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Mononuclear lanthanide complexes with tetradentate bis(phosphorylamino)-substituted 1,8-naphthyridine ligand: Synthesis and structural studies

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ABSTRACT

The complexes of 2,7-bis(diphenylphosphorylamino)-1,8-naphthyridine (**L**) with lanthanide nitrates $Ln(NO_3)_3$ (Ln = Nd, Lu) were investigated to elucidate the coordination ability of a novel type of potentially tetradentate ligands – bis(phosphorylamino) substituted naphthyridines. Mononuclear complexes of 1:1 and 1:2 composition, namely, $[Nd(L)(NO_3)_3]$ (**1a**), $[Nd(L)(NO_3)_3]\cdot H_2O$ (**1b**), $[Lu(L)(NO_3)_2(H_2O)](NO_3)$ (**2**), $[Nd(L)_2(NO_3)_2(H_2O)](NO_3)$ (**3**), $[Lu(L)_2(NO_3)(H_2O)](NO_3)_2\cdot 0.75CH_3CN\cdot H_2O$ (**4a**) and $[Lu(L)_2(NO_3)(H_2O)](NO_3)_2$ (**4b**) were synthesized and studied by IR, Raman, and ^{31}P NMR spectroscopy in solid state and in solution. Structures of the complexes **1b** and **4a** were determined by X-ray diffraction. According to X-ray crystallography, vibrational spectroscopy and C, H, N, P elemental analysis data in solid 1:1 complexes one neutral molecule of **L** serves most likely as *O*,*O*,*N*,*N*-tetradentate ligand while in the 1:2 complexes only one ligand molecule coordinates in the same *O*,*O*,*N*,*N*-tetradentate fashion, and the second one serves as *O*-monodentate one. In solution the coordination mode of the ligand is preserved in all complexes.

1. Introduction

Derivatives of aromatic *N*-heterocycles attract attention of researchers in different fields of contemporary chemistry, medicine, and material science owing to their capability to bind and strongly retain metal ions, including rare earth. The design of ligand systems comprising *N*-heterocycle with additional donor groups offers new prospects for the efficient and selective extraction of trivalent lanthanides and actinides [1], and promotes the development of novel organolanthanide electroluminiphores [2], and lanthanide complexes for biomedical [3] and analytical applications [4].

The derivatives of 1,8-naphthyridine with coordination-active groups (phosphino, phosphoryl, carbonyl, or nitrogen-containing donors) at 2- or 2,7-positions of naphthyridine ring are intensely studied as chelating agents [5]. The ligand cavity of such polydentate compounds provides a possibility to form mono-, bi-, and poly-nuclear complexes depending on the nature of metal and donor groups as well as the length and nature of linkers between these donor centers and the naphthyridine moiety [6]. In this context, systems that form complexes with the f-block elements are of special interest [7].

In the course of our investigation of lanthanide(III) complexation by some naphthyridine-based ligands [8–10], the molecule of 2,7-bis(diphenylphosphorylamino)-1,8-naphthyridine (**L**) attracted our attention because its architecture (a flexible framework) allows various possibilities of coordination to cations. Although this ligand was synthesized previously [11], but its coordination properties were not studied yet.

Here in, we report certain properties of ligand **L**, namely, its capacity to self-association by hydrogen bonding and coordination behavior toward lanthanide cations. Lanthanides were chosen for several reasons: in particular, in order to study fundamental features of 4f-elements complex formation, and to determine the coordination mode of the studied ligand. Moreover, many lanthanide complexes show a number of interesting and useful properties that allow one to use them as catalysts, molecular sensors, electroluminescent devices, and NMR shift reagents [7]. The reference metals used were neodymium and lutetium located in the middle and at the end of lanthanide series. Furthermore, neodymium is often used as a typical cation in studies of lanthanides, while lutetium cation is not paramagnetic, that makes it possible to use NMR spectroscopy for studying its compounds.

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2. Experimental

2.1. Materials

Salts $Nd(NO_3)_3 \cdot 6H_2O$ (Fisher Scientific Company), 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 solvents were purified and dried using standard techniques [12]. Deuterated solvents (CD_3CN, $CDCl_3$, $(CD_3)_2SO$) manufactured by the Prikladnaya Khimiya FGUP Russian Research Center, St. Petersburg, were used as received. Solutions for spectral studies ($c = 0.02$ or 0.01 M) were prepared by volumetric/gravimetric method.

2.2. Preparations

2.2.1. 2,7-Bis(diphenylphosphorylamino)-1,8-naphthyridine (**L**)

The ligand **L** was obtained by the reaction of 2,7-diaminonaphthyridine with diphenylchlorophosphinate in the presence of triethylamine in boiling chloroform as described previously [11]. As distinct from the previously published data [11], we detected only decomposition temperature rather than melting temperature (with decomposition) of the reaction product. Our ^{31}P NMR spectrum ($CDCl_3$ solution) and signal assignment in ^1H NMR spectrum ($CDCl_3$ solution) differed slightly from the data of [11], although there is no doubt about the structure of the obtained compound. Yield: 70%, decomposition temperature >320 °C (from ethanol-hexane) [lit. m.p. (with decomp.) 321–323 °C (from ethanol) [11]]. ^1H NMR ($CDCl_3$, 0.02 M, δ/ppm, J/Hz): 6.97 (d, br, 2H, 4,5-H_{napy}, $^3J_{H,H} = 8.5$); 7.41 (td, 8H, m-H_{Ph}, $^3J_{H,H} = 7.3$, $^4J_{H,H} = 3.2$); 7.48 (t, 4H, p-H_{Ph}, $^3J_{H,H} = 6.8$); 7.55 (d, br, 2H, 3,6-H_{napy}, $^3J_{H,H} = 8.8$); 7.87 (dd, 8H, o-H_{Ph}, $^3J_{H,P} = 12.5$, $^3J_{H,H} = 7.1$). ^1H NMR (DMSO-d_6, 0.02 M, δ/ppm, J/Hz): 7.06 (d, br, 2H, 4,5-H_{napy}, $^3J_{H,H} = 7.3$); 7.38–7.66 (m, 12H, m-H_{Ph}, p-H_{Ph}); 7.73–7.87 (m, 8H, o-H_{Ph}); 7.94 (d, br, 2H, 3,6-H_{napy}, $^3J_{H,H} = 8.5$); 9.35 (d, br, 1H, NHP(O), $^3J_{H,H} = 7.6$). ^{31}P NMR ($CDCl_3$, 0.02 M, δ/ppm, $W_{1/2}$/ppm): 20.6 (s, br, 1.2). ^{31}P NMR (DMSO-d_6, 0.02 M, δ/ppm, $W_{1/2}$/ppm): 17.3 (s, br, 0.2).

