

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Bis(Carbamoylmethylphosphine Oxide) Ligands Fixed on the Arene Core via 1,2,3-Triazole Linkers: Novel Effective Extractants for Palladium, Lanthanides and Actinides

Alexander N. Turanov,^a Vasilii K. Karandashev,^{*b,c} Elena V. Sharova,^d Galina K. Genkina,^d and Oleg I. Artyushin.^d

Received,
Accepted

Novel polydentate neutral organophosphorus ligands containing two diphenyl-(diethylcarbamoylmethyl)phosphine oxide moieties fixed on the arene platform via methylene-1,2,3-triazole linkers (Ar-CMPO) were synthesized by the method of “click” chemistry and studied as an extractant for Pd(II), U(VI), Th(IV) and lanthanides(III) ions from HNO₃ solutions. The influence of aqueous and organic phases on the extraction efficiency was elucidated and stoichiometry of the complexes extracted was determined. The introduction of a 1,2,3-triazole fragment into the methylene bridge of a CMPO molecule resulted in a considerable increase of the efficiency of Pd(II) extraction. This modification of a CMPO molecule does not essentially change the extraction efficiency towards U(VI) and Ln(III) but drastically decreases the Th(IV) extraction and change the order in the extractability of U(VI) and Th(IV) from HNO₃ solutions. Bis-CMPO ligands containing two 1,2,3-triazole moieties (Ar-CMPO) were found to possess a higher extraction efficiency towards Pd(II), U(VI), Th(IV) and lanthanides(III) ions than their mono analog 2-(diphenylphosphoryl)-N,N-diethyl-3-(1-phenyl-1H-1,2,3-triazol-4-yl)propanamide.

Introduction

Solvent extraction is a widely used technique for the recovery and separation of actinides and lanthanides from high-level liquid wastes (HLLW) of nuclear fuel cycles. HLLW can be a valuable source of platinum group metals. The recovery of fission palladium is of particular interest and is being investigated world-wide.^[1] Bidentate neutral organophosphorus compounds such as diaryl- or alkyl(aryl)[dialkylcarbamoylmethyl]phosphine oxides (CMPO) are known to be efficient extractants for the extraction of hard actinides and lanthanides ions from nitric acid solutions.^[2,3] However, these compounds do not show any appreciable ability to extract soft

Pd(II) ions from nitric acid solutions.^[1] A difference in extractabilities of Pd(II) and Ln(III) ions with polyfunctional neutral extractants depends on the nature of coordinating moieties of an extractant molecule. It is known that the diamide extractant tetraoctyldiglycolamide (TODGA) with hard oxygen donors extract lanthanides and actinides from nitric acid solutions more strongly than Pd(II).^[4] Replacement of the central ether oxygen in the molecule of diamides of diglycolic acid by soft nitrogen donors changes the relation between the extractabilities of lanthanides and Pd(II). Sasaki et al. showed that 2,2'-(methylimino)bis(N,N-diethylacetamide), which has a frame similar to that of TODGA and a nitrogen atom instead of the ether oxygen, effectively extracts Pd(II) from nitric acid solutions whereas the extractability of Am(III) and lanthanides is low.^[5]

Recently, we have found that the introduction of a 1,2,3-triazole fragment into the methylene bridge of a CMPO molecule resulted in a considerable increase of the efficiency of Pd(II)

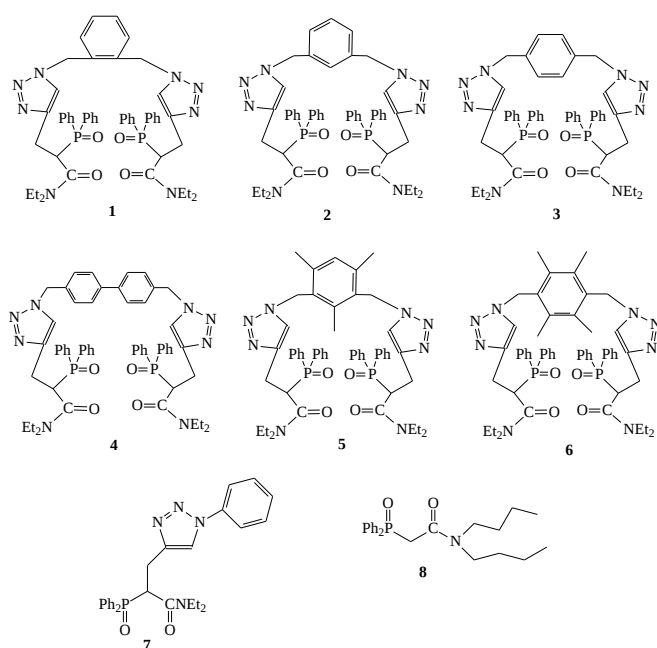
^a Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Russia

^b Institute of Microelectronics Technology and High Purity Materials, Russian Academy of Sciences, 142432 Chernogolovka, Russia

^c National University of Science and Technology MISiS, 119049, Moscow, Russia
E-mail: karan@iptm.ru

^d A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russia

extraction.^[6] However, the extraction efficiency of 2-(diphenylphosphoryl)-*N,N*-diethyl-3-(1-phenyl-1*H*-1,2,3-triazol-4-yl)propanamide towards Ln(III) slightly decreased as compared with that of unsubstituted CMPO.^[6] It is known that the efficiency and selectivity of CMPO type ligands usually increase with an increase in the amount of CMPO residues in a molecule.^[7, 8] Attachment of CMPO groups to molecular platforms such as calixarenes^[9-11] and cavitands^[12-15] led to further increase of extraction efficiencies and selectivities. Therefore, it seemed reasonable to attempt the synthesis of novel polyfunctional neutral organophosphorus compounds Ar-CMPO **1-7** and estimate their extraction properties towards Pd(II), U(VI), Th(IV) and lanthanides(III). This study was carried as part of the research on the specific features of the extraction ability of polyfunctional neutral organophosphorus compounds, depending on the variation in their molecule structure. In this report we describe the results of our studies on some extraction properties of Ar-CMPO **1-7** compounds towards Pd(II), U(VI), Th(IV) and lanthanides(III) in nitric acid media. The extraction behavior of these compounds is compared with that of its structural mono analog **8**.



Scheme 1. The comparative mono- and bis-CMPO ligands used in the study.

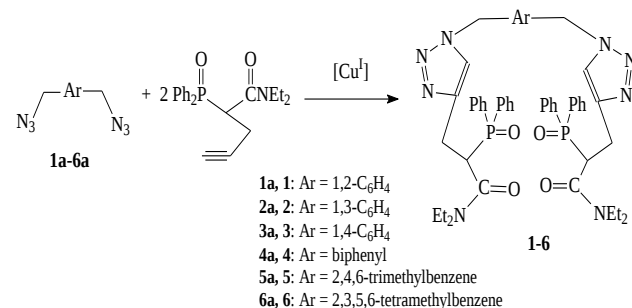
Experimental

The NMR spectra were recorded on a Bruker AMX-400 instrument in CDCl₃ solution. The chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (¹H and ¹³C) or externally to H₃PO₄ (³¹P). The ¹³C NMR spectra were registered using the JMODECHO mode; the signals for the C atoms bearing odd and even numbers of protons have opposite polarities. IR spectra were recorded on a Magna-IR 750 FTIR spectrometer (Nicolet Co., resolution 2 cm⁻¹, scan number 128, KBr pellets). Melting points were determined with an Electrothermal IA9100 DigitalMelting Point Apparatus and were uncorrected. Chemical and analytical grade hexane, acetone, 1,2-dichloroethane, tert-butanol and methanol were used as diluents.

The ligand **6**^[6] was obtained by coupling a phenylazide with 2-propargyl-diphenyl(*N,N*-diethylcarbamoyl-methyl)phosphine oxide by procedure of “click” chemistry. The synthesis of compound **8**^[16] was described previously.

