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Uranium complexes of cyclic *O,O*-bidentate ligands with the P–N–P backbone

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ABSTRACT

The formation of uranium complexes of novel ligands belonging to phosphorylated 2-oxo-1,2-azaphospholane series, namely 2-ethoxy-1-diethoxyphosphoryl-2-oxo-1,2λ^5-azaphospholane (**1a**) and both individual *R**,*R**- and *R**,*S**-diastereomers of the related 2-oxo-2-phenyl-1,2λ^5-azaphospholanes **1b**,**c** with different surrounding at the exocyclic phosphorus atom, has been studied. The structures of the complexes of ML composition obtained in the reaction with uranyl nitrate in 1:1 ratio were found to depend on the difference in donor properties of the oxygen atom of endo- and exocyclic phosphoryl groups. The ligand **1a** possessing the greater difference, serves as *O*-monodentate one with metal–oxygen bonding via the endocyclic P═O function while both isomers of **1b**,**c** coordinate to uranyl cation in a *O,O*-bidentate fashion. In solutions the ML complexes reacted with air oxygen to afford (μ_2-peroxo)-bridged uranium complexes [{UO_2(L)NO_3}$_2$(μ_2-O_2)] which structures were confirmed by X-ray crystallography data.

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1. Introduction

The rapid development of coordination chemistry of f-elements, i.e., lanthanides and actinides, is connected with complementary fundamental and applied investigations and it is difficult to say in which particular area – coordination chemistry or material science – the most impressed results were achieved. The complexes of f-elements attract considerable attention due to their unique luminescent and magnetic properties defining their relevance to luminescent systems with long lifetimes, photostability, and line-like emission bands [1], diagnostic tools in biological sciences, e.g., markers for immunofluorescent assays or paramagnetic contrast agents in magnetic resonance imaging [1c,f,2], second-order nonlinear optical (NLO) chromophores [3] as well as practical reprocessing of nuclear wastes [4].

Due to the highly oxophylic nature of f-elements they interact strongly with phosphoryl donors forming stable complexes and various monodentate and bidentate organophosphorus compounds found application for extraction and separation of these elements [5]. Among the bidentate ligands, imidodiphosphorus derivatives, bearing flexible (X)P–N–P(Y) skeleton and displaying a broad diversity of coordination pattern in neutral or deprotonated form with a variety of metals, are of undoubted interest due to potential industrial uses in metal extraction or application of the complexes as catalytic systems, new luminescent materials for photonic devices and sensors, NMR shift reagents for carboxylic acids, phenols and carboxylates or even biologically active compounds [6]. It is worth noting that all metal complexes formed by the above mentioned P–N–P ligands were derived from the linear compounds whereas the cyclic ones are advantageous for selectivity over the complex formation owing to increased rigidity and modification in the electronic effects and may provide the other coordination pattern [7]. Recently, we have developed the facile and general cascade synthesis of phosphoryl substituted 2-oxo-1,2-azaphospholanes, i.e., the first cyclic ligand systems with the P–N–P backbone [8]. In order to understand the impact of adding the cyclic skeleton to the ligand backbone which provides one endocyclic and one exocyclic phosphorus atoms differing in electronic and steric properties, it seems reasonable to estimate and compare the coordination behavior of these cyclic ligands with that for the known acyclic analogs.

In the present study, we report the complexing features of two recently developed ligands [8] and a new one belonging to the above family of the cyclic P–N–P ligands towards uranyl cation, i.e., UO_2^{2+}, known to be the most stable form of uranium existing in the liquid acidic radioactive wastes [9]. Noteworthy, in the case of the ligands with chiral phosphorus atoms pure diastereomers were used. The choice of uranium as a metal was dictated by a few basic motives, namely, a desire to explore the fundamental aspects of 5f-elements reactivity and coordination behavior, understand the bonding interactions between the metal center and the particular ligand as well as the fact that a number of uranium-containing complexes possess optical [10] and magnetic [11] properties and have been shown to be useful in such applications as

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catalysis, anion and neutral molecule sensing, and small molecule activation [12].

2. Experimental

2.1. Materials and methods

The NMR spectra were recorded on a Bruker AMX-400 instrument in $CDCl_3$, CD_3CN, and CD_3NO_2 solutions. The chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^1H and ^{13}C) or externally to H_3PO_4 (^{31}P). The ^{13}C NMR spectra were registered using the *J*MODECHO 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 or nujol). Melting points were determined with an Electrothermal IA9100 Digital Melting Point Apparatus and were uncorrected. Ph(EtO)PCl was obtained via the known procedure [13], other reagents were used as purchased without further purification (Acros).

2.2. Synthesis of the ligands

The known 2-oxo-2-phenyl-1,2-azaphospholanes **1a**,**b** were obtained via the reported procedure developed by us recently [8].

2.2.1. 1-[Methyl(phenyl)phosphoryl]-2-oxo-2-phenyl-1,2λ^5-azaphospholane (**1c**)

A solution of Ph(EtO)PCl (7.6 g, 40 mmol) in benzene–$CHCl_3$ (2:1, 30 mL) mixture was added dropwise to a stirred suspension of $HBr{\cdot}NH_2(CH_2)_3Br$ (4.6 g, 21 mmol) and Et_3N (6.4 g, 63 mmol) in the same mixed solvent (60 mL) at 0–2 °C. The reaction mixture was refluxed for 1 h and cooled to ambient conditions. Then MeI (8.9 g, 63 mmol) was added and the mixture was gently refluxed for 2 h. On cooling, hexane (60 mL) was added and the mixture was kept overnight. The precipitate of $Et_3N{\cdot}HHal$ was filtered off and the solvent was removed *in vacuo*. The residue was purified by column chromatography (silica gel, $CHCl_3$–MeOH, gradient elution from 100:1 to 100:10) to give the individual *R**,*S**- and *R**,*R**-diastereomers as colorless thick oils. Both isomers crystallized on treatment with Et_2O. Total yield: 2.5 g (50%). *Anal.* Calc. for $C_{16}H_{19}NO_2P_2$: C, 60.19; H, 5.96; N, 4.39; P, 19.44. Found: C, 59.97; H, 5.96; N, 4.45; P, 19.09%.

