J Therm Anal Calorim (2010) 100:253–260
DOI 10.1007/s10973-009-0195-0

# Preparation and characterization of uranyl complexes with phosphonate ligands

**Z. Hnatejko · S. Lis · Z. Stryła**

Received: 2 March 2009 / Accepted: 28 May 2009 / Published online: 9 July 2009

**Abstract** The preparation, spectroscopic characterization and thermal stability of neutral complexes of uranyl ion, $UO_2^{2+}$, with phosphonate ligands, such as diphenylphosphonic acid (DPhP), diphenyl phosphate (DPhPO) and phenylphosphonic acid (PhP) are described. The complexes were prepared by a reaction of hydrated uranyl nitrate with appropriate ligands in methanolic solution. The ligands studied and their uranyl complexes were characterized using thermogravimetric and elemental analyses, ESI-MS, IR and UV–Vis absorption and luminescence spectroscopy as well as luminescence lifetime measurements. Compositions of the products obtained dependent on the ligands used: DPhP and DPhPO form $UO_2L_2$ type of complexes, whereas PhP forms $UO_2L$ complex. Based on TG and DTG curves a thermal stability of the complexes was determined. The complexes $UO_2PhP{\cdot}2H_2O$ and $UO_2(DPhPO)_2$ undergo one-step decomposition, while $UO_2PhP \cdot 2H_2O$ is decomposed in a two-step process. The thermal stability of anhydrous uranyl complexes increases in the series: DPhPO < PhP < DPhP. Obtained IR spectra indicate bonding of P–OH groups with uranyl ion. The main fluorescence emission bands and the lifetimes of these complexes were determined. The complex of DPhP shows a green uranyl luminescence, while the uranyl emission of the $UO_2PhP$ and $UO_2(DPhPO)_2$ complexes is considerably weaker.

**Keywords** Uranyl complexes · Phosphonate ligands · Thermal stability · Spectroscopy

## Introduction

Uranium binds two axial oxygen atoms to form the linear uranyl species $UO_2^{2+}$, which shows a good stability and high solubility in a wide range of organic solvents [1]. In aqueous solutions, the hydrated uranyl entity is equatorially pectacoordinated by five water molecules as $[UO_2(H_2O)_5]^{2+}$. Hydrolysis and steric requirements of equatorial coordination play an important role in studies of uranyl complexes in aqueous solution [2].

The uranyl ion is a hard Lewis acid and has a high affinity for hard donor groups [3]. This ion shows very characteristic absorption and emission spectra. The UV–Vis spectra of uranyl ion in solution are composed with 24 absorption bands (12 bands in the visible and 12 bands in the ultraviolet region). The emission spectrum is a result of energy transfer from two excited levels to five vibrational levels in the ground state [4, 5]. Emission properties of the $UO_2^{2+}$ ion are characterized by a high quantum yield under UV excitation. The luminescence of the uranyl ion is influenced by several factors: such as dynamic quenching of the non-dissociated ligand, static quenching due to the complex formation, and water molecules surrounding the uranium(VI) atom, as well as pH, counter ions and a solvent type [6–10]. Compounds containing the P=O and P–OH groups are known to possess excellent ligand properties towards a wide range of metal centers and the coordination properties these ligands has been extensively studied [11]. In previous works the synthesis, complexation and photophysical characterizations of $UO_2^{2+}$ complexes with phenylphosphonic acids have been studied [12–15].

Z. Hnatejko · S. Lis (✉)
Faculty of Chemistry, Adam Mickiewicz University,
Grunwaldzka 6, 60-780 Poznań, Poland
e-mail: blis@amu.edu.pl

Z. Stryła
Faculty of Physics, Adam Mickiewicz University,
Umultowska 85, 61-614 Poznań, Poland

The complexes are layered, linear or tunnel types. Phenylphosphonic acids were also used for complexation of the 4*f* elements [16–18].

As a part of our research on the metal phosphonate chemistry [19–22] we prepared of uranyl complexes with phenylphosphonic acid, diphenylphosphonic acid and diphenyl phosphate. The obtained solid complexes were characterized using elemental and thermal analyses, IR and luminescence spectra. The thermal decomposition of the complexes has been also used to infer their structure.

## Experimental

Chemicals of reagent grade quality were obtained from commercial companies (Aldrich, Merck). Uranyl nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, was recrystallized from water and other compounds were used without further purification.

Uranyl complexes were prepared by reaction of methanolic solutions $[UO_2(NO_3)_2 \cdot 6H_2O]$ with DPhP, PhP and DPhPO ligands (molar ratio 1:3). The solutions were separately heated for a short time and then mixed together. The reaction mixtures were refluxed for 2 h at temperature 323–330 K. Next day light yellow and yellow precipitates were removed from the solutions by suction, washed with methanol and dried under laboratory conditions.

