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# Dioxouranium complexes with pentadentate *s*-triazine Schiff base ligands: synthesis, crystal structure and optical properties

Lubomír Pavelek <sup>a</sup>,\*, Vít Ladányi <sup>b,c</sup>, Marek Nečas <sup>b,d</sup>, Silvie Vallová <sup>a</sup>, Kamil Wichterle <sup>a</sup>

- <sup>a</sup> Department of Chemistry, Faculty of Metallurgy and Materials Engineering, VŠB-Technical University of Ostrava, 17. listopadu 15, Ostrava-Poruba CZ-70833, Czech Republic
- <sup>b</sup> Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno CZ-61137, Czech Republic
- <sup>c</sup> RECETOX, Faculty of Science, Masaryk University, Kamenice 5, 62500 Brno CZ-62500, Czech Republic
- <sup>d</sup> CEITEC Central European Institute of Technology, Masaryk University, Kamenice 5, 625 00 Brno-Bohunice CZ-62500, Czech Republic

\* Corresponding author. Tel.: +420 704735413; E-mail address: lubomir.pavelek@vsb.cz

**Abstract:** Using the reactions of 2,4-dihydrazino-(R)-*s*-triazine (R – methoxy (**DHMT**)) with salicylaldehyde and *o*-vanillin ligands 2,4-Bis(2-hydroxybenzylidenehydrazino)-6-methoxy-*s*-triazin (**L1**) and 2,4-Bis(2-hydroxy-3-methoxybenzylidenehydrazino)-6-methoxy-s-triazin (**L2**) were obtained. Using the reaction of 2,4-dihydrazino-(R)-*s*-triazine (R – amino (**DHAT**)) with *o*-vanillin ligand 2,4-Bis(2-hydroxy-3-methoxybenzylidenehydrazino)-6-amino-*s*-triazine (**L3**) was obtained. By the reactions of the prepared ligands, derivatives of hydrazo-*s*-triazine, with uranyl acetate or nitrate, four new complexes were prepared. X-ray diffraction shows that the UO<sub>2</sub><sup>2+</sup> ion is in a pentagonal bipyramidal coordination environment. Two oxygen atoms of the UO<sub>2</sub><sup>2+</sup> ion occupy the axial positions and three atoms of nitrogen and two atoms of oxygen construct the equatorial plane. The uranyl(VI) complexes were characterized by single-crystal X-ray diffraction, UV-vis, fluorescence and IR spectroscopy. Thermal stabilities of the complexes were investigated using thermogravimetric analysis.

Keywords: Uranyl(VI), Complexes, Triazine ligands, X-ray structure, Optical properties

### 1. Introduction

The chemical compound 1,3,5-triazine,  $(C_3N_3H_3)$ , also known as *s*-triazine, is a symmetric sixmembered N-heterocyclic aromatic ring consisting of alternating carbon and nitrogen atoms. Chlorinated derivative of *s*-1,3,5-triazine called cyanuric chloride ( $C_3N_3Cl_3$ ) and its derivatives are currently intensively studied heterocyclic compounds with interesting biological qualities for pharmaceutical industry, mainly antifungal, antibacterial, antimalaric and antineoplastic [1-6]. In

addition to the applications of s-1,3,5-triazine derivatives, their usage in rubber-making or textile industry is extremely important as well [7]. Nitrogen-rich derivatives have potential to be used as energetic explosives [8].

By simple substitution of chlorine atoms in cyanuric chloride, using controlled conditions (temperature) and different nucleophiles, various 2,4,6-mono, di- and trisubstituted, symmetrical and non-symmetrical derivatives bearing different substituents can be prepared [9-11]. Cyanuric chloride has temperature-dependent differential reactivity for displacement of chlorides with nucleophiles during  $S_NAr$  as shown in reaction Scheme 1 [12, 13].

### Please insert Scheme 1 here

Cyanuric chloride reacts efficiently with hydrazine hydrate to give mono-, di- or tri- substituted hydrazo- derivatives [14]. Several prepared and well explored hydrazo- *s*-triazines derivatives already exist. *s*-Triazine derivatives are of considerable current interest in coordination chemistry and supramolecular chemistry [15]. 2,4,6-trisubstituted-triazine derivatives proved their great potential in field of material chemistry, both for their  $\pi$ -interaction abilities and for their aptitude to be involved in intricate H-bond networks [16, 17].

Ramírez et al. published a study on the complexation of two bis-tridentate triazine ligands with large metal ions Hg(II) and Pb(II) [18, 19]. A new triazine-based ligand with threefold symmetry gave five heptacoordinate complexes in reaction with Mn(II) [20]. By the reaction of 2,4,6-tris(2-isopropylidene-1-yl)hydrazono-1,3,5-triazine with Zn(II) salt, a mononuclear complex with a trigonal bipyramidal geometry around the Zn(II) was prepared [21]. Tei and coworkers published the preparation of powdered Eu(III) and Gd(III) complexes by the reaction with triazine-dihydrazino-tetracetate polydentate ligands [22].

