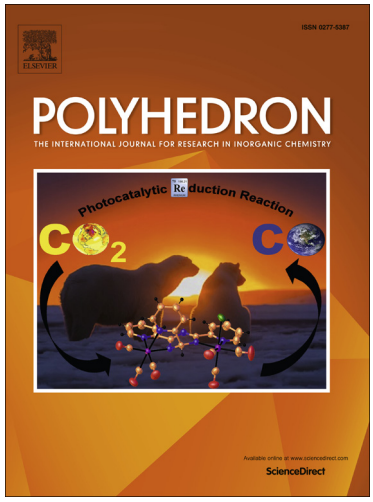

Synthetic and structural studies of piperidine carboxamide uranyl ion complexes

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Synthetic and structural studies of piperidine carboxamide uranyl ion complexes.

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ABSTRACT

New piperidine based ligands of the type [$C_5H_{10}NCONR_2$] (where R = CH_3 (**L1**), C_2H_5 (**L2**) and $^iC_3H_7$ (**L3**)) have been prepared and characterized. The complex chemistry of these ligands with uranyl chloride, bromide, nitrate and β-diketonates has been studied using IR and NMR spectroscopic methods. Crystal structures for the complexes [$UO_2Cl_2(L3)_2$] (**1**), [$UO_2Br_2(L3)_2$] (**2**) [$UO_2(NO_3)_2(L3)_2$] (**5**) and [$UO_2(C_4H_3SCOCHCOCF_3)_2(L3)$] (**8**) have been determined by the X-ray diffraction method. The structures of **1** and **2** show that the uranyl ion is surrounded by two of the ligands and two halogen atoms in an octahedral geometry. The structure of **5** shows that the uranyl group is surrounded by two nitrate groups and two ligands in a hexagonal bipyramidal geometry. The structure of **8** shows that the uranyl group is surrounded by two β-diketonates and one ligand in a pentagonal bipyramidal geometry. The structures show that the carboxamide ligands are strongly bonded to the uranyl group, showing a near linear geometry for the U-O-C bond (angle 150-159°). The prepared chloro and bromo compounds are air and moisture stable and show good solubility in normal organic solvents.

Keywords: Piperidine carboxamide, Uranyl Chloride, Bromide, Nitrate, β-Diketonate, Structures

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1. Introduction

Actinide separation from high level liquid waste emanating from the back end fuel cycle of the nuclear industry is very challenging [1]. Study of actinide coordination chemistry with various extractants containing different functional groups is very much essential to develop the technologies for the reprocessing of the irradiated fuel and safe handling of the actinides [2-6]. N-substituted amides are proposed to be very promising extractants for the solvent extraction removal of actinides from other fission products in nitric acid medium [7-11]. Their ease of synthesis, complete incinerability and high stability constants with actinides make them very good competitors with respect to tributyl phosphate. Moreover, the solvent extraction ability of uranium(VI) from acidic medium can be enhanced by using a mixture of β-diketone and neutral ligands [12]. Previously, we reported the chemistry of isobutyramide based ligands with uranium(VI) ions and showed that the ligands selectively separate the uranium(VI) ion from a large excess of thorium and lanthanide ions [13]. This property indicates their applicability as suitable extractants for the selective partitioning of ^{233}U in AHWR spent fuel reprocessing [14]. In addition, isobutyramide based ligands form air and moisture stable uranyl halide compounds and these compounds are used as synthetic precursors for making uranyl halide compounds [15]. In continuation of our interest in the chemistry of the uranyl ion with newly synthesized ligands, we report herein the synthesis, characterization and complex chemistry of piperidine based carboxamide ligands with uranyl chloride, bromide, nitrate and β-diketonates.

2. Experimental

2.1 Materials and methods

All the chemicals were purchased from commercial source and used without further purification. Infrared spectra were recorded using a JASCO-610 FITR spectrometer as KBr pellets in the range 400-4000 cm^{-1}. NMR spectra were recorded on a Brucker AMX-300 spectrometer using $CDCl_3$ as the solvent.

2.2 Synthesis of **L1**

To a solution of N,N-dimethyl carbamoyl chloride (10.75 g, 0.1 mol) in (50 mL) benzene, a solution of piperidine (8.52 g, 0.1 mol) and triethyl amine (12.1 g, 0.12 mol) in benzene (50 mL) was added slowly with stirring. The reaction mixture was refluxed for 2 hours and treated with 100 ml. of 5% HCl solution. The organic layer was separated, dried over anhydrous sodium sulfate and filtered. The solution on evaporation yielded a colorless liquid. Yield: 62%. *Anal*. Found: C, 60.5; H, 10.1; N, 17.5. Calcd. for $C_8H_{16}N_2O$: C, 61.5; H,10.25; N, 17.9 % . ^{1}H NMR ($CDCl_3$, 25 °C) δ: 2.85 (br, 4H, 2,6-piperidyl CH_2), 2.50 (s, 6H, $N(CH_3)_2$), 1.26 (br, 6H, piperidyl CH_2). IR (cm^{-1}) ν: 1653 (C=O).

2.3 Synthesis of **L2**

This was prepared similarly to **L1** in 76% yield by taking N,N-diethyl carbamoyl chloride. *Anal*. Found: C, 64.5; H, 10.3; N, 15.5. Calcd. for $C_{10}H_{20}N_2O$: C, 65.2; H, 10.9; N, 15.2 %. ^{1}H NMR ($CDCl_3$, 25 °C) δ: 3.15 (8H, 2,6-piperidyl CH_2 and $N(C_2H_5)_2$ CH_2), 1.55 (br, 6H, 3,4,5-piperidyl CH_2), 1.09 (t, J = 7.0 Hz, 6H, $N(C_2H_5)_2$ CH_3). IR (cm^{-1}) ν: 1622 (C=O).