Synthesis of the ligands.

The desired polydentate neutral organophosphorus ligands **1-6** were synthesized using the general synthetic procedure of “click” chemistry detailed by us earlier for compound **7**, namely by copper(I)-catalyzed 1,3-dipolar cycloaddition of corresponding diazides **1a-6a** to 2-propargyl-diphenyl(*N,N*-diethylcarbamoylmethyl)phosphine oxide,^[6] according to the general route depicted in the Scheme 2.



Scheme 2. Synthesis of the Ar-CMPO ligands **1-6**.

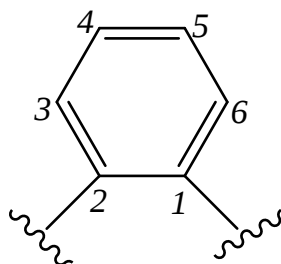
The starting diazides **1a**,^[17] **2a** and **3a**,^[18] **4a**,^[19] **5a**,^[20] and **6a**^[21] were obtained *via* the procedures described in the literature, and their physicochemical constants matched the literature data.

A general procedure for the preparation of 1-6

To a solution of 2-propargyl-diphenyl(*N,N*-diethylcarbamoylmethyl)phosphine oxide (0.5 g, 1.35 mmol) and corresponding diazide **1a-6a** in *t*-BuOH/H₂O (5 mL) in the ratio 5:2 was added CuSO₄·5H₂O (5 mol %, 17 mg, 0.0675 mmol) and sodium ascorbate (10 mol %, 27 mg, 0.135 mmol) with stirring. The mixture was stirred at room temperature for 60-70 h. The reaction was completed as verified by TLC and ³¹P NMR control. Then, the solvent was evaporated under reduced pressure and CH₂Cl₂ was added to the residue (30 mL). The product was washed with 3% aq NH₃ (3×15mL). The collected organic layers were dried over Na₂SO₄, filtered and the solvent was evaporated *in vacuo*. The residue was purified by thin-layer column chromatography (SiO₂) using hexane-acetone (from 100:20 to 10:100, v/v) and then CH₂Cl₂-methanol (100:10, v/v). The identity and the purity of the reaction products were established by their spectral (¹H, ³¹P, ¹³C NMR, IR) data.

Note that isolated ligands after careful drying over P₂O₅ in vacuum contained 1 or 1.5 mol of water according to the ¹H NMR, IR and elemental analysis data. The numeration of the central arene core in Ar-CMPO **1-6** is presented in the figures (*vide infra*)

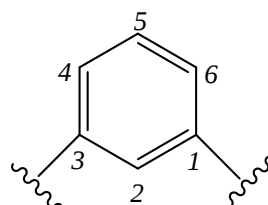
1,1'-(Benzene-1,2-diylldimethanediyl)bis{4-[2-(diphenylphosphoryl)-*N,N*-diethylpropanamide]-1*H*-1,2,3-triazole} (1).



Yield: 60%. Mp: 189-193°C. IR (KBr, cm⁻¹): 3431 (ν_{OH}), 2969, 2929, 1631 (ν_{C=O}), 1460 (ν_{Ar}), 1437, 1215 (ν_{P=O}), 1190, 1118, 1099, 705, 516. ¹H NMR (400 MHz, CDCl₃, ppm, J/Hz): 0.72 and 0.75 (both t, 6H+6H, NCH₂CH₃, ³J_{HH}=7.2); 2.78 and 2.96 (both dd, 2H+2H, CH₂CH(P(O)Ph₂)-, ³J_{HH}=11.1, ³J_{PH}=13.0); 3.10-3.45 (m, 8H, NCH₂CH₃); 4.19 (ddd, 2H, PCH, ²J_{PH}=14.8, ³J_{HH}=11.1); 5.48 (br. s, 4H, -CH₂-Ar-CH₂-); 7.03-7.08 (m, 2H, H(C⁴)+H(C⁵) in Ar); 7.23 (br. s, 2H, CH in triazole cycle); 7.26-7.32 (m, 2H,

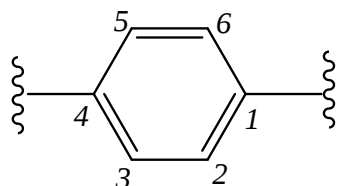
H(C³)+H(C⁶)); 7.42-7.60, 7.83-7.92, 8.05-8.15 (all m, 12H+4H+4H, C₆H₅-P). ³¹P NMR (161.97 MHz, CDCl₃): 30.11 ppm. ¹³C NMR (100.61 MHz, CDCl₃, ppm, J/Hz): 12.42 and 13.76 (both s, CH₃CH₂N), 23.30 (br. s, CH₂CH(P(O)Ph₂)-), 40.85 and 42.49 (both s, CH₃CH₂N), 45.76 (d, P-CH, ¹J_{PC}=60.9), 50.78 (s, -CH₂-Ar-CH₂-), 122.24 (s, =CH- in triazole cycle), 128.29 and 128.46 (both d, o-C in C₆H₅, ²J_{PC}=11.7), 129.40 (s, C³, C⁶ in Ar), 129.81 (s, C⁴, C⁵ in Ar), 130.68 and 130.77 (both d, *ipso*-C in C₆H₅, ¹J_{PC}=99.4), 131.67 and 131.84 (both d, *m*-C in C₆H₅, ³J_{PC}=9.2), 131.94 and 132.02 (both d, *p*-C in C₆H₅, ⁴J_{PC}=2.6), 133.27 (s, *ipso*-C¹, C² in Ar), 144.98 and 145.00 (both d, -C=CH- in triazole cycle, ³J_{PC}=15.5), 167.20 (s, C=O). Anal. Calcd for C₅₀H₅₆N₈O₄P₂·1.5H₂O: C, 65.13; H, 6.91; N, 12.15; P, 6.72. Found: C, 65.32; H, 6.78; N, 12.38; P, 6.54.

1,1'-(Benzene-1,3-diylldimethanediyl)bis{4-[2-(diphenylphosphoryl)-*N,N*-diethylpropanamide]-1*H*-1,2,3-triazole} (2).



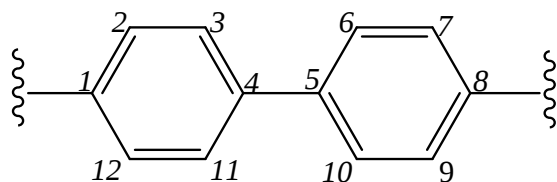
Yield: 57%. Mp: 180-183°C. IR (KBr, cm⁻¹): 3436 (ν_{OH}), 2974, 2932, 1630 (ν_{C=O}), 1461 (ν_{Ar}), 1437, 1190 (ν_{P=O}), 1117, 1099, 728, 705, 516. ¹H NMR (400 MHz, CDCl₃, ppm, J/Hz): 0.50 and 0.54 (both t, 6H+6H, NCH₂CH₃, ³J_{HH}=7.1); 2.53-2.63, 2.73-2.83, 2.90-3.06, 3.15-3.27 (all m, 12H, NCH₂CH₃ + CH₂CH(P(O)Ph₂)-); 4.02 (ddd, 2H, PCH, ²J_{PH}=13.4, ³J_{HH}=11.1); 5.21 (br. s, 4H, -CH₂-Ar-CH₂-); 6.93 (d, 2H, H(C⁴)+H(C⁶) in Ar, ³J_{HH}=7.6); 7.03 (br. s, 2H, CH in triazole cycle); 7.07 (t, 1H, H(C⁵), ³J_{HH}=7.6); 7.14 (s, 1H, H(C²)); 7.25-7.43, 7.65-7.75, 7.84-7.95 (all m, 12H+4H+4H, C₆H₅-P). ³¹P NMR (161.97 MHz, CDCl₃): 30.06 ppm. ¹³C NMR (100.61 MHz, CDCl₃, ppm, J/Hz): 11.97 and 13.31 (both s, CH₃CH₂N), 24.14 (s, CH₂CH(P(O)Ph₂)-), 40.32 and 42.06 (both s, CH₃CH₂N), 44.63 (d, P-CH, ¹J_{PC}=60.9), 52.92 (s, -CH₂-Ar-CH₂-), 121.87 (s, =CH- in triazole cycle), 127.19 (s, C² in Ar), 127.53 (s, C⁴, C⁶ in Ar), 128.00 and 128.07 (both d, o-C in C₆H₅, ²J_{PC}=12.1), 129.14 (s, C⁵ in Ar), 130.14 and 130.30 (both d, *ipso*-C in C₆H₅, ¹J_{PC}=99.0), 131.16 and 131.38 (both d, *m*-C in C₆H₅, ³J_{PC}=9.5), 131.69 and 131.70 (both d, *p*-C in C₆H₅, ⁴J_{PC}=2.0), 135.26 (s, *ipso*-C¹, C³ in Ar), 144.41 (d, -C=CH- in triazole cycle, ³J_{PC}=15.7), 166.79 (s, C=O). Anal. Calcd for C₅₀H₅₆N₈O₄P₂·1.5H₂O: C, 65.13; H, 6.91; N, 12.15; P, 6.72. Found: C, 65.25; H, 6.98; N, 12.10; P, 6.65.

