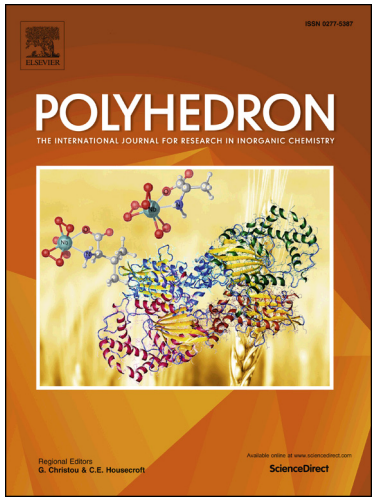

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Coordination and extraction of lanthanides(III) with tripodal ligands on the triphenylphosphine oxide platform: Effect of uncoordinating substituents

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Abstract
A ligand system containing three carbamoyl moieties secured onto a triphenylphosphine oxide platform ($2\text{-}R_2NC(O)CH_2OC_6H_4)_3PO$, where R = Me (**1**), Bu (**2**), and *cyclo*-Hex (**3**)) has been developed for lanthanide complexation and extraction from aqueous solutions. The influence of non-coordinating alkyl substituents at the nitrogen atoms in the carbamoyl side arms on coordination and extraction properties of tripodal ligands **1**–**3** was studied. Two new ligands **1** and **3** with alkyl substituents of different bulkiness were synthesized and characterized by spectroscopic methods. Single-crystal X-ray structures have been determined for ligands **1** and **2**. The selected coordination chemistry of ligands **1**–**3** with $Ln(NO_3)_3$ (Ln = La, Nd, Lu) has been evaluated. The 1:1 complexes of all ligands **1**–**3** were synthesized and characterized *via* elemental analysis and IR spectroscopy; in addition, the crystal structure of the ligand **1** complex with neodymium nitrate was determined by X-ray diffraction. Solution structure of 1:1 complexes was examined by IR and multinuclear (^1H, ^{13}C, and ^{31}P) NMR spectroscopy. A formation of 1:2 complexes with lanthanum and lutetium nitrates (IR, NMR, ESI-MS) has been examined and structure of the major components of 1:2 complexes solutions has been suggested for ligands **1**–**3**. Preliminary extraction studies of Ln(III) (Ln = La, Nd, Eu, Lu) from 3 M NH_4NO_3 into 1,2-dichloroethane show that ligands **2** and **3** recover lanthanides much better than their mono analog $[2\text{-}(Bu_2NC(O)CH_2O)\text{-}5\text{-}Et\text{-}C_6H_3]P(O)Ph_2$ and known extractant $Ph_2P(O)CH_2C(O)NBu_2$.

Key words: tripodal ligand, lanthanide complexes, X-ray diffraction, solution structure, liquid extraction

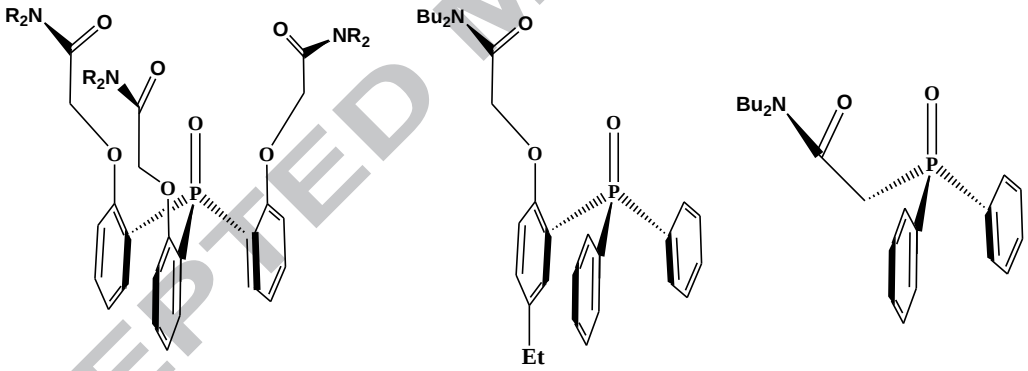
1. Introduction

Growing interest in lanthanide complexes is determined by both rich coordination chemistry of these elements and their unique physical and chemical properties allowing application of these compounds in different multidisciplinary areas such as bioinorganic chemistry and materials science [1]. Since the structure and properties of lanthanide complexes are affected by not only the unique properties of Ln(III) but also the structural features of organic ligand, the search for new ligating systems remains a challenging problem [2]. Among the most interesting ligands for Ln(III) cations, multidentate tripodal ligands attract special attention. The complexes and ligands of this type find an application in medical imaging and therapy [3], for transmembrane

transport [4], as synthetic sensors and receptors [5], as extractants [6], for designing single-molecule magnets [7], *etc*.

Recently, we reported the synthesis of tripodal ligand on $Ph_3P(O)$ platform with anchored carbamoyl side arms $(2\text{-}Bu_2NC(O)CH_2OC_6H_4)_3PO$ [8]. In the context of further development of this field, we have prepared new ligands of this type **1** and **3** (Scheme 1) and studied their coordination behavior toward lanthanide cations, which is determined by the same scaffold and may be affected by non-coordinating alkyl substituents at the nitrogen atoms in the side arms. As substituents, we selected methyl, butyl, and cyclohexyl groups. The ligand **1** with the smallest methyl group provides an example of a molecule with minimal hydrophobic and steric effects. Compounds with butyl (**2**) and cyclohexyl (**3**) groups will exhibit close lipophilicity. At the same time, cyclohexyl is bulkier than butyl and this fact can affect ligand coordination mode. We selected La(III), Nd(III), and Lu(III), located in the beginning, the middle and the end of lanthanide series. Furthermore, neodymium is often used as a typical cation in studies of lanthanides, while lanthanum and lutetium cations are not paramagnetic, that makes it possible to use NMR spectroscopy for studying their complexes.

In this paper, we disclose the preparation of new tripodal ligands (**1** and **3**) and 1:1 complexes of ligands **1**–**3** with lanthanide(III) nitrates, the characterization of all compounds in the solid state (X-ray crystallography for **1** and **2** and complex $[Nd(\mathbf{1})(NO_3)_3]$) and in solution by IR and multinuclear NMR (^1H, ^{13}C, ^{31}P) spectroscopy. Furthermore, we examined the possibility to form 1:2 complexes in solution. Complex stoichiometry was established by ESI-MS. Finally, the lanthanide extraction ability of these ligands from aqueous solution was studied using the mono analog **4** and known extractant **5** containing the same donor groups as reference compounds (Scheme 1).



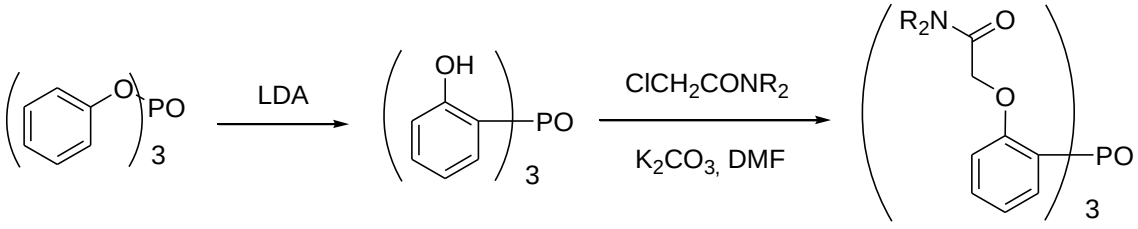
R = Me (**1**), Bu (**2**), *cyclo*-C_6H_{11} (**3**) **4** **5**

Scheme 1. Chemical structure of tripodal ligand **1**–**3** and reference compounds **4**, **5**.

2. Results and discussion

2.1. Synthesis and characterization of ligands 1, 3

The ligands **1**–**3** were obtained from available initial compounds in two stages by the following scheme:



1-3

Scheme 2. Synthesis of tripodal ligands **1**–**3**.

Initial tris(2-hydroxyphenyl)phosphine oxide (2-$HOC_6H_4)_3P(O)$ was obtained by the treatment of triphenyl phosphate with lithium diisopropylamide (LDA) [9] and next reacted with the appropriate N,N-dialkylchloroacetamides to give the corresponding ligands **1**–**3**. Both stages proceed in high preparative yield (82–90%) and allow preparation of the target compounds of high purity. We described the synthesis and spectral characteristics of ligand **2** in detail previously [8].

The composition and structure of the new ligands **1** and **3** were confirmed by the data of elemental analysis, IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. IR spectra of compounds **1** and **3** exhibit the bands of stretching vibrations of P=O at 1178 and 1183 cm^{-1}, respectively, and C=O in the region 1641–1670 cm^{-1}. Vibrations ν(C–O–C) are observed within the range 1260–1210 cm^{-1}. According to quantum chemical calculations, this mixed modes are related mainly to vibrations of three C_{Ar}–O bonds, containing some contribution of ν(P=O) [8].

^1H NMR spectra of compound **1** display signals of alkyl substituents at the nitrogen atoms in the expected region (2.73–2.84 ppm for ligand **1** and 1.15–3.24 ppm for ligand **3**). The proton signals of the CH_2O groups are observed at 4.52 and 4.31 ppm for ligands **1** and **3**, respectively. The aromatic protons appear at ~ 7.0 ppm as doublet of doublets (H-3), at 7.03 ppm as triplet (H-5), at ~ 7.44 as triplet (H-4) for both compounds, and at 7.64 and 7.73 ppm as doublet of doublets (H-6) for ligands **1** and **3**, respectively. ^{13}C NMR spectra display signals of alkyl and aryl carbon atoms of both compounds in the expected regions. Carbon resonances of C=O and CH_2O fragments are observed as singlets at ~ 167 and ~ 69 ppm, while that of C–P fragment appears as doublet at ~ 122 ppm ($^1J_{C,P}$ ~ 110 Hz). Phosphorus signal appears as singlet in the expected region at 23.9 and 24.8 ppm for **1** and **3**, respectively.

The structure of ligands **1** and **2** was finally established by X-ray diffraction.

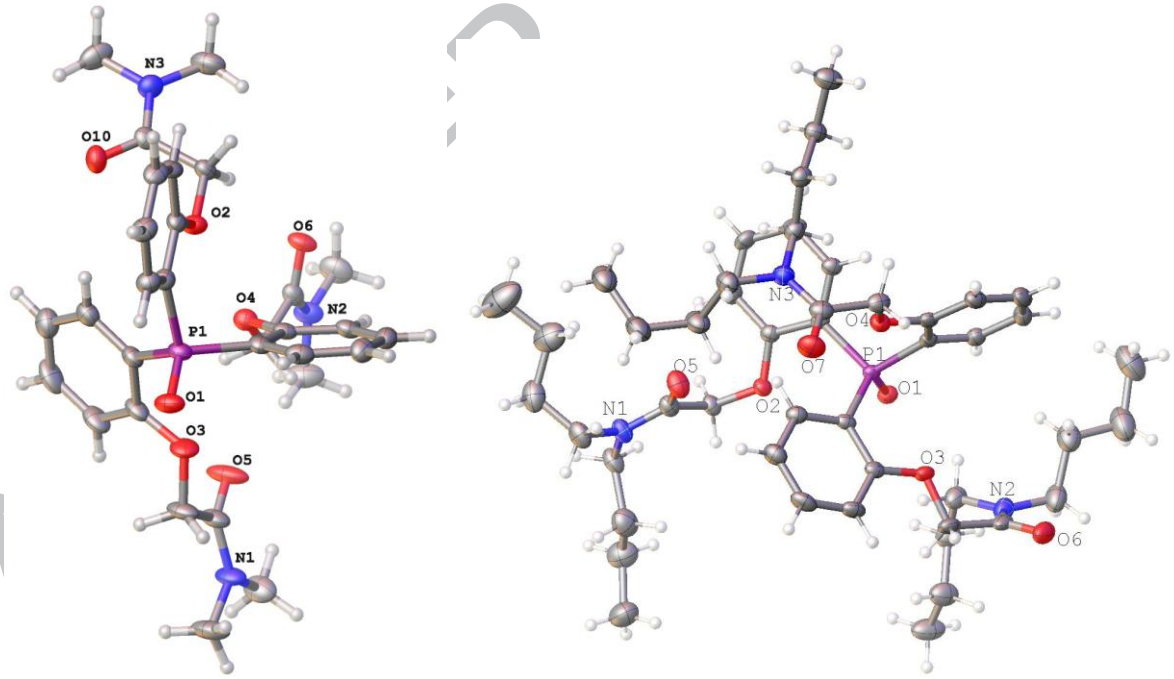


Fig. 1. Molecular view of ligands **1** (a) and **2** (b) in representation of atoms with thermal ellipsoids (given with 50% probability).

