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Pierre Thuéry[a,*], Youssef Atoini,[b] Jack Harrowfield[c,*]

[a] *Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette, France*
[b] *Technical University of Munich, Campus Straubing, Schulgasse 22, 94315 Straubing, Germany*
[c] *Université de Strasbourg, ISIS, 8 allée Gaspard Monge, 67083 Strasbourg, France*

* Corresponding authors.

E-mail addresses: pierre.thuery@cea.fr (P. Thuéry), harrowfield@unistra.fr (J. Harrowfield)

Abstract

2,5-Thiophenedicarboxylic acid (H_2tdc) has been reacted with uranyl nitrate hexahydrate under solvo-hydrothermal conditions with *N,N*-dimethylacetamide (dma) as an organic cosolvent, giving the complex [UO_2(tdc)(dma)] (**1**), isomorphous to the previously reported [UO_2(tdc)(nmp)] (nmp = *N*-methyl-2-pyrrolidone). With tdc^{2-} adopting the bis(μ_2-κ^1O:κ^1O')-bridging coordination mode, complex **1** crystallizes as a triperiodic framework with the point symbol $\{4^2.8^4\}$. With acetonitrile as an organic cosolvent and in the presence of [$Ni(PPh_3)_2Br_2$], triphenylphosphine oxide is formed *in situ* and it binds to uranyl to give [UO_2(tdc)($OPPh_3$)] (**2**). Complex **2** is also a triperiodic framework, with the point symbol $\{4.10^2\}_2\{4^2.10^4\}$ and the **dmd** topological type with uranium as 3-coordinated (3-c) nodes and tdc^{2-} as either a 4-c node in its bis(μ_2-κ^1O:κ^1O')-bridging binding mode, or a simple edge in the bis(κ^2O,O')-chelating mode. In both **1** and **2**, as in the previously described nmp complex, but not in [UO_2(tdc)(dmf)] (dmf = *N,N*-dimethylformamide), coordination of a unidentate ligand disrupts the most common formation of diperiodic networks with tdc^{2-} and tris-chelated uranyl, and promotes formation of frameworks in which channels accommodate the pendant, unidentate ligands. Complex **2** has a photoluminescence quantum yield of 3% in the solid state, and its emission spectrum displays the typical vibronic progression with peak positions in the range usual for complexes with an O_5 equatorial uranyl environment; the "hot band" observed at room temperature disappears at 77 K.

Keywords: Uranyl ion, Metal–organic networks, Triperiodic frameworks, Structure elucidation, Photoluminescence

1. Introduction

2,5-Thiophenedicarboxylate (tdc^{2-}) is a rigid, ditopic ligand which has been used with moderate frequency in uranyl ion chemistry, resulting in 43 crystal structures of complexes being reported in the Cambridge Structural Database (CSD, Version 5.45) [1]. The first examples, reported by Cahill's group, are discrete, binuclear complexes in which two tdc^{2-} ligands bridge two uranyl cations in the bis(κ^1O) mode, the uranium coordination sphere being completed by chelating terpyridine or 2,4,6-tripyridyltriazine [2,3]. Another case of a discrete, but larger heterometallacycle, with all carboxylate groups κ^2O,O'-chelating, was formed when tdc^{2-} was accompanied by the [Ni(tpyc)$_2$] zwitterion ($tpyc^-$ = 2,2′:6′,2″-terpyridine-4′-carboxylate) [4]. All the other uranyl ion complexes with tdc^{2-} pertain to the class of uranyl-based coordination polymers, and they span all the range of periodicities. Chains, simple or double-stranded and ribbon-like, are formed in particular in the presence of additional, terminal ligands such as water [5], 2,2′-bipyridine [6], *N,N*-dimethylformamide [7], nitrate [8], acetate [6], formate [7], 4-(ammoniomethyl)benzoate [9], but also partially deprotonated $Htdc^-$ itself [8], or heterometal-bearing decorating groups [10,11]. Diperiodic polymers are common in this system, with a particular abundance of honeycomb networks [5–8,10,12–15], sometimes involved in interpenetration [5–7] or polycatenation [8,10], and other, less frequent topologies [5–8]. Triperiodic frameworks have much less often been encountered, with the only examples being two complexes with bis(μ_2-κ^1O:κ^1O')-bridging tdc^{2-} and coordinated *N*-methyl-2-pyrrolidone (nmp) [16], and two heterometallic complexes involving Na^+ [17] or Cu^{2+} [11]. We report here the synthesis and crystal structure of two uranyl ion complexes with tdc^{2-} which crystallize as triperiodic frameworks. Both have the peculiarity of involving a unidentate auxiliary ligand, either *N,N*-dimethylacetamide (dma), giving a complex isomorphous to that obtained with nmp [16], or the bulky $OPPh_3$.