The coordination chemistry of uranium has experienced increasing attention over recent years [23-25]. Uranium element in oxidation state VI typically forms a particularly stable uranyl(VI) ion  $(UO_2^{2^+})$  [26, 27]. Some uranyl(VI) complexes are based on structural motifs of 2,6-diacetylpyridine derivatives. These complexes exhibit pentagonal bipyramidal or hexagonal bipyramidal coordination spheres [28-30].

This study reports a preparation of three chelating ligands from the reaction of *s*-triazine as a common base with salicylaldehyde and *o*-vanillin as demonstrated in Scheme 2. By the reaction of these ligands with uranyl salts (acetate and nitrate), three complexes of uranyl(VI) featuring pentagonal bipyramidal  $UO_2^{2+}$  metal ions were prepared.

### 2. Experimental

#### 2.1. Reagents and techniques

The chemicals used in this experiment were commercially available reagents and were used without further purification.  $UO_2(OCOCH_3)_2 \cdot 2H_2O$  (Lachema),  $UO_2(NO_3)_2 \cdot 6H_2O$  (Lachema), N,N-Dimethylformamide (Sigma-Aldrich, 98%), cyanuric chloride (Aldrich, 99%), hydrazine hydrate (Sigma-Aldrich, 50-60%), sodium bicarbonate (Sigma-Aldrich), methanol (Sigma-

FT-IR spectra were recorded using ATR technique by ALPHA FT-IR spectrometer (Bruker) in the 4000 – 400 cm<sup>-1</sup> region. The reported FT-IR signal intensities were defined as w = weak, m = medium and s = strong. Elemental analysis (C, H and N) were performed using Elementar Vario EL III. Single-crystals were collected on a Rigaku MicroMax-007 HF rotating anode four-circle diffractometer with Mo-K $\alpha$  radiation. The temperature during data collection was 120(2) K. The structures were solved by direct methods and refined using the full-matrix least-squares method on  $F^2$  with anisotropic thermal parameters for all nonhydrogen atoms (SheIXTL) [31, 32]. A summary of the crystallographic data and structure refinement parameters is given in Table 3. The molecular graphics as well as additional structural calculations were drawn and interpreted using Diamond, ver. 3.2 (http://www.crystalimpact.com/diamond/Default.htm).

UV-vis absorption spectra of ligands and complexes were recorded using a Shimadzu UV-1602 spectrophotometer or GBC Scientific Equipment Cintra 2020 spectrophotometer in 1-cm quartz cuvette. The fluorescence emission spectra were performed on a FLS 920 fluorescence spectrometer (Edinburgh instruments) equipped with a 450 W Xe lamp and PMT detector with a double grating monochromator for both the excitation and the emission. The measurements were performed in 1-cm fluorescence cuvettes in front face-geometry arrangement.

The thermogravimetric analyses of the complex **1** was performed using simultaneous TG-DTA apparatus Netzsch STA 409 EP equipped with a high-sensitive analytical balance for measuring the mass change of the sample as a function of temperature or time (TG curves). The sample carrier system contains the type S thermocouples (Pt10%Rh-Pt) to measure the temperature and the temperature difference (DTA curves). Thermal analyses of the complexes **2** and **3** (TG/DSC) were done on a Netzsch STA 449C Jupiter apparatus. Samples (1-10 mg in weight) were heated up to 1000 °C in the crucibles ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) in a dynamic atmosphere of a dry air (flow rate of 100 cm<sup>3</sup> min<sup>-1</sup>; complex **1**) or a synthetic air (flow rate of 70 cm<sup>3</sup> min<sup>-1</sup>; complexes **2** and **3**) at a heating rate of 10 °C min<sup>-1</sup>.

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance X-ray diffractometer with silicon strip detector LynxEye. The diffractometer operated at: radiation CoK $\alpha$ , 40 kV and 40 mA, step mode with steps 0.014° 2 $\theta$  and time 1s on steps. For the calculations of the lattice parameters and the size of the coherent diffraction domain the Rietveld method was used (Bruker Diffrac Topas program, version 4.2).

### 2.2. Synthesis of ligands L1, L2 and L3

The synthetic pathways to obtain intermediate and final compounds are shown in Scheme 2.

