Novel diamides of 2,2⁻-dipyridyl-6,6⁻-dicarboxylic acid: synthesis, coordination properties, and possibilities of use in electrochemical sensors and liquid extraction

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The procedure was proposed for the synthesis of various dipyridyldiamides. Their various properties in the series of rare-earth elements were studied. The possibility to use the synthesized compounds in polymer membranes of electrochemical sensors for the development of novel types of sensors was shown. A comparison of the influence of the ligand structure on the extraction and sensor characteristics was performed.

Key words: diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid, chemical sensors, liquid extraction.

The separation of actinides (americium, curium) from the fission products, e.g., rare-earth elements from lanthanum to terbium, is one of the most difficult chemical problems in the fractionation processes of radioactive waste. The known methods of separation by complexones (TALSPEAK or SETFISC processes)^{1,2} do not provide the complete separation of actinides from lanthanides; in addition, solutions with a larger content of salts are used. The most attractive candidates for separation are polydentate nitrogen-containing extracting agents.^{3,4} These compounds are highly selective towards actinides as compared to lanthanides (in some cases, the separation coefficients in the americium-europium pair exceed 100). Unfortunately, the extracting agents proposed to date are not often appropriate for technological use because of low solubility, low chemical stability, or the loss of the extraction ability in an acidic medium.

Therefore, search for novel, more efficient compounds is being actively continued.^{5,6} One of the directions in this search is the study of amides of heterocyclic acids, which are attractive due to the relative simplicity of the synthesis. It has earlier been shown that diamides of 2,6-pyridinedicarboxylic acid⁷ preferably extract americium with an americium—europium separation coefficient of ~8. Diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid⁸ are more selective to americium. In addition to good extraction properties, these compounds can be used in polymer membranes of potentiometric sensors, which makes it possible to obtain ion-selective electrodes with a high sensitivity to various metals.⁹

In this work, we describe the synthesis, coordination properties, and use of novel derivatives of diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid of diverse structure in liquid extraction and in polymer membranes for the development of new electrochemical sensors.

Synthesis of the studied compounds

The synthesis of studied compounds 1-8 (Table 1) can be divided into three stages: synthesis of the stating acids, synthesis of various substituted amines, and acylation of amines by diacids or their derivatives.



The synthesis of 2,2'-dipyridyl-6,6'-dicarboxylic acid from 2-amino-6-methylpyridine has previously been described.⁹ Since the direct introduction of acceptor substit-

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Table 1. Structures of compounds 1-8

Product	Х	R	R´
1	Н	Ph	Et
2	Н	<i>n</i> -Bu	<i>n</i> -Bu
3	Н	<i>n</i> -Oct	n-Oct
4	Br	Ph	Et
5	Н	$3-FC_6H_4$	Et
6	Н	$4-FC_6H_4$	Et
7	Н	$4 - (n - C_6 H_{13}) C_6 H_4$	Et
8	Br	$4 - (n - C_6 H_{13}) C_6 H_4$	Et

uents into the pyridine ring is hindered, the synthesis of 4,4'-disubstituted 2,2'-dipyridyls requires the preliminary preparation of 2,2'-dipyridyl di-N,N'-oxides to facilitate the electrophilic substitution in the pyridine ring. We proposed synthetic Scheme 1 for the synthesis of 4,4'-dibromo-6,6'-dimethyl-2,2'-dipyridyl (9).

Substituted 6,6'-dimethyl-2,2'-dipyridyl **9** was oxidized to 4,4'-dibromo-2,2'-dipyridyl-6,6'-dicarboxylic acid (**13**) by analogy to unsubstituted 6,6'-dimethyl-2,2'-dipyridyl, and target acid **13** was obtained in high yield. The introduction of donor substituents into the pyridine

ring can increase the acidity of the compounds in nitric acid media used in extraction and, therefore, we do not consider them in this work.

A set of commercially available amines (dibutylamine, dioctylamine, and *N*-ethylaniline) was used as an amine The results obtained for *N*-ethylaniline diamide prompted us to study analogous compounds substituted in the aromatic ring. As these anilines, we synthesized *m*- and *p*-fluoro-*N*-ethylanilines and *p*-hexyl-*N*-ethylaniline.

The available fluoroanilines were successfully alkylated by triethyl orthoformate followed by the acidic hydrolysis of the formed formyl derivative (Scheme 2).

The selective nitration of 4-hexylbenzene has been described^{10,11}; however, the solid-phase catalysts used do not allow one to prepare 4-hexylbenzene in sufficient amounts. It is impossible to nitrate hexylbenzene by standard nitrating mixtures with high selectivity and, hence, initially it was assumed to separate the formed mixture of *ortho-* and *para*-isomers at the stage of acetanilides, using the low solubility of 4-hexylacetanilide in saturated hydrocarbons (Scheme 3).

In addition to the necessity of isomer separation, a serious drawback of this method is the formation of a considerable amount of 2-hexylaniline. The three-stage

Scheme 1



Scheme 2







method including the synthesis of 4-hexylacetophenone **16**, the Schmidt rearrangement, and the reduction of the formed 4-hexylacetanilide **17** with lithium alumohydride is free of these disadvantages (Scheme 4).