The substance is practically insoluble in nitromethane, acetonitrile and sparingly soluble in chloroform, alcohol, and DMSO.

2.2.2. $[Nd(L)(NO_3)_3]$ (**1a**) and $[Nd(L)(NO_3)_3] \cdot H_2O$ (**1b**)

A solution of $Nd(NO_3)_3 \cdot 6H_2O$ (0.0438 g, 0.1 mmol) in acetonitrile (2 mL) was added dropwise to a stirred solution of ligand **L** (0.0560 g, 0.1 mmol) in chloroform (5 mL) at room temperature. The mixture was concentrated *in vacuo* (~5 Torr) down to volume of ~4 mL. The precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo* (1 Torr) at 120 °C, and then dissolved in acetonitrile. Resulting whity-pink microcrystalline powder was collected by filtration and dried (120 °C) *in vacuo* (~1 Torr) to give 0.0790 g (89%) of $[Nd(L)(NO_3)_3]$ (**1a**). Decomposition temperature >210 °C. *Anal.* Calc. for $C_{32}H_{26}N_7NdO_{11}P_2$: C, 43.15; H, 2.94; N, 11.01; P, 6.95. Found: C, 43.35; H, 2.99; N, 11.21; P, 7.00%. The complex **1a** was characterized by vibrational spectra, which were identical to those of **1b** except for the IR bands of water solvent molecules.

Light lilac monocrystals of **1b** suitable for X-ray diffraction studies were obtained by ultra slow diffusion of diethyl ether into a nitromethane solution of **1a**. Yield: 0.0395 g, 50%. *Anal.* Calc. for $C_{32}H_{28}N_7NdO_{12}P_2$: C, 42.29; H, 3.11; N, 10.79; P, 6.82. Found: C, 42.35; H, 3.00; N, 10.90; P, 6.90%.

2.2.3. $[Lu(L)(NO_3)H_2O](NO_3)$ (**2**)

A solution of $Lu(NO_3)_3 \cdot 3H_2O$ (0.0415 g, 0.1 mmol) in acetonitrile (1.5 mL) was slowly added dropwise to a stirred solution of **L** (0.0560 g, 0.1 mmol) in chloroform (4 mL) at room temperature. The mixture was concentrated *in vacuo* (~5 Torr) down to ~3 mL. The precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo* (1 Torr) at 120 °C, and then dissolved in acetonitrile. White microcrystalline powder was obtained by slow isothermal evaporation, collected by filtration, and dried *in vacuo* at ambient temperature to give 0.0657 g (70%) of $[Lu(L)(NO_3)_2\text{-}H_2O](NO_3)$ (**2**). Decomposition temperature >202 °C. *Anal.* Calc. for $C_{32}H_{28}LuN_7O_{12}P_2$: C, 40.91; H, 3.00; N, 10.44; P, 6.59. Found: C, 41.18; H, 2.92; N, 10.29; P, 6.60%.

2.2.4. $[Nd(L)_2(NO_3)_2(H_2O)](NO_3)$ (**3**)

To a stirred solution of **L** (0.0448 g, 0.08 mmol) in chloroform (4 mL), a solution of $Nd(NO_3)_3 \cdot 6H_2O$ (0.0175 g, 0.04 mmol) in acetonitrile (1 mL) was added dropwise at room temperature. The mixture was concentrated *in vacuo* (~5 Torr) down to ~3 mL. The precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo* (1 Torr) at 120 °C, and then dissolved in acetonitrile. White microcrystalline powder was obtained by slow isothermal evaporated, collected by filtration, and dried *in vacuo* (1 Torr) at 120 °C to give 0.0469 g (80%) of $[Nd(L)_2(NO_3)_2(H_2O)](NO_3)$ (**3**). Decomposition temperature >240 °C. *Anal.* Calc. for $C_{64}H_{54}N_{11}NdO_{14}P_4$: C, 52.32; H, 3.70; N, 10.49; P, 8.43. Found: C, 51.85; H, 3.53; N, 10.30; P, 8.20%.

2.2.5. $[Lu(L)_2(NO_3)(H_2O)](NO_3)_2 \cdot 0.75CH_3CN \cdot H_2O$ (**4a**) and $[Lu(L)_2(NO_3)(H_2O)](NO_3)_2$ (**4b**)

To a stirred solution of **L** (0.0448 g, 0.08 mmol) in chloroform (4 mL), a solution of $Lu(NO_3)_3 \cdot 3H_2O$ (0.0175 g, 0.04 mmol) in acetonitrile (1 mL) was added dropwise at room temperature. The mixture was concentrated *in vacuo* (~5 Torr) down to ~3 mL. The precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo* (1 Torr) at 120 °C, and then dissolved in acetonitrile. Colorless crystals of **4a**, including transparent ones suitable for X-ray diffraction studies, were obtained by slow isothermal evaporation at room temperature. Yield: 0.0434 g, 70%. *Anal.* Calc. for $C_{65.50}H_{58.25}LuN_{11.75}O_{15}P_4$: C, 50.79; H, 3.79; N, 10.63; P, 8.00. Found: C, 51.01; H, 3.63; N, 10.58; P, 8.16%.

A drying of the crystals of **4a** (0.0200 g, 0.0129 mmol) *in vacuo* (1 Torr) at 120 °C led to a white microcrystalline powder **4b**, which composition according to the elemental analysis data correspond to the formula $[Lu(L)_2(NO_3)(H_2O)](NO_3)_2$. Yield: 0.0193, 92%. Decomposition temperature >231 °C. *Anal.* Calc. for $C_{64}H_{54}LuN_{11}O_{14}P_4$: C, 51.24; H, 3.63; N, 10.27; P, 8.26. Found: C, 51.38; H, 3.41; N, 10.28; P, 8.28%. The vibrational spectra of **4b** in the region of ligand and nitrato groups vibrations were identical to those of **4a**, with the exception of the IR bands and the Raman lines of outer-sphere solvent molecules (acetonitrile and water).

2.3. X-ray crystallography

Single-crystal X-ray diffraction experiments were carried out with a Bruker KAPPA APEX II CCD (**1b**) and a Bruker APEX II CCD (**4a**) diffractometers with monochromated Mo Kα radiation at 295 and 100 K, respectively. Reflection intensities were integrated using SAINT software [13]. The structure of complex **1b** was solved and refined with a twinned crystal. The contribution of the second domain (BASF parameter) was 0.421. Absorption correction for **1b** was made using TWINABS program [14]. Absorption correction for **4a** was made using semi-empirical method SADABS [13].