Stage 1: Cyanuric chloride (13.0 g, 70 mmol) was added into a solution of sodium bicarbonate (6.5 g, 77 mmol) in methanol (100 ml) at 10 °C and the resulting suspension was stirred for 1 h at room temperature. Solid white product was removed by filtration. Dry product was recrystallized in hot hexane to give 2,4-dichloro-6-methoxy-*s*-triazine (**DCMT**). **DCAT** (2,4-dichloro-6-amino-

*s*-triazine) was prepared by using a similar procedure: cyanuric chloride (13.0 g, 70 mmol) was dissolved in acetone (30 mL) at 0 °C and poured into 35 mL of iced-water to form a very fine suspension. The resulting suspension was stirred for 15 min at 0 °C and then ammonium hydroxide solution (13.6 g, 28%, 108 mmol) was being gradually added. The mixture was stirred at 0 °C for 30 min and room temperature for 30 min. White solid was filtered, washed with water (2x 100 mL) and dried to obtain pure **DCAT**.

Stage 2: **DCMT** (10.05 g, 55.56 mmol) or **DCAT** (9.2 g, 55.56 mmol) was suspended in tetrahydrofuran (200 ml) and stirred vigorously for 10 min. One portion of hydrazine hydrate (11.5 g, 0.227 mol) was added at room temperature and stirred for 1 h. After that, the mixture was refluxed for additional 12 h. The solution was cooled at room temperature. Cold distilled water was added into solutions and the precipitated products were collected by filtration and dried to obtain pure **DHMT** (2,4-Dihydrazino-6-methoxy-*s*-triazine) and **DHAT** (2,4-Dihydrazine) and **DHAT** (2,4-Dih

Stage 3: A reaction sequence according to Scheme 2 for L1 and L2: DHMT (1.37 g, 8 mmol) was dissolved in 200 mL of anhydrous tetrahydrofuran and then added in one step salicylaldehyde (L1) (1.95 mL, 16 mmol) or *o*-vanillin (L2) (2.43 g, 16 mmol). The solution was heated under reflux over the night. After cooling the solutions to room temperature, the crude products were obtained as a white (L1) and yellow powders (L2). Ligand L3 was prepared by a similar procedure: DHAT (1.25 g, 8 mmol) was dissolved in 200 mL of anhydrous tetrahydrofuran and then *o*-vanillin (L1) (1.95 ml, 16 mmol) was added to produce ultrafine powders.

For **L1** (white powder): Yield: 31%. Elemental analysis (calcd) for  $C_{18}H_{17}N_7O_3$  (379.37): C, 56.99; H, 4.52; N, 25.84%. Found: C, 56.78; H, 4.61; N, 25.69%. IR (ATR, v/cm<sup>-1</sup>): v = 3568 (w); 2914 (w); 1618 (s); 1574 (s); 1516 (s); 1479 (s); 1366 (s); 1268 (m); 1156 (m); 951 (w); 799 (m); 742 (s).

For L2 (yellow powder): Yield: 32%. Elemental analysis (calcd) for  $C_{20}H_{21}N_7O_5$  (439.42): C, 54.67; H, 4.82; N, 22.31%. Found: C, 54.53; H, 4.71; N, 22.19%. IR (ATR, v/cm<sup>-1</sup>): v = 3542 (w); 2933 (w); 1621 (s); 1578 (s); 1516 (s); 1461 (m); 1371 (s); 1269 (m); 1172 (m); 952 (w); 804 (m); 748 (s).

For L3 (yellow powder): Yield: 38%. Anal. Calcd. for  $C_{19}H_{20}N_8O_4$  (424.41): C, 53.77; H, 4.75; N, 26.40%. Found: C, 53.62; H, 4.89; N, 26.28%. IR (ATR, v/cm<sup>-1</sup>): v = 3484 (w); 3268 (w); 3177 (w); 2978 (w); 1566 (s); 1471 (m); 1422 (s); 1246 (s); 1077 (w); 725 (w).

Please insert Scheme 2 here

### 2.3. Synthesis of complex $[UO_2(L1)] \cdot 2(DMF)$ (1)

*Caution:* Uranium salts were used during the procedure of these experiments, which entailed radioactive hazards associated with uranium salts. Uranium is a toxic metal so care had to be taken during the manipulation.

A suspension of L1 (379.4 mg; 1 mmol) in DMF (30 mL) and UO<sub>2</sub>(OCOCH<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (424 mg; 1 mmol) was treated with Et<sub>3</sub>N (1.51 mL; 1.5 mmol). The final solution was stirred for 1 h and

subsequently filtered. The dark red filtrate was left to evaporate slowly, giving dark red crystals suitable for X-ray diffraction analysis, formed after three weeks. The crystals were filtered off, washed with a little diethyl ether and stored under vacuum. Yield: 23%. Elemental analysis (calcd) for  $C_{24}H_{29}N_9O_7U$  (793.59) (1): C, 36.32; H, 3.68; N, 15.89%. Found: C, 36.19; H, 3.81; N, 15.34%. IR (ATR, v/cm<sup>-1</sup>): v = 3141 (w); 2956 (w); 1651 (s); 1602 (m); 1537 (s); 1461 (m); 1385 (w); 1357 (m); 1092 (w); 889 (s); 797 (m); 752 (m); 662 (w).

