Electrochemical Synthesis of Coordination Compounds of Lanthanides: Effective Luminophores

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Contents

Abstract

The problems of electrochemical synthesis of complex compounds of lanthanides with organic acids are discussed. It was shown that the resulting complex compounds are thermally stable and can be used as effective luminophores.

Keywords

Electrochemical synthesis · Lanthanides · Luminescence

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Electrochemical synthesis is an accessible and effective preparative method to obtain coordination compounds of *d* and *f* elements. In the electrochemical reactions, metals in a free form are used as reagents instead of metal salts. This approach allows one to avoid the contamination of the final product with impurities originated from salts. Electrochemical processes basically proceed in one step and can be easily controlled. The abovesaid factors make electrochemical synthesis to be used to produce pure and ultrapure complex compounds with useful properties (e.g., biologically active compounds, pharmaceuticals, new functional materials, etc.). Such compounds are often difficult to synthesize by other methods. In general, the difficulties in obtaining many coordination compounds by the classical methods are generally associated with low solubility of a ligand and metal salt in the same solvent or mixture of solvents.

The unique luminescent properties of lanthanide coordination compounds with a number of aromatic carboxylic acids are widely known. These properties allow one to use lanthanide carboxylates in various fields of modern science and technology – as protective coatings, luminescent probes, and emitters in chemosensors, in electroluminescent devices, and in OLEDs (organic light emitting diodes).

As it was shown [1], beta-diketonate and pyrazolinate lanthanide complexes known to date revealed good luminescence yields and are relatively easy to obtain. However, these complex compounds have a number of disadvantages, the main one being low thermal stability and a marked tendency to decompose in the air. The coordination compounds of lanthanides with aromatic carboxylic acids as ligands lacked these disadvantages, as they have more pronounced thermal stability and photostability. They also are more stable in air and show characteristic narrow and intense luminescence bands, which allow one to use the compounds for the production of high-quality luminophores in various industrial products.

By introducing various substituents into the aromatic ring, one can influence the physicochemical properties of the synthesized compounds, thereby obtaining substances with parameters of interest (e.g., luminescent properties, thermal stability, resistance to various environmental factors).

However, classical chemical methods for the synthesis of coordination compounds (generally based on ion-exchange reactions) do not always succeed in obtaining substances that completely satisfy the requirements imposed on them, due to hydrolysis, hydration, or contamination of the target substance by the possible reaction by-products. Thus, the presence of coordinated water in a complex compound can decrease the quantum yields of luminescence. However, no these disadvantages are encountered when the electrochemical methods used instead. The electrochemical approach allows one to perform the synthesis in one step, to obtain anhydrous compounds with no extraneous ions, and also to define the structure of the target products and the directions of reactions.

Uncommon Methods of Electrochemical Synthesis of Coordination Compounds

To date, there are a number of variants of electrochemical synthesis of coordination compounds that are known, such as **electrochemical synthesis in a cell with a bipolar liquid electrode, ultrasound electrochemical synthesis, anodic synthesis using a ligand as a background electrolyte, and anodic synthesis in a ligand medium** [2–6].

The method of electrochemical synthesis in a cell with a bipolar liquid electrode, mentioned in [2], remained as theory until the present work. In this paper, we also consider such variants of the electrochemical synthesis as anodic synthesis in a ligand medium and anodic synthesis using a ligand as the background electrolyte. They were developed and successfully tested by our group [7, 8] and allowed us to obtain a number of interesting results.

Anodic Synthesis Using a Ligand as a Background Electrolyte

We proposed a method of electrochemical synthesis without using a special background electrolyte. This is possible when an organic compound dissociating in the selected system and providing an acceptable electrical conductivity of the solution was taken as a ligand. As the starting points, we used aqueous and nonaqueous solutions of some carboxylic, hydroxy, and amino acids. Their dissociation in all cases proceeds according to the general scheme (1):

$$\mathrm{H_nL} \Leftrightarrow \mathrm{nH^+} + \mathrm{L^{n-}} \tag{1}$$

The resulting protons and L^{n-} ions allowed the desired electrical conductivity and the current transfer to the cathode and anode, where the following electrode processes occur, leading to the formation of a complex compound at the anode:

$$\begin{array}{l} \mathrm{K}/2\mathrm{H}^+ + 2e \rightarrow \mathrm{H_2} \\ \mathrm{A}/\mathrm{L^{n-}} + \mathrm{M^{m+}} - \mathrm{ne} \rightarrow \mathrm{M_nL_m} \end{array} \tag{2}$$

The advantage of this technique is to minimize the number of components in the solution, which leads to a minimal contamination of the synthesized substances with ionic impurities. Also, when the target product is solid, this method allows to exclude the contamination of a precipitate due to occlusion and adsorption of the background electrolytes. In this case, the decrease in electrical conductivity in comparison with solutions containing a background electrolyte is insignificant and does not lead to a significant decrease in the rate of the process.

Anodic Synthesis in a Ligand Medium

The authors of papers [2, 6] proposed a new method of anode synthesis of complexes using a liquid or molten ligand as a medium or a solvent. This method can be successfully applied to low-melting ligands. Such ligands could be maintained for a long time in the melted state with no decomposition. In addition, the ligand should be markedly stable above the melting point. This approach requires no special glassware or laboratory equipment.

In our studies, we have used lactic, malic, and citric acids as ligands. In the case of lactic acid, the synthesis could be carried out at the room temperature (25 °C) or slightly elevated temperature, since the ligand has a low melting point (18 °C). Malic acid has a relatively low melting point (100 °C) and is sufficiently stable at the temperature range of 140–150 °C. Thus, synthesis should be carried out in the temperature range from 100 °C to 120–130 °C. In this case, the higher temperature limit was 130 °C. Citric acid has relatively high melting point of 153 °C and starts to decompose above 175 °C. So in this case, we carried out the synthesis at 160 °C. The background electrolyte was formed directly in the melt of the ligand with the addition of inorganic chlorides according to the reactions:

$$\mathrm{nLiCl} + \mathrm{H_nL} \rightarrow \mathrm{Li_nL} + \mathrm{nHCl}\uparrow \tag{3}$$

Hydrogen chloride formed during the reaction readily evaporates at elevated temperatures, so the equilibrium shifts to the formation of coordination compounds.

In general, the synthesis with the selected ligands did not match our expectations and cannot be recommended for practical application, due to the too high viscosity of the ligand melts, the low solubility of the background electrolyte, and, as a consequence, the low rate of electrode processes. In addition, it is rather difficult to work with high-melting compounds.

Advantages of this method are the absence of water and other side substances, including organic solvents. As a last resort, it is possible to exclude a background electrolyte, especially taking into account the fact that background electrolyte does not increase substantially the electrical conductivity of the systems because of the aforementioned problems. Thus, the composition of the system is ideal – it contains only the metal, ligand, and other substances only in the form of impurities, the content of which depends on the degree of purification of the components. The method can be used if there is sufficient time, and it is necessary to obtain a complex compound containing only ligand and metal. It also allows to exclude the formation of solvates and hydrates. The method is also applicable for the synthesis of substances that cannot be obtained by any other methods.

Problem of Anode Passivation in the Electrochemical Synthesis

The electrosynthesis of coordination compounds often accompanied with problems associated with the passivation of the anode by a film of sparingly soluble and non-conductive reaction products. This surface film rapidly increases in thickness and shields the anode from the ligand molecules and also prevents the transfer of metal cations into the solution. All this leads to a decrease in the current density during the synthesis and a significant decrease of the process rate. Also, due to a high electrical resistance, the overall electrical conductivity of the system decreases.

The simplest way to avoid the passivation of anodes is to mechanically peel an insoluble product from the anode. However, this procedure requires the periodical interruption of the process for cleaning and opening of the cell which might not always be desirable due to air access and possible oxidation. In addition, in the case of certain metals, this procedure leads to the scrapping of some visible amounts of metal from the surface of the electrode, along with the insoluble solid. These metal particles could not be separated from the reaction product.

The main efforts of researchers are aimed at solving the problem of premature passivation of electrodes. In this review, we have considered the methods that allow to reduce or exclude the passivation of anodes, thereby improving the parameters of the electrosynthesis of complex compounds. The discussed methods are the electrosynthesis using alternating current [2, 7–10] and the method based on ultrasonic treatment of an electrochemical cell [2–5].

Electrochemical Synthesis of Complex Compounds Using Alternating Current

A group of researchers [9] proposed the use of alternating current for the synthesis of insoluble complex compounds of *d* elements with azole ligands in order to reduce the reaction time and increase the yield of the products. When the alternating current is passing through the anode system, the same processes occur on the electrode as at the anode during electrolysis using direct current. However, when the cathode pulse passes, a partial (due to low solubility) decomposition of the complex takes place. In the first turn, the molecules in the layer closest to the surface of the metal decompose, which cleans the surface for the subsequent anode pulse.

The authors noted that the current yield with the use of alternating current remains practically constant in time, while using a direct current, the yields are high at first and then rapidly decrease.

It was concluded that there is no significant change in the current yield using sinusoidal, rectangular, or sawtooth pulses. As the frequency of the current increases, the current yield of the synthesized complex decreases.

In the papers [2, 7, 8, 10], the elimination of passivation and the stable proceeding of the synthesis of insoluble complexes of *d* and *f* elements with carboxyl- and carbonyl-containing ligands were provided by using an asynchronous current with pulses of a rectangular frequency of 1–10 Hz. The ratio of the durations of the forward and backward pulses was [1:10÷1:5]. In some cases, a technique has been tested, whereby a sinusoidal potential difference is applied to the electrodes rectified half-way using a single diode connected in series with the cell. This is due to the fact that any semiconductor rectifier has a so-called inverse characteristic – a very weak current (in microampere range) flowing through the circuit in the closed state of the *p-n* junction. The authors have successfully used this approach to separate hardly soluble compounds from the anode. Such a rationalization of the synthesis is well suited for industrial use since it simplifies and reduces the cost of the procedure. The corresponding diode can be selected by empirical means or by comparing their inverse characteristics given in the literature.

The drawbacks of this method include its uncontrollability, which is due to the inability to change the process parameters depending on the synthesis conditions without rewiring the electrical circuit.

A method for controlled electrosynthesis using a variable pulse current was developed [10]. The current density does not exceed 10 mA/cm^2. The pulse time is controlled by means of a pulse-shaping unit connected in parallel to the electrolyzer.

Electrochemical Synthesis of Complex Compounds Using Ultrasound

To eliminate the passivation of the anode, the group led by Kharisov [2–5] carried out the electrochemical synthesis with simultaneous ultrasonic treatment of the reaction mixture. For this purpose, an ultrasonic bath or a more powerful ultrasound source was used.

In application to electrosynthesis, ultrasound performs the following additional functions: it accelerates the dissolution kinetics of the starting material and increases mass transfer to/from the surface of the electrodes, thereby reducing the reaction time and optimizing the chemical and electrochemical yields of the product.

Ultrasonic treatment of the reaction system was carried out by electrochemical dissolution of lanthanides in solutions of phthalocyanine precursors.

While studying the behavior of various metals as anodes in electrochemical processes, it was noted that the nature of metal (which partially determines the solubility of the complexes formed) plays a key role in the adhesion of the reaction product to the anode surface.

In the case of using phthalonitrile as a ligand for templating of complex compounds of lanthanides (La, Nd, Pr, and Sm), the use of ultrasound was not only an additional treatment of the reaction system, but also it was found to be an extremely necessary procedure due to the extreme complexity of the electrolysis using these metals. In contrast to the *d* elements, a thick layer of product was formed on the metal surface in the case of the abovementioned lanthanides even if the metals were highly polished. The voltage in the cell is increased greatly.

Amalgam Systems: Structure, Properties, and the Application in Electrochemical Synthesis

Amalgam systems (amalgams) are metal systems, in which mercury is included as one of the components. Depending on the ratio of the components, the nature of metal, and the temperature, amalgams could be homogeneous liquids, solid solutions, solid intermetallides, or heterogeneous systems. Solid intermetallides are formed in most of studied metal-mercury systems.

The nature of the M-Hg interaction is the main factor determining the internal structure of the alloy, and it depends on the nature of the metal introduced into the mercury. There are the following basic models of the structure of amalgam [11]:

(A) *Atomic model.* The M-Hg system is regarded as a mixture of atoms with a certain short-range order. The type of the order, as well as the energy of amalgam formation, is described with the help of statistical thermodynamics and quasi-chemical theory of solutions [12–14]. The choice of the energy variables of the corresponding criterial relationships is usually made on the basis of experimental data.