The structures were solved by direct method and refined by full-matrix least-squares against F^2 in anisotropic (for non-hydrogen atoms) approximation [13]. Hydrogen atoms H(Ow) in **1b** and disordered MeCN molecules in **4a** were not located, however, these H atoms were included in molecular formula and moiety formula. Hydrogen atoms H(N) (in **1b** and **4a**) and H(Ow) (in **4a**) were located from difference Fourier maps and refined in isotropic

Table 1
Crystal data and structural refinement details for $[Nd(L)(NO_3)_3]\cdot H_2O$ (**1b**) and $[Lu(L)_2(NO_3)(H_2O)](NO_3)_2\cdot 0.75CH_3CN\cdot H_2O$ (**4a**).

	1b	**4a**
Empirical formula	$C_{32}H_{28}N_7NdO_{12}P_2$	$C_{65.50}H_{58.25}LuN_{11.75}O_{15}P_4$
M_r	908.79	1548.84
T (K)	293(2)	100(2)
Scan mode	φ- and ω-scan	ω-scan
Crystal system	monoclinic	triclinic
Color of crystals	lilac	colorless
Habit of crystals	prism (fragment)	plate
Space group	$P2_1/n$	*Pbar*1
a (Å)	11.0208(5)	17.5397(17)
b (Å)	21.9413(9)	20.9060(19)
c (Å)	16.1977(7)	21.676(2)
α (°)	90.00	67.432(2)
β (°)	97.215(2)	81.825(2)
γ (°)	90.00	65.780(2)
V (Å^3)	3885.8(3)	6692.4(11)
Z	4	2
ρ_c (g cm^{-3})	1.553	1.537
μ (mm^{-1})	1.486	1.646
Crystal size (mm)	0.24 × 0.18 × 0.14	0.35 × 0.25 × 0.15
F(000)	1820	3138
$2\theta_{max}$ (°)	60.00	50.00
hkl range	$-15 < h < 15$, $-30 < k < 30$, $-22 < l < 22$	$-20 < h < 20$, $-24 < k < 24$, $-25 < l < 25$
Date/restraints/parameters	25 118/0/488	23 502/14/1727
Independent reflections (R_{int})	25 118 (0.0591)	23 502 (0.1153)
Completeness	0.988	0.997
Reflections collected	97 801	57 747
Independent reflections [$I > 2\sigma(I)$]	14 362	12 201
Goodness of fit on F^2	0.890	1.017
R_1, wR_2 [$I > 2\sigma(I)$]	0.0472, 0.0990	0.0537, 0.0884
R_1, wR_2 (all data)	0.1002, 0.1118	0.1071, 0.1368
Largest diff. peak/hole (e Å^{-3})	1.39, −0.67	2.539, −1.758

approximation with constrained NH and HO distances. The H(C) atoms in **1b** and **4a** were placed in geometrically calculated positions and refined in isotropic approximation in riding model with the Uiso(H) parameters equal to n Ueq(Ci), where U(Ci) are respectively the equivalent thermal parameters of the atoms to which corresponding H atoms are bonded, $n = 1.2$ for CH and CH_2 groups, $n = 1.5$ for CH_3 groups.

Crystal data and structure refinement parameters are listed in Table 1. CCDC 833989 (**1b**), and 833962 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

2.4. Measurements

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance TM-400 spectrometer operating at 400.13 and 161.98 MHz, respectively, using the residual signals of the protons of deuterated solvents as an internal reference (^1H) and 85% H_3PO_4 as an external standard (^{31}P). We failed to detect the signals of neodymium complexes **1a** and **3** in $^{31}P\ \{^1H\}$ NMR spectra on account of considerable signal broadening probably owing to paramagnetic properties of the cation.

IR spectra in the region 400–3700 cm^{-1} were recorded using a Nicolet Magna IR-750 FTIR spectrometer. The samples were KBr pellets, mulls in Nujol and hexachlorobutadiene as well as 0.01 M solutions ($CHCl_3$, $CDCl_3$, CD_3CN and CH_3CN) in NaCl and CaF_2 cuvettes.

Raman spectra of the solid samples were obtained in the region 200–3700 cm^{-1} using a Jobin–Yvon LabRAM 300 last-generation laser Raman spectrometer equipped with a microscope and a cooled CCD detector. Excitation was accomplished at 632.8 nm with a He-Ne laser with 10 mW output power.

The identity of crystalline samples used for X-ray investigation and for recording vibrational spectra was checked with a Bruker Apex 2 diffractometer.

Elemental analyses were made in the Laboratory of Microanalysis, Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

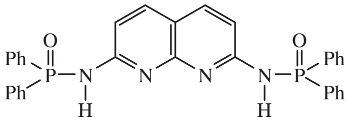
3. Results and discussion

3.1. 2,7-Bis(diphenylphosphorylamino)-1,8-naphthyridine (L)

The molecule of the ligand **L** (Scheme 1) contains four donor atoms that can participate in complex formation: two phosphoryl oxygens and two nitrogen atoms of naphthyridine ring.

At the same time, the presence of two NH groups along with two phosphoryl groups and two nitrogen atoms of naphthyridine ring makes this molecule favorable for hydrogen bondings. As shown in [15–17], the phosphoryl- and carbonyl-containing naphthyridines to the studied ligand **L** are associated *via* hydrogen bonds both in the solid state and in solutions, thus, similar hydrogen bonds can be expected for **L**. In fact, the N–H…O=P bonding is evidenced by the broadened signals in ^1H and ^{31}P NMR spectra (see Section 2), low-frequency shifts in the IR spectra, poor solubility of **L** in aprotic polar solvents, and its high decomposition temperature.

The IR spectrum of the solid ligand **L** shows a ν(P=O) band at 1171 cm^{-1} and a ν(NH) band at 3136 cm^{-1}, these values being shifted compared to those of the free groups [18]. In the spectrum of 0.01 M solution of **L** in $CDCl_3$, the bands of P=O and N–H vibrations appear at higher frequencies at 1210 and 3380 cm^{-1},



Scheme 1. Ligand L.

Table 2
The frequencies (ν, cm^{-1}) of the salient analytical bands in the vibrational spectra of the ligand **L**, and its complexes **1b–4a** in solid state and in solution (CH_3CN, CD_3CN, and $CDCl_3$, 0.01 M).