### 2.4. Synthesis of complex $[UO_2(L2)]$ ·2(DMF) (2)

The synthesis of **2** was performed in the same way as the preparation of **1**, using ligand L2 (439.4 mg; 1 mmol). Dark red plate crystals in 20% yield. Elemental analysis (calcd) for  $C_{26}H_{33}N_9O_9U$  (853.64) (**2**): C, 36.58; H, 3.90; N, 14.77%. Found: C, 36.42; H, 3.77; N, 14.61%. IR (ATR, v/cm<sup>-1</sup>): v = 3451 (w); 2933 (w); 2833 (w); 1654 (s); 1531 (s); 1455 (m); 1384 (s); 1248 (m); 1215 (w); 1082 (m); 889 (s); 744 (w); 726 (w); 663 (w).

### 2.5. Synthesis of complex [UO<sub>2</sub>(L3)]·2(DMF) (3)

A suspension of L3 (424.4 mg; 1 mmol) in DMF (30 mL) and UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (502 mg; 1 mmol) was treated with Et<sub>3</sub>N (1.51 mL; 1.5 mmol). The resulting solution was stirred for 1 h and subsequently filtered. The dark red filtrate was left to evaporate slowly, giving dark red pillar crystals suitable for X-ray diffraction analysis, formed after three weeks. The crystals were filtered off, washed with a little diethyl ether and stored under vacuum. Yield: 30%. Elemental analysis (calcd) for:  $C_{25}H_{32}N_{10}O_8U$  (838.64) (3): C, 35.81; H, 3.85; N, 16.70%. Found: C, 35.55; H, 3.98; N, 16.60%. IR (ATR, v/cm<sup>-1</sup>): v = 3420 (w); 3341 (m); 3250 (w); 2927 (w); 1651 (s); 1614 (s); 1508 (m); 1437 (s); 1247 (m); 1081 (m); 890 (s); 745 (m).

### 3. Results and discussion

### 3.1. IR spectra

The infrared spectra of the three complexes 1-3 were recorded in the region 4000-500 cm<sup>-1</sup> (Fig. S1-S3 in ESI). The vibrational spectrum is one of the most effective methods to characterize the U=O bonding in uranyl complexes. This study shows that the ligands are well suited to form stable complexes with dioxouranium(VI) units. In the spectra of  $[UO_2(L1)]\cdot 2(DMF)$  (1),  $[UO_2(L2)]\cdot 2(DMF)$  (2) and  $[UO_2(L3)]\cdot 2(DMF)$  (3), the presence of the  $UO_2^{2+}$  unit is confirmed by a strong band at 890 cm<sup>-1</sup> (Table 1) [33]. After coordination, the various vibrations of U-O are assigned to bands occurring at 550-520 cm<sup>-1</sup> and U-N are assigned to weak bands occurring at 420-410 cm<sup>-1</sup>, respectively, which confirms the involvement of the oxygen and nitrogen atoms in the coordination sphere of uranyl(VI) [34]. The characteristic C=N stretching of triazine ring in L1, L2 and L3 appears as a strong signal in the range of 1580-1560 cm<sup>-1</sup>. Weak absorption bands in the range 1270-1150 cm<sup>-1</sup> are typical of the C-O-C bonds [35]. The absorption bands around 3450-3250 cm<sup>-1</sup> in complex **3** are assigned to antisymmetric and

#### Please insert Table 1 here

#### 3.2. UV-vis and luminescence properties

Solutions of the ligands and complexes for absorption and fluorescence spectra were prepared in DMF. The calculation of molar absorption coefficients of the ligands and complexes is presented in Table 2. The L1 ligand has two strong absorption bands at 302 nm, 342 nm and a weak absorption band with maximum around 375–405 nm (Fig. 1). The L2 ligand has one strong absorption band with maximum at 318 nm and a weak absorption band with maximum around 392–410 nm. The hump in 360–366 nm region is caused by changing the lamp in a spectrophotometer. The L3 ligand has one strong absorption band with maximum at 314 nm. The absorption maxima of the uranyl complexes are found at 321 nm (1), 320 nm (2) and 311 nm (3). All the three uranyl complexes have weaker absorption properties than the respective ligands and their spectra are bathochromically shifted by long tail up to 600 nm.

Please insert Table 2 here

### Please insert Figure 1 here

Fluorescence spectra of ligands and complexes were measured upon the excitation wavelength around their absorption maximum. Presented spectra were collected from three repetitions.

