Extraction and Coordination Properties of 2,3-Bis(diphenylphosphinyl)buta-1,3-diene and 3,4-Bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene

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Abstract—The extraction properties of 2,3-bis(diphenylphosphinyl)buta-1,3-diene (L^1) and 3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L^2) with respect to f elements are studied for the extraction of microquantities of U(VI) and Th(IV) from HNO_3 solutions with solutions of the extracting agents in 1,2-dichloroethane. The introduction of methyl groups into the 1,3-butadiene carbon skeleton of bis(phosphine oxide) increases the efficiency of U(VI) extraction. The coordination properties of bis(phosphine oxides) L^1 and L^2 are studied for the complexes with uranyl nitrate. The crystal structures of bis(phosphine oxide) L^1·THF (CIF file CCDC no. 2107403) and its complexes with uranyl nitrate **I** and **II** (CIF files CCDC nos. 2107404 and 2107405, respectively) are confirmed by X-ray diffraction data.

INTRODUCTION

In spite of a rather long history of studying phosphorus oxides, increased interest in the synthesis of efficient and selective organophosphorus ligands to various metal ions has been observed in recent decades. The brief list of areas actively using mono-, di-, and polydentate phosphine oxides is as follows: bioinorganic chemistry [1], catalysis [2], production of new materials [3], separation and extraction of rare and scattered elements [4], and hydrometallurgy and decontamination of nuclear waste of electric power stations from radioactive elements [5]. Metal complexes with bis(phosphine oxides) demonstrating a richer structural topology than monophosphine oxides are of most interest. For example, metal-organic frameworks [6–9], macrocyclic compounds [10], and cage complexes [11] based on bis(phosphine oxides) were described.

The structures of the synthesized complexes mainly depend on the structure of the bis(phosphine oxide) used. As a rule, methylene bis(phosphine oxide) chelates metal ions to form six-membered complexes [12, 13]. In the case of the elongation of the bridge linking two phosphine oxide groups $Ph_2P(O)(CH_2)_nP(O)Ph_2$ ($n = 2$, 4, or 6), dimeric or polymeric complexes are usually formed [14–16].

Continuing the study of the coordination properties of alkylenebis(phosphine oxide) [17] and its analogs [18], we performed studies related to an attempt to reveal the influence of structural changes in the carbon skeletons of bis(phosphine oxides) on their coordination and extraction properties. The bis(phosphine oxide) ligands on the 1,3-alkadiene platform, 2,3-bis(diphenylphosphinyl)buta-1,3-diene (L^1) [19] and 3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L^2) [20], were chosen as objects of the study.

EXPERIMENTAL

Solvents $CHCl_3$, CH_2Cl_2, and acetonitrile (reagent grade) were distilled over P_2O_5 for dehydration and stored over CaH_2, and THF was distilled and stored over CaH_2 and distilled off prior to use. Commercial 1,2-dichloroethane and ethanol were used as received.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 spectrometer (400.13, 100.61, and 161.98 MHz, respectively). The H^1 and ^{31}P NMR spectra of the complex were recorded in

DMF-d_7. IR spectra were recorded on a VERTEX 70v Fourier-transform IR spectrometer (Germany). High-resolution mass spectra were detected on a Bruker micrOTOF II instrument using the electrospray ionization (ESI) method. Elemental analyses (C, H, N) were carried out on a CarloErba 1106 automated analyzer.

Synthesis of 3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L²) was carried out in an inert atmosphere. 2,5-Dimethyl-3-hexyne-2,5-diol (0.9 g, 6.4 mmol) was added to a suspension of NaH (0.31 g, 12.8 mmol) in THF (6 mL) with vigorous stirring, and after 5 min diphenylchlorophosphine (3.12 g, 14.1 mmol) was added dropwise maintaining the temperature of the reaction mixture at 20°C. After the cessation of gas release, the mixture was stirred at 20°C for 4 h. A precipitate was filtered off and washed with THF (2 × 3 mL), and $Cu(OTf)_2$ (0.2 g, 0.7 mmol, 10 mol %) was added to the filtrate. After the formation of a yellow-orange solution, the mixture was left to stay for 48 h. Then CH_2Cl_2 (20 mL) was added, the reaction mixture was washed with a 25% solution of NH_3 (2 × 3 mL) and water (2 × 5 mL), and dried over Na_2SO_4. The drying agent was filtered off and washed with CH_2Cl_2 (2 × 5 mL), and the filtrate was evaporated in vacuo. Chromatography on silica gel in a $CHCl_3$–benzene–methanol (30 : 30 : 1) system gave 3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L²) (2.39 g, 72%), (5-chloro-2,5-dimethylhex-3-in-2-yl)diphenylphosphine oxide (L³) (0.21 g, 9%), and (2,5-dimethylhex-5-en-3-in-2-yl)diphenylphosphine oxide (L⁴) (0.14 g, 7%).

