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The impact of alicyclic substituents on the extraction ability of new family of 1,10-phenanthroline-2,9-diamides†

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Development of efficient extractants for the separation of actinides and lanthanides in the technologies of nuclear fuel cycle is one of the most urgent and complex tasks in modern nuclear energetics. New family of 4,7-dichloro-1,10-phenanthroline-2,9-dicarboxylic acid diamides based on cyclic amines was synthesized and shown to exhibit high selectivity in the La/Am pair separation (SF (Am/La \approx 10)) and in the Am/Eu pair separation (SF (Am/Eu \approx 12)). It was shown that pyrrolidine derived diamide is more efficient extractant for americium, curium and lanthanides from highly acidic HNO₃ solution than its non-cyclic *N,N,N',N'*-tetraalkyl analogues. The structures of synthesized compounds were studied in details by IR, NMR spectroscopy, and single crystal X-ray diffraction. According to spectroscopy data, incorporation of aromatic rings to the amide fragment of ligand leads to complex dynamic behavior in solutions what is believed to strongly affect the extraction ability of synthesized ligands.

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Introduction

More than 10% of the world's electricity in 2020 will be supplied by nuclear power plants and the contribution of nuclear power into world's energy production is steadily growing as one of the sources with lowest carbon dioxide emissions.¹ The most serious drawbacks of nuclear power is the need to reprocess and dispose spent nuclear fuel (SNF) due to its long-term and high radiotoxicity generated by the minor actinides (mAn = Am, Cm, Np) and plutonium. Partitioning and transmutation strategy (P&T)²⁻⁴ is an approach aimed at the separation (partitioning) of the SNF into its components, followed by transmutation of mAn into radionuclides with shorter half-times that makes them less

hazardous in long term perspective. However, due to their high neutron-poisoning capacity, the lanthanides (Ln) need to be separated from SNF prior to transmutation of mAn. Due to their very similar chemical properties, the partitioning of mAn and Ln is the most challenging hydrometallurgical separation known.²⁻⁵

Solvent extraction relied on the use of complexing organic ligands which is a common technique for the separation of mAn and Ln. Therefore, the molecular design of such compounds determines the efficiency and selectivity of their binding to metal in an aqueous solution.⁶

To date, a large number of chelators and extractants have been proposed for this purpose.^{3,5,7} Extraction chemistry of diglycolamides (DGA) and bis-triazinyl N-heterocycles is described in separate reviews^{8,9}

1,10-Phenanthroline-2,9-dicarboxylic acid and its diamides is an important class of *N,N',O,O'*-tetradentate ligands. According to Pearson HSAB concept they contain both "hard" (carbonyl oxygen atoms) and "soft" (heterocyclic nitrogen atoms) donor coordination centers. Having moderate Brønsted basicity but high Lewis basicity, these ligands are capable to effective binding with metal cations in strongly acidic media and form stable complexes with cations of transition and post-transition metals, which are soluble in polar organic solvents.¹⁰⁻¹⁴ Their high resistance in respect to oxidation and hydrolysis allows one to use them as perspective extractants for the separation of metal

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cations of very similar nature in “organic solvent/acidic aqueous solution” two-phase systems.^{11,12,15–18}

Diamides of 1,10-phenanthroline-2,9-dicarboxylic acid have been found to demonstrate high values of selectivity factors for actinides and lanthanides separation.^{15,16} Extraction properties of these compounds can be customized by varying the substituents in phenanthroline core and/or at the amide nitrogen atoms. In spite of the fact that a number of variations are known (*N,N'*-dialkyl-,^{19,20} *N,N'*-diaryl-,²¹ *N,N'*-dialkyl-,²² *N,N,N',N'*-tetraalkyl-^{19,23,24} and *N,N'*-dialkyl-*N,N'*-diaryl amides of 1,10-phenanthroline-2,9-dicarboxylic acid^{17,18,25}) it is still difficult to link the structural features of these ligands with their extraction properties.

A deep search allows us to find only few examples of amides of 1,10-phenanthroline-2,9-dicarboxylic acid with alicyclic substituents in the amide function, however without any extraction tests performed.²⁶

In the present work we have synthesized a new family of 4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamides based on commercially available cyclic secondary amines. We also performed extraction experiments in the partitioning of lanthanides, americium and curium to evaluate the effects of structure variations on the selectivity and efficiency of the separation.

The incorporation of chlorine atoms into the phenanthroline core was carried out in order to reduce the Brønsted basicity of the synthesized ligands and to increase their solubility in extraction tests. Such modification permits to have ligands 100 times less basic than nonsubstituted phenanthroline which is important for the separation of f-elements in highly acidic solutions.²⁷ In order to satisfy the CHON principle,²⁸ chlorine atoms can be subsequently replaced with more radiation-resistant CN-groups using cross-coupling reactions catalyzed by palladium salts,^{29,30} maintaining required extraction properties and solubility of resulting ligands.

Results and discussion

Synthesis of 1,10-phenanthroline-2,9-dicarboxamides

Synthesis of 4,7-dichloro-1,10-phenanthroline-2,9-dicarboxylic acid **1** has been described previously.¹⁸

Diamides **3a–h** were prepared by the interaction of acyl dichloride **2** with the corresponding cyclic secondary amines in CH_2Cl_2 media with yields up to 90% (Table 1). An excess of the corresponding secondary cyclic amine was used as an acceptor of HCl for the synthesis of **3a–e**, whereas triethylamine was used for the synthesis of **3f–h**. As a result, new family of ligands was prepared very efficiently to give target amides in up to 90% yield.

Compounds **3a–h** are white or slightly colored high-melting solids. Diamides **3a–e** are soluble in dichloromethane and acetone and sparingly soluble in hexane. The solubility of diamides **3f–h** is significantly lower being compared with **3a–e**.

It was a matter of practical interest to measure the solubility of diamides **3a–h** in solvent “F-3” (3-nitrobenzotrifluoride), which is widely used for its high solvation ability towards actinide complexes and its ability to reveal the best extraction properties of N-heterocyclic diamides.^{31,32}

Expectedly, the solubility increases in the rows **3a–3c** and **3f–3g** with increase of lipophilicity (Table 1).

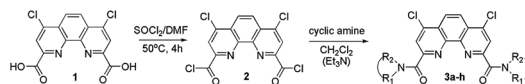
It should be noted, that solubility of diamides **3a–3e** within a range of 0.015–0.023 mol L⁻¹ is sufficient for the intended use in extraction systems for separation of Ln and mAn.³³ However, the solubility of diamides **3f–h** is significantly lower in comparison to known *N,N,N',N'*-tetraalkyl and *N,N'*-dialkyl-*N,N'*-diarylsubstituted diamides.^{23–25}

The structures of **3a–h** were confirmed by IR, ¹H NMR, ¹³C NMR spectrometry and high-resolution mass spectrometry (HRMS). An assignment of signals in NMR spectra was made using two-dimensional ¹H/¹³C hetero-nuclear correlation techniques (HSQC, HMBC). The structures of diamides **3a**, **3b**, **3f** and starting acid **1** were also determined by X-ray diffraction.