All fluorescence spectra have uniform shape with one broad band and one maximum (Fig. S4 in ESI). Spectra of ligands L2 and L3 and all uranyl(VI) complexes 1–3 have the emission maximum around 415 nm (L2: 414 nm, L3: 414.5 nm, 1: 416 nm, 2: 416.5 nm, 3: 415 nm). The emission maximum of the ligand L1 (Fig. 2) is from these values slightly bathochromically shifted to 429 nm (ca. 14 nm shift). The emission intensity of the uranyl(VI) complexes decreases steeply towards longer wavelengths to the emission maximum, unlike in the case of ligands L2 and L3.

#### Please insert Figure 2 here

Fluorescence emission spectra of uranyl(VI) complexes are very similar to emission spectra of ligands which indicates that emission especially comes from the ligands, not from uranyl(VI) cation. We assume that uranyl(VI) central ion specifically affected ligand fluorophores by coordination that causes characteristic shape and emission maximum of the complexes.

### 3.3. X-ray structure of complexes 1, 2 and 3.

In all the present compounds,  $UO_2$  units are perpendicularly embedded in approximate pentagonal formations (Fig. 3) of donor atoms, giving overall seven-coordinate uranium atoms

(Fig. 4). The uranium atom and the five donor atoms of the ligand fit in least-squares planes with r.m.s. deviations ranging from 0.0324 Å in **1** to 0.1165 Å in **3**. The deviations from planarity are further developed in the ligand frameworks, being particularly pronounced in **2** and **3**. The planes of aromatic rings C1 to C6 and C12 to C17 are progressively deflected from the aforementioned least-squares planes through the uranium and the donor atoms (Fig. 5). All methoxy groups are essentially in-plane with the attached aromatic rings, giving rise to torsion angles not larger than  $4.8(5)^{\circ}$ .

Selected bond lengths and angles are listed in Table 4. The present structures are best compared 2,6-diacetylpyridine-bis(4with related uranyl complexes derived from methoxybenzoylhydrazone) (x1), 2,6-diacetylpyridine-bis(N4-phenylsemicarbazone) (x2) and 2,6diacetylpyridine(benzoylhydrazone)-(N4-phenylsemicarbazone) (x3) [38, 39]. While the N-U-N bond angles in 1 to 3 are very similar to related angles in x1 to x3, the O-U-N angles are significantly wider as a result of larger bite distances of donor atoms attached to aromatic rings in 1 to 3. Accordingly, the O-U-O angles in 1 to 3 are narrower, while still larger than in sterically less confined environments in seven-coordinate uranium complexes with a tridentate and two monodentate ligands [40, 41]. All the 1 to 3 crystallize with two molecules of DMF per formula unit. In spite of the presence of DMF which is often found to complete coordination polyhedra of uranyl complexes with salen-type ligands [42-44], interactions between DMF and the uranium atoms in 1 to 3 were not observed. Obviously, the narrow O-U-O angles prevent an increase of the uranium coordination number to eight that is observed for the related complex  $x^2$  in the presence of DMSO.

Although coordinate bonds were not observed between DMF molecules and the uranium atoms, N-H...O hydrogen bonds connect all the NH moieties of the ligands with the DMF molecules. While in **2** and **3** this results in  $[UO_2(L2)]\cdot 2(DMF)$  and  $[UO_2(L3)]\cdot 2(DMF)$  units, respectively, due to a simple 1:1 N-H...O bonding pattern, in **1** supramolecular dimers are formed through 1:2 N-H...O bonds, as shown in Figure 6. The N...O donor-to-acceptor distances in these hydrogen bonds range from 2.691(6) to 3.065(6) Å. The presence of NH<sub>2</sub> moiety in **3** leads to the formation of a group of N-H...O interactions between neighboring  $[UO_2(L3)]$  molecules, with N...O donor-to-acceptor distances ranging from 2.966(3) to 3.147(3) Å. A linear hydrogen-bonded chain is thus formed which extends along the crystallographic *c*-direction (Fig. 7).

Please insert Figure 3 here

Please insert Figure 4, 5, 6, 7 here

Please insert Table 3 here

Please insert Table 4 here 

### 3.4. Thermal analyses

TG and DTA/DSC experiments show that the complexes 1 and 2 follow similar decomposition pathways. The first weight losses up to 200 °C correspond to the evaporation of DMF. The thermal degradation proceeds in two stages in temperature range 300-600 °C (Figs. S5(1)-S6(2) in ESI), starting with a precipitous mass decrease accompanied by strong exothermic effects with a maximum at 380 °C for 1 and 351 and 422 °C for 2, respectively. The following decomposition proceeds over a broader temperature range between 400 and 600 °C.

