



Synthesis, crystal structure and spectroscopic studies of some organic/inorganic hybrid materials containing isostructural monomeric uranyl complexes bridged by bipyridyl typed ligands



Samson Jegan Jennifer, Packianathan Thomas Muthiah*

School of Chemistry, Tiruchirappalli 620024, Tamil Nadu, India

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ABSTRACT

Three uranyl complexes $[\text{UO}_2(\text{TPC})_2(\text{NO}_3)](4,4\text{BIPY})_{0.5}(\text{H}-4,4\text{BIPY})_{0.5}$ (**1**), $[\text{UO}_2(5\text{-TPC})_3]_2(\text{H}-1,4\text{PYPI})(\text{H}_2\text{O})_2$ (**2**), $[\text{UO}_2(\text{NO}_3)_2(4\text{NBPY})_2(\text{H}_2\text{O})]_{0.5}(\text{H}_2\text{O})$ (**3**) (where TPC = thiophene-2-carboxylate, 5-TPC = 5-chlorothiophene-2-carboxylate, 4,4BIPY = 4,4'-bipyridine, H-4,4BIPY = 4,4'-bipyridinium, H-1,4PYPI = 1,4-pyridyl piperazinium and 4NBPY = -4,4-dipyridyl N,N'-dioxide) have been synthesized and characterised using single crystal X-ray diffraction studies. The common structural feature of complexes (**1**, **2**) is the presence of $[\text{UO}_2\text{X}_3]^-$ anionic unit (X = TPC and NO_3 in **1**, 5-TPC in **2** respectively). In both of these complexes the (UO_2^{2+}) uranyl cation is chelated by different thiophene carboxylates. The back bone that transforms these structures into organic/inorganic hybrid materials are the presence of bipyridyl typed ligands. The coordination polymer $\text{UO}_2(\text{NO}_3)_2(4\text{NBPY})_2(\text{H}_2\text{O})_{0.5}(\text{H}_2\text{O})$ (**3**) is quite different from that of (**1,2**) was obtained unexpectedly while trying to synthesize a similar typed. In all the three complexes the space filling, structure direction as well as charge neutralisation roles are played by the organic ligand. Further, the two of the similar typed complexes reported by us with the similar typed $[\text{UO}_2\text{X}_3]^-$ anionic unit; $[\text{UO}_2(5\text{-TPC})_2(\text{NO}_3)](\text{H}-4,4\text{BIPY})_{0.5}(\text{H}_2\text{O})$ = (**U44B**), and $[\text{UO}_2(5\text{-TPC})_2(\text{NO}_3)](\text{H}-1,2\text{BIPY})_{0.5}(\text{H}_2\text{O})$ = (**U12B**) [where H-1,2BIPY = 1,2-bis(4-pyridinium)ethane cation] have also been compared with these present structures. This family of uranyl organic framework materials (UOFs) show a similar type of primary building unit (PBU) which is the $[\text{UO}_2\text{X}_3]^-$ unit despite of different type of carboxylate or heterocyclic ligands.

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1. Introduction

Uranium is a naturally occurring actinide which is an essential raw material for most of the nuclear power sources; hence uranium chelation is an interesting study [1]. Simple ligands that can effectively chelate and remove actinides from the environment or in vivo are of quite interest in these times [2–5]. UO_2^{2+} is one of the most tempting metal centre from which more polymeric and frame work materials have been formulated. The UO_2^{2+} cation has a linear skeleton in square, pentagonal and hexagonal bipyramidal geometries when connected to carboxylate groups [6]. This uranyl ion is the more stable form of uranium that exists in nuclear fuel processing. This uranyl cation maintains a linearity to within a couple of degrees in all of its coordination complexes, relegating coordinative variation to an equatorial plane perpendicular to the $\text{O}=\text{U}=\text{O}$ [7–11]. The oxo moieties at the apical position are essen-

tially non reactive and are typically only observed to interact with Lewis acids in solid state. There are exceptions to this behaviour which typically invoke bulky ligands like Cp^5 , in which the uranyl cation may deviate more than 11° from the linearity and coordinating atoms distort out of the equatorial coordination plane [1]. All these make the study of uranyl bearing hybrid materials as an interesting topic.