The molecules of ligand **1** and **2** in crystal have asymmetrical propeller conformations (Fig. 1). In the molecule of ligand **1**, one of the three *ortho* OCH_2 substituents is oriented to the same direction as the P=O group, while two other substituents are oriented to the opposite direction. On the contrary, in the molecule of ligand **2**, two *ortho* substituents are oriented to the same direction as the P=O group, while the third *ortho* substituent is directed to the opposite side. Ligands **1** and

2 display typical bond lengths and angles (Fig. 1). Selected bond distances are given in Table 1. The realization of coordination mode with concerted orientation of substituents to provide metal binding for these ligands requires the rotation of donor arms as compared with these conformations in the crystalline state. According to quantum chemical calculations [8], this coordination mode is the most probable.

2.2. Synthesis and solid state characterization of the complexes

Compounds **1**–**3** are tripodal polytopic ligands, whose molecules include strong donor P=O and C=O groups and weaker ether oxygen atoms of C–O–C groups, which also can participate in coordination to lanthanide cations. Worth mentioning that Fawcett and Platt [10] on the basis of X-ray data reported coordination of the ether oxygen atoms in lanthanide complexes of bis[(2-diphenylphosphino)phenyl]ether dioxide along with coordination of two P=O groups.

1:1 Complexes of ligands **1**–**3** with lanthanides nitrates—[$La(NO_3)_3$(**1**)] (**6**), [$Nd(NO_3)_3$(**1**)] (**7**), [$Lu(NO_3)_3$(**1**)] (**8**), [$La(NO_3)_3$(**2**)] (**9**), [$Nd(NO_3)_3$(**2**)] (lit. [8]) (**10**), [$Lu(NO_3)_3$(**2**)] (**11**), [$La(NO_3)_3$(**3**)] (**12**), [$Nd(NO_3)_3$(**3**)] (**13**), [$Lu(NO_3)_3$(**3**)] (**14**)—were prepared by the reaction of stoichiometric amounts of the ligand and the salts in a mixture of aprotic solvents. In the case of **8**, ligand **1** and lutetium nitrate were dissolved in MeCN. The composition and structures of the complexes in the solid state were studied using elemental analysis, and IR spectroscopy. The structure of the crystalline complex **7** was also elucidated by X-ray diffraction.

2.2.1. X-ray structure. According to the data of single-crystal X-ray diffraction, compound **7** is a neutral mononuclear complex, where the neodymium atom coordinates three nitrate anions in a bidentate-chelate mode (Fig. 2).

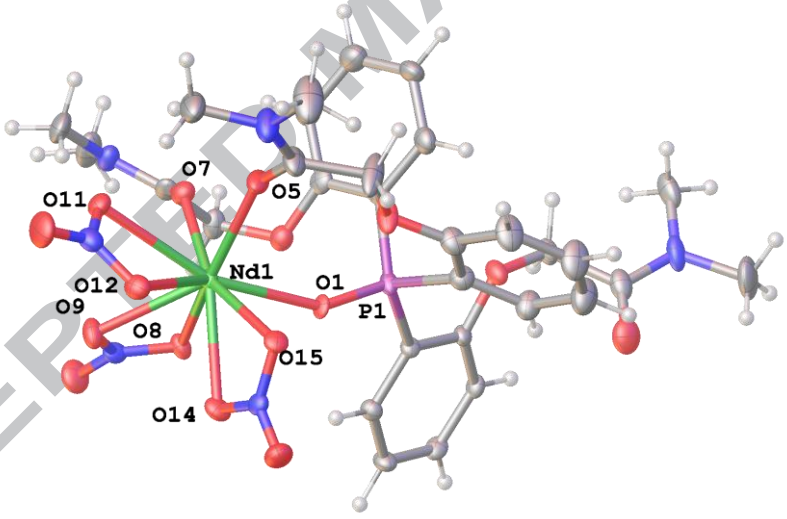


Fig. 2. Molecular view of complex **7** in representation of atoms with thermal ellipsoids (given with 50% probability).

The ligand **1** coordinates to the neodymium atom through the oxygen atoms of P=O and two C=O groups, while the third carbonyl group and all C–O–C oxygen atoms remain uncoordinated. The resulting NdO_9 coordination polyhedron adopts the tricapped trigonal prismatic geometry with oxygen atoms of **1** in one prism base and those of three nitrate anions in the second prism base and three "cap" atoms. The Nd–O bonds to the ligand **1** are significantly shorter than those between metal atom and the anions (Table 1).

Table 1. Selected bond distances (Å) in **1**·DMF, **2** and **7**·0.5MeCN.

Bond	**1**· DMF	**2**	**7**· 0.5MeCN
Ln–O(P)			2.359(3)
Ln–O(C)			2.397(4) – 2.424(4)
Ln–O(N)			2.531(4) – 2.644(4)
P=O	1.486(3)	1.485(1)	1.518(4)
C=O (free)	1.223(5) – 1.232(4)	1.225(2) – 1.239(2)	1.220(8)

C=O (coordinated)	1.256(7) – 1.279(7)

The coordinated C=O and P=O bonds are elongated as compared with the free ones, and ligand conformation also differs from that of crystalline ligand **1**. In complex, two of three carbonyl groups and oxygen atoms of C–O–C groups are oriented to the same direction as the P=O group in contrast to crystalline **1** where only one carbonyl group is directed in the same mode as the P=O group.

2.2.2. IR spectroscopy characterization. The data of IR spectra for complex **7** agree well with the coordination modes from the X-ray data. The formation of the P=O → Nd coordination bond results in the shift of the ν(P=O) band in the IR spectra of crystalline complexes **7** by ~50 cm^{-1} to the low frequency region with respect to the band of the free ligand (1178 cm^{-1}). The formation of two C=O → Nd coordination bonds in complex **7** causes a shift of the ν(C=O) bands to the low frequency region. A strong band appears at 1629 cm^{-1} and a weak band appears at 1647 cm^{-1} that corresponds to vibrations of coordinated C=O groups. The weak band at 1660 cm^{-1} unambiguously refers to the noncoordinated C=O group. The oxygen atoms of C–O–C groups are non-coordinated, however, the bands in the region 1270–1210 cm^{-1} that belong to ν(C–O–C) vibrations change, thus responding to coordination of phosphoryl group (Table. 2). Let us note that the spectral appearance of coordination of C–O–C groups could not be determined unambiguously because, according to quantum chemical calculations [8], the bands in the region 1260–1210cm^{-1} are related to mixed modes and include contribution of both C_{Ar}–O and ν(P=O) bond vibrations.

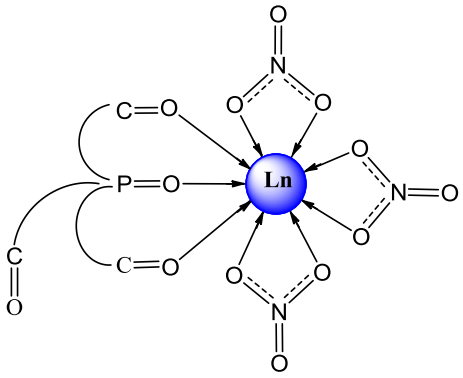
Table 2. Selected IR (ν, cm^{-1}) spectroscopic data for ligands **1**–**3** and their 1:1complexes with lanthanide nitrates **6**–**14** in crystalline[a] and solid state

Compound	ν(P=O)	ν(C=O)	ν(C–O–C)
1[a]	1178m	1671vs, 1666vs	1260m, 1238s
6	1121m	1660sh, 1631vs	1245m, 1228sh
7[a]	1126m	1660sh, 1647sh, 1629s	~1250sh, 1232m
8	1185sh,1180m	1670s, 1660sh, 1630s	1258m, 1239m
2[a]	1181s,	1669s, 1654vs, 1648sh	1244sh, 1236m, 1221sh, 1212m
9	1121m	1665sh, 1630sh, 1610vs	1255m, 1233m, 1218m
10 [8]	1128m	1658sh, 1632sh, 1608vs	1245sh,1235sh, 1218m
11	~1120sh[b]	1660sh, 1638sh, 1613s	1238m, 1216m
3	1183m	1660sh, 1641vs	1225m, 1210sh
12	1122m	1656m, 1630sh, 1606vs	1230m, 1210sh
13	1123m	1660sh, 1625sh, 1604s	1230m, 1210sh
14	1123m	1659s, 1630sh, 1608s	1230m, 1210sh

[b] Shoulder of band at 1142 cm^{-1}.

The strong broad IR bands of bidentately coordinated NO_3 groups are detected at 1480 and 1290 cm^{-1} and relatively weak band is revealed at 1032 cm^{-1}. According to X-ray crystallographic data, crystalline complex **7** contains 0.5 solvate acetonitrile, but the IR spectra of this sample exhibit no absorption for the CN group.

The IR spectra of complexes **6**, **9**–**14** are similar to those of crystalline complex **7** (Table 2), which indicates tridentate P(O),C(O),C(O)-coordination of the corresponding ligand and bidentate coordination of three NO_3 groups in these complexes (Scheme 3).



Scheme 3. 1:1 Complexes in the crystalline (**7**) and solid (**6**, **9**–**14)** state as well as in CD_3CN (**6**, **7**) and in $CDCl_3$ (**9**–**14**) solutions.

Ln(III) cations in these complexes have coordination number 9.

Complex **8** has another structure. In this complex, the P=O group of ligand **1** remains free (the spectrum retains band at 1180 cm^{-1} with a shoulder at 1185 cm^{-1}). Bands at 1630 cm^{-1} and 1670 cm^{-1} with a shoulder at ~ 1660 cm^{-1} refer to vibrations of coordinated and free C=O groups, respectively (Table 2). Taking into account that complex **8** is virtually insoluble in common organic solvents, one can suppose that ligand **1** exhibits chelate-bridge C(O),C(O)-coordination and binds two lutetium cations, whereas the P=O group and one C=O group remain free and three nitrate ions are coordinated in bidentate mode. Complex **8** has polymer structure. The coordination number of lutetium is eight.