The total yield of the target compound obtained by this scheme is 55%.

To synthesize the studied diamides, we tested various procedures of amine acylation using 1-hydroxybenzotriazole or carbonyldiimidazole derivatives for activation. However, the low conversion of the acids makes these methods lowly efficient. The most successful method was the application of acid dichlorides obtained by the interaction of the starting acids with thionyl chloride and used without isolation (Scheme 5). The reaction of rare-earth element nitrates with the amides (Scheme 6) was studied for model ligand 1 containing the phenyl and ethyl substituents at the nitrogen atom of the amide group.

The complexes are formed by reflux of a mixture of the ligand and corresponding inorganic salt for 6 h. The synthesized REE complexes are poorly soluble in acetonitrile, and the solubility decreases with an increase in the atomic number of the element. The data of IR spectroscopy show that the coordination of metal ions in the complexes is the same: the metal is arranged in the compounds in the pseudo-plane of the ligand formed by the nitrogen atoms of the dipyridyl fragment and amide groups. The oxygen atoms of the amide groups are involved in the coordination of the metal ion along with the nitrogen atoms of dipyridyl. This is indicated by the decrease in the frequency of stretching vibrations of the amide I band from 1639 cm⁻¹ in free ligand **1** to 1610 cm⁻¹ in the complexes due to the formation of a five-membered quasi-aromatic metallocycle, including, in addition to the metal ion, the nitrogen atom of dipyridyl and the oxygen atom of the amide group. The vibration frequency of the amide group decreases due to some equalization of the bond lengths in this cycle. In addition, the IR spectrum exhibits vibrations of the nitrate ion coordinated with the metal ion. The band of stretching N=O vibrations of the NO₃ anion is observed for all complexes at 1464 and 1469 cm^{-1} . According to the data of MALDI-TOF mass spectrometry, the spectrum of each complex contains only one peak corresponding to the fragmentation cation formed upon the loss of one nitrate ion by the complex.

Scheme 5



Compound	CH ₃	CH ₂	CH _{5′-Py}	CH _{Ph}	CH _{4´-Py}	CH _{3′-Py}
1	1.18 (t)	3.93 (q)	7.03–7.32 (m)		7.74 (t)	7.57 (d)
1 La(NO ₃) ₃ 1 Eu(NO ₃) ₃ 1 Lu(NO ₃) ₃	1.26 (t) -0.27 (br.t) 1.29 (t)	4.09 (q) 2.34 (br.s) 4.10 (q)	6.99 (d) 3.42 (br.d) 6.85 (d)	7.31–7.53 (m) 7.39 (br.s) 7.38–7.45 (m) 7.48–7.58	7.80 (t) 5.29 (br.s) 7.90 (t)	8.19 (d) 3.64 (br.d) 8.30 (d)

Table 2. Chemical shifts of the protons of ligand 1 and its complexes with lanthanum, europium, and lutetium

Scheme 6



i. $Ln(NO_3)_3 \cdot 6H_2O$, CH_3CN , Δ .

The structures of the synthesized complexes were additionally confirmed by the NMR spectral data. According to the data of ¹H NMR spectra (Table 2), the complexes have a similar symmetric structure, due to which the type and multiplicity of all main signals in their spectra coincide. Compared to the spectra of ligand **1**, a downfield shift of the protons of the pyridine ring and protons of the phenyl ring of the amide substituent is observed. The maximum shift is observed for the protons of the pyridine ring in positions 3 and 4, which is associated with the coordination of the metal ion to the nitrogen atom of the pyridine rings. The shift of the proton in position 5 of the pyridine ring is weak compared to other signals of the pyridine ring because of the influence of the phenyl substituent in the amide group.

Study of the extraction ability

It is known that the extraction ability of the diamide extracting agents depends, to a great extent, on two factors: the type of the solvent used¹² and the structure of the diamide itself.¹³ The polar fluorinated solvent was used: *meta*-nitrobenzotrifluoride (F-3). Solvents of this type make it possible to provide high distribution coefficients for extracted metals. We have earlier studied two diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid differing by sub-

stituents at the amide nitrogen atom: 1 and 2. The extraction ability of the diamide towards actinides and lanthanides was studied and the principal possibility of using diamides of this type for the separation of Am from rareearth elements (separation coefficient ~10) was shown. However, the solubility of 1 and 2 was very low: 0.03 and 0.1 *M*, respectively, which did not allow one to attain high values of distribution coefficients.9 It should be mentioned that diamide 2 characterized by a higher solubility has a lower extraction ability than 1. As for diamides of dipicolinic acid, the effect of aryl strengthening is fulfilled for diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid. The diamides bearing both aryl and alkyl substituents at the amide nitrogen atom have a higher extraction ability that the diamides with alkyl substituents only. A series of eight diamides was synthesized in order to improve the extraction and physical properties of this class of extracting agents. Taking into account the earlier obtained data,⁹ the structure of the diamide in which one of the substituents at the amide nitrogen atom is ethyl and another is substituted phenyl was taken as a basis. The bromide substituent was also introduced into the pyridine ring to determine the influence of an acceptor in the pyridine ring on the extraction ability and sensitivity and selectivity of metal determination in the membrane.

