1416 *Russian Chemical Bulletin, International Edition, Vol. 58, No. 7, pp. 1416—1422, July, 2009*

# Coordination of 2-phosphorylalkyl-substituted 1,8-naphthyridines in complexes with lanthanide nitrates

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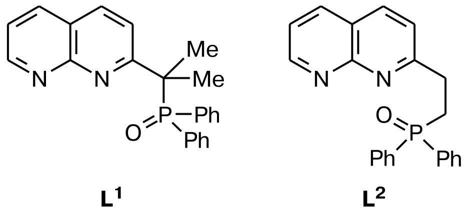
The reaction of 2-phosphorylalkyl-substituted 1,8-naphthyridines, *viz.*, 2-[2-(diphenylphosphoryl)propan-2-yl]-1,8-naphthyridine (**L$^1$**) and 2-[2-(diphenylphosphoryl)ethyl]-1,8-naphthyridine (**L$^2$**), with lanthanide nitrates (Nd, Eu, or Lu) afforded complexes with the metal-to-ligand molar ratio of 1 : 1 and 1 : 2. Based on the IR and Raman spectroscopic data, it was found that the coordination of the ligands **L$^1$** and **L$^2$** in all complexes occurs through the P=O group and the nitrogen atoms of the naphthyridine moiety.

**Key words:** phosphorus-containing 1,8-naphthyridines, complexes, lanthanides, structure, IR spectra, Raman spectra.

In the past decade, the synthetic and coordination chemistry of 1,8-naphthyridine and its derivatives has attracted great interest due to the diverse use of these compounds and their complexes.[1,2] Among 1,8-naphthyridine derivatives, compounds containing coordinatively active substituents at position 2 or positions 2 and 7 are of particular interest. Coordination compounds of this family are used in metal-complex catalysis,[3] some of these compounds exhibit biological activity;[1,2,4] furthermore, some complexes have very interesting photophysical properties,[5] such as luminescence.[6] Although complexes with metal cations belonging to the majority of Groups of the Periodic Table have been investigated,[1,2,7] complexes with lanthanides have been studied to a much lesser extent.[8,9] At the same time, it is known that lanthanide complexes with organic polynitrogen- and oxygen-containing ligands are extensively studied and are used for the preparation of organic light emitting diodes (OLED).[10]

The field of our research is the preparation of new 1,8-naphthyridine systems and the synthesis of the complexes of these systems with lanthanides. Taking into account that tertiary phosphine oxides can form a strong coordination bond with many metals (including lanthanides) through the lone electron pair of the phosphoryl oxygen atom, we synthesized new phosphorus-containing ligands, *viz.*, monosubstituted phosphorylalkyl 1,8-naphthyridines.[11,12]

The coordination properties of this type of ligands were investigated using the example of the complexation of 2-[2-(diphenylphosphoryl)propan-2-yl]-1,8-naphthyridine (**L$^1$**) and 2-[2-(diphenylphosphoryl)ethyl]-1,8-naphthyridine (**L$^2$**) containing linkers of different length with lanthanide nitrates Ln(NO$_3$)$_3$ (Ln = Nd, Eu, or Lu).



**L$^1$** **L$^2$**

## Experimental

The solvents were purified and dried according to known procedures[13] and saturated with argon. The salts Nd(NO$_3$)$_3$·6H$_2$O, Eu(NO$_3$)$_3$·5H$_2$O (Fisher Scientific Company), and Lu(NO$_3$)$_3$·$x$H$_2$O (Aldrich) were used without additional purification. The water content ($x$ = 3) in commercial lutetium nitrate was determined experimentally.

**2-[2-(Diphenylphosphoryl)propan-2-yl]-1,8-naphthyridine (L$^1$) and 2-[2-(diphenylphosphoryl)ethyl]-1,8-naphthyridine (L$^2$)** were synthesized according to procedures described previously.[11,12]

**Synthesis of lanthanide complexes 1—12 (general procedure).** To a solution of a ligand (**L$^1$** or **L$^2$**) (0.3 mmol) in chloroform (1—2 mL), a solution of stoichiometric amount (0.3 or 0.15 mmol) of Ln(NO$_3$)$_3$·$n$H$_2$O in acetonitrile (2 mL) was slowly added dropwise at room temperature, and the mixture was concentrated *in vacuo* (~5 Torr) to ~1 mL. The precipitate that formed was filtered off, washed with diethyl ether, and dried *in vacuo* (~1 Torr) at 100 °C. The decomposition temperatures, the elemental analysis data, the appearance, and the yields of the complexes are given in Table 1.