Let us note that complexes of monoligand **4** with lanthanide nitrates are unknown, however, the structure of several complexes of model ligand **5** were studied by X-ray diffraction and IR spectroscopy [11,12]. The bidentate coordination of ligand **5** with lanthanide cation in the IR spectra of crystalline complexes results in the shift of ν(P=O) and νC=O bands by 30–50 and 30–40 cm^{-1}, respectively. The wide strong bands at ~1480 and ~1300 cm^{-1} and weak band at ~1032 cm^{-1} correspond to nitrato groups coordinated in bidentate mode. Nd(III), Pr(III), and Eu(III) cations in these complexes have coordination number 9 or 10.

2.3. Solution-state characterization of the complexes

The structure of the lanthanide nitrate complexes with ligands **1**–**3** in solutions was studied by IR and multinuclear NMR spectroscopy. The complexes of ligands **2** and **3** were studied in $CDCl_3$, while complexes of ligand **1** were investigated in CD_3CN because they are insoluble in chloroform.

The selected suitable for analysis parameters of IR and ^{31}P, ^{1}H, and ^{13}C NMR spectra for the solution of 1:1 complexes **6**, **7**, **9**–**14** in comparison with the data for the free ligands **1**–**3** are given in Tables 3–5. The tables also include the data for model solutions with metal : ligand ratios 1:2 for lanthanum and lutetium complexes. Model solutions for neodymium complexes were not studied, because neodymium paramagnetism hampers the use of NMR spectroscopy.

The coordination of the P=O group can be reliably determined from the NMR spectra of complexes. The signals of the phosphorus nuclei as well as carbon nuclei C-1 of neighboring groups exhibit corresponding downfield shifts (Tables 3–5) close to those for the known complexes of akin phosphoryl-containing ligands [13]. The signals of the paramagnetic neodymium complex show considerable broadening.

The participation of the C=O group in coordination appears in the ^{13}C and ^{1}H NMR spectra as a downfield shift of the carbon signals of the C=O group relative to the free ligand signals [13a,14]. The proton and carbon resonances of neighboring CH_2 groups also display the corresponding shifts (Tables 3–5). The participation of C–O–C ethereal oxygen atoms in coordination should result in the shift of resonances for neighboring C-2 and CH_2 groups. The shift of C-2 nucleus is more reliable indicator of ethereal oxygen coordination, because the signal of –CH_2– group will respond to coordination of both carbonyl and ethereal oxygen atoms.

Table 3. Selected IR (ν, cm^{-1}) and $^{31}P\{^{1}H\}$, ^{1}H and ^{13}C NMR (δ, ppm; ($W_{½}$)[a], ppm) spectroscopic data for the ligand **1** and their complexes with lanthanide nitrates in CD_3CN (0.01 M) at 25 °C

Sample	ν(P=O)	ν(C=O)	δ_P ($W_{½}$)	δ_H ($OC\underline{H}_2$)	δ_C (C=O)	δ_C ($O\underline{C}H_2$)
1	1178m	1669vs, 1654s	23.9 s (0.01)	4.48 s	166.98 s	67.47 s
6	1126m	1669m,1650sh, 1630vs	32.0 s (0.05)	4.73 s	168.48 s	65.82 s
(**6**+**1**[b])[c]	1123m	1668m, 1653sh, 1635s	30.7 s (0.26);	4.6 br s	–[d]	65.97 s
7	1128m	1669m, 1643sh, 1625s	121 (1)	3.4-3.6 v br s	–[d]	62.0 s

[a] The band width at half-height (in ppm);
[b] Ligand **1** added to solution of complex (Ln:L = 1:2) (see Section 4.4.);
[c] The medium band at 1356 cm^{-1} – $\nu_E(NO_3)$; signals of minor component in ^{1}H and ^{31}C NMR spectra; additional singlet at 44.9 ppm (~ 3%) in ^{31}P NMR spectrum (see Section 2.3.2.1.);
[d] Not observed.

Table 4. Selected IR (ν, cm^{-1}) and $^{31}P\{^{1}H\}$, ^{1}H and ^{13}C NMR (δ, ppm) spectroscopic data for the ligand **2** and their complexes with lanthanide nitrates in $CDCl_3$ (0.02 M) at 25 °C

Sample	ν(P=O)	ν(C=O)	δ_P ($W_{½}$)[a]	δ_H ($OC\underline{H}_2$)	δ_C (C=O)	δ_C ($O\underline{C}H_2$)	δ_C (C-1)
2[16]	1175m	1662s, 1639vs	24.4 (0.01)	4.40 s	167.34 s	68.71 s	122.21 d
9	1128m	1662m, 1630sh, 1619s	31.4 (0.4)	4.7 v br s	167.7 v br s	65.97 s	~117.7 v br d
(**9**+**2**[b])[c]	1123m	1660s, 1620vs	30.0 (0.5)[d]	4.6 br s	167.6 v br s	66.5 br s	~118 v br d
10[16]	1130m	1661m, 1630sh, 1616s	121 (7.6)	3.4–3.8 v br s	–[e]	ca. 62 v br s	–[e]
11	1175[f]	1625s	34.2 (0.3)	4.7 br s	167.80 s	65.60 s	117.44 d
(**11**+**2**[b])[c]	1128m	1658s, 1642sh, 1617s	34.0 (0.9)[g]	4.6 br s	167.7 v br s	65.4_5 br s	~117.6 v br d

[a] The band width at half-height (in ppm);
[b] Ligand **2** added to solution of complex (Ln:L = 1:2) (see Section 4.4.);
[c] The medium band at 1356 cm^{-1} – $\nu_E(NO_3)$ (see Section 2.3.2.2.);
[d] Additional overlapping signal at 31.1 ppm;
[e] Not observed;
[f] Shoulder of the band at 1166 cm^{-1};
[g] Minor signal at 25.3 ppm.

Table 5. Selected IR (ν, cm^{-1}) and $^{31}P\{^{1}H\}$, ^{1}H and ^{13}C NMR (δ, ppm) spectroscopic data for the ligand **3** and their complexes with lanthanide nitrates in $CDCl_3$ (0.02 M) at 25 °C

Sample	ν(P=O)	ν(C=O)	δ_P ($W_{½}$)[a]	δ_H (OC<u>H</u>$_2$)	δ_C (C=O)	δ_C (O<u>C</u>H$_2$)	δ_C (C-2)
3	1183m	1659s, 1636m	24.8 (0.01)	4.29 s	166.81 s	70.33 s	161.24 d
12	1125m	1659m, 1625sh, 1606vs	31.4 (0.5)	4.6 br s	167.3 br s	69.0 v br s	159.97 s
(**12**+**3**[b])[c]	1125m	1658s, 1625sh, 1608vs	31.2 (1.1)[d]	4.25 br.s, ~4.8 v br s	~167.8 br s	70.0 v br s, 66.1 br s	160.0 br s;165.0 br s
13	1125m, 1150sh[e]	1659m, 1625sh, 1606vs	93 (5.4)	–[f]	–[f]	66.5 v br s	–[f]
14	1125m	1656s, 1623s, 1608sh	35.7 (0.6); 35.1 (0.5)[g]	4.7 br s	~166.6 v.br s	68.1 br s	160.18 d
(**14**+**3**[b])[c]	1125m,1183w	1656s, 1630sh, 1608s	37.0 (1.5), 35.0 (1.1), 25.2 (0.6)[h]	4.32 br s, 4.0–4.7 vv br s	166.79 s, 169.3 br s;	70.0 br s; 68.2 br s, 67.2 br s	161.11 s;160.15 br s, 165.0 br s

[a] The band width at half-height (in ppm);
[b] Ligand **3** added to solution of complex (Ln:L = 1:2) (see Section 4.4.);
[c] The medium band at 1356 cm^{-1} – $\nu_E(NO_3)$ (see Section 2.3.2.3.);
[d] Minor signals at 36.5 and 45.4 ppm;
[e] Shoulder of the band at 1166 cm^{-1};
[f] Not observed;
[g] Integral intensity ratio ~2:1;
[h] Integral intensity ratio ~ 1.1:2.8:1.

2.3.1. 1:1 Complexes

The IR spectrum of complex **7** in solution virtually retained when compared with the spectrum of the crystalline sample (Tables 2, 3). The band of the coordinated P=O group is detected at 1128 cm^{-1}, the bands of coordinated C=O and free C=O groups are observed at 1625 and 1669 cm^{-1}, respectively. The bands at ~1450 and ~1310 cm^{-1} correspond to nitrato groups coordinated in bidentate mode. One can suppose that the ligand **1** is coordinated in a P(O),C(O),C(O)-tridentate mode and compound **7** in CD_3CN solution is present as mononuclear neutral complex $[Nd\{P(O),C(O),C(O)\text{-}\mathbf{1}\}(OO\text{-}NO_3)_3]^0$ (Scheme 3).

NMR spectra of complex **7** provide little information owing to paramagnetic properties of Nd but generally agree well with the proposed structure. The ^{31}P NMR spectrum displays only one broadened signal at 121 ppm. The signals in ^{1}H NMR spectrum are very broadened and could not be interpreted. In ^{13}C NMR spectrum, no signals of *ipso*–Ph and C=O were observed. On account of the lack of fine structure, the assignment of signals of aromatic protons is impossible; the signals of Me and CH_2O groups display expected shifts (Table 3).

The IR spectra of complexes **6** and **7** are virtually identical (Table 3), which enables us to suppose that the complexes have the same structure (Scheme 3). NMR spectral data agree well with the suggested structure (Table 3). The $^{31}P\{^{1}H\}$ NMR spectrum of solution of complex **6** shows one broadened ($W_{½}$ = 0.5 ppm) singlet at 32.0 ppm shifted downfield toward the signal of the free ligand. The participation of the C=O groups in coordination appears in the ^{13}C NMR spectrum as a downfield shift of the carbon signals of the C=O groups. Signal change for neighboring groups (OCH_2, C-2, etc.) in ^{1}H and ^{13}C NMR spectra (Table 3, Fig. B1, B2) confirms the conclusion on the coordination of P=O and two C=O groups. No signal of C-1 nucleus is observed in the spectrum because it falls in the solvent signal at ~117 ppm on expected upfield shift by ~4.5 ppm. One can suppose that compound **6** in CD_3CN solution, like complex **7**, is present as mononuclear neutral complex $[La\{P(O),C(O),C(O)\text{-}\mathbf{1}\}\ (OO\text{-}NO_3)_3]^0$ (Scheme 3).

The analysis of spectral data for solutions of 1:1 complexes of the studied ligands **1**–**3** with lanthanum and neodymium nitrates (Tables 3–5) indicate that they have similar structure. The structure of 1:1 complexes in solution is the same as in solid state. Irrespective of the nature of substituent at the nitrogen atom, ligand molecules **1**–**3** in the corresponding mononuclear neutral complexes **6**, **7**, **9**, **10**, **12**, and **13** exhibit P(O),C(O),C(O)-tridentate coordination (Scheme 3).

In contrast to the spectra of 1:1 complexes of light lanthanides, the structure of 1:1 lutetium complexes changes on passing from solid state to solutions. The spectral data for lutetium complex of ligand **2** are the most unusual. The IR spectrum of solution of lutetium complex **11** shows the band of free P=O groups at 1174 $cm^{\subseteq 1}$. The sole band with maximum at 1625 $cm^{\subseteq 1}$ belongs to coordinated C=O groups. The bands of nitrate ions with bidentate coordination mode are observed. The ^{1}H and ^{13}C NMR spectral data agree well with assumption on the coordination of all three C=O groups (Table 4).