Elemental analysis of carbon and hydrogen in the prepared complexes was carried out on a Perkin Elmer 2400 CHN microanalyzer. Mass spectra of $UO_2(DPhPO)_2$ in methanolic solutions ($\sim 10^{-4}$ M) were determined with the use of a Waters Micromass ZQ spectrometer. Scanning was performed from $m/z = 200$ to 1,000. All luminescence spectra of solid samples were recorded with the use of Perkin Elmer MPF-3 spectrofluorimeter. The IR spectra of the ligand and $UO_2^{2+}$ complexes were registered over the range 4,000–400 $cm^{-1}$ on a infrared spectrophotometer FT-IR IFS 66v/S, Bruker, using KBr pellets. Thermogravimetric (TG) and differential thermalanalysis (DTA) curves were obtained in a SETRAM sets 12 system thermoanalyser. The 10 mg samples of the studied complexes were heated in the air atmosphere (in $Al_2O_3$ crucibles) to 1,073 K at a heating rate 10 K $min^{-1}$ with a full scale. The X-ray diffraction patterns were measured on a Bruker AXS D8 Advance diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å) in the $2\theta$ ranges from 10° to 60°, using powder XRD method.

The luminescence lifetime measurements of $UO_2^{2+}$ were carried out with the use of the detection system consisting of a nitrogen laser, as described in details earlier [23]. The luminescence decays were recorded on a Tektronix TDS 210 oscilloscope. Luminescence lifetimes were obtained by fitting the time curves to a single exponential function with correlation coefficients of 0.99–0.999.

## Results and discussion

A schematic presentation the ligands studied is shown in Chart 1. Results of the microanalysis (C, H, N) of the compounds studied and their molecular formulae proposed are presented in Table 1. The results are in a very good agreement with the theoretical values obtained for the structures proposed. The complex compositions were also confirmed by the ESI-MS study. This method is very sensitive and generally applied for characterization of large molecular architectures occurring in solutions. For the ESI-MS study the $UO_2(DPhPO)_2$ complex was used in methanol solution at the concentration of $10^{-4}$ M. The ESI spectrum reveals the peaks corresponding to the species of $m/z = 799$ ($\{UO_2(L)_2CH_3O\}^-$), 519 ($UO_2\{L\}^+$), 551 ($\{UO_2LCH_3OH\}^+$), 301 ($\{UO_2CH_3O\}^+$) and 249 ($\{L\}^-$). The results implied that the complex dissociation takes place in the experimental conditions applied.

### IR study

The main IR bands of the ligands studied and their complexes with uranyl ion (in KBr pellets) were divided into three groups according to the wavelength ranges of occurrence. The absorption bands were assigned to the vibrations of the groups O–H, P=O, P–O–H, P–O–U and U=O. Also characteristic bands corresponding to vibrations of C–C and C–H bonds from the aromatic rings present in the complexes were observed.

The spectra of the ligands (Fig. 1) in the range 4,000–2,000 $cm^{-1}$ show broad bands with the maxima in the range 2,759–2,567 $cm^{-1}$, assigned to the formation of hydrogen bonds between OH groups of the ligands' molecules [24]. In the range 2,349–2,148 $cm^{-1}$ these spectra reveal the bands assigned to the vibrations of the P–O–H groups. The lack of these bands in the spectra of complexes **1**–**3** (corresponding to: $UO_2PhP \cdot 2H_2O$, $UO_2(DPhP)_2$, and $UO_2(DPhPO)_2$, respectively) points to the absence of $PO_3H_2$ groups in the solid state samples, which is in agreement with the chemical formulae proposed (Table 1).

The other region taken for analysis covered the range 1,250–950 $cm^{-1}$ in which a few bands assigned to the

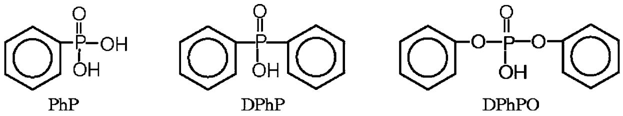

**Chart 1** Schematic presentation of the ligands studied

**Table 1** Analytical data of the studied uranyl complexes

| Compound | Formula | Calculated molar mass | Colour | Found (calculated) (%) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | P | U |
| **1** | $[UO_2PhP] \cdot 2H_2O$ $C_6H_9O_4PUO_2$ | 462.20 | Light yellow | 15.88<br>(15.60) | 2.11<br>(1.97) | – | –<br>(6.70) | –<br>(51.51) |
| **2** | $UO_2(DPhP)_2$ $C_{24}H_{20}O_4P_2UO_2$ | 704.49 | Light yellow | 41.18<br>(40.92) | 3.01<br>(2.86) | – | –<br>(8.79) | –<br>(33.79) |
| **3** | $UO_2(DPhPO)_2$ $C_{24}H_{20}O_8P_2UO_2$ | 768.49 | Yellow | 37.82<br>(37.52) | 2.91<br>(2.83) | – | –<br>(8.06) | –<br>(30.98) |