**IR spectra** of the compounds prepared as KBr pellets and as Nujol or hexachlorobutadiene mulls were recorded in the region

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1375—1381, July, 2009.

400—4000 cm$^{-1}$ on a Nicolet Magna IR-750 FT-IR spectrometer.

**Raman spectra** of the solid samples in the region 200—4000 cm$^{-1}$ and of a solution of complex **12** in nitromethane ($c$ = 0.186 mol L$^{-1}$) were obtained using a LabRAM laser Raman spectrometer equipped with a cooled CCD detector. The excitation line was that at 632.8 nm of a He—Ne laser with an output power not exceeding 10 mW.

The computer curve fitting analysis of the spectral lines with a complicated profile was carried out with the use of the Origin 7.5 program.

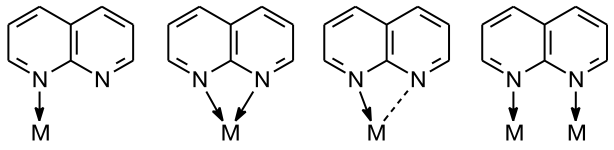
**Quantum chemical calculations** of the geometry and the normal coordinate analysis were carried out with the use of the Gaussian03 program package[14] by the DFT method with the PBE functional and the 6-31G(d,p) basis set.[15]

## Results and Discussion

The reactions of naphthyridines **L**$^1$ and **L**$^2$ with lanthanide nitrates $\mathrm{Ln(NO_3)_3}$ (Ln = Nd, Eu, or Lu) taken in the molar ratios M : L = 1 : 1 and 1 : 2 afford complexes **1**—**12**, which were isolated in the solid state (Table 1).

In studies of the coordination properties of naphthyridines **L**$^1$ and **L**$^2$ with respect to lanthanide cations, the question about the ligands denticity, in particular, about the involvement of the nitrogen atoms in the coordination is the most interesting. The structures of both potentially tridentate naphthyridines **L**$^1$ and **L**$^2$ favor the simultaneous coordination of the P(O) group and one or two nitrogen atoms to one metal ion.

In complexes with metal ions, 1,8-naphthyridine and its derivatives exhibit different coordination modes. According to the Cambridge Structural Database,* unsubstituted 1,8-naphthyridine in mononuclear complexes can act as both the monodentate[7,16,17] (I) and bidentate ligand and can be bound to metal ions either symmetrically[7,18,19] (II) or nonsymmetrically[7,20] (III).



I II III IV

In bi- and polynuclear complexes with 1,8-naphthyridine,[17,21] the ligand is coordinated in a bridging mode (IV) through both nitrogen atoms (the symmetric or non-

**Table 1.** Yields, decomposition temperatures, elemental analysis data, and the color of powder-like complexes **1**—**12**