3,4-Bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L²). Colorless crystals, m.p. = 186−188°C [20]. ¹H NMR (δ, ppm): 8.00−7.96 m (4H, *o*-H, Ph), 7.48−7.44 m (6H, *o*,*p*-H, Ph), 7.38−7.35 m (2H, *p*-H, Ph), 7.20−7.16 m (4H, *m*-H, Ph), 7.14−7.08 m (4H, *m*-H, Ph), 1.76 s (6H, 2CH₃), 1.69 s (6H, 2CH₃). ¹³C NMR (δ_C, ppm): 153.88 dd ((CH₃)₂**C**=C), $^2J_{P,C}$ = 8.02 Hz), 134.75 d (*ipso*-C, $^1J_{P,C}$ = 102.13 Hz), 134.20 d (*ipso*-C, $^1J_{P,C}$ = 99.21 Hz), 132.15 dd (*p*-C, Ph, $^4J_{P,C}$ = 11.68 Hz, $^4J_{P,C}$ = 10.21 Hz), 131.20 br.d. (*o*-C, Ph, $^2J_{P,C}$ = 31.36 Hz), 129.02 d ((CH₃)₂C=**C**, $^1J_{P,C}$ = 8.02 Hz), 128.38 d (*m*-C, Ph, $^3J_{P,C}$ = 10.95 Hz), 128.38 d (*m*-C, Ph, $^3J_{P,C}$ = 11.68 Hz), 25.30−25.23 m ((**C**H₃)₂C=C), 25.12−25.09 m ((**C**H₃)₂C=C). ³¹P NMR (δ_P, ppm): 27.60 s. IR (ν, cm⁻¹): 3051 ν(CH, Ph); 2910, 1436 ν(CH₃); 1608, 1589 ν(Ph); 1628 ν(C=C); 1162 ν(P=O). MS, *m/z*: 511.1950 [*M* + H]⁺ (calculated for $C_{32}H_{33}O_2P_2$: 511.1961).

(5-Chloro-2,5-dimethylhex-3-in-2-yl)diphenyl-phosphine oxide (L³). Colorless oil. ¹H NMR (δ, ppm): 7.72−7.68 m (4H, *o*-H, Ph), 7.52−7.50 m (2H, *p*-H, Ph), 7.48−7.43 m (4H, *m*-H, Ph), 1.46 d (6H, 2CH₃, $^3J_{P,H}$ = 6.0 Hz), 1.44 s (6H, 2CH₃). ¹³C NMR (δ_C, ppm): 133.29 d (*ipso*-C, Ph, $^1J_{P,C}$ = 104.32 Hz),

131.74 d (*p*-C, Ph, $^4J_{P,C}$ = 2.91 Hz), 131.36 d (*o*-C, Ph, $^2J_{P,C}$ = 9.48 Hz), 128.25 d (*m*-C, Ph, $^3J_{P,C}$ = 11.67 Hz), 102.95 br.s. (**C**≡C), 101.93 br.s. (C≡**C**), 99.74 d (**C**−P, $^1J_{P,C}$ = 13.86 Hz), 73.57 d (**C**−Cl, $^4J_{P,C}$ = 5.11 Hz), 30.74 d (2CH₃, $^5J_{P,C}$ = 2.91 Hz), 19.00 d (2CH₃, $^2J_{P,C}$ = 5.84 Hz). ³¹P NMR (δ_P, ppm): 34.37 s. MS, *m/z*: 345.1170 [*M* + H]⁺ (calculated for $C_{20}H_{23}ClOP$: 345.1181).

(2,5-Dimethylhex-5-en-3-in-2-yl)diphenylphos-phine oxide (L⁴). Colorless crystals, m.p. = 152−154°C. ¹H NMR (δ, ppm): 7.70−7.65 m (4H, *o*-H, Ph), 7.47−7.39 m (8H, Ph), 5.46 s (1H, =C(**H**)H), 5.02 s (1H, =C(H)**H**), 1.84 s (3H, **CH₃**(=CH₂)), 1.36 d (6H, 2CH₃, $^3J_{P,H}$ = 6.1 Hz). ¹³C NMR (δ_C, ppm): 136.17 d (**C**H₂=C−CH₃, $^5J_{P,C}$ = 7.29 Hz), 133.21 d (*ipso*-C, Ph, $^1J_{P,C}$ = 105.04 Hz), 131.18 s (*o*-C, Ph, $^2J_{P,C}$ = 9.48 Hz), 131.41 s,[1] Ph, 128.14 d (Ph, $^3J_{P,C}$ = 12.41 Hz), 117.12 d (CH₂=**C**−CH₃, $^4J_{P,C}$ = 3.65 Hz), 101.09 br.s (**C**≡C), 100.08 br.s (C≡**C**), 99.45 d (**C**−P, $^1J_{P,C}$ = 13.14 Hz), 23.00 d (CH₂=C−**C**H₃, $^5J_{P,C}$ = 5.84 Hz), 19.10 d (2CH₃, $^2J_{P,C}$ = 5.83 Hz). ³¹P NMR (δ_P, ppm): 31.57 s. MS, *m/z*: 309.1403 [*M* + H]⁺ (calculated for $C_{20}H_{22}OP$: 309.1414).