2.2.1.1. Data for (R,S*)-**1c**.* Mp 129.5–131.0 °C (diethyl ether). IR (KBr): ν = 3055, 2858, 1440, 1219 (P═O), 1198 (P═O), 1120, 1060, 1032, 1023, 1006, 983. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.54 (d, $^2J_{PH}$ = 14.4 Hz, 3H, CH_3), 2.00–2.30 (m, 4H, PCH_2CH_2), 3.22–3.36, 3.58–3.73 (2 m, 1H + 1H, NCH_2), 7.49–7.63, 7.92–8.06 (2 m, 10H, 2 × C_6H_5). ^1H NMR (400 MHz, CD_3NO_2): δ = 1.92 (d, $^2J_{PH}$ = 14.4 Hz, 3H, CH_3), 2.47–2.76 (m, 4H, PCH_2CH_2), 3.66–3.79, 3.87–4.02 (2 m, 1H + 1H, NCH_2), 7.90–8.10, 8.23–8.37 (2 m, 10H, 2 × C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.3 (d, $^1J_{PC}$ = 87.0 Hz, CH_3), 21.9 (d, $^2J_{PC}$ = 7.3 Hz, PCH_2CH_2), 29.4 (dd, $^1J_{PC}$ = 80.0 Hz, $^3J_{PC}$ = 3.7 Hz, PCH_2), 47.5 (dd, $^2J_{PC}$ = 13.9 Hz, $^2J_{PC}$ = 2.2 Hz, NCH_2), 128.5 (d, $^3J_{PC}$ = 13.2 Hz, C_m), 128.8 (d, $^3J_{PC}$ = 13.2 Hz, C_m), 131.3 (d, $^2J_{PC}$ = 10.6 Hz, C_o), 131.5 (d, $^2J_{PC}$ = 10.5 Hz, C_o), 131.6 (d, $^1J_{PC}$ = 124.0 Hz, C_i), 131.8 (d, $^4J_{PC}$ = 2.9 Hz, C_p), 132.4 (d, $^4J_{PC}$ = 2.9 Hz, C_p), 132.8 (d, $^1J_{PC}$ = 121.0 Hz, C_i). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.9 (s), 48.0 (s). ^{31}P NMR (162 MHz, CD_3NO_2): δ = 30.6 (d, $^2J_{PP}$ = 5.2 Hz), 48.2 (d, $^2J_{PP}$ = 5.1 Hz).

2.2.1.2. Data for (R,R*)-**1c**.* Mp 125.5–127.5 °C (diethyl ether). IR (KBr): ν = 3057, 2970, 1589, 1444, 1437, 1215 (P═O), 1200 (P═O), 1117, 1071, 1020, 1005, 990, 906. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.93 (d, $^2J_{PH}$ = 18.9 Hz, 3H, CH_3), 2.04–2.54 (m, 4H, PCH_2CH_2), 3.53–3.68, 3.90–4.05 (2 m, 1H + 1H, NCH_2), 7.19–7.66 (m, 10H, 2 × C_6H_5). ^1H NMR (400 MHz, CD_3NO_2): δ = 2.11 (d, $^2J_{PH}$ = 14.2 Hz, 3H, CH_3), 2.50–2.75 (m, 4H, PCH_2CH_2), 3.65–3.75, 4.00–4.11 (2 m, 1H + 1H, NCH_2), 7.60–7.88, 7.89–7.97, 7.98–8.08, 8.14–8.25 (4 m, 10H, 2 × C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.6 (d, $^1J_{PC}$ = 89.5 Hz, CH_3), 22.4 (d, $^2J_{PC}$ = 7.0 Hz, PCH_2CH_2), 29.4 (dd, $^1J_{PC}$ = 88.4 Hz, $^3J_{PC}$ = 3.3 Hz, PCH_2), 47.5 (d, $^2J_{PC}$ = 13.9 Hz, NCH_2), 127.8 (d, $^3J_{PC}$ = 13.1 Hz, C_m), 128.1 (d, $^3J_{PC}$ = 13.1 Hz, C_m), 129.9 (C_i), 130.9 (d, $^2J_{PC}$ = 10.6 Hz, C_o), 131.2 (d, $^2J_{PC}$ = 10.6 Hz, C_o), 131.7 (d, $^4J_{PC}$ = 2.9 Hz, C_p), 131.8 (d, $^4J_{PC}$ = 2.9 Hz, C_p), 132.2 (d, $^1J_{PC}$ = 122.5 Hz, C_i). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.7 (d, $^2J_{PP}$ = 5.8 Hz), 45.9 (d, $^2J_{PP}$ = 4.4 Hz). ^{31}P NMR (162 MHz, CD_3NO_2): δ = 31.5 (d, $^2J_{PP}$ = 3.7 Hz), 47.5 (d, $^2J_{PP}$ = 3.7 Hz).

2.3. Synthesis of complexes

2.3.1. [UO_2(**1a**)$(NO_3)_2$](**2**)

A solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (0.260 g, 0.517 mmol) in ethanol (3 mL) was added dropwise to a solution of the ligand **1a** (0.184 g, 0.646 mmol) in the same solvent (2 mL) at 20 °C. In 3 h at 20 °C, the mixture was concentrated to *ca.*1 mL *in vacuo* and then diethyl ether (2 mL) was added and the mixture was kept overnight at 20 °C. The precipitated yellow solid product was filtered off, washed with diethyl ether and dried *in vacuo*. Yield: 0.220 g (63%). Mp 135.5–142.5 °C (ethanol-diethyl ether). *Anal.* Calc. for $C_9H_{21}N_3O_{13}P_2U$: C, 15.90; H, 3.09; N, 6.18; P, 9.13. Found: C, 15.94; H, 2.95; N, 5.76; P, 9.17%. IR (nujol): ν = 2998, 2937, 1530, 1480, 1280, 1273 (P═O), 1178 (P═O), 1158, 1041, 1028, 992, 932 (UO_2), 811. ^1H NMR (400 MHz, CD_3CN): δ = 1.19 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3), 1.22 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3), 1.56 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3), 2.30–2.60 (m, 4H, PCH_2CH_2), 3.58–3.75 (m, 2H, NCH_2), 4.15–4.38 (m, 4H, OCH_2), 4.55 (q, $^3J_{HH}$ = 6.7 Hz, 2H, OCH_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 1.80 (d, $^2J_{PP}$ = 16.1 Hz), 56.0 (br. s).

2.3.2. [{UO_2(**1a**)(NO_3)}$_2$(μ_2-O_2)](**3**)

A solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (0.200 g, 0.400 mmol) in ethanol (3.5 mL) was added dropwise to a solution of the ligand **1a** (0.114 g, 0.400 mmol) in the same solvent (3 mL) at 20 °C. In 3 days, the resulting yellow crystals of **3** were filtered off, washed with ethanol and dried *in vacuo*. Yield: 0.042 g (17%). *Anal.* Calc. for $C_{18}H_{42}N_4O_{22}P_4U_2$: C, 17.06; H, 3.32; N, 4.42; P 9.79. Found: C, 17.12; H, 3.30; N, 4.37; P, 9.81%. IR (nujol): ν = 1495, 1293, 1272,1218(P═O), 1191, 1174(P═O), 1159, 1033, 995, 918(UO_2), 906, 816, 744.^1H NMR (400 MHz, $CDCl_3$): δ = 1.23–1.36 (m, 3H, CH_3), 1.60–1.72 (m, 7H, 6H 2 × CH_3 + 1H PCH_2CH_2), 1.80–1.97 (m, 1H, PCH_2CH_2), 1.97–2.14, 2.16–2.34 (2m, 1H + 1H, PCH_2), 3.47–3.78 (m, 2H, NCH_2), 4.61 - 4.90 (m, 6H, 3 × OCH_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 6.30–7.00 (m), 58.6 (d, $^2J_{PP}$ = 10.0 Hz), 58.9 (d, $^2J_{PP}$ = 10.0 Hz), 59.0 (d, $^2J_{PP}$ = 9,8 Hz).

