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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.

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),