Compound	ν(P=O)	Vibrations of naphthyridine moiety			ν(N=O)	ν_{as}(NO_2)	ν(NO_3)
	IR	IR	Raman	Raman	IR	IR	IR
L	1171s (*1210s*)[a]	1540 m (*1540m*)[a]	1375	787			
[Nd(L)(NO_3)$_3$]·H_2O (**1b**)	1162s (*1160s*)[c]	[b] ([b])[c]	1400	810	1480s (*1490s*)[c]	1320s (*1300s*)[c]	–
[Lu(L)(NO_3)H_2O](NO_3) (**2**)	1162s (*1160s*)[c]	[b] ([b])[c]	1410	813	1500s (*1490s*)[c]	1295s (*1300s*)[c]	1345m (*1350m*)[c]
[Nd(L)$_2$(NO_3)$_2$(H_2O)](NO_3) (3)	1190m, 1162s (*1200m*, *1160s*)[c]	[b], 1542w ([b], *1540w*)[c]	1397, 1382	808, 792	1480s (*1480m*)[c]	1320s (*1310m*)[c]	1341m (*1340s*) [c]
[Lu(L)$_2$(NO_3)(H_2O)](NO_3)$_2$· 0.75CH_3CN·H_2O (4a)	1190 m, 1160s (*1200m*, *1160s*)[c]	[b], 1539w ([b], *1539w*)[c]	1407, 1381	813, 794	1500s (*1500w*)[c]	1309s (*1300w*)[c]	1346s (*1340s*)[c]

s – strong; m – medium; w – week.

[a] The data for solution in $CDCl_3$ are given in parentheses.

[b] The region of higher frequencies is obscured by intense adsorption other bands of the ligand.

[c] The data for solution in CH_3CN and CD_3CN are given in parentheses.

respectively, while the bands of the naphthyridine moiety remain almost unchanged (Table 2). It should be noted that an akin compound containing $Ph_2P(O)NH$ fragment, namely, $Ph_2P(O)NH$[–C=CMeNMeNPhC(O)–], according to X-ray diffraction in solid state exists as dimers united by NH…O=C bonds, and its IR spectrum shows the ν(P=O) band of the free P=O group at 1210 cm^{-1}. When the compound is dissolved, ν(NH) changes from 3150 to 3370 cm^{-1}, the frequency of P=O group remains constant [19].

Thus, it is evident that the molecules of **L** in the solid state are associated *via* intermolecular N–H…O=P hydrogen bonds while both N-atoms of naphthyridine moiety remain intact.

The goal of present work is to study the coordination properties of a new ligand **L** toward lanthanide cations, to determine the composition of the resulting complexes as well as their structures in the solid state and in solutions.

The reaction of **L** with lanthanide nitrates Ln(NO_3)$_3$ (Ln = Nd, Lu) at metal/ligand molar ratios of 1:1 and 1:2 leads to the formation of complexes **1a–4b** isolated as solids. They were studied by the IR, Raman, and ^{31}P NMR spectroscopy. The structures of the complexes **1b** and **4a** were also elucidated by X-ray diffraction. The parameters of vibrational spectra for the complexes **1b–4a** in comparison with the data for the free ligand **L** are given in Table 2.

3.2. Complexes of 1:1 composition

Complexes Ln(L)(NO_3)$_3$·nH_2O (Ln = Nd, Lu, n = 0, 1) are readily formed at the reactant ratio of 1:1. A crystalline complex **1b** with composition Nd(L)(NO_3)$_3$·H_2O was isolated on crystallization of the complex [Nd(L)(NO_3)$_3$] (**1a**) from nitromethane, the structure of **1b** was established by X-ray diffraction. The crystal structure of **1b** contains separate neutral complexes [Nd(L)(NO_3)$_3$] and solvate water molecules (Fig. 1).

Ligand molecule is coordinated to central neodymium cation in *O,O,N,N*-tetradentate fashion, and three nitrate ions are coordinated in a chelated fashion. The coordination number of neodymium cation is 10: eight oxygen atoms and two nitrogen atoms. If each nitrato group is considered to occupy one coordination position, then the coordination polyhedron of neodymium atom can be described to a first approximation as a distorted pentagonal bipyramid, whose equatorial plane is formed by two oxygen atoms O(1), O(2) and two nitrogen atoms N(2), N(3) of ligand molecule as well as the midpoint O6(7) between the coordinated oxygen atoms of nitrate group O(6)···O(7) (Fig. 2). Maximal deviation of equatorial atoms of the coordination polyhedron from their least-squares plane is 0.45 Å for O(1), average deviation is ±0.33 Å. Two other nitrato groups occupy apical positions.

Solvate water molecule in the structure of **1b** forms a hydrogen bond with one of the NH groups of the coordinated ligand molecule (Fig. 1). Hydrogen bond parameters are as follows: r(N···O) = 2.888(3) Å, r(H···O) = 2.06 Å, angle (N–H...O) = 162.5°. Several bond distances for **1b** are presented in Table 3. Geometrical parameters of the ligand molecule are typical for this class of compounds [8,15,20,21].

The IR spectrum of complex **1b** (Table 2) does not show any band in the region typical for free P=O group (~1210 cm^{-1}). The single band corresponding to the P=O bond stretching is observed at 1162 cm^{-1}, which evidences the equivalence of both coordinated P=O groups in this complex. The IR band at ~1540 cm^{-1} corresponding to vibrations of non-coordinated naphthyridine ring is absent, while the higher frequency region to where the band of the coordinated naphthyridine moiety should be shifted [8,9,22] is obscured by the intense absorption of other groups of the ligand. The bands of the NO_3 groups appear at 1480 and 1320 cm^{-1}, that corresponds to their bidentate coordination [23]. Absorption of the solvate water molecule appears

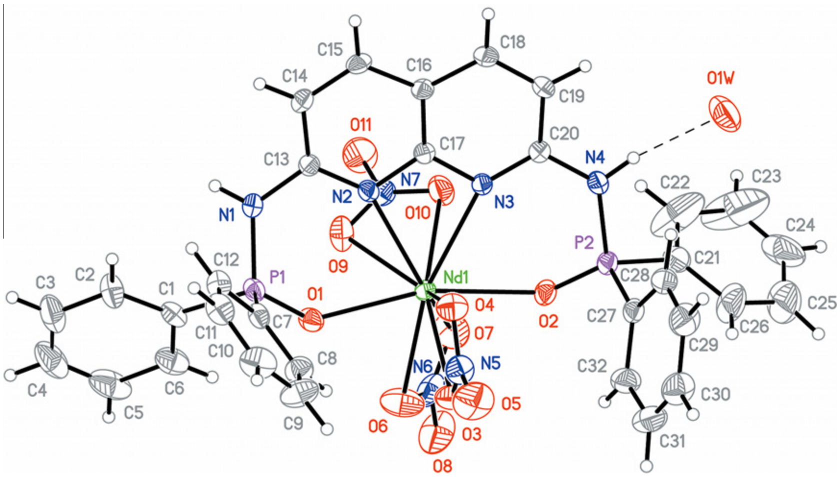


Fig. 1. Structure of the neutral complex **1b**. The thermal ellipsoids are given at 30% probability level.