| Compound | Composition | Yield (%) | T.decomp./°C | Found / Calculated (%) | | | | Molecular formula | Color of the powder |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | P | | |
| **1** | $\mathrm{Nd}(\mathbf{L}^1)(\mathrm{NO_3})_3\cdot 4\mathrm{H_2O}$ | 83 | >205 | 35.71 | 3.72 | 9.25 | 3.97 | $\mathrm{C_{23}H_{21}N_5NdO_{10}P\cdot 4H_2O}$ | Pale-lilac |
| | | | | 35.66 | 3.77 | 9.04 | 4.00 | | |
| **2** | $\mathrm{Eu}(\mathbf{L}^1)(\mathrm{NO_3})_3$ | 90 | >290 | 38.79 | 2.97 | 9.64 | 4.41 | $\mathrm{C_{23}H_{21}EuN_5O_{10}P}$ | Cream |
| | | | | 38.89 | 2.98 | 9.86 | 4.36 | | |
| **3** | $\mathrm{Lu}(\mathbf{L}^1)(\mathrm{NO_3})_3$ | 81 | >210 | 37.68 | 2.88 | 9.58 | 4.21 | $\mathrm{C_{23}H_{21}LuN_5O_{10}P}$ | White |
| | | | | 37.67 | 2.89 | 9.55 | 4.22 | | |
| **4** | $\mathrm{Nd}(\mathbf{L}^1)_2(\mathrm{NO_3})_3\cdot 4\mathrm{H_2O}$ | 75 | >223 | 51.50 | 3.87 | 9.20 | 5.80 | $\mathrm{C_{46}H_{42}N_7NdO_{11}P_2\cdot 4H_2O}$ | White |
| | | | | 51.39 | 3.94 | 9.12 | 5.76 | | |
| **5** | $\mathrm{Eu}(\mathbf{L}^1)_2(\mathrm{NO_3})_3\cdot \mathrm{H_2O}$ | 85 | >220 | 49.68 | 3.93 | 9.02 | 5.53 | $\mathrm{C_{46}H_{42}EuN_7O_{11}P_2\cdot H_2O}$ | White lustrous |
| | | | | 50.18 | 4.09 | 8.97 | 5.63 | | |
| **6** | $\mathrm{Lu}(\mathbf{L}^1)_2(\mathrm{NO_3})_3$ | 80 | >219 | 49.49 | 3.69 | 8.93 | 5.42 | $\mathrm{C_{46}H_{42}LuN_7O_{11}P_2}$ | White |
| | | | | 49.96 | 3.83 | 8.87 | 5.60 | | |
| **7** | $\mathrm{Nd}(\mathbf{L}^2)(\mathrm{NO_3})_3$ | 74 | >180 | 38.02 | 2.81 | 9.80 | 4.32 | $\mathrm{C_{22}H_{19}N_5NdO_{10}P}$ | Pale-lilac |
| | | | | 38.38 | 2.78 | 10.17 | 4.50 | | |
| **8** | $\mathrm{Eu}(\mathbf{L}^2)(\mathrm{NO_3})_3\cdot 4\mathrm{H_2O}$ | 82 | >120 | 34.31 | 3.45 | 8.98 | 3.95 | $\mathrm{C_{22}H_{19}EuN_5O_{10}P\cdot 4H_2O}$ | Cream |
| | | | | 34.39 | 3.54 | 9.11 | 4.03 | | |
| **9** | $\mathrm{Lu}(\mathbf{L}^2)(\mathrm{NO_3})_3$ | 85 | >150 | 36.75 | 2.67 | 9.59 | 4.30 | $\mathrm{C_{22}H_{19}LuN_5O_{10}P}$ | White |
| | | | | 36.73 | 2.66 | 9.74 | 4.31 | | |
| **10** | $\mathrm{Nd}(\mathbf{L}^2)_2(\mathrm{NO_3})_3\cdot 4\mathrm{H_2O}$ | 79 | >165 | 50.35 | 3.59 | 9.23 | 5.88 | $\mathrm{C_{44}H_{38}N_7NdO_{11}P_2\cdot 4H_2O}$ | White |
| | | | | 50.47 | 3.66 | 9.39 | 5.92 | | |
| **11** | $\mathrm{Eu}(\mathbf{L}^2)_2(\mathrm{NO_3})_3$ | 86 | >141 | 49.89 | 3.55 | 9.14 | 5.79 | $\mathrm{C_{44}H_{38}EuN_7O_{11}P_2}$ | White |
| | | | | 50.11 | 3.63 | 9.30 | 5.88 | | |
| **12** | $\mathrm{Lu}(\mathbf{L}^2)_2(\mathrm{NO_3})_3$ | 87 | >145 | 48.87 | 3.41 | 8.99 | 5.72 | $\mathrm{C_{44}H_{38}LuN_7O_{11}P_2}$ | Yellowish |
| | | | | 49.04 | 3.55 | 9.10 | 5.75 | | |

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* More than 50 crystal structures of 1,8-naphthyridine complexes are available in the Cambridge Structural Database (CSD); in the present study, we give references to only some of these structures.

symmetric coordination depending on the nature of the complex-forming agent).

In the presence of active electron-donating substituents in positions 2 and 7 of the naphthyridine core, the new coordination possibilities could arise.

The coordination modes of the ligands and the structures of complexes **1**—**12** were studied by vibrational spectroscopy. The IR and Raman spectra of both the free ligands and their complexes were recorded.

