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Coordination and extraction properties of new bis- and tetrakis(diphenylphosphoryl)-substituted pyrazines towards *f*-block elements

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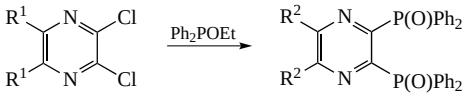
2,3-Bis- and 2,3,5,6-tetrakis(diphenylphosphoryl)-substituted pyrazines have been synthesized from the corresponding polychloropyrazines and ethyl diphenylphosphinite. They may serve as new *N*,*O*-bidentate organophosphorus ligands for extraction and recovery of *f*-block metal ions from nitric acid solutions.



R^1 = H, Cl, –CH=CH–CH=CH– R^2 = H, $P(O)Ph_2$, –CH=CH–CH=CH–

extragents for *f*-block metal ions

Keywords: 2,3-bis(diphenylphosphoryl)pyrazine, 2,3,5,6-tetrakis(diphenylphosphoryl)pyrazine, organophosphorus compounds, pyrazines, quinoxalines, complexes, *f*-block elements, X-ray diffraction analysis, extraction.

N,*O*-Donor ligands containing phosphine oxide P=O fragments linked to *N*-heterocyclic scaffold exhibit high extraction properties toward U^{VI}, Th^{IV} and trivalent rare earth elements on recovery even from acid solutions.[1–4] They are also promising precursors for preparing complexes, including water soluble species, which show unique electrooptical properties.[5] First compounds of this class were obtained in 1978,[6] however, these ligands remained unavailable until recently because of their complicated synthesis. Recently, attempts were made to improve the syntheses of these compounds using palladium-catalyzed reactions.[7] However, because of high cost of the catalysts and poor availability and low stability of initial reagents, in particular $Ph_2P(O)H$, this approach remains academic.

Previously,[8–11] we proposed a simple and efficient approach to prepare organophosphorus di- and tetrasubstituted benzenes and pyridines, which behave as rather efficient extractants for the recovery of *f*-block elements from nitric acid solutions[8–11] and serve to produce complexes of unusual composition. In the present report, we propose new approaches for the synthesis of analogous di- and tetrasubstituted pyrazines showing unexpected extraction properties toward U^{VI}, Th^{IV} and trivalent rare earth elements in nitric acid solutions.

The traditional phosphorylation of pyrazines based on the reaction of sodium diphenylphosphide with (het)aryl fluorides was inefficient in this case. In this study (Scheme 1), all phosphorus-substituted pyrazines **2a**–**c** were obtained by the Arbuzov reaction of ethyl diphenylphosphinite with known[12,13] di- and tetrachloropyrazines **1a**–**c** at high temperature.† Phosphorylated pyrazines **2a**,**b** are powders poorly soluble in non-polar organic solvents and therefore readily isolable from reaction mixtures after cooling. The structures of **2a**,**b** were established by NMR and IR spectroscopy as well as elemental analysis. It should be noted that quinoxaline derivative **2c** was previously described in the literature,[13] however, the lack of any spectral data for that compound and incorrect melting point can drop a hint of doubt on the purity of the previously obtained compound. Phosphorylated pyrazines **2a**,**b** are new.

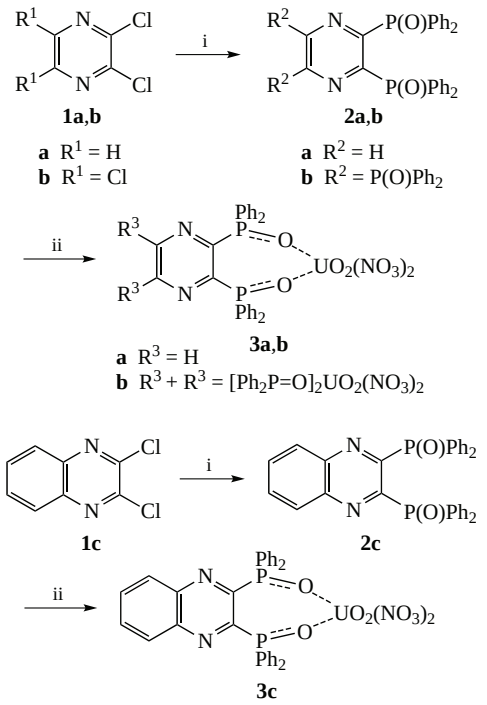
We studied complexing properties of the obtained compounds **2a**–**c** using the reaction with uranyl nitrate. In the case of ligand **2b**, product **3b** precipitated from acetonitrile solution as $[(UO_2)_2\mathbf{2b}(NO_3)_4]\cdot 2\,MeCN$ (Figure 1).‡ Tetrakis(phosphine