1,1'-(Benzene-1,4-diyl dimethanediyl)bis{4-[2-(diphenylphosphoryl)-N,N-diethylpropanamide]-1H-1,2,3-triazole} (3).



Yield: 50%. Mp: 195-198°C. IR (KBr, cm^{-1}): 3436 (ν_{OH}), 2973, 2931, 1630 ($\nu_{\text{C=O}}$), 1461 (ν_{Ar}), 1437, 1217 ($\nu_{\text{P=O}}$), 1188, 1099, 705, 516. ^1H NMR (400 MHz, CDCl_3 , ppm, J/Hz): 0.71 and 0.76 (both t, 6H+6H, NCH_2CH_3 , $^3J_{\text{HH}}=7.2$); 2.75-2.87, 2.93-3.08, 3.10-3.30, 3.32-3.48 (all m, 12H, NCH_2CH_3 + $\text{CH}_2\text{CH}(\text{P}(\text{O})\text{Ph}_2)$); 4.21 (ddd, 2H, PCH, $^2J_{\text{PH}}=13.4$, $^3J_{\text{HH}}=11.5$); 5.41 (br. s, 4H, $-\text{CH}_2-\text{Ar}-\text{CH}_2-$); 7.18 (br. s, 4H, $\text{H}(\text{C}^2)+\text{H}(\text{C}^3)+\text{H}(\text{C}^5)+\text{H}(\text{C}^6)$ in Ar); 7.24 (br. s, 2H, CH in triazole cycle); 7.45-7.65, 7.85-7.96, 8.07-8.18 (all m, 12H+4H+4H, $\text{C}_6\text{H}_5-\text{P}$). ^{31}P NMR (161.97 MHz, CDCl_3): 30.09 ppm. ^{13}C NMR (100.61 MHz, CDCl_3 , ppm, J/Hz): 12.41 and 13.75 (both s, $\text{CH}_3\text{CH}_2\text{N}$), 24.65 (s, $\text{CH}_2\text{CH}(\text{P}(\text{O})\text{Ph}_2)$), 40.79 and 42.52 (both s, $\text{CH}_3\text{CH}_2\text{N}$), 45.65 (d, P-CH, $^1J_{\text{PC}}=60.1$), 53.26 (br. s, $-\text{CH}_2-\text{Ar}-\text{CH}_2-$), 122.03 (s, $=\text{CH}-$ in triazole cycle), 124.90 (s, C^2 , C^3 , C^5 , C^6 in Ar), 128.33 and 128.47 (both d, *o*-C in C_6H_5 , $^2J_{\text{PC}}=13.9$), 130.81 (d, *ipso*-C in C_6H_5 , $^1J_{\text{PC}}=99.4$), 131.69 and 131.87 (both d, *m*-C in C_6H_5 , $^3J_{\text{PC}}=9.2$), 131.94 and 132.01 (both d, *p*-C in C_6H_5 , $^4J_{\text{PC}}=3.6$), 135.20 (s, *ipso*-C 1 , C^4 in Ar), 145.03 (d, $-\text{C}=\text{CH}-$ in triazole cycle, $^3J_{\text{PC}}=15.4$), 167.24 (s, $\text{C}=\text{O}$). Anal. Calcd for $\text{C}_{50}\text{H}_{56}\text{N}_8\text{O}_4\text{P}_2 \cdot 1.5\text{H}_2\text{O}$: C, 65.13; H, 6.91; N, 12.15; P, 6.72. Found: C, 65.40; H, 6.90; N, 12.32; P, 6.83.

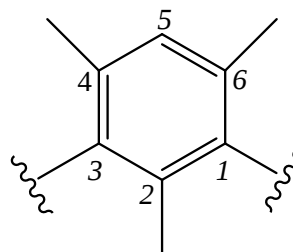
1,1'-(Biphenyl-4,4'-diyl dimethanediyl)bis{4-[2-(diphenylphosphoryl)-N,N-diethylpropanamide]-1H-1,2,3-triazole} (4).



Yield: 62%. Mp: 110-115°C. IR (KBr, cm^{-1}): 3436 (ν_{OH}), 2974, 2932, 1630 ($\nu_{\text{C=O}}$), 1461 (ν_{Ar}), 1437, 1188 ($\nu_{\text{P=O}}$), 1117, 1099, 704, 515. ^1H NMR (400 MHz, CDCl_3 , ppm, J/Hz): 0.70 and 0.72 (both t, 6H+6H, NCH_2CH_3 , $^3J_{\text{HH}}=7.6$); 2.70-2.82, 2.93-3.03, 3.06-3.25, 3.33-3.42 (all m, 12H, NCH_2CH_3 + $\text{CH}_2\text{CH}(\text{P}(\text{O})\text{Ph}_2)$); 4.17 (ddd, 2H, PCH, $^2J_{\text{PH}}=13.5$, $^3J_{\text{HH}}=11.1$); 5.45 (dd, 4H, $-\text{CH}_2-\text{Ar}-\text{CH}_2-$, $^2J_{\text{HH}}=14.9$, $^2J_{\text{HH}}=18.0$); 7.21 and 7.44 (both d, 4H+4H, $\text{H}(\text{C}^2)+\text{H}(\text{C}^3)+\text{H}(\text{C}^6)+\text{H}(\text{C}^7)+\text{H}(\text{C}^9)+\text{H}(\text{C}^{10})+\text{H}(\text{C}^{11})+\text{H}(\text{C}^{12})$ in Ar, $^3J_{\text{HH}}=8.4$); 7.28 (br. s, 2H, CH in triazole cycle); 7.45-7.55, 7.84-7.90, 8.06-8.12 (all m, 12H+4H+4H, $\text{C}_6\text{H}_5-\text{P}$). ^{31}P NMR (161.97