The changes in chemical shifts ($\Delta\delta_H$) for the $C\underline{H}_2O$ and ($\Delta\delta_C$) for C=O and $\underline{C}H_2O$ groups (Table 4) confirm the assumption on the coordination of all three C=O group. Let us note that the ^{13}C NMR spectra of complex **11** (Fig. B3) and previously studied $[\{Lu(NO_3)_3\}_2(\mathbf{2})]$ complex [8] show no broadening for all ^{13}C nuclei, as distinct from the spectra of other complexes of ligand **2** (Table 4). At the same time, the $^{31}P\{^{1}H\}$ NMR spectrum shows the only signal at 34.2 ppm shifted relative to the signal of free ligand by 9.8 ppm, which evidences the formation of P=O→Lu coordination bond.

Thus, according to NMR spectra, the ligand in complex **11** is coordinated in tetradentate mode, but, as distinct from the data of IR spectroscopy, there are no direct evidences on the presence of non-coordinated P=O group. This contradiction seems to be explained by the nature of both methods. The chemical shift of nuclei in lanthanide complexes is determined by contact (along the chain of chemical bonds) and pseudocontact (through the space) interaction of the nuclei with lanthanide atom [15]. The spatial structure of the coordination site of ligand **2** (Fig. 3) has such a configuration that, at symmetrical tridentate coordination of all three C=O groups, the lutetium

atom will be disposed virtually above the P=O group even in the lack of P(O)→Lu coordination bond and the pseudocontact interaction of O and Lu nuclei will be sufficiently strong (Fig. 3)

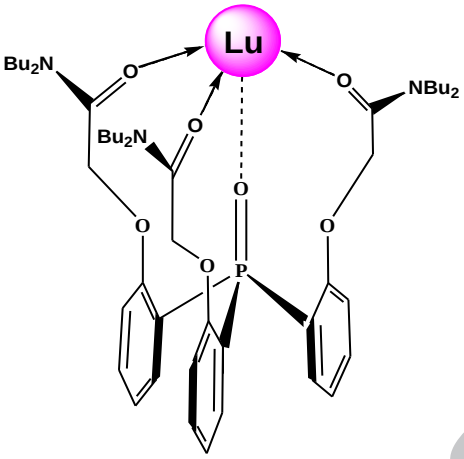


Fig. 3. Visualization for the spatial structure of C(O),C(O),C(O)-coordinated ligand **2** in 1:1 complex with Lu(III). Ligand conformation corresponds to the global minimum [8].

We believe that this type of coordination of ligand **2** (without involvement of the P=O group) occurs in solutions of lutetium complexes with metal : ligand ratio 1:1 (this work) and 2:1 [8]. All nitrate ions in complex **11** are coordinated in bidentate mode, lutetium cation has coordination number 9.

Although IR spectrum of 1:1 complex **14** (Table 5) is the same as the spectrum of solid complex (Table 2), the data of NMR spectra allow us to suppose the presence in solution of two (or several) complex forms. This assumption is supported by the presence of two signals in $^{31}P\{^{1}H\}$ NMR spectrum at 35.7 and 35.1 ppm with integral intensity ratio ~ 2:1. Usually, such a shape of spectrum is explained by the presence of equilibrium between neutral and cationic (as a contact ion pair) complexes of ligand with coordinated P=O group (*vide infra*, [13c]). The structures $[Lu\{P(O),C(O),C(O)\text{-}\mathbf{2}\}(NO_3)_3]^0$ (Scheme 3) and $[Lu\{P(O),C(O),C(O)\text{-}\mathbf{2}\}(NO_3)_2]^+\cdot(NO_3)^-$ are the most likely. The data of ^{1}H and ^{13}C NMR (Table 5) do not contradict this assumption. The coordination number of lutetium in these complexes is 9 or 7.

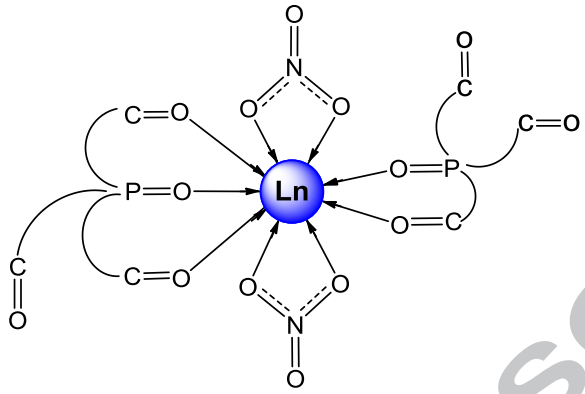
Thus, the nature of substituents at the nitrogen atom has no effect on the structure of 1:1 complexes of light lanthanides in both solid state and solutions. In neutral mononuclear lanthanum and neodymium complexes, the ligands display tridentate P(O),C(O),C(O)-coordination. For lutetium, which has the smallest radius, the structure of complexes in solution considerably differs from that in solid state and depends on the nature of substituent at the nitrogen atom. Ligand **2** shows C(O),C(O),C(O)-coordination mode instead of P(O),C(O),C(O)-mode, whereas ligand **3** produces ionic complex along with neutral one.

2.3.2. Formation of 1:2

Since lanthanides(III) have large coordination numbers (up to 12), we examined the possibility for the formation of 1:2 complexes with lanthanum and lutetium nitrates. The spectral data for model solutions of 1:2 composition are given in Tables 3–5.

The major feature of IR spectra of all 1:2 complexes as compared with 1: 1 complexes is the emergence of a band of "free" nitrate ion at ~1355 cm^{-1} and intensity redistribution for the bands of coordinated and uncoordinated C=O group. The band of coordinated P=O group, as previously, is observed at ~ 1125 cm^{-1}. The spectrum retains the bands of nitrato groups coordinated in bidentate mode. ^{31}P NMR spectra exhibit additional minor signals and broadening of the main signal of coordinated P=O group. The signals in ^{1}H NMR spectra undergo considerable broadening, which prevents adequate interpretation of the spectra. The ^{13}C NMR spectra also display additional minor signals, but the main difference consists in change in the chemical shift for C-2 nucleus in the spectra of 1:2 complexes of ligand **3** (*vide infra*).

2.3.2.1. Ligand 1 complexation with $La(NO_3)_3$ at La:L ratio of 1:2 in CD_3CN. In accordance with the spectral data in Table 3 and the arguments given above, one can suppose that 1:2 complex of ligand **1** is a contact or solvent-separated ion pair where one ligand molecule is coordinated in a P(O),C(O),C(O) tridentate mode, while another molecule coordinates in P(O),C(O)-bidentate mode; lanthanum coordination number is 9 (Scheme 4).



Scheme 4. Cation of 1:2 complexes of ligands **1**, **2** with $Ln(NO_3)_3$ (Ln = La, Lu) in solution.

Taking into account the typical lanthanum coordination number of ten, one can also suppose that coordination of acetonitrile molecule is possible. The ^{31}P NMR spectrum shows additional narrow singlet at 44.9 ppm of a minor component (~3%) that causes supplementary signals in ^{1}H and ^{13}C NMR spectra. Let us note that NMR spectra of 1:2 complexes of ligand **1** display the least number of additional signals and the smallest broadening as compared with the spectra of complexes from ligands **2** and **3** (*cf*. Tables 3–5). No signal of C-1 nucleus expected due to shift at ~117 ppm was observed because it is obscured by the solvent signal, while the shift of signal from C-2 is small (0.32 ppm).

2.3.2.2. Ligand 2 complexation with $Ln(NO_3)_3$ (Ln = La, Lu) at Ln:L ratio of 1:2 in $CDCl_3$. The spectral data for solution with La:L = 1:2 for ligand **2** are close to those for ligand **1** (*cf*. Table 3 and 4) except for larger line broadening in NMR spectra and emergence of an additional signal in ^{31}P NMR spectrum at ~ 31.1 ppm. In accordance with these data, one can suppose that bisligand complex of ligand **2** also has structure shown in Scheme 5. Since La(III) cation typically has coordination number 10 and chloroform does not show coordinating properties, one can suppose that the main component $[La\{P(O),C(O),C(O)\text{-}\mathbf{2}\}\{P(O),C(O)\text{-}\mathbf{2}\}(NO_3)_2]^+\cdot(NO_3)^-$ is in equilibrium with a second complex where both ligand molecules are coordinated in tridentate mode $[La\{P(O),C(O),C(O)\text{-}\mathbf{2}\}_2(NO_3)_2]^+\cdot(NO_3)^-$. This assumption explains the presence of two close broadened signals in ^{31}P NMR spectrum. The data of ^{1}H and ^{13}C NMR spectra agree well with suggested structures.

Spectral data for solution with Lu:L = 1:2 (Table 4) allow us to suppose that the lutetium and lanthanum complexes of 1:2 composition have the same structure (Scheme 4). Difference is the presence of trace signals of minor component at δ_P ~ 25.3 ppm in the spectrum of the lutetium complex, which enables one to suppose either ligand coordination without participation of the P=O group or the presence of free ligand. ^{1}H and ^{13}C NMR spectra provide no possibility to clarify the structure of the minor component.

2.3.2.3. Ligand 3 complexation with $Ln(NO_3)_3$ (Ln = La, Lu) at Ln:L ratio of 1:2 in $CDCl_3$. The IR spectrum of solution at La:L = 1:2 is the same as for other 1:2 complexes (Tables 3–5). Certain variations in spectra in the region 1270–1210 cm^{-1} could not be interpreted unambiguously. Difference is visible in NMR spectra (Table 5).

The signal in $^{31}P\{^{1}H\}$ NMR spectrum is shifted downfield by 6 ppm relative to the signal of free ligand and considerably broadened (Table 5). Moreover, the spectrum exhibits trace signals at 36.5 and 45.4 ppm, which can be related to cationic complexes with larger charge than that of the main complex species. The signals in ^{1}H NMR spectrum are considerably broadened and poorly interpretable. Analytical signals in the ^{13}C NMR spectrum presented in Table 5 are broadened. The

shift of broadened signal by $\Delta\delta_C$(C=O) ~ 1 ppm indicates that a part of C=O groups are involved in coordination. The major feature of ^{13}C NMR spectrum is the emergence of a broadened signal of C-2 at ~ 165 ppm along with a signal at 160.0 ppm (Fig. B4). We believe the first signal to indicate bidentate coordination of ligand molecule *via* P=O group and the ethereal oxygen atom (Fig. 4), while the second signal present in the spectra of all studied complexes and shifted relative to the corresponding signal of free ligand by 1.0–1.2 ppm is related to the ligand in P(O),C(O),C(O)-tridentate coordination mode.