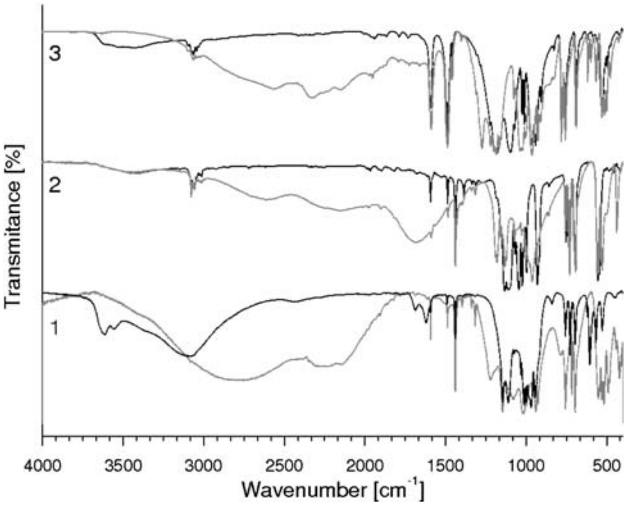

**Fig. 1** The IR spectra of studied systems: (1) $UO_2PhP \cdot 2H_2O$; (2) $UO_2(DPhP)_2$; (3) $UO_2(DPhPO)_2$ (the complexes are noted *black colour* and suitable ligands *grey*)

vibrations of P=O and P–O–H groups appeared [14, 25]. The P=O group gives the absorption band at ~1,170 cm$^{-1}$ [26–29]. Comparison of the positions of the bands assigned to the vibrations of P=O (Table 2) has shown that the spectra of the ligands and the complexes occur at the same frequencies. This fact implies that the P=O group is not involved in the complexation of the uranyl ion, so the complexation of the $UO_2^{2+}$ ion is realised only via the P–O–H groups. The IR spectra reveal the bands corresponding to the vibrations of P–O–U, involved in the complex formation, at ~1,100 and ~970 cm$^{-1}$.

The third analysed range covered the frequencies 950–400 cm$^{-1}$. This range comprised further bands attributed to P–O–U at ~600 and ~540 cm$^{-1}$ and the bands assigned to the asymmetric $\nu_{as}$, and symmetric $\nu_s$ vibrations of $UO_2^{2+}$; the asymmetric ones at 944–905 and 527–449 cm$^{-1}$, while the symmetric ones in the range 854–826 cm$^{-1}$. The positions of these bands in the spectra of the complexes studied are consistent with the relevant earlier reports [25, 30, 31].

**Table 2** Characteristic IR bands of the ligands studied and their uranyl complexes

| PhP | $UO_2PhP$ | DPhP | $UO_2(DPhP)_2$ | DPhPO | $UO_2(DPhPO)_2$ | Assignment |
|---|---|---|---|---|---|---|
| – | 3,083 | – | – | – | – | $\nu$ O–H |
| 2,759 | – | 2,615 | – | 2,567 | – | $\nu$ P–O(H) |
| 2,349 | – | 2,156 | – | 2,320 | – | |
| 2,138 | – | | | 2,148 | – | |
| – | 1,619 | – | | – | – | $\delta$ O–H |
| 1,439 | 1,438 | 1,439 | 1,438 | – | – | $\nu$ P–C$_{Ar}$ |
| 1,220 | – | 1,189 | – | 1,273 | – | $\nu$(P=O, P–O(H)) |
| 1,145 | 1,144 | 1,155 | 1,159 | 1,199 | 1,195 | |
| 1,079 | – | 1,122 | – | 1,170 | – | |
| | | 961 | – | 1,038 | – | |
| – | 1,110 | – | 1,109 | – | 1,096 | $\nu$ P–O–U |
| – | 968 | – | 997 | – | 940 | |
| – | 605 | – | 542 | – | 533 | |
| – | 944 | – | 930 | – | 905 | $\nu_{as}$ U=O |
| – | 527 | – | 508 | – | – | |
| – | 449 | – | 457 | – | – | |
| | 839 | | 854 | | 826 | $\nu_s$ U=O |

As follows from the IR spectra and results of the elemental analysis, water molecules occur only in complex **1.** The presence of water in this complex is confirmed by the broad band with the maximum at about 3,083 $\mathrm{cm}^{-1}$ and a narrow band at 1,619 $\mathrm{cm}^{-1}$, assigned to the vibrations of $\nu(\mathrm{OH})$ and $\delta(\mathrm{OH_2})$, respectively [13, 32, 33].

## Thermal study

The thermogravimetric analysis of the compounds studied was performed on heating them from 298 to 1,073 K. The compounds are stable in the air at room temperature but on heating they undergo decompositions along different pathways (Fig. 2, Table 3), discussed below on the basis of the mass loss noted. The TG curves of compounds **1–3** are shown in Fig. 2, while Table 3 presents the mass loss (found and calculated) for all the complexes studied as a function of temperature.

Figure 2(1) presents results of the thermal analysis of the $\mathrm{UO_2PhP \cdot 2H_2O}$ complex that undergoes two-step decomposition. The DTG curve shows two peaks in the ranges 343–418 and 710–821 K, while the DTA curve shows a small endothermic peak with the maximum at 383 K and a high exothermic peak at 763 K. At the first endothermic stage of decomposition (343–418 K) the observed mass loss was 7.68% (the calculated value was 7.78%) corresponding to elimination of two water molecules, most probably occurring in the outer coordination sphere of the complex (lattice water). The water eliminated from the complexes below 423 K is considered as the lattice water, while the water removed above this temperature is treated as water coordinated to the central ion [34, 35]. The second stage of decomposition of compound **1** started above 673 K and demonstrated a strong exothermic effect. The corresponding mass loss of 6.23% indicated elimination of two benzyl groups and hence the total decomposition of the ligand.