2. Experimental section

2.1. Synthesis

Caution! Uranium is a radioactive and chemically toxic element, and uranium-containing samples must be handled with suitable care and protection. Small quantities of reagents and solvents were employed to minimize any potential hazards arising both from the presence of uranium and the use of pressurized vessels for the syntheses.

Dioxouranium(VI) nitrate hexahydrate, $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (RP Normapur, 99%) was purchased from Prolabo. 2,5-Thiophenedicarboxylic acid and $[Ni(PPh_3)_2Br_2]$ were from Aldrich. The mixtures in demineralized water/organic cosolvent were placed in 10 mL tightly closed glass vessels and heated at 140 °C in a sand bath, under autogenous pressure. The crystals characterized were those deposited under the reaction conditions and not from subsequent cooling and depressurization.

*2.1.1. $[UO_2(tdc)(dma)]$ (**1**)*

H_2tdc (17 mg, 0.10 mmol), and $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (35 mg, 0.07 mmol) were dissolved in a mixture of water (0.6 mL) and dma (0.2 mL). A few yellow crystals of complex **1** were obtained within four days.

*2.1.2. $[UO_2(tdc)(OPPh_3)]$ (**2**)*

H_2tdc (17 mg, 0.10 mmol), $[Ni(PPh_3)_2Br_2]$ (38 mg, 0.05 mmol) and $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (35 mg, 0.07 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL). Yellow crystals of complex **2** were obtained within two weeks (34 mg, 68% yield based on U). *Anal.* Calc. for $C_{24}H_{17}O_7PSU$: C, 40.12; H, 2.38. Found: C, 40.19; H, 2.47%.

2.2. *Crystallography*

The data were collected at 100(2) K on a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source (IμS 3.0 Mo) and a PHOTON III area detector, and operated through the APEX4 software [18]. The data were processed with SAINT [19], and absorption effects were corrected empirically with SADABS [20,21]. The structures were solved by intrinsic phasing with SHELXT [22] and refined by full-matrix least-squares on F^2 with SHELXL, using the ShelXle interface [23]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3). In complex **2**, three aromatic rings of $OPPh_3$ ligands are disordered over two positions which were refined as idealized hexagons and with occupancy parameters constrained to sum to unity. Restraints on displacement parameters were applied for the disordered groups and for some other misbehaving atoms. Some voids in the structure of **2** are probably occupied by disordered and unresolved water molecules, whose contribution to the structure factors was subtracted with SQUEEZE [24]. Crystal data and structure refinement parameters are given in Table 1. Drawings were made with ORTEP-3 [25,26] and VESTA [27]. Topological analyses were made with ToposPro [28].

2.3. *Luminescence measurements*

The emission spectrum of **2** at room temperature was recorded on a solid sample using an Edinburgh Instruments FS5 spectrofluorimeter equipped with a 150 W CW ozone-free xenon arc lamp, dual-grating excitation and emission monochromators (2.1 nm/mm dispersion; 1200 grooves/mm), and an R928P photomultiplier detector. The powdered compound was pressed to the wall of a quartz tube, and the measurement was performed using the right-angle mode in the SC-05 cassette. An excitation wavelength of 420 nm was used and the emission was

monitored between 450 and 600 nm. The measurement at 77 K was conducted on a solid sample using an Edinburgh Instruments SC-80 and an OptistatDN (Oxford Instruments) cryostat equipped with a temperature controller and using liquid nitrogen as cooling agent. The quantum yield measurement was performed by using a Hamamatsu Quantaurus C11347 absolute photoluminescence quantum yield spectrometer and exciting the sample between 300 and 400 nm.