The complete vibrational spectrum of 1,8-naphthyridine was first published in 1973 along with the assignment of normal modes to symmetry species but not to particular forms.[22] The refinement of this assignment based on normal mode calculations was reported in the study.[23] For the correct band assignment, we have carried out quantum chemical calculations[24] of the geometry, as well as of normal mode frequencies and eigenvectors, for the free 1,8-naphthyridine molecule and its model 1 : 1 complex with $FeCl_3$. The complex with the Fe ion was chosen as the model to simplify the computation. The most intense lines in the Raman spectra of the 1,8-naphthyridine and 2-methyl-1,8-naphthyridine molecules are the lines of totally symmetric modes with frequencies at ~1360, ~770, and ~530 $cm^{-1}$.[24] According to the results of the normal coordinate analysis (NCA), all these modes belong to the naphthyridine moiety and are heavily mixed (group vibrations). The most intense line at ~1360 $cm^{-1}$ corresponds to a totally symmetric mode of complex origin with the participation of $\nu_{C=C}$ and $\delta_{C-H}$ coordinates, and the lines at ~770 and ~530 $cm^{-1}$ correspond to "breathing" vibrations of the aromatic moiety with the participation of both nitrogen atoms. In the IR spectrum, the naphthyridine core is characterized by a band of medium intensity at ~1550 $cm^{-1}$, which also belongs to a mixed mode with the participation of the nitrogen atoms.

The calculation for the model complex $[Fe(napy)Cl_3]$ (*napy* is 1,8-naphthyridine) optimized the geometry with two unequal Fe—N bonds and showed that the complex formation should shift the above-mentioned naphthyridine modes to higher frequencies by 15—20 $cm^{-1}$. High-frequency shifts of some IR bands of 1,8-naphthyridine in the case of its bidentate coordination with lanthanides have been reported previously.[8] The same shifts are observed in the spectra of all the complexes studied in the present work. However, it should be emphasized that due to complex mode eigenvectors, these shifts do not allow one to distinguish between particular coordination modes of the nitrogen atoms, *i.e.*, to chose between the structures I—III. The coordination of the phosphoryl oxygen atom to metal ions, including lanthanide ions, leads to a shift of the ν(P=O) band by 30—35 $cm^{-1}$ to lower frequencies.[25]

The spectral manifestations of the free and coordinated nitrato groups were also investigated in detail.[26] The free nitrato groups are observed in the IR spectra at ~1370 $cm^{-1}$, whereas the bidentate nitrato groups appear in the IR spectra[26] as ν(NO) at ~1500 $cm^{-1}$, $\nu_s(NO_2)$ at 1030 $cm^{-1}$, and $\nu_{as}(NO_2)$ at ~1300 $cm^{-1}$. It is the latter bands that are observed in the IR spectra of complexes **1**—**12**, whereas these bands could not be identified in the Raman spectra because of their low intensities.

The frequencies of the salient analytical bands of the complexes under study compared to those of the free ligands are given in Tables 2 and 3.

The IR spectra of some complexes (**1**, **4**, **5**, **8**, and **10**) exhibit bands at 3200—3650 $cm^{-1}$ characteristic of outer-sphere water molecules.

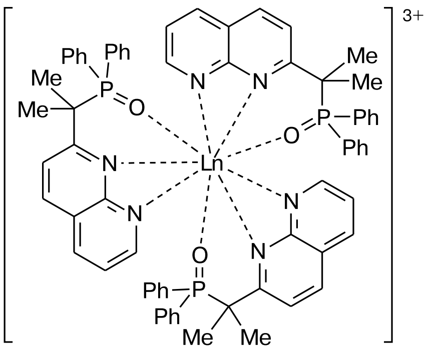
**Complexes $[Ln(L^1)(NO_3)_3] \cdot nH_2O$ (1—3).** In the IR spectra of complexes **1**—**3**, the P=O absorption bands are shifted to low frequencies of ~1130 $cm^{-1}$, and the bands of nitrato groups suggest their bidentate coordination. The bands of free nitrato (~1370 $cm^{-1}$) and phosphoryl (~1177 $cm^{-1}$) groups are absent. The frequencies of the naphthyridine core in the IR and Raman spectra (see Table 2) are shifted to high frequencies by approximately 20 $cm^{-1}$ and suggest the coordination of the nitrogen atoms. However, as mentioned above, these data do not allow the determination of the coordination mode of the ligands. Attempts to prepare crystals of complexes **1**—**3** suitable for X-ray diffraction failed. The X-ray powder diffraction pattern of complex **1** shows the amorphous state of the sample. Therefore, we compared the vibrational spectra of complexes **1**—**3** with those of the crystalline complexes of another stoichiometric composition, *viz.*, $[Nd(L^1)_3]^{3+} \cdot 3(NO_3)^- \cdot MeCN$ (**13**), $[Eu(L^1)_3]^{3+} \cdot 3(NO_3)^- \cdot [Eu(NO_3)_3 \cdot 4H_2O] \cdot MeCN$ (**14**), and $[Lu(L^1)_3]^{3+} \cdot 3(NO_3)^- \cdot [Lu(NO_3)_3 \cdot 3H_2O] \cdot 2\ MeCN \cdot 0.5H_2O$ (**15**),