The data on the maximum solubility of diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid in F-3 are listed in Table 3. Compounds **3** and **5** are very poorly soluble, which can be explained by steric hindrances. In the case of compound **3**, the long alkyl substituents prevent the free spa-

 Table 3. Maximum solubility of the diamides

 in meta-nitrobenzotrifluoride

Diamide	Maximum solubility/mol L ⁻¹				
1	0.03				
2	~0.10				
3	< 0.01				
4	0.05				
5	< 0.01				
6	>0.05				
7	>0.05 (~0.1)				
8	>0.05				



Fig. 1. Distribution coefficients (*D*) of metals vs diamide structure. Extraction from 5 M HNO₃, 0.05 M diamide 2–8 in F-3 (0.03 M 1 in F-3) as an extracting agent.

tial rotation of the molecule about the C—C axis. In the case of compound **5**, the fluoride substituent in the *meta*-position sharply decreased the solubility of this compound.

The comparative data on the extraction of americium and europium from a solution of 5 M nitric acid for diamides of different structure are presented in Fig. 1. The introduction of the additional substituent into the pyridine ring of the diamide decreases the extraction ability of the diamide compared to the extracted metals, which is clearly seen by the comparison of two pairs of diamides 1/4 and 7/8. The introduction of the long alkyl radical into position 4 of aniline increases the distribution coefficients.

Thus, all studied compounds, regardless of the structure, extract americium better than europium. The separation coefficients for the studied compounds reach values of ~10, which allows one to use these extracting agents for the selective extraction of actinides from acidic solutions.

Electrochemical sensors based on dipyridyldiamides

To study the sensitivity of the developed sensors, we carried out potentiometric measurements with these sensors in REE solutions: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, and ytterbium in an acidic medium at pH 2. The results are given in Fig. 2. The sensors based on diamides 4, 7, and 8 have no significant sensitivity to the cations studied. The sensors based on compounds 1 and 6 is a series of REE solutions demonstrate the sensitivity close to the Nernst sensitivity (19.7 mV dec⁻¹), and the sensitivity to heavy lanthanides (gadolinium, vtterbium) is $5-10 \text{ mV} \text{ dec}^{-1}$ lower than that to lighter lanthanides. This fact agrees well with the data obtained in liquid extraction,⁹ and the distribution coefficients for the REE of the beginning of the series are about 300 and decrease to 50 with an increase in the atomic number of the extracted metal.

It was shown that, similarly to the dependence observed for extraction, the introduction of acceptor substituents (bromine) into the pyridine ring results in a sharp decrease in the sensitivity towards lanthanides. The decrease in the sensitivity of lanthanide determination for 7 does not correspond to the increase in the extraction ability observed for extraction. Perhaps, the alkyl substituents in the *para*-position of the phenyl rings in the composition of the polymer sensor membrane favor the formation of a more ordered structure.

The logarithms of selectivity coefficients of the sensors towards REE cations are presented in Fig. 3. As a whole, the developed sensors have a low selectivity in the series of REE and possess a high cross sensitivity (especially 1 and 6),



Fig. 2. Electrode sensitivity (α) of the sensors to rare-earth metal cations in their aqueous solutions at fixed values of pH of the medium (pH 2).



Fig. 3. Logarithms of selectivity coefficients $\log K_{La/Ln}$ of the sensors to the REM cations in nitric acid solutions at pH = 2 and pLa = 3 estimated by the method of bionic potentials.

and the sensors based on **2** are predominantly more selective towards lanthanum cations.

The pH dependence of the potential of the sensors was studied in the range from 2 to 12 pH units. When pH of the measured solution changed in the indicated range, the potential of the first five types of the sensors decreased by at most 200 mV on all the studied range, which indicates an insignificant influence of the pH on the potential of the sensors. The decrease started at the pH of the solution higher than 6, whereas the potential remained almost unchanged under the conditions of lower pH. The decrease in the potential of the sensor based on **8** in the pH range from 2 to 6 was close to the decrease in the hydrogen electrode potential, indicating the strong pH dependence of this sensor.

Thus, we proposed the procedure for the synthesis of diamides of 2,2'-dipyridyl-6,6'-dicarboxylic acid with various substituents on the amide nitrogen atoms. Using IR and NMR spectroscopy, we studied the processes of complex formation of these compounds with lanthanides. It was shown that the oxygen atoms of the amide groups participate in coordination. The synthesized dipyridyl-amides can successfully be used in liquid extraction for the selective extraction of actinides from acidic solutions. The incorporation of the synthesized ligands into the polymer plasticized membranes makes it possible to obtain chemical sensors with the expressed sensitivity to lanthanide cations in acidic aqueous solutions.

Experimental

¹H NMR spectra were recorded on a Bruker Avance-400 instrument in $(CD_3)_2SO$ at ambient temperature. The chemical shifts are presented in the δ scale relative to SiMe₄. Thin

layer chromatography was carried out on Merck Silica gel 60 F_{256} and Merck Aluminium Oxide F_{256} neutral plates. Column chromatography was carried out on silica gel (Merck, 70–230 mesh).