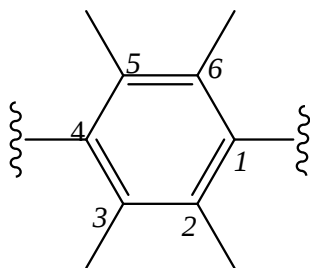
MHz, CDCl_3): 29.95 ppm. ^{13}C NMR (100.61 MHz, CDCl_3 , ppm, J/Hz): 12.44 and 13.79 (both s, $\text{CH}_3\text{CH}_2\text{N}$), 24.75 (s, $\text{CH}_2\text{CH}(\text{P}(\text{O})\text{Ph}_2)$), 40.83 and 42.55 (both s, $\text{CH}_3\text{CH}_2\text{N}$), 45.79 (d, P-CH, $^1J_{\text{PC}}=60.9$), 53.23 (br. s, $-\text{CH}_2-\text{Ar}-\text{CH}_2-$), 121.95 (s, $=\text{CH}-$ in triazole cycle), 127.55 (s, C^3 , C^6 , C^{10} , C^{11} in Ar), 128.48 (s, C^2 , C^7 , C^9 , C^{12} in Ar), 128.28 and 128.47 (both d, *o*-C in C_6H_5 , $^2J_{\text{PC}}=11.7$), 130.73 and 130.86 (both d, *ipso*-C in C_6H_5 , $^1J_{\text{PC}}=98.7$), 131.70 and 131.87 (both d, *m*-C in C_6H_5 , $^3J_{\text{PC}}=9.1$), 131.94 and 132.02 (both d, *p*-C in C_6H_5 , $^4J_{\text{PC}}=3.0$), 133.95 and 140.61 (both s, *ipso*-C in Ar), 145.05 (d, $-\text{C}=\text{CH}-$ in triazole cycle, $^3J_{\text{PC}}=15.8$), 167.24 (s, $\text{C}=\text{O}$). Anal. Calcd for $\text{C}_{56}\text{H}_{60}\text{N}_8\text{O}_4\text{P}_2 \cdot \text{H}_2\text{O}$: C, 68.00; H, 6.32; N, 11.33; P, 6.26. Found: C, 67.84; H, 6.54; N, 11.19; P, 6.21.

1,1'-(2,4,6-Trimethylbenzene-1,3-diyl) dimethanediyl)bis{4-[2-(diphenylphosphoryl)-N,N-diethylpropanamide]-1H-1,2,3-triazole} (5).



Yield: 50%. Mp: 77-87°C. IR (KBr, cm^{-1}): 3436 (ν_{OH}), 2973, 2932, 1631 ($\nu_{\text{C=O}}$), 1461 (ν_{Ar}), 1438, 1214 and 1191 ($\nu_{\text{P=O}}$), 1117, 1099, 1047, 705, 516. ^1H NMR (400 MHz, CDCl_3 , ppm, J/Hz): 0.65 and 0.68 (both t, 6H+6H, NCH_2CH_3 , $^3J_{\text{HH}}=7.2$); 2.10 and 2.20 (both s, 6H+3H, $\text{CH}_3(\text{C}^2)+\text{CH}_3(\text{C}^4)+\text{CH}_3(\text{C}^6)$ in Ar); 2.66-2.75, 2.88-2.98, 3.00-3.15, 3.17-3.27 (all m, 12H, NCH_2CH_3 + $\text{CH}_2\text{CH}(\text{P}(\text{O})\text{Ph}_2)$); 4.09 (ddd, 2H, PCH, $^2J_{\text{PH}}=14.0$, $^3J_{\text{HH}}=11.2$); 5.38 (br. s, 4H, $-\text{CH}_2-\text{Ar}-\text{CH}_2-$); 6.84 (s, 1H, $\text{H}(\text{C}^5)$ in Ar); 7.43 (s, 2H, CH in triazole cycle); 7.32-7.50, 7.75-7.82, 7.96-8.05 (all m, 12H+4H+4H, $\text{C}_6\text{H}_5-\text{P}$). ^{31}P NMR (161.97 MHz, CDCl_3): 30.09 ppm. ^{13}C NMR (100.61 MHz, CDCl_3 , ppm, J/Hz): 12.41 and 13.77 (both s, $\text{CH}_3\text{CH}_2\text{N}$), 19.71 (s, $\text{CH}_3(\text{C}^4)+\text{CH}_3(\text{C}^6)$ in Ar), 19.84 (s, $\text{CH}_3(\text{C}^2)$ in Ar), 24.71 (s, $\text{CH}_2\text{CH}(\text{P}(\text{O})\text{Ph}_2)$), 40.79 and 42.50 (both s, $\text{CH}_3\text{CH}_2\text{N}$), 45.68 (d, P-CH, $^1J_{\text{PC}}=60.5$), 48.17 (s, $-\text{CH}_2-\text{Ar}-\text{CH}_2-$), 120.61 (s, C^5 in Ar), 121.07 (s, $=\text{CH}-$ in triazole cycle), 128.19 and 128.40 (both d, *o*-C in C_6H_5 , $^2J_{\text{PC}}=12.1$), 129.72 (d, *ipso*-C in C_6H_5 , $^1J_{\text{PC}}=112.2$), 131.62 and 131.78 (both d, *m*-C in C_6H_5 , $^3J_{\text{PC}}=9.2$), 131.89 and 131.96 (both d, *p*-C in C_6H_5 , $^4J_{\text{PC}}=2.5$), 137.71 (s, *ipso*-C 4 , C^6 in Ar), 137.84 (s, *ipso*-C 2 in Ar), 138.74 (s, *ipso*-C 1 , C^3 in Ar), 144.32 (d, $-\text{C}=\text{CH}-$ in triazole cycle, $^3J_{\text{PC}}=15.8$), 167.18 (s, $\text{C}=\text{O}$). Anal. Calcd for $\text{C}_{53}\text{H}_{62}\text{N}_8\text{O}_4\text{P}_2 \cdot 1.5\text{H}_2\text{O}$: C, 66.03; H, 6.80; N, 11.62; P, 6.43. Found: C, 66.23; H, 6.75; N, 11.58; P, 6.30.

1,1'-[(2,3,5,6-Tetramethylbenzene-1,4-diyl)dimethanediyl]bis(4-methyl-1H-1,2,3-triazole)bis{4-[2-(diphenylphosphoryl)-N,N-diethylpropanamide]-1H-1,2,3-triazole} (6).



Yield: 65%. Mp: 129-130°C. IR (KBr, cm^{-1}): 3436 (ν_{OH}), 2971, 2930, 1631 ($\nu_{\text{C=O}}$), 1461 (ν_{Ar}), 1438, 1217 and 1191 ($\nu_{\text{P=O}}$), 1117, 1099, 705, 516. ^1H NMR (400 MHz, CDCl_3 , ppm, J/Hz): 0.77 (br. t, 12H, NCH_2CH_3 , $^3J_{\text{HH}}=7.6$); 2.20 (s, 12H, $\text{CH}_3(\text{C}^2)+\text{CH}_3(\text{C}^3)+\text{CH}_3(\text{C}^5)+\text{CH}_3(\text{C}^6)$ in Ar); 2.76-2.90 and 3.00-3.40 (both m, 12H, $\text{NCH}_2\text{CH}_3 + \text{CH}_2\text{CH}(\text{P}(\text{O})\text{Ph}_2)$); 4.21 (ddd, 2H, PCH, $^2J_{\text{PH}}=14.0$, $^3J_{\text{HH}}=11.2$); 5.57 (s, 4H, $-\text{CH}_2-\text{Ar}-\text{CH}_2-$); 6.93 (s, 2H, CH in triazole cycle); 7.45-7.65, 7.82-7.95, 8.06-8.18 (all m, 12H+4H+4H, C_6H_5 -P). ^{31}P NMR (161.97 MHz, CDCl_3): 30.24 ppm. ^{13}C NMR (100.61 MHz, CDCl_3 , ppm, J/Hz): 12.44 and 13.81 (both s, $\text{CH}_3\text{CH}_2\text{N}$), 16.33 (s, $\text{CH}_3(\text{C}^2)+\text{CH}_3(\text{C}^3)+\text{CH}_3(\text{C}^5)+\text{CH}_3(\text{C}^6)$ in Ar), 24.79 (s, $\text{CH}_2\text{CH}(\text{P}(\text{O})\text{Ph}_2)$), 40.87 and 42.61 (both s, $\text{CH}_3\text{CH}_2\text{N}$), 45.73 (d, P-CH, $^1J_{\text{PC}}=80.5$), 48.90 (s, $-\text{CH}_2-\text{Ar}-\text{CH}_2-$), 121.20 (s, $=\text{CH}-$ in triazole cycle), 128.24 and 128.47 (both d, $o\text{-C}$ in C_6H_5 , $^2J_{\text{PC}}=16.1$), 130.77 and 130.69 (both d, $ipso\text{-C}$ in C_6H_5 , $^1J_{\text{PC}}=132.4$), 131.21 (s, $ipso\text{-C}^2, \text{C}^3, \text{C}^5, \text{C}^6$ in Ar), 131.75 and 131.80 (both d, $m\text{-C}$ in C_6H_5 , $^3J_{\text{PC}}=12.0$), 132.00 (br. s, $p\text{-C}$ in C_6H_5), 134.72 (s, $ipso\text{-C}^1, \text{C}^4$ in Ar), 144.31 (d, $-\text{C}=\text{CH}-$ in triazole cycle, $^3J_{\text{PC}}=21.2$), 167.25 (s, $\text{C}=\text{O}$). Anal. Calcd for $\text{C}_{54}\text{H}_{64}\text{N}_8\text{O}_4\text{P}_2\cdot\text{H}_2\text{O}$: C, 66.93; H, 6.86; N, 11.56; P, 6.39. Found: C, 66.78; H, 6.81; N, 11.62; P, 6.25.