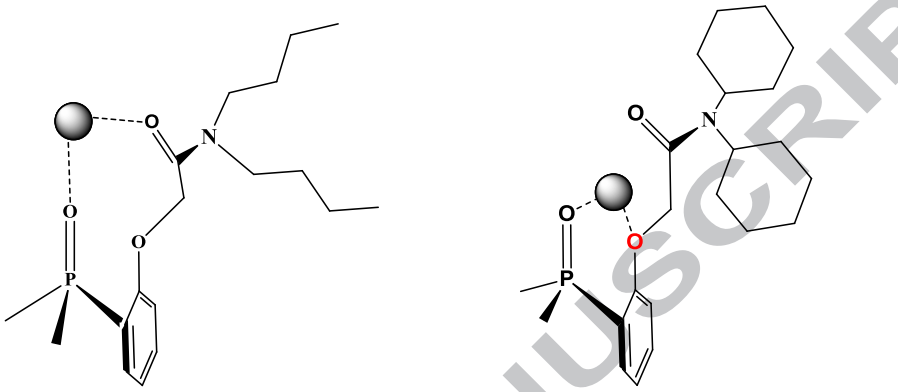
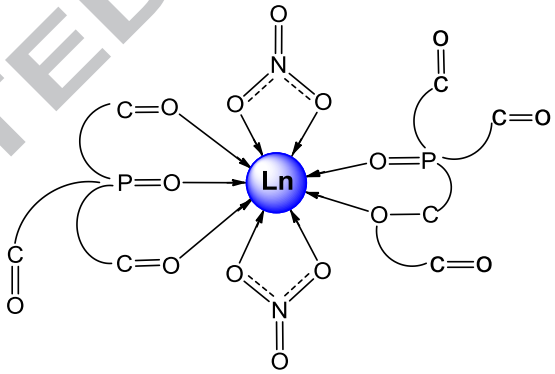


Fig. 4. Visualization for the portion of the spatial structure of P(O),C(O)-coordinated ligand **2** (a) and of P(O),O_{eth}-coordinated ligand **3** (b) in 1:2 complexes with Ln(III).

In accordance to the body of IR and NMR spectral data, the structure of the major component of 1:2 complex can be represented by Scheme 5. Lanthanum has coordination number 9.



Scheme 5. Cation of 1:2 complexes of ligand **3** with $Ln(NO_3)_3$ (Ln = La, Lu) in chloroform solution.

Other cationic complexes, in particular cationic complex in Scheme 5, seem to exist in equilibrium with this complex, which agrees well with change in the band intensity of C=O groups observed on comparison of IR spectra of 1:2 lanthanum complexes of ligands **2** and **3** (see Tables 4 and 5).

Such considerable changes in ligand coordination mode are caused by the replacement of butyl substituents at the nitrogen atom by the bulkier cyclohexyl fragments. In spite of much lower donor ability of the ethereal oxygen atom as compared with carbamoyl one $R_2NC(O)$, the steric hindrances on coordination of the second ligand molecule lead to change in coordination mode. Let us note that P(O),P(O),O_{eth}-tridentate coordination mode with participation of ethereal oxygen atom was detected by X-ray diffraction method in 1:2 complexes of bis[(2-diphenylphosphino)phenyl]ether dioxide with lanthanide halides [10].

The IR spectrum of solution at Lu:L = 1:2 in the region of C=O vibrations is similar to the spectrum of solution at La:L ratio of 1:2 for this ligand (see Table 5). However, in contrast to the

latter spectrum, the spectrum of 1:2 solution with lutetium nitrate shows a weak band of uncoordinated P=O group at 1183 cm^{-1}, while the intensity of the band of "free" nitrate ion at ~ 1360 cm^{-1} is larger. The $^{31}P\{^{1}H\}$ NMR spectrum displays three broadened signals at 37.0, 35.0, and 25.2 ppm with integral intensity ratio ~ 1.1 : 2.8 : 1 (Fig. B5). The signals of OCH_2 group in ^{1}H NMR spectrum are considerably broadened. In ^{13}C NMR spectrum, the signals of diagnostic C=O, O<u>C</u>H_2, and C-2 groups are complicated and detected at several values (Table 5). Thus, the signals of C-2 atom are detected at ~160.15 (br), 161.11, and ~165.1 (br) ppm, while broadened singlets of O<u>C</u>H_2 are observed at 70.0, 68.2, and 67.2 ppm. The signals of C=O are observed at 169.3 (broadened) and 166.79 ppm. The body of these data allows us to suppose the presence in solution of several complexes where the ligand exhibits coordination in different modes: P(O),C(O),C(O)-tridentate, P(O),O_{eth}-bidentate, as well as C(O),C(O)- and P(O),C(O)-bidentate coordinations. Moreover, cationic complexes may include two or one nitrate ions in coordination sphere, which makes spectral pattern more complicated.

Furthermore, using this solution as an example, we elucidate the reason of emergence of additional signals in $^{31}P\{^{1}H\}$ NMR spectra shifted downfield relative of the signal of free ligand. Previously (see above), we supposed that two phosphorus signals shifted downfield correspond to two complexes with the same ligand coordination mode but different number of nitrate ions in coordination sphere. These are exemplified by molecular complex $[Ln(NO_3)_3(\mathbf{L})_n]^0$ and cationic species as solvent-separated and/or contact ion pairs $[Ln(L)_n(NO_3)_2]^+ \cdot (NO_3)^-$. We described in detail the separate detection of molecular and ionic complexes earlier [13c]. Indeed, the addition of 10 moles of Bu_4NNO_3 to a solution with $Lu(NO_3)_3$: **3** = 1:2 leads to disappearance of signal at 37.0 ppm (Fig. B6), *i.e.*, the equilibrium is shifted toward molecular complex.

We used also ESI-MS to determine complex composition. Positive-ion electrospray mass spectral data for solutions of 1:1 complexes of ligands **2** and **3** in MeCN were recorded under the same experimental conditions. Peak assignment was made on the basis of analysis of isotope distribution and fragmentation of ions. The data of ESI-MS spectra for solutions of Ln(III) complexes are given in Table B1. Almost all spectra show a dominant peak corresponding to $[LnL_2(NO_3)]^{2+}$ ion (see as an example Fig. B7) and a number of additional peaks, such as $[LnL_2]^{3+}$, and $[LnL(NO_3)_2]^+$. However, there are no peaks that may be related to tris-ligand complex.

Let us note that, according to preliminary data, the majority of Ln(III) cations are extracted with ligands **2** and **3** as bis-ligand complexes (the study of extraction properties is in progress).

Thus, the structure of complexes of related ligands in solutions is determined by not only the main coordination modes caused by the same structure of ligand frame but also is considerably affected by the spatial properties of non-coordinated alkyl substituents at the nitrogen atom. In solutions of 1:1 complexes with light lanthanide nitrates possessing large coordination sphere, all three ligands **1**–**3** display P(O),C(O),C(O)-tridentate coordination mode. However, on coordination of ligand **2** with butyl substituents at the nitrogen atom to lutetium nitrate, the ligand unexpectedly displays the C(O),C(O),C(O)-tridentate coordination mode, in contrast to its homolog, ligand **3**. Even more differences in coordination mode occur upon formation of 1:2 complexes. The ligands **1** and **2** commonly show two coordination modes: P(O),C(O),C(O) and P(O),C(O), irrespectively of lanthanide nature, whereas ligand **3** along with these modes also displays the P(O),O_{eth}-bidentate coordination in 1:2 complexes with both light and heavy lanthanides.

2.4. Solvent extraction of lanthanides(III)

The extraction ability of ligands **2** and **3** was studied by the example of the extraction of certain lanthanides(III) (La, Nd, Eu, Lu) from neutral aqueous solutions (3 M NH_4NO_3) into 1,2-dichloroethane (DCE). Ligand **1** with methyl substituents at the nitrogen atom was prepared as a model compound to study coordination properties and was not studied in extraction experiments because it is markedly soluble in water. Distribution ratio ($D_L = [L_{org}]/[L_{aq}]$) between organic and

aqueous phases for ligand **1** is 0.53, whereas D_L values for ligands **2** and **3** are equal to ~ 10000 and 8000, respectively.

To compare the efficiency and selectivity of the studied ligands **2** and **3** as well as their mono analog **4** [16] and well-known extractant **5**, we compared the distribution ratios of the lanthanides ($D = [Ln]_{org}/[Ln]_{aq}$) for extractants **2**–**5** under the same experimental conditions (Fig. 5).

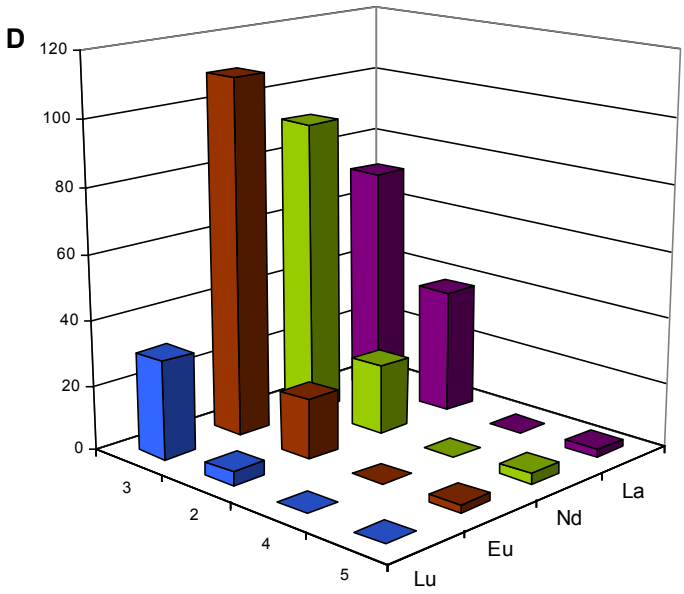


Fig. 5. Comparative data on Ln(III) extraction with ligand **2**–**5** from 3 M NH_4NO_3 in DCE (0.05 M ligand in DCE and $4 \cdot 10^{-6}$ M metal in aqueous phase)

Fig. 5 shows that both compounds **2** and **3** extract Ln(III) much more efficiently than their mono analog **4**. This fact indicates the cooperative interaction of coordinating centers of the polytopic system of ligands **2**, **3** with lanthanide cations, which agrees well with structure of complexes (see Section 2.3). Furthermore, compounds **2** and **3** recover Ln(III) much better than the known extractant **5** containing the same donor centers P=O and C=O involved into coordination with metal.

Extraction efficiency and selectivity is known to be dependent in complicated manner on numerous factors, including the strength and structure of extracted complexes, hydrophilicity/lipophilicity balance of a ligand and its complexes. Although ligands **2** and **3** exhibit almost equal lipophilicity (see above), they differ considerably in Ln(III) extraction efficiency (Fig. 5). We suppose that the different structure of their 1:2 lanthanide complexes in solution is one of the reasons of this difference. Such a structural difference should affect the strength and lipophilicity of extracted complexes. Moreover, it was found preliminary that, in contrast to ligand **2**, the stoichiometry of extracted complexes of ligand **3** is also dependent on lanthanide atomic number (in progress).

The selectivity of both ligands differs insignificantly but it is slightly higher for ligand **2** (see Fig. 5). Thus, separation factor ($SF = D_{La}/D_{Lu}$) for ligand **2** is 9, while that for ligand **3** is only 2.3.

Thus, the nature of the tested substituents at the nitrogen atom has little effect on ligand lipophilicity but considerably affects ligand coordination mode and its ability to recover metals into organic phase.

3. Conclusion

Coordination and extraction properties of new type of tripodal ligands on the triphenylphosphine oxide platform were studied. Two new tripodal ligands with alkyl substituents of different bulkiness

were synthesized. The influence of non-coordinating alkyl substituents (Me, *n*-Bu, *cyclo*-Hex) at the nitrogen atoms in the side arms on coordination and extraction properties of tripodal ligands **1**–**3** was studied. Eight new mononuclear 1:1 complexes of **1**–**3** ligands with $Ln(NO_3)_3$ (Ln = La, Nd, Lu) were studied in the solid state (elemental analysis, IR, X-ray) and in solution (IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR).