Synthesis of 2,3-bis(diphenylpphosphinyl)-but-1,3-diene uranyl dinitrate (I). A solution of $UO_2(NO_3)_2$· $6H_2O$ (104 mg, 0.2 mmol) in acetonitrile (5 mL) was slowly added to a solution of phosphine oxide L¹ (90.8 mg, 0.2 mmol) in chloroform (5 mL), and the reaction mixture was stirred for 1 h. The precipitated yellow crystals were filtered off, washed with acetonitrile (2 × 5 mL), recrystallized from a DMF−diethyl ether (1 : 1) mixture, and dried in a vacuum of 0.1 mmHg to a constant weight. The yield of complex **I** was 160 mg (80%), T_{decomp} = 255−257°C. IR (KBr; ν, cm⁻¹): 539, 582, 692, 730, 929 (UO₂), 1122, 1145, 1161, 1273 (UO₂), 1292, 1385, 1487 (NO₃), 1516. ¹H NMR (400 MHz; DMF-d_7; δ, ppm): 8.4−7.6 m (20H, 4C₆H₅), 6.87 d (2H, $^2J_{HH}$ = 42 Hz, CH₂=), 6.18 br.s. (2H, CH₂=). ¹³C NMR (100 MHz; DMF-d_7; δ, ppm): 138.94 dd ($^1J_{PC}$ = 95.0 Hz, $^2J_{PC}$ = 8.0 Hz, P−C=), 136.38 br.s (H₂C=), 134.04 br.s (C₆H₅), 132.57 d ($^3J_{PC}$ = 9.7 Hz, C₆H₅), 129.68 d ($^2J_{PC}$ = 12.0 Hz, C₆H₅). ³¹P NMR (162 MHz; DMF-d_7; δ, ppm): 46.44 br.s.

For $C_{28}H_{24}N_2O_{10}P_2U$

	C	H	N
Anal. calcd., %	C, 39.64	H, 2.85	N, 3.30
Found, %	C, 39.40	H, 2.89	N, 3.44

Synthesis of 2,3-bis(diphenylphosphinyl)-1,1,4,4-tetramethylbut-1,3-diene uranyl dinitrate (II). A solu-

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[1] The signal of the left part of the *p*-C coalesces with the left part of the *o*-C doublet.

tion of $UO_2(NO_3)_2 \cdot 6H_2O$ (104 mg, 0.2 mmol) in ethanol (5 mL) was carefully added onto the surface of a solution of phosphine oxide L^2 (102 mg, 0.2 mmol) in DMF (5 mL). The light green crystals precipitated on the next day were filtered off, washed with diethyl ether, and dried in a vacuum of 0.1 mmHg to a constant weight. The yield of complex **II** was 150 mg (73%), $T_{decomp} = 320-322°C$. IR (KBr; ν, cm^{-1}): 545, 575, 699, 748, 932 (UO_2), 1097, 1121, 1144, 1278 (UO_2), 1296, 1385, 1439, 1484 (NO_3), 1512, 1529.

For $C_{32}H_{32}N_2O_{10}P_2U$

Anal. calcd., %	C, 42.21	H, 3.54	N, 3.08
Found, %	C, 42.00	H, 3.54	N, 3.10

Study of the extraction properties for compounds L^1, L^2, and L^5. 1,2-Dichloroethane (reagent grade) was used as the organic solvent. Solutions of the extracting agents were prepared using exact weighed samples. The starting aqueous solutions of U(VI) and Th(IV) were prepared by the dissolution of the corresponding nitrates in water followed by the addition of HNO_3 to a required concentration. The starting concentration of metal ions was 2×10^{-6} mol/L. Equal volumes of the organic and aqueous phases were stirred at room temperature on a rotary instrument with a rate of 60 rpm for 1 h, which is sufficient for establishing constant distribution coefficients.

The concentration of U(VI) and Th(IV) in the starting and equilibrium aqueous solutions was determined by mass spectrometry using sample ionization in inductively coupled plasma (ICP-MS) on an XSeriesII mass spectrometer (Thermo Scientific, United States) at the following operation parameters: generator output 1300 W, package of standard nickel cones, PolyCon concentric sprayer, quartz conic spraying chamber cooled to 3°C, plasma forming argon flow rate 13 L/min, auxiliary argon flow rate 0.9 L/min, argon flow rate in the sprayer 0.95 L/min, and analyzed sample flow rate 0.8 mL/min. The spectrometer was calibrated using single- and multicomponent standards (High-Purity Standards, United States). The concentration of U(VI) and Th(IV) in the equilibrium organic phase was determined as a difference between the concentrations in the starting and equilibrium aqueous solutions. The distribution coefficients of elements (D) were calculated as the ratio of their concentrations in the equilibrium organic and aqueous phases. An inaccuracy of distribution coefficient determination did not exceed 5%. The concentration of HNO_3 in the equilibrium aqueous phase was determined by potentiometric titration with a standard solution of NaOH.

X-ray diffraction (XRD). Single crystals of compound $L^1 \cdot THF$ were obtained by recrystallization from THF, and complexes **I** and **II** were taken from the reaction mixture. Reflection intensities were measured on Bruker Apex II ($L^1 \cdot THF$ and **I** at 120 K) and Bruker Quest (**II**, 100 K) diffractometers using MoK_α radiation ($\lambda = 0.71073$ Å). The structures were solved using the SHELXT algorithm [21] and refined in the full-matrix approximation against F^2 (*hkl*). Non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were found from geometric concepts and refined in the isotropic approximation by the riding model with $U_{iso}(H) = 1.2U_{eq}(X)$. Single crystals of $L^1 \cdot THF$ are twins that were separated using the PLATON program [22] and refined using the BASF/HKLF 5 instructions. All calculations were performed using the SHELXL2014 [23] and OLEX2 [24] programs. The parameters of the crystals and refinement results are given in Table 1.