Please insert Figure 8 here

#### Please insert Table 5 here

The TG curve of **3** again shows the loss of DMF up to 230 °C and subsequent decomposition of the organic part of the complex. In opposite to **1** and **2**, the thermal degradation of **3** is initiated by a gradual mass decrease over a broad temperature range up to 500 °C, followed by a sudden weight drop accompanied by a strong exothermic effect with a maximum at 550 °C. As suggested by a shoulder peak near the exothermic maximum, the step consists of at least two reaction processes. Powder XRD measurement done on the residue left after the thermal decomposition of **3** confirmed the U<sub>3</sub>O<sub>8</sub> phase (Fig. S7 in ESI). The thermal analysis data are summarized in Table 5 including theoretical weight losses calculated for the transformation of the complexes to U<sub>3</sub>O<sub>8</sub>.

#### 4. Conclusions

This work has presented the preparation of three novel pentadentate triazine-based ligands and their mononuclear  $U^{VI}O_2$  complexes, which were characterized by X-ray crystallography and IR, UV-vis, fluorescence spectroscopy and TG/DTA/DSC. The ligands are bound to the  $U^{VI}O_2$  units using one of the triazine N atoms and two chelate arms, giving overall five-coordinate uranyl cations. Higher metal coordination numbers resulting from the saturation of the coordination sphere by DMF were not achieved due to small O-U-O angles. The DMF molecules interact with the NH units of the ligands by hydrogen bonding and a supramolecular 1D chain is allowed through N-H…O hydrogen bonding in the presence of the ligand with NH<sub>2</sub> moiety.

The prepared ligands L1-L3 confirm the usefulness of novel pentadentate triazine-based derivatives as excellent in-plane chelating ligands, which are easily derivatized and can be considered as interesting alternatives to salen ligands.

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### Appendix A. Supplementary Data

X-ray crystallographic files in CIF format have been deposited at the Cambridge Crystallographic Data Center, CCDC Nos. 1060125, 1060126 and 1432228. This material is available free of charge on the Internet at via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>. Supplementary data associated with this article can be found, in the online version.

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### **Figure captions**

Scheme 1. Differential reactivity of cyanuric chloride with  $R-NH_2$ ,  $R^1-NH_2$ ,  $R^2-NH_2 = N$  nucleophiles.

Scheme 2. Reagents and conditions: (a)  $NH_3$  (aq),  $CH_3COCH_3$ , 0 °C, 1 h; (b)  $CH_3OH$ ,  $NaHCO_3$ , 10 °C, 1 h; (c)  $N_2H_4$ · $H_2O$ , THF, reflux 12 h; (d)  $CH_3OH$ , reflux 24 h.

Fig. 1. The molar absorption coefficients spectra of ligands L1–L3, complexes 1–3.

**Fig. 2.** Fluorescence emission spectra of ligand L1 and complex 1. Concentration and excitation wavelength of L1:  $c = 5.5 \cdot 10^{-4}$  M,  $\lambda_{exc} = 300$  nm, 1:  $c = 6.3 \cdot 10^{-5}$  M,  $\lambda_{exc} = 321$  nm.

Fig. 3. Coordination polyhedron of the uranium atom in 1.

**Fig. 4.** The structure of **1** showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level.

Fig. 5. Conformations of 1, 2 and 3 (from top). Angles of aromatic ring planes to equatorial coordination planes (see text) are  $8.3/7.8^{\circ}$  (1),  $26.1/7.9^{\circ}$  (2), and  $28.6/28.7^{\circ}$  (3).

Fig. 6. Hydrogen bonding pattern in 1.

Fig. 7. Linear polymers of 3 resulting from multiple N-H...O hydrogen bonds.

Fig. 8. TG and DSC curves for 3.







Scheme 2.

















Fig. 8.

|         | I riazine bands        | Selected Type           | v <sub>asym</sub> U- | v <sub>sym</sub> U-O | 0-0        | U-N |
|---------|------------------------|-------------------------|----------------------|----------------------|------------|-----|
| complex |                        | of stretching           | 0                    |                      | (phenolic) |     |
| L1      | 1573 (C=N)             | 1038-952 (N-N);         | -                    | -                    | -          | -   |
| 1       | 1651, 1602, 1537, 1461 | 1032-969 (N-N)          | 889                  | 860                  | 520        | 409 |
| L2      | 1578 (C=N)             | 1048-942 (N-N)          | -                    | -                    | -          | -   |
| 2       | 1645, 1599, 1527, 1459 | 1055-959                | 890                  | 863                  | 518        | 414 |
| L3      | 1566 (C=N)             | 1020-940 (N-N)          | -                    | -                    | -          | -   |
| 3       | 1651, 1614, 1551, 1508 | 1032-969 (N-N);         | 890                  | 858                  | 521        | 412 |
|         |                        | 3338 (NH <sub>2</sub> ) |                      |                      |            |     |
|         |                        |                         |                      |                      |            |     |
| C       |                        |                         |                      |                      |            |     |

Table 1 Selected infrared spectral data of ligands L1, L2, L3 and complexes 1, 2 and 3 (v/cm<sup>-1</sup>).