Irrespective of the type of substituent at the nitrogen atom, ligands **1**–**3** exhibit P(O),C(O),C(O)-denticity in all studied solid 1:1 complexes (except for [Lu(**1**)$(NO_3)_3$]). In solution, this coordination mode is retained for all 1:1 complexes except for [Lu(**2**)$(NO_3)_3$] (**11**). In complex **11**, the ligand displays symmetrical C(O),C(O),C(O)-dentate coordination mode to form so-called "hammock" for lutetium cation without coordination with the P=O group.

The possibility for the formation of 1:2 complexes with lanthanum and lutetium nitrates (IR, NMR, ESI-MS*)* has been examined and solution structure of the major components of 1:2 complexes has been suggested. In solutions of 1:2 complexes, steric switching of coordination mode from P(O),C(O),C(O)- and P(O),C(O)-dentate for ligands **1** and **2** to P(O),C(O),C(O)- and P(O),O_{et}-dentate for ligand **3** is observed.

New polytopic tripodal ligands **2** and **3** extract Ln(III) much more efficiently than their mono analog **4** and the known ditopic CMPO ligand **5**. The efficiency and selectivity of lanthanide extraction with ligand **3** is much higher than that with ligand **2**, which seems to be due to change in coordination mode in 1:2 complexes because the lipophilicity of ligands **2** and **3** is almost the same.

Further application of tripodal ligands on the triphenylphosphine oxide platform in coordination and extraction chemistry is expected.

4. Experimental

4.1. General

Solvents were purified and dried using standard procedures [17]. Deuterated solvents, CD_3CN (99.8% D, Sigma–Aldrich) and $CDCl_3$ (99.8% D, Sigma–Aldrich), were used as received. Multinuclear ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance 400 spectrometer (operating at 400.23, 100.61, and 161.98 MHz, respectively) and a Bruker Avance 500 instrument (operating at 500.15, 202.46 and 125.75 MHz, respectively) at ambient temperature using CD_3CN (c = 0.01 M) or $CDCl_3$ (c = 0.02 M) solution. Chemical shifts (ppm) refer to the residual protic solvent peaks (for ^{1}H and ^{13}C), and 85% H_3PO_4 (for ^{31}P) as external standards and coupling constants are expressed in hertz (Hz), the band width at half-height ($W_{1/2}$) is given in ppm (for ^{31}P{^{1}H} NMR spectra). IR spectra in the region 400–4000 cm^{-1} were obtained on a Bruker Tensor 37 FTIR spectrometer. The samples were KBr pellets and mulls in Nujol as well as 0.01 and 0.02 M solutions in CD_3CN, and $CDCl_3$, respectively, in CaF_2 cuvettes. The content of C, H, and N was determined on a Carlo Erba 1106 instrument. The content of P was determined according to the published procedures [18]. Melting points were determined in open capillary tubes on a Stanford Research Systems MPA120 EZ-melt automated melting point apparatus and were not corrected.

The reagents—tris(2-hydroxyphenyl)phosphine oxide [9]**,** tris(2-N,N-dibutylcarbamoylmethoxyphenyl)phosphine oxide (**2**) [8] model compound (N,N-dibutylcarbamoylmethyl)diphenylphosphine oxide (**5**) [19], N,N-dimethylchloroacetamide [20] and N,N-dicyclohexylchloroacetamide [21]—were prepared by the literature procedures.

Salts $La(NO_3)_3{\cdot}6H_2O$ (reagent grade), $Nd(NO_3)_3{\cdot}6H_2O$ (reagent grade), $Eu(NO_3)_3{\cdot}6H_2O$ (pure grade), and $Lu(NO_3)_3{\cdot}xH_2O$ (Aldrich) were used without further purification. The water content (x = 3) in commercial lutetium nitrate was determined experimentally.

The following reagents were used for the preparation of solutions in the extraction study: bidistilled water, 1,2-dichloroethane (reagent grade), HNO_3 (high purity grade). Solutions for spectral and extraction studies were prepared by volumetric/gravimetric method.

4.2. Ligand synthesis

4.2.1. Tris[2-(N,N-dimethylcarbamoylmethoxy)phenyl]phosphine oxide (**1**). A mixture of 0.98 g (3 mmol) of tris(2-hydroxyphenyl)phosphine oxide, 4.15 g (30 mmol) of K_2CO_3 , 1.24 g (10 mmol) of N,N-dimethylchloroacetamide (see ESI), and 15 mL of DMF was heated with magnetic stirring at 60 °C for 3 h. The mixture was evaporated to dryness in vacuum, 30 mL of water and 30 mL of CH_2Cl_2 was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined extracts were washed with water (2×10 mL) and dried with Na_2SO_4. The solvent was removed in a vacuum to dryness and the residue was crystallized from chloroform–hexane mixture to give **1** (1.58 g, 90.6%). Mp 183–184 °C. *Anal.* Calc. for $C_{30}H_{36}N_3O_7P$: C, 61.95; H, 6.24; N, 7.22; P, 5.33%. Found: C, 61.79; H, 6.20; N, 7.07; P, 5.49. IR (KBr disk): ν_{max}/cm^{-1} 1671vs, 1666vs (C=O), 1178m (P=O). ^{1}H NMR (500.13 MHz, $CDCl_3$, 0.02 M): δ 2.73 (9H, s, CH_3), 2.84 (9H, s, CH_3), 4.52 (6H, s, CH_2), 7.00 (3H, dd, $^3J_{3,4}$ = 8.4, $J_{H,P}$ = 5.6, H-3), 7.05 (3H, td, $^3J_{4,5} = J_{5,6}$ = 7.5, $^4J_{3,5}$ = 1.2, H-5), 7.46 (3H, t, $^3J_{3,4} = {}^3J_{4,5}$ = 7.8, H-4), 7.64 (3H, ddd, $^3J_{HP}$ = 14.8, $^3J_{5,6}$ = 7.6, $^4J_{4,6}$ = 1.4, H-6). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$, 0.02 M): δ 35.53 (s, N-CH_3), 36.47 (s, N-CH_3), 68.67 (s, O$\underline{C}H_2$), 112.93 (d, $^3J_{C,P}$ = 6.3, C-3), 121.39 (d, $^3J_{C,P}$ = 12.7, C-5), 121.67 (d, $^1J_{C,P}$ = 110.4, C-1), 133.53 (d, $^4J_{C,P}$ = 1.8, C-4), 134.40 (d, $^2J_{C,P}$ = 8.6, C-6), 160.19 (d, $^2J_{C,P}$ = 2.1, C-2), 167.63 (s, C=O). ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$, 0.02 M): δ 23.9 (s). Slow crystallization from the mother liquor resulted in single crystals of DMF solvate of ligand **1** (mp 171–172 ºC) suitable for X-ray diffraction study.

4.2.2. Tris[2-(N,N-dicyclohexylcarbamoylmethoxy)phenyl]phosphine oxide (**3**) was obtained in similar manner. Yield 82%, mp 145–147 °C. *Anal.* Calc. for $C_{60}H_{84}N_3O_7P$: C, 72.77; H, 8.55; N, 4.24; P, 3.13%. Found: C, 72.74; H, 8.69; N, 4.25; P, 3.21. IR (KBr disk): ν_{max}/cm^{-1} 1660sh, 1641vs (C=O), 1183m (P=O). ^{1}H NMR (500.13 MHz, $CDCl_3$, 0.01 M): δ 1.00–1.80 (54H, m, CH_2 (*cyclo*-Hex)), 2.39 (6H, br s, CH_2 (*cyclo*-Hex)), 2.91 (3H, br s, N–CH), 3.20–3.30 (3H, m, N–CH), 4.29 (6H, s, CH_2O), 6.97 (3H, dd, $^3J_{3,4}$ = 8.3, $^4J_{H,P}$ = 5.3, H-3), 7.02 (3H, td, $^3J_{5,6} = {}^3J_{5,4}$ = 7.5, $^4J_{5,3}$ = 1.5, H-5), 7.39 (3H, t, $^3J_{4,5} = {}^3J_{4,3}$ = 7.5, H-4), 7.74 (3H, dd, $^3J_{6,5}$ = 7.3, $^3J_{H,P}$ = 14.3, H-6). ^{13}C{^{1}H} NMR (125.76 MHz, $CDCl_3$, 0.01 M): δ 25.25 (s, CH_2 (*cyclo*-Hex)), 25.30 (s, CH_2 (*cyclo*-Hex)), 25.68 (s, CH_2 (*cyclo*-Hex)), 26.55 (s, CH_2 (*cyclo*-Hex)), 29.77 (s, CH_2 (*cyclo*-Hex)), 31.20 (s, CH_2 (*cyclo*-Hex)), 55.90 (s, N–CH), 56.85 (s, N–CH), 70.33 (s, CH_2O), 114.74 (d, $^3J_{CP}$ = 6.4, C-3), 121.60 (d, $^2J_{CP}$ = 12.5, C-5), 122.94 (d, $^1J_{CP}$ = 110.3, C-1), 133.04 (d, $^4J_{CP}$ = 1.3, C-4), 134.43 (d, $^2J_{CP}$ = 8.8, C-6), 161.26 (d, $^2J_{CP}$ = 2.5, C-2), 166.83 (s, C=O). ^{31}P{^{1}H} NMR (202.46 MHz, $CDCl_3$, 0.01 M): δ 24.82 (s).

4.3. Synthesis of lanthanides(III) complexes

4.3.1. General procedure for the synthesis of 6–14. The complexes **6–14**, including those suitable for X-ray analysis, were prepared according to a similar procedure, with a ratio of reagents of 1 : 1. A solution of $Ln(NO_3)_3{\cdot}xH_2O$ in acetonitrile was added dropwise with stirring to a solution of ligand in chloroform or MeCN. The yields were 70–90%, but no attempts were made to optimize the yield for each individual complex.

4.3.1.1. [La(1)(NO$_3$)$_3$], 6. A solution of 0.0335 g (0. 0773 mmol) of $La(NO_3)_3{\cdot}6H_2O$ in 3 mL of acetonitrile was added dropwise with stirring to a solution of 0.0449 g (0.0773 mmol) of ligand **1** in 3 mL of chloroform. The resultant transparent solution was stirred at ambient temperature for 1 h. The solution was evaporated to dryness under reduced pressure to give 0.06 g of solid. The residue was washed with anhydrous ether and dried in vacuo (~ 1 Torr) at 62 °C to give 0.057 g (81%). Mp 162–163 ºC. *Anal.* Calc. for $C_{30}H_{36}LaN_6O_{16}P$: C, 39.75; H, 4.00; N, 9.27%. Found: C, 38.97; H, 3.71; N, 9.44. IR (KBr disk): ν_{max}/cm^{-1} 1631s, 1660sh (C=O), 1121m (P=O), 1460s (N=O), 1290s (NO_2)as, 1032w (NO_2)s. ^{1}H NMR (500.13 MHz, CD_3CN, 0.01 M): δ 2.88 (9H, s, CH_3), 2.92 (9H, s, CH_3), 4.73 (6H, s, CH_2), 7.12–7.15 (6H, m, H-3 + H-5), 7.50 (3H, dd, $^3J_{HP}$ = 15, $^3J_{5,6}$ = 10, H-6,), 7.66 (3H, t, $^3J_{3,4} = {}^3J_{4,5}$ = 7.5, H-4). ^{13}C{^{1}H} NMR (125.75 MHz, CD_3CN, 0.01 M): δ 35.20 (s, N–CH_3), 35.62 (s, N–CH_3), 65.82 (s, CH_2O), 113.48 (d, $^3J_{CP}$ = 6.3, C-3), 121.89 (d, $^3J_{CP}$ = 12.5, C-5), 134.41 (d, $^2J_{CP}$ = 10.0, C-6), 135.00 (s, C-4), 159.94 (s, C-2), 168.48 (s, C=O). No signal of C-1 nucleus expected due to shift at ~117 ppm was observed because

it is obscured by the solvent signal. $^{31}P\{^{1}H\}$ NMR (202.46 MHz, CD_3CN, 0.01 M): δ 32.0 (s, $W_{1/2}$ = 0.05).