† *2,3,5,6-Tetra(diphenylphosphoryl)pyrazine* **2b**. Under an argon atmosphere, a mixture of ethyl diphenylphosphinite (1.9 g, 8.1 mmol) and 2,3,5,6-tetrachloropyrazine **1b** (0.43 g, 2.0 mmol) was heated in *o*-xylene (10 ml) at 140 °C for 10 h. The resultant precipitate was separated by filtration, washed with dry diethyl ether, and dried under reduced pressure. Yield 1.25 g (74%), mp 320 °C, off-white powder. Compounds **2a**,**c** were obtained similarly from 2,3-dichloropyrazine **1a** or 2,3-dichloroquinoxaline **2c** (2 mmol) and Ph_2POEt (4.1 mmol) in yields of 57 and 83%, respectively.

[*2,3,5,6-Tetra(diphenylphosphoryl)*]*bis(uranyl dinitrate)* **3b**. A solution of ligand **2b** (88 mg, 0.1 mmol) in chloroform (2 ml) was slowly added dropwise to a solution of $UO_2(NO_3)_2\cdot 6H_2O$ (100.3 mg, 0.2 mmol) in acetonitrile (2 ml). Next day, the resultant crystals were separated by filtration and dried under reduced pressure. Yield 159 mg (91%), mp >350 °C (decomp.), yellow crystals.

Complexes **3a**,**c** were obtained similarly from ligands **2a** or **2c** (1 mmol) and $UO_2(NO_3)_2\cdot 6H_2O$ (1 mmol) in 90 and 93% yields, respectively.

‡ *Crystal data for* **3b**·2MeCN. $C_{56}H_{46}N_8O_{20}P_4U_2$, M = 1750.95, monoclinic, space group $P2_1/n$, at 140.0(2) K, a = 11.7575(19), b = 21.340(4) and c = 12.6231(16) Å, β = 93.996(4)°, V = 3159.5(8) Å^3, Z = 2, d_{calc} = 1.840 g cm^{-3}, μ(MoKα) = 5.300 mm^{-1}, F(000) = 1684; 18703 reflections were measured, 9464 independent reflections (R_{int} = 0.112) were used in further refinement. Refinement converged at wR_2 = 0.114 and GOF = 0.988 for independent reflections [R_1 = 0.058



Scheme 1 *Reagents and conditions*: i, Ph_2POEt (stoichiometric amount), *o*-xylene, 140 °C, 10 h; ii, $UO_2(NO_3)_2 \cdot 6H_2O$ (stoichiometric amount), $CHCl_3$/MeCN, room temperature, 24 h.

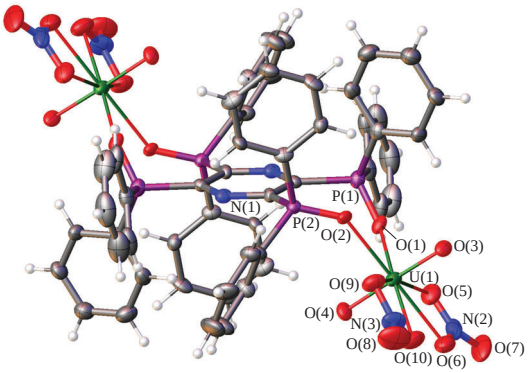


Figure 1 Molecular structure of complex **3b** $[(UO_2)_2\mathbf{2b}(NO_3)_4]$. Atoms are represented by thermal ellipsoids. Non-carbon atoms of the asymmetric unit are labeled. Average distances (Å): U=O, 1.759; U–O(P), 2.385; U–O(NO_3), 2.502; P=O, 1.505.

Table 1 Distribution ratios for U^{VI} and Th^{IV} on their extraction from 3 M HNO_3 with 0.001 M solutions of compounds **2a–c** and BDPP in 1,2-dichloroethane.