Table 1

Crystal data and structure refinement details.

	1	**2**
Chemical formula	$C_{10}H_{11}NO_7SU$	$C_{24}H_{17}O_7PSU$
M_r	527.29	718.43
Crystal system	orthorhombic	orthorhombic
Space group	*Pbcn*	*Pna2₁*
a (Å)	12.3611(4)	49.9431(19)
b (Å)	12.7499(4)	10.9216(5)
c (Å)	18.2594(6)	27.2565(11)
V (Å^3)	2877.73(16)	14867.3(11)
Z	8	24
No. of reflections collected	176895	283308
No. of independent reflections	4383	28234
No. of observed reflections [$I > 2\sigma(I)$]	4033	26860
R_{int}	0.060	0.075
No. of parameters refined	184	1931
R_1	0.017	0.042
wR_2	0.032	0.099
S	1.114	1.069
$\Delta\rho_{min}$ (e Å^{-3})	–1.20	–2.34
$\Delta\rho_{max}$ (e Å^{-3})	0.66	4.41

3. Results and discussion

3.1. Synthesis

While the synthesis of complex **1** provides an example of an apparently simple solvothermal process involving no more than deprotonation of H_2tdc, possibly facilitated by co-solvent hydrolysis, that of complex **2** shows that this reaction can be accompanied by various others. [Ni(PPh$_3$)$_2$Br$_2$] was included in the reaction mixture in the belief that replacement of the relatively labile bromido ligands by carboxylate donors could lead to the presence of terminal

or bridging $Ni(PPh_3)_2$ units, depending on the stereochemistry at Ni^{II}, within a uranyl ion coordination polymer formed with tdc^{2-}. The isolated product contains no Ni^{II} but at least partial aquation of the PPh_3 ligands of the reactant, followed by oxidation, must have occurred to give the $OPPh_3$ ligands bound as unidentate species to U^{VI}. We have observed similar oxidation of a phosphine to a phosphine-oxide under solvothermal conditions in the case of the tripodal ligand tris(2-carboxyethyl)phosphine [29] and recent studies [30] have shown that oxidations of similar types are due to nitrate present because of the use of $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ as a reactant and not due to U^{VI}, although it is possible that coordination of nitrate to U^{VI} serves to activate it. Thus, through a considerably more complicated process, the complex isolated as **2** has the same composition, $[UO_2(tdc)L]$ (L = unidentate O-donor), not only as **1** but also as the two previously isolated complexes where L = nmp. There again, some components of the reaction mixture were not present in one of the isolated crystalline products and it is worthy of note that the two complexes were not deposited at the same temperature (one of the two forms being deposited upon cooling). This is perhaps a factor of relevance in considering all known structures (see ahead), the structure of $[UO_2(tdc)(dmf)]$ (dmf = *N,N*-dimethylformamide) [7] obtained under conditions similar to those employed with complex **1** but with dmf replacing dma, adding a fifth case for comparison.

Our development of the habit of taking only crystals deposited at the temperature of the solvothermal reaction was based upon recognition of the temperature dependence of solubility in general and thus the possibility that crystals deposited at the reaction temperature need not be the same as those deposited on cooling, especially when reaction temperatures and pressures are elevated. Although but a single example, our earlier isolation of different polymorphs of $[UO_2(tdc)(nmp)]$ depending on the conditions of crystallization we consider an indicator of a not always recognized complication in solvothermal synthesis. In our experience in practice with uranyl ion complexes, cooling of solvothermal reaction mixtures also often results in

deposition of amorphous material in addition to crystals, so that reaction temperature deposition ensures greater purity, albeit that may be at the expense of a low yield.

