2-(*N*-Phosphorylamino)-substituted 1,8-naphthyridines. Synthesis and structure

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The previously unknown 2-(*N*-phosphorylamino)-substituted 1,8-naphthyridines were synthesized by the direct phosphorylation of 2-amino-5,7-dimethyl-1,8-naphthyridine with phosphoryl chlorides of different structures. The structures of the reaction products were confirmed by mass spectrometry, ^{1}H and ^{31}P NMR spectroscopy, and X-ray diffraction study (for one of the compounds).

Key words: phosphorylation, 1,8-naphthyridines, phosphoryl chlorides, synthesis, structure, mass spectra, NMR spectra, X-ray diffraction study.

The search for new original ligands, that can selectively form stable complexes with metals belonging to different Groups of the Periodic table, is an interesting and important problem of modern chemistry. Investigations in this area are associated with the necessity of solving problems related to the purification and separation of nuclear waste in industry, as well as the problems of metal-complex catalysis and the creation of materials for the design of energy-saving equipment. In this context, coordination compounds containing ligand groups of several types[1] have attracted growing attention and have found increasing application. Polynitrogen-containing heterocyclic ligands have attracted great interest. Complexes of these ligands with f elements, for example, with lanthanides, often display interesting photophysical (in particular, luminescence) properties and, hence, they can serve as materials for the design of electroluminescent diodes.[2] Along with pyridines, triazoles, triazines, and phenanthrolines, particular attention is given to 1,8-naphthyridines[3,4] in which the endocyclic nitrogen atoms are in the favorable arrangement for the formation of chelate complexes with different metal cations, including actinides and lanthanides. The introduction of additional groups capable of forming coordination bonds at positions 2 and 7 of the heterocyclic moiety of 1,8-naphthyridine results in the formation of oligodentate polyfunctional ligands, which can form complexes of different types with metal salts. The presence of P^{III}-containing fragments in the side chains of these ligands gives rise to an additional coordination center and, correspondingly, to new coordination properties of 1,8-naphthyridine derivatives.[1]

Previously,[5,6] we have synthesized a series of phosphoalkyl derivatives of 1,8-naphthyridine, in which the phosphoryl fragment is bound to the heterocyclic moiety by structurally different alkylene linkers of different lengths. The coordination properties of these systems have been studied, and these systems have shown to act as tridentate ligands in complexes with lanthanides, both the nitrogen atoms of the heterocyclic moiety and the oxygen atom of the phosphoryl group being involved in coordination bonds.[7]

These data have stimulated the continuation of the search for and design of tridentate organophosphorus ligands based on 1,8-naphthyridine. It would be expected that the best conditions for the complexation would be achieved with the use of the —NH— bridge as a linker that connects the ligand fragments (the heterocycle and the phosphoryl group). In the presence of this bridge, not only the distances between the endocyclic nitrogen atoms and the phosphorus atom are optimized but also the electron system of the chelating center is delocalized.

It is also known that 2-amino-1,8-naphthyridine derivatives have a strong ability to form hydrogen bonds,[8—10] due to which these compounds can be used as modern tools for biochemical studies.[11—14]

The aim of the present study was to develop a convenient and efficient method for the synthesis of 2-(phosphorylamino)-substituted derivatives of 1,8-naphthyridine.

Results and Discussion

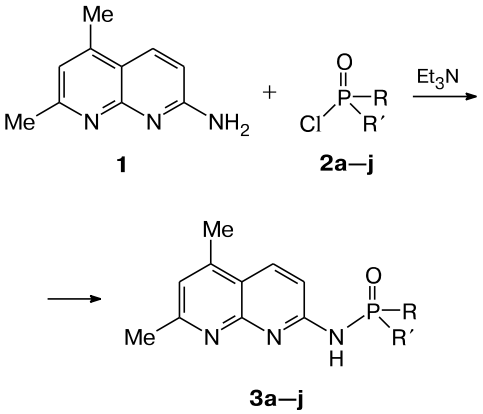
The above-mentioned compounds were successfully synthesized by the direct phosphorylation of 2-amino-1,8-naphthyridines with phosphoryl chlorides (Scheme 1).

We chose 2-amino-5,7-dimethyl-1,8-naphthyridine (**1**), which can easily be synthesized from cheap and com-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1404—1409, July, 2009.