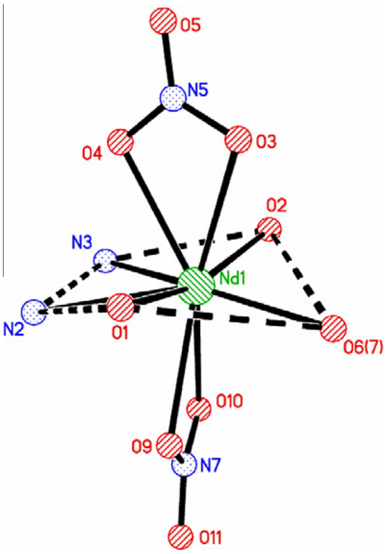
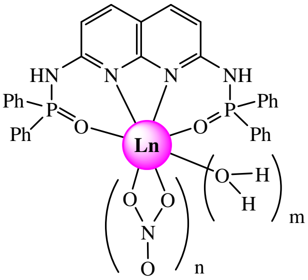


Fig. 2. Visualization of the distorted pentagonal bipyramidal environment around Nd^{III} in **1b**. One nitrate group N(6)O(6)O(7)O(8) is presented as one point O6(7) (midpoint between the coordinated oxygen atoms of nitrate group O(6)…O(7)).

Table 3
Selected bond lengths (Å) for the structure **1b**.

Bond	(Å)
Nd1–O1	2.426(2)
Nd1–O2	2.388(2)
Nd1–N2	2.646(2)
Nd1–N3	2.658(2)
Nd1–O3(NO_3)	2.566(2)
Nd1–O4(NO_3)	2.583(2)
Nd1–O6(NO_3)	2.559(2)
Nd1–O7(NO_3)	2.587(2)
Nd1–O9(NO_3)	2.554(2)
Nd1–O10(NO_3)	2.658(2)
P1–O1	1.494(2)
P2–O2	1.491(2)



Scheme 2. Complexes **1a**,**b** (Ln = Nd, *n* = 3, *m* = 0), and complex cation **2** (Ln = Lu, *n* = 2, *m* = 1).

in the range of ν(OH) vibrations at 3500–3400 cm^{-1}. This region overlaps that of the free ν(NH) bands. We managed to detect this band at 3402 cm^{-1} only in the IR spectrum of anhydrous complex **1a** after careful removal of solvate water. The lines of coordination-sensitive vibrations of naphthyridine moiety in the Raman spectrum of the complex **1b** are recorded at 1400 and 810 cm^{-1}, being shifted to the high-frequency region by 23–25 cm^{-1}, which is typical for the coordination of both nitrogen atoms to lanthanide cation [8,9].

In the IR spectrum of the acetonitrile solution of **1b** the bands of the P=O and nitrate groups are virtually unchanged, the free naphthyridine bands are absent. This data allows to conclude that the neutral complex [Nd(*O*,*O*,*N*,*N*-L)(*O*,*O*-NO_3)$_3$] retains its structure in solution (Scheme 2).

The main difference between the IR spectra of solid lutetium complex **2** and neodymium complex **1b** is the presence in the former one of a band of free nitrate ion at 1345 cm^{-1} and a band of metal-coordinated water at 3200 cm^{-1} [23]. According to these data, compound **2** has most likely a structure of cationic complex [Lu(*O*,*O*,*N*,*N*-L)(*O*,*O*-NO_3)$_2$(H_2O)](NO_3), in which the ligand shows maximal tetradentate coordination, and the inner coordination sphere includes also two chelate nitrate ions and one water molecule (Scheme 2). The coordination number of lutetium in the complex cation is equal to nine.

In the IR spectrum of the acetonitrile solution of **2**, the bands of the P=O groups and those related to coordinated and free nitrate groups are virtually unchanged, and there is no vibrational band of the free naphthyridine moiety. In the ^{31}P {^1H} NMR spectrum of **2** a broadened signal of coordinated[1] phosphoryl groups is

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[1] Unfortunately, the ligand **L** is virtually insoluble in acetonitrile. However, by analogy with the related compounds one can expect that in this solvent the signal of **L** in ^{31}P {^1H} NMR spectrum should be in the range 17–20 ppm. Upon coordination with Lu(NO_3)$_3$, the signal of phosphoryl-containing ligands is usually shifted downfield by ~10–12 ppm [24,25]. For example, the ^{31}P {^1H} NMR spectrum of complex **4a** (see below) shows the signal of the free P=O group at 17.4 ppm ($W_{1/2} = 0.3$ ppm), while the signal of the coordinated one is detected at 31 ppm ($W_{1/2} = 2.3$ ppm).

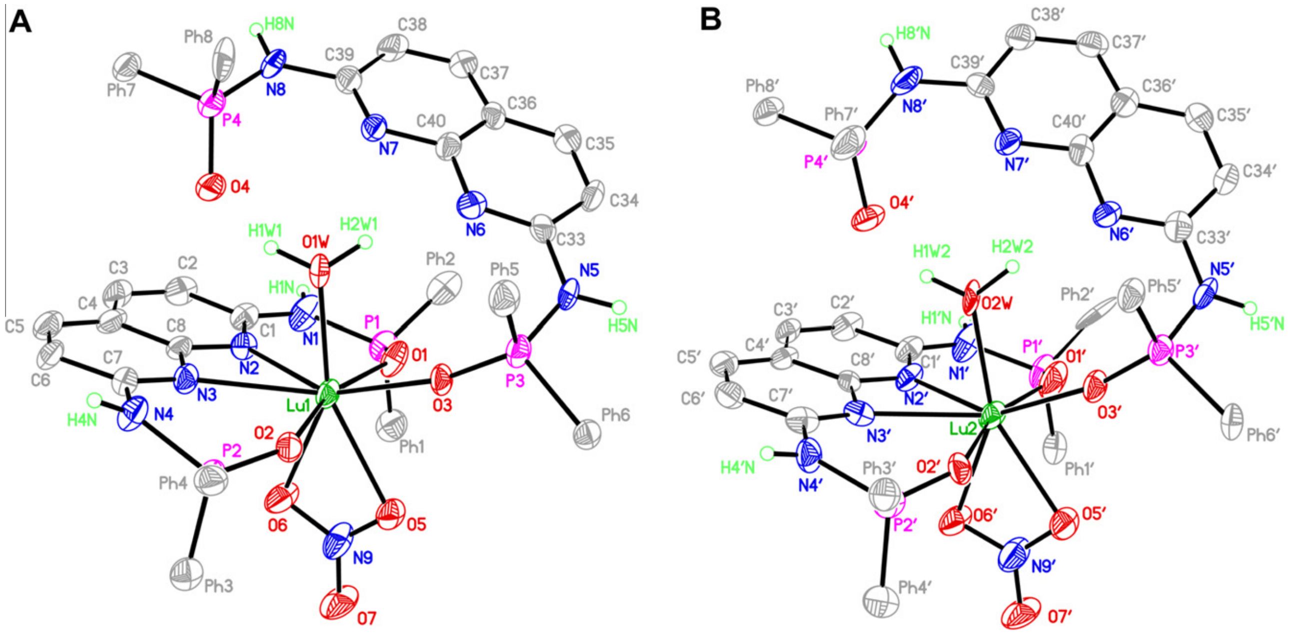
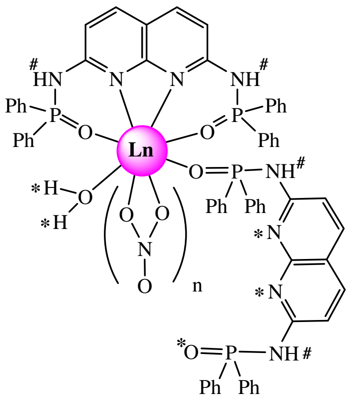


