N-Alkyl-*N*´-[(alkyl/aryl)(alkoxy/aroxy)phosphoryl]ureas: synthesis and extraction properties toward f-elements*

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A reaction of chlorophosphonates $R^1R^2P(O)Cl$ with NaOCN and subsequent treatment with octylamine lead to phosphorylureas $R^1R^2P(O)NHC(O)NHC_8H_{17}$-*n* ($R^1$ = EtO, PhO; R^2 = Me, Ph). Their extraction capability toward U^{VI} and a number of tervalent lanthanides (La^{III}, Nd^{III}, Ho^{III}, Yb^{III}) was studied. Efficiency and selectivity of these ligands in the extraction of f-elements from nitric acid solutions to chloroform were compared with extraction properties of a model phosphine oxide-type phosphorylurea $MePhP(O)NHC(O)NHC_8H_{17}$-*n* and carbamoylphosphine oxide $Ph_2P(O)CH_2C(O)NBu_2$.

Key words: phosphorylureas, chlorophosphonates, one-pot processes, extraction, lanthanides, actinides.

Extraction as a method for recovery of valuable components and separation of elements with close properties is widely used in atomic industry for reprocessing spent nuclear fuel, in hydrometallurgy for obtaining hafnium-free zirconium, for separation of copper and iron, nickel and cobalt, as well as for separation of rare earth elements. The advantage of this method is its high productivity and relatively simple automation. Therefore, a search for new extractants possessing high extraction capability and selectivity is still a relevant problem. Among organophosphorus extractants, the most frequently used are neutral organophosphorus compounds (OPC), which contain one or several donor centers capable of coordination with metal cations (mono-, bi-, and polydentate ligands).[1—3] The properties of bidentate neutral OPC are well studied; they have two coordination centers, one of which is the oxygen atom of the P=O group, whereas the second center can be either similar P=O oxygen atom (diphosphine dioxides, diphosphonates, and diphosphinates $R^1R^2P(O)—X—P(O)R^1R^2$, here and further X is alkylene bridges of different nature, R is different alkyl, alkoxy, and aryl groups), or the oxygen atom of the C=O group (for example, compounds with a carbamoyl fragment $R^1R^2P(O)—X—C(O)NR^3_2$ and $R^1R^2P(O)—X—C(O)NHR^3$). General correlations between the extractant structure and its extraction capability were established.[3,4] However, evaluation of practical importance of extractants, besides efficiency, should also include the cost of the starting materials and processability of the synthesis of target compounds. Lately, a new family of synthetically more available (as compared to carbamoylmethylphosphine oxides (CMPO)) acetyl-containing phosphine oxides[5—7] $R^1R^2P(O)—X—C(O)Me$ was studied. A number of diorganylphosphorylmonoureas and -bisureas[8—12] were synthesized, which are the structural analogs of CMPO containing an NH imide fragment instead of the CH_2 methylene bridge between the phosphoryl and the carbonyl groups. A simple and technological one-pot method was developed for the synthesis of this type of compounds,[13] and it appears that extraction properties of diorganylphosphorylmonoureas toward f-elements are significantly better than those of the corresponding carbamoyl analogs. In this case, *N*-diphenylphosphoryl-*N*´-*n*-alkylureas, especially *N*´-*n*-octyl derivatives, were found to be the most efficient.[12] Note that earlier *N*-dialkoxyphosphorylureas were reported as possible extractants for actinides.[14] At the same time, there are no literature data on the extraction capability of phosphorylureas, whose molecules simultaneously contain a P—C and a P—O—C fragments (the phosphonate type). In continuation of our studies on the search for efficient and selective extractants for extraction and separation of lanthanides and actinides, it seemed reasonable to synthesize a number of this type phosphorylureas and study their extraction properties.

In the present work, we synthesized a series of earlier unknown phosphonate-type phosphorylureas **1**—**4**, in the

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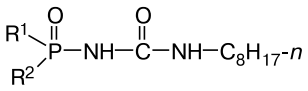
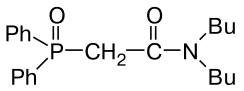
molecules of which simple alkyl, aryl, alkoxy, and aroxy fragments are attached to the phosphorus atom in different combinations, with the *n*-octyl substituent being attached to the terminal nitrogen atom in all the cases. This allowed us to highly correctly evaluate the influence of substituents at the phosphorus atom on the extraction parameters of the ligands obtained.



1—5



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R^1 = EtO, R^2 = Me (**1**); R^1 = PhO, R^2 = Me (**2**); R^1 = EtO, R^2 = Ph (**3**); R^1 = PhO, R^2 = Ph (**4**); R^1 = Me, R^2 = Ph (**5**)

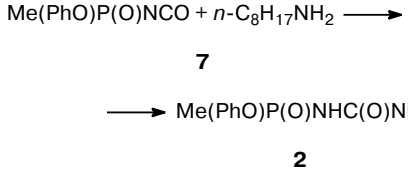
Extraction of f-elements was chosen as an example to study extraction capability of phosphorylureas **1—4**, whereas the phosphine oxide-type phosphorylurea $PhMeP(O)NHC(O)NHC_8H_{17}$-*n* (**5**) and CMPO structurally close to ureas $Ph_2P(O)CH_2C(O)NBu_2$ (**6**) were used as reference compounds.