The literature search provides the structures of a large number of complexes of 1,10-phenanthroline-2,9-dicarboxylic acid and its diamides with cations of transition and post-transition metals.^{11,13,14,34–38} However, information about the structures of the acid itself, its diamides and/or derivatives with substituents in the phenanthroline core, is very limited. The search in the Cambridge Crystallographic Database (CSD release 2020.0) revealed several hits, namely: DMSO solvate of 1,10-phenanthroline-2,9-dicarboxylic acid³⁹ *N,N'*-bis(2-pyridyl)-1,10-phenanthroline-2,9-

Table 1 Synthesis and solubility data for diamides **3a–h**

Code	Starting amine	Yield, %	Solubility in “F-3”, mol L ⁻¹	Solubility in CHCl_3 , mol L ⁻¹
3a	Pyrrolidine	82	0.015	0.33
3b	Piperidine	81	0.020	0.40
3c	Azepane	82	0.023	0.67
3d	Morpholine	71	0.015	0.44
3e	<i>N</i> -Methyl-piperazine	79	0.018	0.62
3f	Indoline	76	0.0008	0.03
3g	1,2,3,4-Tetra-hydroquinoline	90	0.002	0.20
3h	9 <i>H</i> -Carbazole	63	0.0002	0.0002



dicarboxamide,²¹ *N,N'*-bis(2-amino-6-pyridyl)-1,10-phenanthroline-2,9-dicarboxamide,²¹ methanol solvate of *N,N'*-diethyl-*N,N'*-ditolyl-1,10-phenanthroline-2,9-dicarboxamide,¹⁷ hemihydrate of 4,7-bis(2-methylpropoxy)-*N,N'*-diphenyl-1,10-phenanthroline-2,9-dicarboxamide and 4,7-bis(2-methylpropoxy)-9-[(1-phenylethyl)-carbamoyl]-2-(phenylcarbamoyl)-1,10-phenanthroline-1-ium trifluoromethane-sulfonate.²⁰

Molecular and crystal structures of acid 1 and its diamides

In the present work molecular and crystal structures of starting dicarboxylic acid **1** and its diamides **3a**, **3b**, **3f** were examined by single-crystal X-ray diffraction.

The X-ray data and full description of molecular and crystal structures of **1**·H₂O·DMF are given in ESI (see Fig. S4, Tables S2–S8†).

Molecular structures and packing diagrams of three diamide ligands are presented in Fig. 1–3, and full data on bond lengths, flat and dihedral angles and intermolecular contacts in the studied structures are given in ESI (Tables S10–S15, S17–S22 and S24–S30†). Compound **3b** crystallizes as the **3b**·H₂O hydrate, with the water molecules being rotationally disordered as mentioned below in Experimental section.

In all three structures, the phenanthroline cores are essentially planar, with the mean deviations of atoms from the planes not exceeding 0.05 Å. All compounds crystallize in the twisted asymmetric conformations, in which the oxygen atoms of the amide groups are positioned far away from each other. These conformations significantly differ from those adopted by the

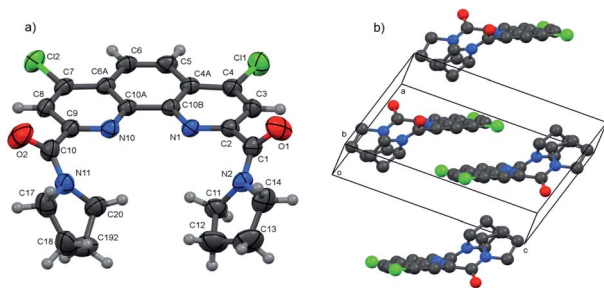


Fig. 1 Molecular structure of **3a** (a) and packing diagram showing the dimeric arrangement (b). Thermal ellipsoids are drawn at the 50% probability level. In the packing diagram, all H atoms are omitted.

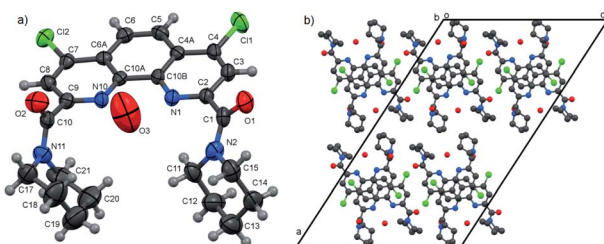


Fig. 2 Asymmetric part of **3b**·H₂O (a) and packing diagram drawn along the *b* axis direction showing stacks and layers (b). Thermal ellipsoids are drawn at the 50% probability level. In the packing diagram, all H atoms are omitted.

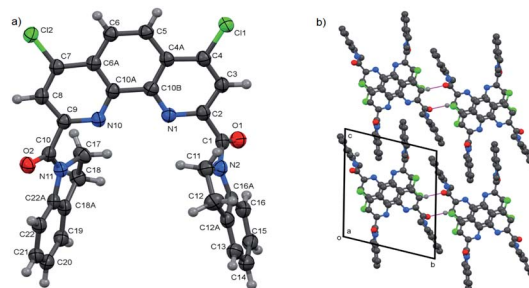


Fig. 3 Molecular structure (a) and packing diagram (b) of **3f**. Thermal ellipsoids are drawn at the 70% probability level. The contacts C–H...O are presented by violet lines, other H atoms are omitted for clarity.

ligands in the complexes with metal ions, where the carbonyl oxygen atoms are brought together and deviate only slightly from phenanthroline tricycle plane in *syn-syn* conformation. The amide groups are nearly planar, with π -conjugation in the O=C–N fragments evident from the C–N and C=O bond lengths. Their least-squares planes are inclined to the phenanthroline fragments at 51.07(9)° and 41.1(1)° (**3a**), 48.16(9)° and 81.26(9)° (**3b**), and 64.1(4)° and 74.0(4)° (**3f**). In **3a** and **3b**, the amide oxygen atoms lie in periplanar position with respect to the phenanthroline fragments, whereas in **3f** they are oriented *anti*-periplanar.

The five-membered amide cycles in **3a** and **3f** adopt the “envelope” conformations, whereas the six-membered cycles in **3b** have the “chair” conformations. The angles C–N–C in the amide five- and six-membered cycles increase in the row **3f** < **3a** < **3b** (see ESI, Table S30†). Because of their large size, the piperidine groups in **3b** hinder free rotation about the C–C and C–N bonds. In the molecule of **3f**, the five-membered cycles are compact, but rotation about the C–C bonds by 360° is hindered by the bulk and rigid aromatic groups. Consequently, molecule of **3a** seems to be the most flexible.