All solvents were purified by standard procedures prior to used.

6,6'-Dimethyl-2,2'-dipyridyl di-N,N'-oxide (10). A threenecked 250-mL flask equipped with a stirrer and a thermometer was loaded with glacial acetic acid (70 mL, 1.2 mol) and 6,6'-dimethyl-2,2'-dipyridyl (19.5 g, 0.106 mol), which dissolved within 10 min with vigorous stirring. The temperature of obtained solution was brought to 70 °C, a 50% solution of H₂O₂ (20 mL, 0.35 mol) was added, and the mixture was stirred for 7 h at a specified temperature. The reaction mixture was cooled to ~20 °C. After 12 h, 250 mL of water were poured in two manipulations (by portions of 150 and 100 mL), and the solvent was evaporated on a water-jet pump to 70-80 mL. Then a saturated solution of potassium carbonate (100 g in 100 mL of water) was poured to the obtained liquid. The floated insoluble substance was filtered off and washed with small portions of chloroform. A light vellow powder was obtained in a yield of 21.5 g (93.9%), m.p. 181-182 °C. ¹H NMR (CDCl₃), δ: 2.58 (s, 6 H); 7.24 (t, 2 H, J = 7.74 Hz); 7.35 (d, 2 H, J = 3.79 Hz); 7.37 (d, 2 Hz); 7.37 (d,J = 2.81 Hz). IR (KBr), v/cm⁻¹: 1470–1450.

6,6 '-Dimethyl-4,4 '-dinitro-2,2 '-dipyridyl di-*N*,*N*'-oxide (**11**). 6,6 '-Dimethyl-2,2 '-dipyridyl di-*N*-oxide (7.50 g, 0.035 mol) was introduced into a nitrating mixture obtained from concentrated sulfuric (20 mL) and fuming nitric (27 mL) acids. The obtained solution was stirred for 2 h at 90 °C and poured into ice (200 mL). The reaction mixture was neutralized to pH 6. The precipitate was filtered off, washed with water and methylene dichloride, and dried in air. The target dinitro compound was obtained as a yellow powder with the temperature of decomposition >300 °C in a yield of 7.74 g (78%). ¹H NMR (DMSO-d₆), δ : 2.53 (s, 6 H); 8.52 (d, 2 H, *J*=3.4 Hz); 8.60 (d, 2 H, *J*=3.4 Hz).

4,4 - **Dibromo-6,6** - **dimethyl-2,2** - **dipyridyl** di-*N*,*N* - **oxide** (12). Compound 11 obtained at the previous stage (30 g, 0.098 mol)

was suspended in carbon tetrachloride (300 mL), acetyl bromide (100 mL) was added, and the mixture was refluxed with stirring for 4 h. After cooling, the precipitate was filtered off, washed with a solution of soda and water, and dried in air. The target dibromide was obtained as a white powder with the temperature of decomposition >300 °C in a yield of 22 g (59%). ¹H NMR (DMSO-d₆), δ : 2.51 (s, 6 H); 7.84 (d, 2 H, *J* = 1.7 Hz); 7.92 (d, 2 H, *J* = 1.7 Hz).

4,4 '-Dibromo-6,6 '-dimethyl-2,2 '-dipyridyl (9). A mixture of 4,4 '-dibromo-6,6 '-dimethyl-2,2 '-dipyridyl di-*N*-oxide (20 g, 0.053 mol) and phosphorus tribromide (20 mL) in methylene dichloride (150 mL) was stirred at ambient temperature for 4 h and left to stay for 16 h. The solution was poured into ice (300 mL) and neutralized by the addition of soda until carbon dioxide stopped evolving. The obtained solution was extracted with methylene dichloride (4×50 mL). The extract was dried over anhydrous sodium sulfate. After the solvent was evaporated, the product was obtained in a yield of 14.8 g (81%), m.p. 158–160 °C. ¹H NMR (CDCl₃), δ : 2.41 (s, 6 H); 8.48 (d, 2 H, *J* = 1.7 Hz); 8.76 (d, 2 H, *J* = 1.7 Hz).

4,4 \cdot **Dibromo-2,2** \cdot **dipyridyl-6,6** \cdot **dicarboxylic acid (13).** The starting 4,4 \cdot dibromo-6,6 \cdot dimethyl-2,2 \cdot dipyridyl (5 g, 0.015 mol) was dissolved at 50 °C in concentrated sulfuric acid (70 mL), and chromium anhydride (7.5 g, 0.075 mol) was introduced by portions, controlling the temperature increase not higher than 75 °C. The obtained solution was stirred for 2 h at 70 °C and poured into ice (300 mL). The precipitate formed was filtered off, washed on the filter with water, ethanol, and diethyl ether, and dried in air. The target diacids was obtained as a white powder in a yield of 4.8 g (80%), m.p. 274–275 °C (with decomp.). ¹H NMR (DMSO-d₆), δ : 8.91 (br.s, 2 H); 8.29 (br.s, 2 H).