Results and Discussion

The phosphonate-type phosphorylureas were synthesized according to the following scheme: phosphoryl chloride → phosphoryl isocyanate → phosphorylurea, which is thought[15] to be the most rational approach to the preparation of different types of *N*-phosphorylated ureas. It should be noted that a key step in this scheme, which determines its overall effectiveness, is the synthesis of the corresponding phosphoryl isocyanates.

Earlier,[16] we have developed a simple, efficient, and technological method for the preparation of monoisocyanates of pentavalent phosphorus oxoacids consisting in the reaction of phosphoryl chlorides with cheap commercially available NaOCN in anhydrous acetonitrile in the presence of anhydrous magnesium chloride as a catalyst. In particular, this method was used to synthesize methyl(phenoxy)phosphoryl isocyanate (**7**) in 73% yield, which violently reacted with *n*-octylamine in anhydrous benzene at ~20 °C to give *N*-[methyl(phenoxy)phosphoryl]-*N*′-octylurea (**2**) in 87% yield (Scheme 1).

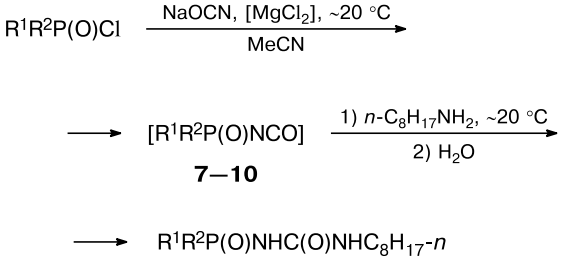
Scheme 1



Phosphoryl isocyanate **7** appeared to be not stable enough, and even on storage under inert atmosphere when air moisture is absent, it gradually decomposes with the formation of a white solid products, most likely, of the polymeric nature. Since other representatives of phosphonic acid isocyanates can be similarly unstable, we decided to develop practical one-pot processes for the synthesis of the corresponding phosphonate-type *N*-phosphorylureas.

A possibility to carry out such processes was demonstrated for the synthesis of urea **2** taken as an example (Scheme 2).* In the first step, phosphoryl chloride reacted with NaOCN in the presence of $MgCl_2$ in anhydrous acetonitrile at ~20 °C.[16] In the second step, a calculated amount of octylamine was added to the *in situ* obtained phosphoryl isocyanate **7**. After the reaction mixture was worked-up, the target compound **2** was isolated in 88% yield (calculated on the starting chlorophosphonate).

Scheme 2



R^1 = EtO, R^2 = Me (**1**, **8**); R^1 = PhO, R^2 = Me (**2**, **7**); R^1 = EtO, R^2 = Ph (**3**, **9**); R^1 = PhO, R^2 = Ph (**4**, **10**)

Compounds **1**, **3**, and **4** were obtained similarly.

$^{31}P\{^1H\}$ NMR spectroscopy showed that the corresponding phosphoryl isocyanates $R^1R^2P(O)NCO$ **8—10** are mainly formed in the first step of these processes for all the phosphoryl chlorides under study. After their treatment with *n*-octylamine, the target phosphorylureas **1**, **3**, and **4** were obtained in high yields (73—86%) (Table 1).

The ureas **1—4** are white crystalline compounds, stable in air and melting without decomposition. They are virtually insoluble in water, hexane, and heptane and fairly well soluble in chloroform and DMSO. The structure of these compounds was confirmed by elemental analysis, as well as by IR spectroscopy and NMR spectroscopy (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$). The ^1H NMR spectra of compounds **1—4**, whose molecules contain an asymmetric phosphorus atom, exhibit magnetic nonequivalence of both the geminal protons in the $P—O—CH_2$ fragments and (in most cases) the protons of the methylene groups in the

* Chlorophosphonates used in this work were synthesized based on the most efficient procedures described in the literature. An original method was developed for the preparation of Ph(EtO)P(O)Cl (see Experimental), which allowed us to obtain this compound in the yield close to quantitative based on the commercially available products $PhP(O)(OEt)_2$ and PCl_5.

Table 1. One-pot synthesis of the phosphonate-type *N*-phosphorylureas $R^1R^2P(O)NHC(O)NHC_8H_{17}$-*n* **1—4**

R^1	R^2	Duration of the first step of the process/h	Phosphoryl isocyanate formed	Content of isocyanate in the mixture (%) ($^{31}P\{^1H\}$ NMR)	Phosphoryl-urea obtained	Yield (%)
Me	EtO	2	**8**	88	**1**	86
Me	PhO	3	**7**	—	**2**	88
Ph	EtO	2	**9**	96	**3**	77
Ph	PhO	10	**10**	72	**4**	73

C(O)—NH—CH_2 fragment, that naturally results in a significant complication of the spectral pattern in the region characteristic of the signals for the protons of the corresponding groups.

This one-pot method for the synthesis of phosphorylureas **1—4** is distinguished by its simplicity and processability and, if necessary, can be easily reproduced on a large scale. It is reasonable to suggest that this process can be also used for the preparation of other representatives of the phosphonate-type *N*-phosphorylureas.*

Extraction properties of phosphorylureas **1—4** toward f-elements were studied for extraction of uranium(VI) and the group of lanthanides(III) from aqueous nitric acid into the organic phase, with the concentration of nitric acid being varied and the concentrations of the salt in the aqueous phase and the ligand in $CHCl_3$ being constant.