2.4 Synthesis of **L3**

This was prepared similarly to **L1** in 94% yield by taking N,N-diisoproyl carbamoyl chloride. *Anal*. Found: C, 66.6; H, 10.7; N, 13.0. Calcd. for $C_{12}H_{24}N_2O$: C, 67.9; H, 11.3; N, 13.2 %. ^{1}H NMR ($CDCl_3$, 25 °C) δ: 3.48 (m, 2H, N(^{i}Pr$_2$) CH), 2.91 (br, 4H, 2,6-piperidyl CH_2), 1.44 (br, 6H, 3,4,5-piperidyl CH_2), 1.15 (d, J = 6.6 Hz, 12H, N(^{i}Pr$_2$) CH_3). IR (cm^{-1}) ν: 1651 (C=O).

2.5 Synthesis of **1**

Solid UO_3 (300 mg) was dissolved in 4 mL of concentrated HCl and the volume of the solution was reduced completely to dryness on a hot plate. The orange colored solid thus obtained was dissolved in 10 mL of methanol to give a clear solution. To this solution N,N-diisopropylpiperidine-1-carboxamide was added and heated for 2 min. The volume of the solution was reduced to 2mL, and 20 mL of diethyl ether was added into it with stirring. The yellow product formed was filtered, washed with ether and dried in air. This product was recrystallized from a chloroform/isooctane mixture to give a crystalline solid. Yield 89%. *Anal*. Found: C, 37.2; H, 6.0; N, 7.2. Calcd. for $C_{24}H_{48}N_4O_4Cl_2U$: C, 37.6; H, 6.3; N, 7.3 %. IR (cm^{-1}) ν: 1524 (C=O), 924 ($U=O_{assy}$).

2.6 *Synthesis of* **2**

This was synthesized similar to **1**, by taking concentrated HBr instead of HCl. Yield 85%. *Anal*. Found: C, 33.2; H, 5.2; N, 6.2. Calcd. for $C_{24}H_{48}N_4O_4Br_2U$: C, 33.7; H, 5.6; N, 6.6 %. IR (cm^{-1}) ν: 1525 (C=O), 928 ($U=O_{assy}$).

2.7 Synthesis of **3**

To a solution of N,N-dimethylpiperidine-1-carboxamide (200 mg, 1.29 mmol) in chloroform, solid $UO_2(NO_3)_2.6H_2O$ (300 mg, 0.59 mmol) was added with stirring. The solution was allowed to stir until all the uranyl nitrate dissolved to give a clear solution. This solution was filtered and layered with isooctane. This solution on slow evaporation yielded a yellow crystalline solid. This was filtered, washed with hexane and air dried. Yield: 89%. *Anal*. Found: C, 26.7; H, 4.2; N, 11.5. Calcd. for $C_{16}H_{32}N_6O_{10}U$: C, 27.2; H, 4.5; N, 11.9 %. ^{1}H NMR ($CDCl_3$, 25 °C) δ: 3.55 (br, 4H, 2,6-piperidyl CH_2), 3.14 (s, 6H, $N(CH_3)_2$), 1.63 (br, 6H, 3,4,5-piperidyl CH_2). IR (cm^{-1}) ν: 1525 (C=O), 925 ($U=O_{assy}$).

2.8 Synthesis of **4**

This was prepared similarly to **3** by taking $UO_2(NO_3)_2.6H_2O$ (300 mg, 0.59 mmol) and N,N-diethylpiperidine-1-carboxamide (240 mg, 1.3 mmol). Yield 86%. *Anal*. Found: C, 31.1; H, 4.8; N, 10.7. Calcd. for $C_{20}H_{40}N_6O_{10}U$: C, 31.5; H, 5.2; N, 11.0 %. ^{1}H NMR ($CDCl_3$, 25 °C) δ: 3.52 (br, 8H, 2,6-piperidyl CH_2 and $N(C_2H_5)_2$ CH_2), 1.63 (br, 6H, 3,4,5-piperidyl CH_2), 1.26 (s, 6H, $N(C_2H_5)_2$ CH_3). IR (cm^{-1}) ν: 1521 (C=O), 928 ($U=O_{assy}$).

2.9 Synthesis of **5**

This was prepared similarly to **3** by taking $UO_2(NO_3)_2.6H_2O$ (300 mg, 0.59 mmol) and N,N-diisopropylpiperidine-1-carboxamide (270 mg, 1.27 mmol). Yield 85%. *Anal*. Found: C, 35.1; H, 5.8; N, 10.1. Calcd. for $C_{24}H_{48}N_6O_{10}U$: C, 35.2; H, 5.9; N, 10.2 %. ^{1}H NMR ($CDCl_3$, 25 °C) δ: 3.90 (br, 2H, $N(^iPr_2)$ CH), 3.40 (br, 4H, 2,6-piperidyl CH_2), 1.56 (br, 6H, 3,4,5-piperidyl CH_2), 1.41 (d, J = 6.0 Hz, 12H, $N(^iPr_2)$ CH_3). IR (cm^{-1}) ν: 1522 (C=O), 932 ($U=O_{assy}$).

2.10 Synthesis of **6**

To a dichloromethane solution of N,N-dimethylpiperidine-1-carboxamide (70 mg, 0.44 mmol), solid $UO_2(C_8H_5F_3O_2S)_2.2H_2O$ (300 mg, 0.4 mmol) was added and refluxed for 2 hours with constant stirring. This solution was filtered and layered with isooctane. This solution on slow evaporation yielded bright yellow colored needle shaped crystals in 94% yield. *Anal*. Found: C, 32.8; H, 2.7; N, 3.1. Calcd. for $C_{24}H_{24}N_2O_7F_6S_2U$: C, 33.2; H, 2.8; N, 3.2 %. ^{1}H NMR ($CDCl_3$, 25 °C) δ: 8.26 (s, 2H, thiophene CH), 7.83 (t, J = 6.6 Hz, 2H, thiophene CH), 7.28 (q, J = 4.5 Hz, 2H, thiophene CH), 6.79 (s, 2H, TTA CH), 3.59 (br, 4H, piperidyl CH_2), 3.22 (s, 6H, $N(CH_3)_2$), 1.63 (br, 6H, piperidyl CH_2). IR (cm^{-1}) ν: 1618 (C=O, TTA), 1540 (C=O, L1), 919 ($U=O_{assy}$).