(B) *Intermetallic model.* The concept of "short-range order" is absolutized. It is assumed that in the liquid amalgam, phase consists of pseudomolecules capable to dissociate according to the scheme:

$$\mathrm{MHg_m} \leftrightarrow \mathrm{MHg_m}\ (\text{in mercury}) \leftrightarrow \mathrm{M} + \mathrm{mHg} \tag{4}$$

(C) *The ion model.* Starting from the suggestion that any metal is a set of ionic cores M^{m+} and collectivized electrons, it is assumed that a metal is completely ionized when it is dissolved in mercury. The dissolution is accompanied by a transition of the valence electrons M to the conduction zone Hg. The charge of M^{z+} cations is often taken equal to the group number of the periodic table of elements.

(D) *The ion solvation model* is the development of the ion model. It is assumed that the emerging M^{z+} cations are solvated (hydrated), that is, a known analogy with solutions of electrolytes is drawn.

As it could be seen, it is clear that there is no any general view on the structure of amalgams. This is due to the presence in the amalgam systems of a variety of emerging forms of chemical bonding, methods for packing particles, and characteristics of the background free electrons.

Amalgams are formed by direct contact of metal and mercury (preferably under heating conditions), electrolysis of aqueous and nonaqueous solutions of salts, as well as low-temperature melts on the Hg cathode. In the case of hydrolyzable cations (e.g., Ln^{3+}), electrolysis of aqueous solutions is effective only in the presence of buffering agents and complexing agents.

A method of contact exchange between M^{z+} ions and amalgams of alkali metals and other active metals has found wide application. Solid M-Hg alloys are expedient to be obtained directly from the elements, since the concentration of electrically synthesized amalgams requires the subsequent separation of the solid phase and partial distillation of mercury. When mercury is applied to the surface of appreciably soluble metals, a wetting film of liquid amalgam is formed. This process is called amalgamation.

The solubility of various metals in mercury varies very widely and depends on the position of metal in the periodic system, its melting point, and the strength of the crystal lattice [11–15].

Practical Implementation of the Method of Electrochemical Synthesis of Coordination Compounds in a Cell with a Bipolar Liquid Amalgam Electrode

In the anodic synthesis of complex compounds of transition elements, one may face the problem of accessibility of expensive metal (lanthanide) anodes. In this case, we propose a principally new method of electrosynthesis of coordination compounds, which allows us to avoid the use of metals in a free form. The method is based on the use of a liquid amalgam bipolar membrane as an electrode. The membrane separates a metal salt solution and a ligand solution in an electrochemical cell. Schematically, the principle of operation of this method can be represented as follows (Fig. 1).

In accordance with this scheme, the electrolyzer contains two inert electrodes made of platinum or graphite and a bipolar electrode made of mercury. When a voltage is applied, the bipolar electrode turns into an amalgam due to cathodic deposition of metal ions on it. In the electrosynthesis of coordination compounds, the membrane on the metal side is a cathode and on the side of the ligand, an anode, and it completely isolates the solutions of the metal salt and ligand from each other. During the process, a metal cation reduces at the cathode, and then a metal diffuses through the phase of liquid mercury membrane and oxidizes from the side of a ligand at anode. Anolyte (a solution, where inert electrode is an anode) contains components for cathodic deposition of the corresponding metal; catholyte (a solution where inert electrode is a cathode) contains background electrolyte and a ligand or only a ligand. With the appropriate selection of the potentials of the anode and cathode in the cell, the following processes must occur:

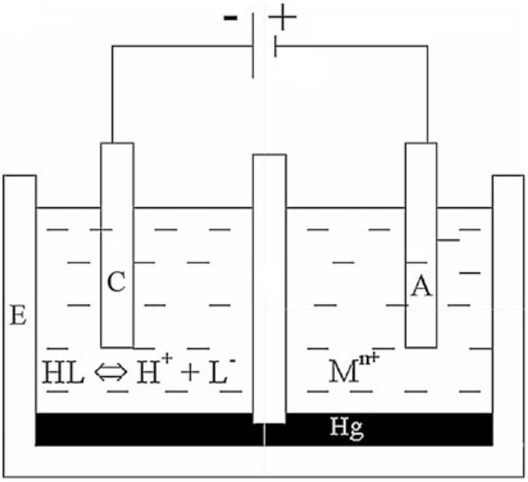


Fig. 1 Diagram of a cell with a liquid bipolar electrode

Anolyte: inert electrode-anode, liquid metal-cathode

$$\begin{array}{l}\mathbf{A}/\mathrm{Pt}/2\mathrm{H_2O} - 4e \rightarrow \mathrm{O_2} + 4\mathrm{H}^+ \\ \mathbf{K}/\mathrm{mHg} + \mathrm{M}^{\mathrm{n}+} + \mathrm{ne} \rightarrow \mathrm{Hg_mM}\end{array} \tag{5}$$

Catholyte: liquid metal (amalgam)-anode, inert electrode-cathode

$$\begin{array}{l}\mathbf{A}/\mathrm{Hg_mM} - \mathrm{ne} \rightarrow \mathrm{mHg} + \mathrm{M}^{\mathrm{n}+}; \\ \mathbf{K}/\mathrm{Pt}/\mathrm{H_mL} + \mathrm{me} \rightarrow \mathrm{L}^{\mathrm{m}-} + {}^{\mathrm{m}}/{}_{2}\mathrm{H_2}; \\ \mathrm{M}^{\mathrm{n}+} + \mathrm{L}^{\mathrm{m}-} \rightarrow \mathrm{M_mL_n}\end{array} \tag{6}$$

This method has great prospects, since it represents a fundamentally new approach to the electrochemical synthesis of complex compounds. It makes possible to perform the synthesis without appropriate metals as complexing agents, using far more accessible metal salts instead; this is crucial factor for rare and rare-earth elements.

It is noteworthy that it is possible to use a variety of different combinations of mechanically isolated systems – a metal salt solution (anolyte) and a ligand solution (catholyte). This approach extends the range of complexes obtained and simplifies the synthesis of already known compounds. Thus, using this method, anhydrous lanthanide complexes could be synthesized easily from aqueous solutions of lanthanide salts, which is extremely important for modern coordination chemistry.

The above method of electrosynthesis could be applied to the preparation of complexes of transition metals that can dissolve in mercury as well as those of the lanthanide group which include lanthanum, cerium, neodymium, praseodymium, samarium, europium, ytterbium, and gadolinium [11, 15, 16]. To introduce this method into practice, it is necessary to develop and test an appropriate electrochemical cell.

Development of an Electrochemical Cell with a Bipolar Amalgam Electrode

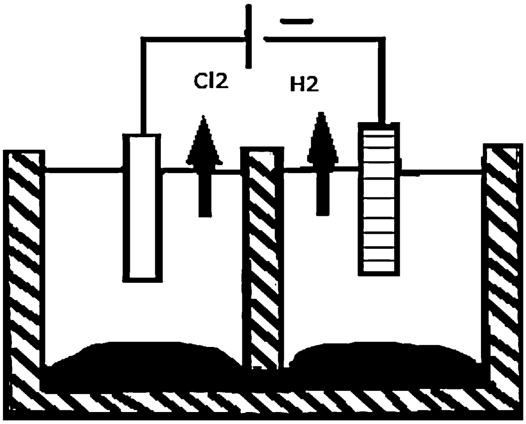
To date, a number of cells with a bipolar liquid electrode using an alkali metal amalgam (Li, Na, K) were described [16]. They are widely used in industry to produce various organic and inorganic substances by electrochemical way and to reduce energy consumption. The simplest construction of such a cell useful for electrolytic production of chlorine and an alkali is shown in Fig. 2.

In the above construction, a bipolar liquid electrode is located at the bottom of the vessel, and the cathode and anode spaces are separated by a septum, the end of which is fixed to a bipolar electrode. We have modified this scheme and developed a cell for the synthesis of lanthanide coordination compounds, which can be called *coaxial*.

Coaxial Cell

In this system (Fig. 3), the glass tube is coaxially located inside a cylindrical vessel having a bipolar electrode placed on the bottom. The lower end of the tube

Fig. 2 A cell with a bipolar liquid electrode used for chlorine-alkali electrolysis



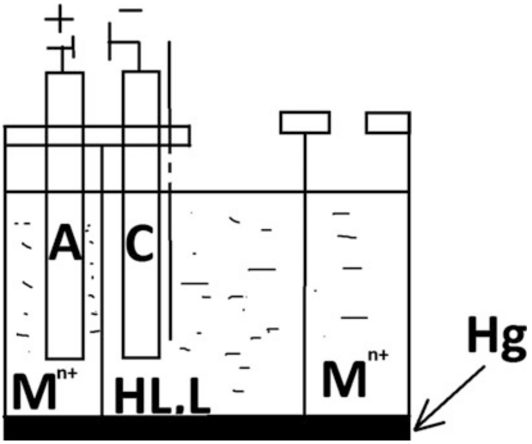


Fig. 3 A *coaxial* cell with a liquid amalgam bipolar electrode, where C is a cathode and A is an anode

is in contact with the liquid electrode. A catholyte is inside the tube, and an anolyte is placed inside the cylindrical vessel (or vice versa). The lower end of the tube is covered with a silver layer, which undergo amalgamation in contact with mercury. As a result, the bipolar electrode is tightly connected to the end of the tube, thus isolating catholyte and anolyte from each other.

The application of a silver layer onto the glass tube was carried out by the method of burning pastes at 400 °C. The ignition paste consisted of a mixture of rosin, silver carbonate, and turpentine taken in a weight ratio of 1:8:4, respectively.

However, when using this type of cell for electrosynthesis of lanthanide complex compounds, a number of difficulties arose due to a slow increase in the lanthanide concentration in the anode part of the membrane. It makes the synthesis significantly long, about 10–15 or more days. This is due to the large thickness of the membrane in this cell, low rate of diffusion of lanthanides in mercury, and low value of the limiting density of the cathodic current for the reduction of most REE in mercury.

These problems can be solved partially using the stirring of a mercury membrane. However, it makes impossible to fix a mercury on the silvered ends of the inner tube of the cell. In this case, the tube should be immersed in the mercury layer to save the isolation of catholyte and anolyte, with no contact with a stirrer located at the bottom. As a result, it will lead to thickening of the mercury membrane layer. Thus, when stirring was used, the amount of mercury in the cell will increase three to four times, and about 300–500 g of mercury is required for the synthesis with one lanthanide. The work with such quantities of mercury is dangerous. In addition, for the synthesis of complexes with different lanthanides, it is necessarily to clean the membrane before each change of metal, which further lengthens and complicates the process.

All the above drawbacks make the use of a coaxial cell for the electrosynthesis of lanthanide complex compounds problematic. So we have developed another cell for the electrochemical synthesis of lanthanide coordination compounds using an amalgam bipolar membrane in a form of U-shaped tube (Fig. 4).

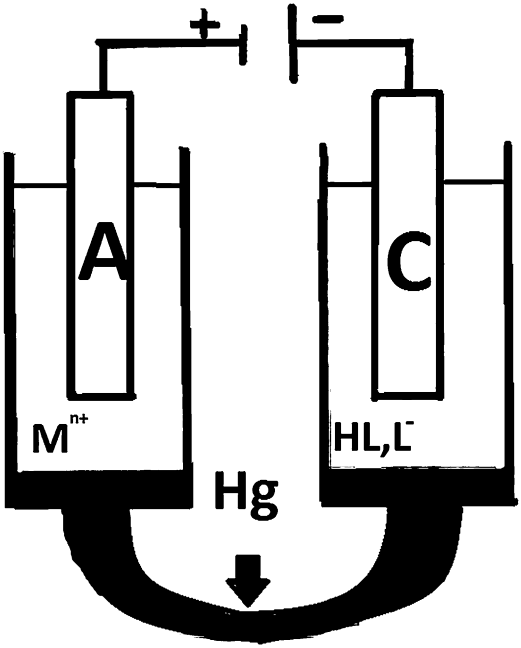


Fig. 4 A U-shaped cell with a liquid amalgam bipolar electrode, where C is a cathode, A is an anode, and IT is a current source

U-Shaped Cell

Such a cell has several advantages over a coaxial cell. This cell is easier and faster to maintain, it requires 15–20 times less amounts of mercury to create a bipolar membrane, and often the membrane regeneration step could be avoided.

However, the above cell construction also has some drawbacks, e.g., a large length of the membrane along with a low cross-sectional area of the bipolar electrode. It makes the diffusion of lanthanide from the cathode to the anode parts of the membrane a very long process. The rate of synthesis in this system is only 2–2.5 times higher than in a coaxial cell (5–10 days), and it is extremely difficult to apply stirring for this cell design (Fig. 4).

Thus, considering all the above drawbacks, it can be concluded that liquid bipolar amalgam electrode must be thin, have a large cross-sectional area, and contain a small amount of mercury to achieve a reasonable electrosynthesis rate.