4.3.1.2. [Nd(1)(NO$_3$)$_3$], **7**. A solution of 0.0472 g (0.1078 mmol) of $Nd(NO_3)_3 \cdot 6H_2O$ in 3 mL of acetonitrile was added dropwise on stirring to a solution of 0.0627 g (0.1078 mmol) of ligand **1** in 3 mL of chloroform. The resultant transparent solution was stirred at ambient temperature for 1 h. The solution was evaporated to dryness under reduced pressure to give 0.100 g of solid. The residue was washed with anhydrous ether and dried in vacuo (~ 1 Torr) at 62 °C to give 0.082 g (83%). Mp 233ºC. *Anal.* Calc. for $C_{30}H_{36}N_6NdO_{16}P$: C, 39.52; H, 3.98; N, 9.22%. Found: C, 39.47; H, 3.94; N, 9.00. The residue (40 mg) was dissolved in 4.5 ml CH_3CN. After a few days, a light lilac crystals of $[Nd(\mathbf{1})(NO_3)_3]\cdot 0.5CH_3CN$, formed, some of them were suitable for X-ray diffraction study. The crystals were separated by decantation, washed with anhydrous ether and dried in air (20 mg, 50%). On storage in air, especially upon trituration, the complex easily loses solvent of crystallization. The IR band and Raman lines of the acetonitrile molecules were not observed in the vibrational spectra of sample. The elemental analysis indicated that the formula of crystals of is $[Nd(\mathbf{1})(NO_3)_3]$. Complex is not soluble in chloroform. IR (KBr disk): ν_{max}/cm^{-1} 1629, 1647sh, 1670sh (C=O), 1126 (P=O), 1465s (N=O), 1290s (NO_2)as, 1032w (NO_2)s. ^{1}H NMR (400.23 MHz, CD_3CN, 0.01 M): the signals are very broad because of paramagnetic properties of neodymium and could not provide precise integration and interpretation. $^{13}C\{^{1}H\}$ (100.61 MHz, CD_3CN, 0.01 M): δ 35.42 (s, N–CH_3), 35.74 (s, N–CH_3), 61.99 (br s, OCH_2), 112.89 (s), 122.63 (d, $^{3}J_{CP}$ = 2.0), 135.37 (s), 137.43 (br s,),161.71 (s). No signals of *ipso*–Ph and C=O were observed. $^{31}P\{^{1}H\}$ NMR (161.98 MHz, CD_3CN, 0.01 M): 121 (br s, $W_{½}$ = 1).

4.3.1.3. [Lu(1)(NO$_3$)$_3$], **8**. A solution of 44.1 mg (0.1062 mmol) $Lu(NO_3)_3 \cdot 3H_2O$ in 2 ml of MeCN was added dropwise on stirring to a solution of 61.7 mg (0.1062 mmol) **1** in 2 ml of MeCN. The resultant transparent solution was stirred at ambient temperature for 1 h. In an hour, a white fine-crystalline precipitate of **8** formed. One day later, the crystals were separated by decantation, washed with anhydrous ether and dried in vacuo (~ 1 Torr) at 62 °C to give 0.093 g (93%). Mp (with decomp.) 307–308 °C. *Anal.* Calc. for $C_{30}H_{36}LuN_6O_{16}P$: C, 38.23; H, 3.85; N, 8.92%. Found: C, 38.14; H, 3.79; N, 9.00. IR (KBr disk): ν_{max}/cm^{-1} 1630s, 1660sh, 1670s (C=O), 1180m,1185sh (P=O), 1480s (N=O), 1300s (NO_2)as, 1035w (NO_2)s. Complex is virtually insoluble in common solvents for NMR.

4.3.1.4. [La(2)(NO$_3$)$_3$], **9**. This compound was synthesized according to the general method similar to preparation of complex **7**, starting with 0.0367 mmol (26.2 mg) $La(NO_3)_3 \cdot 6H_2O$ and 0.0367 mmol (36.3 mg) **2**. The mixture was concentrated in vacuo (~5 Torr) up to a volume of ~1.3 mL. The fine-crystalline white precipitate formed was filtered, washed by diethyl ether and dried in vacuo (~1 Torr) at 62 °C to give 0.050 g (74.6%) of **9**. Mp 112–114 °C. *Anal.* Calc. for $C_{48}H_{72}N_6LaO_{16}P$: C, 49.74; H, 6.28; N, 7.25%. Found: C, 49.47; H, 6.24; N, 7.10. IR (KBr disk): ν_{max}/cm^{-1} 1610vs, 1630sh, 1665sh (C=O), 1121m (P=O), 1480s (N=O), 1300s (NO_2)as, 1035w (NO_2)s. ^{1}H NMR (400.13 MHz, $CDCl_3$, 0.02 M): δ 0.86–0.91 (18H, m, CH_3), 1.19–1.30 (12H, m, CH_3–C$\underline{H}_2$), 1.37–1.48 (12H, m, N–CH_2–C$\underline{H}_2$), 3.03–3.07 (6H, m, N–C$\underline{H}_2$), 3.24–3.36 (6H, v br s, N–C$\underline{H}_2$), 4.7 (6H, br s, CH_2O), 6.96 (3H, br s, H-3), 7.04 (3H, br s, H-5), ca 7.4 (extremely br s, H-6), 7.51–7.56 (3H, m, H-4). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $CDCl_3$, 0.02 M): δ 13.78 (s, CH_3), 13.92 (s, CH_3), 19.99 (s, CH_3–$\underline{C}H_2$), 20.05 (s, CH_3–$\underline{C}H_2$), 29.41 (s, N–CH_2–$\underline{C}H_2$), 30.51 (s, N–CH_2–$\underline{C}H_2$), 46.73 (s, N–CH_2), 47.08 (s, N–CH_2), 65.97 (s, CH_2O), 133.33 (s, C-3), ~117.7 (br d, $^{1}J_{CP}$ ~ 112, C-1), 112.10 (d, $^{3}J_{CP}$ = 12.5, C-5), 134.62 (s, C-4), 134.98 (s, C-6), 160.04 (s, C-2), ~167.7 (br s, C=O). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, $CDCl_3$, 0.02 M): δ 31.4 (s, $W_{1/2}$ = 0.4 ppm).

4.3.1.5. [Lu(2)(NO$_3$)$_3$], **11**. This compound was synthesized according to the general method similar to the preparation of complex **9**, starting from 0.0837 mmol (34.7 mg) $Lu(NO_3)_3 \cdot 3H_2O$ and 0.0837 mmol (69.8 mg) **2**. The white precipitate, 0.080 g (80%). Mp 84–85 °C. *Anal.* Calc. for $C_{48}H_{72}N_6LuO_{16}P$: C, 48.24; H, 6.07; N, 7.03%. Found: C, 47.97; H, 6.14; N, 7.10. IR (KBr disk): ν_{max}/cm^{-1} 1613s, 1638sh, 1660sh(C=O), 1120sh (P=O), 1480s (N=O), 1300s (NO_2)as, 1035w (NO_2)s. ^{1}H NMR (400.13 MHz, $CDCl_3$, 0.02 M): δ 0.91–0.95 (18H, m, CH_3), ~1.3 (12H, br s, CH_3–C$\underline{H}_2$), ~1.5 (12H, br s, N–CH_2–C$\underline{H}_2$), ~3.1 (6H, br s, N–C$\underline{H}_2$), ~3.3 (6H, br s, N–

C<u>H</u>$_2$), 4.7 (6H, br s, CH_2O), 6.9 (3H, br s, H-3), 7.0 (3H, br s, H-5), ca 7.4 (~ 3H, v br s, H-6), 7.5 (3H, br s, H-4). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, 0.02 M): δ 13.75 (s, CH_3), 13.83 (s, CH_3), 19.99 (s, CH_3–<u>C</u>H_2), 20.06 (s, CH_3–<u>C</u>H_2), 29.39 (s, N–CH_2–<u>C</u>H_2), 30.66 (s, N–CH_2–<u>C</u>H_2), 46.83 (s, N–<u>C</u>H_2), 47.21 (s, N–<u>C</u>H_2), 65.60 (s, CH_2O), 112.85 (s, C-3), 117.44 (d, $^1J_{CP}$ = 115, C-1), 121.73 (d, $^3J_{CP}$ = 12.0, C-5), 134.62 (d, $^2J_{CP}$ = 10.0, C-6), 134.75 (s, C-4), 160.40 (s, C-2), 167.80 (s, C=O). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 0.02 M): δ 34.2 (br. s, $W_{1/2}$ = 0.3)

4.3.1.6. [La(3)(NO$_3$)$_3$], **12**. This compound was synthesized according to the general method similar to preparation of complex **9**, starting with 0.0532 mmol (23 mg) $La(NO_3)_3·6H_2O$ and 0.0532 mmol (52.7 mg) **3**. The white fine-crystalline precipitate, 0.061 g (87%). Mp 208–209 °C. *Anal.* Calc. for $C_{60}H_{84}LaN_6O_{16}P$: C, 54.79; H, 6.44; N, 6.39%. Found: C, 54.32; H, 6.48; N, 6.53. IR (KBr disk): ν_{max}/cm^{-1} 1606vs, 1630sh, 1656m (C=O), 1122m (P=O), 1480s (N=O), 1300s (NO_2)as, 1035w (NO_2)s. ^1H NMR (500.13 MHz, $CDCl_3$, 0.02 M): δ 1.15–1.70 (br m, 60H, CH_2 (*cyclo*-Hex)), ~2.9 (~3H, br s, CH (*cyclo*-Hex)), ~3.1 (~ 3H, br s, CH (*cyclo*-Hex)), ~4.6 (~ 6H, br s, CH_2O), 6.90–7.15 (9H, br m, Ar-H), 7.5–7.65 (~ 3H, br m, Ar-H). $^{13}C\{^1H\}$ NMR (125.75 MHz, $CDCl_3$, 0.02 M): δ 24.98 (s, CH_2 (*cyclo*-Hex)), 25.66 (s, CH_2 (*cyclo*-Hex)), 26.42 (s, CH_2 (*cyclo*-Hex)), 29.47 (s, CH_2 (*cyclo*-Hex)), 30.76 (br s, CH_2 (*cyclo*-Hex)), 57.2 (br s, N–CH), ~ 69.0 (v br s, CH_2O), ~ 117.3 (v br s, C-1), 122.68 (s, C-5), 134.67 (s, C-6 + C-4), 159.97 (s, C-2), 167.30 (br s, C=O). $^{31}P\{^1H\}$ NMR (202.46 MHz, $CDCl_3$, 0.02 M): δ 31.4 (br s, $W_{1/2}$ = 0.5).