2.11 Synthesis of **7**

This was prepared similarly to **6** in 89% yield by taking $[UO_2(C_8H_5F_3O_2S)_2.2H_2O]$ (300 mg, 0.4 mmol) and N,N-diethylpiperidine-1-carboxamide (80 mg, 0.43 mmol). *Anal*. Found: C, 34.6; H, 2.9; N, 3.0. Calcd. for $C_{26}H_{28}N_2O_7F_6S_2U$: C, 34.8; H, 3.1; N, 3.1 %. ^{1}H NMR ($CDCl_3$, 25 °C) δ: 8.26 (br, 2H, thiophene CH), 7.84 (br, 2H, thiophene CH), 7.28 (d, J = 4.7 Hz, 2H, thiophene CH), 6.79 (s, 2H, TTA CH), 3.52 (br, 8H, piperidyl CH_2 and $N(C_2H_5)_2$ CH_2), 1.61 (br, 6H, piperidyl CH_2), 1.23 (br, 6H, $N(C_2H_5)_2$ CH_3). IR (cm^{-1}) ν: 1591 (C=O, TTA), 1539 (C=O, L2), 922 ($U=O_{assy}$)

2.12 Synthesis of **8**

This was prepared similarly to **6** in 88% yield by taking $[UO_2(C_8H_5F_3O_2S)_2.2H_2O]$ (300 mg, 0.4 mmol) and N,N-diisopropylpiperidine-1-carboxamide (90 mg, 0.42 mmol). *Anal*. Found:

C, 35.8; H, 3.0; N, 3.0. Calcd. for $C_{28}H_{32}N_2O_7F_6S_2U$: C, 36.4; H, 3.5; N, 3.0 %. ^{1}H NMR ($CDCl_3$, 25 °C) δ: 8.25 (t, 2H, thiophene CH), 7.82 (d, 2H, thiophene CH), 7.29 (br, 2H, thiophene CH), 6.79 (s, 2H, TTA CH), 3.91 (s, 2H, N(^{i}Pr$_2$) CH), 3.46 (s, 4H, piperidyl CH_2), 1.56 (s, 6H, piperidyl CH_2), 1.46 (d, J = 6.6 Hz, 12H, N(^{i}Pr$_2$) CH_3). IR (cm^{-1}) ν: 1618 (C=O, TTA), 1540 (C=O, L3), 922 ($U=O_{assy}$).

2.13 Synthesis of **9**

To a solution of N,N-dimethylpiperidine-1-carboxamide (80 mg, 0.51 mmol) in dichloromethane, solid $UO_2(C_6H_5COCHCOC_6H_5)_2.2H_2O$ (350 mg, 0.47 mmol) was added and the resulting mixture was refluxed for 2 hours with constant stirring. The solution was filtered and layered with dodecane. This on slow evaporation yielded an orange red crystalline solid product in 92% yield. *Anal*. Found: C, 51.8; H, 3.9; N, 3.0. Calcd. for $C_{38}H_{38}N_2O_7U$: C, 52.3; H, 4.4; N, 3.2 % . ^{1}H NMR ($CDCl_3$, 25 °C) δ: 8.46 (d, 8H, Ph, DBM), 8.0 (d, 4H, Ph, DBM), 7.58 (br, 8H, Ph, DBM), 7.24 (s, 2H, CH, DBM), 3.53 (br, 4H, piperidyl CH_2), 3.14 (br, 6H, $N(CH_3)_2$), 1.55 (br, 6H, piperidyl CH_2). IR (cm^{-1}) ν: 1591 (C=O, DBM), 1542 (C=O, L1), 907 ($U=O_{assy}$).

2.14 Synthesis of **10**

This was prepared similarly to **9** in 94% yield by taking $[UO_2(C_6H_5COCHCOC_6H_5)_2.2H_2O]$ (350 mg, 0.47 mmol) and N,N-diethylpiperidine-1-carboxamide (90 mg, 0.49 mmol). *Anal*. Found: C, 52.8; H, 4.5; N, 3.0. Calcd. for $C_{40}H_{42}N_2O_7U$: C, 53.3; H, 4.7; N, 3.1 %. ^{1}H NMR ($CDCl_3$, 25 °C): δ 8.49 (br, 8H, DBM Ph), 8.0 (d, 4H, DBM Ph), 7.58 (s, 8H, DBM Ph), 7.25 (s, 2H, DBM CH), 3.53 (br, 8H, piperidyl CH_2 and $N(C_2H_5)_2$

CH_2), 1.52 (s, 6H, piperidyl CH_2), 1.23 (t, J = 6.6 Hz, 6H, $N(C_2H_5)_2$ CH_3). IR (cm^{-1}) ν: 1591 (C=O, DBM), 1542 (C=O, L2), 905 ($U=O_{assy}$).

2.15 Synthesis of **11**

This was prepared similarly to **9** in 89% yield by taking $[UO_2(C_6H_5COCHCOC_6H_5)_2.2H_2O]$ (350 mg, 0.47 mmol) and N,N-diisopropylpiperidine-1-carboxamide (105 mg, 0.5 mmol). *Anal*. Found: C, 53.9; H, 4.5; N, 2.8. Calcd. for $C_{42}H_{46}N_2O_7U$: C, 54.3; H, 4.9; N, 3.0 %. ^1H NMR ($CDCl_3$, 25 °C) δ: 8.61 (br, 4H, DBM Ph), 8.40 (br, 4H, DBM Ph), 8.0 (d, 4H, DBM Ph), 7.59 (s, 8H, DBM Ph), 7.27 (s, 2H, DBM CH), 3.94 (s, 2H, $N(^iPr_2)$ CH), 3.42 (s, 4H, piperidyl CH_2), 1.49 (s, 18H, piperidyl CH_2 and $N(^iPr_2)$ CH_3). IR (cm^{-1}) ν: 1592 (C=O, DBM), 1541 (C=O, L3), 901 ($U=O_{assy}$).

