ligand concentrations by gradually raising the content of a ligand to the maximum possible value at a given temperature. For the amino acid systems, this means that the concentration can be raised from 0.005 M to the point of saturation (Fig. 2). It was found that such a procedure frequently makes it possible to avoid passivation of copper and zinc electrodes.

Copper easily dissolves in all the systems studied, with a high current efficiency at small shifts of the potential from the equilibrium value and high dissolution current densities.

Zinc dissolves well in the system with a stronger polarization, at higher anode potentials and lower current densities. Hydrogen is evolved at the cathode at the beginning of the process. Then, as metal ions are accumulated in the electrolyte, a parallel process of zinc separation commences, which decreases the current efficiency of the anodic process. The metal ions are discharged at the cathode to form dendrites, which are accumulated on the cell bottom because of the poor adherence to the electrode, thus creating additional difficulties in isolation of the final product. This difficulty is eliminated if a cell with separated electrode compartments is used. In all probability, the high current efficiencies by the zinc compounds are due to the simultaneous spontaneous dissolution of the zinc electrodes:

$$Zn + 2HL \rightarrow ZnL_2 + H_2\uparrow.$$

The electrosynthesis of the complex nickel compounds with hydroxy acids (except γ-hydroxy butyric acid) poses certain difficulties. When the electrode potentials are low (1–2 V), the electrode in the system chosen is passivated, the electrolysis proceeds very slowly, and the anodic products cannot be identified by analysis as individual compounds. At high anode potentials (up to 3 V), oxygen evolution from water proceeds at the anode, which makes the nickel electrode completely inert. The successful synthesis of the nickel(II) complex with γ-hydroxy butyric acid is probably favored by the fact that it is synthesized from the preligand (2-butenolide), the true concentration of the ligand near the anode surface is very low, and its loss is continuously compensated for by hydrolysis of 2-butenolide directly at the anode surface:



It was established for copper in an analogous system that copper compounds with different states degrees oxidation are formed by electrochemical synthesis at different temperatures: a pale green copper(II) complex insoluble in water (compound **VI**) is formed at 25°C, and a copper(I) complex insoluble in water (compound **VII**), at 65°C.

Comparison of the IR spectra of the compounds obtained in the REE(Nd, Tb)/HAcac system, which have, according to the results of an analysis, the composition $LnAcac_3$, with the spectrum of the pure ligand (shift of the carbonyl vibrational band at around 1650 cm^{-1} by 50–60 cm^{-1}) shows that a chemical carbonyl bond is formed [22]. The thermogravimetric