Fig. 3. Complex cations **A** (left) and **B** (right) in the structure of compound **4a**. The thermal ellipsoids are given at 50% probability level. Phenyl rings are represented as one atom (Ph), the hydrogen atoms of the naphthyridine fragments are omitted for clarity.

Table 4
Selected bond lengths (Å) for the structure **4a**.

Bond	Cation **A** (Ln = Lu1)	Cation **B** (Ln = Lu2)
Ln–O1/O1′	2.212(5)	2.202(6)
Ln–O2/O2′	2.266(5)	2.252(5)
Ln–O3/O3′	2.201(4)	2.196(4)
Ln–N2/N2′	2.464(6)	2.496(6)
Ln–N3/N3′	2.485(6)	2.441(6)
Ln–O1W/O2W	2.216(5)	2.232(5)
Ln–O5/O5′(NO_3)	2.403(5)	2.425(5)
Ln–O6/O6′(NO_3)	2.383(5)	2.371(5)
P1/P1′–O1/O1′	1.508(5)	1.516(6)
P2/P2′–O2/O2′	1.482(5)	1.490(5)
P3/P3′–O3/O3′	1.490(5)	1.482(5)
P4/P4′–O4/O4′	1.479(5)	1.491(5)



Scheme 3. Complex cations present in the structures of **3** (Ln = Nd, *n* = 2) and **4a**,**b** (Ln = Lu, *n* = 1). The sign ∗ designates atoms participating in the formation of intramolecular hydrogen bonds, the sign # designates atoms participating in the formation of intermolecular hydrogen bonds.

detected at 30 ppm ($W_{1/2} = 2$ ppm). In accordance with these data, we can suppose the presence of an equilibrium between the complex cation [Lu(*O*,*O*,*N*,*N*-L)(*O*,*O*-NO_3)$_2$]$^+$ and free ion NO_3^- in solution.

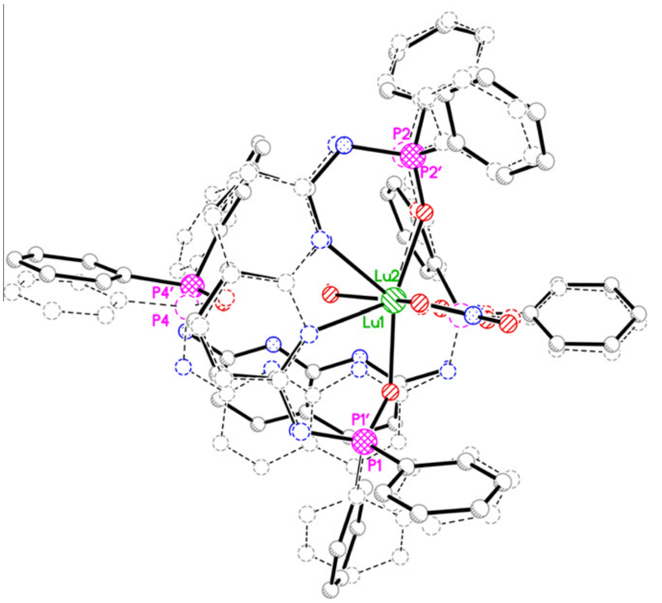


Fig. 4. Comparison of the two independent cations **A** (Lu1) и **B** (Lu2) present in the structure of compound **4a**, demonstrating the difference in the turns of aromatic fragments. Hydrogen atoms are omitted for clarity.

Thus, at the ratio M:L = 1:1, the reaction of the ligand with lanthanide nitrates leads to the formation of mononuclear complexes where the ligand exhibits maximal *O*,*O*,*N*,*N*-tetradentate coordination. The number of nitrate groups and water molecules coordinated by lanthanide cation varies when passing from neodymium to lutetium, the latter is known to have smaller coordination sphere (see Scheme 2).

3.3. Complexes of 1:2 composition

The reaction of ligand **L** with lanthanide nitrates at 1:2 ratio leads to complexes **3**, **4a**,**b** that have Ln(L)$_2$(NO$_3$)$_3$·nSolv