2.16 Crystallography

Crystal data for **1**, **2**, **5** and **8** were measured on an Agilent SuperNova system equipped with a Titan CCD detector at 293(2) K using CuK_α radiation (λ = 1.5418 Å). The crystals were positioned 101 mm from the CCD. 1008, 643, 1750 and 1016 frames were measured respectively for compounds **1**, **2**, **5** and **8** with a counting time of 1s. Data analysis was carried out with the CrysAlis program [16a]. The structures were solved using direct methods with the Shelxs97 program [16b]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were included in the geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they were attached. Empirical absorption corrections were carried out using the ABSPACK program [16c]. The

structures were refined to convergence on F^2 using Shelxl972 [16b]. Selected crystallographic data for **1**, **2**, **5** and **8** are given in Table 1 .

3. Results and Discussion

3.1 Synthesis of the piperidine carboxamide ligands.

Ligands **L1-L3** were prepared by reacting piperidine and N,N'-dialkyl carbamoyl chloride in presence of triethyl amine (Scheme 1). The IR spectra of all ligands show the presence of carbamoyl group in the synthesized ligands. The ^{1}H NMR spectra of all the ligands show the expected peaks and integrations.

3.2 Synthesis of piperidine carboxamide uranyl halo compounds

The reaction of $[UO_2X_2{\cdot}nH_2O]$ (X = Cl or Br) with the ligand **L3** yielded compounds **1** and **2** (Scheme 1). However, similar reactions with **L1** and **L2** yielded hydroscopic products which were therefore not characterized. C, H and N analyses of **1** and **2** revealed that the ratio of ligand to uranyl halide is 2:1 in both compounds. The IR spectra of **1** and **2** show that the water molecules from the starting compounds $[UO_2X_2{\cdot}nH_2O]$ are replaced completely by the ligand. The observed frequency difference for the carbamoyl group ($\Delta\nu_{CO}$ = 125 cm^{-1}, where $\Delta\nu_{CO} = \nu_{CO(\text{free ligand})} - \nu_{CO(\text{coordinated})}$) shows that the carbamoyl group is bonded to the uranyl group directly. This difference is comparable/greater in magnitude than those observed in $[UO_2X_2\{^iC_3H_7CON(^iC_4H_9)_2\}_2]$ (X = Cl or Br) [15], $[[UO_2(NO_3)_2\{^iC_3H_7CON(^iC_4H_9)_2\}_2]$ [13] $UO_2(NO_3)_2$(N-cyclohexyl,2-pyrrolidone)$_2$] [17], $[UO_2(NO_3)_2$(1,3-dimethyl,2-imidazolidone)$_2$] [17] and $[UO_2(NO_3)_2(^iC_3H_7)_2NCOCH_2CON(^iC_3H_7)_2]$ [18].

The ^{1}H NMR spectra of **1** and **2** show the expected peaks and integrations. All the protons are deshielded with respect to the free ligand indicating that the bonding between the

ligand and uranyl group persists in solution. It is apparent from the IR and NMR spectra that the ligand bonds through the carbamoyl groups to the uranyl group. The structures of **1** and **2** have been determined by the single crystal X-ray diffraction method, which confirms these spectral results.

*3.3 Structure of **1** and **2***

The structures of **1** and **2** are shown in Figures 1 and 2, respectively, and selected bond distances and angles are given in Table 2. The structures of both **1** and **2** show a centrosymmetric uranium(VI) ion surrounded by four oxygen atoms and two halogen atoms in an octahedral geometry. The two uranyl oxygen atoms occupy the axial positions. Two oxygen atoms of the two piperidine carboxamide ligands together with two halogen atoms form the equatorial square plane.

This type of coordination is similar to that observed in the compounds of uranyl chloro or bromo compounds such as $[UO_2X_2\{^iC_3H_7CON(^iC_4H_9)_2\}_2]$ (X = Cl or Br) [15] and $[UO_2Cl_2(OPPh_3)_2]$ [19] with monodentate ligand. The average U-O(amide) distance of 2.322(10) Å in **1** and 2.317(5) Å in **2** are comparable in magnitude with those of earlier reported uranyl halide-amide compounds $[UO_2X_2\{^iC_3H_7CON(^iC_4H_9)_2\}_2]$ (2.3151(18) Å for X = Cl and 2.281(4) Å for X = Br) [15]. The observed average U-Cl bond distance 2.683(5) Å in **1** and U-Br distance 2.8073(10) Å in **2** are normal [13,19]. The angles subtended at the metal atom show that the uranium atom has a slightly distorted octahedral geometry.

3.4 Synthesis of uranyl nitrate piperidine carboxamide compounds

The reaction of ligands **L1-L3** with $[UO_2(NO_3)_2 \cdot 6H_2O]$ yielded compounds **3-5** (Scheme 1). C, H and N analyses revealed that the ratio of ligand to uranyl nitrate is 2:1 in all the compounds. The IR spectra of **3-5** show that the water molecules from the starting compound $[UO_2(NO_3)_2 \cdot 6H_2O]$ are completely replaced by the ligand and the ligand is bonded through the carbamoyl oxygen atom to the uranyl group. The observed frequency difference for the carbamoyl group ($\Delta\nu_{CO}$ = 120 cm^{-1}, where $\Delta\nu_{CO} = \nu_{CO\ (free\ ligand)} - \nu_{CO(coordinated)}$) is consistent with the supposition that the carbamoyl group is bonded to the uranyl group directly. This difference is comparable in magnitude with those observed in $[UO_2(NO_3)_2$(N-cyclohexyl,2-pyrrolidone$)_2$] [17], $[UO_2(NO_3)_2$(1,3-dimethyl,2-imidazolidone$)_2$] [17], $[UO_2(NO_3)_2\{^iC_3H_7CON(^iC_4H_9)_2\}_2]$ [13] and $[UO_2(NO_3)_2(^iC_3H_7)_2N\ COCH_2CON(\ ^iC_3H_7)_2]$ [18].

The ^{1}H NMR spectra of **3-5** show the expected peaks and integrations. The protons of the piperidine carboxamide ligands are deshielded by ca. 0.5-0.8 ppm with respect to the free ligand, indicating that the bonding between the carbamoyl oxygen and uranyl group persists in solution. The structure of **5** has been determined by single crystal X-ray diffraction methods and confirms the spectral results.