1066-5285/09/5807-1445

Scheme 1



2,3	R	R′	2,3	R	R′
a	Ph	Ph	**f**	Ph	Me
b	OPh	OPh	**g**	OPh	Me
c	OC_6H_4Me-*o*	OC_6H_4Me-*o*	**h**	Ph	OEt
d	OC_6H_4Me-*m*	OC_6H_4Me-*m*	**i**	Me	OEt
e	OC_6H_4Me-*p*	OC_6H_4Me-*p*	**j**	OEt	OEt

mercially available reactants,[15] as the starting amino-substituted naphthyridine and various phosphoric, phosphonic, and phosphinic acid monochlorides (**2a—j**) as phosphorylating agents. This allowed us to widely vary the nature of the substituents at the ligand phosphoryl group.

Taking into account that the starting heterocyclic amine **1** is poorly soluble in most of organic solvents, 2-phosphorylamino-1,8-naphthyridines (**3**) were initially synthesized by refluxing a solution of amine **1** in pyridine with the phosphorylating agent in the presence of triethylamine, which is much more basic than pyridine as the hydrogen chloride acceptor (method ***A***). However, it appeared that, although this method affords phosphorylamides **3a—g** in high (71—83%) yields (Table 1), the yield of amide **3h** is substantially lower (45%); moreover, attempts to prepare phosphorylamides **3i,j** according to the method ***A*** failed because the corresponding starting phosphoryl chlorides **2i,j** undergo the destruction under these conditions.

Hence, we developed an alternative, much milder approach to the synthesis of 2-phosphorylamino-1,8-naphthyridines **3** based on the reaction of phosphoryl chlorides **2** with a suspension of aminonaphthyridine **1** in chloroform in the presence of triethylamine under heating (method ***B***). Under these conditions, we succeeded in preparing phosphoramides **3i,j** and synthesized compounds **3a—h** in higher yields (the yield of phosphoramide **3h** was substantially higher) than those obtained according to the method ***A*** (see Table 1).

All 2-(*N*-phosphorylamino)-substituted 1,8-naphthyridines **3a—j** are air-stable white or pale-yellow solid compounds, which are readily soluble in such organic solvents as *N*,*N*-dimethylformamide, dimethyl sulfoxide, pyridine,

Table 1. Yields, melting points, and elemental analysis data for naphthyridines **3**

Compound	Yield (%)	M.p./°C	Found / Calculated (%)				Molecular formula
			C	H	N	P	
3a	86 (78)*	191—192	70.85	5.29	11.30	8.45	$C_{22}H_{20}N_3OP$
			70.77	5.40	11.25	8.30	
3b	80 (71)	67—68	65.18	5.03	10.21	7.46	$C_{22}H_{20}N_3O_3P$
			65.18	4.97	10.37	7.64	
3c	82 (80)	138—139	66.37	5.49	9.70	7.10	$C_{24}H_{24}N_3O_3P$
			66.50	5.58	9.69	7.15	
3d	80 (74)	98—99	66.61	5.52	9.74	7.23	$C_{24}H_{24}N_3O_3P$
			66.50	5.58	9.69	7.15	
3e	84 (83)	127—128	66.42	5.60	9.78	7.07	$C_{24}H_{24}N_3O_3P$
			66.50	5.58	9.69	7.15	
3f	83 (72)	229—230	65.74	5.80	13.50	9.67	$C_{17}H_{18}N_3OP$
			65.59	5.83	13.50	9.95	
3g	79 (74)	186—187	62.14	5.49	12.75	9.43	$C_{17}H_{18}N_3O_2P$
			62.38	5.54	12.84	9.46	
3h	78 (45)	98—99	63.40	5.94	12.35	9.01	$C_{18}H_{20}N_3O_2P$
			63.34	5.91	12.31	9.07	
3i	82 (0)	203—204	55.83	6.44	15.11	10.97	$C_{13}H_{18}N_3O_2P$
			55.91	6.50	15.05	11.09	
3j	71 (0)	117—118	54.55	6.41	13.66	10.10	$C_{14}H_{20}N_3O_3P$
			54.36	6.52	13.59	10.01	

*The yields of naphthyridines **3** synthesized according to the method ***A*** are given in parentheses.

benzene, and chloroform and are poorly soluble in hexane, diethyl ether, and water. The purity and the structures of the reaction products were confirmed by elemental analysis and NMR spectroscopy ($^{31}P\{^1H\}$ and ^1H) (Table 2). In all cases, the $^{31}P\{^1H\}$ NMR spectra show a singlet in the region characteristic of the corresponding environment of the phosphorus atom. The ^1H NMR spectra have several types of signals. Thus, the low-field signals characterize the presence of the naphthyridine moiety, and the high-field signals correspond to aliphatic substituents at the phosphorus atom, as well as to the methyl groups at the naphthyridine moiety. In addition, signals

Table 2. Mass-spectrometric data and the $^{31}P\{^1H\}$ and ^1H NMR spectroscopic data ($CDCl_3$) for naphthyridines **3**