**Table 2.** Frequencies of coordination-sensitive bands in the vibrational spectra (ν/$cm^{-1}$) of the ligand $L^1$, complexes **1**—**6**, and crystalline complexes **13**—**15**

| Compound | ν(P=O) (IR) | Vibrations of the naphthyridine core | | | ν(N=O) (IR) | $\nu_{as}(NO_2)$ (IR) |
|---|---|---|---|---|---|---|
| | | IR | Raman | | | |
| $L^1$ | 1177 | 1544 | 1368 | 777 | — | — |
| **1** | 1129 | 1563 | 1382 | 795 | 1490 | 1303 |
| **2** | 1133 | 1564 | 1383 | 797 | 1480 | 1308 |
| **3** | 1136 | 1567 | 1390 | 801 | 1498 | 1300 |
| **4** | 1127 | 1562 | 1383,<br>1371* | 795,<br>781* | 1470 | 1300 |
| **5** | 1131 | 1564 | 1383,<br>1370 | 797,<br>777 | 1480 | 1314 |
| **6** | 1133 | 1566 | 1388,<br>1370 | 800,<br>777 | 1497 | 1315 |
| **13** [24] | 1128 | 1563 | 1383 | 797 | — | — |
| **14** [24] | 1130 | 1564 | 1383 | 798 | 1482 | 1300 |
| **15** [24] | 1133 | 1566 | 1390 | 802 | 1498 | 1314 |

* The frequency was obtained by the computer curve fitting analysis of the spectral lines with a complicated profile.

whose structures have been established by X-ray diffraction previously.[24] In spite of the different compositions, compounds **13—15** contain the complex cation $[Ln(\mathbf{L}^1)_3]^{3+}$ as the main structural fragment. For all the lanthanides (Ln = Nd, Eu, and Lu) under study, these cations are isostructural, the three ligands $\mathbf{L}^1$ being coordinated to the central lanthanide atom in the *O*,*N*,*N*-tridentate fashion. Thus, the coordination polyhedron is formed by nine atoms.



$[Ln(\mathbf{L}^1)_3]^{3+}$

The vibrational spectra of crystalline complexes **13—15** in the region of analytical frequencies of the ligand are identical to the spectra of the corresponding monoligand complexes **1—3** (see Table 2 and Fig. 1). Therefore, it may be concluded with certainty that the ligand $\mathbf{L}^1$ in the complexes under consideration is also coordinated in a tridentate fashion.

Complexes **1—3** are soluble in polar solvents. The above-mentioned data suggest that the interaction of the ligand $\mathbf{L}^1$ with lanthanide nitrates affords the neutral monodentate complexes $[Ln(\eta^3\text{-}O,N,N\text{-}\mathbf{L}^1)(\eta^2\text{-}O,O\text{-}NO_3)_3] \cdot nH_2O$ (Ln = Nd, Eu, or Lu, $n$ = 0 or 4), in which the ligand is coordinated in a tridentate fashion, and the coordination sphere is completed by three bidentate nitrato groups.

**Table 3.** Frequencies of coordination-sensitive bands in the vibrational spectra ($\nu$/cm$^{-1}$) of the ligand $\mathbf{L}^2$ and complexes **7—12**

| Compound | ν(P=O) (IR) | Vibrations of the naphthyridine core | | | ν(N=O) (IR) | $\nu_{as}(NO_2)$ (IR) |
|---|---|---|---|---|---|---|
| | | IR | Raman | | | |
| $\mathbf{L}^2$ | 1183 | 1549 | 1374 | 781 | – | – |
| **7** | 1144 | 1567 | 1382 | 791 | 1480 | 1299 |
| **8** | 1144 | 1568 | 1383 | 792 | 1500 | 1304 |
| **9** | 1146 | 1571 | 1387 | 796 | 1500 | 1301 |
| **10** | 1144 | 1566 | 1383,<br>1371* | 791,<br>777* | 1470 | 1304 |
| **11** | 1148 | 1565,<br>1554 | 1382,<br>1369 | 792,<br>777 | 1480 | 1309 |
| **12** | 1158,<br>(1143)* | 1557,<br>1570 sh | 1387,<br>1368 | 795,<br>775 | 1500 | 1306 |

* The frequency was obtained by the computer curve fitting analysis of the spectral lines with a complicated profile.