An additional crystallographic information for $L^1 \cdot THF$, **I**, and **II** was deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2107403 ($L^1 \cdot THF$), 2107404 (**I**), and 2107405 (**II**); http://www.ccdc.cam.ac.uk/structures).

The surfaces of the Voronoi polyhedra were constructed and examined in the ToposPro structural topological program package [25].

RESULTS AND DISCUSSION

Compound **I** was synthesized using a previously described procedure [19]. The synthesis of 1,3-alkadiene **II** was based on the modified procedure [20]. 2,5-Dimethyl-3-hexyne-2,5-diol was introduced in the reaction with diphenylchlorophosphine in the presence of NaH and 10 mol % $Cu(OTf)_2$ in THF at 20°C (Scheme 1).
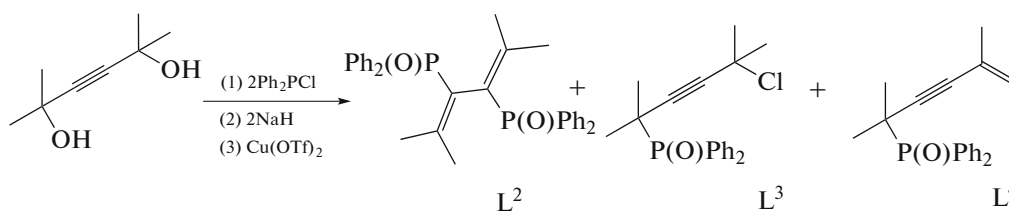
Scheme 1.

The target product (alkadiene L^2) was synthesized and isolated by column chromatography in a yield of 72%. (5-Chloro-2,5-dimethylhex-3-in-2-yl)diphenylphosphine oxide (L^3) and (2,5-dimethylhex-5-en-3-

Table 1. Crystallographic data and experimental parameters for compounds $L^1 \cdot THF$, **I**, and **II**

Parameter	Value		
	$L^1 \cdot THF$	**I**	**II**
Formula	$C_{32}H_{32}O_3P_2$	$C_{28}H_{24}N_2O_{10}P_2U$	$C_{32}H_{32}N_2O_{10}P_2U$
FW	526.51	848.46	904.56
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1$	$P2_1/n$	$P2_12_12_1$
Z	2	4	4
a, Å	8.3734(8)	12.1672(13)	9.5958(2)
b, Å	16.2032(15)	19.666(2)	16.4917(3)
c, Å	11.1046(10)	12.8628(14)	20.7474(4)
β, deg	112.1243(18)	105.899(4)	90
V, Å^3	1395.7(2)	2960.1(6)	3283.30(11)
ρ(calcd.), g cm^{-3}	1.253	1.904	1.830
μ, cm^{-1}	0.187	5.651	5.101
$F(000)$	556	1632	1760
Measured reflections	12645	39731	106772
Independent reflections (R_{int})	12645 (0.080)	9080 (0.048)	10047 (0.045)
Reflections with $I > 2\sigma(I)$	11567	7023	9671
Number of parameters	333	388	429
R_1	0.0442	0.0273	0.0173
wR_2	0.0907	0.0544	0.0385
GOOF	0.996	1.020	1.005
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.54/−0.33	0.55/−1.39	1.29/−0.42
Flack parameter	−0.01(3)		0.040(3)

in-2-yl)diphenylphosphine oxide (L^4) are formed as by-products in 9 and 7% yields, respectively. The structures of compounds L^2-L^4 were determined by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and IR spectroscopy, and the compositions were determined using elemental analyses and mass spectrometry.

The extraction properties of compounds L^1 and L^2 with respect to f elements were studied for the extraction of microquantities of U(VI) and Th(IV) from HNO$_3$ solutions with solutions of the extracting agents in 1,2-dichloroethane. 1,2-Bis(diphenylphosphinyl)ethane Ph$_2$P(O)CH$_2$CH$_2$P(O)Ph$_2$ (L^5) served as the reference compound.

The influence of the HNO$_3$ concentration in the equilibrium aqueous phase on the changes in the distribution coefficients of U(VI) (Fig. 1) and Th(IV) (Fig. 2) was considered for the extraction with 0.001 M solutions of compounds L^1, L^2, and L^5 in dichloroethane. An increase in the concentration to 1−2 M HNO$_3$ is accompanied by an increase in D_U and D_{Th}, which is related to the salting-out effect of NO$_3^-$ ions and corresponds to the extraction of these ions as coordinatively solvated nitrates [26]. The further increase in the HNO$_3$ concentration results in some decrease in D_U and D_{Th} due to the coextraction of nitric acid leading to the concentration of the free extracting agent in the organic phase.

The stoichiometric metal to extracting agent ratio in the extracted complexes was determined by the equilibria shifting method. The obtained data (Figs. 3, 4) show that compounds L^1, L^2, and L^5 in dichloroethane extract Th(IV) from nitric acid solutions in the form of disolvates, whereas U(VI) is predominantly extracted in the form of monosolvates.