The thermal decomposition of compound **2** was significantly different from **1**. The DTG curve (Fig. 2(2)) showed a single signal in the range 748–863 K with the minimum at 808 K. This signal was assigned to the elimination of four benzyl groups and decomposition of **2.** This process was accompanied by an exothermic effect, similarly to those observed in the case of the compounds **1** and **3**. The experimental (44.91%) and calculated (44.71%) values of the mass loss are consistent each other.

Compound **3** showed a little different pattern of the thermal decomposition, which is similar to that of compound **2.** The DTG curve minimum was observed at 668 K; the corresponding mass loss was related to the elimination of organic molecules and exothermic effect on the DTA

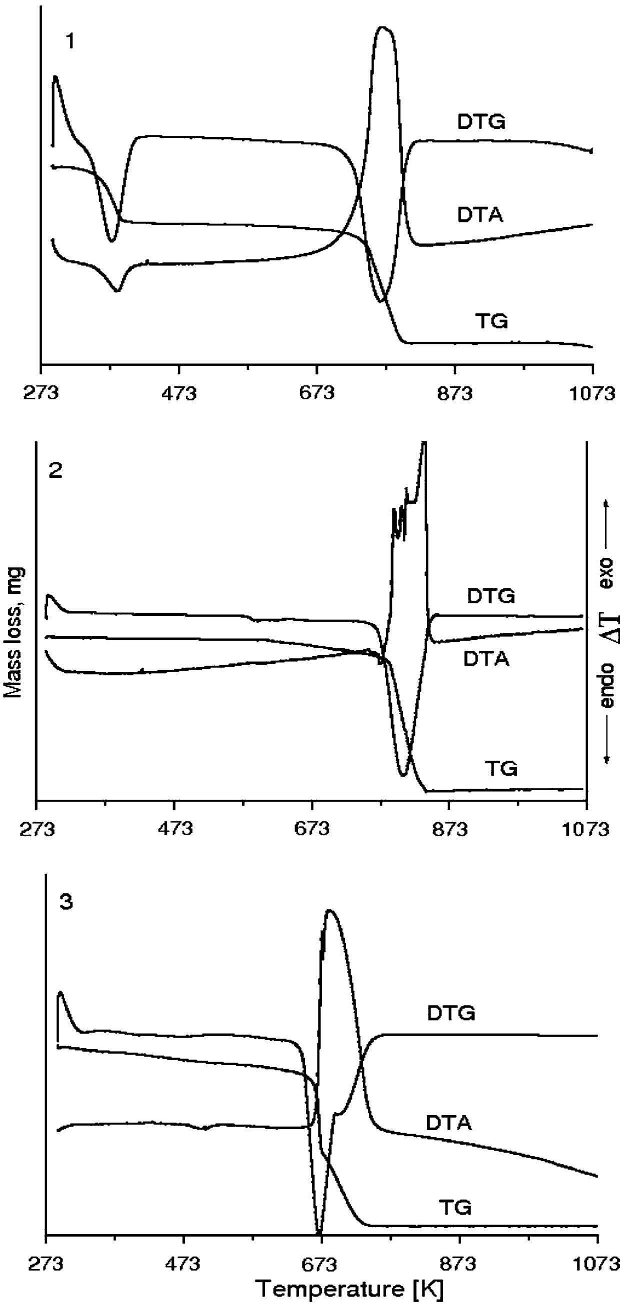

**Fig. 2** TG, DTG and DTA curves of the complexes studied: (1) $\mathrm{UO_2PhP \cdot 2H_2O}$; (2) $\mathrm{UO_2(DPhP)_2}$ and (3) $\mathrm{UO_2(DPhPO)_2}$

**Table 3** Thermogravimetric analysis results of the uranyl complexes

| Compounds | $\Delta T_1$ K | $\Delta T_2$ K | Mass loss % | |
|---|---|---|---|---|
| | | | Found | Calc. |
| $\mathrm{UO_2PhP \cdot 2H_2O}$ | 343–418 | 710–821 | 7.68 | 7.78 |
| | | | 16.23 | 16.90 |
| $\mathrm{UO_2(DPhP)_2}$ | | 747–863 | 44.91 | 44.71 |
| $\mathrm{UO_2(DPhPO)_2}$ | | 608–773 | 44.90 | 44.81 |

$T_1$ Dehydratation, $T_2$ decomposition curve. The observed value of the mass loss, 44.90%, was in a good agreement with the calculated value of 44.81%.

The experimental results indicate that the thermal decomposition of uranyl complexes can be presented in the following way:

$$\mathrm{UO_2PhP \cdot 2H_2O \rightarrow UO_2PhP \rightarrow (UO_2)_2P_2O_7 + (UO_2)_3(PO_4)_2 \cdot 0.5H_2O;} \quad (1)$$

$$\mathrm{UO_2(DPhP)_2 \rightarrow UP_2O_7;} \quad (2)$$

$$\mathrm{UO_2(DPhPO)_2 \rightarrow UP_2O_7.} \quad (3)$$

The final products of thermal decomposition were determined from the TG/DTG curves and based on the XRD patterns obtained in the temperature range above 973 K (Fig. 3). The final decomposition product of **1** was a mixture of $(UO_2)_2P_2O_7 + (UO_2)_3(PO_4)_2 \cdot 0.5H_2O$, while **2** and **3** give $UP_2O_7$, as identified from their XRD patterns. The XRD results are consistent with the data of the calcination products [$(UO_2)_2P_2O_7$ and $UP_2O_7$] obtained from the TG/DTG curves.