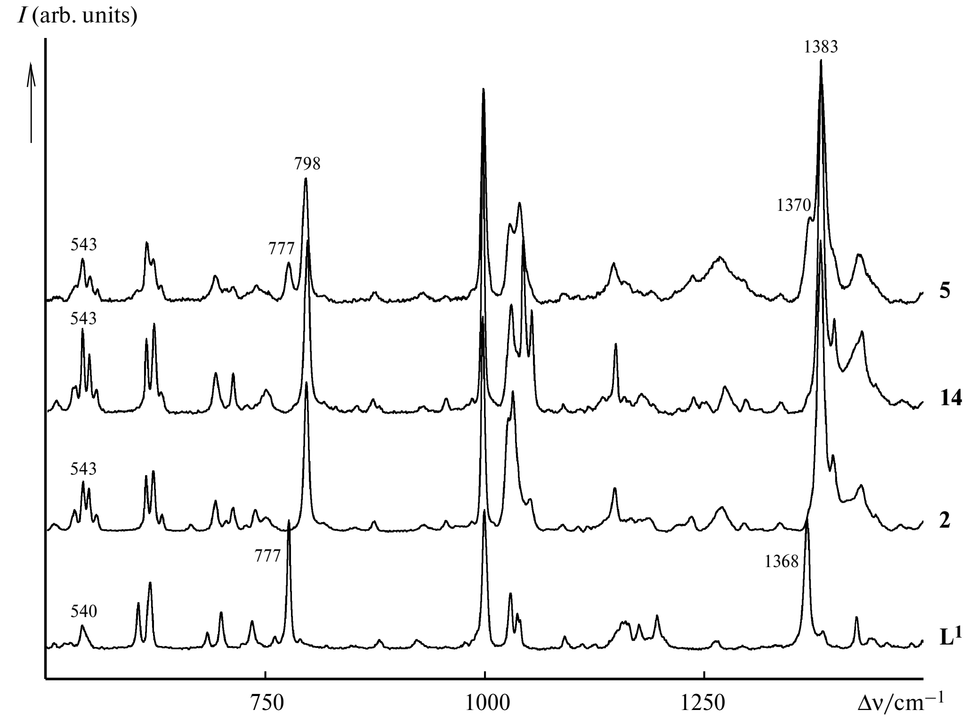
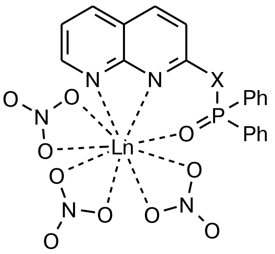


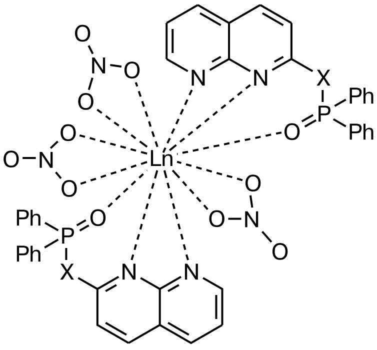
**Fig. 1.** Raman spectra of the free ligand $\mathbf{L}^1$ and its complexes with europium nitrate with a metal-to-ligand ratio of 1 : 1 (**2**) and 1 : 2 (**5**) and of crystalline complex **14**.



X = $CMe_2$ (**L$^1$**), $CH_2CH_2$ (**L$^2$**)

The coordination sphere of the lanthanide cation in complexes **1—3** is formed by nine atoms, *viz.*, two nitrogen atoms of the naphthyridine moiety, one phosphoryl oxygen atom of the ligand, and six oxygen atoms of three bidentate nitrato groups, and the complexes have the following composition [$LnN_2O_7$].