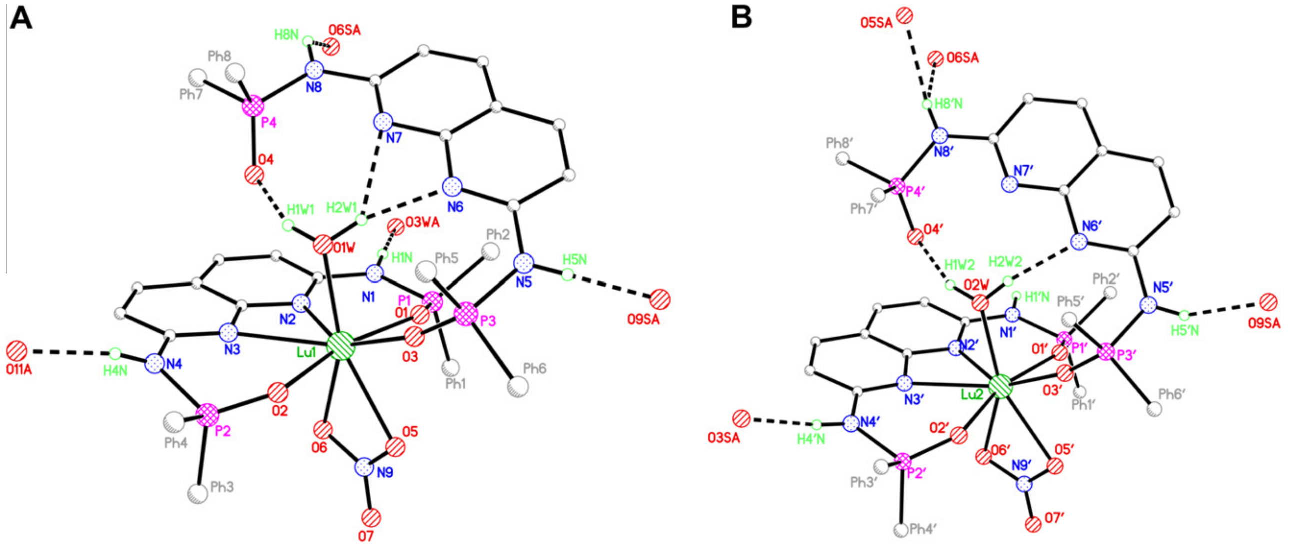


Fig. 5. Drawings of complex cations A (left) and B (right) demonstrating the H-bonds in the structure **4a**. Phenyl rings are represented as one atom (Ph), the hydrogen atoms of naphthyridine fragments are omitted for clarity.

composition, where Solv is a solvent molecule (water, acetonitrile) and Ln = Nd, Lu. The structure of lutetium complex **4a** with composition $Lu(L)_2(NO_3)_3{\cdot}0.75CH_3CN{\cdot}2H_2O$ was established by X-ray diffraction.

The crystal of **4a** contains two crystallographically independent complex cations $[Lu(L)_2(NO_3)H_2O]^{2+}$ (designated further as **A** and **B**) that differ insignificantly in their structure (Fig. 3), as well as NO_3^- anions and solvate molecules of water and acetonitrile. The main bond distances are given in Table 4.

Both complex cations contain two coordinated ligand molecules, one molecule has *O*,*O*,*N*,*N*-tetradentate coordination to lutetium, while another molecule shows monodentate coordination *via* oxygen atom of one of the P═O groups. The coordination polyhedron is supplemented by oxygen atoms of a water molecule and those of a nitrate group coordinated in a bidentate mode: $\{LuO_6N_2\}$. The coordination number of lutetium in both complex cations equals to eight (see Fig. 3 and Scheme 3). The lengths of coordination bonds in complexes **A** and **B** are close to each other (Table 4), the main difference consists in the orientation of the aromatic fragments of the ligand (Fig. 4) and different number of intra- and intermolecular hydrogen bonds that stabilize the corresponding conformation (see Fig. 5).

In cation **A**, one of the hydrogen atoms of the coordinated water molecule forms a bifurcated hydrogen bond with both nitrogen atoms of the naphthyridine fragment of the monocoordinated ligand molecule. This is in contrast with the cation **B** (Fig. 5) where a “normal” H-bond is formed with only one of the naphthyridine nitrogen atoms: O2W–H2W2···N6′. Moreover, the structure of the cation **A** comprises four intermolecular H-bonds between the NH groups and the oxygen atoms of NO_3^- counterions and the solvate water molecules, while the structure of the cation **B** contains only three such H-bonds, one NH group remaining free. The X-ray parameters of the hydrogen bonds are shown in Table 5.

To a first approximation, the coordination polyhedron of lutetium in both complex cations of structure **4a** can be represented as a distorted pentagonal bipyramid. The equatorial plane of the bipyramid is formed by five atoms N(2),N(3),O(1),O(2),O(3) that are coplanar (±0.2 Å). Two nitrogen atoms N(2), N(3) and two oxygen atoms O(1), O(2) are provided by one ligand molecule, and one

Table 5
Hydrogen bonds for structure **4a** [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
O1W–H1W1...O4#1	0.85	1.85	2.650(8)	156
O1W–H2W1...N6#1	0.85	2.11	2.944(8)	168
O1W–H2W1...N7#1	0.85	2.36	2.982(8)	130
N1–H1N...O3W#1	0.90	1.90	2.793(9)	170
N4–H4N...O11S#2	0.90	1.90	2.76(1)	160
N5–H5N...O9S#1	0.90	2.03	2.84(1)	149
N8–H8N...O6S#3	0.90	2.30	2.950(9)	128
O2W–H1W2...O4′#1	0.85	1.90	2.707(8)	159
O2W–H2W2...N6′#1	0.85	2.09	2.906(9)	162
N4′–H4′N...O3S#4	0.90	1.88	2.779(9)	173
N5′–H5′N...O9S#5	0.90	2.05	2.84(1)	146
N8′–H8′N...O6S#6	0.90	2.22	2.94(1)	136
O3W–H2W3...O4S#3	0.85	2.22	2.97(1)	147
O3W–H1W3...O10′#1	0.85	2.18	2.76(1)	124
O4W–H1W4...O11′#1	0.85	1.96	2.77(1)	157
O4W–H1W4...O11S#1	0.85	2.24	2.93(1)	137
O4W–H2W4...O5′#2	0.85	2.24	3.09(1)	179

Symmetry transformations used to generate equivalent atoms:
#1 *x*, *y*, *z*; #2 −*x* + 1, −*y* + 1, −*z* + 1; #3 −*x* + 2, −*y* + 1, −*z* + 1.
#4 −*x*, −*y* + 2, −*z*; #5 −*x* + 1, −*y* + 2, −*z* + 1; #6 *x* − 1, *y* + 1, *z* − 1.

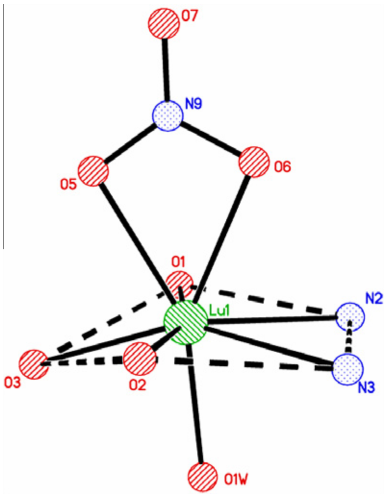


Fig. 6. Visualization of the distorted pentagonal bipyramidic environment around Lu^{III} in the structure of **4a** (for complex cations **A**).

oxygen atom (O3) belongs to another ligand molecule. One water molecule and one bidentate NO_3 group occupy the apical positions (Fig. 6).