Compound	MS, m/z (I_{rel} (%))	NMR, δ (J/Hz)	
		^{31}P	^1H
3a	373 $[M]^+$ (55.5), 372 $[M - H]^+$ (100), 296 $[M - C_6H_5]^+$ (42.6), 278 $[C_{16}H_{13}N_3P]^+$ (6.6), 248 $[C_{16}H_{13}N_3]^+$ (19.5), 218 $[C_{12}H_{13}NOP]^+$ (17.8), 199 $[C_{12}H_{10}NP]^+$ (6.4)	16.8	2.49 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 7.08 (s, 1 H, $H_{naphth}(6)$), 7.26 (d, 1 H, $H_{naphth}(3)$, $J = 9.1$), 7.46—7.54 (m, 6 H, *m*-Ph + *p*-Ph), 7.81—7.86 (m, 4 H, *o*-Ph), 8.23 (d, 1 H, $H_{naphth}(4)$, $J = 9.1$)
3b	405 $[M]^+$ (8.0), 404 $[M - H]^+$ (13.5), 328 $[M - C_6H_5]^+$ (6.2), 312 $[M - C_6H_5O]^+$ (93.1), 294 $[M - (C_6H_5O + H_2O)]^+$ (22.5), 249 $[C_{12}H_{12}NO_3P]^+$ (100), 248 $[C_{12}H_{11}NO_3P]^+$ (86.3), 218 $[C_{11}H_7O_3P]^+$ (36.2)	−3.0	2.52 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 6.94 (s, 1 H, $H_{naphth}(6)$), 7.10—7.13 (m, 3 H, $H_{naphth}(3)$ + *p*-Ph), 7.27—7.28 (m, 8 H, *o*-Ph + *m*-Ph), 7.95 (dd, 1 H, $H_{naphth}(4)$, $^2J = 9.4$, $^3J = 1.8$)
3c	433 $[M]^+$ (15.2), 326 $[M - C_7H_7O]^+$ (62.7), 308 $[M - (C_7H_7O + H_2O)]^+$ (20.4), 263 $[C_{14}H_{16}O_3P]^+$ (97.4), 262 $[C_{14}H_{15}O_3P]^+$ (100), 236 $[C_{10}H_{11}N_3O_2P]^+$ (9.8), 218 $[C_{10}H_{19}N_3OP]^+$ (20.2)	−2.7	2.27 (s, 6 H, $C_6H_4C\underline{H}_3$), 2.51 (s, 3 H, Me_{naphth}), 2.55 (s, 3 H, Me_{naphth}), 6.93 (s, 1 H, $H_{naphth}(6)$), 6.99—7.16 (m, 7 H, $H_{naphth}(3)$ + *m*-$C_6\underline{H}_4CH_3$ + *p*-$C_6\underline{H}_4CH_3$), 7.37 (d, 2 H, *o*-$C_6\underline{H}_4CH_3$, $J = 8.0$), 7.94 (d, 1 H, $H_{naphth}(4)$, $J = 9.4$)
3d	433 $[M]^+$ (6.1), 326 $[M - C_7H_7O]^+$ (66.9), 308 $[M - (C_7H_7O + H_2O)]^+$ (16.1), 263 $[C_{14}H_{16}O_3P]^+$ (93.6), 262 $[M - C_{10}H_9N_3]^+$ (100), 218 $[M - 2\,C_6H_4CH_3]^+$ (23.3), 173 $[C_{10}H_{11}N_3]^+$ (8.7)	−3.5	2.28 (s, 6 H, $C_6H_4C\underline{H}_3$), 2.51 (s, 3 H, Me_{naphth}), 2.54 (s, 3 H, Me_{naphth}), 6.91 (d, 2 H, *m*-$C_6\underline{H}_4CH_3$, $J = 7.1$), 6.93 (s, 1 H, $H_{naphth}(6)$), 7.05—7.17 (m, 7 H, $H_{naphth}(3)$ + + *o*-$C_6\underline{H}_4CH_3$ + *p*-$C_6\underline{H}_4CH_3$), 7.95 (d, 1 H, $H_{naphth}(4)$, $J = 9.4$)
3e	433 $[M]^+$ (10.6), 326 $[M - C_7H_7O]^+$ (54.3), 308 $[M - (C_7H_7O + H_2O)]^+$ (19.6), 263 $[C_{14}H_{16}O_3P]^+$ (100), 262 $[M - C_{10}H_9N_3]^+$ (83.7), 236 $[C_{10}H_{11}N_3O_2P]^+$ (11.3), 218 $[M - 2\,OC_6H_4CH_3]^+$ (20.0)	−3.2	2.27 (s, 6 H, $C_6H_4C\underline{H}_3$), 2.52 (s, 3 H, Me_{naphth}), 2.55 (s, 3 H, Me_{naphth}), 6.95 (s, 1 H, $H_{naphth}(6)$, 7.04—7.16 (m, 9 H, $H_{naphth}(3)$ + $C_6\underline{H}_4CH_3$), 7.97 (d, 1 H, $H_{naphth}(4)$, $J = 9.4$)
