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Synthesis, coordination and extraction properties of 2,3-bis(diphenylphosphoryl)pyridine toward *f*-block elements

Oleg I. Artyushin,[a] Anna V. Vologzhanina,[a] Aleksandr N. Turanov,[b] Vasilii K. Karandashev[c] and Valery K. Brel*[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 6373; e-mail: v_brel@mail.ru*
[b] *Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation*
[c] *Institute of Problems of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation*

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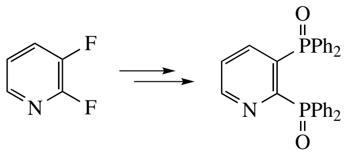
2,3-Bis(diphenylphosphoryl)pyridine, a novel N,O-donor bidentate organophosphorus ligand, can serve as an efficient extractant for recovery of *f*-block elements from nitric acid solutions.

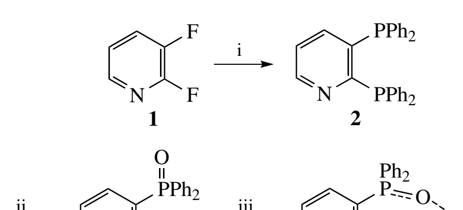


Keywords: 2,3-bis(diphenylphosphoryl)pyridine, organophosphorus compounds, complexes, *f*-block elements, X-ray diffraction analysis, extraction.

Dedicated to the memory of Nikolay S. Zefirov (1935–2017)

Monodentate organophosphorus ligands (OPLs) showed excellent performance in the reprocessing of spent nuclear fuel for recovery of uranium, thorium, and plutonium;[1–4] however, they proved to be inefficient for the isolation of minor actinides mAn (mAn = Am, Cm, Np) and especially for their separation from each other and from lanthanides. Therefore, in recent years extraction practice has been focused on the use of polydentate OPLs containing different substituents, including nitrogen-containing heterocycles.[5–11] Such an approach showed excellent results in terms of both increase in extraction from nitric acid solutions and Am/Ln, Am/Cm, Am/Eu separation efficiency.[12] However, the synthesis of these promising extractants is rather complicated at present because it includes palladium-catalyzed P–C bond formation using unavailable and unstable in storage diphenylphosphine oxide. Therefore, the search for and development of approaches to the synthesis of new and efficient polydentate N,O-donor OPLs based on N-heterocycles is the topical and demanding task.

In the present report, we propose a simple and convenient two-step synthesis of new bidentate OPL on pyridine platform (Scheme 1), namely, 2,3-bis(diphenylphosphoryl)pyridine **3**.



Scheme 1 *Reagents and conditions*: i, Ph_2PNa, THF, –20 °C, 1 h, then room temperature, 4 h, 60 °C, 3 h; ii, H_2O_2, $CHCl_3$, room temperature, 3 h; iii, $UO_2(NO_3)_2\cdot 6H_2O$, MeCN, room temperature, 1 h.

Ligand **3** was prepared in two stages form 2,3-difluoropyridine **1**. At the first stage, the reaction of compound **1** with sodium diphenylphosphide in THF resulted in 2,3-bis(diphenylphosphino)pyridine **2** (see Scheme 1), which attracts interest, like the majority of similar compounds, as a ligand for preparing light-emitting materials.[13,14] Bis-phosphine **2** is a stable compound, however, on treatment with hydrogen peroxide under mild conditions, it would readily convert into bis-phosphine oxide **3** in quantitative yield.† The structure of compounds **2** and **3** was established by NMR and IR spectroscopy.

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† *2,3-Bis(diphenylphosphino)pyridine* **2**. Sodium foil (0.50 g, 21.7 mmol) was added to a solution of diphenylphosphine (4.04 g, 21.7 mmol) in dry THF (50 ml), and the mixture was stirred for 4 h until complete dissolution. 2,3-Difluoropyridine (1.00 g, 8.68 mmol, 80% of theoretical amount) was added dropwise to the resultant brown solution on cooling to –20 °C, and the mixture was stirred at the same temperature for 1 h. Next, the reaction mixture was stirred at 20 °C for 4 h and finally at 60 °C for 3 h, and cooled to 20 °C. Methanol (5 ml) and water (50 ml) were added sequentially, a half of the solvent was distilled off under reduced pressure, the resultant precipitate was filtered off and washed with water (2 × 50 ml), dried under reduced pressure, and recrystallized from ethanol–toluene (1 : 10) mixture. Yield 2.63 g (68%), mp 194–195 °C, colourless crystals.

2,3-Bis(diphenylphosphoryl)pyridine **3**. Hydrogen peroxide (30% H_2O_2, 1.9 ml, 16.77 mmol) was added dropwise with vigorous stirring to a solution of bis-phosphine **2** (2.5 g, 5.59 mmol) in chloroform (50 ml), and the mixture was stirred for 3 h. Water (20 ml) was added, the organic layer was separated and evaporated to dryness under reduced pressure. The residue was kept in a vacuum (0.1 Torr) at 80 °C until constant weight to afford bis-phosphine oxide **3** as a monohydrate. Yield 2.78 g (100%), mp 87–88 °C, colourless crystals.