It is obvious that in the absence of crystal packing effects, the rotation around the C_{2,9}–C(O) bonds between the phenanthroline fragments and the amide C atoms gives rise to a number of conformers, as confirmed by the spectral data for solutions presented below.

Another typical feature of the crystal structures of diamides under study is the formation of dimers and stacks due to the π – π interactions between the phenanthroline fragments. In crystals, the molecules of **3a** are packed into the centrosymmetric dimers (Fig. 1b), with the distance between the planes of phenanthroline nuclei of 3.414(1) Å. In the structure of **3b**·H₂O, the molecules related by the screw axis 2₁ form stacks with the shortest intercentroid separation of 3.641(1) Å between the central aromatic ring and the terminal ring containing the N10 atom. In the crystals of **3f**, the molecules are connected by the inversion centers into the stacks along the *a* axis direction, the distances between the phenanthroline planes being 3.316(2) and 3.368(2) Å. Thus, the formation of π – π associates in aqueous solutions due to such interactions is also possible.



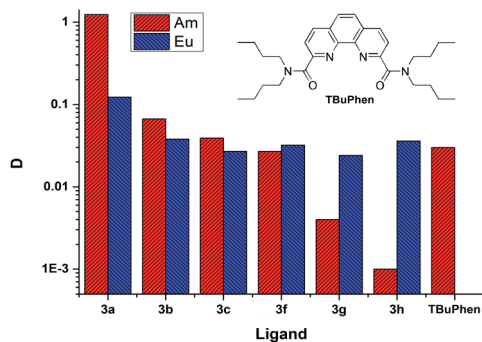


Fig. 4 The distribution ratios D (Am) and D (Eu) for extraction from 3 mol L^{-1} nitric acid. The organic phase is saturated solutions of ligands in "F-3".

Thus, we unambiguously confirmed the structure of synthesized diamides and found out some features of their crystal packaging.

Extraction of lanthanides, americium and curium by diamides 3 \ddagger

Separation of a pair of Am^{3+} and Eu^{3+} cations is usually acts as a model test when evaluating the extraction properties organic ligands. Saturated solutions of diamides 3 in "F-3" were used in the extraction of these cations from 3 mol L^{-1} solution of nitric acid. The values of the D between the organic and aqueous phases are shown in Fig. 4. \S

D is the distribution ratio of the metal cation in a biphasic system which is calculated as follows: $D = [\text{M}]_{\text{org}}/[\text{M}]_{\text{aq}}$, where $[\text{M}]_{\text{org}}$ and $[\text{M}]_{\text{aq}}$ is metal cation concentration in organic and aqueous phases, respectively.

As it seen from Fig. 4, ligand **3a** extracts $\text{Am}(\text{III})$ and $\text{Eu}(\text{III})$ with the highest distribution ratios. An increase in the cycle size at the amide nitrogen atom per one methylene group (ligand **3b**) leads to a drastic decrease in the extraction capacity in this solvent and to about five times decrease in selectivity towards Am/Eu pair. The same patterns are observed when extracting from nitric acid solutions of 1 mol L^{-1} to 5 mol L^{-1} . The distribution ratios D and separation factors SF ($\text{SF} = D_1/D_2$, where D_1 and D_2 are distribution ratios for "metal 1" and "metal 2", $D_1 > D_2$, $\text{SF} > 1$) for both ligands grow monotonously with an increase in the nitric acid content in this interval, which is typical for all diamides of 4,7-dichloro-1,10-phenanthroline-2,9-dicarboxylic acid^{16,18} (Fig. 4, 5, Table 2). Extraction data for ligand **3d** can be found in ESI (Fig. S1 \dagger). Comparison data for N,N,N',N' -tetrabutyl-1,10-phenanthroline-2,9-dicarboxamide (TBuPhen) was taken from ref. 40.

When one and then two benzene rings are incorporated into the structure of amide fragment of the **3a** and **3b** ligands, their extraction ability with respect to $\text{Am}(\text{III})$ decreases sharply, while

\ddagger In experiments with **3e** a precipitate appeared at the phase interface. The most probable explanation of this fact is fast protonation of this ligand in nitric acid media and subsequent collapse of this strongly basic compound.

\S Note that for all the graphs below the uncertainties in a range of $0.01 < D < 10$ are within $\pm 10\%$.

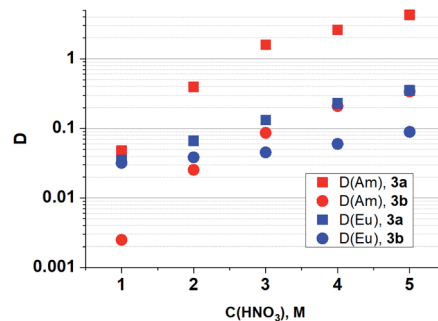


Fig. 5 Dependences of D (Am) and D (Eu) on the concentration of HNO_3 in the equilibrium water phase for extraction by **3a** and **3b** solutions in "F-3".

Table 2 SF values for extraction by **3a** and **3b** solutions in "F-3"

Ligand	$\text{C}(\text{HNO}_3), \text{mol L}^{-1}$	1	2	3	4	5
3a	SF (Am/Eu)	1.4	5.9	12	12	12
	SF (Am/Eu)	0.1	0.7	2	4	4

the extraction ability with respect to $\text{Eu}(\text{III})$ remains almost constant. As a result, the separation factor $\text{SF}_{\text{Am/Eu}}$ inverts when coming from the ligands **3a–3c** to the ligands **3f–3h**.

It should be noted, that for the several types of extractants among of which are diamides of pyridine-2,6-dicarboxylic and 1,10-phenanthroline-2,9-dicarboxylic acids,^{40–45} the "effect of abnormal aromatic strengthening" is known. Attachment of aryl-substituent to the amide nitrogen significantly increases their extraction efficiency. An origin of the phenomenon considered in.⁴⁶ Regrettably, the solubility of **3g**, **3h** and **3f** in "F-3" is too low for correct comparison of their extraction efficiency with the same of N,N' -dialkyl- N,N' -diaryl-1,10-phenanthroline-2,9-dicarboximides.

The stoichiometry of complexes formed during extraction in "F-3" was determined by the slope analysis of " $\lg D - \lg C(L)$ " dependence.

The distribution ratios D (Am) and D (Eu) depending on the concentration of **3a** during extraction from the 5 mol L^{-1} HNO_3 aqueous phase are presented in ESI (Fig. S2 and Table S1 \dagger). The obtained solvate numbers, which are 1.32 for $\text{Am}(\text{III})$ and 1.04 for $\text{Eu}(\text{III})$, show that $\text{Am}(\text{III})$ is extracted into the organic phase as complexes of 1 : 1 and 1 : 2 composition, and $\text{Eu}(\text{III})$ as a complex 1 : 1 only.