2.3.3. [UO_2(**L**)$(NO_3)_2$](**4**,**5**) (general procedure)

A solution of $UO_2(NO_3)_2{\cdot}6H_2O$ (0.32 mmol) in ethanol (3 mL) was added dropwise to a solution of a single diastereomer of the corresponding ligand (**1b**,**c**, 0.32 mmol) in ethanol (2 mL) at 20 °C. In one day (**1b**) or 1 h (**1c**), the resulting precipitate was collected by filtration, washed with diethyl ether, and dried *in vacuo*.

2.3.3.1. Data for [UO_2{(R,S*)-**1b**}$(NO_3)_2$] ((R*,S*)-**4**).* Yellow solid; yield: 0.174 g (73%). *Anal.* Calc. for $C_{17}H_{21}N_3O_{11}P_2U$: C, 27.46; H, 2.83; N, 5.65; P, 8.34. Found: C, 27.39; H, 2.81; N, 5.59; P, 8.27%. IR (nujol): ν = 3065, 2995, 1524, 1440, 1284, 1165 (P═O), 1145 (P═O), 1117, 1037, 1025, 1007, 935 (UO_2). ^1H NMR (400 MHz, CD_3CN): δ = 1.25 (t, $^3J_{HH}$ = 6.9 Hz, 3H, CH_3), 2.40–2.62 (m, 2H, PCH_2CH_2), 2.64–2.82, 2.87–3.08 (2 m, 1H + 1H, PCH_2), 3.70–3.90, 4.00–4.16 (2 m, 1H + 1H, NCH_2), 4.27 (q, $^3J_{HH}$ = 7.6 Hz, 2H, OCH_2),

7.28–7.40, 7.53–7.64, 7.68–7.85 (3 m, 10H, 2 × C_6H_5). ^{31}P NMR (162 MHz, CD_3CN): δ = 23.4 (s), 66.8 (s).

*2.3.3.2. Data for [UO_2{(R^*,R^*)-**1b**}$(NO_3)_2$] ((R^*,R^*)-**4**).* Bright yellow crystalline solid; yield: 0.173 g (73%). *Anal.* Calc. for $C_{17}H_{21}N_3O_{11}P_2U$: C, 27.46; H, 2.83; N, 5.65; P, 8.34. Found: C, 27.61; H, 2.93; N, 5.46; P, 8.32%. IR (nujol): ν = 3064, 2685, 1593, 1522, 1493, 1442, 1288, 1264, 1161 (P═O), 1146 (P═O), 1129, 1114, 1031, 1019, 998, 987, 938 (UO_2). ^1H NMR (400 MHz, CD_3NO_2): δ = 1.71 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 2.63–2.82 (m, 2H, PCH_2CH_2), 3.02–3.18, 3.16–3.35 (2 m, 1H + 1H, PCH_2), 3.76–3.88, 4.11–4.25 (2 m, 1H + 1H, NCH_2), 4.60–4.75 (m, 2H, OCH_2), 7.68–7.84, 7.85–8.00, 8.15–8.26, 8.35–8.45 (4 m, 10H, 2 × C_6H_5). ^{31}P NMR (162 MHz, CD_3NO_2): δ = 25.7 (s), 68.3 (s).

*2.3.3.3. Data for [UO_2{(R^*,S^*)-**1c**}$(NO_3)_2$] ((R^*,S^*)-**5**).* Bright yellow crystalline solid; yield: 0.180 g (81%). *Anal.* Calc. for $C_{16}H_{19}N_3O_{10}P_2U$: C, 26.93; H, 2.66; N, 5.89; P, 8.70. Found: C, 26.84; H, 2.85; N, 5.97; P, 8.62%. IR (nujol): ν = 3063, 2918, 1592, 1521, 1439, 1281, 1143 (P═O), 1111 (P═O), 1050, 1035, 1026, 989, 933 (UO_2), 892. ^1H NMR (400 MHz, CD_3NO_2): δ = 2.58 (d, $^2J_{PH}$ = 13.2 Hz, 3H, CH_3), 2.68–3.40 (m, 4H, PCH_2CH_2), 4.10–4.28, 4.29–4.44 (2m, 1H + 1H, NCH_2), 7.48–7.65, 7.66–7.86, 7.87–7.97, 7.98–8.20 (4 m, 10H, 2 × C_6H_5). ^{31}P NMR (162 MHz, CD_3CN): δ = 53.2, (s), 66.0 (s).

*2.3.3.4. Data for [UO_2{(R^*,R^*)-**1c**}$(NO_3)_2$] ((R^*,R^*)-**5**).* Yellow solid; yield: 0.150 g (66%). *Anal.* Calc. for $C_{16}H_{19}N_3O_{10}P_2U$: C, 26.93; H, 2.66; N, 5.89; P, 8.70. Found: C, 26.93; H, 2.65; N, 5.65; P, 8.66%. IR (nujol): ν = 3061, 2919, 1592, 1522, 1490, 1440, 1289, 1265, 1147 (P═O), 1109 (P═O), 1053, 1031, 1024, 986, 937 (UO_2). ^1H NMR (400 MHz, CD_3NO_2): δ = 2.60–2.86 (m, 2H, PCH_2CH_2), 2.73 (d, $^2J_{PH}$ = 14.3 Hz, 3H, CH_3), 3.00–3.13, 3.14–3.31 (2m, 1H + 1H, PCH_2), 3.68–3.83, 3.99–4.15 (2m, 1H + 1H, NCH_2), 7.70–7.86, 7.87–8.02, 8.13–8.27, 8.30–8.46 (4m, 10H, 2 × C_6H_5). ^{31}P NMR (162 MHz, CD_3NO_2): δ = 54.1 (s), 67.3 (s).