3.5 Structure of **5**

The structure of **5** is shown in Figure 3, and selected bond distances and angles are given in Table 2. The structure of **5** shows that the uranium atom is surrounded by eight oxygen atoms in a hexagonal bipyramidal geometry. Six oxygen atoms of the two bidentate nitrate groups together with two oxygen atoms of piperidine carboxamide ligands form the equatorial hexagonal plane. The two uranyl oxygen atoms occupy the axial positions.

This type of coordination is similar to that observed in the compounds of monodentate ligands with uranyl nitrate, such as $[UO_2(NO_3)_2$(N-cyclohexylmethyl,2-pyrrolidone$)_2]$ [17], $[UO_2(NO_3)_2$(1,3-dimethyl,2-imidazolidone$)_2]$ [17], $[UO_2(NO_3)_2\{^iC_3H_7CON(^iC_4H_9)_2\}_2]$ [13], $[UO_2(NO_3)(DMF)_2]$ [20], $[UO_2(NO_3)_2$(tetrabutylglutaramide$)_2]$, $[UO_2(NO_3)_2$(tetrabutylglutaramide$)_2]$ [21] and $[UO_2(NO_3)_2(PhN(CH_3)CO(CH_3)NPh)_2]$ [22]. The U-O(amide) distance (2.378(6) Å) in **5** is comparable in magnitude with those of earlier reported uranyl nitrate-amide compounds, such as $UO_2(NO_3)_2$(N-cyclohexylmethyl,2-pyrrolidone$)_2]$ (2.374(2) Å) [17], $[UO_2(NO_3)_2$(1,3-dimethyl,2-imidazolidone$)_2]$ (2.383(2) Å) [17], $[UO_2(NO_3)_2\{^iC_3H_7CON(^iC_4H_9)_2\}_2]$ (2.349(6) Å) [13], $[UO_2(NO_3)(DMF)_2]$ (2.397(6) Å) [20], $[UO_2(NO_3)_2$(tetrabutylglutaramide$)_2]$ (2.378(6) Å), $[UO_2(NO_3)_2$(dibutyldecanamide$)_2]$ (2.37(2) Å) [21] and $[UO_2(NO_3)_2(PhN(CH_3)CO(CH_3)NPh)_2]$ (2.381(2) Å) [22]. The observed average U-O(NO_3) bond distance of 2.527(9) Å is normal. The angles subtended at the metal atom show that the uranium atom has a slightly distorted hexagonal bipyramidal geometry.

3.6 Synthesis of uranyl bis(β-diketonates) piperidine carboxamide compounds

The reactions of **L1-L3** with $[UO_2(OO)_2.2H_2O]$ (OO = $C_4H_3SCOCHCOCF_3$ or $C_6H_5COCHCOC_6H_5$) yielded the compounds **6-11** (Scheme 1). C, H and N analyses revealed that the ratio of ligand to uranyl bis(β-diketonate) is 1:1 in all the compounds. The IR spectra of **6-11** show that the water molecules from the starting compound $[UO_2(OO)_2.2H_2O]$ are completely replaced by the ligand and furthermore the observed frequency difference for the carbamoyl group ($\Delta\nu_{CO}$ = 100-120 cm^{-1}, where $\Delta\nu_{CO} = \nu_{CO\ (free\ ligand)} - \nu_{CO(coordinated)}$) is consistent with the supposition that the carbamoyl group is bonded to the uranyl group directly. This difference is comparable in magnitude with those observed in

$[UO_2(DBM)_2\{^iC_3H_7CON(^iC_3H_7)_2\}_2]$ [13], $[UO_2(NO_3)_2$(N-cyclohexyl,2-pyrrolidone$)_2]$ [17] and $[UO_2(NO_3)_2$(1,3-dimethyl,2-imidazolidone$)_2]$ [17].

The ^{1}H NMR spectra of **6-11** show the expected peaks and integrations. The piperidine carboxamide protons are deshielded by ca. 0.5 ppm with respect to the free ligand, indicating that the bonding between the ligand and uranyl group persists in solution. The structure of **8** has been determined by the single crystal X-ray diffraction method and confirms the spectral and analysis results.

3.7 Structure of **8**.

The structure of **8** is shown in Figure 4 together with the numbering scheme, and selected bond distances and angles are given in Table 2. The structure shows that the uranyl group is bonded to two $C_4H_3SCOCHCOCF_3$ groups and one piperidine carboxamide ligand to give a coordination number of seven. The piperidine carboxamide ligand acts as a monodentate ligand and is bonded through the carbamoyl oxygen to the uranyl group. Four oxygen from two bidentate $C_4H_3SCOCHCOCF_3$ groups and one oxygen from the piperidine carboxamide ligand form the equatorial plane, which together with two oxygen atoms of the uranyl group form a pentagonal bipyramidal geometry around the uranium(VI) ion. The thiophene ring is disordered due to 180° rotation of this ring about the C16-C17 and C24-C25 bonds. A hybrid scattering factor consisting of 50% sulfur and 50% carbon was used to model this disorder.

Similar structures are also observed in the compounds of phosphine oxides, sulfoxides, ketones, N-oxides and amides with uranyl bis(β-diketoantes), viz: $[UO_2(DBM)_2(OPPh_3)]$ [23], $[UO_2(DBM)_2(C_6H_5CH_2SOCH_3)]$ [24], $[UO_2(TTA)_2(DBA)]$ [25], $[UO_2(TTA)_2(C_5H_5NO)]$ [26], $[UO_2(TTA)_2$(camphor)] [27] and $[UO_2(DBM)_2(^iC_3H_7CON\{^iC_3H_7)_2)]$ [13] . The observed U-O

amide bond distance (2.375(5) Å) is comparable in magnitude with that reported in $[UO_2(DBM)_2(^iC_3H_7CON\{^iC_3H_7)_2)]$ (2.379(5) Å) [13] .