3f	311 $[M]^+$ (18.0), 310 $[M - H]^+$ (19.9), 296 $[M - CH_3]^+$ (100), 278 $[M - (CH_3 + H_2O)]^+$ (5.4), 234 $[M - C_6H_5]^+$ (4.5), 218 $[C_{11}H_{13}N_3P]^+$ (18.5), 173 $[C_{10}H_{11}N_3]^+$ (9.6)	30.1	1.95 (d, 3 H, P—CH_3, $^2J_{HP} = 14.4$), 2.50 (s, 3 H, Me_{naphth}), 2.59 (s, 3 H, Me_{naphth}), 6.94 (s, 1 H, $H_{naphth}(6)$), 7.20 (d, 1 H, $H_{naphth}(3)$, $J = 9.1$), 7.41—7.51 (m, 3 H, *o*-Ph + *p*-Ph), 7.94 (d, 1 H, $H_{naphth}(4)$, $J = 9.1$), 7.97—8.02 (m, 2 H, *m*-Ph)
3g	326 $[M]^+$ (2.3), 252 $[M - C_6H_3]^+$ (9.6), 250 $[M - C_6H_5]^+$ (8.5), 249 $[M - C_6H_6]^+$ (38.8), 235 $[M - H, C_6H_4O]^+$ (19.7), 234 $[M - C_6H_5O]^+$ (100), 216 $[M - (C_6H_5O + H_2O)]^+$ (43.9), 173 $[C_{10}H_{11}N_3]^+$ (8.7)	29.4	2.06 (d, 3 H, P—CH_3, $^2J_{HP} = 17.6$), 2.56 (s, 3 H, Me_{naphth}), 2.65 (s, 3 H, Me_{naphth}), 7.00—7.06 (m, 2 H, *m*-Ph), 7.05 (d, 1 H, $H_{naphth}(3)$, $J = 9.0$), 7.11—7.15 (m, 4 H, *o*-Ph + *p*-Ph + $H_{naphth}(6)$), 8.01 (d, 1 H, $H_{naphth}(4)$, $J = 9.0$)
3h	341 $[M]^+$ (11.6), 340 $[M - H]^+$ (15.4), 312 $[M - C_2H_5]^+$ (20.0), 297 $[M - C_2H_4O]^+$ (11.4), 296 $[M - C_2H_5O]^+$ (10.0), 294 $[M - (C_2H_5 + H_2O)]^+$ (19.8), 248 $[C_{11}H_{11}N_3O_2P]^+$ (50.1), 236 $[M - (C_6H_5 + C_2H_5)]^+$ (99.4), 220 $[M - (C_6H_5 + C_2H_5O)]^+$ (90.3), 173 $[C_{10}H_{11}N_3]^+$ (100)	18.4	1.34 (t, 3 H, O—CH_2—$\underline{CH}_3$, $J = 7.0$), 2.49 (s, 3 H, Me_{naphth}), 2.58 (s, 3 H, Me_{naphth}), 4.15—4.23 (m, 2 H, O—$\underline{CH}_2$—CH_3), 6.94 (s, 1 H, $H_{naphth}(6)$, 7.20 (d, 1 H, $H_{naphth}(3)$, $J = 9.1$), 7.38—7.43 (m, 2 H, *m*-Ph), 7.48 (m, 1 H, *p*-Ph), 7.88—7.97 (m, 3 H, *o*-Ph + $H_{naphth}(4)$)
3i	279 $[M]^+$ (20.1), 250 $[M - C_2H_5]^+$ (5.0), 236 $[M - (C_2H_4 + CH_3)]^+$ (21.8), 235 $[M - (C_2H_5 + + CH_3)]^+$ (19.1), 220 $[M - (C_2H_4O + CH_3)]^+$ (100), 173 $[C_{10}H_{11}N_3]^+$ (60.2), 157 $[C_{10}H_9N_2]^+$ (8.2)	29.5	1.26 (td, 3 H, O—CH_2—$\underline{CH}_3$, $J_{HH} = 7.1$, $J_{HP} = 2.0$), 1.90 (d, 3 H, P—CH_3, $^2J_{HP}$=17.6), 2.55 (s, 3 H, Me_{naphth}), 2.63 (s, 3 H, Me_{naphth}), 3.98—4.04 (m, 1 H, O—$\underline{CH}_2$—CH_3), 4.13—4.17 (m, 1 H, O—$\underline{CH}_2$—CH_3), 6.98 (s, 1 H, $H_{naphth}(6)$), 7.25 (d, 1 H, $H_{naphth}(3)$, $J = 8.9$), 8.07 (d, 1 H, $H_{naphth}(4)$, $J = 8.9$)
3j	309 $[M]^+$ (14.1), 281 $[M - C_2H_4]^+$ (10.9), 265 $[M - C_2H_4O]^+$ (4.2), 253 $[M - 2C_2H_4]^+$ (4.7), 236 $[C_{12}H_{15}N_3O_2P]^+$ (13.1), 201 $[C_{12}H_{15}N_3]^+$ (6.2), 173 $[C_{10}H_{11}N_3]^+$ (100)	1.8	1.32 (t, 6 H, O—CH_2—$\underline{CH}_3$, $J = 7.0$), 2.57 (s, 3 H, Me_{naphth}), 2.62 (s, 3 H, Me_{naphth}), 4.10—4.21 (m, 4 H, O—$\underline{CH}_2$—CH_3), 7.00 (s, 1 H, $H_{naphth}(6)$, 7.27 (d, 1 H, $H_{naphth}(3)$, $J = 8.9$), 8.10 (d, 1 H, $H_{naphth}(4)$, $J = 8.9$)