It is known that efficiency and selectivity of extraction depends on many factors, and this dependence is complex. These factors include stability of extracted complexes (structure of complexes, steric availability and basicity of coordinating groups, ligand denticity, *etc.*), as well as the hydrophilic-lypophilic balance of ligand and its complexes. Our analysis of the dependence of the metal distribution ratios (*D*) from the ligand structure included the fact that the electron effect of substituents at the phosphorus atom[17] usually correlates with both basicity of the phosphoryl group and stability of the extracted complexes. The constants $\Sigma\sigma^P$, characterizing electron effects of substituents at phosphorus atom, rather considerably vary for the ligands **1**, **2**, **3**, and **4**: −1.17, −1.02, −0.69, and −0.54, respectively. Such a change in the $\Sigma\sigma^P$ values for this series of related structures corresponds to the changes in the basicity of these compounds in nitromethane[18] by 1 p*K* unit. The $\Sigma\sigma^P$ value for the model ligand **5** is −1.44, *i.e.*, this ligand should be the most basic among compounds **1—5**, other things being equal.

Steric effect of bulky substituents at phosphorus atom has also important influence on the coordination with metal, sometimes even higher than basicity.[19] However, preliminary data obtained by conformational analysis (molecular mechanics) showed that steric availability of both centers (P(O) and C(O)) capable of coordination with metal cation is virtually the same in all the ureas under study.

At the same time, variations of substituents at the phosphorus atom, namely, the replacement of one C—P bond with C—O—P, considerably changes lipophilicity of both the ligand itself and its complexes, that, in turn, changes solubilities and extraction properties of compounds. For example, the solubility of acids $(PhO)_2P(O)OH$ and $Ph_2P(O)OH$ in water differ by almost 300 times ($1.03 \cdot 10^{-1}$ and $3.6 \cdot 10^{-3}$ mol L^{-1}, respectively).[20]

The results of the studies of liquid extraction of uranyl and lanthanide ions for the same concentration of phosphorylureas **1—5** in $CHCl_3$ and the salt in aqueous phase are given in Fig. 1.

From the data obtained for uranium (see Fig. 1, *a*), it follows that the dependence of the distribution ratios D_U from the concentration of HNO_3 is similar for ligands **1—5**: the D_U values increase with concentration of HNO_3. The efficiency of uranium extraction is low for all the ligands, and the maximum values are reached at the highest concentration of nitric acid. Also note a certain symbatic character in the change of extraction capability with the change of electron properties of substituents at the phosphorus atom. Distribution ratios found at the maximum concentration of HNO_3, as well as the $\Sigma\sigma^P$ value characterizing induction properties of substituents, decrease in the order **1**, **2**, **5** > **3** > **4**.

As a first approximation, similarly to other OPC,[5,7,21] it can be suggested that in the extraction of U^{VI}, neutral $[UO_2(L)_n(NO_3)_2]^0$ and cationic $[UO_2(L)_n(NO_3)]^+ \cdot NO_3^-$ (in the form of ion pairs) complexes ($n \geq 2$) (for convenience, coordinated water molecules are not given) are the main extracted species. In this case, an increase in the concentration of nitric acid should lead to the increase in the efficiency of extraction due to the shift of the equilibrium to the side of the formation of the better extracted neutral complexes.

The structure and composition of complexes formed during extraction of uranium with phosphorylureas under study are unknown. There are only first pub-

* In fact, in the case of *N*-diorganylphosphorylureas the corresponding one-pot procedure developed for the synthesis of *N*-diphenylphosphoryl-*N*′-*n*-alkylureas[13] became afterwards a general method for the design of a great variety of this class of compounds.[12]