Extractant	logD_U	logD_{Th}
2a	1.37	–1.22
2b	1.35	0.95
2c	3.00	2.67
BDPP[a]	3.10	2.21

[a] Reference compound 2,3-bis(diphenylphosphoryl)pyridine.

Table 2 Distribution ratios (log*D* values) for trivalent rare earth elements on their extraction from 3 M HNO_3 with 0.05 M solutions of compounds **2c** and BDPP in 1,2-dichloroethane.

Ligand	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
2c	1.73	2.07	2.18	2.19	2.44	2.40	2.32	2.50	2.45	2.36	2.26	2.21	2.13	1.99
BDPP	1.39	1.77	1.86	1.87	1.99	1.98	1.86	1.96	1.89	1.78	1.72	1.70	1.69	1.57

oxide) **2b** acts as a tetradentate bridge-chelate ligand towards two uranyl atoms, and four nitrate anions act as bidentate-chelate ligands. Uranium(VI) atom presents a bicapped hexagonal prismatic coordination with two oxygen atoms of the uranyl group in apical positions. Uranyl group is linear [OUO angle is 178.5(2)°] but asymmetrical {*r*[U(1)–O(3)] and *r*[U(1)–O(4)] are 1.749(5) and 1.769(5) Å, respectively}. Bond distances U–O increase from U=O to U–O(P) and to U–O(NO_3). Neighboring phosphine oxide groups are involved in the formation of two chelating seven-membered $UO_2P_2C_2$ rings with two oxygen and metal atoms situated on opposite sides of the mean plain formed by the heterocycle and phosphorus atoms. Overall molecular scaffold presents a pseudo-chair conformation previously observed for $[(UO_2)_2(tpp)(NO_3)_4]$.[11]

Ligands **2a** and **2c** containing two phosphoryl groups form with uranyl nitrate complexes **3a**,**c** $[L(UO_2)(NO_3)_2]$ of 1 : 1 composition, which is confirmed by elemental analysis.

The extraction properties of compounds **2a–c** toward *f*-block elements from 3 M HNO_3 aqueous solutions into 1,2-dichloroethane were compared with those of 2,3-bis(diphenylphosphoryl)-pyridine (BDPP) as the reference having excellent extraction properties.[10] Table 1 shows that the most efficient extractant of three new phosphorylated pyrazines was 2,3-bis(diphenylphosphoryl)quinoxaline **2c** with the efficiency at the level of reference BDPP. Di- and tetraphosphorylated pyrazines **2a**,**b** extract U^{VI} and Th^{IV} thousand times poorer than compound **2c**.

Extraction of trivalent rare earth elements from 3 M HNO_3 with leader compound **2c** was further studied (Table 2), which showed that ligand **2c** exceeded reference compound BDPP in extraction ability for all studied cations.

The compositions of extracted complexes calculated from the slopes of log*D*–log[*L*] dependences are presented in Table 3 which shows that the majority of complexes has composition close to 1 : 2, *i.e.*, one metal ion binds to two ligand molecules. The extraction properties of diphosphorylated quinoxaline **2c** are very close to those previously obtained for 2,3-diphosphorylated pyridine BDPP, exhibiting the best extraction among the three pyrazine ligands **2a–c**.

In summary, we have proposed simple and convenient synthesis of phosphorylated pyrazines possessing different substitution pattern. Study of their complexing and extraction

Table 3 Composition of extracted complexes ML_x with ligands **2a–c** and BDPP.

Ligand	Ligand/metal ratio					
	Th^{IV}	U^{VI}	La^{III}–Eu^{III}	Lu^{III}	Tm^{III}	Yb^{III}
2a	1.62	1.24	–	–	–	–
2b	1.57	1.30	–	–	–	–
2c	2.20	1.74	2.5	2.05	2.29	2.13
BDPP	2	1.50	2.5	2	–	–

calculated on F^2 for 4314 observed reflections with $I > 2\sigma(I)$]. The data were collected on a Bruker Apex II 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[14] and OLEX2[15] programs. Hydrogen atoms were added in ideal positions using the riding model.

CCDC 2164553 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.

properties revealed that the most promising compound was 2,3-bis(diphenylphosphoryl)quinoxaline **2c**.

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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.2022.09.032.

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