assigned to aromatic substituents at the phosphorus atom and a signal for the proton of the NH group can be observed at low field depending on the type of the compound (see Table 2).

Since the phosphorylamide derivatives of 1,8-naphthyridine synthesized in the present work contain various substituents at the phosphorus atom, these compounds differ in stability. Hence, it was of interest to investigate the stability of these compounds to electron impact.

The mass-spectrometric study showed that naphthyridine **3a** containing the diphenylphosphoryl group is most stable to electron impact. The mass spectrum of this compound has the most intense molecular ion peak M^+ and the maximum related stabilizing effect giving the base ion at m/z = 372 with the intensity of approximately 100%. For compounds **3f** and **3h** (containing one phenyl group at the phosphorus atom), this effect is much less pronounced. In turn, the least intense molecular ions are observed for naphthyridines **3b—e** and **3g** containing the phenoxy substituents (for naphthyridine **3g**, the intensity is as low as 2.3%) and for compounds **3h—j** containing the alkoxy groups at the phosphorus atom.

The main fragmentation pathways of the phosphorylamide derivatives of naphthyridine were also investigated by mass spectrometry. The analysis of the mass spectra showed that the favorable fragmentation pathway for some of the 1,8-naphthyridines synthesized in the present study involves the elimination of one of the substituents (for example, of the phenyl group) from the phosphorus atom rather than the cleavage of the P—N bond, which is relatively labile in most cases (see Table 2). Thus, the intensity of the ion corresponding to the elimination of one phenyl group from naphthyridine **3a** is 42.6%. The intensity of the ion at m/z = 296 that is formed as a result of the elimination of the methyl group from compound **3f** and the intensity of the ion at m/z = 234 assigned to the elimination of the phenoxy group from naphthyridine **3g** are 100%. The intense ion peaks at m/z = 173, which are indicative of the P—N bond cleavage, are observed only in the mass spectra of naphthyridines **3h—j** containing the ethoxy groups at the phosphorus atom.

Naphthyridine **3j** containing two ethoxy groups at the phosphorus atom was studied by X-ray diffraction. According to the X-ray diffraction data, the bond lengths and bond angles (Table 3) in the heteroaromatic moiety are typical of this class of compounds.[16] The deviations of the atoms of the naphthyridine system from the mean plane are, on the average, 0.02(1) and 0.04(1)Å for two crystallographically independent molecules in the structure of **3j**. These data confirm the aromaticity of the phosphorus-containing naphthyridine. The C—C bond lengths of the methyl substituents in the naphthyridine moiety and of the ethyl substituents at the phosphorus atom vary from 1.487(3) to 1.509(3)Å. According to the X-ray diffraction data (see Table 3), the P(1)—N(3) bond is single,

Table 3. Selected geometric parameters for two independent molecule in the structure of **3j**