Synthesis of 3- and 4-fluoro-*N*-ethylanilines (14 and 15) from substituted anilines was carried out by analogy to the procedure for 4-chloro-*N*-ethylaniline.¹⁵ The total yields of the final products were 43% for 3-fluoro-*N*-ethylaniline (14) and 52% for 4-fluoro-*N*-ethylaniline (15).

<u>Compound 14</u>, b.p. 130–134 °C (25 Torr). ¹H NMR (CDCl₃), δ : 0.93 (t, 3 H, J = 7.1 Hz); 2.74 (q, 2 H, J = 7.1 Hz); 3.43 (br.s, 1 H); 6.11 (br.m, 2 H), 6.27 (t, 1 H, J = 8.1 Hz); 6.90 (m, 1 H).

<u>Compound 15</u>, b.p. 112–114 °C (25 Torr). ¹H NMR (CDCl₃), δ : 0.72 (t, 3 H, J = 7.3 Hz); 2.52 (q, 2 H, J = 7.3 Hz); 3.04 (br.s, 1 H); 6.01 (m, 2 H), 6.53 (t, 2 H, J = 6.8 Hz).

4-Hexylacetophenone (16). Acetyl chloride (0.22 mol) was added on cooling with ice and stirring to a suspension of AlCl₃ (28 g, 0.23 mol) in CH₂Cl₂ (100 mL). The resulting solution was stirred for 15 min. Hexylbenzene (32.4 g, 0.2 mol) was added on cooling with ice and stirring. The obtained solution was stirred for 2 h. After the end of stirring, the reaction mixture was poured into a mixture of concentrated hydrochloric acid (200 mL) and ice (200 g). The organic fraction was separated, and the aqueous fraction was extracted with methylene dichloride (2×50 mL). The combined organic extracts were washed with water and dried over calcium dichloride. The solvent was removed on a rotary evaporator. The residue was distilled in vacuo, collecting the fraction with b.p. 130-132 °C (2 Torr). Target acetophenone was obtained in a yield of 33.86 g (83%). ¹H NMR (CDCl₃), δ : 0.89 (t, 3 H, J = 6.6 Hz); 1.37 (m, 4 H); 1.66 (quint, 4 H, J = 7.2 Hz); 2.52 (s, 3 H); 2.81 (t, 2 H, J = 7.7 Hz); 7.35 (d, 2 H, J = 8.1 Hz) 7.95 (d, 2 H, J = 8.1 Hz).

4-Hexylacetanilide (17). 4-Hexylacetophenone (40.8 g, 0.2 mol) was dissolved in acetic acid (200 mL) containing concentrated sulfuric acid (50 mL, 92 g) at 60-70 °C. Sodium azide (0.3 mol) was introduced by small portions with vigorous stirring avoiding too intense dinitrogen evolution (the addition took about 2 h). Stirring was continued for 3 h more under the same conditions. Then the mixture was poured into ice (3 L) and left to warm to ambient temperature. The precipitate was filtered off and washed with water containing a small amount of soda to remove adsorbed acids. A white powder with m.p. 92-92.5 °C. (Ref. 14: 91-92 °C) was obtained in a yield of 37.23 g (71%). ¹H NMR (CDCl₃), δ : 0.98 (t, 3 H, J = 6.7 Hz); 1.29 (m, 6 H); 1.58 (quint, 2 H, J = 7.5 Hz); 2.30 (s, 3 H); 2.55 (t, 2 H, J = 7.7 Hz); 7.12 (d, 2 H, J = 8.2 Hz), 7.30 (br.s, 1 H); 7.39 (d, 2 H, J = 8.2 Hz). ¹³C NMR (CDCl₃), δ: 14.06, 22.58, 24.51, 28.88, 31.43, 31.70, 35.34, 119.99, 128.81, 135.45, 139.10, 168.20.

4-Hexyl-N-ethylaniline (18). A solution of 4-hexylacetanilide (26.2 g, 0.119 mol) in anhydrous tetrahydrofuran (150 mL) was added on cooling in a water bath and stirring to a suspension of lithium alumohydride (5.24 g, 0.138 mol) in anhydrous tetrahydrofuran (50 mL). After the end of dihydrogen evolution, the reaction mixture was refluxed for 6 h and left to stay for 16 h. The reaction mixture was decomposed by the consecutive addition of water (5.24 mL), a 15% solution of sodium hydroxide (5.24 mL), and water (3×5.24 mL) with stirring and cooling in a water bath. The precipitate was filtered off and washed with tetrahydrofuran (3×30 mL). The solution was dried over anhydrous calcium dichloride. Tetrahydrofuran was evaporated, and the obtained amine was distilled in vacuo collecting the fraction with b.p. 139-140 °C (3 Torr). The target compound was obtained as a viscous yellow liquid* in a yield of 22.8 g (93%). ¹H NMR (CDCl₃), δ : 0.87 (t, 3 H, J = 3.9 Hz); 1.02 (t, 3 H, J = 6.9 Hz); 1.28 (m, 4 H); 1.55 (m, 2 H); 2.64 (m, 2 H); 2.90 (t, 2 H, J = 5.9 Hz); 3.46 (s, 1 H); 3.58 (q, 2 H, J = 6.9 Hz); 6.38(d, 2 H, J = 4.8 Hz); 6.89 (d, 2 H, J = 4.8 Hz).