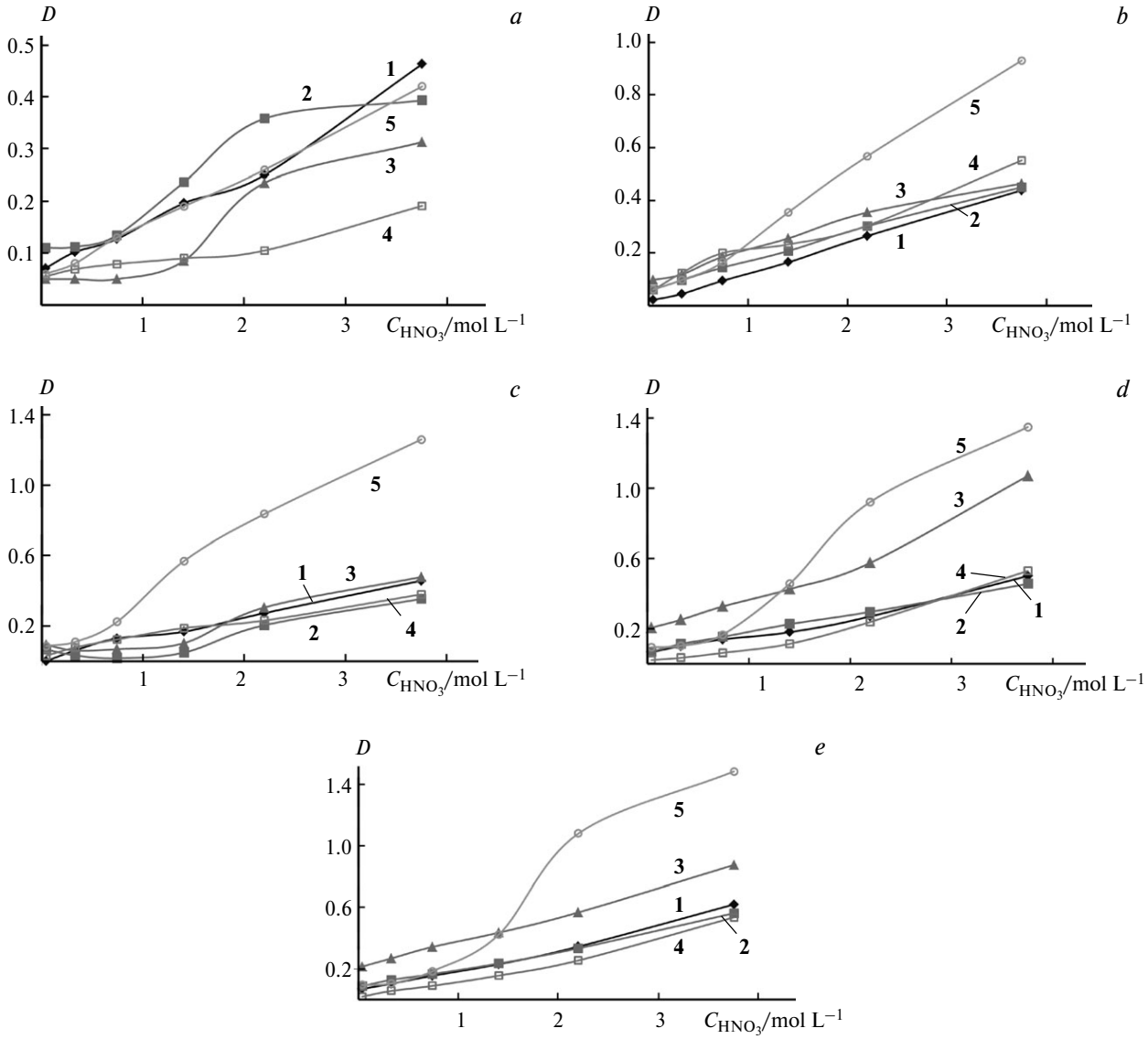


Fig. 1. Dependence of distribution ratios for U^{VI} (*a*), La^{III} (*b*), Nd^{III} (*c*), Ho^{III} (*d*), and Yb^{III} (*e*) from the concentration of HNO_3 in the extraction with phosphorylureas **1**—**5** (0.01 *M* solution in $CHCl_3$).

lications on the structure of 1 : 1 complexes of $Ph_2P(O)NHC(O)NHC_8H_{17}$-*n* with uranyl, thorium(IV), and europium(III) nitrates, in which a bidentate coordination of the ligand involving P=O and C=O groups and a bidentate coordination of all the nitrato groups was suggested according to the data of IR spectroscopy.[22] Nonetheless, it should be indicated that during extraction the structure and composition of complexes can considerably differ from those of crystalline and solid complexes synthesized in the model experiments, that, for example, was the case[23] in the studies of the extraction mechanism of CMPO.

In contrast to extraction of U^{VI}, phosphorylureas **1**—**4** virtually similarly extract La^{III} and Nd^{III}, with the distribution ratios being quite low, which insignificantly rise with the raising in the concentration of HNO_3 (see Fig. 1, *b*, *c*). It can be suggested that for the extraction of these lanthanides, the effect caused by the change in lipophilicity of ureas **1**—**4** due to the presence of the C—O—P bond considerably exceeds the influence on the extraction of the differences in electron properties of substituents at the phosphorus atom, R^1 and R^2. As a result, the efficiency of extraction of La^{III} and Nd^{III} with ligands **1**—**4** is virtually the same within entire range of HNO_3 concentrations. In the case of ligand **5** (two C—P bonds), an increase in the extraction capability with the increase in the acidity of the medium is of pronounced character, and in the range of acid concentrations 1.4—3.75 mol L^{-1} urea **5** extracts La^{III} and Nd^{III} considerably more efficiently than the phosphonate derivatives **1**—**4**.

In the extraction of Ho^{III} and Yb^{III}, the distribution ratios of all five phosphorylureas also rise with the raising in the concentration of HNO_3 (see Fig. 1, *d*, *e*). The plots of dependences for ligands **1**—**4** are almost linear, whereas the plot for ligand **5** has somewhat more complicated pattern: the *D* value changes unevenly in the region of HNO_3 concentrations 0.074—2.20 mol L^{-1}. Like in the extraction of La^{III} and Nd^{III}, the distribution ratios for all the ligands reach the maxima at the highest acidity of the aqueous phase, with ligand **5** demonstrating the highest efficiency. However, in contrast to extraction of La^{III} and Nd^{III}, ligand **3** extracts both heavy lanthanides Ho^{III} and Yb^{III} better than related ligands **1**, **2**, and **4** within entire range of HNO_3 concentrations.

Similarly to other organophosphorus ligands,[5,21] it can be suggested that the tervalent lanthanides are extracted by phosphorylureas **1**—**5** as cationic $[Ln(L)_n(NO_3)_2]^+ \cdot (NO_3)^-$ and neutral $[Ln(L)_n(NO_3)_3]^0$ complexes ($n \geq 2, 3$), existing in the equilibrium. It is expected that with the increase in the concentration of HNO_3, the content of the better extracted neutral complexes should increase.