2.4. X-ray crystallography

Single crystals of the compounds (R^*,S^*)-**1c** and **6** were grown by crystallization from benzene and acetonitrile, respectively. The suitable for X-ray study crystal of **3** (head-to-tail form) was obtained by sublimation from chloroform solution. All diffraction data for **3** and **6** were collected on a Bruker SMART APEX II CCD diffractometer [λ(Mo Kα) = 0.71072 Å, ω-scans] at 100 K, those for (R^*,S^*)-**1c** on a Bruker SMART 1000 CCD diffractometer [λ(Mo Kα) = 0.71072 Å, ω-scans] at 120 K. The substantial redundancy in data allows the empirical absorption correction to be made with the SADABS program [14] using multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F_2 in the anisotropic-isotropic approximation. All calculations were performed with the SHELXTL software package [15]. Crystal data and structure refinement parameters are listed in Table 1.

Table 1
Crystal data and structure refinement parameters for (R^*,S^*)-**1c**, **3**, and **6**.

	(R^*,S^*)-**1c**	**3**	**6**
Empirical formula	$C_{19}H_{22}NO_2P_2$	$C_{20}H_{44}Cl_6N_4O_{22}P_4U_2$	$C_{36}H_{44}N_6O_{16}P_4U_2$
Formula weight	358.32	1505.23	1416.71
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Z	2	2	2
a (Å)	8.9423(10)	9.5495(9)	11.9708(14)
b (Å)	10.2986(12)	13.6464(13)	10.5641(12)
c (Å)	11.5088(13)	17.5531(17)	18.365(2)
α (°)	91.806(2)	–	–
β (°)	108.893(3)	99.598(2)	103.647(2)
γ (°)	111.072(2)	–	–
V (Å^3)	922.49(18)	2255.4(4)	2256.9(5)
D_{calc} (g cm^{-1})	1.290	2.216	2.085
Linear absorption, μ (cm^{-1})	2.46	77.47	73.83
F(0 0 0)	378	1428	1348
$2\theta_{max}$ (°)	54	58	54
Reflections measured	8559	21 672	18 355
Independent reflections	3995	5992	4895
Observed reflections [with $I > 2\sigma(I)$]	3221	4558	3922
Parameters	218	298	291
R_1	0.0468	0.0349	0.0587
wR_2	0.1168	0.0916	0.1611
Goodness-of-fit	1.006	1.009	1.145
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.518/−0.378	1.825/−1.107	4.446/−2.016

3. Results and discussion

3.1. Synthesis of the cyclic ligands with the P–N–P backbone **1a–c**

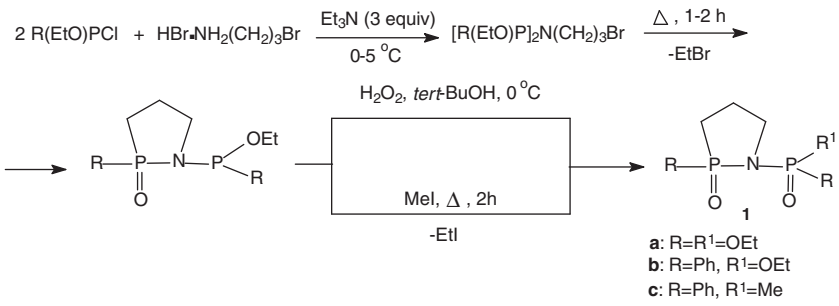
The cyclic *O,O*-bidentate ligands with the P–N–P backbone used in this investigation represent 1-phosphorylated 2-oxo-1,2-azaphospholanes. The recently developed synthetic approach to the first representatives of this family of compounds, i.e., **1a**,**b** [8], was based on the intramolecular Arbuzov reaction of the *N,N*-bis-P(III)-substituted 3-bromopropylamines generated *in situ* from phosphorus(III) acid chlorides, followed by oxidation of the intermediate cyclic P(III)-species. The related ligand **1c** was first obtained in the present study by modification of the above-mentioned one-pot procedure where the intermolecular Arbuzov reaction under the action of methyl iodide was used at the last synthetic step (Scheme 1).

Similar to the ligand **1b** [8], two diastereomers of **1c** were separated by column chromatography and characterized by IR and multinuclear NMR spectroscopy. The structure of one of the diastereomers of **1c** that demonstrated the upfield chemical shift for the exocyclic phosphorus atom and low-field signal for the endocyclic one was determined by a single crystal X-ray diffraction study. According to these data, the isomer crystallizing as a crystallosolvate with benzene molecule possesses the opposite configuration of the chiral centers, i.e., (R^*,S^*)-**1c** (Fig. 1). In a crystal, the molecules of this ligand, which lack any convenient proton donor, are hold together by a number of weak C–H···O, C–H···π, and H···H contacts; the smallest C···O and C···C distances being 3.374(3), 3.748(3), and 4.201(3) Å, respectively. The formation of the 3D framework is completed by C–H···O (C···O 3.273(3)–3.288(3) Å) and C–H···π (C...C 3.611(3) Å) interactions with the solvate benzene species.

Noteworthy, the comparison of X-ray data and the ^{31}P NMP spectra for individual diastereomers of **1b**,**c** allowed to conclude that the isomer of 1-phosphoryl-2-oxo-1,2λ^5-azaphospholane with the opposite configuration of chiral phosphorus atoms (R^*,S^*) demonstrates a downfield chemical shift of the endocyclic phosphorus atom in the ^{31}P NMR spectra in $CDCl_3$ solution and a smaller J_{PP} coupling constant as compared to that with the identical configuration of the P*-atoms (see Supplementary data, Table S1).

3.2. Complexes of cyclic *O,O*-bidentate ligands **1a–c** with uranylnitrate

Organophosphorus *O,O*-ligands such as methylene bisphosphine oxides [16], carbamoylmethylphosphine oxides [17], phosphorylated ureas [18], and acyclic ligands with the P–N–P



Scheme 1. One-pot synthesis of *N*-phosphoryl-2-oxo-1,2-azaphospholanes **1a**–**c**.