Synthesis of diamides 1-8 (general procedure). The starting acid was refluxed in thionyl chloride (5 mL of SOCl₂ per 1 g of the acid), adding dimethylformamide (0.5 mL) for 2.5 h. Thionyl chloride was removed by distillation, and the remained acid chloride was dried in a vacuum of a water-jet pump and dissolved in anhydrous tetrahydrofuran (10 g of THF per 1 g of the starting acid). The obtained solution was added with stirring in portions to a mixture of the starting amine taken in an amount of 2.1 equivalents to the acid and in the equal volume with the amount of triethylamine in anhydrous tetrahydrofuran (10 mL of THF per 1 g of the amine). After the end of addition, the obtained mixture was protected from moisture with a calcium dichloride tube, stirred for 4–5 h at 40–50 °C, and left to stay for 16 h. The equal volume of water was added to the reaction mixture, and the organic layer was separated. The aqueous fraction was three times extracted with diethyl ether. The combined organic fractions were washed with water and dried over anhy-

^{*} An increase in the amount of the used alumohydride and reduced acetanilide does not increase the amount of isolated amine. This is related, most likely, to the fact that an insoluble layer of metallized amine and an amide layer poorly soluble in THF are formed on the lithium alumohydride surface. Therefore, to obtain larger amounts of *N*-ethylanilines, it is reasonable to carry out several parallel reactions with the indicated loads and to combine the obtained filtrates.

drous sodium sulfate. After the solvents were evaporated, the reaction mixture was treated depending on the amine used.

(1) Amides obtained from aliphatic diamines (dibutylamine, dioctylamine) or 4-hexyl-*N*-ethylaniline were treated with hexane. The precipitate formed was filtered off, washed with hexane. and dried in air.

(2) Derivatives of *N*-ethylanilines were treated with a minimum amount of ethyl acetate. The precipitate formed was washed cold ethyl acetate and dried in air.

The yields of the diamides were 65–80%. The spectral characteristics of the diamides are given in Table 4.

Synthesis of lanthanum, europium, and lutetium complexes with diamide 1. A mixture of lanthanide nitrate hydrate (0.52 mmol) and ligand 1 (0.52 mol) in anhydrous acetonitrile (80 mL) was refluxed for 6 h. After cooling to ambient temperature, the precipitate of the complex was filtered off and washed with cold

acetonitrile (1 mL). The mother liquor was evaporated *in vacuo* and an additional portion of the complex was filtered off.

 N^6 , N^6 -Diethyl- N^6 ', N^6 '-diphenyl-[2,2'-dipyridyl]-6,6'-dicarboxamidolanthanum(III) nitrate (1[La(NO₃)₃]). The yield was 70%. Found (%): C, 43.37; H, 3.43; N, 12.42. C₂₈H₂₆N₇O₁₁La. Calculated (%): C, 43.37; H, 3.38; N, 12.64. IR (KBr), v/cm⁻¹: 1610.27, 1571.70, 1494.56, 1463.71, 1428.99, 1294.00. MS, m/z(I_{rel} (%)): 713 [La1(NO₃)₂]⁺ (100). ¹H NMR (acetonitrile-d₃), 8: 1.26 (t, 3 H, J = 7.15 Hz); 2.27 (s, 1 H); 4.09 (d, 2 H, J = 7.21 Hz); 6.99 (d, 1 H, J = 7.82 Hz). ¹³C NMR (acetonitrile-d₃), 8: 11.91, 48.94, 125.77, 128.42, 128.92, 130.23, 131.22, 140.92, 141.88, 151.57, 154.65, 163.45.

 N^6 , N^6 -Diethyl- N^6 , N^6 '-diphenyl-[2,2'-dipyridyl]-6,6'-dicarboxamidoeuropium(III) nitrate (1[Eu(NO₃)₃]). Found (%): C, 42.81, 42.61; H, 3.30, 3.34; N, 12.27, 12.31. C₂₈H₂₆N₇O₁₁Eu.