4.3.1.7. [Nd(3)(NO$_3$)$_3$], **13**. This compound was synthesized according to the general method similar to preparation of complex **9**, starting with 0.0530 mmol (23.2 mg) $Nd(NO_3)_3·6H_2O$ and 0.0530 mmol (52.5 mg) **3**. The fine-crystalline precipitate, 0.0567 g (81%). Mp 203–204 °C. *Anal.* Calc. for $C_{60}H_{84}N_6NdO_{16}P$: C, 54.57; H, 6.41; N, 6.36%. Found: C, 54.45; H, 6.28; N, 6.40. IR (KBr disk): ν_{max}/cm^{-1} 1604s, 1625sh, 1660sh (C=O), 1123m (P=O), 1480s (N=O), 1300s (NO_2)as, 1035w (NO_2)s. In ^1H NMR spectrum, the proton signals of CH_2 *c*-Hex groups are considerably broadened. No signals for the remaining groups the CH and CH_2 protons are observed. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, 0.02 M): δ 24.71 (s), 24.91 (s), 25.26 (s), 26.35 (s), 28.8 (br s), 30.0 (br s), 56.7 (br s), 58.4 (v br s), 66.5 (v br s), 114.3 (v br s), 123.45 (br s), 134.90 (br s). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 0.02 M): δ 93 (br s, $W_{1/2}$ = 5.4).

4.3.1.8. [Lu(3)(NO$_3$)$_3$], **14**. This compound was synthesized according to the general method similar to preparation of complex **9**, starting with 0.0518 mmol (21.5 mg) $Lu(NO_3)_3·3H_2O$ and 0.0518 mmol (51.3 mg) **3**. The white fine-crystalline precipitate, 0.060 g (85%). Mp 198–199 °C. *Anal.* Calc. for $C_{60}H_{84}LuN_6O_{16}P$: C, 53.33; H, 6.27; N, 6.22%. Found: C, 53.02; H, 6.38; N, 6.33. IR (KBr disk): ν_{max}/cm^{-1} 1608s, 1630sh, 1659s (C=O), 1123m (P=O), 1480s (N=O), 1300s (NO_2)as, 1035w (NO_2)s. In ^1H NMR spectrum, the proton signals of all groups are considerably broadened and could not be integrated (Fig. S19). ^1H NMR (400.13 MHz, $CDCl_3$, 0.02 M): δ 1.13–1.83 (br m, CH_2 *c*-C_6H_{11}), ~2.9 (v br s), ~3.1 (v br s), ~4.7 (v br s, CH_2O), 7.0 (br s, Ar-H), 7.1 (br s, Ar-H), ca 7.6 (v br m, Ar-H). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, 0.02 M): δ 25.04 (s, CH_2 (*cyclo*-Hex)), 25.65 (s, CH_2 (*cyclo*-Hex)), 26.44 (s, CH_2 (*cyclo*-Hex)), 29.75 (s, CH_2 (*cyclo*-Hex)), 30.82 (s, CH_2 (*cyclo*-Hex)), 56.88 (s, N–CH), 57.28 (s, N–CH), ~ 68.1 (v br s, CH_2O), 114.92 (s, C-3), 122.45 (d, $^3J_{CP}$ = 12.5, C-5), 134.82 (s, C-4), 134.99 (s, C-6), 160.18 (d, $^2J_{CP}$ = 2.5, C-2), 166.50 (v br s, C=O). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 0.02 M): δ 35.7 (br. s, $W_{1/2}$ = 0.6), 35.1 (sh).

4.4. General procedure for the preparation of model solution with metal:ligand ratios of 1:2

To prepare solution with metal : ligand molar ratio of 1:2, a calculated amount of ligand was added to a solution of corresponding 1:1 complex in CD_3CN or $CDCl_3$.

4.5. X-ray crystallography

Single crystals of the **1**·DMF, **2,** and **7**·0.5 MeCN were grown from their saturated solutions in DMF, $CHCl_3$ and MeCN, respectively, at room temperature. The intensities of reflections were measured with a Bruker Apex II CCD diffractometer using graphite monochromated MoK_α radiation (for **1**·DMF and **7**·0.5MeCN, λ = 0.71073 Å) or CuK_α radiation with multilayer optics (for **2**, λ = 1.54178 Å). The structures were solved by the direct method and refined by full-matrix

least squares on F^2. Non-hydrogen atoms were refined in anisotropic approximation. The unit cell of crystal of ligand **1** contains one solvate DMF molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON [22]. Chemical formula, formula weight and d_c were calculated taking the solvate molecules into account. Positions of the hydrogen atoms were calculated. All hydrogen atoms were included in the refinement by the riding model with $U_{iso}(H) = nU_{eq}(C)$, where n = 1.5 for methyl groups and 1.2 for the other atoms. All calculations were made using the SHELXL-2015 [23]] and OLEX2 [24] program packages. The main crystallographic data and experimental details are collected in Table 6.

Table 6. Crystallographic data and refinement parameters for **1**·DMF, **2** and **7**·0.5MeCN

Compound	**1**·DMF	**2**	**7**·0.5MeCN
Empirical formula	$C_{33}H_{43}N_4O_8P$	$C_{48}H_{72}N_3O_7P$	$C_{31}H_{37.5}N_{6.5}NdO_{16}P$
Fw	654.68	834.05	932.38
Color, habit	Light yellow, prism	Colorless, plate	Light pink, prism
Crystal size (mm^3)	0.32 × 0.31 × 0.26	0.26 × 0.10 × 0.04	0.32 × 0.31 × 0.26
F(000)	1392	904	944
T, K	120	120	120
Space group, Z	Monoclinic, $P\,2_1/c$, 4	Triclinic, $P\bar{1}$, 2	Triclinic, $P\bar{1}$, 2
a (Å)	16.082(3)	12.3182(1)	10.6694(16)
b (Å)	22.421(4)	13.7729(2)	12.1311(19)
c (Å)	9.0671(15)	16.0655(2)	15.608(2)
α (°)	90	68.309(1)	93.779(4)
β (°)	95.266(4)	68.382(1)	95.448(3)
γ (°)	90	85.757(1)	91.022(3)
V ($Å^3$)	3255.7(9)	2348.38(5)	2006.1(5)
d_c (g/cm^3)	1.336	1.180	1.544
μ(MoKα) (cm^{-1})	0.142	0.927	1.409
θ_{max} (°)	29.64	67.79	28.99
I_{hkl}coll/uniq	18015 / 7918	29268 / 7988	15721 / 10398
R_{int}	0.082	0.024	0.024
Obs. refl. / N / restraints	3865 / 370 / 0	7207 / 538 / 0	9158 / 509 / 1
R,[a] % [I > 2σ(I)]	0.088	0.039	0.060
R_w,[b] %	0.181	0.085	0.142
GOF[c]	1.05	1.00	1.03
Refcode[d]	1574776	1574777	1574778

[a] $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(w(F_o^2))]^{1/2}$. [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$ [d] Code of compound at the CSD.

4.6. Electrospray ionization mass spectrometry (ESI-MS)

The ESI mass spectra were recorded using a Finnigan LCQ Advantage mass spectrometer with 50–2000 m/z range octapole ion trap mass analyzer (Thermo Electron Corp., San Jose, CA, USA) and XCalibur version 1.3 equipped with Surveyor MS pump and Surveyor autosampler with MeCN as mobile phase. The temperature of heated capillary was kept at 120 °C. Nitrogen was used as the sheath and auxiliary gas and was set at 10 and 10 psi, respectively. The spray voltage was kept under 4.5 kV. The distance between the needle and the counter electrode was 1 cm. Samples were introduced directly in source with 5 μL min^{-1} by syringe pump. The full scan modes from 50 to 1800 Da and constant cone voltage at 13 V were used. For sample preparation, the measured amount (0.9–1.2 mg) of compounds was dissolved in 1.00 mL MeCN and sonicated. The stock solutions were further series diluted up to concentrations $1.5 \cdot 10^{-5}$ M. The fresh analyte solutions were immediately introduced into the mass spectrometer. The spectra of all studied compounds were recorded under the same conditions and at the same concentrations.

4.7. Extraction of lanthanides(III)

1,2-Dichloroethane (DCE) of reagent grade was used without additional purification as the organic solvent. Solutions of extractants at 0.05 M concentration were prepared from accurately weighed samples. The initial aqueous lanthanide(III) solutions were prepared by dissolving the respective nitrates in water, followed by the addition of NH_4NO_3. The initial concentrations of metal ions were $4 \cdot 10^{-6}$ M, the concentration of NH_4NO_3 was 3 M. The phases were contacted at room temperature by agitation with a stirrer at 60 rpm for 1 h, which is sufficient to establish constant values of distribution ratios. The concentration of lanthanides(III) in the initial and equilibrated aqueous solutions was determined by mass spectrometry with inductively coupled plasma ionization of samples (ICP-MS), using a Thermo Elemental X-7 mass spectrometer according to a published method [25]. The content of elements in the organic phase was determined after back extraction with a 0.1 M solution of 1-hydroxyethane-1,1-diphosphonic acid. The distribution ratios for the elements were calculated as ratios of the equilibrium concentration in the organic and aqueous phases ($D_M = [M_{org}]/[M_{aq}]$). The error of the determined D_M values did not exceed 5%.

The distribution ratios ($D_L = [L_{org}]/[L_{aq}]$) for the extractants **1**–**3** were calculated as ratios of the equilibrium concentration in the organic and aqueous phases. The initial concentration of the extractants in DCE was 0.05 M, the concentration of NH_4NO_3 in aqueous solution was 3 M. The concentration of extractants in the equilibrium aqueous solutions was evaluated by phosphorus content determination using inductively coupled plasma atomic emission spectrometry (ICP-AES) on an ICAP-61 spectrometer (Thermo Jarrel Adh).

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Appendix A. Supplementary data CCDC 1574776–1574778 contains the supplementary crystallographic data for **1**, **2** and **7**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Appendix B. Supplementary data associated with this article can be found, in the online version, at http://...

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Coordination and extraction of lanthanides(III) with tripodal ligands on the triphenylphosphine oxide platform: Effect of uncoordinated substituents

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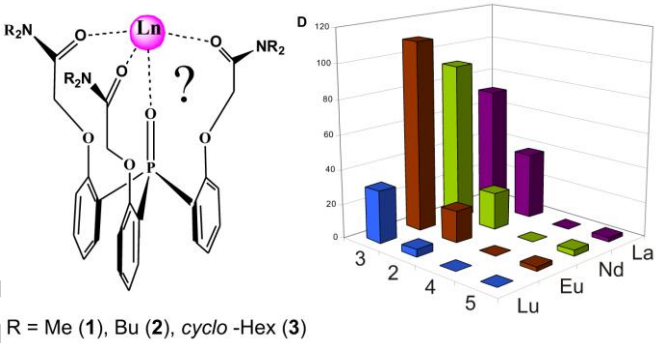
New tripodal ligands were synthesized and characterized. Nine lanthanide 1:1 complexes were synthesized and studied by IR and X-ray diffraction. Solution structure of 1:1 and 1:2 complexes was studied by IR, multinuclear NMR spectroscopy, and ESI-MS. Effect of non-coordinating substituents at N atom on coordination and extraction properties was revealed.



R = Me (**1**), Bu (**2**), *cyclo* -Hex (**3**)