A Cell with a Bipolar Electrode Deposited on an Inert Matrix

It is known that mercury can be fixed on a surface of nickel due to the interelectronic interaction of unsaturated surface metal atoms, but no further interaction occurs between these metals. This points to the possibility to use nickel as an inert matrix to deposit a layer of mercury and create a liquid bipolar electrode. Such a liquid-metal membrane is thin (1.5–2 mm) and has a large cross-sectional area; it will require a small amount of mercury (10–20 times less than for a U-shaped cell). These parameters of the membrane allow one to believe that the rate of electrosynthesis of complex compounds of lanthanides will be much higher than when using other of the above systems. As an inert matrix, it is reasonable to use a nickel grid. The design of an electrochemical cell with such a bipolar electrode is given below (Fig. 5).

Before mercury will be applied, a nickel grid should be wetted with concentrated hydrochloric acid to activate surface-layer nickel atoms.

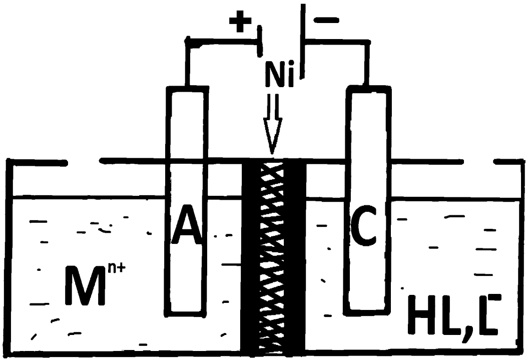


Fig. 5 A cell with a *bipolar electrode deposited on an inert matrix*, where C is the cathode and A is the anode

In our opinion, among all the systems described, a cell with bipolar electrode on a nickel matrix is the most optimal for the electrochemical synthesis of lanthanide coordination compounds.

Electrochemical Synthesis of Lanthanide Coordination Compounds Using a Bipolar Liquid Amalgam Electrode

Synthesis of already known anhydrous coordination compounds such as neodymium (III), terbium (III), and gadolinium (III) complexes with lactic acid was carried out by electrochemical method using a bipolar liquid amalgam electrode. A solvent and a background electrolyte were the same as in the classical anodic synthesis of these complexes – acetonitrile and lithium chloride, respectively.

The Preparation of Nonaqueous Solvent and Background Electrolyte

Acetonitrile is suitable solvent for the synthesis of coordination compounds since it readily dissolves many organic and inorganic substances and has a wide range of electrochemical resistance.

Useful for electrochemical synthesis, acetonitrile should contain minimum amounts of water. Therefore, the solvent should be dried before the synthesis and also purified.

A combined method for acetonitrile purification and dehydration was used [17, 18]. First, acetonitrile was distilled, and a fraction with bp > 82.0 °C was collected. The fractions boiling at lower temperatures were discarded. Then the solvent was dried for 2 days over 3A molecular sieves pre-calcined at 250–300 °C for 8–10 h. Finally, the solvent was again subjected to fractional distillation.

Lithium chloride used as a background electrolyte is hygroscopic. When working with nonaqueous LiCl solutions in cases where the presence of water should be excluded, thorough purification of LiCl from both water and other contaminants is necessary.

Lithium chloride used for the preparation of a solution was purified as follows: LiCl was preliminarily dried in an Alundum pot at 250–300 °C with constant stirring for 5–7 h. Then the pot was transferred to a muffle oven, and the temperature was raised to $\approx$700 °C. In this case, melting of lithium chloride (MP_{LiCl} 613 °C) was observed. The melt was aged for 2–3 h, and then it was cooled in a vacuum desiccator over CaO.

Synthesis of Coordination Compounds of Neodymium (III), Terbium (III), and Gadolinium (III) with Lactic Acid

The processes were carried out in the cell depicted in Fig. 5. The inert electrodes were graphite rods. The anolyte was 1 M aqueous solution of $(CH_3COO)_3Ln$, catholyte – 0.5 M solution of lactic acid in acetonitrile. Lithium chloride (0.05 M) was used as the background electrolyte in both parts of the cell.

In some cases, to increase the rate of the process, it was divided into two stages: (1) pre-electrolysis in order to concentrate lanthanide atoms in the mercury membrane and (2) further use of the amalgam membrane as a bipolar electrode.

The voltage applied to the cell was 1–2.5 V. At higher voltage, the side processes of anodic oxidation of mercury and cathodic reduction of hydrogen ions have started on the surface of the membrane. It led to a slowing down of the synthesis process and contamination of a resulting complex. The current density during the processes was 0.1–0.2 mA/cm^2.

As a result, anhydrous and poorly soluble coordination compounds of the composition LnL_3 were obtained.

In the study of the coordination compounds, we found that their composition, properties, and IR spectra were the same as those described for the previously prepared samples [18]. Mercury-containing impurities in the synthesized compounds were not detected. Thus, the electrochemical synthesis could be successfully performed using a bipolar liquid amalgam electrode.

Electrochemical Synthesis of Terbium (III) Complex Compounds and Gadolinium (III) with Aromatic Acids

A direct electrochemical synthesis of complex compounds was carried out by the soluble anode method using a direct current source in a two-electrode cell under constant stirring.

The cell consists of a tightly stoppered glass reactor with electrodes – an anode made of the corresponding lanthanide metal and a platinum cathode. A magnetic stirring bar was placed in the bottom of the cell for constant stirring of the solution.

Water-free acetonitrile was used as a nonaqueous solvent in the electrochemical synthesis. The concentration of ligands depended on their solubility and ranged from 0.001 to 0.015 M. The reaction time was determined from the initial concentration of ligands according to the Faraday law; it was 2–3.5 h. The processes were carried out in an inert atmosphere and in an airtight system.

The following ligands were used in the synthesis	
1,10-Phenanthroline	Phen
1,10-Phenanthroline-2,9-dicarboxylic acid	$PhdicH_2$
2-(4-Fluorobenzoyl)benzoic acid	2(4Fben)BenzH
2-(4-Chlorobenzoyl)benzoic acid	2(4Clben)BenzH
2-(4-Chloronitrobenzoyl)benzoic acid	2(4ClNitben)BenzH
2,2′-Dipyridyl	bipy
2,3-Dimethoxybenzoic acid	2,3-MeOBenzH
2,3-Pyridinedicarboxylic acid	2,3-$DpirH_2$
2,4-Dihydroxybenzoic acid	2,4-HOBenzH
2,4-Dimethoxybenzoic acid	2,4-MeOBenzH
2,5-Dimethoxybenzoic acid	2,5-MeOBenzH
2,6-Dimethoxybenzoic acid	2,6-MeOBenzH
2,6-Pyridine dicarboxylic acid	2,6-$DpirH_2$
2-Acetylbenzoic acid	2-AcBenzH
2-Benzoylbenzoic acid	2-BenzolBenzH

(*continued*)

The following ligands were used in the synthesis	
2-Hydroxybenzoic acid	2-HydBenzH
2-Hydroxinicotinic acid	2-OHNicH
2-Methylbenzoic acid	o-MBAH
2-Pyrazinecarboxylic acid	PyrazH
2-Phenoxybenzoic acid	2-FenOBenzH
2-Chlorobenzoic acid	2-ClBenzH
2-Chloro-5-nitrobenzoic acid	2-Cl-5-NO_2BenzH
3,4-Dimethoxybenzoic acid	3,4-MeOBenzH
3,4-Diethoxybenzoic acid	3,4-EtOBenzH
3,5-Dihydroxybenzoic acid	3,5-HOBenzH
33,5-Diisopropylsalicylic acid	3,5-IzopropSalH
3,5-Dimethoxybenzoic acid	3,5-MeOBenzH
3-Methylsalicylic acid	MeSalH
3-Pyridinecarboxylic acid	3-PircarbH
3-Chlorobenzoic acid	3-ClBenzH
4-Acetylbenzoic acid	4-AcBenzH
4-Hydroxybenzoic acid	4-HydBenzH
4-Pyridinecarboxylic acid	4-PircarbH
4-Tert-butyl-benzoic acid	4-TbutBenzH
4-Chlorobenzoic acid	4-ClBenzH
5-Bromonicotinic acid	BrNicH
5-Bromosalicylic acid	5-BrSalH
5-Sulfosalicylic acid	5-SulfoSalH
6-Hydroxinicotinic acid	6-OHNicH
Acrylic acid	AcrH
Acetylacetone	AcacH
Acetylsalicylic acid	AcetSalH
Benzoic acid	BenzH
Hexadecylphthalic acid	C_{16}FtalH
Maleic acid	$MalH_2$
Monotetradecylphthalic acid	C_{14}FtalH
Phthalaminic	FtalaminH
Phthalic acid	$FtalH_2$
Fumaric acid	$FumH_2$
Benzoylacetone	BAcH
Dibenzoylmethane	dBMH
Ethanol	EtOH
Thenoyltrifluoroacetone	TTAH

It is known, it is necessary to determine the optimum conditions and parameters of synthesis when using electrochemical synthesis methods to achieve maximum process efficiency. The conditions and parameters are the composition of electrolyte system, applied voltage, current strength, current density, temperature, and current yield. In the present work, the volt-ampere characteristics and processes occurring at the electrodes were not studied in details, since, as it was shown by Tuk et al. [19–25], "in non-aqueous solvents, when we neglect electrochemistry details it does not hinder the synthesis of individual complexes." However, it could be assumed that the preliminary recording of volt-ampere characteristics may give a detailed information on the nature of the processes and their mechanism.

The optimum current during the synthesis of terbium (III) coordination compounds and gadolinium (III) with the ligands used was 15–30 mA. To achieve the optimum values of the current intensity, a voltage of 4–9 V was applied to the electrochemical cell. The choice of this range of operating current is due to the fact that at lower values the synthesis rate decreases significantly and at the higher current intensities, the solution may overheat, which, in turn, may lead to the occurrence of side processes. As a result, the target product either decomposes or becomes significantly contaminated. For this reason, the synthesis was carried out at the temperature not exceeding 35 °C. The optimal anode current density during the processes was set in the range 8–13 $\mathrm{mA/cm^2}$. At higher values of the current density, the destruction of the anode began, which led to a decrease in the efficiency of electrochemical processes and contamination of a reaction mixture with hard-to-separate particles of the electrode material.

In the course of the synthesis of terbium (III) and gadolinium (III) complexes in a number of cases, e.g., with 3,5-diisopropylsalicylic and 3,4-dimethoxybenzoic acids, the adhesion of the resulting sparingly soluble complex compounds at the anode was observed, which led to passivation of the anode. As a result of passivation, almost total reduction in the current density was observed, which caused the synthesis process to slow down significantly. There was also an increase in the electrical resistance of the system, leading to a decrease in the overall electrical conductivity. To solve these problems, the electrochemical cell was subjected to ultrasonic treatment during the synthesis, which resulted in a significant decrease of passivation of the anode and stabilization of the synthesis processes. The use of ultrasound to prevent the passivation is a common method for all syntheses where poorly soluble compounds are formed. The heating of the reaction mixture also gave positive results, but in this case, the synthesis becomes more complicated due to the use of a low-boiling solvent.

In the cases when soluble complexes (e.g., with 2,4-dimethoxybenzoic acid) were formed during the synthesis, which are harder to separate in the solid form, it is necessary to minimize the number of components of the electrolyte system. For this reason, the synthesis was carried out by using a ligand as the background electrolyte, which avoids contamination of the reaction product with ions included in the background electrolyte, and also by reducing the number of components to a minimum, to simplify the isolation of the complex compound in solid form. However, this can only be done if a ligand dissociates well in acetonitrile. In other cases, to increase the electrical conductivity of the system, lithium perchlorate should be used as the background electrolyte. It is readily soluble in the solvents used, and the ions have a low coordinating power.

Complex compounds of terbium (III) and gadolinium (III) with acetylsalicylic and phthalamic acids, which could not be obtained chemically due to the hydrolysis of ligands, were easily obtained by anodic dissolution of the corresponding lanthanides in an acetonitrile medium. The starting ligands are readily soluble, but due to the low conductivity of the solutions, a background electrolyte was used. As a result, soluble complex compounds for acetylsalicylic acid and insoluble for phthalamic acid were prepared.

At the end of the electrochemical process, the slightly soluble white complexes precipitated were filtered off, washed with acetonitrile, and dried in a vacuum oven at 30–50 °C.

In the case of the formation of soluble products (e.g., with 2,4-dimethoxybenzoic acid), the complexes were preliminarily isolated by dilution of the reaction mixture with a mixture of toluene and chloroform. A white precipitate of the complex compound was filtered off and then dried to a constant weight.

The Synthesis of Terbium (III) and Gadolinium (III) Complex Compounds with Ligands Used in the Work

The synthesis based on the exchange interaction of a metal salt and a ligand. As it was already noted above, aromatic carboxylic acids were used as ligands in our work, since the resulting compounds have good luminescence and a number of other useful properties (thermal stability and photostability). Terbium was chosen as a complexing metal because of its high probability to give green luminescence in the visible range. Complex compounds with gadolinium (III) were used to determine the triplet levels of ligands, the intensity of their phosphorescence, and also other luminescence characteristics.