**Complexes [Ln($L^1$)$_2$($NO_3$)$_3$] · *n*$H_2O$ (4—6).** The vibrational frequencies of complexes **4—6** are similar to those of the complexes with composition 1 : 1 (see Table 2). However, unlike the Raman spectra of monoligand complexes **1—3**, the spectra of bis-ligand complexes **4—6** show the doublet splitting of the lines corresponding to the vibrations of the aromatic naphthyridine system (see Fig. 1). Apparently, the splitting is caused by a certain nonequivalence of the coordinated ligand molecules due to the steric hindrance in the crowded coordination polyhedron [$LnN_4O_8$], which is formed by 12 atoms in the bis-ligand complexes. It should be noted that such a high coordination number is not unusual for lanthanide complexes.[27] For example, the X-ray diffraction data[19] showed that the praseodymium atom in the complex with 1,8-naphthyridine has the coordination number 12; the same coordination number is suggested for the complexes of 1,8-naphthyridine with lanthanide nitrates and perchlorates.[8] Therefore, it can be concluded that bis-ligand complexes **4—6** are also neutral, and both ligands are coordinated in a tridentate fashion, whereas the three nitro groups are coordinated in a bidentate fashion: [Ln($\eta^3$-*O*,*N*,*N*-**L$^1$**)$_2$($\eta^2$-*O*,*O*-$NO_3$)$_3$] · *n*$H_2O$ (Ln = Nd, Eu, or Lu, *n* = 0, 1, or 4).



X = $CMe_2$ (**L$^1$**), $CH_2CH_2$ (**L$^2$**)

**Complexes [Ln($L^2$)($NO_3$)$_3$] · *n*$H_2O$ (7—9).** The positions of the IR bands and the Raman lines in the vibrational spectra of complexes **7–9** (see Table 3) indicate that the ligand is coordinated both through the phosphoryl oxygen atom and the nitrogen atoms of the naphthyridine core.

Attempts to prepare crystalline complexes with the ligand **L$^2$** failed. However, the spectra of complexes **7—9** are similar to the spectra of the corresponding complexes **1—3**, although the shifts of the analytical bands of the ligand in the spectra of complexes **7—9** (see Table 3) are somewhat smaller than those in the spectra of related complexes **1—3** containing the ligand with the short linker (see Table 2). Complexes **7—9** are moderately soluble in polar solvents. The above-considered data suggest that both groups of the monoligand complexes are structurally similar, *i.e.*, the ligand **L$^2$** in complexes **7—9** is also coordinated in a tridentate fashion, whereas the three nitrato groups are bidentate: [Ln($\eta^3$-*O*,*N*,*N*-**L$^2$**)($\eta^2$-*O*,*O*-$NO_3$)$_3$] · *n*$H_2O$ (Ln = Nd, Eu, or Lu, *n* = 0 or 4). The coordination number of the lanthanide cation is nine.

**Complexes [Ln($L^2$)$_2$($NO_3$)$_3$] · *n*$H_2O$ (10—12).** The frequencies of the vibrations of bis-ligand complexes **10—12** are similar to the corresponding frequencies of monoligand complexes **7—9** (see Table 3). In addition, the vibrational spectra of complexes **10—12**, like the spectra of bis-ligand complexes **4—6** containing the ligand **L$^1$** with the short linker, also exhibit the splitting of the Raman lines corresponding to the vibrations of the naphthyridine moiety (see Table 3, Fig. 2 (the lutetium complexes)).

As opposed to the complexes containing the ligand with the short linker, the splitting is observed not only in the Raman spectra but also in the IR spectra (the band at ~1570 cm$^{-1}$). As exemplified by the Raman spectrum of readily soluble bis-ligand complex **12** (see Fig. 2), this splitting is not the Davydov splitting because it is retained in the spectrum of a solution. Hence, it can be suggested that complexes **10—12** are structurally similar to complexes **4—6**, [Ln($\eta^3$-*O*,*N*,*N*-**L$^2$**)($\eta^2$-*O*,*O*-$NO_3$)$_3$] · *n*$H_2O$ (Ln = Nd, Eu, or Lu; *n* = 0 or 4). Both ligand molecules are coordinated in a tridentate fashion but not strictly equivalent, and three nitrato groups are coordinated in a bidentate fashion. The coordination number of lanthanide is 12, and the coordination polyhedron has the composition [$LnN_4O_8$]. Of all the complexes under study, compounds **10—12** are most readily soluble in polar solvents (acetonitrile, nitromethane, acetone, and ethanol).