The data on the extraction of U(VI) and Th(IV) from nitric acid solutions under comparable conditions are given in Table 2 to compare the extraction abilities of compounds L^1, L^2, and L^5 with respect to U(VI) and Th(IV) and the separation factors of thorium and uranium ($\beta_{Th/U} = D_{Th}/D_U$). It can be seen that the introduction of allyl and especially methyl substituents into the alkylene bridge of the Ph$_2$P(O)CH$_2$CH$_2$P(O)Ph$_2$ (L^5) molecule leads to an increase in the efficiency of U(VI) extraction and some decrease in the extraction ability of compounds L^1 and L^2 with respect to Th(IV).
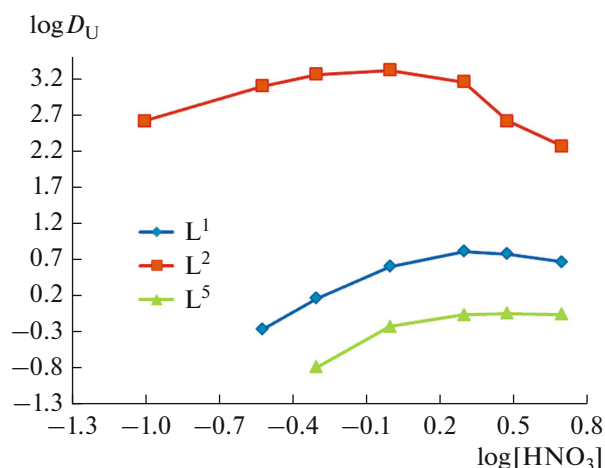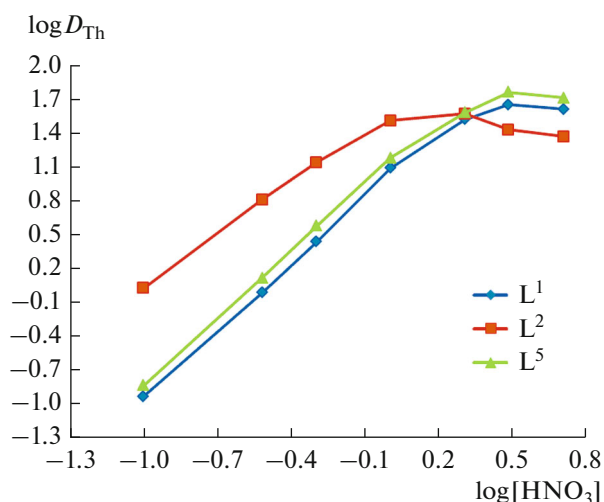
Fig. 1. Dependences of the distribution coefficients of U(VI) on the equilibrium concentration of HNO_3 in the equilibrium aqueous phase for extraction with 0.001 M solutions of compounds L^1, L^2, and L^5 in dichloroethane.
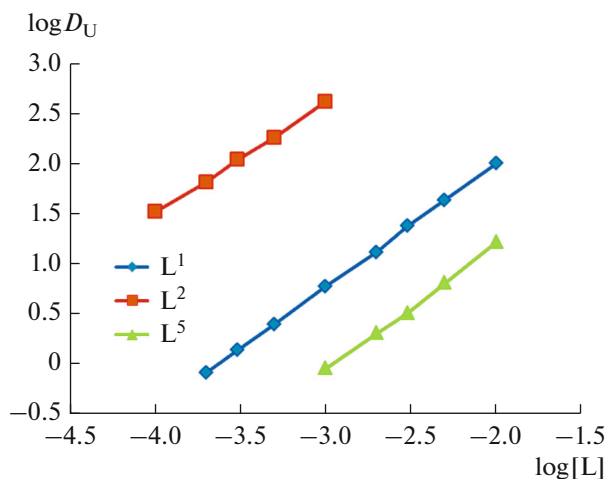

Fig. 2. Dependences of the distribution coefficients of Th(IV) on the equilibrium concentration of HNO_3 in the equilibrium aqueous phase for extraction with 0.001 M solutions of compounds L^1, L^2, and L^5 in dichloroethane.

Fig. 3. Dependences of the distribution coefficients of U(VI) on the concentration of compounds L^1, L^2, and L^5 in dichloroethane for extraction from a 3 M solution of HNO_3.
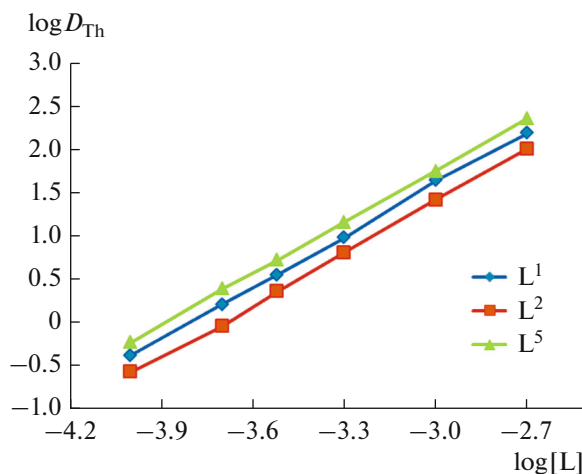

Fig. 4. Dependences of the distribution coefficients of Th(IV) on the concentration of compounds L^1, L^2, and L^5 in dichloroethane for extraction from a 3 M solution of HNO_3.