Extraction studies

In the extraction experiments, 1,2-dichloroethane of chemical grade without any additional purification was used as an organic solvent. Extractant solutions were prepared using precisely weighed samples. Stock aqueous solutions of lanthanides(III), U(VI), Th(IV) and Pd(II) were prepared by dissolving the corresponding nitrates in water followed by the addition of HNO_3 . The initial concentration of metal ions was $1\cdot 10^{-5}$ M. All lanthanides (III) (except Pm) were present in the initial aqueous phase when simultaneous extraction of Ln(III) was studied. The extraction experiments were performed in tubes equipped with sealing plugs

at room temperature and the 1:1 volume ratio of organic and aqueous phases. The phases were contacted in a rotar mixer at the rate 60 rpm for 1 h, this time being sufficient to reach constant values of the distribution ratio (D).

The concentration of Ln(III), U(VI), Th (IV) and Pd(II) in the initial and equilibrium aqueous solutions was determined using inductively coupled plasma mass spectrometry (ICP-MS) on a mass spectrometer X-7 (Thermo Electron, USA) according to the previously described procedure.^[22] The content of U, Th and lanthanides in the organic phase was determined after back-extraction with 0.1 M solution of 1-hydroxyethane-1,1-diphosphonic acid. The distribution ratio of metal ions was calculated as a ratio of their concentrations in the equilibrium phases. Duplicate experiments showed that the reproducibility of the D measurements was generally within 10%. The concentration of HNO_3 in the equilibrium aqueous phase was determined by potentiometric titration with KOH solution.

Results and Discussion

Characterization of compounds 1-6

The pure ligands **1-6** demonstrate a singlet at ca. 30 ppm in the ^{31}P NMR spectrum, i.e., the region characteristic for the given phosphorus atom environment. The ^1H NMR spectrum corresponds to the depicted structure and is comprises a doublet doublet doublet (ddd) of protons of the PCH group at ca. 4.17 ppm with coupling constants of 11.0 and 14.2 Hz along with the other characteristic signals of the hydrogen atoms located in the typical regions. In the IR spectrum characteristic absorption bands at 1631 cm^{-1} ($\text{C}=\text{O}$), 1461 cm^{-1} (Ar) and 1215 cm^{-1} ($\text{P}=\text{O}$) along with the absorption of OH group appearing as a broad band at 3436 cm^{-1} (valent oscillations) were observed.

Extraction of Pd(II) from HNO_3 and HCl Solutions

To compare the extraction efficiency of compounds **1-8** towards Pd(II), the D_{Pd} values were measured at the Pd(II) extraction from

3M HNO_3 containing 0.001M Pd(II) with 0.001M solutions of compounds **1-7** and 0.01 M compound **8** in 1,2-dichloroethane. The data in Table 1 show that the extraction efficiency of compounds **1-7** towards Pd(II) is considerably higher than that for compound **8**.

This suggests the participation of a 1,2,3-triazole fragment of extractants **1-7** molecule in the complexation with Pd^{2+} ions. Earlier, the formation of Pd-N bonds was reported by Khisamutdinov et al. [23] for complexes of Pd(II) with 1-(2,4-dichlorophenyl)-propyl-1,3-dioxolan-2-yl-methyl-1H-1,2,4-triazol. However, it is difficult to discuss the participation of CMPO moieties in the complex formation with Pd^{2+} ions in detail because of the lack of information on the real coordination fashion of extracted complexes since no direct structural parameters under the same extraction conditions have been obtained yet.

The data in Table 1 show that the efficiency of Pd(II) extraction with compounds **1-3**, **5** and **6** containing two triazole fragments is higher than that for their mono analog **7**. Pd(II) forms square-planar complexes, which could make the symmetrical phenyl-bridged bis-CVPO-triazol ligands especially effective for the extraction of Pd(II).

Table 1. The extraction of Pd(II) from 3 M HNO_3 solutions containing 0.001M Pd(II) with 0.001M solutions of extractants **1-7** and 0.01 M solution of extractant **8** in 1,2-dichloroethane.

extractant	$\lg D_{\text{Pd}}$	extractant	$\lg D_{\text{Pd}}$
1	1.48	5	1.62
2	1.70	6	1.79
3	1.60	7	1.33
4	0.92	8	-1.27

A similar increase in the efficiency of Pd(II) extraction was observed on going from benzoylthiourea to 1-benzoyl-3[6-(3-benzoyl-thioureido)-hexyl]-thiourea. [24] However, the extraction efficiency of compound **4** with biphenyl spacer between triazole groups is lower than that for its mono analog **7**. This can be due to a larger distance between triazole fragments, as compared with compounds **1-3**, **5** and **6**.

The effect of HNO_3 and HCl concentrations in the equilibrium aqueous phase on the extraction of Pd(II) ions with solutions of compound **6** in 1,2-dichloroethane is shown in Fig. 1.

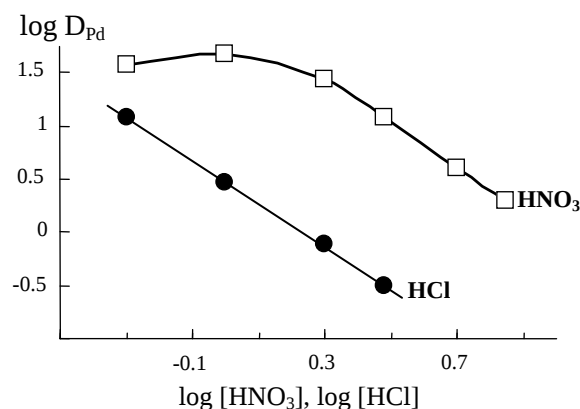


Figure 1. The effect of HNO_3 and HCl concentration in the aqueous phase on the extraction of Pd(II) with $2 \cdot 10^{-5}$ M solutions of compound **6** in 1,2-dichloroethane. Solid lines are guide for the eyes.

The $\log D_{\text{Pd}}$ vs $\log[\text{HNO}_3]$ curve exhibits a maximum at $[\text{HNO}_3] = 1\text{M}$. This can be due to the combined effect of HNO_3 salting out and competition for the extractant, as well as to the formation of Pd(II) anionic complexes in the aqueous phase. [25] The data in Fig. 1 suggest that compound **6** extracts Pd(II) from HNO_3 solutions more effectively than from HCl solutions. This is connected with a high stability of $[\text{PdCl}_4]^{2-}$ complexes in the aqueous phase. [25]

The stoichiometric ratio of palladium(II) to extractant in the extracted complexes was determined by the slope analysis method. The variations in D_{Pd} as a function of compounds **6** and **7** concentration in 1,2-dichloroethane for 3M HNO_3 solutions are shown in Fig. 2.