Using the obtained $\lg D(\text{Am}) - \lg C(L)$ relationship, the extraction efficiency can be extrapolated to the concentration of 0.5 mol L^{-1} and calculated $D(\text{Am})$ is about 600. In similar conditions TBuPhen⁴⁰ shows $D(\text{Am})$ about 10. Also as it presented in Fig. 4, **3a** possess much higher extraction ability towards Am when comparing it with TBuPhen in similar conditions. This clearly shows a sharp increase in extraction efficiency due to the volume reduction and hardening of substituents at the amide nitrogen atom.



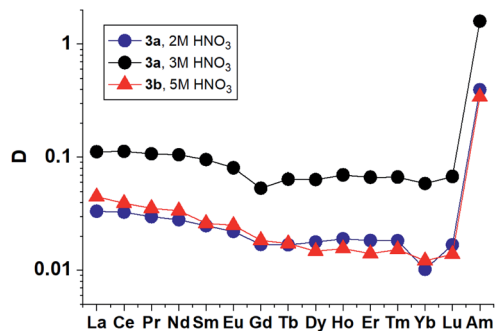


Fig. 6 Distribution ratios for lanthanides(III) and Am(III) for extraction by **3a** and **3b** solution in "F-3".

The extraction of the entire set of lanthanides (except promethium) from solutions containing 2–5 mol L⁻¹ nitric acid by **3a** and **3b** solutions in "F-3" (Fig. 6) demonstrates monotonous decrease in distribution ratios with increasing atomic number of Ln that has already been observed previously for diamides of 1,10-phenanthroline-2,9-dicarboxylic acid.¹⁸

The results obtained show that **3a** and **3b** in their selectivity to the Am/La pair (SF (Am/La) \approx 10) are close to TBuPhen²³ and derivatives of diamides of 2,2'-bipyridyl-6,6'-dicarboxylic acid.^{47,48}

Also, we should mention that in some cases of the Cm and Ln distribution ratios are very low (\approx 0.01). Since the content in the organic phase was calculated as the difference in the initial water phase and the equilibrium water phase, these values should be considered as semi-quantitative (very low). However, for $D(\text{Eu})$, it is clear that the values obtained by two methods (ICP-OES and gamma-spectrometry) are consistent.

Extractive separation of neighboring radionuclides Am/Cm is a complicated and urgent task in modern nuclear technologies. We studied the extraction of Cm(III) from nitric acid solutions by diamides **3a** and **3b** in "F-3". The values of obtained D and SF (Am/Cm) are presented in Table 3.

Thus, diamides **3a** and **3b** in their selectivity are inferior to N,N' -diethyl- N,N' -di(*p*-hexylphenyl)-4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamide¹⁶ which demonstrates SF (Am/Cm) values as high as 7.

To determine the cause of the observed unexpected "structure–property" patterns we conducted a thorough study of structural behavior of synthesized ligands **3a–3h** by IR (both in solid and in solution state) and NMR spectroscopy.

Peculiarities of structure and dynamics of diamides **3**

Rather important general factor determining structure – extraction efficiency relationship for diamides under study is

Table 3 The D and SF values for extraction of Am/Cm by **3a** and **3b**

Ligand	C(HNO ₃), mol L ⁻¹	D (Am)	D (Cm)	SF (Am/Cm)
3a	1	0.125	0.033	3.8
3a	2	0.3	0.1	3.0
3a	3	1.24	0.46	2.7
3b	5	0.37	0.15	2.6

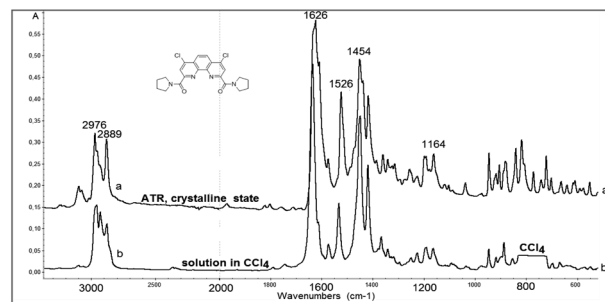


Fig. 7 View of IR-spectra of **3a** in crystalline state (above) and in CCl₄ solution (below). Solvent absorption in the area of 800 cm⁻¹ is excluded.

"the ligand preorganisation energy" which is a difference in energies between conformation of free ligand and its conformation in complex with metal cation. In this regard, the noticeable decrease in the distribution coefficients D found by comparing diamides **3a** and **3b** with diamide **3f** is quite expected, since the amide fragments in **3a** and **3b** in the crystals are in the periplanar position, while in **3f** they are *anti*-periplanar. However, in the solution, the diamides **3** can take on conformations different from those in the solid. In this case, the extraction properties of these ligands will be substantially determined as well by activation barriers that separate such conformations. These obvious considerations prompted us to study the structures of diamides **3** in solutions using IR and NMR spectroscopy.

Fig. 7 shows the overview IR spectra of compound **3a** in the solid state and in CCl₄ solution. At first glance, the solid state and solution IR spectra of diamides **3a–h** are very similar. A thorough study of stretch bands of C=O groups in IR-spectra of diamides **3** in solid state revealed a complicated structure, as shown in Fig. 8.

Complicated contours of these bands clearly indicate that carbonyl groups in crystals exist in different spatial environment. All diamides **3** contain C–C(O)–N fragment, which can be expected to provide conformational mobility with respect to the C–C(O) and N–C(O) bonds. Most likely, the complication of the spectra is associated with the formation of different rotamers with respect to these bonds during crystallization leading to the formation of polymorphic forms of crystals. The spectra can be further complicated by the Fermi resonances with overtones or combinations bands of non-planar deformation oscillations of C–H aromatic rings, which are manifested in the region of 820–870 cm⁻¹.

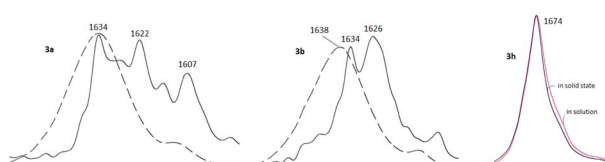


Fig. 8 Stretch vibrations of C=O groups of **3a**, **3b** and **3h** in crystalline state (black solid lines) and in CCl₄ solutions (dashed or colored lines).



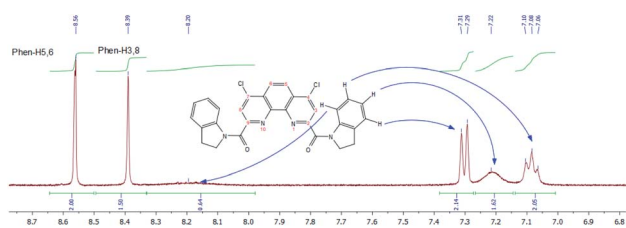


Fig. 12 ^1H NMR spectra of **3f** in DMSO-d_6 at $55\text{ }^\circ\text{C}$ (fragmental view).

leading to the interconversion of conformers. To confirm this assumption, we used ROESY NMR technique (Fig. 11).