Table 4. Spectra	l characteristics of 2,2	´-dipyridyl-6,6	'-dicarboxylic acid	diamides 1–8
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Di- amide	Yield	/ield ¹ H NMR		IR, ν/cm ⁻¹ ν(C=O) ν(C=N)		Found (%) Calculated			Empirical formula
	(%)	Aromatic region Aliphatic region							
						С	Н	Ν	
1	79	7.62 (t, 3 H, <i>J</i> = 7.32); 7.12 (br.m, 5 H)	4.02 (q, 2 H, <i>J</i> = 6.97); 1.24 (t, 3 H, <i>J</i> = 6.97)	1639	1576	<u>75.01</u> 74.65	<u>6.12</u> 5.82	<u>12.58</u> 12.44	$C_{28}H_{26}N_4O_2$
2	80	7.60 (d, 1 H, <i>J</i> = 7.82); 7.89 (t, 1 H, <i>J</i> = 7.70); 8.42 (d, 1 H, <i>J</i> = 7.82)	0.74 (t, 3 H, <i>J</i> = 7.34); 1.00 (t, 3 H, <i>J</i> = 7.34); 1.11 (qt, 2 H, <i>J</i> = 7.34, <i>J</i> = 7.43); 1,44 (qt, 2 H, <i>J</i> = 7.34, <i>J</i> = 7.43); 1.69 (m, 4 H); 3.36 (t, 2 H, <i>J</i> = 7.34); 3.54 (t, 2 H, <i>J</i> = 7.34)	1640	1571	<u>72.12</u> 72.07	<u>9.21</u> 9.07	<u>12.23</u> 12.01	$C_{28}H_{42}N_4O_2$
3	68	7.57 (d, 1 H); 7.85 (t, 1 H); 8.40 (d, 1 H)	0.83 (t, 3 H, <i>J</i> = 7.25); 0.89 (m, 6 H); 1.27 (m, 17 H); 1.67 (tt, 2 H, <i>J</i> = 7.48, <i>J</i> = 7.29); 1.72 (tt, 2 H, <i>J</i> = 7.68, <i>J</i> = 6.76); 3.36 (t, 2 H, <i>J</i> = 7.68); 3.50 (t, 2 H, <i>J</i> = 7.68)	1641	1578	<u>76.54</u> 76.47	<u>10.52</u> 10.79	<u>8.26</u> 8.11	$C_{44}H_{74}N_4O_2$
4	65	7.97 (d, 1 H, <i>J</i> = 3.02); 7.41 (d, 1 H, <i>J</i> = 3.02); 7.26 (br.m, 2 H); 7.14 (br.m, 1 H); 7.06 (br.m, 2 H)	4.02 (q, 2 H, <i>J</i> = 6.85); 1.26 (t, 3 H, <i>J</i> = 6.85)	1642	1574	<u>54.99</u> 55.28	<u>4.15</u> 3.98	<u>9.52</u> 9.21	$C_{28}H_{24}Br_2N_4O_2$
5	78	7.67 (m, 3 H); 7.12 (td, 1 H, J = 7.95, J = 6.60); 6.89 (d, 1 H, J = 9.78); 6.87 (t, 2 H, J = 6.60)	4.01 (q, 2 H, <i>J</i> = 7.09); 1.28 (t, 3 H, <i>J</i> = 7.09)	1643	1578	<u>69.14</u> 69.12	<u>5.05</u> 4.97	<u>12.01</u> 11.52	$C_{28}H_{24}F_2N_4O_2$
6	67	7.65 (m, 2 H); 7.57 (br.t, 1 H, $J = 7.15$); 7.04 (m, 2 H); 6.87 (t, 2 H, $J = 7.15$)	3.96 (q, 4 H, <i>J</i> = 7.03); 1.25 (t, 3 H, <i>J</i> = 7.03)	1644	1578	<u>68.92</u> 69.12	<u>5.04</u> 4.97	<u>11.87</u> 11.52	$C_{28}H_{24}F_2N_4O_2$
7	72	7.61 (m, 3 H); 6.98 (br.m, 4 H)	3.99 (q, 2 H, <i>J</i> = 7.05); 2.47 (t, 2 H, <i>J</i> = 7.83); 1.47 (tt, 2 H, <i>J</i> = 6.93, <i>J</i> = 7.09); 1.27 (m, 9 H); 0.97 (t, 3 H, <i>J</i> = 6.97)	1641 ;	1570	<u>77.58</u> 77.67	<u>8.24</u> 8.14	<u>9.19</u> 9.05	$C_{40}H_{50}N_4O_2$
8	73	7.73 (d, 1 H, <i>J</i> = 1.84); 7.35 (d, 1 H, <i>J</i> = 1.84); 6.94 and 7.02 (AA´BB´, 4 H, <i>J</i> = 7.77, <i>J</i> = 7.42)	3.97 (q, 2 H, $J = 6.71$); 2.41 (t, 2 H, $J = 7.42$); 1.41 (tt, 2 H, $J = 6.36$, J = 5.65); 1.21 (m, 9 H); 0.84 (t, 3 H, $J = 6.36$)	1645	1577	<u>62.03</u> 61.86	<u>90.6</u> 6.23	<u>7.01</u> 7.21	$C_{40}H_{48}Br_2N_4O_2$

Calculated (%): C, 42.65; H, 3.32; N, 12.43. MS, m/z (I_{rel} (%)): 727 [Eu1(NO₃)₂]⁺ (100), 812 [Eu1(NO₃)(PhCHCHCO₂H)]⁺ (13), 449 [1 – H]⁺ (20). ¹H NMR (acetonitrile-d₃), δ : -0.27 (br.s, 3 H); 2.34 (br.s, 2 H); 3.42 (br.d, 1 H, J = 7.34 Hz); 3.64 (br.d, 1 H, J = 7.83 Hz); 5.29 (br.t, 1 H, J = 7.58 Hz); 7.39 (br.s, 5 H).