Generally, the efficiency of extraction of lanthanides with ligands **1**—**5** obeys a known[24] rule on the change in stability of lanthanide coordination complexes ("gadolinium angle"): (La > Nd) < (Ho < Yb), though for phosphorylureas **1**, **2**, **4**, and **5**, the selectivity toward pairs of heavy and light lanthanides is low. A noticeable selectivity is exhibited only by ligand **3**. The distribution ratios in the extraction with this compound for Ho^{III} and Yb^{III} are equal to 1.07 and 0.88, respectively, whereas for La^{III} and Nd^{III} they are 0.46 and 0.48, that allows one to consider ligand **3** as a group extractant for separation of heavy and light lanthanides.

Extraction properties of phosphorylureas **1**—**4** were also compared with the properties of one of the most known bidentate extractant CMPO **6**, which were studied under the same experimental conditions (Fig. 2). The reference ligand **6** extracts uranium slightly better, than all the ureas studied. At the same time, the extraction coefficients of La^{III} and Nd^{III} for all the ligands **1**—**4** and **6** lie within the same range. Noticeable differences were observed only in the extraction of heavy lanthanides. Phosphorylurea **3** extracts Ho^{III} and Yb^{III} significantly more efficiently than related compounds **1**, **2**, **4**, and the reference ligand **6** (see Fig. 2).

In conclusion, we have developed a two-step scheme for the synthesis of earlier unknown phosphonate-type *N*-phosphorylureas based on the use of the most efficient and technological approaches of modern synthetic chemistry: the catalytic reactions and one-pot processes. Extraction properties of the ligands synthesized toward a number of f-elements were studied. Phosphorylurea (EtO)PhP(O)NHC(O)NHC$_8$H$_{17}$-*n* (**3**), in contrast to other ligands of this type **1**, **2**, **4** and the reference compounds (urea **5** and CMPO **6**), can be considered as a group extractant for the separation of heavy and light lanthanides from solutions of nitric acid into chloroform.

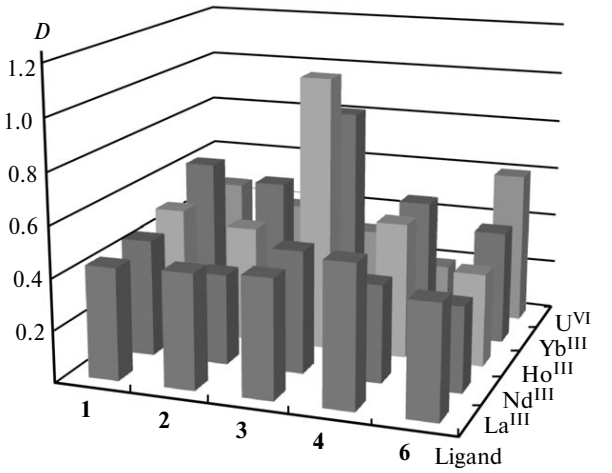


Fig. 2. Comparison of distribution ratios of La^{III}, Nd^{III}, Ho^{III}, Yb^{III}, and U^{VI} in the extraction with ligands **1**—**4** and **6** (0.01 *M* solutions in $CHCl_3$) from 3.75 *M* HNO_3, the initial concentration of lanthanide and uranyl nitrates in aqueous phase was $2.5 \cdot 10^{-4}$ mol L^{-1}.

Experimental

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AV-400 spectrometer (400.13 MHz (^1H), 100.61 MHz ($^{13}C\{^1H\}$), and 161.98 MHz ($^1P\{^1H\}$), solvent $CDCl_3$). The signals for the residual protons of the deuterated solvent and the signals for the carbon atoms of the deuterated solvent were used as references for the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively; 85% aqueous H_3PO_4 was used as an external standard for the $^{31}P\{^1H\}$ NMR spectra.

IR spectra were obtained on a Magna-IR 750 (Nicolet) Fourier-transform IR spectrometer in KBr pellets.

Elemental analysis was performed in the Laboratory of microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences.

The salt NaOCN (Aldrich, 98%) was dried for 4 h at 120 °C *in vacuo* over P_2O_5; *n*-octylamine (Acros, 99+%) was distilled over solid KOH before use; tetrachloromethane (pure grade), benzene (reagent grade), and acetonitrile (Acros, 99+%) were distilled over P_2O_5 before use. Phosphorus pentachloride (analytical grade) before the reaction was finely crushed and allowed to stand for 2 h *in vacuo* (~1 Torr) at ~20 °C. Diethyl phenylphosphonate (Alfa Aesar, 97%) and anhydrous $MgCl_2$ (Aldrich, ≥98%) were used as purchased.

Methyl(phenoxy)phosphoryl isocyanate[16] (**7**), phenyl chloro(methyl)phosphonate,[25] phenyl chloro(phenyl)phosphonate,[26] and ethyl chloro(methyl)phosphonate,[27] as well as the model compounds urea (**5**)[11] and (*N*,*N*-dibutylcarbamoylmethyl)diphenylphosphine oxide $Ph_2P(O)CH_2C(O)NBu_2$ (**6**)[28] were synthesized and purified according to the known procedures.

Ethyl chloro(phenyl)phosphonate. Finely crushed PCl_5 (26.3 g, 0.126 mol) was added in portions over 2.5 h to a solution of diethyl phenylphosphonate (27.0 g, 0.126 mol) in anhydrous

CCl_4 (94 mL) under argon with stirring on a magnetic stirrer and heating (~50 °C). After addition of PCl_5, the reaction mixture was allowed to stand for 12 h at the same temperature. The solvent and $POCl_3$ formed were evaporated at ~20 °C *in vacuo* using a water-jet pump (60 Torr). The residue was fractionally distilled *in vacuo*. The yield was 24.9 g (97%), b.p. 98—98.5 °C (1 Torr) (*cf.* Ref. 29: b.p. 82 °C at 0.01 Torr).