The selectivity of Th(IV) extraction decreases in the series of compounds $L^5 > L^1 > L^2$, and compound L^2 extracts U(VI) much more efficiently than Th(IV). The separation factor of uranium and thorium ($\beta_{U/Th}$) for this compound decreases from 200 to 16 with an increase in the HNO_3 concentration in the equilibrium aqueous phase from 0.3 to 3 mol/L. The difference in the stoichiometry of the extracted U(VI) and Th(IV) complexes results in a decrease in $\beta_{U/Th}$ with an increase in the concentration of compound L^2 in the organic phase.

In order to establish factors affecting the extraction properties of bis(phosphine oxides) L^1 and L^2, their structural studies were carried out. The structures and compositions of ligands L^1 and L^2 were determined by XRD. Bis(phosphine oxide) L^2 crystallizes as monohydrate similarly to the earlier presented data [20], whereas compound L^1 crystallizes with a THF molecule. The XRD data show that molecule L^1 in the crystal of L^1·THF adopts the planar *s-trans* conformation (with the C=C–C=C angle equal to 162.6(3)°) (Fig. 5), whereas L^2 in L^2·H_2O [20] takes the *gauche s-cis* conformation with the turning angle between the unsaturated fragments $-C=C(CH_3)_2$ equal to 86.5(2)°.

Table 2. Distribution coefficients of U(VI) and Th(IV) for their extraction from a 3 M HNO$_3$ solution with 0.001 M solutions of L^1, L^2, and L^5 in dichloroethane

Extracting agent	$\log D_{Th}$	$\log D_U$	$\beta_{Th/U}$
L^1	1.64	0.78	7.2
L^2	1.42	2.62	0.06
L^5	1.75	−0.04	61.6

A violation of complanarity of the alkadiene fragment for compound L^2 is probably induced by steric interactions between the terminal methyl groups with the bis(phosphine oxide) fragments. The coplanarity of the 1,3-alkadiene fragment in L^1 favors the charge density delocalization along this chain, which results in some elongation of the C=C bonds (Table 2). In addition, the bonds of the phosphoryl group P=O and the bonds of phosphorus with the 1,3-alkadiene skeleton P–C are elongated in L^1 compared to L^2.

UV spectroscopy was used to establish the conformational compositions of compounds L^1 and L^2 in the liquid phase. It is known that electron spectroscopy is widely used to determine the conformational composition of flexible molecules of the 1,3-alkadiene type [27]. In particular, it was found that the violation of conjugation between the vinyl fragments of the carbon skeleton and the formation of the *gauche s-cis* conformation are accompanied by an appreciable decrease in the absorption band intensity in the UV spectra. This effect was demonstrated for organophosphorus 1,3-alkadienes [28]. Using this approach, we succeeded to show that the UV spectra of compounds L^1 and L^2 detected in solutions differ strongly. The intensity of the band at 220 nm for compound L^1 is nearly 1.5 times higher than that for compound L^2 (Fig. 6). Thus, it can be asserted with a high probability that the conformational compositions of bis(phosphine oxides) L^1 and L^2 in the solid phase and solution are identical.

The coordination properties of bis(phosphine oxides) L^1 and L^2 were studied for their reactions with UO$_2$(NO$_3$)$_2$·6H$_2$O (Scheme 2). Uranyl complexes **I** and **II** were synthesized using CH$_3$CN as the solvent for ligand L^1 and DMF for ligand L^2.
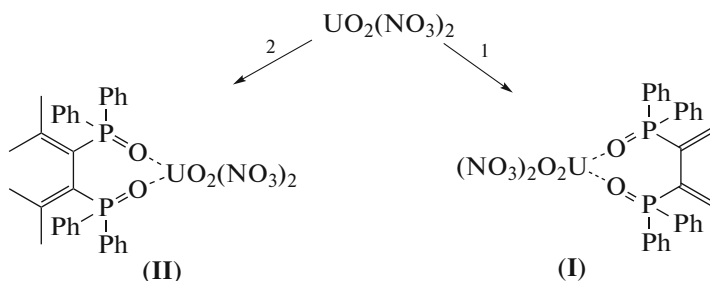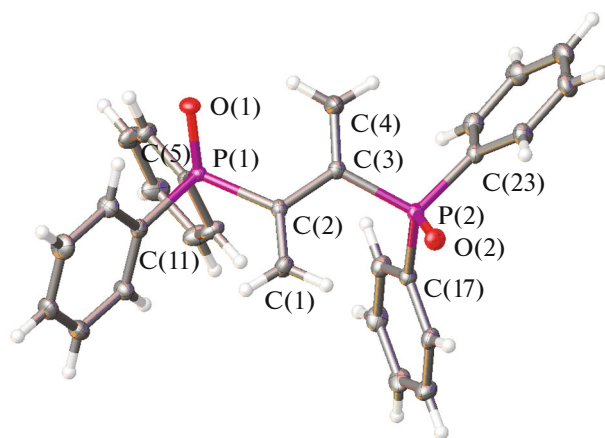
Scheme 2.