Many inexhaustible varieties of resulting architecture are obtained in the case of UOFs [7–11]. Recently there is an increased interest in UOFs particularly that of hexavalent uranium containing a carboxylate and an aromatic pyridyl/pyridyl typed functionalized linker [12–15]. The use of these materials are due to two advantages, carboxylates have a high affinity of uranyl ions and preferentially coordinates to the uranyl center, whereas the dipyridyl is directly coordinated to the uranyl cation or lies at the lattice and acts to be a space filler. 5-TPC not only show versatile coordination modes but also exhibit non covalent interactions like $\text{Cl}\cdots\pi$ and $\text{C}-\text{H}\cdots\text{Cl}$ [16–21]. Reported herein are the synthesis and crystal structures of three uranyl complexes. We have already reported

* Corresponding author. Tel.: +91 0431 2407053; fax: +91 431 2407045.

E-mail address: tommtrichy@yahoo.co.in (P.T. Muthiah).

similar typed uranyl complexes (**U44B** and **U12B**) with 4,4-bipyridinium and 1,2-bis(4-pyridinium)ethane cation [16]. The bipyridinium cation contains two pyridine rings connected directly by a C–C bond, while in the 4,4'-(ethane-1,2-diyl)dipyridinium cation the pyridine rings are connected by a small alkyl chain which extends the distance between the rings. This leads to small elongations in the a and b unit-cell axes of the otherwise quite similar unit cells. As an extension of our previous work we replaced the carboxylate and the bridging ligand with TPC and 1,4-PYPI to study the influence of these ligands on the supramolecular architectures.

2. Experimental

2.1. Materials and methods

All reagents and solvents for syntheses were purchased from commercial sources and used as received. TPC, 4,4BIPY, 1,4PYPI (Aldrich), 5-TPC (Hoechst Aktiengesellschaft), methanol (Qualigens, India), were used. IR spectra of the complex in region 400–4000 cm^{-1} were recorded as pressed disks (1% by weight in KBr) on a Shimadzu FT IR spectrophotometer. CHNS analysis was carried out using Elementar Vario EL III in solid state (Table 1). Thermal stability studies were carried out on a STA 409 PL Luxx thermal analyzer at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere.

Caution! With uranium being a radioactive and chemically toxic element, uranium-containing samples must be handled with suitable care and protection. All starting materials used in these synthetic reactions are available commercially and were used as obtained from supplier. Characterisation and identification of other products of these syntheses will be discussed below.

2.2. Preparation of $\text{UO}_2(\text{TPC})_2(\text{NO}_3)_2 \cdot (4,4\text{BIPY})_{0.5}(\text{H}-4,4\text{BIPY})_{0.5}$ (**1**)

The chemicals for the synthesis of the compounds were used as purchased. For the preparation of the title compound, (**1**), Dioxouranium(VI)nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 0.1505(g) was

suspended into a 20 ml solution containing (1:1) methanol/water mixture. Similarly TPC 0.0850 (g) was suspended into a 20 ml of acetonitrile. Both the solutions were stirred separately for 30 min at 40 $^{\circ}\text{C}$. On mixing both the solution resulted in a yellowish solution which was continued to stir for another half an hour at 40 $^{\circ}\text{C}$. The 4-4'-bipyridine ligand 0.0442(g) was weighed and directly added to the beaker containing the above boiling suspensions, and the stirring was continued. A sudden colour change with the formation of turbid yellow solution was observed on adding the 4-4'Bipyridine ligand. 20 ml of acetonitrile was added into the reaction vessel and the turbidity disappeared (Scheme 1). The resulting clear yellowish solution was kept undisturbed for crystallisation. After 30 days clear yellow plate like crystals were formed which floated on the surface of the mother liquor. The crystals were filtered and washed with small portions of methanol and was dried in air. IR selected bands (cm^{-1}): 3101(m), 2924(m), 2852(m), 2736(m), 1653(s), 1512(s), 1490(s), 1438(s), 1384(s), 1323(s), 1273(s), 1219(s), 1118(s), 1085(s), 1029(s), 1002(m), 862(s), 817(s), 771(s), 748(s), 717(s), 657(s), 609(s), 513(s).