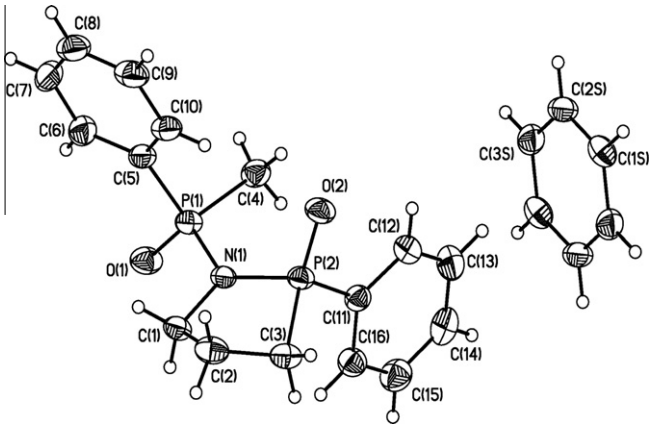
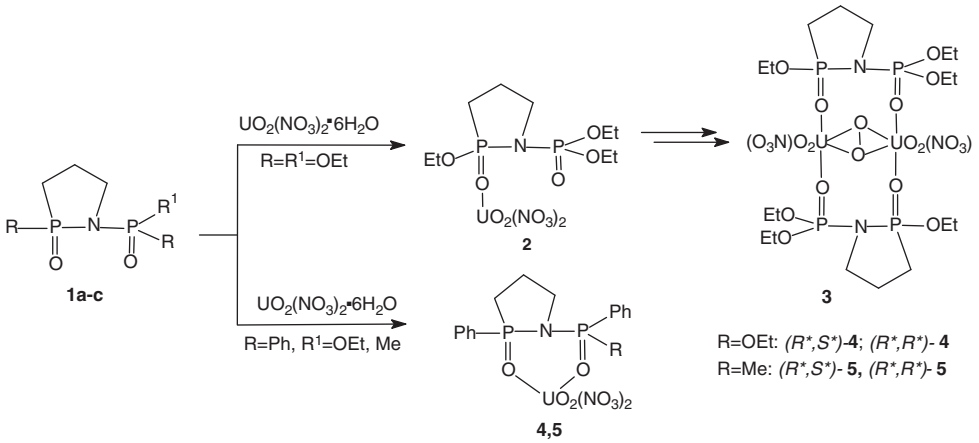


Fig. 1. General view of the (*R**,*S**)-**1c**·C_6H_6 in representation of atoms *via* thermal ellipsoids at 50% probability level.

backbone [19] are known to form uranium complexes via *O,O*-bidentate chelating fashion. It should be noted that according to the spectroscopic and structural studies, uranium coordinates the linear prototypes of 1-phosphoryl-2-oxo-1,2-azaphopholanes **1a**–**c** to afford chelate complexes of 1:1 composition independent from the bulkiness of the additional substituent at the nitrogen atom (methyl or isopropyl), counteranion in the starting uranium salt (perchlorate or nitrate), nature of the substituents at the phosphorus atoms in the ligand, and reaction conditions. The cyclic ligands **1a**–**c** also readily form complexes reacting with uranyl nitrate in 1:1 ratio in neutral solutions. In this case the coordination mode of the ligand and structure of the complexes were found to depend upon the ligand nature and the experimental conditions.

Therefore, the ligand **1a** bearing ethoxy groups at both phosphorus atoms, was found to form two different uranium complexes depending on the reaction time. In other words, if reaction mixture (EtOH) was worked-up in less than 3 h (see Section 2), only light yellow crystalline complex of ML composition $[UO_2(\mathbf{1a})(NO_3)_2]$ (**2**) was isolated in 63% yield (Scheme 2). At the same time, if the reaction mixture was kept for 3 d under ambient conditions and on exposure to air before the work-up, the other uranium complex **3**, $[\{UO_2(\mathbf{1a})NO_3\}_2(\mu_2\text{-}O_2)]$, was obtained (17% yield).

According to the IR and NMR spectroscopy data, in the complex **2** the ligand serves as the *O*-monodentate one with the phosphoryl-metal bonding *via* the endocyclic P═O group. Thus, the IR spectrum of the complex **2** demonstrated two strong absorption bands of P═O valence vibrations at 1273 and 1174 cm^{-1}, respectively. Compared with the corresponding data for the free ligand **1a** (ν(PO) 1273 and 1234 cm^{-1}), the first band remained unchanged upon complexation, while the second one is significantly shifted to a lower frequency. These data are consistent with the participation of only one phosphoryl moiety in the complex formation. Two broad intense bands at 1530 and 1280 cm^{-1} point to the presence of bidentate chelated nitrate groups [20]; in addition, the asymmetric uranyl stretching frequency appears at 932 cm^{-1}. In the $^{31}P\text{-}\{^1H\}$ spectrum of the complex **2**, which has revealed two signals at 1.80 ppm (d, J_{PP} = 16.1 Hz) and 56.0 ppm (br, s) assigned to the exo- and endocyclic phosphorus atoms, respectively, the signal of the latter one is downfield shifted (for *ca.* 10 ppm) relative to that in the free ligand. Moreover, in ^1H NMR spectrum of **2** the signals of cyclic CH_2 protons along with those of the ethoxy group at the endocyclic phosphorus atom also were downfield shifted compared to the corresponding signals in the free **1a**. It should be noted that ^{31}P NMR monitoring of the reaction of **1a** and uranyl nitrate in 1:1 ratio has revealed the formation of complex **2** in a few minutes after mixing of the reactants. The participation in coordination of



Scheme 2. Different uranium complexes formed by *N*-phosphoryl-2-oxo-1,2-azaphospholanes **1a**–**c**.

the endocyclic phosphoryl oxygen only can be explained by its higher donor properties compared with that of the related exocyclic functionality due to the presence of cyclic methylene group as a substituent at the *endo*-P atom.

Vice verse, the complex **3** possesses the (μ_2-peroxo)-bridged structure [{UO_2(**1a**)NO_3}$_2$ (μ_2-O_2)] with two fused eight-membered cycles and bridging *O,O*-bidentate coordination mode of the ligands to uranium (Scheme 2). The presence of two absorption bands due to coordinated P═O groups (at 1218 and 1174 cm^{-1}) in the IR spectrum of **3** explicitly confirm *O,O*-bidentate coordination mode for the ligand. The broad intense absorption bands at 1469 and 1293 cm^{-1} correspond to the vibrations of coordinated nitrate groups and antisymmetric uranyl vibration at 918 cm^{-1} is shifted to a lower frequency compared with the complex **2**. A medium-weak absorption band at 816 cm^{-1} may be assigned to the ν(O–O) peroxo vibration [21]. Furthermore, downfield chemical shifts in the ^{31}P-{^{1}H} NMR spectrum of **3** (unresolved multiplet in the range 6.30–7.00 ppm for the exo-P atom and three doublets in the range from 58 to 59 ppm for the endo one) indicate the coordination of the uranium with oxygen atoms of both P═O functions. Additionally, in the ^{1}H NMR spectrum of **3** the signals of the PCH_2, NCH_2, and all OCH_2 hydrogen atoms are downfield shifted compared to those in the free ligand due to coordination. Apparently, bonding of the ligand **1a** in complex **3** is realized via head-to-tail manner. In such a way, the three doublets for the endo-phosphorus atom in the ^{31}P NMR spectrum may be explained by the presence of two different conformers of the compound in solutions, i.e., two closely located doublets with spin coupling constants of *ca.*10 Hz are assigned to the conformer having non-equivalent endo-P atoms while the doublet with $^3J_{PP}$ 9.8 Hz – to the conformer possessing two equivalent ones. Finally, the proposed structure of head-to-tail form of **3** (being a crystallosolvate with chloroform, Fig. 2) was unambiguously confirmed by a single crystal X-ray diffraction analysis.