Fig. 5. Molecular structure of ligand L^1 in representation of atoms by thermal ellipsoids ($p = 50\%$).
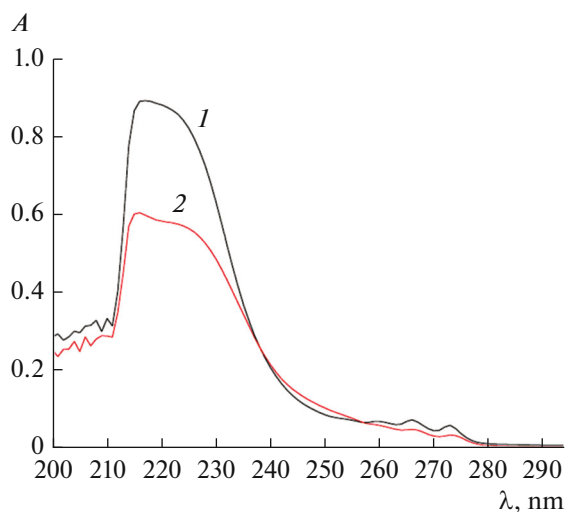
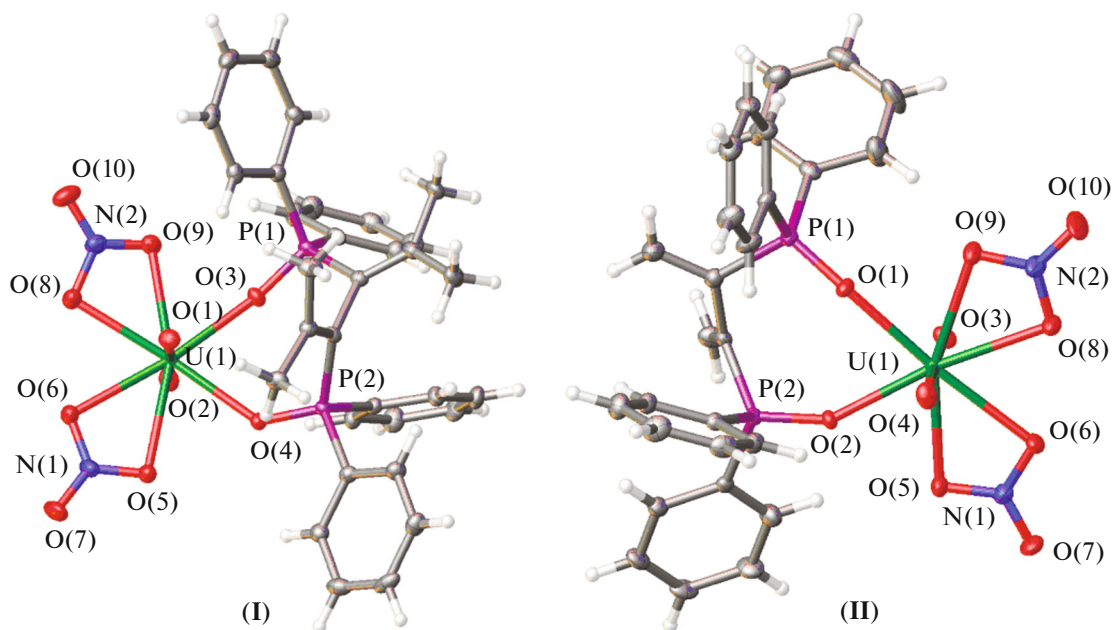**Fig. 6.** UV spectra of (*1*) L^1 and (*2*) L^2.

Fig. 7. Molecular structures of compounds **I** and **II** in representation of atoms by thermal ellipsoids (p = 50%).

Ligands L^1 and L^2 form uranyl complexes in the ratio UO_2 : L = 1 : 1, which was found by XRD of single crystals of complexes **I** and **II**. The molecular structures of the complexes are shown in Fig. 7. The coordination polyhedra U(VI)O_8 are hexagonal bipyramids with the oxygen atoms of uranyl in the axial positions and six oxygen atoms in the equatorial positions. The uranyl groups in complexes **I** and **II** are nearly linear (177.2(1)° and 178.2(1)°, Table 3).

The U(VI)−OP=O bonds are shorter than the U(VI)−O(N) bonds. The bond lengths in bis(phosphine oxides) L^3 and L^4 are close to the bonds in the starting ligand $L^2·H_2O$ [20]. The similarity of the con-

formations of the ligands for L^2, **I**, and **II** compared to L^1 is shown in Fig. 8.

As follows from Fig. 8, the configurations of the ligand in complexes **I** and **II** are very close to each other due to the rigidity of the seven-membered metallocycle, which assumes rotation only along the P−CPh bonds. The conformations of free phosphine oxide in $L^2·H_2O$ [20] and in complex **II** are also close to each other on the whole, except for the turn of one $Ph_2P=O$ fragment along the P−C_{diene} bond at the angle about 120°. At the same time, the configuration of molecule L^1 in $L^1·THF$ differs considerably from the configuration in L^3 because of the unusual torsion angles C=C−P=O. Thus, the *s-trans* conformation of