***N*-[Ethoxy(methyl)phosphoryl]-*N′*-*n*-octylurea (1).** Finely powdered anhydrous $MgCl_2$ (44 mg, 0.47 mmol) was added to a solution of ethyl chloro(methyl)phosphonate (2.00 g, 0.0187 mol) in anhydrous acetonitrile (20 mL) with stirring on a magnetic stirrer under argon at ~20 °C. The stirring was continued until complete dissolution of $MgCl_2$, followed by addition of NaOCN (2.44 g, 0.037 mol) and stirring for another 2 h at this temperature. *n*-Octylamine (2.32 g, 0.018 mol) was added to the suspension obtained, which was stirred for 1 h at ~20 °C. The mixture was quenched with DI water (60 mL) and stirred for another 1 h at this temperature, then it was allowed to stand for ~14 h. A precipitate was filtered off and further treated similarly to the synthesis of **2** (method *B*). The yield was 3.95 g (86%), m.p. 96 °C (heptane—chloroform). Found (%): C, 51.75; H, 9.79; N, 10.17. $C_{12}H_{27}N_2O_3P$. Calculated (%): C, 51.79; H, 9.78; N, 10.07. IR, ν/cm^{-1}: 1210 (P=O); 1680, 1695 (d, C=O); 3420, 3335, 3170, 3095 (NH). $^{31}P\{^1H\}$ NMR (c = 0.05 mol L^{-1}), δ: 29.6 (s). ^1H NMR (c = 0.05 mol L^{-1}), δ: 0.86 (t, 3 H, Me, $^3J_{H,H}$ = 6.8 Hz); 1.16—1.33 (m, 10 H, Me(C$\underline{H}_2$)$_5$); 1.32 (t, 3 H, C$\underline{H}_3$CH$_2$O, $^3J_{H,H}$ = 7.0 Hz); 1.48 (quint, 2 H, C$\underline{H}_2$CH$_2$N, $^3J_{H,H}$ = 7.0 Hz); 1.68 (d, 3 H, MeP, $^2J_{P,H}$ = 17.5 Hz); 3.08—3.23 (m, 2 H, CH$_2$N); 3.97—4.16 (m, 2 H, CH$_2$O); 6.40 (br.s, 1 H, N$\underline{H}$CH$_2$); 7.60 (d, 1 H, NHP(O), $^2J_{P,H}$ = 6.8 Hz).

***N*-[Methyl(phenoxy)phosphoryl]-*N′*-*n*-octylurea (2).** Method *A*. A solution of *n*-octylamine (0.414 g, 3.2 mmol) in anhydrous benzene (2 mL) was added dropwise to a solution of methyl(phenoxy)phosphoryl isocyanate (**7**) (0.579 g, 2.9 mmol) in anhydrous benzene (8 mL) with stirring on a magnetic stirrer under argon at ~20 °C, the mixture was stirred for 1 h at this temperature. The solvent was evaporated *in vacuo*, the syrup-like residue was diluted with hexane (10 mL) and stirred for 15 min, a precipitate formed was filtered off, washed with hexane on the filter (2×7 mL), and dried in air. The yield was 0.85 g (87%), m.p. 86—87 °C. Found (%): C, 58.99; H, 8.28; N, 8.60; P, 9.40. $C_{16}H_{27}N_2O_3P$. Calculated (%): C, 58.88; H, 8.34; N, 8.59; P, 9.49. IR, ν/cm^{-1}: 1235, 1200 (d, P=O); 1695 sh, 1675 (C=O); 3320, 3140, 3090 (NH). $^{31}P\{^1H\}$ NMR (c = 0.05 mol L^{-1}), δ: 28.7 (s). ^1H NMR (c = 0.05 mol L^{-1}), δ: 0.88 (t, 3 H, C$\underline{H}_3$CH$_2$, $^3J_{H,H}$ = 6.5 Hz); 1.15—1.35 (m, 10 H, Me(C$\underline{H}_2$)$_5$); 1.42 (quint, 2 H, C$\underline{H}_2$CH$_A$CH$_B$N, $^3J_{H,H}$ = 6.4 Hz); 1.83 (d, 3 H, MeP, $^2J_{H,P}$ = 17.8 Hz); 3.09 (ddt, 1 H, CH$_B$N, $^2J_{H_A,H_B}$ = 13.2 Hz, $^3J_{H,H}$ = 6.5 Hz); 3.15 (ddt, 1 H, CH$_A$N, $^2J_{H_A,H_B}$ = 13.2 Hz, $^3J_{H,H}$ = 6.8 Hz); 6.01 (br.s, 1 H, CH$_A$CH$_B$N$\underline{H}$); 7.09—7.22 (m, 3 H, *o*,*p*-Ph); 7.28 (t, 2 H, *m*-Ph, $^3J_{H,H}$ = 7.8 Hz); 8.09 (d, 1 H, NHP(O), $^2J_{H,P}$ = 5.6 Hz). $^{13}C\{^1H\}$ NMR (c = 0.1 mol L^{-1}), δ: 13.96 (d, MeP, $^1J_{C,P}$ = 134.2 Hz); 14.10 (s, C$\underline{H}_3$CH$_2$); 22.66 (s, MeC$\underline{H}_2$); 26.77 (s, C$\underline{H}_2$CH$_2$N); 29.24 (s, C$\underline{H}_2$(CH$_2$)$_3$N); 29.27 (s, C$\underline{H}_2$(CH$_2$)$_2$N); 29.81 (s, C$\underline{H}_2$(CH$_2$)$_4$N); 31.82 (s, MeCH$_2$C$\underline{H}_2$); 39.92 (s, CH$_2$N); 121.03 (d, *o*-Ph, $^3J_{C,P}$ = 4.4 Hz); 125.26 (d, *p*-Ph, $^5J_{C,P}$ = 2.2 Hz); 129.62 (d, *m*-Ph, $^4J_{C,P}$ = 1.5 Hz); 149.71 (d, *ipso*-Ph, $^2J_{C,P}$ = 9.5 Hz); 154.93 (d, C=O, $^2J_{C,P}$ = = 2.2 Hz).