At the same time, the ligand nature also influenced on the result of the complexation. Thus, reaction of any diastereomer of **1b** or **1c** with uranyl nitrate in 1:1 ratio in EtOH solution resulted in the complexes ((*R**,*R**)-**4**, (*R**,*S**)-**4**, (*R**,*R**)-**5**, and (*R**,*S**)-**5**) of ML composition [UO_2(L)(NO_3)$_2$] which precipitated from ethanol solution as yellow solids in a day (*L* = (*R**,*R**)-**1b**, (*R**,*S**)-**1b**) or 0.5–1 h (*L* = (*R**,*R**)-**1c**, (*R**,*S**)-**1c**) (Scheme 2). Based on the significant coordination shift of P═O absorption bands ($\Delta\nu$(PO) = 68–79 and 55–91 cm^{-1} for the exo- and endo-phosphorus atoms, respectively) and typical asymmetric stretching frequency of the uranyl cation (933–938 cm^{-1}) in the IR spectra, downfield shifting both of the corresponding phosphorus resonances in the ^{31}P-{^{1}H} NMR spectra and signals of all hydrogen atoms in the ligand structure in the ^{1}H NMR spectra of isomeric complexes **4** and **5**, the bidentate chelating coordination mode of the ligands **1b**,**c** to uranium has been suggested in these cases (IR and ^{31}P NMR data for complexes are summarized in Tables S2 and S3, see Supplementary). Such difference in complexing behavior between the ligands **1a** and **1b**,**c** may be explained by increased donor properties of both oxygen atoms in the ligands **1b**,**c** as well as comparability of such properties for both coordinating P═O functions.

Finally, when the reaction of (*R**,*S**)-**1c** and uranyl nitrate was performed in acetonitrile, in which the above complex (*R**,*S**)-**5** was more soluble than in EtOH, in a few days the (μ_2-peroxo)-bridged uranium complex [{UO_2(*R**,*S**)-**1c**)NO_3}$_2$(μ_2-O_2)] (**6**) was isolated in trace quantities along with the major desired product. The structure of this peroxo uranium complex was elucidated by the X-ray diffraction analysis (Fig. 3).

Although the severe disorder of the peroxo and NO_3 groups in **3** does not allow analyzing its molecular geometry in detail, the mutual disposition of the constituting moieties can still be assessed. Thus, the UO_2U and NO_3 planes are not parallel, and the corresponding dihedral angle is *ca.* 40° (36.4(5)–38.4(5)°); the latter deviation from planarity, although being a rare case, was previously reported for several peroxo complexes of uranium [22]. In contrast, the O═U═O moiety in **3** is nearly perpendicular to the NO_3 plane (the angle they form is 83.7(5)–87.7(5)°) that is characteristic of such systems. The disposition of the envelope-shaped heterocycles (the C(2) atom deviates by 0.56(1) Å) of the two chelating ligands is a transoid one relative to the mean UO_2U plane. In a crystal, these complexes together with the solvate chloroform molecules are assembled into the 3D framework by a number of weak C–H···O, C–H···Cl, C–Cl···O, and H···H contacts.

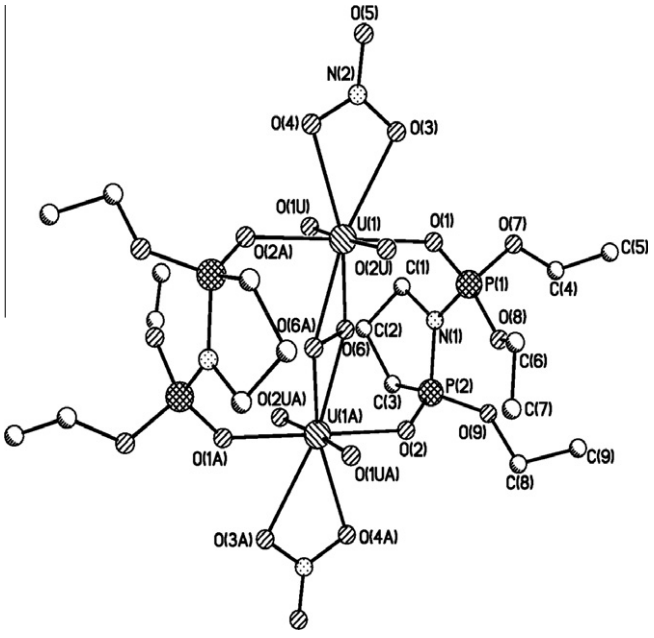


Fig. 2. General view of the complex **3**. Hydrogen atoms, atoms of the minor component of the disordered moieties, and solvate chloroform molecules are not shown. The atoms labeled with A are obtained from the basic ones by the symmetry operation $-x+1, -y+1, -z$.

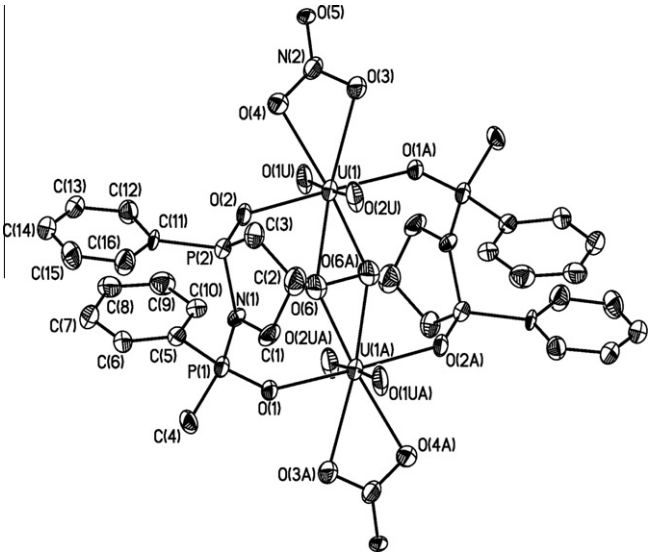


Fig. 3. General view of the complex **6** in representation of atoms *via* thermal ellipsoids at 50% probability level. Hydrogen atoms and solvate acetonitrile molecules are not shown. The atoms labeled with A are obtained from the basic ones by the symmetry operation $-x, -y, -z+1$.

The structure of complex **6** is somewhat similar to that of the complex **3**. In particular, the phosphorus heterocycles, which have the same envelope conformation with the C(2) atom deviating by 0.59(1) Å, are directed in opposite directions from the UO_2U plane. The latter moiety is characterized by the peroxo O(6)–O(6A) distance equal to 1.513(15) Å that is similar to those in its 2,2′-bipyridyl (1.483 Å) [23] and *N*,*N*′-ethylenebis(2-pyrrolidone) (1.468 Å) [22c] analogs. This UO_2U fragment is, however, in the same plane as the nitrate species with the O═U═O group being almost perpendicular with the corresponding angle of 85.2(7)°. Hence, the above deviation of $NO_3UO_2UNO_3$ from planarity in **3** can come out of its disorder. As in the crystal of **3**, the molecules of the complex **6** are hold together through a number of weak C–H···O and C–H···π contacts complemented by those of the C–H···N type with the solvate acetonitrile molecules, thus forming the 3D framework.