Table 3. Selected interatomic distances (Å) in the structures of compounds L^1, L^2, **I**, and **II**

| Parameter	L^1	L^2 [20]	**I**	**II**	$[Mn(L^1)_3][MBr_4]$ [29]	$[Mn(L^1)_3][M(SCN)_4]$ [30]
			U(VI)		Mn(II)	
U(VI)=O			1.750(2)−1.768(2)	1.768(2)−1.769(2)		
M−O$_{P=O}$			2.356(2)−2.371(2)	2.334(2)−2.367(2)	2.140(3)−2.154(3)	2.131(2)−2.168(2)
M−O$_{NO_3}$			2.515(2)−2.540(2)	2.513(2)−2.546(2)		
P=O	1.489(2)−1.494(2)	1.475(1)−1.479(1)	1.503(2)−1.505(2)	1.509(2)−1.517(2)	1.486(3)−1.493(3)	1.483(2)−1.488(2)
P−C$_{diene}$	1.828(2)−1.834(2)	1.803(2)−1.806(2)	1.810(3)− 1.812(3)	1.812(3)−1.814(3)	1.804(3)−1.811(4)	1.801(3)−1.818(4)
P−C$_{Ph}$	1.801(3)−1.812(2)	1.788(2)−1.796(2)	1.787(3)−1.796(3)	1.792(3)−1.808(3)	1.794(4)−1.811(5)	1.785(3)−1.803(3)
C=C	1.341(3)−1.350(3)	1.333(2)−1.338(2)	1.333(4)−1.336(4)	1.344(4)−1.347(4)	1.307(5)−1.326(6)	1.309(5)−1.323(5)
C$_{diene}$−C$_{diene}$	1.489(3)	1.494(3)	1.490(4)	1.515(4)	1.499(6)−1.511(6)	1.496(5)−1.500(6)
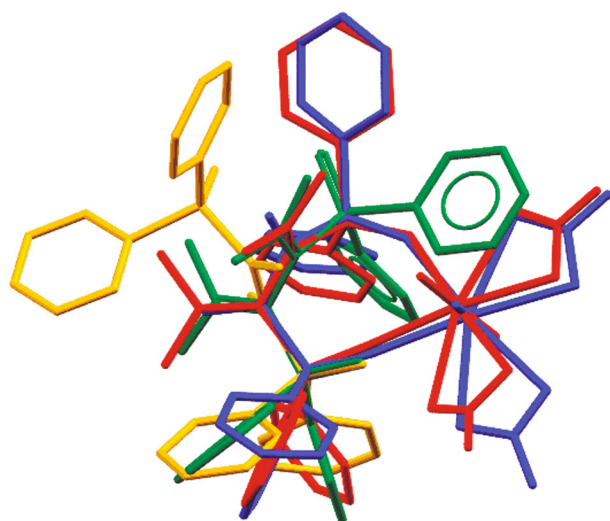
Fig. 8. Comparison of conformations of the ligands in the crystals of compounds (orange) $L^1 \cdot$THF, (green) $L^2 \cdot H_2O$ [20], (blue) **I**, and (red) **II**. The atoms of the P=O groups are superimposed. Hydrogen atoms are omitted.

ligand L^1 can be a reason for its decreased extraction ability to f elements compared to its alkyl-substituted analogs, in particular, ligand L^2.

Another possibility of different behaviors of ligands L^1 and L^2 during extraction can be related to different compositions of the atoms that form the molecular surface and, as a consequence, affecting the solubility of the substance in hydrophobic solvents. The surfaces of the molecular Voronoi polyhedra formed by all regions of the crystal, which are closer to this molecule than to the molecules (or ions) of the environment, provide a convenient approximation that makes it possible to estimate the contributions from diverse atoms to the surface area of the molecular surface and their participation in various intermolecular contacts [31]. This representation of molecules in crystal makes it possible to successfully analyze specific features of packing and intermolecular interactions in polymorphs [31−33], conformationally flexible molecules [33, 34], and homological series of compounds [35]. In particular, it has previously been found that an increase in the contribution of hydrophobic H...H contacts and C...H contacts to the total molecular surface area of monocarboxylic acids is accompanied by an increase in their ability to form polynuclear complexes with double uranium(VI) salts [35]. In the cases of $L^1 \cdot$THF and $L^2 \cdot H_2O$, the surface area of the Voronoi molecule, which corresponds to hydrophobic interactions C...C, C−H...C, and C−H...H−C, is equal to 460 and 506 Å^2 (or 87.5 and 91.7% of the total surface area of the molecule). In complexes **I** and **II**, the partial contribution of the hydrophobic interactions to the surface area of the molecule is 52.9 and 59.6% (327 and 387 Å^2). Thus, as should be expected,

alkyl-substituted dienes and their complexes should have a large molecular surface area capable of forming hydrophobic interactions.

The extraction and coordination properties of 2,3-bis(diphenylphosphinyl)buta-1,3-diene (L^1) and 3,4-bis(diphenylphosphinyl)-2,5-dimethylhexa-2,4-diene (L^2) were studied in this work. Compound L^1 was found by XRD and electron spectroscopy to have a predominantly planar *s-cis* conformation. The introduction of additional substituents as methyl groups (compound L^2) into the 1,3-butafiene fragment leads to a *gauche s-cis* conformation with the turning angle between the unsaturated fragments C=C(CH$_3$)$_2$ equal to 86.5(2)°. A similar conformation of the ligands was determined for uranyl complexes **I** and **II**. The study of the extraction properties of bis(phosphine oxides) L^1 and L^2 revealed a significant efficiency of extracting agent L^2 compared to compound L^1 for the extraction of microquantities of U(VI) from HNO$_3$ solutions. Probably, this can be explained by an enhanced hydrophobicity of bis(phosphine oxide) L^2 and uranyl complex **II** and a more favorable conformation of ligand L^2 for the formation of a complex with U(VI).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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