In addition to the electrochemical synthesis, chemical synthesis of the corresponding lanthanide complexes in water-ethanol solutions was also carried out at the molar ratio of the metal salt/ligand Ln:HL 1:3 for the comparison. The chosen ratio is the most optimal, since it leads to the formation of neutral complex compounds, which can minimize the presence of extraneous ions in the coordination sphere.

A water-alcohol solution was used as a solvent for the synthesis of complex compounds. This is due to a number of factors: Firstly, in pure water or ethanol, sufficient solubility of the starting components is not always achieved, which greatly complicates the synthesis. Secondly, when water is used, the hydration of complex compounds increases, which is highly undesirable for luminescent materials. In nonaqueous solvents, the lanthanide (III) ion is loosely isolated by solvent molecules from the reaction with an aromatic acid. When alcohol is used instead of water (i.e., when the concentration of water molecules decreases), the number of solvent molecules in a solvate shell of lanthanide (III) ions decreases from 9 to 3. The resulting solvatocomplexes are much less stable than similar aquacomplexes. It is also necessary to note the decrease in the processes of hydrolysis during complexation. The use of ethanol as an organic phase in most similar syntheses is explained by its availability, low toxicity, good solubility of ligands, and low coordination ability.

The choice of the pH range from 5 to 7 is due to several reasons. At low pH values, the ligand is not deprotonated; hence, complexation does not occur. Since the dissociation of carboxylic acids is a reversible process, one of the factors that

Table 1 pK_a values of some of the aromatic acids used (water, 25 °C)

Name of acid	pK_a values
Benzoic acid	4.20
2-Hydroxybenzoic acid	2.97
Acetylsalicylic acid	3.70
2,6-Dimethoxybenzoic acid	3.98
3,4-Dimethoxybenzoic acid	4.44
3,5-dimethoxybenzoic acid	3.96
3,4-Diethoxybenzoic acid	4.39
2-Acetylbenzoic acid	4.16
2,3-Pyridinedicarboxylic acid	2.52
2,6-Pyridinedicarboxylic acid	2.21
5-Sulfosalicylic acid	2.85
3-Pyridinecarboxylic acid	4.81
3-Methylsalicylic acid	2.80

stabilize the carboxylate ion relative to the undissociated form of the ligand is to increase the pH value to the required level. For the selected ligands, the acidity constant lies in the range pK_a 4–5 (Table 1). Therefore, it is necessary to increase the pH above this value. On the other hand, an increase in the pH above 6 in the synthesis of coordination compounds leads to an increase in the probability of formation of the corresponding hydroxocomplexes $LnOHL_2$, $Ln(OH)_2L$.

Complex compounds obtained by chemical synthesis from the elemental analysis data are hydrates corresponding to the composition $Ln_mL_3 \cdot nH_2O$, where $m = 1$ for monocarboxylic and 2 for dicarboxylic acids; the content of water molecules is $n = 4–5$. Depending on the nature of the ligand, complex compounds are either highly soluble in water and alcohol or, conversely, extremely badly soluble. Soluble complex compounds were purified by recrystallization from ethyl alcohol, resulting in the formation of hydrated compounds containing up to eight water molecules. Anhydrous coordination compounds are practically insoluble in most of the solvents used: ethanol, acetonitrile, tetrahydrofuran, chloroform, benzene, carbon tetrachloride, dioxane, diethyl ether, and others. This can be explained by the fact that lanthanide ions have rather high coordination numbers and when water molecules are removed they will be coordinated with ligands from neighboring complex molecules in order to compensate for coordination unsaturation. It will result in the formation of a polymer structure, and, as it is known, inorganic polymers have an extremely low solubility in most solvents and are also characterized by a low volatility.

Electrochemical synthesis of complex compounds. The electrochemical cell for the anodic synthesis of anhydrous complex compounds is a hermetically and tightly sealed glass vessel with electrode holders. Two electrodes are fixed in the holders – working (anode) and auxiliary electrode (cathode). The choice of the material for the cell is determined by the inertness of the glass, its relative hardness (it should not be scratched and should not contaminate the reaction products), and thermal stability.

As an anode, a plate made of the corresponding lanthanide was used and platinum as the cathode. Metallic terbium and gadolinium are relatively active, especially in aqueous solutions, where they are gradually eroded to form hydroxides. This process is especially fast upon action of electric current. It is also necessary to take into account the fact that they are capable of direct interaction with a number of aromatic carboxylic acids, which we used as ligands. Although this process is slow, nevertheless it should not be neglected. Therefore, a reliable calculation of the current yield of the product is not possible since we do not know which part of metal is reacted directly and which is dissolved upon the action of electric current. So the calculation is carried out by the substance or by the ligand. The yields on the material in the electrochemical synthesis exceeded 80%, which is evidence of a high efficiency of the anodic synthesis for preparation of these substances.

To achieve maximum process efficiency in the electrochemical synthesis, it is necessary to determine the optimum synthesis conditions: the composition of the electrolyte system, applied voltage, current strength, current density, and temperature.

The choice of acetonitrile as a solvent for most cases is due to the fact that this solvent meets the requirements for electrochemical synthesis: electrochemical stability, poor coordination ability, solubility in it of the starting ligands and background electrolyte, availability, and ease of purification. A fairly high value of the vapor pressure of acetonitrile allows its simple removal upon heating, especially in vacuum. We also made an attempt to synthesize benzoates and salicylates of gadolinium (III) and terbium (III) in aqueous medium. However, we failed to obtain the desired complexes by this method because of the strong erosion of the electrodes. At the same time, the hydrates of the corresponding complex salts formed did not differ in composition from those obtained by chemical means.

In the electrochemical cell, the following electrode processes occur in the synthesis of complex compounds:

$$\begin{array}{l} \mathrm{A} \mid \mathrm{Ln} - 3e \rightarrow \mathrm{Ln}^{3+} \\ \mathrm{K} \mid \mathrm{HL} + e \rightarrow \tfrac{1}{2}\mathrm{H}_2 \uparrow + \mathrm{L}^- \\ \mathrm{Ln} + 3\mathrm{HL} \rightarrow \mathrm{LnL}_3 + {}^3/{}_2\mathrm{H}_2 \uparrow , \end{array} \tag{7}$$

where HL is a ligand.

As we noted above, charge transfer and diffusion of the components are the processes determining the kinetics of the reaction. A definite relationship between the electrode potential ε and the current density j can be drawn in most cases of dissolving a metal on the anode (Fig. 6).

For the case when the metal is passivated during the electrochemical dissolution process, the graph of the dependence is shown in Fig. 6a. At the first stage, active dissolution of the metal takes place, at which the current density increases (segment *ab*). At the next stage, a passivation process occurs, accompanied by a drop in the current density (segment *bc*). After that, the metal is in a passive state (*cd*). This stage is characterized by a low rate of dissolution of the metal due to a decrease in the current density. For some metals under certain conditions, a

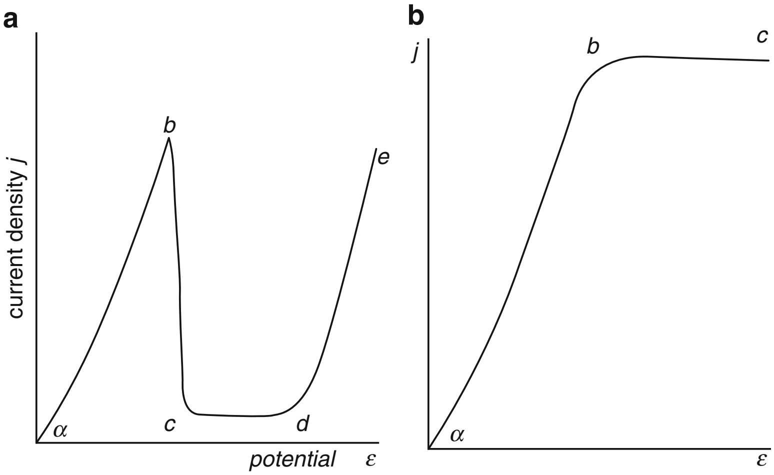


Fig. 6 Correlation of the current density change from the electrode potential at the anodic dissolution of a metal

transpassive state may occur when a noticeable increase in the current density is observed and the rate of the process increases again (segment de). This is possible in the case where the metal is capable to be oxidized to a state with an increased oxidation state or a process of high polarization of the electrode is possible (the release of gaseous oxygen at the anode is observed).

The case with no passivation of the metal during its anodic dissolution is shown in Fig. 6b. As can be seen, at the initial stage (segment ab), active dissolution of the metal takes place, while the current density is constantly growing. After the electrode potential reaches a sufficiently positive value, the rate of dissolution of the metal slows down significantly (segment bc), and this segment is characterized by the appearance of the so-called anodic limiting current. At this stage of synthesis, the adsorption of the complex compound is possible on the surface of the metal electrode leading to the passivation of its working region. In this case, the further anode dissolution rate of a metal will depend on the adhesion of the given complex compound to the metal surface and is also determined by the rate of dissolution of this complex, i.e., processes of desorption. Under certain conditions, metal reduction can also occur in addition to the process of active metal dissolution. This reaction also affects the kinetics of the process and pointed to a poorly selected electrosynthesis conditions.

Sometimes, at the first stage of the synthesis, the initial drop in the density of the electric current was observed, followed by its subsequent rise (Fig. 7). This can be explained by a special mechanism of metal dissolution. Initially, dissolution occurs at the active points of the metal surface, formed in the microheterogeneous zones. The presence of these zones is associated with the heterogeneity of the metal surface (the presence of microprotrusions), which causes a significant contact area of the phases, and hence high values of the electric current density at these protrusions.

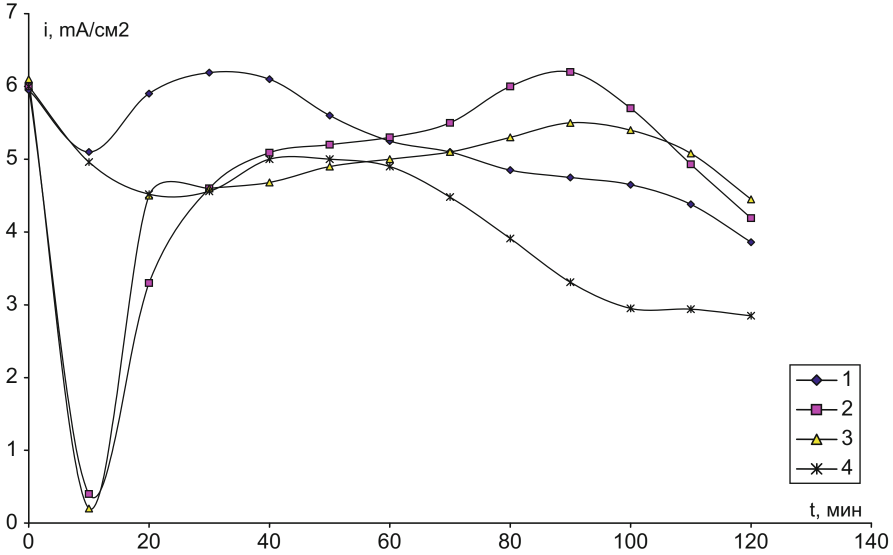


Fig. 7 Dependence of current density on the synthesis time of terbium (III) coordination compounds. 1- 2-Hydroxybenzoic acid, 2-benzoic acid, 3-pyridinecarboxylic acid, 4-3,4-dimethoxybenzoic acid

During the synthesis, these protrusions dissolve in the first place, which reduces the surface area of the electrode and, correspondingly, decreases the current density. Further dissolution at the intergranular boundary again leads to the appearance of microroughness, which will cause an increase in the rate of anodic dissolution of a metal.

In addition to the phenomena described, effects associated with the adsorption of compounds with high adhesion on the surface of the metal may take place. These effects are due to the nature of the ligand mainly and quite often lead to passivation of the anode. Thus, the current density drop is much higher in the case of benzoic acid than, for example, with 2-hydroxybenzoic acid. This is due to the different structure of ligands, which leads to the formation of complex compounds of different stability (in the second case, more stable complex compounds are formed). As the result of passivation, an increase in the electrical resistance of the system and an almost total reduction in the current density occur, which makes the synthesis process significantly slower. In this case, the application of ultrasonic treatment of the electrochemical cell during the whole synthesis process contributed to its considerable acceleration. Weak ultrasonic waves helped reduce the adhesion of reaction products to the surface of the anode, thereby removing most of the precipitate from its surface, reducing the resistance in the electrochemical cell. Although the voltage in the system was increased over time, it was a much slower process than in the case of electrochemical synthesis without ultrasonic treatment. Nevertheless, in this case, there was no need to stop the synthesis and mechanically peel the surface of the electrodes. Upon ultrasound treatment, the yields of products increased by 5–10% on average. Since electrochemical synthesis also involves the chemical dissolution of lanthanides, the maximum rate of dissolution of a metal is reached when ultrasound is used. However, it should be noted that the ultrasonic treatment may warm the reaction mixture, which can accelerate the process due to an increase in the solubility of substances (dissociation is improved) but also lead to undesirable side reactions. Therefore, careful temperature control during synthesis is also necessary.