The peroxo-complexes of uranium including those containing organic ligands and reflecting the oxophility of the $(UO_2)^{2+}$ group are known from the literature. The targeted synthesis of these species is based on the direct reaction of intermediate U-complexes with hydrogen peroxide [24]. However, in some cases formation of the related peroxo-complexes (mostly in trace amounts) was also observed upon exposure of the reaction mixtures to atmospheric oxygen [21,22c,25] despite the detailed mechanism of dioxygen insertion is still unclear. Taking that into account, (μ_2-peroxo)-bridged complexes as **3** and **6** are also believed to form under the direct action of atmospheric molecular oxygen on soluble intermediate complexes similar to the previously reported examples. The difference in the yields of complexes **3** and **6** may be explained by the difference in the solubility of their precursors. In other words, the soluble monodentate complex **2** apparently can readily undergo dimerization to afford the corresponding complex M_2L_2 followed by oxygen insertion and elimination of nitrato groups. In the case of ligands **1b**,**c**, the similar reaction scheme, including dimerization of the corresponding *O*-monodentate complex and subsequent reaction of the dimer with O_2, seems also rather reasonable. Apparently, in the last cases the above *O*-monodentate species are formed in negligible amounts due to precipitation of *O*,*O*-bidentate complexes **4** and **5** from the reaction media, which, in turn, shifts the equilibrium position between *O*-mono- and *O*,*O*-bidentate complexes.

4. Conclusions

In contrast to the linear *O*,*O*-ligands with the P–N–P backbone forming with uranium exclusively complexes of 1:1 composition *via* bidentate chelate mode, their cyclic counterparts belonging to the phosphorylated 1,2-azaphospholane series were found to form complexes with uranyl nitrate *via* *O*-monodentate or *O*,*O*-bidentate coordination mode depending mostly on the ligand nature, to be more precise, on the donor properties of the oxygen atom of phosphoryl groups. Furthermore, in solutions *O*-monodentate complexes react with molecular oxygen to afford the third type of uranium complexes with (μ_2-peroxo) bridge, [{UO_2(L)NO_3}$_2$(μ_2-O_2)], which structures were confirmed by X-ray crystallography data.

Appendix A. Supplementary material

CCDC 804958, 804959, and 804957 contain the supplementary crystallographic data for complexes *R**,*S**-**1c**, **3** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.04.007.

References

[1] (a) D. Parker, R.S. Dickins, H. Puschmann, C. Crossland, J.A.K. Howard, Chem. Rev. 102 (2002) 1977;
(b) J.P. Cross, M. Lauz, P.D. Badger, S. Petoud, J. Am. Chem. Soc. 126 (2004) 16278;
(c) S. Faulkner, S.J.A. Pope, B.P. Burton-Pye, Appl. Spectr. Rev 40 (2005) 1;
(d) C.F. de Sa, O.L. Malta, C. de Mella Donega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. da Silva Jr., Coord. Chem. Rev. 196 (2000) 165;
(e) S. Yanagida, Y. Hasegawa, K. Murakoshi, Y. Wada, N. Nakashima, T. Yamanaka, Coord. Chem. Rev. 171 (1998) 46;
(f) J.-C.G. Bünzli, G.R. Choppin, Lanthanide Probes in Life, Chemical, and Earth Sciences: Theory and Practice, Elsevier, Amsterdam, 1989;
(g) E. Desurvire, Erbium-Doped Amplifiers. Principles and Applications, John Wiley & Sons, New York, 1994.

[2] (a) N. Hildebrandt, H.-G. Lohmannsroben, Curr. Chem. Biol. 1 (2007) 167;
(b) G. Pompidor, O. Marry, J. Vicat, R. Kahn, Acta Cryst. D66 (2010) 762.

[3] (a) C.E. Powell, M.G. Humphrey, Coord. Chem. Rev. 248 (2005) 725;
(b) E. Cariati, M. Pizzotti, D. Roberto, F. Tessore, R. Ugo, Coord. Chem. Rev. 250 (2006) 1210;
(c) M.G. Humphrey, M. Samoc, Adv. Organomet. Chem. 55 (2008) 61;
(d) A. Valore, E. Cariati, S. Righetto, D. Roberto, F. Tessore, R. Ugo, I.L. Fragala, M.E. Fragala, G. Malandrino, F. De Angelis, L. Belpassi, I. Ledoux-Rak, K.H. Thi, J. Zyss, J. Am. Chem. Soc. 132 (2010) 4966.

[4] (a) A.M. Rozen, B.V. Krupnov, Rus. Chem. Rev. 65 (1996) 973;
(b) E.P. Horwitz, W.W. Schulz, Metal ion separation and preconcentration: progress and opportunities, in: A.H. Bond, M.L. Dietz, R.D. Rogers (Eds.), ACS Symposium Series 712, American Chemical Society, Washington, D.C., 1999, pp. 20–50;
(c) S.M. Cornet, J. May, M.P. Redmond, C.A. Sharrad, O. Rosnel, Polyhedron 28 (2009) 363. and references cited therein.

[5] (a) E.P. Horwitz, M.L. Dietz, D.M. Nelson, J.J. LaRossa, W.D. Fairman, Anal. Chim. Acta 238 (1990) 263;
(b) A.N. Turanov, V.K. Karandashev, N.A. Bondarenko, Rus. J. Inorg. Chem. 53 (2008) 1801;
(c) A.N. Turanov, V.K. Karandashev, E.V. Sharova, O.I. Artyushin, I.L. Odinets, Solv. Extr. Ion Exchange 28 (2010) 579;
(d) I.L. Odinets, E.V. Sharova, O.I. Artyshin, K.A. Lyssenko, Yu.V. Nelyubina, G.V. Myasoedova, N.P. Molochnikova, E.A. Zakharchenko, Dalton Trans. 39 (2010) 4170;
(e) A.M. Safiulina, E.I. Goryunov, A.A. Letyushov, I.B. Goryunova, S.A. Smirnova, A.G. Ginzburg, I.G. Tananaev, E.E. Nifant'ev, B.F. Myasoedov, Mendeleev Commun. 19 (2009) 263.