Parameter	**3j**	**3j´**
Bond	*d*/Å	
P(1)—O(1)	1.4745(13)	1.4656(13)
P(1)—O(2)	1.5665(13)	1.5683(12)
P(1)—O(3)	1.5652(13)	1.5711(13)
P(1)—N(3)	1.6457(14)	1.6561(15)
O(2)—C(11)	1.464(2)	1.443(2)
O(3)—C(13)	1.460(2)	1.454(2)
N(3)—C(1)	1.393(2)	1.389(2)
N(1)—C(1)	1.321(2)	1.320(2)
N(1)—C(8)	1.364(2)	1.362(2)
N(2)—C(8)	1.369(2)	1.365(2)
N(2)—C(7)	1.324(2)	1.323(2)
C(1)—C(2)	1.428(2)	1.427(2)
C(2)—C(3)	1.353(2)	1.354(3)
C(3)—C(4)	1.425(2)	1.417(3)
C(4)—C(5)	1.417(2)	1.422(2)
C(6)—C(7)	1.410(2)	1.416(3)
C(4)—C(8)	1.415(2)	1.424(2)
Angle	ω/deg	
O(1)—P(1)—O(2)	115.95(7)	109.34(7)
O(1)—P(1)—O(3)	107.86(7)	116.18(7)
O(2)—P(1)—O(3)	107.55(7)	104.05(7)
O(1)—P(1)—N(3)	110.04(7)	116.61(8)
O(2)—P(1)—N(3)	103.70(7)	107.88(7)
O(3)—P(1)—N(3)	111.75(8)	101.73(7)
C(1)—N(1)—C(8)	117.06(14)	117.99(14)
N(1)—C(8)—N(2)	114.58(14)	114.93(15)
N(1)—C(8)—C(4)	123.29(14)	122.76(16)
C(8)—N(2)—C(7)	118.04(14)	117.65(15)
N(3)—C(1)—N(1)	118.80(14)	116.00(15)
N(3)—C(1)—C(2)	117.20(14)	120.55(15)
C(1)—C(2)—C(3)	118.90(15)	118.44(16)
C(2)—C(3)—C(4)	119.35(15)	120.46(16)
C(3)—C(4)—C(5)	123.78(15)	124.45(16)
C(4)—C(5)—C(6)	117.44(15)	117.12(16)
C(5)—C(6)—C(7)	120.49(15)	120.73(17)

thus allowing the rotation of the other atoms about this bond and resulting in that the diethoxyphosphoryl fragments in two independent molecules **3j** are in different orientations with respect to the naphthyridine moiety (Fig. 1). In molecule **3j** (the atoms are unprimed), the O(1)—P(1)—N(3)—C(1) torsion angle is 26.4(2)°, and the ethoxy groups are on the opposite sides with respect to the plane of the naphthyridine moiety, whereas the corresponding torsion angle in **3j´** (the atoms are primed) is 68.1(2)°, and the substituents are on the same side of the heterocycle. The proton at the N(3) atom in molecules **3j** or **3j´** and the N(1) atom are in the *trans* and *cis* positions with respect to the N(3)—C(1) bond, respectively (see Fig. 1).

Due to the different orientation of the NH group with respect to the heterocycle, molecules **3j** and **3j´** form dif-