The temperature of the final decomposition of the anhydrous complexes was found to be strictly correlated with the structure of the ligands studied. The ligands having the direct P–$C_{Ar}$ bonds formed complexes of greater thermal stability. The decomposition of complexes **1** and **2** started at 710 and 748 K, respectively. Complex **3** in which the phosphorus atom is bonded to the organic ligand through the oxygen atom (P–O–$C_{Ar}$), was much less thermally stable as its decomposition started at much lower temperature of 623 K. Therefore the thermal stability of the complexes studied show the following pattern: DPhPO < PhP < DPhP.

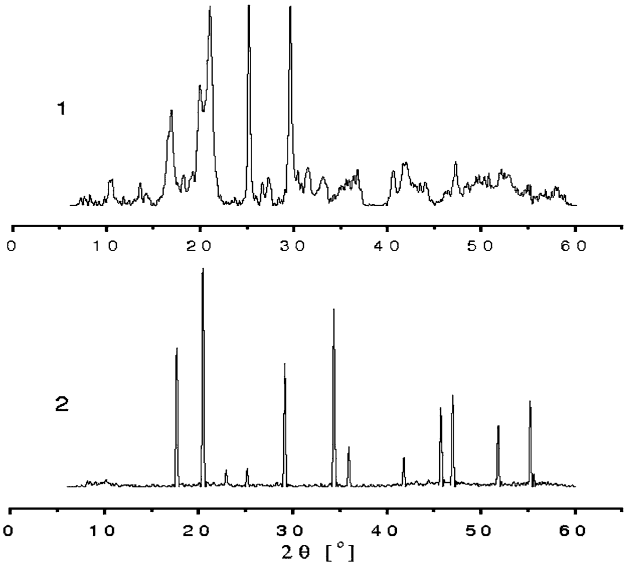

**Fig. 3** XRD patterns of the powdered samples: (1) $UO_2PhP \cdot 2H_2O$; (2) $UO_2(DPhP)_2$

## Luminescence study

The emission spectra of uranyl compounds result from an excited state in which an electron has been transferred from the $UO_2^{2+}$ molecular orbital to the 5*f* U atomic orbital [36]. The luminescence spectra of $UO_2^{2+}$, as $UO_2(ClO_4)_2$ and $UO_2(NO_3)_2$ in aqueous solutions, are composed with six and five emission bands [37, 38].

The emission spectra of uranyl nitrate hexahydrate and the $UO_2(DPhP)_2$ complex, recorded in the solid state at room temperature, consist of a series of bands, which are vibronically structured, while the $UO_2PhP$ and $UO_2(DPhPO)_2$ complexes display only broad bands (Fig. 4). The spectra were recorded in the range 400–700 nm, using the excitation wavelength $\lambda = 337.1$ nm. This excitation wavelength is longer than the maximum absorption wavelengths of the ligands (i.e. 271, 270 and 262 nm for DPhP, PhP and DPhPO, respectively). Therefore, the observed emission is a result of a direct excitation of the uranyl ion. In such conditions the intramolecular energy transfer from ligands to the metal ion does not occur [39].

The observed emission bands in $[UO_2(NO_3)_2 \cdot 6H_2O]$ (Fig. 4) correspond to the $S_{10} \rightarrow S_{0v}$ electronic transition for $v = 0$–4 ($\lambda_{max} = 491, 511, 535, 561$ and 587 nm) [4, 5, 25] and are related to the transitions from the first excited electronic level to the symmetric and anti-symmetric vibrational levels of the uranyl ion [40]. In the case of the DPhP complex the emission intensity is one order of magnitude lower then for $UO_2(NO_3)_2$ with a red shift of the uranyl emission signal (Fig. 4), which is attributed to the $UO_2^{2+}$/DPhP complexation. The solid-state emission spectrum of this complex reveals characteristic emission bands lying at 515, 538, 565 and 592 nm. These bands are located in about the same positions as observed in other uranyl—containing compounds [41–44]. The most intense luminescence bands were observed for uranyl nitrate and the $UO_2(DPhP)_2$ complex at $\lambda_{em} = 511$ and 538 nm (green emission), respectively. The $UO_2(DPhPO)_2$ and $UO_2PhP$ complexes show only a very weak luminescence in room temperature, which is observed together with the emission of the ligands used (Fig. 4). The weak $UO_2^{2+}$ luminescence observed in the case of the $UO_2PhP$ complex is in a good agreement with earlier reports by Grohol and Clearfield [15].