The observed M-$O_{(amide)}$ bond distances (2.322(10), 2.317(5) and 2.376(6) Å) and M-O-C bond angles (154.9, 155.20 and 149.3°) in the uranyl, chloro, bromo and nitrate compounds show clearly that the piperidine based amide ligand forms relatively weaker complexes with the uranyl ion as compared to those of the corresponding iso-butyramide based ligands (2.3151(18) Å, 160.83(15)°, 2.281(14) Å, 171.9(6)° and 2.349(6) Å, 171.2(6)° respectively for the chloro, bromo and nitrate compounds). Interestingly, the chloro and bromo compounds of **L3** are stable to air and moisture and are soluble in normal organic solvents, whereas those with **L1** and **L2** are hydroscopic, giving insoluble products.

4. Conclusions

In conclusion, the piperidine based amide ligands form 2:1 complexes with uranyl chloride, bromide and nitrate and 1:1 complexes with the uranyl bis(β-diketonates). The uranyl chloro and bromo compounds are air and moisture stable and soluble in common organic solvents. The structures of the chloro and bromo complexes show that the uranium(VI) ion is surrounded by two halogen, two uranyl and two amido oxygen atoms in an octahedral geometry. The structures of the uranyl nitrate and uranyl bis(β-diketonates) complexes show hexagonal bipyramidal and pentagonal bipyramidal geometries respectively around the uranium(VI) ion .

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Appendix A: Supplementary data

Electronic Supplementary Information (ESI) is available. CCDC 980684, 980685 980686 and 980687 contain the supplementary crystallographic data for **1**, **2**, **5** and **8** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1233-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 1. Crystal data refinement of compounds **1**, **2**, **5** and **8**

	1	**2**	**5**	**8**
Empirical Formula	$C_{24}H_{48}N_4O_4Cl_2U$	$C_{24}H_{48}N_4O_4Br_2U$	$C_{24}H_{48}N_6O_{10}U$	$C_{28}H_{34}N_2O_7S_2F_6U$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	Pbca	Pbca	P 2_1/n	P 2_1/n
a (Å)	15.2149(6)	15.2003(4)	8.9696(2)	16.0316(3)
b (Å)	12.2538(7)	12.3726(3)	18.2161(4)	9.03822(19)
c (Å)	16.9457(8)	16.9049(4)	10.2600(3)	23.4060(4)
β (°)	90.0	90.0	102.403(3)	94.8813(18)
V (cm^3)	3159.4(3)	3179.24(13)	1637.26	3379.16(12)
Z	4	4	2	4
ρ_{calcd} (g cm^{-3})	1.610	1.785	1.661	1.822
μ (mm^{-1})	16.279	17.576	14.447	15.382
Reflections collected/unique	2957/1360	2981/1769	3088/2010	6283/4965
Data/restrains/ parameters	2957/0/165	2981/72/165	3088/36/202	6283/138/457
Goodness of fit on F^2	1.050	1.000	1.060	1.007
Final R_1 indices [$I > 2\sigma(I)$]	0.0798	0.0452	0.0425	0.0416
R_1 indices (all data)	0.1308	0.0789	0.0688	0.0559

$w = 1/[\sigma^2(Fo^2)+(0.1805P)^2 + 0.8529P]$ for **1**, $w = 1/[\sigma^2(Fo^2)+(0.0646P)^2 +1.6221P]$ for **2**, $w = 1/[\sigma^2(Fo^2)+(0.0649P)^2]$ for **5**, $w = 1/[\sigma^2(Fo^2)+(0.0643P)^2]$ for **8**, where $P = (Fo^2 +2Fc^2)/3$

Table 2. Important bond lengths (Å) and angles (°) for **1**, **2**, **5** and **8**

	1		
U1 – O1	1.739(8)	O1 – U1 – O2	88.1(4)
U1 – O2	2.322(10)	O1 – U1 – Cl1	90.8(3)
U1 – Cl1	2.683(5)	O2 – U1 – Cl1	88.7(3)
C1 – O2	1.262(16)	U1 – O2 – C1	154.9(11)
	2		
U1 – O1	1.754(6)	O1 – U1 – O2	91.4(2)
U1 – O2	2.317(5)	O1 – U1 – Br1	89.99(19)
U1 – Br1	2.8073(10)	O2 – U1 – Br1	88.10(14)
C1 – O2	1.263(9)	U1 – O2 – C1	155.2(5)
	5		
U1 – O1	1.762(6)	O1 – U1 – O2	87.4(2)
U1 – O2	2.378(6)	O3 – U1 – O4	50.0(2)
U1 – O3	2.517(6)	O2 – U1 – O4	65.2(2)
U1 – O4	2.538(6)	U1 – O2 – C1	149.3(6)
C1 – O2	1.253(9)		
	8		
U1 – O1	1.754(5)	U1 – O5	2.393(5)
U1 – O2	1.757(5)	U1 – O6	2.379(5)
U1 – O3	2.375(5)	U1 – O7	2.383(5)
U1 – O4	2.387(5)	C1 – O3	1.256(8)

O1 – U1 – O2	178.2(2)	O4 – U1 – O5	70.29(18)
O6 – U1 – O7	70.06(17)	O5 – U1 – O6	71.18(18)
O4 – U1 – O3	73.97(17)	O3 – U1 – O7	74.60(17)
U1 – O3 – C1	155.6(5)		

Figure Legends

Scheme 1. Synthesis of the ligands and their compounds

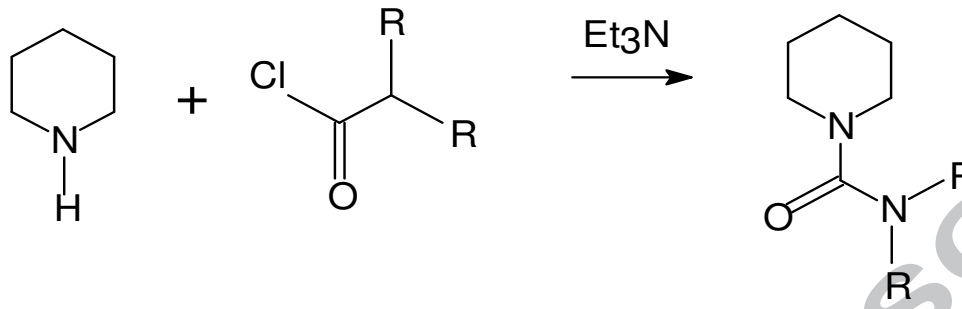
Fig 1. Molecular structure of **1**

Fig 2. Molecular structure of **2**

Fig 3. Molecular structure of **5**

Fig 4. Structure of **8**

Scheme 1



R = CH_3 (**L1**) ; R = C_2H_5 (**L2**) ; R = $^iC_3H_7$ (**L3**)