Method *B*. Finely powdered anhydrous $MgCl_2$ (19 mg, 0.20 mmol) was added to a solution of phenyl chloro(methyl)-phosphonate (1.53 g, 0.008 mol) in anhydrous acetonitrile (15 mL) with stirring on a magnetic stirrer under argon at ~20 °C. The mixture was stirred until complete dissolution of $MgCl_2$, followed by addition of NaOCN (1.04 g, 0.016 mol) and stirring for another 3 h at this temperature. The suspension obtained was treated by octylamine (1.01 g, 7.84 mmol) and stirred for another 1 h at ~20 °C. The solvent was evaporated *in vacuo*, the residue was treated with a mixture of DI water (30 mL) and acetonitrile (5 mL). The suspension obtained was stirred for 2 h, a precipitate formed was filtered off, sequentially washed with a mixture of DI water (17 mL) and acetonitrile (3 mL), a mixture of 1% aq. hydrochloric acid (28 mL) and acetonitrile (2 mL), and DI water (4×20 mL), then dried in air. The yield was 2.30 g (88%), m.p. 85—86 °C. Spectroscopic characteristics of the product obtained were identical to the characteristics of the compound synthesized by method *A*.

***N*-[Ethoxy(phenyl)phosphoryl]-*N′*-*n*-octylurea (3).** Finely powdered anhydrous $MgCl_2$ (19 mg, 0.20 mmol) was added to a solution of ethyl chloro(phenyl)phosphonate (1.63 g, 8 mmol) in anhydrous acetonitrile (15 mL) with stirring on a magnetic stirrer under argon at ~20 °C. The mixture was stirred until complete dissolution of $MgCl_2$, followed by addition of NaOCN (1.03 g, 0.016 mol) and stirring for 2 h at ~20 °C. The suspension obtained was treated with octylamine (0.85 g, 6.56 mmol) and stirred for 1 h at ~20 °C. DI water (30 mL) was added and the mixture was stirred for another 1 h at this temperature and then was allowed to stand for ~14 h. A precipitate was filtered off and further treated similarly to the synthesis of compound **2** by method *B*. The yield was 2.24 g (77%), m.p. 115.5—116 °C. Found (%): C, 60.04; H, 8.64; N, 8.19; P, 9.08. $C_{17}H_{29}N_2O_3P$. Calculated (%): C, 59.98; H, 8.59; N, 8.23; P, 9.10. IR, ν/cm^{-1}: 1215 (P=O); 1680 (C=O); 3320, 3170, 3090 (NH). $^{31}P\{^1H\}$ NMR (c = 0.05 mol L^{-1}), δ: 16.9 (s). ^1H NMR (c = 0.05 mol L^{-1}), δ: 0.86 (t, 3 H, Me, $^3J_{H,H}$ = 7.1 Hz); 1.16—1.32 (m, 10 H, Me(C$\underline{H}_2$)$_5$); 1.38 (t, 3 H, C$\underline{H}_3$CH$_2$O, $^3J_{H,H}$ = 7.0 Hz); 1.34 (quint, 2 H, C$\underline{H}_2$CH$_A$CH$_B$N, $^3J_{H,H}$ = 6.9 Hz); 3.15 (ddt, 1 H, CH$_B$N, $^2J_{H_A,H_B}$ = 13.4 Hz, $^3J_{CH,H}$ = 6.9 Hz, $^3J_{NH,H}$ = 5.9 Hz); 3.17 (ddt, 1 H, CH$_A$N, $^2J_{H_A,H_B}$ = 13.4 Hz, $^3J_{CH,H}$ = 7.1 Hz, $^3J_{NH,H}$ = 5.6 Hz); 4.14—4.27 (m, 2 H, CH$_2$O); 6.94 (br.t, 1 H, CH$_A$CH$_B$N$\underline{H}$); 7.28 (d, 1 H, NHP(O), $^2J_{H,P}$ = 6.5 Hz); 7.44 (dt, 2 H, *m*-Ph, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,P}$ = 4.4 Hz); 7.54 (dtt, 1 H, *p*-Ph, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = $^5J_{H,P}$ = 1.2 Hz); 7.83 (ddd, 2 H, *o*-Ph, $^3J_{H,H}$ = 7.7 Hz, $^3J_{H,P}$ = 13.8 Hz, $^4J_{H,H}$ = 1.4 Hz).