Figure 5 presents the luminescence decay of the uranyl ion in different coordination environments, recorded using excitation wavelength $\lambda = 337.1$ nm in room temperature. The calibration of our system for luminescence lifetime measurements [23] we used the luminescence lifetime of uranyl nitrate hexahydrate. The light source was a nitrogen

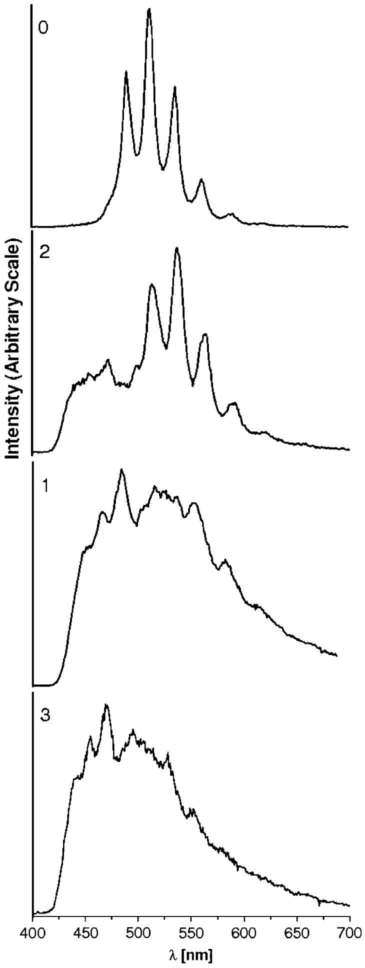

**Fig. 4** Emission spectra of solid powder samples of $UO_2(NO_3)_2 \cdot 6H_2O$ (0), (1) $UO_2PhP \cdot 2H_2O$, (2) $UO_2(DPhP)_2$ and (3) $UO_2(DPhPO)_2$; $\lambda_{ex} = 337.1$ nm

laser (KB 6211 Cobrabid). The luminescence from the solid powder samples passed through green filters (SiF 510 or 535, VEB Carl Zeiss JENA) and then was detected by a photomultiplier (M12 FVC51). For the determination of each lifetime 128 luminescence decays were averaged. The luminescence lifetimes of the $UO_2^{2+}$ ion were calculated with the use of ORIGIN 7, obtained values are shown in Table 4. In the case of the $UO_2(NO_3)_2 \cdot 6H_2O$ salt the calculated value of the lifetime from the luminescence decay at 510 nm was 750 μs with a standard deviation of 12 μs, while for the $UO_2(DPhP)_2$ complex the decay measured at 535 nm gave the lifetime of 70 μs with a standard deviation of 6 μs.

The decay time measured for $UO_2(NO_3)_2 \cdot 6H_2O$ is very close to the values reported earlier [4]. For the $UO_2PhP \cdot 2H_2O$ and $UO_2(DPhPO)_2$ complexes it was impossible to measure the lifetimes because of very weak luminescence signals observed in these cases.

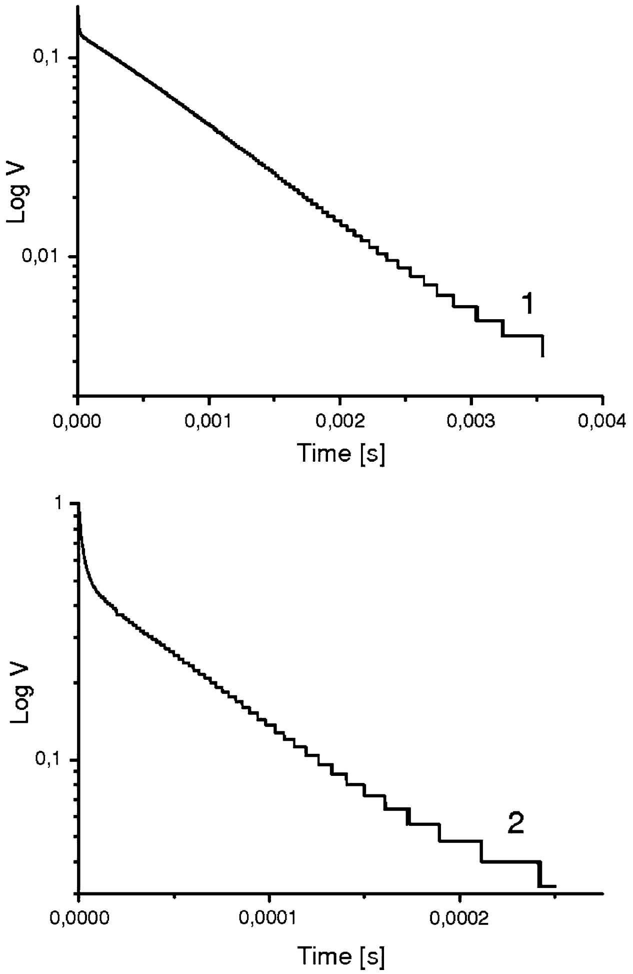

**Fig. 5** The luminescence decay curves of the solid powder samples: (1) $UO_2(NO_3)_2 \cdot 6H_2O$ and (2) $UO_2(DPhP)_2$

**Table 4** Luminescence lifetime data of the emitting uranyl compounds

| Compounds | *T* (μs) | $R^2$ |
|---|---|---|
| $UO_2(NO_3)_2 \cdot 6H_2O$ | 750 ± 12 | 0.998 |
| $UO_2(DPhP)_2$ | 70 ± 6 | 0.993 |

## Conclusions

Synthesized complexes of uranyl with: phenylphosphonic acid, diphenylphosphonic acid and diphenyl phosphate ligands were photophysically and thermally characterized. Based on the results of elemental and thermogravimetric analyses and IR spectra the following compositions $UO_2PhP \cdot 2H_2O$, $UO_2(DPhP)_2$ and $UO_2(DPhPO)_2$ of the obtained complexes were formulated. Thermogravimetric analysis (TG, DTG and DTA) enabled to determine a range of the thermal stability and decomposition pathways of these complexes. The complexes $UO_2(DPhP)_2$ and $UO_2(DPhPO)_2$ undergo one-step decomposition, while the complex $UO_2PhP \cdot 2H_2O$ is decomposed in a two-step process. The thermal stability of anhydrous uranyl complexes increases in the series: DPhPO < PhP < DPhP.