The optimal current strength during the synthesis of complex compounds with the ligands used is 15–30 mA. A voltage in the range of 4–12 V was applied. Optimal anode current density during the processes was in the range of 6–12 mA/cm^2. The choice of these parameters contributed to the most efficient course of the synthesis process.

At large negative potentials, the cathodic reduction of carboxylic acids is possible, leading to the formation of either the corresponding aldehydes (8) (two-electron process) or the corresponding alcohols (9) (four-electron process):

$$\mathrm{RCOOH} \overset{+2e+H^+}{\rightarrow} \mathrm{RCH(OH)_2} \leftrightarrows \mathrm{RCHO} + \mathrm{H_2O} \tag{8}$$

$$\mathrm{RCHO} \overset{+2e+H^+}{\rightarrow} \mathrm{RCH_2OH} \tag{9}$$

Since aldehydes are most often reduced with less negative potentials than analogous carboxylic acids, the termination of the aldehyde reduction process at this stage is rather difficult. In aromatic carboxylic acids, which do not contain substituents that are more easily reducible than the carboxyl group (strong electron-withdrawing groups), only hydrogen is released on electrolysis in aqueous solutions on the cathode. The carboxylate anion formed after the reduction of the proton can hardly be reduced further. So the recovery of non-activated aromatic carboxylic acids in weakly acidic and slightly alkaline media does not occur. At the same time, the situation changes dramatically in a strongly acidic medium, since the protonation of the COOH group can give highly reactive species capable to take electrons by the carbon-oxygen bond. Moreover, other types of reduction of aromatic carboxylic acids may proceed. For example, in 80% ethanol solution, benzoic acid can be reduced to benzil:

$$\mathrm{PhCOOH} \overset{+e+H^+}{\rightarrow} \mathrm{PhC^{\cdot}O} \rightarrow \tfrac{1}{2}\,\mathrm{PhCOCOPh} \tag{10}$$

This reaction takes place in strongly acidic solutions on mercury or lead electrodes. In the presence of tetraalkylammonium salts, the efficiency of this reduction is higher than in the presence of alkali metal cations (used as a background electrolyte). This is due to the fact that when the charge is transferred to the ion pair (the potential-determining stage), the benzoate anion has an essentially delocalized charge. At low pH values, another type of reduction reaction may be the formation of the corresponding aromatic alcohols.

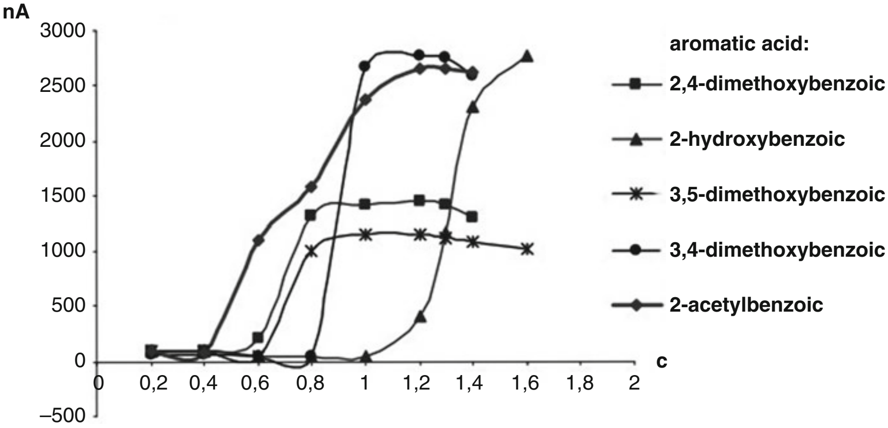


Fig. 8 Voltammograms of some aromatic acids used in the present work

Thus, for electrochemical reduction of aromatic carboxylic acids, it is necessary to create rather hard conditions (a strongly acidic medium and a rather high negative potential (less than −2 V)). In our case, such processes were impossible because of the mild conditions for the processes of synthesis of coordination compounds.

Voltammograms of some of the aromatic acids used in our work are shown in Fig. 8. As can be seen, the oxidation potentials of ligands begin at 0.4 V, and the upper oxidation potential lies in the region of 1.6 V. Consequently, a rather wide range of potentials at which ligands are not subjected to electrochemical transformations allows them to be used in the synthesis of complex compounds under our conditions.

In the synthesis of complexes with ligands easily hydrolyzed (phthalamic acid, acetylsalicylic acid), a standard procedure was also used, without the need to lower the pH value for the deprotonation of the acid (this process took place at the cathode). As a result, the corresponding anhydrous complex compounds with lanthanide ions of the composition LnL_3 were obtained. It should be noted that obtaining them by classical methods requires much more complex and careful management of the process of synthesis and separation of final products. The method of obtaining complex compounds used by us has also shown positive results for ligands, complexation with which is difficult due to steric factors (2,6-dimethoxybenzoic acid). Due to the deprotonation of the ligand on the anode and the formation of its reactive forms, the equilibrium shifted toward the formation of reaction products.

Thermogravimetric Study of Complex Compounds of Lanthanides

Thermal stability is an important characteristic in the study of new materials, since with the possible use of the resulting complex compounds in industry, it is necessary to take into account the operating temperature range of the substances under which they retain their original properties. Since luminophores are applied to conductive substrates by sublimation at elevated temperature and reduced pressure in the preparation of electroluminescent devices, an investigation of the operating temperature range in which the compound does not lose its luminescent properties becomes an important task. The thermal stability of the resulting lanthanide complexes was studied by thermogravimetry.

The shape of the curves on thermograms of complexes with identical ligands does not differ in shape, but there are small differences in the temperature effects. Thermogravimetric analysis is illustrated by the example of some terbium (III) complexes obtained with the selected ligands (Figs. 9, 10, 11, 12, 13, 14, and 15). According to the thermogravimetric analysis, most of the synthesized complexes are thermostable up to 300–400 °C, which makes it possible to deposit them on substrates using the vacuum sublimation method. Thermal analysis of anhydrous complex compounds shows no effects up to 200 °C, corresponding to dehydration processes. Thermograms of hydrated complexes in the temperature range 80–120 °C show endo-effects corresponding to the loss of crystallization water. The residual mass corresponds to lanthanide oxides. In the temperature range 250–600 °C, there are exo-effects accompanied by a sharp loss of mass, which correspond to the thermal-oxidative destruction of the complexes.

For example, the thermal stability region for coordination compound of terbium (III) with 4-tert-butylbenzoic acid is up to 400 °C, with no effects corresponding to dehydration processes up to 200 °C (Fig. 9).

Anhydrous and hydrated complexes for the same ligand generally have a similar type of thermogram, except for the effects associated with the cleavage of water