The dependence $\log D_{\text{Pd}}$ vs $\log([L]_{\text{init}} - s[\text{Pd}]_o)$, where $[L]_{\text{init}}$ is the initial extractant concentration and $[\text{Pd}]_o$ is the equilibrium concentration of Pd(II) in the organic phase, is linear with a slope of 1. Hence, one molecule of compounds **6** and **7** are involved in the formation of complexes with Pd(II) under the experimental conditions used.

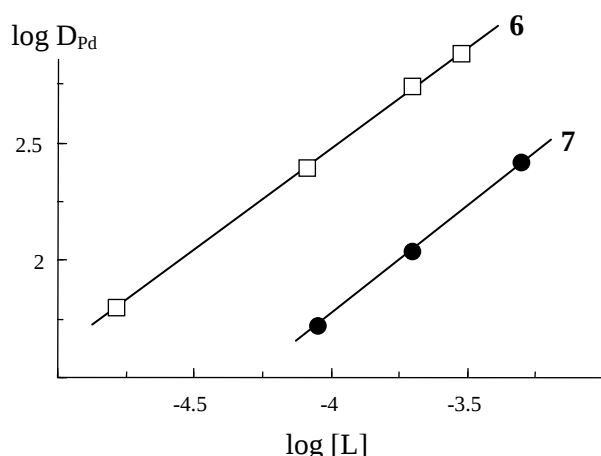


Figure 2. The effect of extractants **6** and **7** concentration in 1,2-dichloroethane on the extraction of Pd(II) from 3 M HNO₃ solutions. Solid lines: linear variation with a slope of $0,94 \pm 0,06$.

Extraction of U(VI), Th(IV) and Ln(III) from Nitric Acid Solutions

The effect of HNO₃ concentration in the equilibrium aqueous phase on the extraction of U(VI), Th(IV) and Eu(III) ions with solutions of compound **6** in 1,2-dichloroethane is shown in Fig. 3. An increase in HNO₃ concentration is accompanied by the growth of distribution ratios of U(VI) and Th(IV).

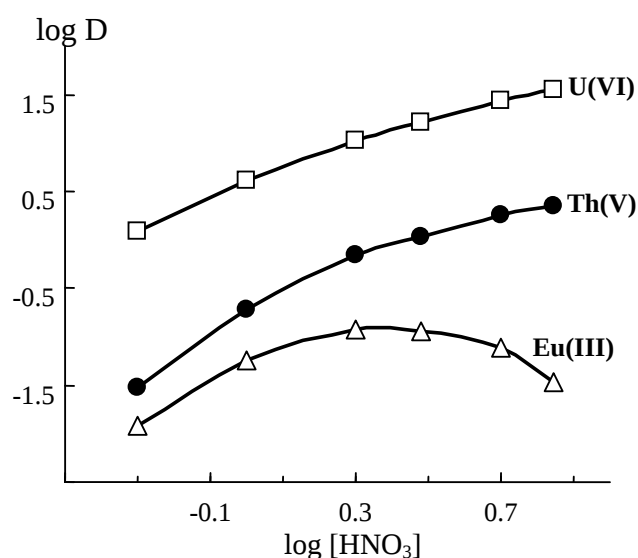


Figure 3. The effect of HNO₃ concentration in the aqueous phase on the extraction of U(VI), Th(IV) and Eu(III) with 0.001 M (for U and Th) and 0.01 M (for Eu) solutions of compound **6** in 1,2-dichloroethane. Solid lines are guide for the eyes.

A similar character of the $\log D - \log [\text{HNO}_3]$ dependence was observed for the extraction of U(VI) and Pu(IV) with CMPO

extractants in the form of coordination-solvated nitrates.^[26] The $\log D_{\text{Eu}}$ vs $\log [\text{HNO}_3]$ curve exhibits a maximum in the range of [HNO₃] between 2 and 3 M (Fig. 3). These maxima are commonly observed in the Ln(III) extraction with neutral organophosphorus compounds and are explained by the combined effect of HNO₃ salting out and competition for extractant, as well as by the change of the activity coefficient values of Ln(III) nitrates depending on [HNO₃].^[27]

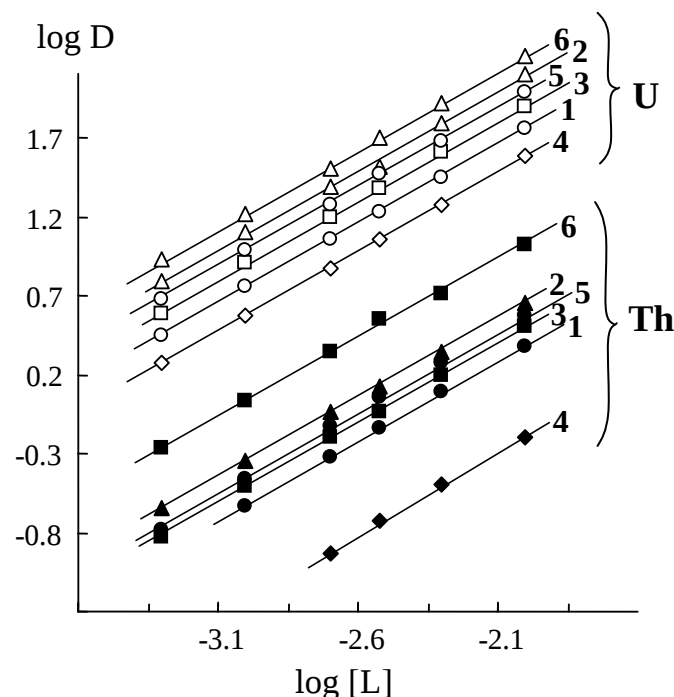


Figure 4. The effect of extractants **1-6** concentration in 1,2-dichloroethane on the extraction of U(VI) and Th(IV) from 3 M HNO₃ solutions. Solid lines: linear variation with a slope of $0,98 \pm 0,06$.

The variations in D_{U} and D_{Th} as a function of extractants **1-6** concentration in 1,2-dichloroethane are shown in Fig. 4. The first power dependence of D_{U} and D_{Th} on [L] points out that U(VI) and Th(IV) ions are extracted with compounds **1-6** from nitric acid solutions mostly as monosolvates. In contrast to the above compounds, their mono analogs compounds **7**^[6] and **8**^[26] extract U(VI) and Th(IV) as a mixture of mono- and disolvates under similar conditions.

For the lanthanides(III) extraction with compound **6**, a non-integer slope of the $\log D_{\text{Ln}}$ vs $\log [L]$ curves is observed (Fig. 5). This can be a result of the formation of a mixture of mono- and

disolvates in the organic phase. In this case, the relation between D_{Ln} and the extractant concentration in the organic phase can be presented as

$$D_{Ln} = [NO_3^-]^3(K_1[L] + K_2[L]^2)$$

where K_1 and K_2 are the extraction constants of Ln(III) as mono- and disolvates, respectively.

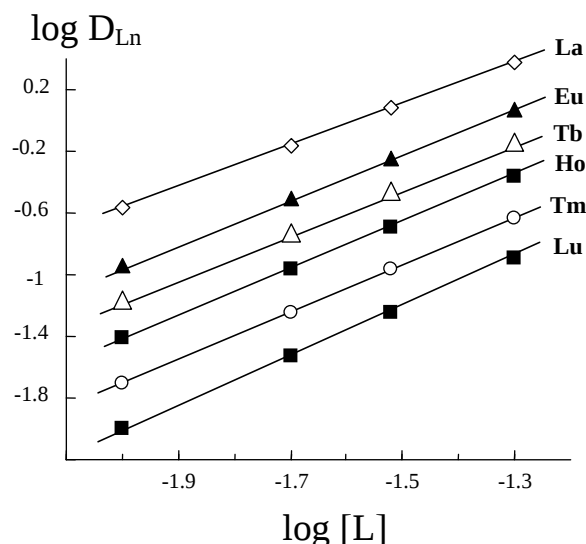


Figure 5. The effect of extractants **6** concentration in 1,2-dichloroethane on the extraction of Ln(III) from 3 M HNO₃ solutions. Solid lines: linear variation with a slope of 1.48 ± 0.12 .