2.3. Preparation of $[\text{UO}_2(5\text{-TPC})_3]_2(\text{H}-1,4\text{PYPI})(\text{H}_2\text{O})_2$ (**2**)

The structure of complex (**1**) inspired us to design the preparation of complex (**2**) with same chelating mode using the 5-TPC ligand. The procedure of preparation of (**2**) is similar to (**1**). Instead of TPC and 4,4BIPY, 5-TPC and 1,4-pyridyl piperazine ligands were used (Scheme 1). IR selected bands (cm^{-1}): 2924(m), 2854(m), 1523(s), 1425(s), 1384(s), 1282(m), 1219(m), 1145(s), 1114(s), 1001(s), 920(s), 815(s), 767(s), 669(s), 526(s), 487(m).

2.4. Preparation of $\text{UO}_2(\text{NO}_3)_2(4\text{NBPY})_2 \cdot (\text{H}_2\text{O})_{0.5}(\text{H}_2\text{O})$ (**3**)

The coordination polymer (**3**) was obtained by serendipity while trying to synthesize an organic inorganic hybrid using 4NBPY. The synthesis procedure of (**3**) was same as that of (**2**), except 4NBPY was used in the place of 1,4PYPI (Scheme 1). IR selected bands (cm^{-1}): 2924(s), 2852(m), 1382(s), 1290(s), 1182(s), 1120(s), 1120(m), 1033(m), 925(m), 835(s), 750(m), 669(s), 561(s), 476(m).

Table 1

Crystal data and structure refinement information for compounds [1–3].

	Compound 1	Compound 2	Compound 3
Empirical Formula	$\text{C}_{10}\text{H}_6\text{NO}_9\text{S}_2\text{U}$, $0.5(\text{C}_{10}\text{H}_{10}\text{N}_2)$, $0.5(\text{C}_{10}\text{H}_8\text{N}_2)$	$2(\text{C}_{15}\text{H}_6\text{C}_{13}\text{O}_8\text{S}_3\text{U})$, $\text{C}_9\text{H}_{14}\text{N}_3$, $2(\text{H}_2\text{O})$	$\text{C}_{10}\text{H}_8\text{N}_4\text{O}_{10}$ U , $3(\text{H}_2\text{O})$
Formula weight	743.52	1709.84	636.28
T (K)	296	296	296
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1$	$C2/c$
a (Å)	17.716(5)	14.2963(3)	16.2001(4)
b (Å)	10.269(5)	17.8701(4)	8.7660(2)
c (Å)	13.121(5)	11.1714(2)	13.5412(4)
α ($^{\circ}$)	90	90	90
β ($^{\circ}$)	104.836(5)	105.105(1)	116.165(2)
γ ($^{\circ}$)	90	90	90
V (Å ³)	2307.5(16)	2755.42(10)	1725.93(8)
Z	4	2	4
Calculated density (g cm^{-3})	2.140	2.061	2.449
Mu(MoKa) (mm)	7.273	6.458	9.485
F(000)	1408	1624	1192
Final R_1 index [$I > 2\sigma(I)$]	0.0392	0.0461	0.0188
wR_2 (all data)	0.1154	0.1434	0.0479
Goodness of fit (GOF) on F^2	1.02	0.80	1.11
Largest difference in peak and hole (e Å^{-3})	−1.24 and 1.88	−0.83 and 0.75	−1.03 and 0.92

3. Crystal structure determination

Intensity data sets were collected at room temperature, on a BRUKER SMART APEXII CCD [22] area-detector diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The data were reduced by using the program SAINT [22] and empirical absorption corrections were done by using the SADABS [22]. The structures were solved by direct methods using SHELXS-97 [23] and subsequent Fourier Difference maps, refined anisotropically by full-matrix least-squares method using SHELXL-97 [23] within the WINGX suite of software, based on F^2 with all reflections. All carbon hydrogen's were positioned geometrically and refined by a riding model with Uiso 1.2 times that of attached atoms. The molecular structure was drawn using the ORTEP-III [24], POV-ray [25] and MERCURY [26].

4. Results and discussion

4.1. IR spectra

On the basis of literature evidences assignment of selected characteristic IR bands (4000–400 cm^{-1}) of the uranyl complexes (**1–3**) have been carried. The IR of complexes **U44B**, **U12B** which were not reported earlier are also used to indicate the bonding site of the uranyl ion UO_2^{2+} . The IR spectra of the complexes (**1**, **2**, **U44B**

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