 N^6 , N^6 -Diethyl- N^6 ', N^6 '-diphenyl-[2,2'-dipyridyl]-6,6'-dicarboxamidolutetium(III) nitrate (1[Lu(NO₃)₃]). The yield was 78%. Found (%): C, 41.67; H, 3.31; N, 12.15. C₂₈H₂₆N₇O₁₁Lu. Calculated (%): C, 41.44; H, 3.23; N, 12.08. IR (KBr), v/cm⁻¹: 1612.28, 1583.35, 1571.78, 1510.06, 1494.64, 1463.78, 1452.21, 1307.56, 1297.92, 1290.21. MS, m/z (I_{rel} (%)): 749 [Lu1(NO₃)₂]⁺ (100). ¹H NMR (acetonitrile-d₃), δ : 1.29 (t, 3 H, J = 7.09 Hz); 4.10 (q, 2 H, J = 7.34 Hz); 6.85 (d, 1 H, J = 7.95 Hz); 7.4 (m, 2 H); 7.52 (m, 3 H); 7.90 (t, 1 H, J = 8.25 Hz); 8.30 (d, 1 H, J = 7.82 Hz). ¹³C NMR (acetonitrile-d₃), δ : 11.81, 50.23, 126.14, 128.84, 130.98, 131.66, 141.46, 144.89, 149.80, 156.57, 173.78.

Study of the solubility and extraction properties of dipyridyldiamides. The solubility of diamides was measured by the consecutive addition of the solvent until an exactly taken weighed sample of diamide was completely dissolved. Initially the weighed sample of diamide was taken in such a way that the solution of a concentration of 0.5 *M* diamide in *meta*-nitrobenzotrifluoride would be prepared. Dissolution was carried out at 20 ± 1 °C with vigorous shaking for 1 h. If the taken weighed sample of diamide was not completely dissolved, an additional amount of the solvent necessary for the preparation of a solution with a concentration of 0.45 *M* diamide in F-3 was added. The procedure was repeated until the complete dissolution of diamide, decreasing the diamide concentration in the subsequent solution by 0.05 *M*.

Experiments on extraction were carried out in 5-mL tubes. An aqueous phase (1 mL) was introduced into the tube. Solutions of HNO₃ of the required concentration $(10^{-5} M \text{Eu}(\text{NO}_3)_3)$ and the indicator amounts of ¹⁵²Eu or ²⁴¹Am were used as an aqueous phase. Then the extracting agent (1 mL) was added to the tube. The phases were vigorously stirred for 3 min at 20 ± 2 °C and separated by centrifugation. Samples of the aqueous and organic phases (0.4 mL) were taken for analysis. The distribution coefficients of Am and Eu were determined radiometrically using a DeskTop InSpector 1270 scintillation gamma spectrometer based on a NaI detector (51×51 mm) with a well (Canberra). The determination inaccuracy was less than 15%.

Production of electrochemical sensors. Polymer sensor membranes were produced from polyvinyl chloride (PVC) plasticized with *o*-nitrophenyl octyl ether (NPOE). Chlorinated cobalt dicarbollide in the H⁺ form (CCD, Katchem, Czechia), which is applied in liquid extraction as a synergetic additive to polydentate neutral extracting agents for REE extraction, was used as a cation-exchange additive. All components for membrane production were from Fluka (Switzerland). The PVC content in all membranes was 33 wt.%. The CCD content was 0.5%. The ligand content was 50 mmol (kg of membrane)⁻¹ (2.3–3.9 wt.% depending in the molecular weight). The NPOE content was varied depending in the composition in the range from 62.6 to 64.2 wt.%.

The following procedure was used for the production of sensor membranes: the components of the membrane were dissolved in freshly distilled tetrahydrofuran with magnetic stirring. The obtained solution was poured into a Teflon beaker with the flat bottom. The beaker was closed with an object-plate and left to stay to the complete evaporation of THF (~48 h). Discs of membranes 7 mm in diameter and a thickness of ~0.3 mm were cut from the obtained films and glued into the body of the PVC electrode. The glue was a solution of PVC in cyclohexanone. Eighteen sensors were produced: the membrane of each type was in three sensors.

Potentiometric measurements were carried out in nitric acid solutions of REE cations at pH 2 in order to suppress hydrolysis. The measurements were carried out in the galvanic cell Cu | Ag | AgCl, KCl_{sat} | studied solution | membrane | 0.01 *M* NaCl | AgCl | Ag | Cu.

EMF readings were detected on a multichannel electronic digital voltmeter with a high input resistance connected to a personal computer for data collection and processing. An EVL 1 M 3.1 silver chloride electrode was used as a reference electrode. An ESL 43-07 glass electrode was used for monitoring pH of solutions. The both electrodes were produced at the ZIP factory (Gomel, Belarus). The sensitivity of the sensors was studied by the calibration method over a series of standard solutions of an individual ion in the concentration range from 10^{-7} to 10^{-3} mol L⁻¹. The sensor sensitivity is determined by the angular coefficient (slope) of the linear region of the electrode function calculated by least squares (the theoretical value is 19.7 mV dec⁻¹ under normal conditions for three-charge ions). The value of the standard electrode potential was obtained by the extrapolation of the linear region of the calibration dependence to $\log C = 0$. The method of biionic potentials was used to study the membrane selectivity. The data presented on various characteristics of the sensors are averaged over three values for sensors of the same type.

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