It should be noted that the changes in the vibrational spectra of the complexes containing the ligand **L$^1$** with the short linker are much more substantial than those observed in the spectra of the complexes containing the ligand **L$^2$** with the longer linker. For example, the shift of the P=O frequency for monoligand complexes **1—3** is 48—41 cm$^{-1}$, whereas the shift for complexes **7—9** is only 39—37 cm$^{-1}$ (see Tables 2 and 3). The shifts of the IR bands and the Raman lines corresponding to the vibrations of the naphthyridine cores of complexes **1—3** are 19—23, 14—22, and 18—24 cm$^{-1}$ for the bands at 1560, 1380, and 790 cm$^{-1}$, respectively, whereas these shifts for complexes

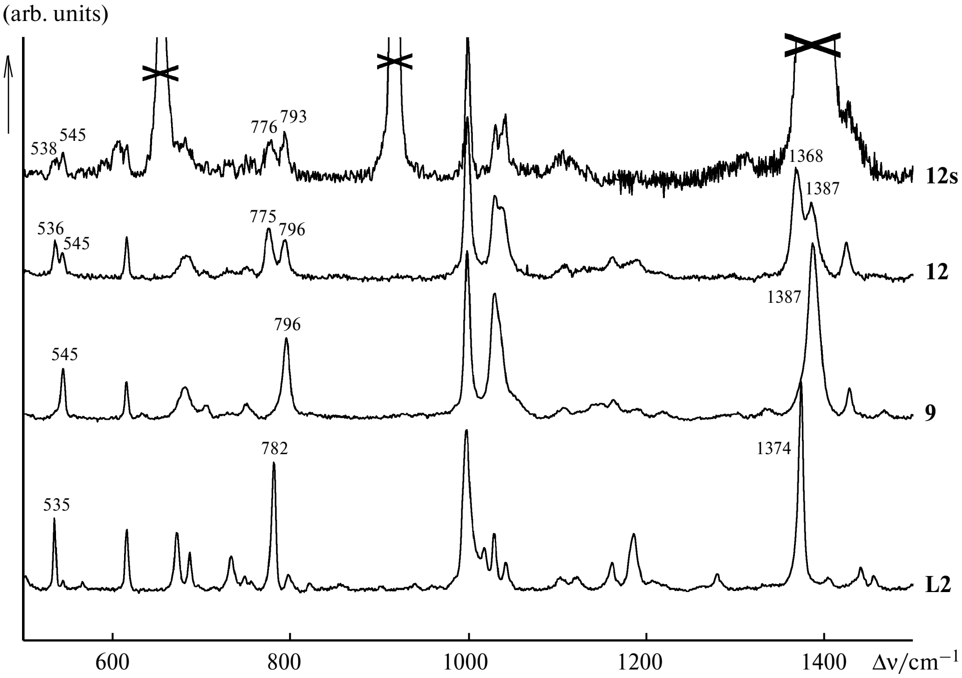


**Fig. 2.** Raman spectra of the free ligand **L$^2$** and its complexes with lutetium nitrate with a metal-to-ligand ratio of 1 : 1 (**9**) and 1 : 2 (**12**) and of a solution of complex **12** in nitromethane (**12s**). The crossed lines refer to the solvent.

**7**—**9** are 18—22, 8—13, and 10—15 cm$^{-1}$, respectively (see Tables 2 and 3). This suggests that the tridentate ligand **L$^1$** with the short linker forms more stable complexes with lanthanide nitrates compared to the analogous ligand **L$^2$** with the longer linker. Most likely, this is due to the fact that the coordination of **L$^1$** leads to the formation of the more stable six-membered metallacycle.

The shifts and splitting of the IR bands and the Raman lines corresponding to the vibrations of the naphthyridine system increase in the series Nd—Eu—Lu in all the groups of the compounds studied. At the same time, the shift of the band of the coordinated P=O groups decreases in the same series. This seems to be associated with a change in the strength of coordination bonds. Presumably, the strength of the bonds with the nitrogen atoms of the naphthyridine core increases, whereas the bond with the phosphoryl oxygen atom becomes weaker with a decrease in the ionic radius of the metal atom.

Thus, 2-phosphorylalkyl-substituted 1,8-naphthyridines **L$^1$** and **L$^2$** in the mononuclear complexes with lanthanide nitrates (neodymium, europium, and lutetium) exhibit the highest possible *O*,*N*,*N*-denticity regardless of the linker length, the composition of the complex, and the size of the lanthanide cation.

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*Received November 19, 2008;*
*in revised form March 3, 2009*