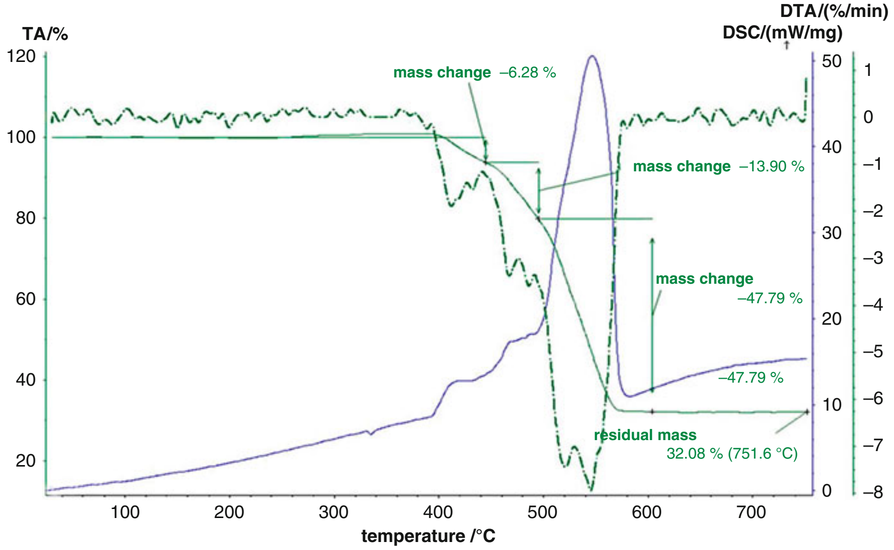


Fig. 9 Thermogram of the complex Tb(4-TbutBenz)$_3$

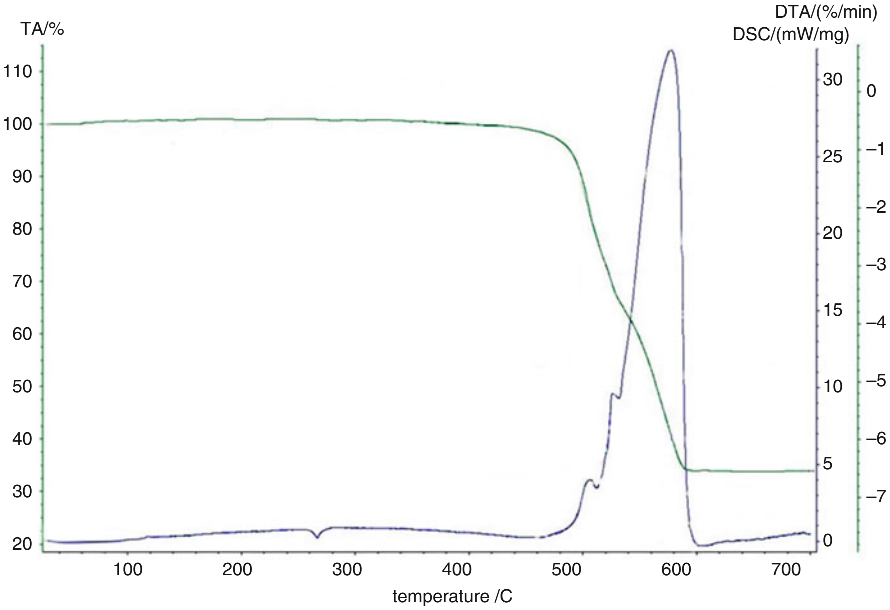


Fig. 10 Thermogram of complex compound Tb(Benz)$_3$

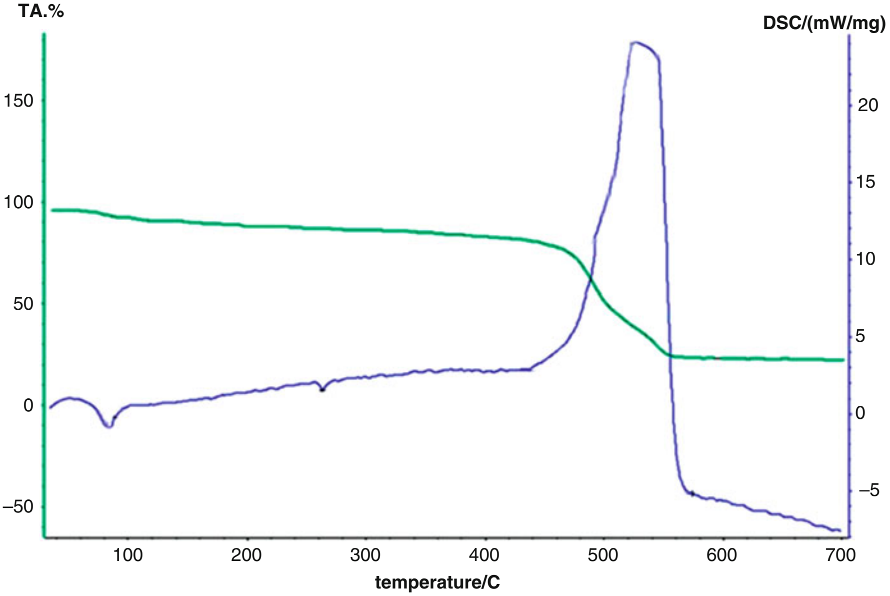


Fig. 11 Thermogram of complex compound Tb(Benz)$_3$·(H$_2$O)$_4$

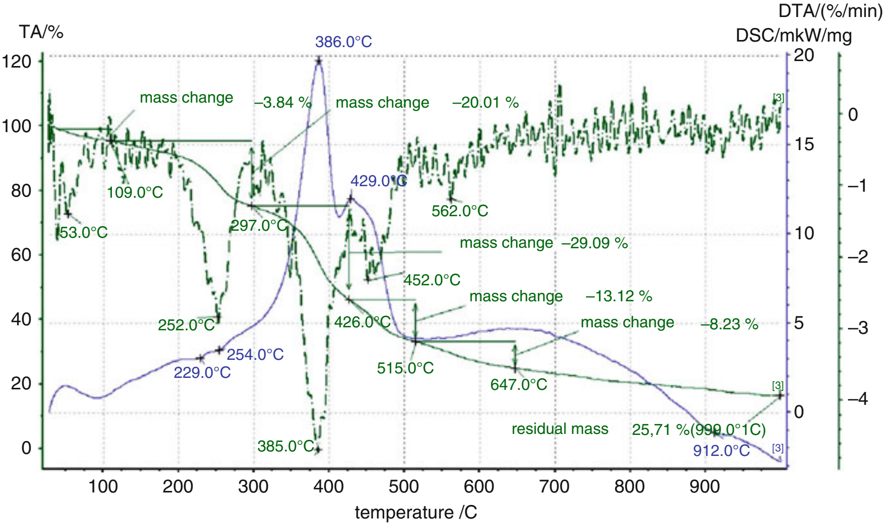


Fig. 12 Thermogram of complex compound Tb(2-HidBenz)$_3$(H$_2$O)$_3$

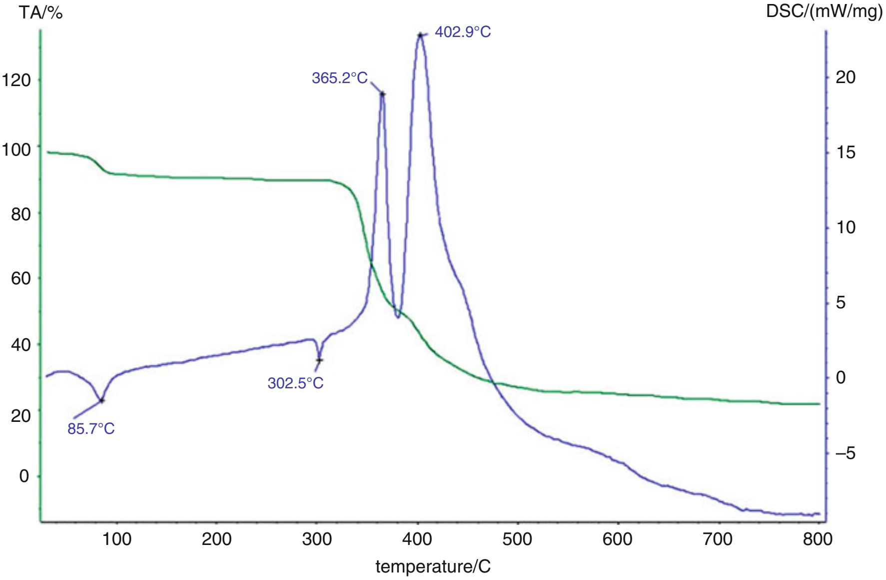


Fig. 13 Thermogram of complex compound Tb(3,4-MeOBenz)$_3$(H$_2$O)$_6$

molecules, other thermal effects are similar, and their differences are insignificant. Thermograms of terbium (III) benzoate and its hydrate (Figs. 10 and 11) show that the cleavage of outer-sphere water molecules occurs in the temperature range

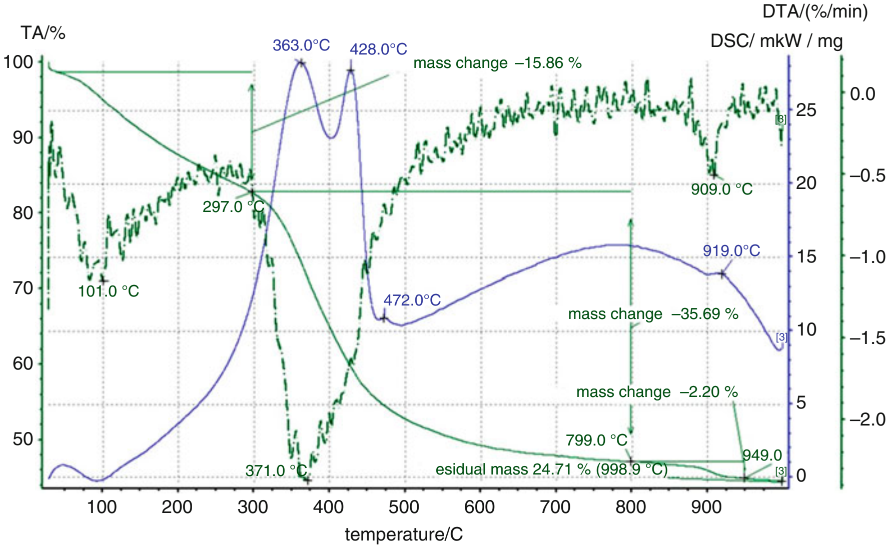


Fig. 14 Thermogram of complex compound Tb(MeSal)$_3$(H$_2$O)$_4$

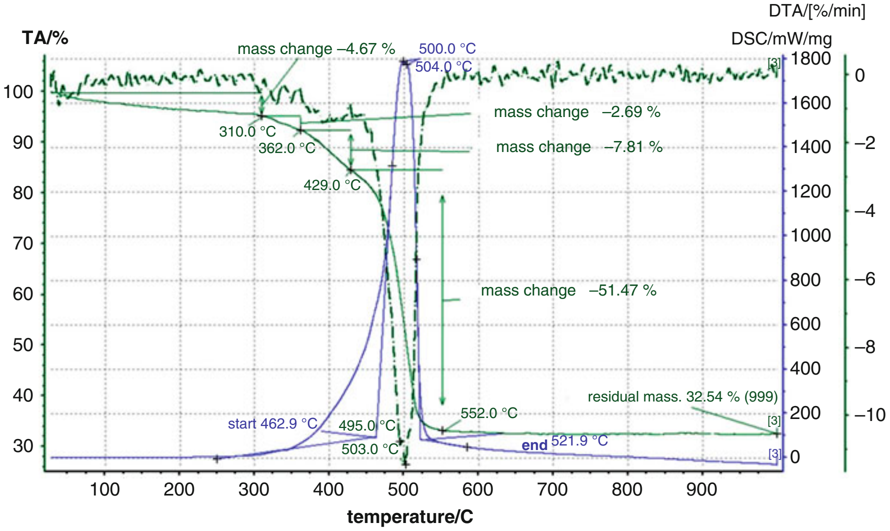


Fig. 15 Thermogram of a complex compound Tb(3-PircarbH)$_3$

70–110 °C and at 460 °C the thermo-oxidative destruction of the complex compound begins, but in general they are similar in appearance. As it can be seen, benzoates are thermostable in the temperature range of 200–400 °C. In Fig. 11, it is shown that even in the region of thermal stability, the hydrated compound exhibits a partial decrease in mass without visible endo-effects. This can be explained by the presence of coordinated water molecules in the compound, the loss of which, as the temperature increases, leads to a weakening of the coordination bond between a ligand and a metal ion, leading to a partial cleavage of the ligand molecules. On the contrary, in anhydrous complex compounds, the thermal stability region emerges on a wide plateau.

In general, the introduction of substituents into the benzoic ring of aromatic acids leads to a decrease in the thermal stability of complex compounds. From the thermogram (Fig. 12) of the terbium (III) complex with 2-hydroxybenzoic acid, it can be seen that at the first stage in the 109 °C region, external-sphere water is cleaved off. Further, in the temperature range 210–300 °C, an endothermic process is observed. Initially, to a temperature of 250 °C, the removal of the 2-HidBenz-ion occurs without its oxidation to form the $Tb_2(C_6H_4COO)_4$ oligomer. When the temperature is raised to 310 °C, its structure changes to $Tb_2(C_6H_4COO)_3$. Then, in the temperature range 310–550 °C, a thermo-oxidative destruction of the intermediate takes place to form Tb_4O_7 with an exothermic effect.

The decomposition scheme of the complex can be represented as follows:

$$\begin{aligned}&4\mathrm{Tb(2\text{-}HidBenz)_3{}^{*}3H_2O} \rightarrow 2\mathrm{Tb_2(2\text{-}HidBenz)_4} + 3\mathrm{H_2O}\\&2\mathrm{Tb_2(2\text{-}HidBenz)_4} \rightarrow 2\mathrm{Tb_2(2\text{-}HidBenz)_3}\\&2\mathrm{Tb_2(2\text{-}HidBenz)_3} \rightarrow \mathrm{Tb_4O_7}\end{aligned} \tag{11}$$

In general, alkoxy groups lower the temperature of thermolysis of complex compounds, compared to benzoates. For example, for the terbium (III) complex with 3,4-dimethoxybenzoic acid (Fig. 13), the DTG curve is more smooth, and the thermal stability region lies at 110–300 °C. The endo-effect at 302 °C without loss of mass corresponds to the melting of the substance; in benzoate it is correspondingly revealed at 262.4 °C.

For the complex compound of terbium (III) with 3-methylsalicylic acid (Fig. 14), an exo-effect is observed at 101 °C, which corresponds to the cleavage of outer-sphere water. The thermal-oxidative destruction of the organic part of the complex is observed in the temperature range 363–472 °C.

The complex compound of terbium (III) with 3-pyridinecarboxylic acid (Fig. 15) is thermally stable up to 300 °C. In the temperature range 462–550 °C, a thermal-oxidative destruction of the organic part is observed, accompanied by an exothermic effect.

It is noteworthy that anhydrous 2,3,4-trimethoxybenzoates of lanthanides (III) have a thermal stability up to 285 °C. The appearance of another additional methoxy group in 2,3-dimethoxybenzoic acid in the position 4 increases the thermal stability by 25 °C. In trimethoxybenzoates of lanthanides (III), thermal stability will increase in the series 2,4,5- <2,3,4- <3,4,5-.

In summary, the thermal stability of lanthanide coordination compounds depends both on the structure of the complex compound and on the structure of the starting ligand. The latter factor can play a decisive role.

Luminescence of Coordination Compounds

Since the energy of the excited triplet level of the ligand has a decisive influence on the process of intramolecular transfer of the excitation energy from the organic ligand to the resonant $^5D_4$ level of the Tb^{3+} ion [26–30], the spectra of phosphorescence of the gadolinium complexes with the studied ligands have been recorded and studied (Figs. 16 and 17). The use of this approach to estimate the energy of the triplet level of the ligand is possible due to the high ratio of the quantum yield of phosphorescence to the quantum yield of fluorescence at liquid nitrogen temperature

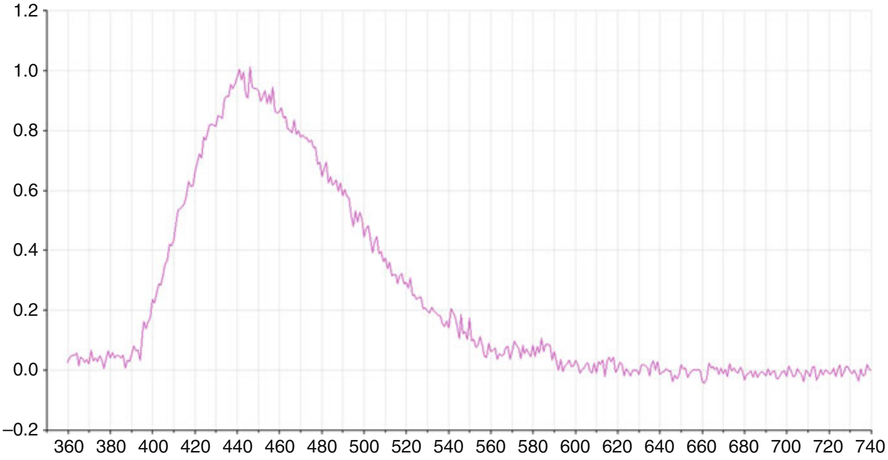


Fig. 16 Spectrum of phosphorescence of anion 2,3-MeOBenz-

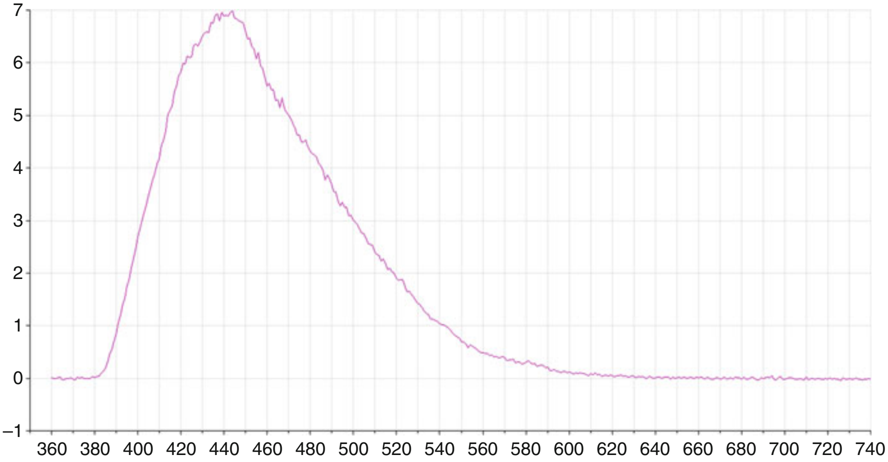


Fig. 17 Spectrum of phosphorescence of anion 2,4-MeOBenz-

(77 K), and in this case, energy transfer from the organic part of the complex compound to the lanthanide ion is not possible, since the lower-resonant-level gadolinium (III) lies well above the triplet levels of the ligands used by us.