$[UO_2X_2.nH_2O]$ + 2L ⟶ $[UO_2X_2.2L]$

X = Cl, L = L3 (**1**) ; X = Br, L = L3 (**2**)

$[UO_2(NO_3)_2.6H_2O]$ + 2L ⟶ $[UO_2(NO_3)_2.2L]$

L = L1 (**3**) ; L = L2 (**4**); L = L3 (**5**)

$[UO_2(TTA)_2.2H_2O]$ + L ⟶ $[UO_2(TTA)_2.L]$

L = L1 (**6**) ; L = L2 (**7**); L = L3 (**8**)

$[UO_2(DBM)_2.2H_2O]$ + L ⟶ $[UO_2(DBM)_2.L]$

L = L1 (**9**) ; L = L2 (**10**); L = L3 (**11**)

Fig 1

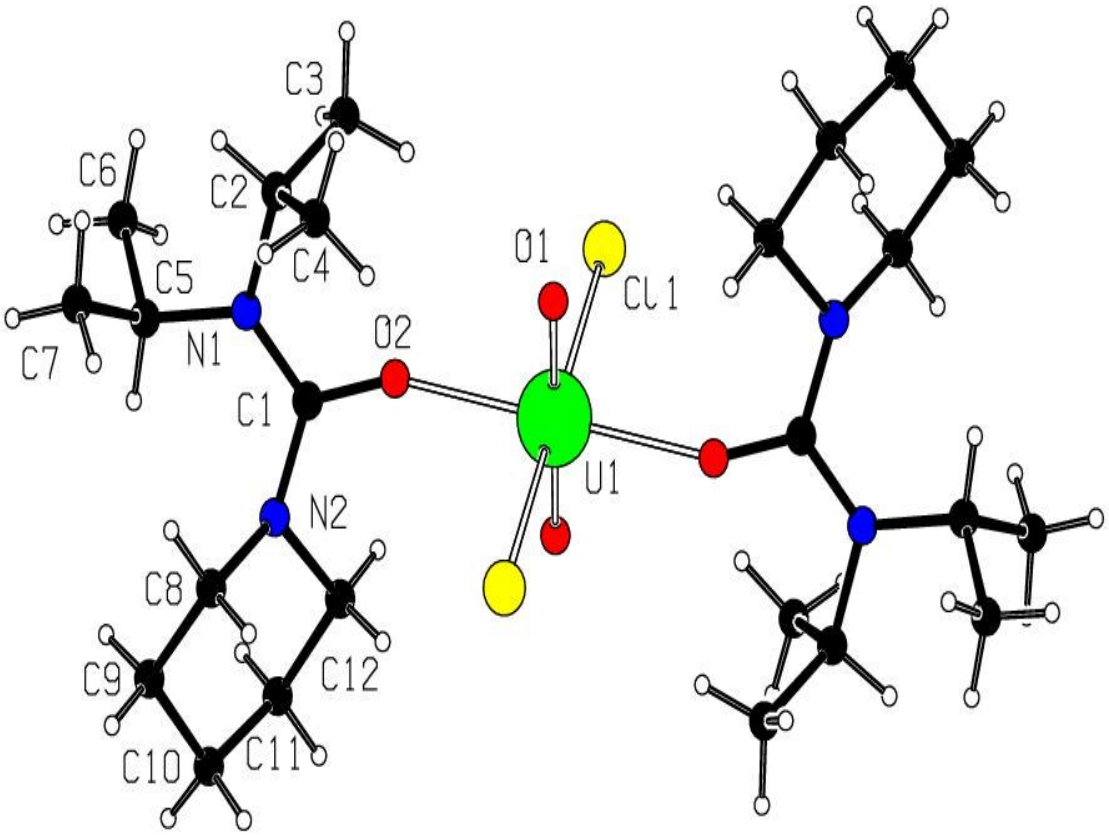


Fig 2

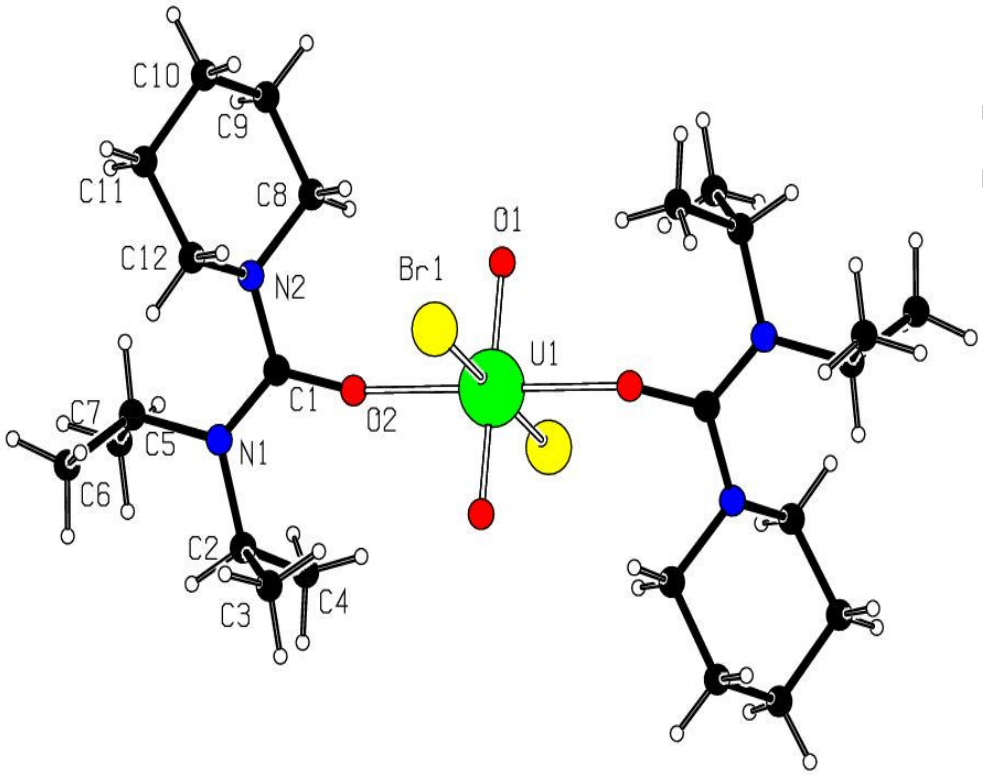


Fig 3

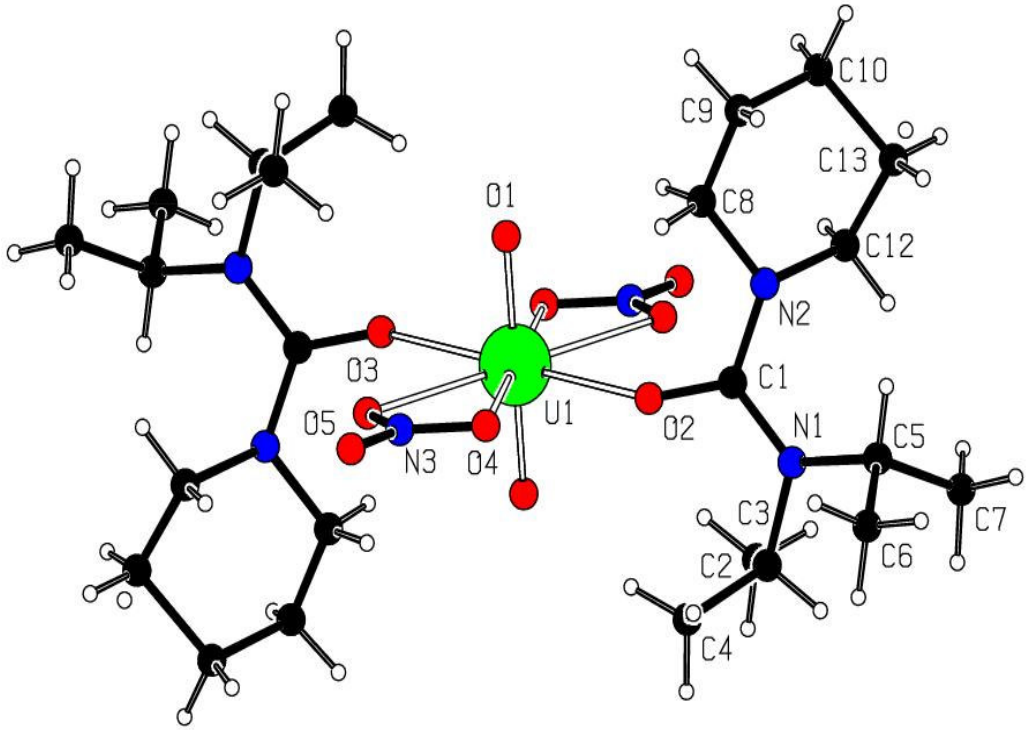
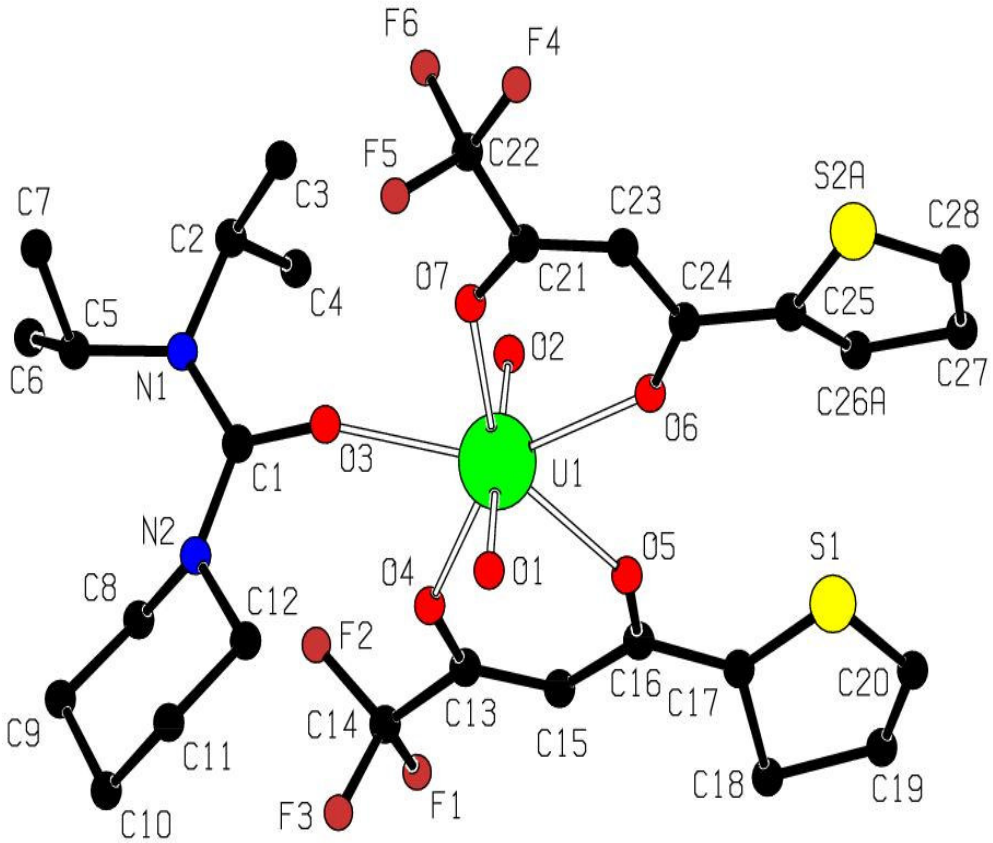


Fig 4



Graphical abstract