Studies of the emission spectra revealed that the uranyl emission observed in room temperature is effective in the case of the $UO_2(NO_3)_2 \cdot 6H_2O$ salt as well as for the $UO_2(DPhP)_2$ complex. The complexes $UO_2PhP$ and $UO_2(DPhPO)_2$ show very weak emission properties. In the case of the $UO_2(DPhP)_2$ complex a batochromic shift of the emission bands was observed comparing with the $UO_2(NO_3)_2 \cdot 6H_2O$ salt. The $UO_2^{2+}$ emission lifetime measured for $UO_2(DPhP)_2$ is one order of magnitude shorter than that obtained for $UO_2(NO_3)_2 \cdot 6H_2O$.

## References

1. Cotton A, Wilkinson G. Advanced inorganic chemistry. New York: Wiley; 1988.
2. Meinrath G. Coordination of Uranyl(VI) carbonate species in aqueous solutions. J Radioanal Nucl Chem. 1996;211:349–62.
3. Pearson GR. Hard and soft acids and bases. J Am Chem Soc. 1963;85:3533–9.
4. Rabinowitch E, Belford RL. Spectroscopy and photochemistry of uranyl compounds, vol. 1. London: Pergamon Press; 1964.
5. Bell JT, Biggers RE. Absorption spectrum of the uranyl ion in perchlorate media. III. Resolution of the ultraviolet band structure; some conclusions concerning the excited state of uranyl ion. J Mol Spectrosc. 1968;25:312–29.
6. Denning RG. Electronic structure and bonding in actinyl ions. Struct Bond. 1992;79:215–76.
7. Matsushima R, Sakuraba S. Quenching of the uranyl fluorescence by aromatic molecules. J Am Chem Soc. 1971;93:7143–5.
8. Hill RJ, Kemp TJ, Allen DM, Cox A. Absorption spectrum, lifetime and photoreactivity towards alcohols of the excited state of the aqueous uranyl ion (UO2+2). J Chem Soc Faraday Trans I. 1974;70:847–57.
9. Matsushima R. Mechanism of quenching of the uranyl fluorescence by organic compounds. J Am Chem Soc. 1972;94:6010–6.
10. Sidhu MS, Anju, Bhatia PVK. Uranyl ion luminescence quenching with benzene derivatives and related to compounds. Linear free energy relantionship. J Radioanal Nucl Chem. 1994;188:243–53.
11. Engel R, Hilderband RL, editors. The role of phosphonates in living systems. Boca Raton, FL: CRC Press; 1988.
12. Poojary DM, Grohol D, Clearfield A. Synthesis and X-ray powder structure of a novel porous uranyl phenylphosphonate containing unidimensional channels flanked by hydrophobic regions. Angew Chem Int Ed Engl. 1995;34:1508–10.
13. Sailaja BBV, Kebede T, Prasada Rao MS. Thermal decomposition of barium dioxodiaquaperoxyoxalato uranate(VI) hydrate. J Therm Anal Calorim. 2002;68:841–9.
14. El-Gamel NEA, Mohamed GG. Synthesis, spectral and thermal characterization of 6-hydroxymethyl pyridine-2-carboxylic acid methyl ester and its complexes. J Therm Anal Calorim. 2005; 81:111–8.
15. Grohol D, Clearfield A. Solid-state water-catalyzed transformation at room temperature of a nonluminescent linear-chain uranyl phenylphosphonate into a luminescent one. J Am Chem Soc. 1997;119:4662–8.
16. Sato N, Goto M, Matsumoto S, Shinkai S. Lipophilic phenylphosphonic acid-lanthanide ion complexes which show efficient energy-transfer luminescence. Tetrahedron Lett. 1993;34: 4847–50.
17. Panigrahi BS. Fluorescence and cofluorescence enhancement of $Tb^{3+}$ and $Eu^{3+}$ using phenyl phosphonic and phenyl phosphinic acids as ligands. J Lumin. 1999;82:121–7.
18. Scarpari SL, Stucci EB. Effects of dispersion by $Gd^{3+}$ upon europium diphenylphosphinate luminescence. J. Alloys Compd. 2001;323–324:740–2.
19. Hnatejko Z, Elbanowski M. Complexation, luminescence and energy transfer of Ln(III) ions with phenylphosphonic acid. J Alloys Compd. 2004;380:181–5.
20. Lis S, Piskuła Z, Hnatejko Z. Spectroscopic studies of lanthanides complexes with diethyl benzylphosphonate and diethylphosphonoacetic acid. J Alloys Compd. 2008;451:388–94.
21. Hnatejko Z, Lis S, Pawlicki G, Meinrath G. Lanthanide complexes with diethyl(2-oxopropyl) phosphonate and diethyl(2-oxo-2-phenylethyl) phosphonate ligands. J Alloys Compd. 2008; 451:395–9.
22. Lis S, Piskula Z, Staninski K, Tamaki S, Inoue M, Hasegawa Y. Luminescence studies of europium(III) tris($\beta$-diketonato)/phosphonat complexes in chloroform. J Rare Earths. 2008;26:185–91.
23. Lis S, Hnatejko Z, Stryła Z. Device for measurements of selective luminescence excitation spectra of europium (III) based on a nitrogen and dye laser system. Opt Appl. 2001;31:643–8.
24. Mar Gómez-Alcántara M, Cabeza A, Aranda MAG, Gougliardi A, Mao JG, Clearfield A. Synthesis and characterization of metal carboxyalkylphosphonates hybrid materials. Solid State Sci. 2004;5:479–87.
25. Jacopin C, Sawicki M, Plancque G, Doizi D, Taran F, Ansoborlo E, et al. Investigation of the interaction between 1-hydroxyethane-1,1'-diphosphonic acid (HEDP) and uranium(VI). Inorg Chem. 2003;42:5015–22.
26. Princz E, Szilagyi I, Mogyorosi K, Labadi I. Lanthanide complexes of ethylenediamine-tetramethylene-phosphonic acid. J Therm Anal Calorim. 2002;69:427–39.
27. Tanner PA, Mak TWC. Synthesis, structure, and spectroscopy of rare earth hypophosphites. 2. Uranyl hypophosphite monohydrate and uranyl hypophosphite−hypophosphorous acid (1/1). Inorg Chem. 1999;38:6024–31.
28. Pouchert ChJ, Behnke J. The aldrich library of FTIR spectra, II edn. 1997.
29. de Aquino AR, Bombieri G, Isolani PC, Vicentini G, Zukerman-Schpector J. Characterization, luminescence and crystal structure of uranyl nitrate complexes with diphenyl-N-ethylphosphine amide and tripiperidinephosphine oxide. Inorg Chim Acta. 2000;306:101–5.
30. Signorini O, Dockal ER, Castellano G, Oliva G. Synthesis and characterization of aquo[N,N'-ethylenebis(3-ethoxysalicylideneaminato)] dioxouranium(VI). Polyhedron. 1996;15:245–55.
31. Arruda AF, Campiglia AD, Chauhan BPS, Boudjouk P. New organosilicon polymer for the extraction and luminescence analysis of uranyl in environmental samples. Anal Chim Acta. 1999;396:263–72.
32. Mohamed GG, Soliman AA, El-Mawgood MA. Structural and thermal characterization of cerium, thorium and uranyl complexes of sulfasalazine. Spectrochim Acta A. 2005;62:1095–101.
33. Ferenc W, Walków-Dziewulska A. Thermal and spectral features of yttrium and heavy lanthanide complexes with 2,4-dimethoxybenzoic acid. J Therm Anal Calorim. 2001;63:865–77.
34. Nikolaev AV, Logvinienko VA, Myachina LJ. Thermal analysis, vol. 2. New York: Academic Press; 1989.
35. Brzyska W, Ożga W. Spectral and thermal investigation of rare earth element 4-methoxy-2-methylbenzoates. J Therm Anal Calorim. 2002;70:467–74.