As it seen from Fig. 11, at $-30\text{ }^\circ\text{C}$ the exchange process is slow and ROESY spectrum at this temperature contains only diagonal peaks (Fig. 11a). Analysis of cross-peaks in the region 3.6–4.8 ppm in the ROESY spectrum at $25\text{ }^\circ\text{C}$ (Fig. 11b) clearly shows that positional exchange between two indoline fragments in minor conformer proceeds through symmetrical conformer.

Similar behavior was observed for ^1H NMR spectra of **3f** in DMSO-d_6 , but the signals of main and minor forms are more broaden in comparison with those in CDCl_3 . A fragmental view of aromatic region with the assignment of signals is given in Fig. 12.

Such spectral changes were also found for **3g** (see ESI †).

In contrast to other diamides **3**, ^1H NMR spectrum of bis-carbazolyl diamide **3h** is quite simple and predictable (Fig. 13). The introduction of two spatially very bulky carbazolyl residues into the molecule leads to the fact that only one conformer of a symmetrical structure is stable.

Thus, according to our study, diamides **3f** and **3g** exist in solutions as equilibrium mixtures of conformers that arise as a result of slow rotation around “Phen”–C(O) bonds and around R_2N –C(O) amide bonds, which leads to the observed temperature dependences in ^1H NMR spectra. These observations may explain the fact of a sharp decrease in selectivity towards Am/Eu pair for diamides **3f** and **3g**.

Another fact that needs to be explained is the sharp decrease in selectivity towards Am/Eu pair when switching from amide **3a** to amide **3b**. It is well known^{58–62} that the ability to bind metal cations for a wide range of extractants is associated with the ability to realize so called “pre-organized” conformation in solution. In the case of this class of compounds, the flexible parts of the extractant are the amide groups where oxygen atoms are involved in binding with the metal cation.

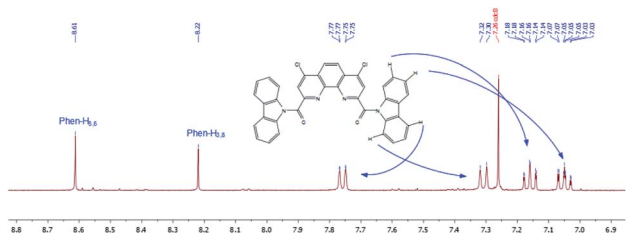


Fig. 13 ^1H NMR spectrum of **3h** in CDCl_3 at $55\text{ }^\circ\text{C}$ (region from 6.9 to 8.7 ppm).

Thus, according to our study, diamides **3f** and **3g** exist in solutions as equilibrium mixtures of conformers that arise as a result of hindered rotation around “Phen”–C(O) bonds and around R_2N –C(O) amide bonds, which leads to the observed temperature dependences in ^1H NMR spectra. Sufficiently high rotation barriers around Phen–CO bonds in **3f** and **3g** compared with those in diamides **3a–3c** may be an additional reason for the decrease in the extraction ability of the first two diamides.

Experimental section

Materials

The list of the studied diamides and their labels (**3a–3h**) are presented in Table 1.

All syntheses were performed in argon inert atmosphere. Dichloromethane was purified by distillation over calcium hydride prior to use. Triethylamine was purified by simple distillation, previously held for 12 hours over sodium hydroxide. All the cyclic amines which are liquid under normal conditions were purified by simple or vacuum distillation. Carbazole was previously purified by recrystallization from toluene.

3-Nitrobenzotrifluoride (“F-3”) analytical grade was purchased from Rhodia (France) and was used as a solvent in the extraction experiments without further purification.

Methods

NMR spectra were recorded using standard 5 mm sample tubes on Agilent 400-MR spectrometer with operating frequencies of 400.1 MHz (^1H) and 100.6 MHz (^{13}C) and Bruker Avance-600 spectrometer with operating frequencies of 600.1 MHz (^1H) and 150.6 MHz (^{13}C). Deuterated solvents CDCl_3 , THF-d_8 , benzene- d_6 , acetonitrile- d_3 , and DMSO-d_6 for NMR spectra were purchased from commercial sources and used without further purification.

The ROESY spectrum was recorded on the Agilent 400-MR spectrometer using standard ROESYAD pulse sequence with a mixing time 200 ms and an acquisition time 150 ms.

IR spectra were recorded on FTIR spectrometer Nicolet iS5 (Thermo Scientific) using an internal reflectance attachment with diamond optical element – attenuated total reflection (ATR) with 45° angle of incidence. Resolution 4 cm^{-1} , the number of scans is 32.

IR spectra in CCl_4 solutions were recorded in a 0.06 cm cuvette with KBr windows at the concentrations of compounds 0.01 mol L^{-1} at room temperature. Ultrasonic bath was used to facilitate dissolution of diamides **3f–3h**.

HRMS ESI – mass spectra were recorded on the MicroTof Bruker Daltonics and Orbitrap Elite instruments.

Single crystals of **1**·DMF· H_2O and **3f** were obtained upon slow isothermal ($25\text{ }^\circ\text{C}$) recrystallization of corresponding substances from DMF-ethyl acetate (50/50) mixture, single crystals of **3a** were obtained upon slow adding of *n*-hexane to a solution of **3a** in ethyl acetate-chloroform (50/50) mixture, and **3b**· H_2O – by recrystallization of **3b** from acetonitrile.



X-ray diffraction experiments for **1**·DMF·H₂O and **3f** were performed on the “Belok” beamline of the National Research Center “Kurchatov Institute” (Moscow, Russian Federation) using a Rayonix SX165 CCD detector and X-ray radiation with $\lambda = 0.78790 \text{ \AA}$ and 0.79272 \AA for **1**·DMF·H₂O and **3f**, respectively. For **3a** and **3b**·H₂O, the STOE STADIVARI diffractometer equipped with the fine-focus Cu GeniX 3D radiation source ($\lambda = 1.54186 \text{ \AA}$) and a Pilatus 100 K detector was used. For **1**·DMF·H₂O and **3f**, data reduction procedure was carried out with the *iMOSFLM* program from the CCP4 program set,⁶³ absorption correction was performed with the *SCALA* program,⁶⁴ whereas for **3a** and **3b**·H₂O, the STOE X-AREA program was applied. All structures were determined by direct methods and refined by full-matrix least-squares on F^2 with all non-H atoms given anisotropically. Hydrogen atoms of hydroxy groups and water molecule in **1**·DMF·H₂O were located from difference Fourier maps and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. For **3b**·H₂O, we failed to determine the positions of water molecule H atoms, which seem to be disordered. All other H atoms were positioned geometrically and refined as riding at parent C atoms with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for all other H atoms. For **1**·DMF·H₂O and **3f**, all calculations were performed with SHELXTL,^{65a} whereas for **3a** and **3b**·H₂O SHELXT^{65b} was used for the structure solution and SHELXL^{65a} – for the refinement. Full crystallographic data are deposited in Cambridge Structural Database, deposition numbers 1938798 (**1**·DMF·H₂O), 1988714 (**3a**), 1983770 (**3b**·H₂O), 1938799 (**3f**).[†] Selected crystal data for the studied compounds are presented below:

1·DMF·H₂O. C₁₇H₁₅Cl₂N₃O₆, $M_r = 428.22$, triclinic, $P\bar{1}$, $a = 7.158(1)$, $b = 8.352(2)$, $c = 15.356(3) \text{ \AA}$, $\alpha = 81.10(3)$, $\beta = 82.92(3)$, $\gamma = 78.62(3)^\circ$, $V = 885.1(3) \text{ \AA}^3$, $Z = 2$, $d_c = 1.607 \text{ g cm}^{-3}$, $\mu = 0.538 \text{ mm}^{-1}$, $F(000) = 440$, $T = 100(2) \text{ K}$, $T_{\text{min}}/T_{\text{max}} = 0.890/0.980$, $2\theta_{\text{max}} = 61.52^\circ$, 15 682 reflections, 4025 unique ($R_{\text{int}} = 0.028$), $R_1 = 0.031$ for 3711 reflections with $I > 2\sigma(I)$, $wR_2 = 0.089$ for all reflections and 268 refined parameters, GoF on $F^2 = 1.073$.

3a. C₂₂H₂₀Cl₂N₄O₂, $M_r = 443.32$, triclinic, $P\bar{1}$, $a = 7.7488(3)$, $b = 10.1002(4)$, $c = 13.5780(5) \text{ \AA}$, $\alpha = 79.974(3)$, $\beta = 76.276(3)$, $\gamma = 83.821(3)^\circ$, $V = 1014.12(7) \text{ \AA}^3$, $Z = 2$, $d_c = 1.452 \text{ g cm}^{-3}$, $\mu = 3.11 \text{ mm}^{-1}$, $F(000) = 460$, $T = 293(2) \text{ K}$, $T_{\text{min}}/T_{\text{max}} = 0.672/0.953$, $2\theta_{\text{max}} = 135.95^\circ$, 8085 reflections, 3593 unique ($R_{\text{int}} = 0.023$), $R_1 = 0.043$ for 2581 reflections with $I > 2\sigma(I)$, $wR_2 = 0.129$ for all reflections and 281 refined parameters, GoF on $F^2 = 1.025$.

3b·H₂O. C₂₄H₂₆Cl₂N₄O₃, $M_r = 489.39$, monoclinic, $C2/c$, $a = 36.3267(15)$, $b = 6.8415(2)$, $c = 22.1880(11) \text{ \AA}$, $\beta = 122.928(3)$, $V = 4628.5(4) \text{ \AA}^3$, $Z = 8$, $d_c = 1.405 \text{ g cm}^{-3}$, $\mu = 2.81 \text{ mm}^{-1}$, $F(000) = 2048$, $T = 293(2) \text{ K}$, $T_{\text{min}}/T_{\text{max}} = 0.865/0.972$, $2\theta_{\text{max}} = 135.37^\circ$, 26 181 reflections, 4179 unique ($R_{\text{int}} = 0.113$), $R_1 = 0.036$ for 2196 reflections with $I > 2\sigma(I)$, $wR_2 = 0.072$ for all reflections and 298 refined parameters, GoF on $F^2 = 0.846$.

3f. C₃₀H₂₀Cl₂N₄O₂, $M_r = 539.40$, triclinic, $P\bar{1}$, $a = 7.2410(14)$, $b = 11.680(2)$, $c = 14.506(3) \text{ \AA}$, $\alpha = 103.259(14)$, $\beta = 95.030(2)$, $\gamma = 97.662(18)^\circ$, $V = 1174.6(4) \text{ \AA}^3$, $Z = 2$, $d_c = 1.525 \text{ g cm}^{-3}$, $\mu = 0.420 \text{ mm}^{-1}$, $F(000) = 556$, $T = 100(2) \text{ K}$, $T_{\text{min}}/T_{\text{max}} = 0.93/0.97$, $2\theta_{\text{max}} = 61.92^\circ$, 18 379 reflections, 5233 unique ($R_{\text{int}} = 0.078$), R_1

$= 0.059$ for 3967 reflections with $I > 2\sigma(I)$, $wR_2 = 0.153$ for all reflections and 344 refined parameters, GoF on $F^2 = 1.021$.

Detailed crystallographic data provided in ESI (see from p. S41[†]).

Synthesis and analytical data

4,7-Dichloro-1,10-phenanthroline-2,9-dicarbonyl chloride 2. 0.35 Mol (118 g) of thoroughly dried dicarboxylic acid **1** was added to 1.4 l of SOCl₂ at room temperature and stirring. 100 μL of DMF was added to the resulting suspension and the reaction mixture was stirred for 4 hours at 50 °C. After that, SOCl₂ was removed at low pressure (200 Torr), then 250 mL of dry benzene was added to the residue, and then the solvent was distilled off again. Absolute diethyl ether was added to the solid rest. It was washed on a filter with cold ether, after that the product **2** was dried in vacuum to a constant mass. Yield 95%, pale-yellow fibers, T.decomp. > 220 °C, ¹H NMR (400 MHz, CDCl₃) δ 8.58 (s, 2H), 8.52 (s, 2H).

General method for synthesis of diamides 3a–e

A solution of the corresponding cyclic amine (50 mmol) in 5 mL of methylene chloride was added at –20 °C under vigorous stirring to a suspension of 10 mmol (3.74 g) of chloride **2** in 25 mL of methylene chloride. Then the reaction mixture was allowed to reach room temperature and stirred overnight. Next, the reaction mixture was diluted with 50 mL of methylene chloride, washed with water (2 × 50 mL), dried over sodium sulfate, and the solvent was distilled off. The residue was treated with hexane, recrystallized from a mixture of chloroform/hexane, obtaining the desired product in the form of a white or slightly colored solid.

(4,7-Dichloro-9-(pyrrolidin-1-ylcarbonyl)-1,10-phenanthroline-2-yl)(pyrrolidin-1-yl)-methanone 3a. Yield 82% (3.64 g), yellowish powder, mp 245–247 °C, R_f 0.78 (acetone); IR (cm⁻¹) 3095, 3073, 2968, 2878 (C–H stretching vibrations), 1634, 1622, 1615 (C=O), 1573, 1522, 1449, 1437, 1416 (C=C, C=N); ¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 2H), 8.31 (s, 2H), 4.09 (t, $J = 6.5 \text{ Hz}$, 4H), 3.74 (t, $J = 6.5 \text{ Hz}$, 4H), 2.01–1.91 (m, 8H); ¹³C NMR (101 MHz, CDCl₃) δ 164.9, 154.3, 145.2, 143.8, 127.5, 124.4, 124.2, 49.2, 47.3, 26.9, 24.2; HRMS (ESI-TOF) (m/z) [$M + H$]⁺ calculated for C₂₂H₂₁Cl₂N₄O₂ 443.1037, found 443.1034.