### Table 2

Absorption properties of ligands L1–L3 and complexes 1–3.

|    | $\lambda_{\rm max}$ , nm, ( $\varepsilon$ , mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup> ) |  |
|----|--|--|
| L1 | 293 (33600), 302 (38800), 332 (36500), 342 (37400), 375 (4900),                                  |  |
|    | 405 (3500)   |  |
| 1  | 308 (25000), 321 (25800), 361 (25200)  |  |
| L2 | 318 (43700), 344 (21500), 392 (3400), 410 (3100)   |  |
| 2  | 320 (28000), 366 (19700)   |  |
| L3 | 315 (39600), 340 (21200)   |  |
| 3  | 311 (32600), 371 (16200)   |  |

Concentration of L1  $c = 1.5 \cdot 10^{-5}$  M, 1  $c = 3.5 \cdot 10^{-5}$  M, L2  $c = 1.4 \cdot 10^{-5}$  M, 2  $c = 4.9 \cdot 10^{-5}$  M, L3  $c = 4.5 \cdot 10^{-5}$  M, 3  $c = 2.7 \cdot 10^{-5}$  M.

### Table 3

ROUT

X-ray structure data collection and refinement parameters for complex  $[UO_2(L1)]\cdot 2(DMF)$  (1),  $[UO_2(L2)]\cdot 2(DMF)$  (2),  $[UO_2(L3)]\cdot 2(DMF)$  (3).

|   | 1                     | 2                     | 3                        |
|---|-----------------------|-----------------------|--------------------------|
| Empirical formula   | $C_{24}H_{29}N_9O_7U$ | $C_{26}H_{33}N_9O_9U$ | $C_{25}H_{32}N_{10}O_8U$ |
| Formula weight  | 793.59                | 853.64                | 838.64                   |
| Crystal system  | monoclinic            | monoclinic            | orthorhombic             |
| Space group   | $P2_{1}/c$            | $P2_{1}/c$            | $P2_{1}2_{1}2_{1}$       |
| a (Å)   | 13.8612(6)            | 8.338(4)              | 12.58820(10)             |
| b (Å)   | 22.7398(8)            | 26.555(3)             | 13.89550(10)             |
| c (Å)   | 8.9752(4)             | 13.767(2)             | 17.5978(2)               |
| α (°)   | 90                    | 90                    | 90                       |
| β (°)   | 102.849(4)            | 90.36(2)              | 90                       |
| γ (°)   | 90                    | 90                    | 90                       |
| V (Å <sup>3</sup> )   | 2758.2(2)             | 3048.2(16)            | 3078.20(5)               |
| Z   | 4                     | 4                     | 4                        |
| $D_{calcd.}$ (g· cm <sup>-3</sup> )   | 1.911                 | 1.860                 | 1.810                    |
| F(000)  | 1536                  | 1664                  | 1632                     |
| $\mu(\text{mm}^{-1})$   | 5.946                 | 5.392                 | 5.336                    |
| Measured/unique reflections   | 15012/5045            | 17135/5562            | 18424/5623               |
| Data/restraints/parameters  | 5045/6/375            | 5562/0/413            | 5623/0/397               |
| $R_1/wR_2 [I > 2\sigma(I)]$   | 0.0337/0.0751         | 0.0481/0.0942         | 0.0151/0.0386            |
| $R_1/wR_2$ [all data]   | 0.0382/0.0785         | 0.0634/0.1013         | 0.0153/0.0387            |
| GooF  | 1.038                 | 1.169                 | 1.088                    |
| $\Delta \rho_{\text{max}} / \Delta \rho_{\text{min}}$ (e. Å <sup>-3</sup> ) | 2.680/-1.256          | 3.491/-1.155          | 0.961/-0.391             |

### Table 4

Selected bond lengths [Å] and angles [°] for  $[UO_2(L1)] \cdot 2(DMF)$  (1),  $[UO_2(L2)] \cdot 2(DMF)$  (2),  $[UO_2(L3)] \cdot 2(DMF)$  (3) and related compounds  $[UO_2(x1)], [UO_2(x2)(DMSO)]$  and  $[UO_2(x3)]$ .