Under the same conditions, compounds **1-5** also extract Ln(III) as a mixture mono- and disolvates. In contrast to above compounds, their mono analogues compounds **7** [6] and **8** [28] extract Ln(III) as disolvates and a mixture of di- and trisolvates, respectively. The decrease in the solvate numbers in the extracted Ln(III) complexes with compounds **1-6** may be caused by polydentate coordination of the ligands during complexation with Ln(III) ions.

To compare the extraction efficiency of compounds **1-8** towards U(VI), Th(IV) and lanthanide(III) ions in nitric acid systems, the D_U , D_{Th} and D_{Eu} values were measured at the extraction with 0.01M solutions of compounds **1-8** in 1,2-dichloroethane from 3M HNO₃ solutions. The data in Table 2 suggest that the introduction of the 1,2,3-triazole fragment into the methylene bridge a CMPO molecule **8** does not essentially change the extraction efficiency of compound **7** towards U(VI) and Eu(III) but drastically decreases the Th(IV) extraction with this compound.

Evidently, the extraction of Th(IV) is more sensitive to an increase in the conformational rigidity of an extractant molecule. In contrast to unsubstituted CMPO **8**, compounds **1-7** extract U(VI) more effectively than Th(IV). The difference in the extractability of U(VI) and Th(IV) by compounds **8** and **1-7** may be due to the difference in the geometry of extracted complexes.

Table 2. The extraction of U(VI), Th(IV) and Eu(III) from 3 M HNO₃ solutions with 0.01M solutions of extractants **1-8** in 1,2-dichloroethane.

extractant	lgD _U	lgD _{Th}	lgD _{Eu}
1	1.76	0.38	-1.26
2	2.10	0.66	-0.94
3	1.90	0.51	-1.14
4	1.59	-0.20	-1.93
5	1.99	0.57	-1.03
6	2.22	1.02	-0.94
7	1.25	0.01	-1.86
8	1.27	3.10	-1.78

Bis-CMPO compounds **1-3**, **5** and **6** extract U(VI), Th(IV) and Eu(III) more effectively than their mono-CMPO analog **7**. Evidently, both CMPO fragments of an extractant molecule take part in the complexation with metal ions. However, the extraction efficiency of bis-CMPO **4** with biphenyl spacer between triazole fragments does not increase in the case of Eu(III), moreover it becomes lower for Th(IV) as compared with that of compound **7**. This can be a result of an increase in the distance between CMPO fragments in the compound **4** molecule and, probably, of a greater conformational rigidity, as compared with compounds **1-3**, **5** and **6**.

Compound **2** extracts U(VI), Th(IV) and Eu(III) more effectively than its *o*- and *p*-isomers – compounds **1** and **3**. The same effect was observed on the extraction of Am(III) and Eu(III) with bis(diarylphosphorylmethyl)benzenes from nitric acid solutions, but in a significantly higher degree: on going from *ortho*- to *meta*-isomers, D_{Am} and D_{Eu} values are three orders of magnitude higher. [29, 30]

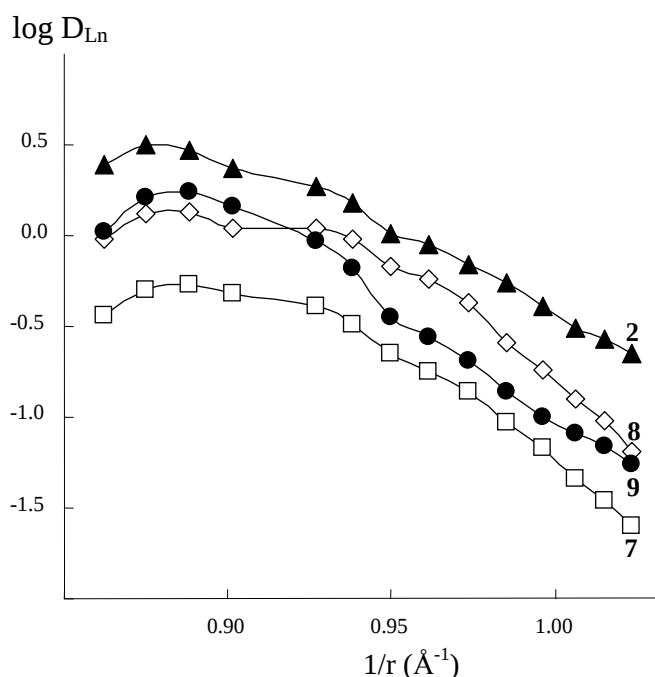


Figure 6. The extraction of lanthanides(III) from 3 M HNO₃ solutions with 0.05M solutions of compounds 7-9 and 2 in 1,2-dichloroethane. The data for 9 from ref. [31]. Solid lines are guide for the eyes.

The effect of the structure of compounds 2, 7 and 8 on the efficiency of lanthanides(III) ions extraction was examined by performing simultaneous extraction of Ln(III) ions from 3M HNO₃ solutions with these compounds in 1,2-dichloroethane (Fig. 6).

The figure also presents our previous data^[31] on the Ln(III) extraction with 1,7-bis(dibutylcarbamoyl)1,7bis(diphenylphosphinyl)-heptane 9, whose molecule contains two Ph₂P(O)CHC(O)NBu₂ coordinating groups linked by a pentamethylene spacer through methylene groups. At this HNO₃ concentration in the equilibrium aqueous phase, the extraction of Ln(III) decreases from La(III) to Lu(III). In general, such lanthanide pattern is typical for the ligands of the CMPO type^[32, 33] as well as for some other neutral bidentate ligands, such as tetraarylmethylenediphosphine dioxides^[34, 35] and alkylsubstituted malonamides^[36] in nitric acid systems. These trends were explained by the rise in the hydration energies of Ln(III) ions as their ionic radii decrease.^[32]

The data in Fig. 6 show that D_{Ln} values for compound 7 are lower than those for compound 8. That is, the replacement of one hydrogen atom in the methylene bridge of CMPO molecule by a

triazole fragment decreases the extraction efficiency of compound 7 towards Ln(III). The same effect was observed on the extraction of Am(III) and Eu(III) with tetraphenyl-methylenediphosphine dioxide^[37] and CMPO^[38] with alkyl or other substituents in the methylene bridge between coordinating groups. This was assigned to a limited conformational mobility of the spacer between P(O) and C(O) groups of the extractant molecule and an associated inhibition of the formation of a six-membered chelate complex with the extracted ion.^[38] This can probably explain the lower extraction efficiency of bis-CMPO 9 towards Sm-Lu than that of its monoanalogue 8.

The data in Fig. 6 suggest that, under comparable conditions, the extraction efficiency of bis-CMPO 2 is significantly higher than that of its monoanalogue 7. The D_{Ln} values for compound 2 are higher than those for bis-CMPO 9 with pentamethylene spacer between CMPO moieties. However, it is difficult to discuss the participation of 1,2,3-triazole groups in the complexation with Ln(III) ions in detail because of the lack of information on the real coordination fashion of extracted complexes since no direct structural parameters under the same extraction conditions have been obtained yet.

Conclusions

Novel polyfunctional neutral organophosphorus compounds - Ar-CMPO were synthesized and studied as extractants for Pd(II), Ln(III), U(VI) and Th(IV) from HNO₃ solutions. The influence of aqueous and organic phases on the extraction efficiency was elucidated and stoichiometry of the complexes extracted was determined. The data obtained showed that one of the ways to modify CMPO aimed at the improvement of their extraction ability towards Pd(II) is to introduce 1,2,3-triazole fragment into the methylene bridge of the CMPO molecule. This modification of an extractant molecule does not essentially change the extraction efficiency towards U(VI) and Ln(III) but drastically decreases the Th(IV) extraction and change the order in the extractability of U(VI) and Th(IV) from HNO₃ solutions. An increase in the number of CMPO- and triazole fragments in extractants molecule leads to

an increase of their extraction efficiency towards Pd(II), Ln(III), U(VI) in nitric acid systems.