(4,7-Dichloro-9-(piperidin-1-ylcarbonyl)-1,10-phenanthroline-2-yl)(piperidin-1-yl)-methanone 3b. Yield 81% (3.82 g), white powder, mp 249–251 °C, R_f 0.58 (acetone : CH₂Cl₂ 1 : 4); IR (cm⁻¹) 3084, 3043, 2938, 2914, 2843 (C–H stretching vibrations), 1634, 1626 (C=O), 1571, 1532, 1456, 1446, 1425 (C=C, C=N); ¹H NMR (400 MHz, CDCl₃) δ 8.36 (s, 2H), 8.10 (s, 2H), 3.79 (t, $J = 5.3 \text{ Hz}$, 4H), 3.72 (t, $J = 5.3 \text{ Hz}$, 4H), 1.82–1.59 (m, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 166.0, 154.5, 145.3, 143.9, 127.3, 124.3, 124.0, 48.7, 43.9, 26.7, 25.7, 24.7; HRMS (ESI-TOF) (m/z) [$M + H$]⁺ calculated for C₂₄H₂₅Cl₂N₄O₂ 471.1350, found 471.1355.

Azepan-1-yl(9-(azepan-1-ylcarbonyl)-4,7-dichloro-1,10-phenanthroline-2-yl)methanone 3c. Yield 82% (4.10 g), white powder, mp 238–241 °C, R_f 0.53 (acetone : CH₂Cl₂ 1 : 5); IR (cm⁻¹) 3037, 2926, 2853 (C–H stretching vibrations), 1634, 1631, 1626 (C=O), 1590, 1530, 1456, 1427 (C=C, C=N); ¹H NMR (400



MHz, CDCl₃) δ 8.38 (s, 2H), 8.11 (s, 2H), 3.82–3.72 (m, 8H), 1.90 (p, $J = 5.9$ Hz, 4H), 1.78 (p, $J = 5.9$ Hz, 4H), 1.71–1.57 (m, 8H); ¹³C NMR (101 MHz, CDCl₃) δ 167.6, 154.9, 145.4, 143.8, 127.3, 124.1, 124.0, 49.9, 47.4, 29.6, 27.6, 27.3, 27.0; HRMS (ESI-TOF) (m/z) [M + H]⁺ calculated for C₂₆H₂₉Cl₂N₄O₂ 499.1663, found 499.1662.

(4,7-Dichloro-9-(morpholin-4-ylcarbonyl)-1,10-phenanthrolin-2-yl)(morpholin-4-yl)methanone 3d. Yield 71% (3.37 g), white powder, mp 236–238 °C, R_f 0.75 (acetone : CH₂Cl₂ 1 : 1); IR (cm⁻¹) 3093, 3026, 2966, 2912, 2852 (C–H stretching vibrations), 1644, 1640, 1634, 1634, 1628, (C=O), 1570, 1528, 1475, 1462, 1444, 1427 (C=C, C=N); ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 2H), 8.21 (s, 2H), 3.98 (t, $J = 4.8$ Hz, 4H), 3.95–3.83 (m, 8H), 3.75 (t, $J = 4.8$ Hz, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 165.8, 153.5, 145.1, 144.3, 127.6, 124.9, 124.3, 67.3, 67.0, 48.2, 43.3; HRMS (ESI-TOF) (m/z) [M + H]⁺ calculated for C₂₂H₂₁Cl₂N₄O₄ 475.0935, found 475.0928.

(4,7-Dichloro-9-(4-methylpiperazin-1-yl)carbonyl)-1,10-phenanthrolin-2-yl(4-methylpiperazin-1-yl)methanone 3e. Yield 79% (3.96 g), white powder, mp 235–238 °C; IR (cm⁻¹) 3041, 2973, 2937, 2894, 2860, 2794, 2749 (C–H stretching vibrations), 1635 (C=O), 1531, 1460, 1446, 1425 (C=C, C=N); ¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 2H), 8.17 (s, 2H), 3.98–3.87 (m, 8H), 2.55 (t, $J = 5.0$ Hz, 4H), 2.42 (t, $J = 5.0$ Hz, 4H), 2.32 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 165.8, 153.9, 145.1, 144.1, 127.5, 124.7, 124.2, 55.7, 54.8, 47.5, 46.2, 42.8; HRMS (ESI-TOF) (m/z) [M + H]⁺ calculated for C₂₄H₂₇Cl₂N₆O₂ 501.1568, found 501.1562.

General method for synthesis of diamides 3f–h

Triethylamine (30 mmol, 3.04 g, 4.20 mL) was added to a suspension of 10 mmol (3.74 g) of chloride 2 in 25 mL of methylene chloride at –20 °C under vigorous stirring and then the solution of the corresponding secondary amine (22.5 mmol) in 10 mL of methylene chloride was added dropwise. After that, the reaction mixture was stirred at –20 °C for 1 hour, allowed to reach the room temperature and was additionally stirred for 24 hours. Then it was washed with water (2 × 50 mL), dried over sodium sulfate and the solvent was distilled off. The residue was washed with chloroform, giving the desired product in the form of slightly colored solid.

(4,7-Dichloro-9-(2,3-dihydro-1H-indol-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)(2,3-dihydro-1H-indol-1-yl)methanone 3f. Yield 76% (4.10 g), yellowish fibers, mp 289–290 °C, R_f 0.74 (EtOAc : CH₂Cl₂ 1 : 10); IR (cm⁻¹) 3109, 3070, 3053, 2971, 2936, 2862 (C–H stretching vibrations), 1634 (C=O), 1597, 1569, 1533, 1481, 1463, 1437, 1403 (C=C, C=N); ¹H NMR (400 MHz, DMSO-*d*₆, recorded at 343.15 K) δ 8.56 (s, 2H), 8.39 (s, 2H), 8.20 (bs, 2H), 7.30 (d, $J = 7.8$ Hz, 2H), 7.22 (bs, 2H), 7.08 (t, $J = 7.8$ Hz, 2H), 4.52 (bs, 4H), 3.17–3.05 (m, 4H); HRMS (ESI-TOF) (m/z) [M + H]⁺ calculated for C₃₀H₂₀Cl₂N₄O₂ 539.1045, found 539.1045.