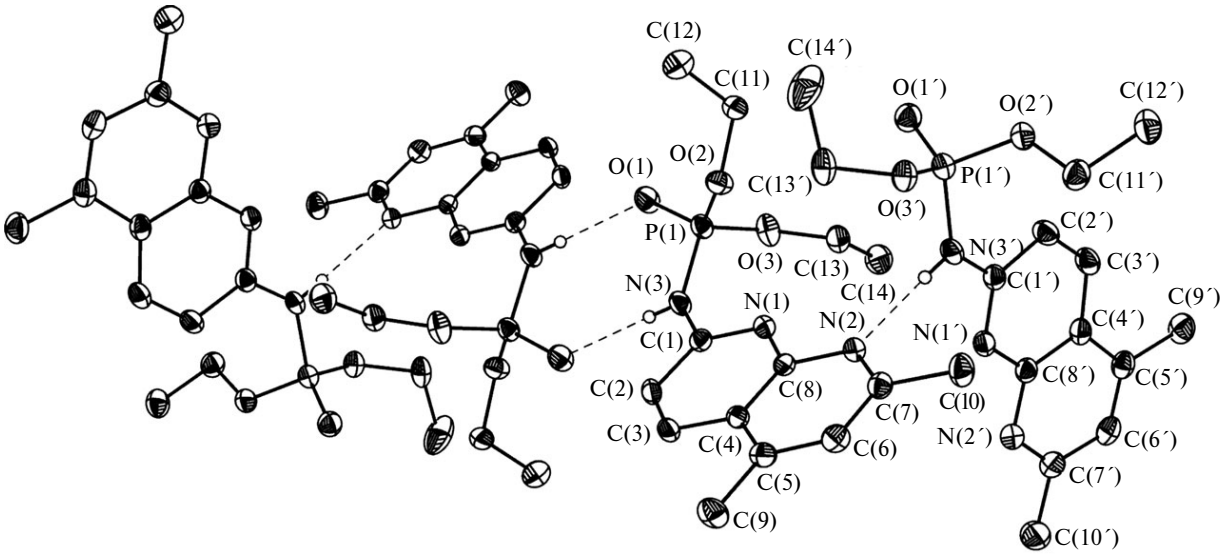


Fig. 1. Structure of the tetramer formed by molecules **3j** through hydrogen bonds (displacement ellipsoids are drawn at the 50% probability level). The atomic numbering scheme is given only for the asymmetric unit cell. The hydrogen atoms, which are not involved in the hydrogen bonding, are omitted. The hydrogen bonds are indicated by dashed lines.

ferent types of hydrogen bonds. Two molecules **3j** form a centrosymmetric dimer through two N(3)—H...O(1) hydrogen bonds between the amino group and the oxygen atom of the phosphoryl group (r(N...O) = 2.801(2) Å, r(H...O) = 2.066 Å, and the N—H—O angle is 173°). Each molecule **3j** is linked to molecule **3j´** through the N(3´)—H...N(2) hydrogen bond between the amino group and the heterocycle (r(N...N) = 2.908(2) Å, r(H...N) = = 2.142 Å, the N—H—N angle is 174°). As a result, the crystal structure of **3j** consists of tetramers formed through strong hydrogen bonds (see Figs 1 and 2). The naphthyridine cores of molecules **3j´** are almost perpendicular to the heterocycles of molecules **3j** (the angle between the heterocycles is 89.82(2)°). In the crystals of **3j**, in addition to the hydrogen bonds, there are also stacking interactions between the heterocycles of the molecules of one type (between two molecules **3j** or **3j´**). In all cases, the naphthyridine moieties that form stacking contacts are related to each other by a center of inversion and, consequently, are strictly parallel to each other (Fig. 2). In molecules **3j** and **3j´**, the heterocycle—heterocycle distance is 3.35 and 3.47 Å, respectively. As a result, the structure of **3j** consists

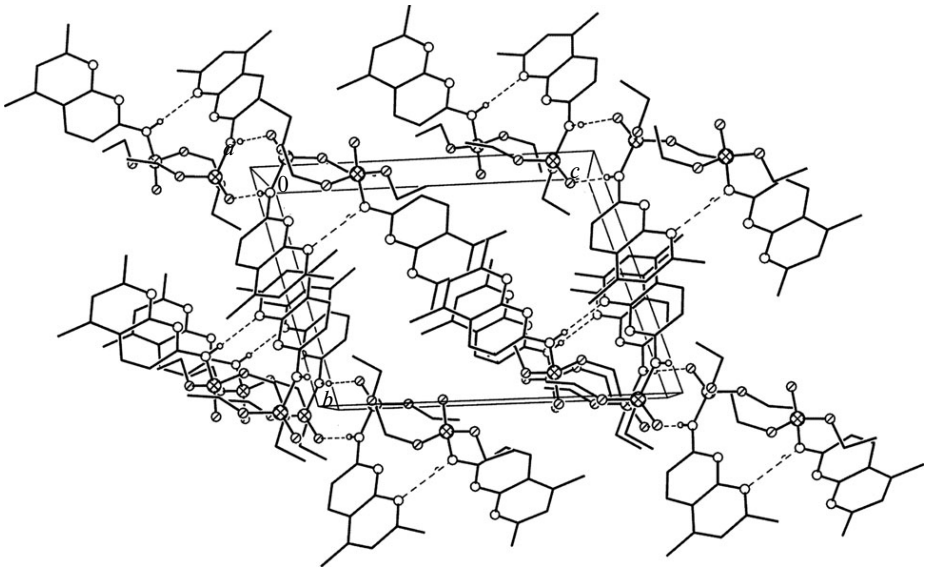


Fig. 2. Fragment of the crystal packing of **3j** projected along the crystallographic *a* axis. The hydrogen atoms, which are not involved in the hydrogen bonding, are omitted. The hydrogen bonds are indicated by dashed lines.

of layers perpendicular to the crystallographic *a* axis, which are formed by the molecules linked together through hydrogen bonds and stacking interactions.

To conclude, let us note that the synthetic approach used in the present study is suitable for the preparation of a wide range of phosphorus- and nitrogen-containing naphthyridine ligands, which, in principle, can act as efficient complex-forming agents for different metal cations, including actinides and lanthanides.