The phosphorescence spectra of complex compounds of gadolinium (III) were recorded at a liquid nitrogen temperature (77 K) (to maximize the leveling of the thermal quenching of the luminescence). The triplet levels of the ligands were determined from the maxima of the emission bands, which are presented in Table 2. Here we also show the values of the integrated intensities in the luminescence spectra of terbium (III) complexes.

The luminescence intensity of the complex compounds terbium (III) was estimated according with respect to the reference compound (anhydrous terbium benzoate), which integrated intensity was taken to be 10. It was chosen because the compound revealed a luminescence of sufficient intensity. In addition, benzoic acid is the simplest compound in the series of aromatic carboxylic acids.

As it can be seen from Table 2, the T_1 value of the anion of benzoic acid, the simplest acid among the ligands used, is 22,830 cm^{-1}. According to the literature data, T_1 for this acid is 21,280 cm^{-1}. The differences can be explained by the fact that in literary data the energy of the triplet state was determined for a complex containing water and for an anhydrous complex in our case. This makes a difference

Table 2 Energy values of excited triplet states of anions of carboxylic acids used

The anion of the acid	Energy T_1, cm^{-1}		$T_1 - {}^5D_0$, cm^{-1}	Integral intensity TbL_3
	Measured	Literature data		
Benz-	22,830	21,280	2330	10
4-TbutBenz-	25,060	24,875	4560	–
2-HidBenz-	23,810	23,800	3310	11.21
4-HidBenz-	23,360	23,530	2860	4.56
3,5-IsopropSal-	24,390	–	3890	8.82
5-SulfoSal-	20,830	–	330	5.058
5-BrSal-	20,280	–	−220	
2,3-MeOBenz-	22,573		2073	5.688 4.105
2,4-MeOBenz-	22,522		2022	15.262
2,6-MeOBenz-	22,675		2175	7.115
3,4-MeOBenz-	21,277		777	18.774
3,5-MeOBenz-	20,491		−9	13.355
2-AcBenz-	20,408		−92	4.675
4-AcBenz-	21,052		552	5.485
2-BenzolBenz-	20,618		118	6.098
2(4Clben)Benz-	21,930		1430	7
2(4Fben)Benz-	22,321		1821	10.264
Ftalamin-	21,978		1478	6.8
2,6-Dpir-	23,585		3085	4.085

in the structure of the coordination node, which causes a distortion of the geometry of the organic ligand itself. As a result, this leads to a change in the energy of the excited triplet state.

As it was found earlier, in order to observe intensive luminescence in complex compounds of terbium (III), it is necessary that the triplet level of the ligand is located above the resonance level of the $^5D_4$ Tb^{3+} ion by 2500–4000 cm^{-1} [31, 32]. At higher values, energy transfer becomes inefficient due to the low probability of such a transition of electrons, and at lower values, due to the thermal vibration of molecules, the reverse transfer of part of the energy to the ligand molecule will increase. For ligands with the difference in energy between the excited triplet level of the ligand and the resonance level of the Tb^{3+} ion is below 200 cm^{-1}, a weak luminescence is observed, which agrees well with the literature data. However, it should be noted that this is not a strict rule and there may be some deviations. In our case, the value of the difference is slightly less than the minimum threshold, so for terbium (III) benzoate, a luminescence of a medium intensity is observed.

In the case of 4-tert-butylbenzoic acid, a significant increase in the energy of the excited triplet state to 25,060 cm^{-1} (according to the data of paper – 24,875 cm^{-1}) is observed. This is due to the fact that the substituent (tert-butyl-) has a significant positive inductive effect and leads to an increase in the electron density on the benzene ring, which in turn leads to an increase in the energy of the $\pi \rightarrow \pi^*$ junction. The difference value for the terbium (III) ion approaches the maximum threshold. However, the luminescence of a moderate intensity was still observed.

The use of an anion of salicylic acid as a ligand raises the energy of the excited triplet state to 23,810 cm^{-1}, which almost completely corresponds to the literature data. This increase in the triplet state energy is due to the predominance of the positive mesomeric effect over the negative inductive, which is revealed by the hydroxyl group in the anion of salicylic acid.

A less increase in energy for isomeric 4-hydroxybenzoic acid is due to the large distance between the two substituents, which weakens the mesomeric effect. For a given type of ligand, the triplet state energy is 23,360 cm^{-1} (literature data – 23,530 cm^{-1}).

When using the 3,5-isopropylsalicylic acid anion as a ligand, the energy of the excited triplet state changes in comparison with 2-hydroxybenzoic acid, under the influence of a positive mesomeric effect and positive inductive effects arising from the presence of two isopropyl substituents in the molecule. As a result, the energy of the excited triplet state rises, which causes the intensive luminescence.

The negative inductive effect in the anion of 5-bromosalicylic acid is associated with the action of bromine on the benzene ring. As a result it gives a negative increase in the energy of the triplet state with respect to benzoic acid (20,280 cm^{-1}).

A similar situation is observed when the anion of sulfosalicylic acid is used. The same negative mesomeric effect, but of lesser force, causes a large energy of the excited triplet state of this ligand (20,830 cm^{-1}).

The anion of 2,3-dimethoxybenzoic acid is characterized by a positive mesomeric effect, which increased the energy of the excited triplet state to 22,573 cm^{-1}. This effect is due to the presence of oxygen atoms in the direct contact with the benzene ring, the unpaired electronic pairs of which are displaced toward the ring, increasing its electron density and, as a consequence, the energy of the excited triplet state. The lower energy of the excited triplet state for the anion of 2,4-dimethoxybenzoic acid is due to the absence of a contact between the 2 and 4 methoxy groups, which is observed in the presence of substituents at position 2,3. In this compound, the mesomeric effect was enhanced by the neighboring substituents in the benzene ring. Similarly, an increase in energy in the anion of 2,6-dimethoxybenzoic acid occurs.

In the anion of 3,4-dimethoxybenzoic acid, the mesomer effect is enhanced by the conjugation of substituents, but the absence of conjugation with the carboxyl group gives a small increase in the energy of the excited triplet state (777 cm^{-1}). The negative increase in the energy of the excited triplet state in 3,5-dimethoxybenzoic acid is due to the absence of any conjugation and the overall small positive mesomeric effect of the methoxy group, which weakens due to the methyl group, which retards a part of the electron density to itself. As a result, we have a negative increase in the energy of the excited triplet state.

In the anion of 2-acetylbenzoic acid, the negative inductive effect of the substituent increases in the ortho-position relative to the carboxyl group, which explains the smaller increase in the energy of the excited triplet state, compared with the anion of 4-acetylbenzoic acid.

In the anion of 2-benzoylbenzoic acid, the negative inductive effect is weakened. As a result, the increase in the energy of the excited triplet state with respect to benzoic acid is insignificant.

For anions of halogenated benzoylbenzoic acids, the energy of the excited triplet state is determined by a negative inductive effect, and the increase in the energy of the excited triplet state is proportional to the electronegativity of the halogen atoms.

In the anion of phthalamic acid, the substituent has a negative inductive effect, which, in addition, is amplified by an amino group. Due to this, a strong increase in the energy of the excited triplet state is obtained.

In the anion of 2,6-pyridinecarboxylic acid, two negative inductive effects are enhanced by a mesomeric positive effect directed toward the nitrogen atom. As a consequence, there is a strong increase in the energy of the excited triplet state with respect to the anion of benzoic acid.

All the terbium (III) complex compounds obtained exhibit good luminescence. The absence of phosphorescence of the organic part of the complex (ligand) indicates an effective redistribution of energy to the Tb^{3+} ion, which is due to the optimal location of the excited triplet level of the ligand and the emitting level of the lanthanide (III) ion. In the photoluminescence spectra, the emission bands characteristic of the Tb^{3+} ion are observed: $^5D_4 \rightarrow {}^7F_6$ (490 nm), $^5D_4 \rightarrow {}^7F_5$ (545 nm), $^5D_4 \rightarrow {}^7F_4$ (585 nm), $^5D_4 \rightarrow {}^7F_3$ (620 nm), and $^5D_4 \rightarrow {}^7F_2$ (650 nm), which confirm the luminescence of only the lanthanide ion.

As can be seen from the obtained data (Fig. 18), the appearance and mutual arrangement of the substituents in the benzoic ring of the ligand relative to each other, and also with respect to the carboxyl group, affect the structure of the coordination node of the binary complexes. Their mutual arrangement can significantly

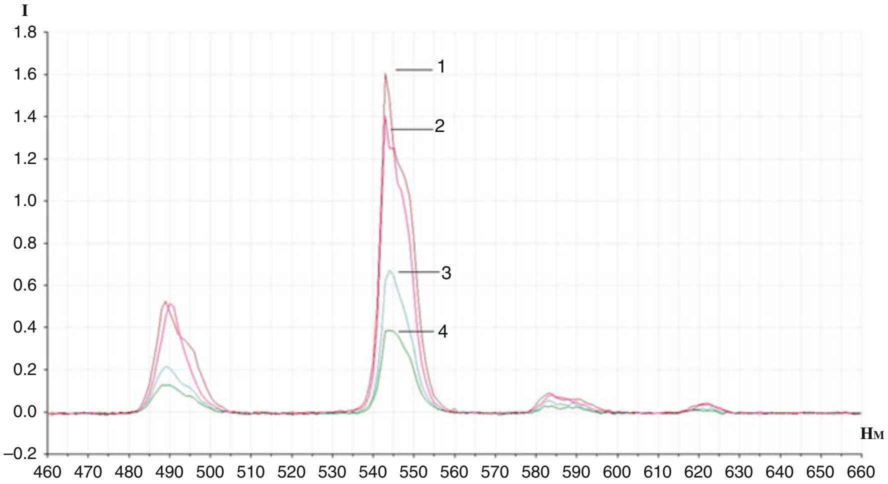


Fig. 18 Comparison of luminescence spectra of complex compounds Tb(3,4-MeOBenz)$_3$ (1), Tb (2,4-MeOBenz)$_3$ (2), Tb(2,6-MeOBenz)$_3$ (3), Tb(2,6-MeOBenz)$_3$ (4) at 298 K

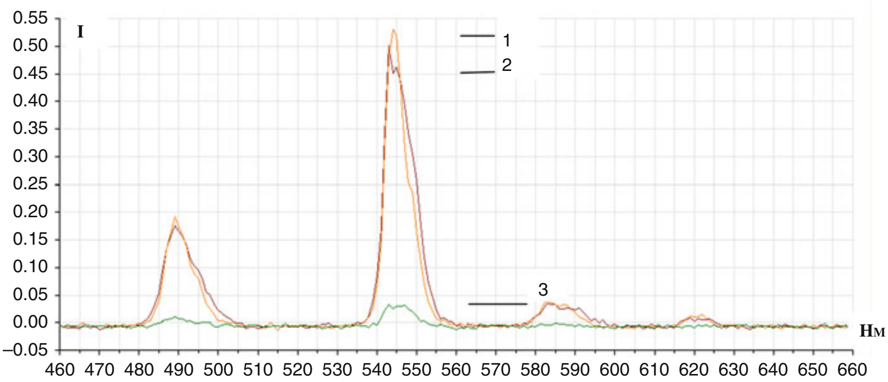


Fig. 19 Luminescence spectra of complex compounds Tb(2-HidBenz)$_3$ (1), Tb(5-SulfoSalH)$_3$ (2), Tb(5-BrSal)$_3$ (3)

change the geometry of the coordination node, and hence the efficiency of energy transfer from the ligand to the lanthanide ion, while changing the intensity of luminescence.

Figure 19 shows the effect of various substituents in 2-hydroxybenzoic acid on the luminescence intensity of complex compounds with terbium (III). As already noted above, in the case of 5-bromosalicylic acid, the lowest luminescence intensity is observed, which is associated with the largest negative mesomeric effect in the 5-bromosalicylic acid anion in comparison with the 5-sulfosalicylic acid anion, which leads to a significant decrease in the energy of the excited triplet state of

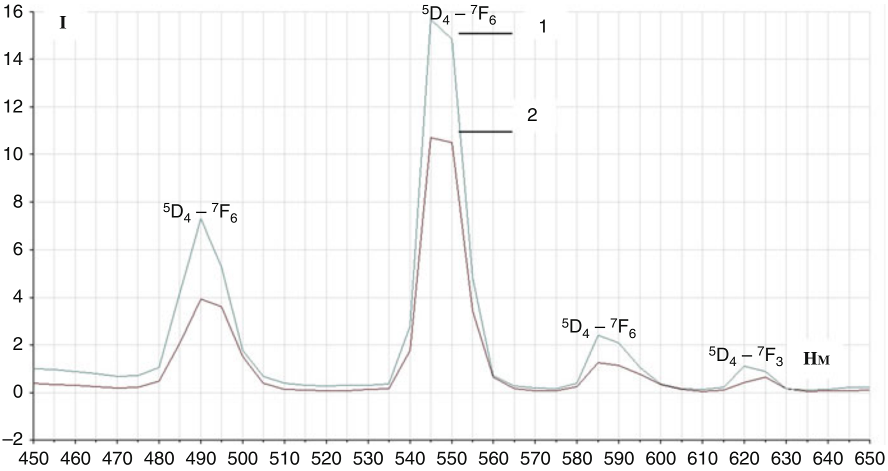


Fig. 20 Luminescence spectra of complex compounds Tb(2,4-MeOBenz)$_3$ (1) и Tb(OH)(2,4-MeOBenz)$_2$

this ligand. As a result, the transfer of energy from the ligand to the resonance level of terbium (III) becomes ineffective.