36. Jørgensen CK. Excited states of the uranyl ion. J Lumin. 1979;18:63–8.
37. Bell JT, Biggers RE. The absorption spectrum of the uranyl ion in perchlorate media. I. Mathematical resolution of the overlapping band structure and studies of the environmental effects. J Mol Spectrosc. 1965;18:247–75.
38. McGlynn SP, Smith JK. The electronic structure, spectra, and magnetic properties of actinyl ions. I. The uranyl ion. J Mol Spectrosc. 1961;6:164–87.
39. Jiang Y-S, Yu Z-T, Liao Z-L, Li G-H, Chen J-S. Syntheses and photoluminescent properties of two uranyl-containing compounds with extended structures. Polyhedron. 2006;25:1359–66.
40. Leung AF, Hayashibara L, Spadaro J. Fluorescence properties of uranyl nitrates. J Phys Chem Solids. 1999;60:299–304.
41. Almond PM, Tallcy CE, Bean AC, Peper SM, Albrecht-Schmitt TE. Hydrothermal syntheses, structures, and fluorescence spectroscopy of new one-dimensional uranium oxyfluorides built from edge-sharing [$UO_2F_5$] pentagonal bipyramids. J Solid State Chem. 2000;154:635–41.
42. Kong X, Ren Y, Long L, Huang R, Zheng L. An organic–inorganic hybrid uranyl nicotinate molybdate polymer and its fluorescent property. Inorg Chem Commun. 2007;10:894–6.
43. de Almeida KCS, Martins TS, Isolani PC, Vicentini G, Zukerman-Schpector J. Uranyl nitrate complexes with diphenylsulfoxide and dibenzylsulfoxide: characterization, luminescence and structures. J Solid State Chem. 2003;171:230–4.
44. Koban A, Bernhard G. Complexation of uranium(VI) with glycerol 1-phosphate. Polyhedron. 2004;23:1793–7.