(4,7-Dichloro-9-(1,2,3,4-tetrahydroquinolin-1-ylcarbonyl)-1,10-phenanthrolin-2-yl)-(1,2,3,4-tetrahydroquinolin-1-yl)methanone 3g. Yield 90% (5.10 g), yellowish powder, mp 238–241 °C, R_f 0.59 (EtOAc : CH₂Cl₂ 1 : 2); IR (cm⁻¹) 3061, 3042, 2946, 2885, 2843 (C–H stretching vibrations), 1651, 1644, 1640, 1637 (C=O), 1602, 1581, 1571, 1530, 1491, 1450, 1439, 1400

(C=C, C=N); ¹H NMR (400 MHz, C₆D₆) δ 7.96 (s, 2H), 7.84 (s, 2H), 7.62 (bs, 2H), 6.93–6.79 (m, 6H), 3.86–3.78 (m, 4H), 2.49 (t, $J = 6.8$ Hz, 4H), 1.70–1.62 (m, 4H); ¹³C NMR (101 MHz, C₆D₆) δ 166.9, 155.5, 145.9, 143.3, 139.7, 131.4, 128.9, 127.2, 126.1, 125.3, 124.9, 124.2, 123.8, 46.2, 27.2, 24.1; HRMS (ESI-TOF) (m/z) [M + H]⁺ calculated for C₃₂H₂₅Cl₂N₄O₂ 567.1350, found 567.1349.

9H-Carbazol-9-yl(9H-carbazol-9-ylcarbonyl)-4,7-dichloro-1,10-phenanthrolin-2-yl)methanone 3h. Yield 63% (4.00 g), white powder, mp 389–393 °C; IR (cm⁻¹) 3097, 3061 (C–H stretching vibrations), 1674 (C=O), 1527, 1491, 1480, 1444, 1381 (C=C, C=N); ¹H NMR (CDCl₃) δ , ppm: ¹H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 2H), 8.22 (s, 2H), 7.80–7.73 (m, 4H), 7.31 (d, $J = 8.5$ Hz, 4H), 7.16 (td, $J = 7.4, 1.1$ Hz, 4H), 7.05 (ddd, $J = 8.5, 7.4, 1.1$ Hz, 4H); HRMS (ESI-TOF) (m/z) [M + H]⁺ calculated for C₃₈H₂₁Cl₂N₄O₂ 635.1035, found 635.1029.

Solvent extraction experiments

Solvent extraction experiments were carried out as follows. 0.5 mL of organic solution of the extractant in 3-nitrobenzotrifluoride (“F-3”) and 0.5 mL of aqueous phase containing nitric acid and radionuclides were mixed in 1.5 mL polypropylene vial. Three sets of aqueous solutions were prepared for extraction experiments. The first one contained trace concentrations of ²⁴¹Am (≈ 1500 Bq mL⁻¹) and ¹⁵²Eu (≈ 2500 Bq mL⁻¹), the second set contained ²⁴¹Am (≈ 1500 Bq mL⁻¹) and ²⁴⁴Cm (≈ 2000 Bq mL⁻¹). The third set contained lanthanum and all lanthanides (except promethium) in total concentration 10⁻⁴ mol L⁻¹. The phases were stirred for 15 minutes on a vortex shaker at 25 ± 1 °C in an air thermostat. Then samples were centrifuged (5 minutes, 6000 rpm) and aliquots of each phase were taken for determination of radionuclide or lanthanide concentration.

Content of ²⁴¹Am ($E_\gamma = 59.5$ keV) and ¹⁵²Eu ($E_\gamma = 121.8$ keV) was determined by gamma-spectrometry using a high-pure germanium detector GR 3818 (Canberra Ind.) in the first set of experiments. Second set of samples was analyzed by alpha-spectrometry ($E_\alpha(^{241}\text{Am}) = 5637$ keV, $E_\alpha(^{244}\text{Cm}) = 5901$ keV) using an alpha spectrometer Model 7401 with Si detectors (Canberra Ind.). Initial aqueous phase and equilibrium aqueous phases of the third set of samples were analyzed by ICP-OES (Agilent ICP-OES 720).

The distribution ratios (D) of metals were calculated for the first set of experiments as the ratio of the counting rate in the organic and aqueous phase. For the second and the third sets of samples activity/concentration in organic phase was calculated as difference between concentrations in initial and equilibrium aqueous phases. The separation factors (SF) were calculated as the ratio of the distribution ratios. All extraction experiments were repeated three times. Uncertainties for 0.01 < D < 100 are within ±10%.

Conclusions

A family of new diamides of 4,7-dichloro-1,10-phenanthroline-2,9-dicarboxylic acid was synthesized starting from the



corresponding dichloride **2** and cyclic amines. The structures of three diamides and starting acid itself were determined by single-crystal X-ray diffraction. Diamides **3a**, **3b** and **3f** crystallize in the twisted asymmetric conformations. In **3a** and **3b**, these fragments are in periplanar positions to each other, while the more bulky indoline fragments in **3f** occupy *anti*-periplanar positions. All structures are stabilized by a network of intramolecular hydrogen bonds. In structures **3b** and **3f**, the π -stacking interaction between aromatic nuclei is clearly manifested. The addition of aromatic rings in the ligand structure leads to complex dynamic behavior in solutions.

In solutions of all diamides **3**, according to NMR data, the rotation along the $R_2N-C(O)$ amide bonds is inhibited. In diamides **3a–3c**, containing small volume monocyclic groups in amide fragments, rotation along the “Phen”–CO bonds at room temperature is free. Insertion of the first aromatic ring into amide moiety complicates the dynamic behavior of the ligands **3f** and **3g** in solutions whereas insertion of bulky carbazolyl groups simplifies the spectra of **3h**. The data of IR spectroscopy showed that in the polycrystalline state and in solutions, diamides **3a–3g** exist as mixtures of conformers differing probably in the dihedral angles around the amide bonds $R_2N-C(O)$ and around CO–Phen bonds.

Liquid–liquid extraction experiments revealed exceptional properties for some of diamides **3** under study. It was shown that diamide **3a** is more efficient extractant for lanthanides, americium and curium from highly acidic HNO_3 solution than their non-cyclic *N,N,N',N'*-tetraalkyl analogues. Also **3a** shows high selectivity in the La/Am pair separation (SF (Am/La) \approx 10) and in the Am/Eu pair separation (SF (Am/Eu) \approx 12)). Its selectivity in the Am/Cm pair separation is moderate (SF (Am/Cm) \approx 3.8). Both selectivity and extraction ability of the ligands under study decrease from **3a** to **3c** with the expansion of alicycle in the amide function despite increase in solubility. In the same time, there is a sharp inversion in selectivity in relation to the Am(III)/Eu(III) pair in the row **3a**, **3f**, **3h**. These unusual properties can be explained by molecular dynamics of such compounds.

In order to unambiguously confirm our assumptions of the sharp decrease in selectivity towards Am/Eu pair when switching from amide **3a** to amide **3b** and to get more information about relationships of dynamic behavior of diamides **3** with their extraction abilities we initiated the study of complexation of lanthanides with diamides **3a** and **3b** using the direct 1H NMR and UV-vis titration and DFT calculations of structures of these ligands and structures of their metal complexes. These results will be presented in a separate paper.

Conflicts of interest

There are no conflicts to declare.

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