As it was expected, the luminescence intensity of hydroxy complexes is considerably lower than luminescence intensity of anhydrous and hydrated coordination compounds (Figs. 20 and 21). The hydroxyl group bonded to an ion of a lanthanide (III) participates in energy transfer from ligand to metal ion of the molecule. At the same time, part of the energy is expended on the natural oscillations, thereby making its negative impact on the luminescence process. Similar phenomena are observed in the presence of coordinated molecules of water; however, their effect on the luminescence intensity is somewhat weaker as compared with the hydroxyl group. Thus, in the synthesis of complex compounds, it is necessary to avoid an increase of the pH value, to exclude the formation of hydroxyl complexes, as we have shown in practice. The synthesis also should be carried out in an anhydrous medium to exclude the coordination of water molecules, if it is possible. It should be noted that the thermal stability of hydrates and hydroxyl complexes is lower than for corresponding anhydrous complex compounds, which negatively affects their application in the art as luminescent materials.

It is well known that the optical spectra of lanthanide (III) ions have a relatively low intensity, which is reflected in the quantum-mechanical description by a parity prohibition. The presence of aromatic acid anions in the close surroundings of the lanthanide (III) ions has a little effect on the configuration of 4f electrons due to the shielding effect by external 5s and 5p shells. However, an insignificant change in the radius of the 4f shell occurs in this case, which leads to the Stark splitting of the $4f^n$-electron configuration of the ion. Under the influence of the neighboring ions, the symmetry of the lanthanide ion decreases. It leads to the polarization, which contributes to an increase in the intensity of the optical transitions. The lifting of the prohibition will be due to the addition of configurations of components having a different parity to the components of the crystalline field of the surrounding lanthanide ion. Therefore, the analysis of the luminescence spectra allows one to determine the structure of the coordination polyhedron. However, in the case of Tb^{3+} ion, this is difficult to do because of the too complicated Stark structure.

The luminescence times of most of the compounds obtained are in the range 0.02–0.6 ms (Figs. 22, 23, 24, and 25). This indicates that the transfer of energy from

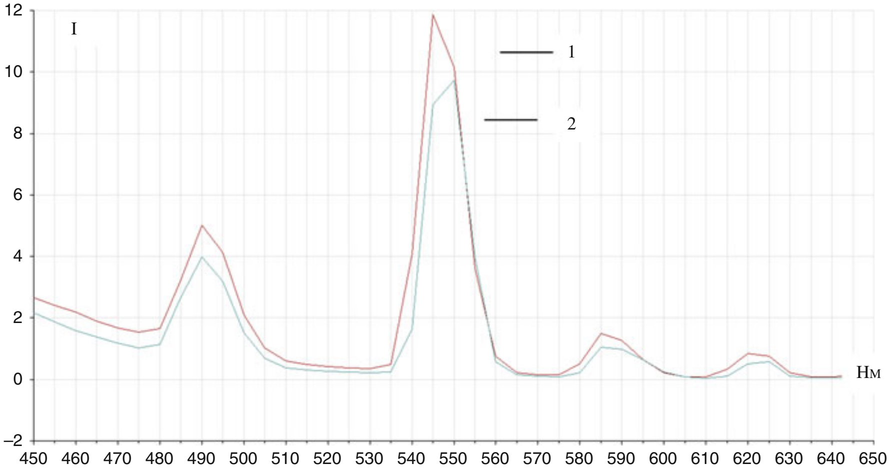


Fig. 21 Luminescence spectra of complex compounds Tb(2-HidBenz)$_3$ (1) и Tb (2-HidBenz)$_3$(H$_2$O)$_6$

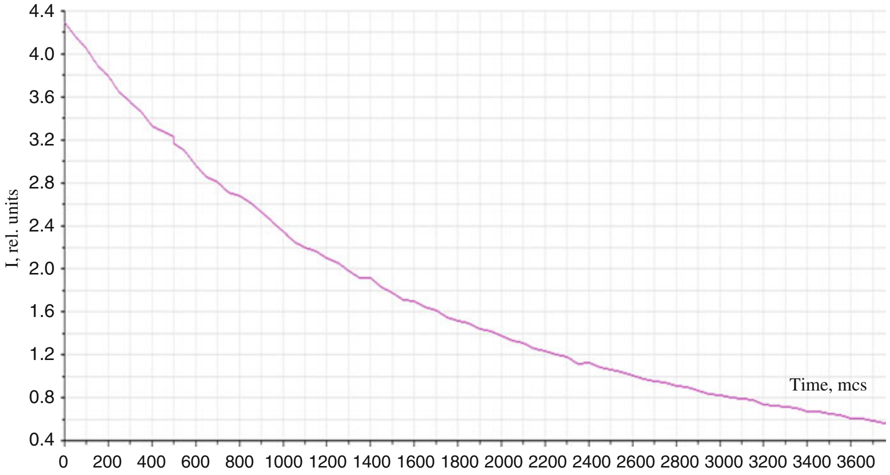


Fig. 22 Spectrum of the kinetics of luminescence Tb(3,4-MeOBenz)$_3$

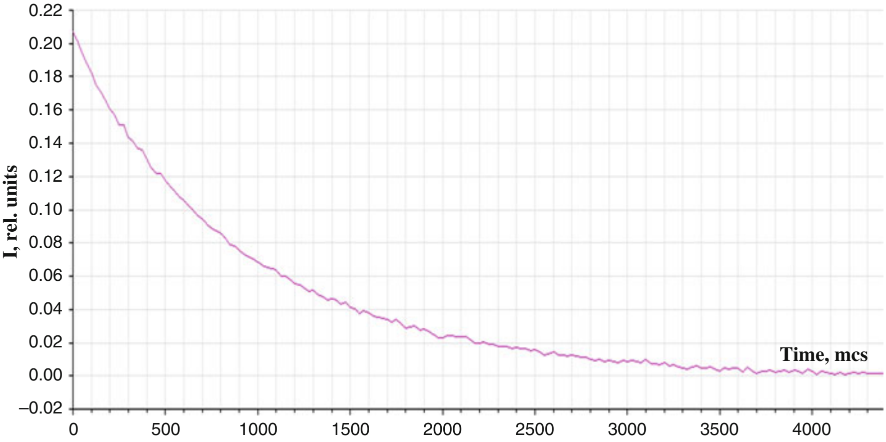


Fig. 23 Spectrum of the kinetics of luminescence Tb(4-AcBenz)$_3$

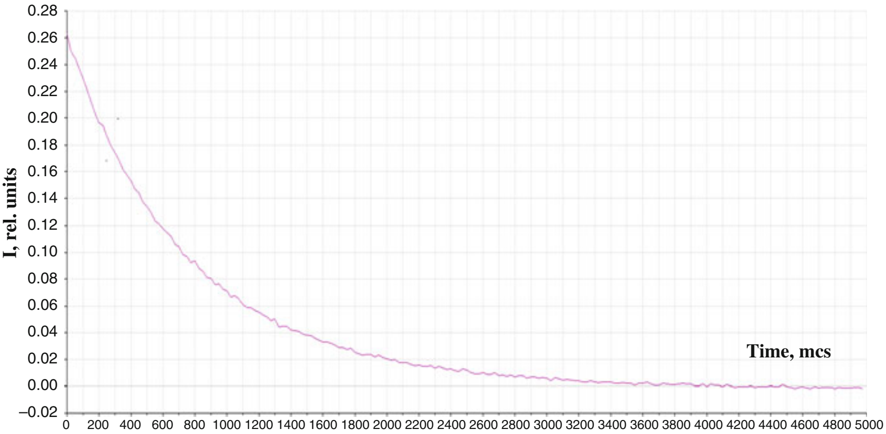


Fig. 24 Spectrum of the kinetics of luminescence Tb(5-SulfoSalH)$_3$

the excited triplet level of the aromatic carboxylic acid to the resonance level of the terbium (III) ion without phosphorescence of an organic part of the complex compound is predominant.

Conclusions and Further Outlook

1. We showed that anhydrous complex compounds of lanthanides possessing effective luminescence could be synthesized using electrochemical methods. The synthesis was carried out by the soluble anode method in anhydrous acetonitrile.

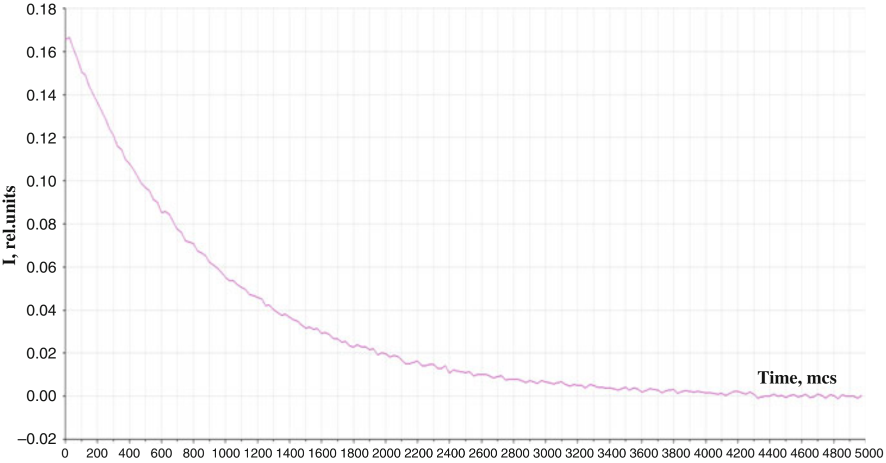


Fig. 25 Spectrum of the kinetics of luminescence $Tb_2(2,6\text{-}Dpir)_3$

Optimum synthesis parameters: voltage 6–12 V, current density 6–10 mA, ligand concentration $3 \cdot 10^{-3}$–$1.5 \cdot 10^{-2}$ mol/L, and solvent – acetonitrile. Ultrasound was used to reduce the passivation of an electrode.

2. The complex compounds of terbium (III) and gadolinium (III) (Ln) with substituted benzoic acids (2-acetyl-, 4-acetyl-, 2-benzoyl-, 2-hydroxy-, 2,4-dihydroxy-, 4-hydroxy-, 2,4-dihydroxy-, 3,5-dihydroxy-, 2-acetyloxy-, 4-tert-butyl-, 2,4-dimethoxy-, 2,3-dimethoxy-, 2,5-dimethoxy-, 2,6-dimethoxy-, 3,4-dimethoxy-, 3,5-dimethoxy-, 3,4-diethoxy-, 2-phenoxy-) LnL3 and pyridine dicarboxylic acids (2,3- and 2,6-pyridinedicarboxylic acids) Ln2L3 were prepared for the first time using electrochemical methods. Complex compounds with phthalamic acid were not obtained previously by chemical synthesis.
3. The composition of the obtained compounds was confirmed by thermogravimetric analysis. It was found that the lanthanide hydroxyl- and alkoxybenzoates are thermostable up to 250 °C, complexes with pyridinedicarboxylic acids – up to 320 °C. Lanthanide alkylbenzoates showed the greatest stability (up to 380–400 °C).
4. The energies of excited triplet states of the ligand anions are determined from the spectra of phosphorescence of gadolinium (III) complexes. It was shown that the introduction of an electron-donating groups leads to an increase in the energy of the triplet level of the anions of benzoic acids and to an increase in luminescence intensity of complex compounds with terbium (III), while the introduction of an electron-withdrawing substituents leads to a decrease in the energy of the triplet level of a ligand and an increase in the luminescence intensity of complex compounds with terbium (III).
5. We found that anhydrous complex compounds of terbium (III) with aromatic carboxylic acids that were obtained by electrochemical method in nonaqueous media revealed a 1.5–2 times higher luminesce than the corresponding complex

compounds obtained by chemical methods and containing water molecules in the internal coordination sphere. The complex compound Tb(3,4-MeOBenz)$_3$ showed the best luminescence, with integrated intensity of 18 times greater than that of terbium (III) benzoate.

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