[6] (a) T.Q. Ly, J.D. Woollins, Coord. Chem. Rev. 176 (1998) 451;
(b) C. Silvestru, J.E. Drake, Coord. Chem. Rev. 223 (2001) 117. and references cited therein;
(c) S.W. Magennis, S. Parsons, Z. Pikramenou, A. Corval, J.D. Woollins, Chem. Commun. (1999) 61;
(d) S.W. Magennis, S. Parsons, Z. Pikramenou, Chem. Eur. J. 8 (2002) 5761;
(e) L. Barkaoui, M. Charrouf, M.-N. Rager, B. Denise, N.-M. Platzer, H. Rudler, Bull. Soc. Chim. Fr. 134 (1997) 167.

[7] (a) F.I. Bel'skii, Yu.M. Polikarpov, M.I. Kabachnik, Russ. Chem. Rev. 61 (1992) 221;
(b) F. Lemasson, H.-J. Gay, G. Raabe, Tetrahedron Lett. 48 (2007) 8752.

[8] I.M. Aladzheva, O.V. Bykhovskaya, Y.V. Nelyubina, A.A. Korlyukov, P.V. Petrovskii, I.L. Odinets, Synthesis (2010) 613.

[9] J.J. Katz, G.T. Seaborg, L.R. Morss, The Chemistry of the Actinide Elements, second ed., Chapman and Hall, London, 1986.

[10] (a) A.C. Bean, S.M. Peper, T.E. Albrecht-Schmitt, Chem. Mater. 13 (2001) 1266;
(b) C. Moulin, P. Decambox, V. Moulin, J.G. Decaillon, Anal. Chem. 67 (1995) 348;
(c) Y.-S. Jiang, Z.-T.Yu, Z.-L. Liao, G.-H. Li, J.-S. Chen, Polyhedron 25 (2006) 1359;
(d) K. Umeda, J. Zukerman-Schpector, P.C. Isolani, Polyhedron 25 (2006) 2447.

[11] (a) L. Salmon, P. Thuerry, E. Riviére, J.-J. Girerd, M. Ephritikhine, J. Chem. Soc., Dalton Trans. (2003) 2872;
(b) L. Salmon, P. Thuerry, E. Riviére, J.-J. Girerd, M. Ephritikhine, Chem. Commun. (2003) 762.

[12] (a) J.L. Sessler, P.J. Melfi, G. Dan Pantos, Coord. Chem. Rev. 250 (2006) 816;
(b) V. van Axel Castelli, R. Cacciapaglia, G. Chiosis, F.C.J.M. van Veggel, L. Mandolini, D.N. Reinhoudt, Inorg. Chim. Acta 246 (1996) 181;
(c) W.D. Wang, A. Bakac, J.H. Espenson, Inorg. Chem. 34 (1995) 6034;
(d) M. Shimazu, K. Shinozuka, Angew. Chem., Int. Ed. Engl. 32 (1993) 870.

[13] E. Steininger, Chem. Ber. 95 (1962) 2993.

[14] G.M. Sheldrick, SADABS, University of Gottingen, 1996

[15] SHELXTL, version 6.1, Bruker AXS Inc., Madison, WI 2005.

[16] (a) S. Kannan, N. Rajalakshmi, K.V. Chetty, V. Venugopal, M.G.B. Drew, Polyhedron 23 (2004) 1527;
(b) A.D. Sutton, G.H. John, M.J. Sarsfield, J.C. Renshaw, I. May, L.R. Martin, A.J. Selvage, D. Collison, M. Helliwell, Inorg. Chem. 43 (2004) 5480;
(c) T.W. Hayton, Guang Wu, J. Am. Chem. Soc. 130 (2008) 2005;
(d) S. Kannan, M.A. Moody, C.L. Arnes, P.B. Duval, Inorg. Chem. 45 (2006) 9206;
(e) S.M. Cornet, I. May, M.P. Redmond, A.J. Selvage, C.A. Sharrad, O. Rosnel, Polyhedron 28 (2006) 363.

[17] (a) S.M. Bowen, E.N. Duesler, R.T. Paine, Inorg. Chem. 22 (1983) 286;
(b) L.J. Caudle, E.N. Duesler, R.T. Paine, Inorg. Chim. Acta 110 (1985) 91;
(c) S. Karthikeyan, R.T. Paine, R.R. Ryan, Inorg. Chim. Acta 144 (1988) 135;
(d) G.S. Conary, R.L. Meline, L.J. Caudle, E.N. Duesler, R.T. Paine, Inorg. Chim. Acta 189 (1991) 59;
(e) E.V. Sharova, O.I. Artyushin, Yu.V. Nelyubina, K.A. Lyssenko, M.P. Passechnik, I.L. Odinets, Rus. Chem. Bul. Int. Ed. 57 (2008) 1890.
[18] E.I. Matrosov, E.I. Goryunov, T.V. Baulina, I.B. Goryunova, P.V. Petrovskii, Ed.E. Nifant'ev, Dokl. AN 432 (2010) 191.
[19] (a) K.P. Lannert, M.D. Joesten, Inorg. Chem. 7 (1968) 2048;
(b) K. Bokolo, J.-J. Delpuech, L. Rodenhüser, P. Rubini, Inorg. Chem. 20 (1981) 992;
(c) L. Rodenhüser, P. Rubini, K. Bokolo, J.-J. Delpuech, Inorg. Chem. 21 (1982) 1061;
(d) K. Bokolo, A. Courtois, J.-J. Delpuech, E. Elkaim, J. Protas, D. Rinaldi, L. Rodenhüser, P. Rubini, J. Am. Chem. Soc. 106 (1984) 6333;
(e) K. Aparna, S.S. Krishnamurty, M. Nethaji, J. Chem. Soc., Dalton Trans. (1995) 2991.
[20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley, Inc., 1986.
[21] G.H. John, I. May, M.J. Sarsfield, H.M. Steele, D. Collison, M. Helliwell, J.D. McKinney, Dalton Trans. (2004) 734. and references cited therein.
[22] (a) P. Charpin, G. Folcher, M. Lance, M. Nierlich, D. Vigner, Acta Crystallogr., C 41 (1985) 1302;
(b) B. Masci, P. Thuery, Polyhedron 24 (2005) 229;
(c) G.A. Doyle, D.M.L. Goodgame, A. Sinden, D.J. Williams, Chem. Commun. (1993) 1170.
[23] I.A. Charushnikova, C. Den Auwer, Russ. J. Coord. Chem. 30 (2004) 511.
[24] (a) M. Bhattacharjee, M.K. Chaudhuri, R.N.D. Purkayastha, Inorg. Chem. 25 (1986) 2354;
. For the first example of uranium peroxo-complexes with organic ligands see:(b) A.D. Westland, M.T.H. Tarafder, Inorg. Chem. 20 (1981) 3992.
[25] (a) R. Haegele, J.C.A. Boeyens, J. Chem. Soc., Dalton Trans. (1977) 648;
(b) D. Rose, Y.-D. Chang, Q. Chen, J. Zubieta, Inorg. Chem. 33 (1994) 5167.