|          | 1          | 2         | 3          | $[UO_2(\mathbf{x1})]^a$ | $[UO_2(\mathbf{x2})(DMSO)]^b$ | $[\mathrm{UO}_2(\mathbf{x3})]^{\mathrm{b}}$ |
|----------|------------|-----------|------------|-------------------------|-------------------------------|---|
| U1–O1    | 1.772(3)   | 1.776(5)  | 1.7791(19) | 1.77(1)                 | 1.752(5)                      | 1.70(2)                                     |
| U1–O2    | 1.770(3)   | 1.775(5)  | 1.7803(19) | 1.77(1)                 | 1.763(5)                      | 1.726(1)                                    |
| U1–O3    | 2.210(4)   | 2.223(5)  | 2.235(2)   | 2.32(1)                 | 2.360(5)                      | 2.30(1)                                     |
| U1–O4    | 2.216(3)   | 2.205(5)  | 2.225(2)   | 2.30(1)                 | 2.368(5)                      | 2.33(1)                                     |
| U1-N1    | 2.613(4)   | 2.596(6)  | 2.597(2)   | 2.47(1)                 | 2.559(6)                      | 2.53(2)                                     |
| U1-N6    | 2.610(4)   | 2.608(6)  | 2.576(2)   | 2.49(1)                 | 2.583(6)                      | 2.55(2)                                     |
| U1-N7    | 2.495(4)   | 2.499(6)  | 2.503(2)   | 2.52(1)                 | 2.610(6)                      | 2.54(2)                                     |
| O1–U1–O2 | 174.07(16) | 175.8(2)  | 176.54(8)  | 178.8(5)                |                               |   |
| O3–U1–O4 | 94.89(13)  | 96.46(18) | 96.43(8)   | 106.8(5)                | 113.7(2)                      | 109.9(6)                                    |
| O3-U1-N1 | 69.62(13)  | 69.84(19) | 69.97(7)   | 63.5(5)                 | 61.5(2)                       | 62.7(5)                                     |
| O4-U1-N6 | 69.89(13)  | 69.73(18) | 70.11(8)   | 63.3(4)                 | 61.3(2)                       | 63.7(6)                                     |
| N1-U1-N7 | 62.75(13)  | 61.92(19) | 62.31(8)   | 63.3(4)                 | 61.6(2)                       | 61.2(5)                                     |
| N6U1N7   | 62.90(13)  | 62.52(19) | 62.11(8)   | 63.3(4)                 | 61.1(2)                       | 62.4(6)                                     |

X-ray diffraction data collected at 295 K<sup>a</sup> and 293 K<sup>b</sup>.

### Table 5

Residual Mass loss I Mass loss II<sup>b</sup> Complex Step I (°C) found/calcd<sup>a</sup> Endo I (°C) Step II<sup>b</sup> (°C) Exo II<sup>b</sup> (°C) massfound  $\Delta m_{tot}(\%)$ (%)  $^{c}$ /calcd  $^{d}(\%)$ (%) 130-170 18.8/18.4 350-415 34.0 65.5 34.5/35.4 1 150 380 66.8 2 16.0/17.1 27.6 33.3/32.9 124-153 140 330-387 351 387-443 14.6 422 66.15 142-235 17.2/17.4 529-600 32.6 33.5/33.5 3 160 550

Thermal analysis data for complexes 1 - 3.

<sup>a</sup> Mass loss calculated for two molecules of DMF.

<sup>b</sup> Values given for prominent exothermic event(s). <sup>c</sup> Values given for t = 650 °C

<sup>d</sup>Residual mass calculated for  $U_3O_8$  established by XRD (Fig. S7).

### <u>Graphical abstract – pictogram</u>

Three new mononuclear uranyl complexes have been synthesized using three new Schiff-base ligands based on *s*-triazine derivative. Crystal structures show pentagonal bipyramidal geometry around uranium atom with the 3-aza and 2-oxo coordinating sites of the ligand.



### **Graphical Abstract – Synopsis**

- Three new uranyl(VI) complexes of a Schiff-base ligands based on *s*-triazine derivative have been synthesized.
- The X-ray crystal structures of [UO<sub>2</sub>(L1)]·2(DMF) (1), [UO<sub>2</sub>(L2)]·2(DMF) (2) and [UO<sub>2</sub>(L3)]·2(DMF) (3) have been determined.
- The luminescence, FTIR and UV-vis spectra of [UO<sub>2</sub>(L1)]·2(DMF) (1), [UO<sub>2</sub>(L2)]·2(DMF) (2) and [UO<sub>2</sub>(L3)]·2(DMF) (3) have been studied.
- The TG and DTA/DSC analyses of [UO<sub>2</sub>(L1)]·2(DMF) (1), [UO<sub>2</sub>(L2)]·2(DMF) (2) and [UO<sub>2</sub>(L3)]·2(DMF) (3) have been determined.