[2,3-Bis(diphenylphosphoryl)pyridine]uranyl dinitrate **4**. A solution of $UO_2(NO_3)_2\cdot 6H_2O$ (55.2 mg, 0.11 mmol) in acetonitrile (3 ml) was added dropwise to a solution of phosphine oxide **3** (54.7 mg, 0.11 mmol) in chloroform (3 ml), and the mixture was stirred for 1 h. The next day, the precipitated crystals were separated and recrystallized from

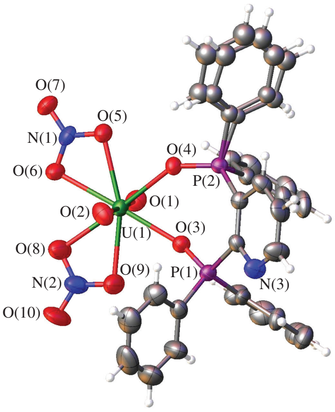

Figure 1 Molecular structure of complex **4**, view as thermal ellipsoids.

The complexing properties of new N,O-donor organophosphorus ligand **3** were shown in its reaction with uranyl nitrate. This reaction in acetonitrile–chloroform solution leads to [2,3-bis(diphenylphosphoryl)pyridine]uranyl dinitrate **4** in quantitative yield (see Scheme 1). The slow crystallization of complex **4** from CH_2Cl_2–hexane mixture afforded single crystals used in X-ray diffraction study (Figure 1).[‡]

The obtained crystals contain complex **4** of composition $[UO_2(L)(NO_3)_2]$ and a solvent molecule in the independent part of unit cell. The ligand molecule behaves as a bidentate chelate ligand toward uranyl cation coordinated through both phosphoryl groups. Two of four phenyl rings are arranged almost in parallel to each other [the angle between their planes is 9.1(4)°, while the distance between the centers of the rings is 4.416(6) Å], which enables one to suppose a C–H···π interaction. Nitrate anions behave as bidentate chelate ligands toward the cation so that uranium(VI) atom has coordination number eight, while the shape of $U^{VI}O_8$ coordination polyhedron is hexagonal bipyramid whose axial positions are occupied by the oxygen atoms of uranyl cation. The uranyl cation is equal-arm [r(U=O) = 1.744(6)–1.746(6) Å] and linear [O=U=O angle is 177.5(3)°]. The equatorial plane is markedly curved, the deviation of oxygen atoms from the plane is 0.13(1) Å on average. The complex has insular structure close to that of previously studied [1,2-bis(diphenylphosphinyl)benzene]uranyl dinitrate,[17] the maximal deviation of atoms for the two complexes is not larger than 1.19 Å.

Table 1 Distribution ratios for U^{VI}, Th^{IV}, and REE^{III} on extraction from 3 M HNO_3 solution with 0.001 M solutions of compounds **3** and **5** into 1,2-dichloroethane.

Extractant	$\lg D_{Th}$	$\lg D_U$	$\lg D_{Nd}$	$\lg D_{Sm}$	$\lg D_{Eu}$	$\lg D_{Ln}$	$\lg D_{Sm}$
3	2.21	3.10	1.87	1.99	1.98	1.39	1.99
5	1.20[18]	0.05[18]	0.04[18]	0.04[18]	–0.02[18]	–0.02[18]	0.04[18]

The extraction properties of bis-phosphine oxide **3** toward *f*-block elements were studied by the example of recovery of micro amounts of U^{VI}, Th^{IV}, and rare earth elements REE^{III} from 3 M HNO_3 solutions into 1,2-dichloroethane. The efficiency of extraction of these elements with solutions of compound **3** was compared with that for the known extractant, diphenyl(dibutylcarbamoylmethyl)phosphine oxide **5** used as a standard in assessment of extraction properties[18] (Table 1).

The data of Table 1 show that 2,3-bis(diphenylphosphoryl)pyridine **3** exhibits high extraction ability toward U^{VI}, Th^{IV}, and REE^{III} and efficiently recovers these elements from nitric acid solutions. The efficiency of compound **3** considerably (by hundreds of times) exceeds that of widely used extractant **5**.

In summary, we developed a convenient method for preparing previously unknown N,O-donor bidentate organophosphorus ligand, 2,3-bis(diphenylphosphoryl)pyridine **3**. This ligand can be used as extractant for recovery of *f*-block elements from nitric acid solutions.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.05.009.

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CH_2Cl_2–hexane mixture. Crystals suitable for X-ray diffraction study were taken from the prepared yellow crystals, the remaining crystals were dried under vacuum (0.1 Torr) until constant weight. Yield of complex **4** was 99 mg (90%), mp 292–293 °C.

[‡] *Crystal data for* $\mathbf{3}\cdot 0.5\,CH_2Cl_2$. $C_{29.5}H_{24}ClN_3O_{10}P_2U$, M = 915.94, monoclinic, space group $P2_1/n$; at 295 K: a = 10.255(4), b = 34.538(15) and c = 10.325(4) Å, β = 105.755(15)°, V = 3520(3) Å^3, Z = 4, d_{calc} = 1.727 g cm^{-3}, μ(MoKα) = 4.833 mm^{-1}, $F(000)$ = 1764, 65799 reflections were measured, 10875 independent reflections (R_{int} = 0.1567) were used in further refinement. Refinement converged at wR_2 = 0.151 and GOF = 1.059 for independent reflections [R_1 = 0.067 calculated on F^2 for 6361 observed reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker Quest diffractometer equipped with monochromatized radiation (λ = 0.71073 Å). The structure was solved by direct method, non-hydrogen atoms were located in difference synthesis of electron density and refined anisotropically using SHELXTL[15] and OLEX2[16] programs on F^2. One of phenyl rings and the carbon atom of CH_2Cl_2 solvent molecule are disordered in two positions, non-hydrogen atoms of these fragments were refined isotropically. Solvent molecule was refined using SADI instructions for C–Cl distance. Hydrogen atoms were added in ideal positions using the Riding model.

CCDC 2070340 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

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