***N*-[Phenoxy(phenyl)phosphoryl]-*N′*-*n*-octylurea (4).** Finely powdered anhydrous $MgCl_2$ (19 mg, 0.20 mmol) was added to a solution of phenyl chloro(phenyl)phosphonate (2.00 g, 7.92 mmol) in anhydrous acetonitrile (15 mL) with stirring on a magnetic stirrer under argon at ~20 °C. The mixture was stirred until complete dissolution of $MgCl_2$ (warmed up with hot water for 15 min). Then, NaOCN (1.04 g, 0.016 mol) was added and the mixture was stirred for 10 h at ~20 °C. The suspension obtained was treated with octylamine (0.84 g, 6.5 mmol) and the mixture was stirred for 1 h at ~20 °C, quenched with DI water (30 mL), and stirred for another 1 h at this temperature, then it was allowed to stand for ~14 h. A precipitate was filtered off and further treated similarly to the synthesis of compound **2** by method *B*. The yield was 1.60 g (73%), m.p. 145—146 °C (hexane—chloroform). Found (%): C, 65.02; H, 7.61; N, 7.21; P, 7.92. $C_{21}H_{29}N_2O_3P$. Calculated (%): C, 64.93; H, 7.53; N, 7.21; P, 7.97. IR, ν/cm^{-1}: 1240, 1205 sh (P=O); 1690 (C=O); 3340, 3160, 3095 (NH). $^{31}P\{^1H\}$ NMR (c = 0.05 mol L^{-1}),

δ: 15.2 (s). ^{1}H NMR (c = 0.05 mol L^{-1}), δ: 0.84 (t, 3 H, Me, $^3J_{H,H}$ = = 6.8 Hz); 1.12—1.32 (m, 10 H, Me(C$\underline{H}_2$)$_5$); 1.38 (quint, 2 H, C$\underline{H}_2$CH$_A$CH$_B$N, $^3J_{H,H}$ = 6.3 Hz); 3.06 (ddt, 1 H, CH$_B$N, $^2J_{HA,HB}$ = 13.2 Hz, $^3J_{H,H}$ = 6.5 Hz); 3.12 (ddt, 1 H, CH$_A$N, $^2J_{HA,HB}$ = 13.2 Hz, $^3J_{H,H}$ = 6.6 Hz); 6.63 (br.t, 1 H, CH$_A$CH$_B$N$\underline{H}$); 7.10—7.19 (m, 1 H, *p*-PhO); 7.20—7.30 (m, 4 H, *o*,*m*-PhO); 7.45 (dt, 2 H, *m*-PhP, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,P}$ = 4.4 Hz); 7.57 (t, 1 H, *p*-PhP, $^3J_{H,H}$ = 7.1 Hz); 7.95 (dd, 2 H, *o*-PhP, $^3J_{H,H}$ = 7.4, $^3J_{H,P}$ = 14.1 Hz); 8.10 (d, 1 H, NHP(O), $^2J_{H,P}$ = 7.2 Hz).

Solutions were prepared using bidistilled water, $CHCl_3$ (reagent grade), arsenazo III (analytical grade), HNO_3 (high purity grade), $UO_2(NO_3)_2 \cdot 6H_2O$ (reagent grade), $La(NO_3)_3 \cdot 6H_2O$ (reagent grade), $Nd(NO_3)_3 \cdot 6H_2O$ (reagent grade), $Ho(NO_3)_3 \cdot 6H_2O$ (pure grade), and $Yb(NO_3)_3 \cdot 6H_2O$ (pure grade). Solutions were prepared by the volumetric gravimetric method. Solution of lanthanide and actinide nitrates were prepared by the dissolution of weighed amounts of the corresponding nitrates in 0.01 *M* HNO_3. The concentration of the metal nitrate solutions (1 mmol L^{-1}) was refined spectrophotometrically according to the procedure described earlier[30] using a Cary50 Scan (Varian) spectrometer. The concentration of the HNO_3 solutions was determined by potentiometric titration with 0.1 *M* NaOH using a pH/ion Analyser Radelkis-125 model OP-300 with the accuracy ±0.01 pH units. The electrode pair was calibrated using the standard buffer solutions with pH 1.68, 4.01, and 9.22 (the values at 20 °C). The concentration of the NaOH solution was refined by potentiometric titration with 0.1 *M* HCl (fixanal).

Extraction of metal cations was studied using the following procedure. A solution of nitric acid (1.5 mL) with the concentration varying from 0.052 to 5.00 mol L^{-1}, a 1 m*M* solution of metal nitrate (0.5 mL), and a 0.01 *M* solution of ligand in $CHCl_3$ (2 mL) were placed into a test-tube with a ground-glass stopper. The phases were stirred for 20 min using a Multi RS-60 multirotator, BioSan, 80 rpm. The time of setting the extraction equilibrium was established by increasing the time of the contact of phases to 120 min and finding no changes in the distribution ratios. The phases were separated by centrifugation. After the phases were separated, the concentration of metals in the aqueous phase was determined using spectrophotometric method.[30] Three or more independent trials were carried out for each concentration. All the experiments were performed at 20±1 °C.

Distribution ratios ($D = [M]_{org}/[M]_{aq}$) were determined at the constant concentrations of the extractant (0.01 mol L^{-1} in $CHCl_3$) and metals (0.25 mmol L^{-1} in aqueous phase).

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