Experimental

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker Avance-400 instrument operating at 400.13 MHz for ^1H and at 161.98 MHz for ^{31}P at 298 K in $CDCl_3$ using the residual signals of the protons of the deuterated solvent as the internal standard (^1H) and of 85% H_3PO_4 as the external standard (^{31}P). The concentration of the solutions was 0.02 mol L^{-1}.

The mass spectra were recorded on a Finnigan Polaris Q mass spectrometer (EI, 70 eV, the temperature of the ion source was 250°C, a direct inlet probe (DIP) with programmed heating of the ampoule from 50° to 100—150 °C). The assignment was made taking into account the ion fragmentation scheme determined by recording the mass spectra in the MS^n mode ($n = 1$—5).

All operations were carried out under argon. The solvents were saturated with argon, purified, and dried according to known procedures.[17] Diphenyl chlorophosphinate **2a**, diphenyl chlorophosphate **2b**, methyl phenyl chlorophosphinate **2f**, and diethyl chlorophosphate **2j** (Aldrich) were purified by distillation *in vacuo*. 2-Amino-5,7-dimethyl-1,8-naphthyridine **1**,[15] bis(*o*-tolyl) chlorophosphate **2c**,[18] bis(*m*-tolyl) chlorophosphate **2d**,[19] bis(*p*-tolyl) chlorophosphate **2e**,[18] *O*-phenyl methyl chlorophosphonate **2g**,[20] *O*-ethyl phenyl chlorophosphonate **2h**,[21] and *O*-ethyl methyl chlorophosphonate **2i** (see Ref. 22) were synthesized according to known procedures.

Synthesis of 2-(*N*-phosphorylamino)-substituted 1,8-naphthyridines 3a—g (method *A*). The corresponding phosphoryl chloride **2** (5 mmol) was added dropwise to a solution of aminonaphthyridine **1** (867 mg, 5 mmol) and anhydrous triethylamine (606 mg, 6 mmol) in anhydrous pyridine (10 mL) at room temperature. The reaction mixture was refluxed for 5 h, pyridine was removed using a water-jet vacuum pump, and the residue was dissolved in $CHCl_3$ (20 mL), washed with water (2×15 mL), dried over $MgSO_4$, and chromatographed on alumina (8 g) using $CHCl_3$ as the eluent. The solvent was removed from the eluate, and the residue was recrystallized from *tert*-butyl methyl ether.

Synthesis of 2-(*N*-phosphorylamino)-substituted 1,8-naphthyridines 3a—j (method *B*). The corresponding phosphoryl chloride **2** (5 mmol) was added dropwise to a suspension of aminonaphthyridine **1** (867 mg, 5 mmol) in anhydrous $CHCl_3$ (20 mL). The reaction mixture was stirred at room temperature for 5 min, and then anhydrous triethylamine (606 mg, 6 mmol) was added dropwise. The reaction mixture was refluxed until the starting aminonaphthyridine was completely dissolved and then cooled, washed with water (2×20 mL), dried over $MgSO_4$, and worked up as described in the method *A*.

X-ray diffraction study. Yellow prismatic crystals of $C_{14}H_{20}N_3O_3P$ (**3j**) (M = 309.3) are triclinic, at 120(2) K a = = 9.8093(4) Å, b = 11.6480(5) Å, c = 14.8087(6) Å, α = 73.393(1)°, β = 85.976(1)°, γ = 68.603(2)°, V = 1508.5(1) Å^3, space group $P\bar{1}$, $Z = 4$, d_{calc} = 1.362 g cm^{-3}. A total of 14364 reflections were collected on a Bruker Smart 1000 diffractometer at 120 K (Mo-Kα radiation, $2\theta_{max}$ = 54.00°) from a single crystal of dimensions 0.32×0.24×0.16 mm. The merging of equivalent reflections gave 6567 independent reflections (R_{int} = 0.0187), which were used for the structure solution and refinement. The structure was solved by direct methods. All nonhydrogen atoms were located in difference electron density maps and refined anisotropically based on F^2_{hkl}. All hydrogen atoms were found in difference electron density maps and refined isotropically using a riding model. All calculations were carried out with the use of the SHELXTL ver. 5.10 program package.[23] The final R factors were as follows: R_1 = 0.0401 (based on F_{hkl} for 5407 reflections with $I > 2\sigma(I)$), wR_2 = 0.0962 (based on F^2_{hkl} for all 6567 reflections), GOOF = 1.001. The completeness of the data set was 99.8%, the number of parameters in the refinement was 387, the maximum and minimum residual peaks were 0.359 and –0.388 e Å^{-3}, respectively.

The complete tables of the atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Structural Database (CCDC 710331).

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Received December 22, 2008;
in revised form April 14, 2009