Acknowledgements

The work was carried out with financial support from the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST «MISiS» (№ K1-2014-026)

Notes and references

- 1 Z. Kolaric, and E.V. Renard, *Platinum Metals Rev.* 2003, **47**, 74.
- 2 E.P. Horwitz, and W.W. Schulz, *Metal Ion Separation and Preconcentration: Progress and Opportunities* (Eds.: A.H. Bond, M.L. Dietz, R.D. Rogers) *ACS Symposium Series 712*, American Chemical Society Washington, D.C., 1999, 20.
- 3 M.K. Chmutova, M.N. Litvina, G.A. Pribilova, L.A. Ivanova, I.B. Smirnov, A.Yu. Shadrin, and B.F. Myasoedov, *Radiokhimiya (in Russian)* 1999, **41**, 331.
- 4 Z.-X. Zhu, Y. Sasaki, H. Suzuki, S. Suzuki, and T. Kimura, *Analyt. Chim. Acta* 2004, **527**, 163.
- 5 Y. Sasaki, M. Ozawa, T. Kimura, and K. Ohashi, *Solvent Extr. Ion Exch.* 2009, **27**, 378.
- 6 A.N. Turanov, V.K. Karandashev, O.I. Artyushin, E.V. Sharova, G.K. Genkina, and A.N. Yarkevich, *Solvent Extr. Ion Exch.* 2014, **32**, 669.
- 7 A.N. Turanov, V.K. Karandashev, E.V. Sharova, O.I. Artyushin, and I.L. Odinets, *Solvent Extr. Ion Exch.* 2010, **28**, 579.
- 8 A.N. Turanov, V.K. Karandashev, E.V. Sharova, O.I. Artyushin, and I.L. Odinets, *Solvent Extr. Ion Exch.* 2012, **30**, 604.
- 9 A. Arduini, V. Bochmer, L. Delmau, J.F. Desreux, J.-F. Dozol, A.G. Carrera, B. Lambert, C. Musigmann, A. Pochini, A. Shivanyuk, and F. Ugozzoli, *Chem. Eur. J.* 2000, **6**, 2135.
- 10 L. Atamas, O. Klimchuk, V. Rudzevich, V. Pirozhenko, V. Kalchenko, I. Smirnov, V. Babain, T. Efremova, A. Varnek, G. Wipff, F. Arnaud-New, M. Roch, M. Saadioui, and V. Bohmer, *J. Supramolecular Chem.* 2002, **2**, 421.
- 11 L.H. Delmau, N. Simon, M.-J. Schwing-Weill, F. Arnaud-New, J.-F. Dozol, S. Eymard, B. Tournois, C. Gruttner, C. Musigmann, A. Tunayar, and V. Bohmer, *Sep. Sci. Technol.* 1999, **43**, 863.
- 12 H. Boerrigter, W. Verboom, and D.N. Reinhoudt, *J. Org. Chem.* 1997, **62**, 7148.
- 13 M.M. Reinoso-Garcia, W. Verboom, D.N. Reinhoudt, F. Brisch, F. Arnaud-New, and K. Liger, *Solvent Extr. Ion Exch.* 2005, **23**, 425.
- 14 P. Amrhein, P.L. Wash, A. Shivanyuk, and J. Rebek, *J. Org. Lett.* 2002, **4**, 319.
- 15 P. Amerhein, A. Shivanyuk, D.W. Jonson, and J. Rebek, *J. Am. Chem. Soc.* 2002, **124**, 10349.
- 16 A.N. Turanov, V.K. Karandashev, A.V. Kharitonov, A.N. Lezhnev, Z.V. Safronova, A.N. Yarkevich, and E.N. Tsvetkov, *Russian J. of General Chemistry* 1999, **69**, 1068.
- 17 Z.-F. Guo, H. Yan, and Z.-F. Li, *Org. Biomol. Chem.* 2011, **9**, 6788.
- 18 L.K. Haridas, Y.K. Sharma, and S. Upreti, *Org. Lett.* 2008, **10**, 1645.
- 19 M. Pascu, A. Ruggi, R. Scopelliti, and K. Severin, *Chem. Commun.* 2013, **49**(1), 45.
- 20 H.R. Seong, D.-S. Kim, S.-G. Kim, H.-J. Choi, and K.H. Ahn, *Tetr. Lett.* 2004, **45**(4), 723.
- 21 A.J. Papa, *J. Org. Chem.* 1966, **31**, 1426.
- 22 [41] A.N. Turanov, V.K. Karandashev, and V.E. Baulin, *Solvent Extr. Ion Exch.* 1996, **14**, 227.
- 23 R.A. Khisamutdinov, Yu.I. Murinov, and O.V. Shitikova, *Zhurnal neorganicheskoi khimii (in Russian)* 2007, **52**, 1041.
- 24 A.N. Turanov, V.K. Karandashev, and A.N. Proshin, *Solvent Extr. Ion Exch.* 2008, **26**, 360.
- 25 J.C. Bailar, H.J. Emeleus, S.R. Nyholm, and A.F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry*, Vol. 3, First Edition; Pergamon Press Ltd.: Oxford, England, 1973.
- 26 M.N. Litvina, M.K. Chmutova, G.A. Pribilova, N.P. Nesterova, and B.F. Myasoedov, *Radiokhimiya (in Russian)* 1998, **40**, 550.
- 27 A.M. Rozen, and B.V. Krupnov, *Russ. Chem. Rev.* 1996, **65**, 73.
- 28 A.N. Turanov, V.K. Karandashev, E.V. Sharova, O.I. Artyushin, and I.L. Odinets, *Tsvetnie metalli (in Russian)* 2012, **3**, 51.
- 29 M. K. Chmutova, G.V. Bodrin, M.N. Litvina, A.G. Matveeva, E.I. Matrosov, Yu.M. Polikarpov, P.L. Khiznyak, B.F. Myasoedov, and M.I. Kabachnik, *Radiokhimiya (in Russian)* 1989, **31**, 83.
- 30 B.F. Myasoedov, G.V. Bodrin, M.K. Chmutova, N.E. Kochetkova, T.Ya. Medved, Polikarpov, and M.I. Kabachnik, *Solvent Extr. Ion Exch.* 1983, **4**, 689.
- 31 A.N. Turanov, V.K. Karandashev, and A.N. Yarkevich, *Radiochemistry* 2012, **54**, 477.
- 32 E.P. Horwitz, K.A. Martin, H. Diamond, and L. Kaplan, *Solvent Extr. Ion Exch.* 1986, **4**, 449.
- 33 M.N. Litvina, M.K. Chmutova, B.F. Myasoedov, and M.I. Kabachnik, *Radiokhimiya (in Russian)* 1996, **38**, 525.
- 34 T. Yaita, and S. Tachimori, *Radiochim. Acta* 1996, **73**, 27.
- 35 A.N. Turanov, V.K. Karandashev, and N.A. Bondarenko, *Radiochemistry* 2007, **49**, 55.
- 36 H. Narita, T. Yaita, K. Tamura, and S. Tachimori, *J. Radioanal. Nucl. Chem.* 1999, **239**, 381.
- 37 N.E. Kochetkova, O.E. Koiro, N.P. Nesterova, T.Ya. Medved, M.K. Chmutova, B.F. Myasoedov, and M.I. Kabachnik, *Radiokhimiya (in Russian)* 1986, **28**, 338.
- 38 B.F. Myasoedov, M.K. Chmutova, N.E. Kochetkova, O.E. Koiro, and G.A. Pribilova, *Solvent Extr. Ion Exch.* 1986, **4**, 61.