Bond distances and valence angles of the ligand molecules in structures **4a** and **1b** are typical for this class of compounds [26]. For instance, the lengths of the P=O bonds in **1b**,**4a** (1.491(2)–1.516(6) Å) are in a good agreement with those for such bonds (1.51–1.53 Å) in lanthanide complexes of phosphoryl containing 1,8-naphthyridine [8] and in the related non-coordinated compounds 2-[2-(diphenylphosphoryl)-2-methylprophyl]-1,8-naphthyridine (1.495(2) [20]) and 2-[(diethoxyphosphoryl)amino)]-5,7-dimethyl-1,8-naphthyridine (1.474(1), 1.466(1) Å [15]).

The IR spectrum of the crystalline complex **4a** (Table 2) exhibits two ν(P=O) bands at 1160 and 1190 cm^{-1}. The former corresponds to metal-coordinated P=O groups while the latter to an H-bonded P=O group. The region of 1600–1570 cm^{-1}, where the band of coordinated naphthyridine system should appear, is obscured by the intense absorption of other groups of the ligand, while the vibrations of intact naphthyridine ring appear as a low-intensity band at 1539 cm^{-1}. The strong broad IR bands of bidentate NO_3 groups of **4a** are detected at 1500 and 1309 cm^{-1}, while a strong narrow band at 1346 cm^{-1} corresponds to vibrations of free (non-coordinated) nitrate ions. In the region of 3200–3400 cm^{-1} an overlap is observed of the bands corresponding to metal-coordinated and solvate water (~3200 and ~3400 cm^{-1}) and bound and free NH groups (~3150 and 3400 cm^{-1}).

According to the data of elemental analysis, the complex **4b** contains no solvate water and acetonitrile. In the IR spectrum of **4b** the absorption of the only free NH group (one of eight) is too weak to be observed. The band of metal-coordinated water is present at 3200 cm^{-1}.

The Raman spectrum of complex **4a** shows lines at 1407 and 813 cm^{-1} corresponding to vibrations of bidentate-coordinated naphthyridine fragment, while the lines at 1381 and 794 cm^{-1} correspond to the vibrations of the naphthyridine moiety which is not involved in coordination, but forms intramolecular H-bond with the hydrogen atoms of an inner-sphere water molecule. Vibration frequencies of non-coordinated naphthyridine moiety in complex **4a** are slightly higher than those for the solid free ligand (Table 2). In general, the vibrational spectra agree well with the X-ray diffraction data, although the both IR and Raman spectra of a crystalline sample of **4a** did not reveal the bands of solvate acetonitrile molecule.

In the IR spectrum of a solution of complex **4a**, the positions of the analytical bands are virtually unchanged (Table 2). The $^{31}P\{^1H\}$ NMR spectrum of the same solution shows two broadened signals at 31 ppm ($W_{1/2} = 2.3$ ppm) and 17.4 ppm ($W_{1/2} = 0.3$ ppm) with the ratio of integral intensities of 3:1, respectively. According to these data, one can suppose that the structure of complex cations $[Lu(O,O,N,N\text{-}L)(O\text{-}L)(O,O\text{-}NO_3)(H_2O)]^{2+}$ in acetonitrile is retained, and the solution contains an equilibrium mixture of the complex cations and free NO_3^- ions. The intensities of the bands of coordinated nitrate groups in the IR spectrum of a solution of **4a** are rather low. This fact allows us to suggest a partial dissociation of the complex, and the equilibrium could also involve complex cations $[Lu(O,O,N,N\text{-}L)(O\text{-}L)(H_2O)]^{3+}$ containing no inner-sphere nitrate ion.

The vibrational spectra of the solid neodymium complex **3** with composition $Nd(L)_2(NO_3)_3 \cdot H_2O$ are almost identical to those of the crystalline complex **4a** (see Table 2). The spectra of **3** do not reveal the bands corresponding to absorption of solvate molecules and exhibit a slightly different intensity ratio for the bands of coordinated and free nitrate ions. According to the elemental analysis data and vibrational spectra, this compound has most likely the structure of cationic complex $[Nd(O,O,N,N\text{-}L)(O\text{-}L)(O,O\text{-}NO_3)_2(H_2O)](NO_3)$ where one ligand molecule is tetradentate, while another one is coordinated only *via* one phosphoryl group. The inner coordination sphere of the cation also involves one water molecule and two chelate NO_3 groups (Scheme 3). Coordination number of neodymium in complex **3** is ten.

According to the data of the IR spectra (Table 2), the structure of complex **3** in solution is mainly retained (the positions of the bands of P=O groups, naphthyridine fragment, and nitrate groups are unchanged). However, the intensity ratio of coordinated and free nitrate groups slightly differs, this fact allows one to suppose that in solution cations with two and one nitrate groups, namely, $[Nd(O,O,N,N\text{-}L)(O\text{-}L)(O,O\text{-}NO_3)_2H_2O]^+$ and $[Nd(O,O,N,N\text{-}L)(O\text{-}L)(O,O\text{-}NO_3)H_2O]^{2+}$, may be in equilibrium with the free NO_3^- ions.

4. Conclusions

Coordination properties of a new tetradentate ligand 2,7-bis(diphenylphosphorylamino)-1,8-naphthyridine (**L**) toward lanthanide(III) were studied. The novel complexes $[Nd(L)(NO_3)_3]$ (**1a**), $[Nd(L)(NO_3)_3]\cdot H_2O$ (**1b**), $[Lu(L)(NO_3)_2(H_2O)](NO_3)$ (**2**), $[Nd(L)_2(NO_3)_2(H_2O)](NO_3)$ (**3**), and $[Lu(L)_2(NO_3)(H_2O)](NO_3)_2\cdot 0.75CH_3CN\cdot H_2O$ (**4a**), $[Lu(L)_2(NO_3)(H_2O)](NO_3)_2$ (**4b**) were synthesized and characterized by IR, Raman, and ^{31}P NMR spectroscopy. Structures of the complexes **1b** and **4a** were determined by X-ray diffraction.

The agreement among X-ray crystallography, vibrational and NMR spectroscopy results as well as elemental analysis data allows the assignment of the structures of all investigated complexes both in solid state and in solutions.

The coordination mode of ligand depends on a particular complex composition: it exhibits *O,O,N,N*-fashion in 1:1 complexes and (*O,O,N,N* + *O*)-fashion in 1:2 complexes. In solutions, the coordination mode of the ligand is preserved in all the complexes studied.

Intramolecular H-bonds were found to play a significant role in formation and stabilization of the bisligand complexes.

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Appendix A. Supplementary material

CCDC 833989 and 833962 contains the supplementary crystallographic data for **1b** and **4a**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.12.010.

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