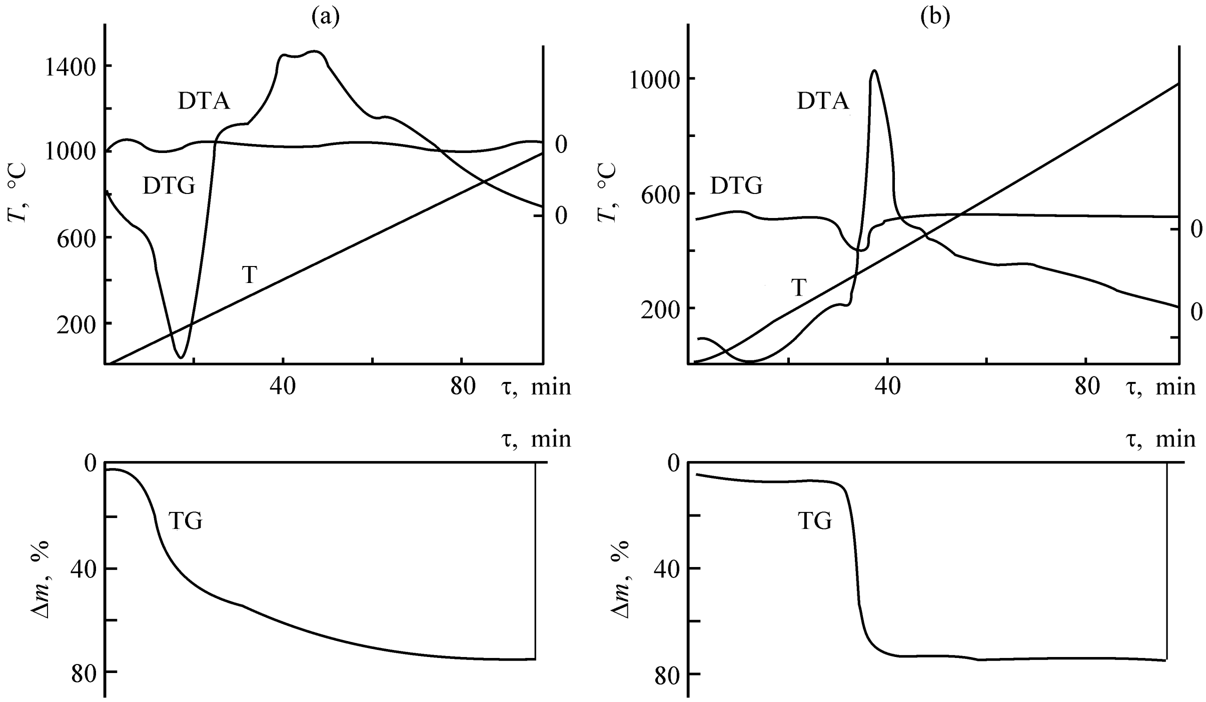


Fig. 3. Thermograms of (a) neodymium and (b) terbium trisacetylacetonates. (*T*) Temperature, (Δ*m*) relative loss of mass, and (τ) time.

data in Fig. 3 suggest that the substances synthesized are volatile: a drastic mass loss (96%) observed at T = 310°C for compound (**XXXIX**) corresponds to a strong exothermic effect, which may be due to sublimation of a sample and its simultaneous combustion in the vapor state; for compound (**XL**), a 75%-loss of mass, accompanied by a pronounced endothermic effect, is observed at T = 220°C. Thus, the electrochemical synthesis of acetylacetonates of rare-earth elements is a simpler and less expensive method, and, which is the most important, it gives anhydrous compounds with a molecular crystal lattice [26].

In the course of synthesis in a system containing copper electrodes and an aqueous solution of lactic acid at high anode potentials (2–3 V), a finely dispersed colorless water-insoluble solid substance is formed at the anode alongside with a compound $CuLac_2 \cdot 5H_2O$, which is obtained in a very low yield (5–10%). An analysis of the compound obtained revealed neutral anhydrous copper carbonate $CuCO_3$. Therefore, it was suggested that the electrochemical anodic reaction of decarboxylation of lactic acid (Kolbe reaction) occurs in such a synthesis as a side process unknown previously for α-substituted hydroxy carboxylic acids and their salts. The process can be used to introduce into the anodic Kolbe synthesis new classes of organic substances, which is important for practice.

Various nonaqueous solvents also differently affect the composition of the products obtained and the process efficiency. Use of aqueous-alcoholic media in synthesis of *d*-element succinates was ineffective. It was found for aprotic solvents that there is a relationship between the solvent chosen and formation of solvated complexes. The formation of solvates (solvation) depends on the relative donor strength of the solvent and the ligand used and on the temperature mode of electrolysis. For example, solvated complexes are always formed in dimethylformamide, whereas in acetonitrile, this occurred only in several cases. It may be concluded that acetonitrile is the most suitable solvent for synthesis of unsolvated compounds.

The electrochemical synthesis has a high efficiency: the yield of substance and the current efficiency (>50%) are considerably higher than those in the conventional chemical syntheses. In addition, the electrochemical synthesis is a single-stage process, which also makes higher the yield of the product. In the general case, the yield of substance and the current efficiency may be different or may coincide.

The effect of the process temperature on the composition of the products obtained was especially strong in interaction of copper with 2-butenolide, when at a comparatively small temperature difference, two products of different compositions were formed, with copper in different oxidation states. In other cases, differently solvated compounds were formed.

CONCLUSIONS

(1) The optimal concentration ranges of the ligand for electrochemical synthesis of complex compounds, temperature, solvent, and gaseous medium of synthesis were determined on the basis of potenstiostatic data.

(2) Anodes made of rare-earth metals were used in electrochemical synthesis for the first time. Thermogravimetric data demonstrated that the physical properties (high volatility) and structure of acetylacetonates of rare-earth elements synthesized by this method in anhydrous acetonitrile differ from the properties of the previously synthesized analogues.

(3) It was shown that the anodic dissolution of the metal facilitates decarboxylation of hydroxy acid.

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