3.2. Crystal structures

The complex $[UO_2(tdc)(dma)]$ (**1**) is isomorphous to one of the two forms of $[UO_2(tdc)(nmp)]$, previously reported [16], but quite different from $[UO_2(tdc)(dmf)]$ [7], although all three compounds were obtained under very similar conditions. The uranium atom in **1** is in a pentagonal-bipyramidal environment, with four carboxylate oxygen donors from four tdc^{2-} ligands and one dma in the equatorial plane [U–O(oxo), 1.7662(16) and 1.7738(17) Å; U–O(carboxylato), 2.3579(17)–2.3894(16) Å; U–O(dma), 2.3760(16) Å] (Fig. 1). Both tdc^{2-} carboxylate groups are bridging in the μ_2-κ^1O:κ^1O' mode, and both metal and dicarboxylate ligand are 4-coordinated (4-c) nodes. The triperiodic framework formed, shown in Fig. 2, has the point symbol $\{4^2.8^4\}$. The two nodes are however distinct, with extended point symbols [4.4.8(4).8(5).8(6).8(7)] and [4.4.8.8(2).8(5).8(6)] for U and tdc^{2-}, respectively. No solvent-accessible voids are present, and the Kitaigorodsky packing index (KPI, evaluated with PLATON [31]) is 0.68.

In the structure viewed down [001] (Fig. 1c), the dma ligands all lie in channels of approximately rectangular profile defined by the $UO_2(tdc)$ framework. Given the lability of the equatorial coordination sites on uranyl ion, solvent exchange in these channels might be possible without disruption of the framework, one factor to be considered there being the volume of the solvent molecules in the solid state (estimated by assigning 18 $Å^3$ to each of the non-hydrogen atoms [32]) and indeed dma (108 $Å^3$) and nmp (126 $Å^3$) do have similar values. However, there are clearly subtleties relating to the detailed interactions of the solvent ligands with their framework, as indicated by the structure of the different form of $[UO_2(tdc)(nmp)]$

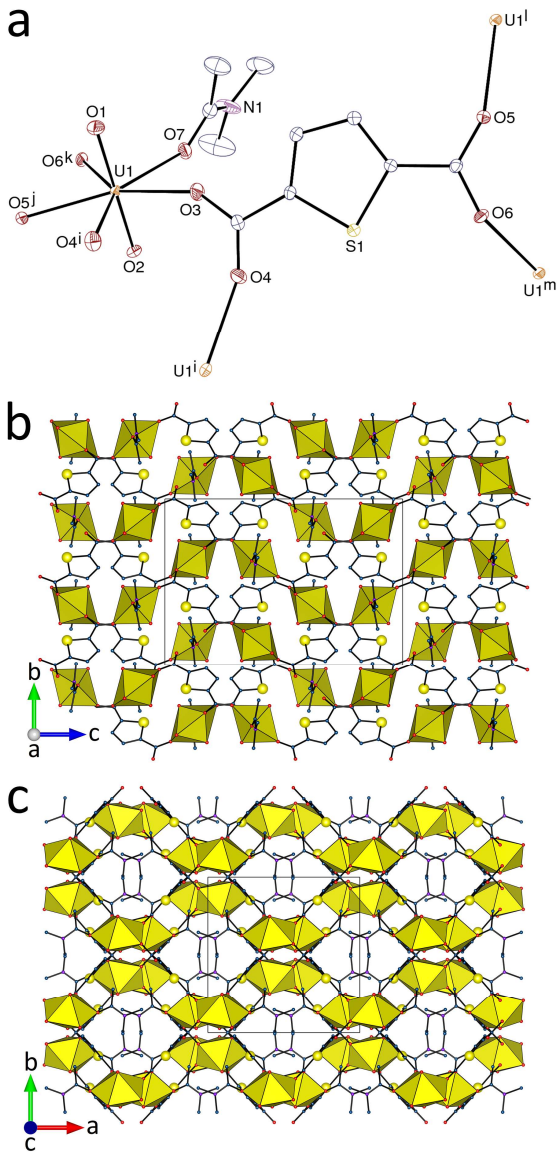

Fig. 1. (a) View of complex **1** with displacement ellipsoids shown at the 50% probability level and hydrogen atoms omitted. Symmetry codes: i = –*x*, *y*, 3/2 – *z*; j = *x* – 1/2, *y* + 1/2, 3/2 – *z*; k = 1/2 – *x*, 3/2 – *y*, *z* + 1/2; l = *x* + 1/2, *y* – 1/2, 3/2 – *z*; m = 1/2 – *x*, 3/2 – *y*, *z* – 1/2. (b) and (c) Two views of the triperiodic framework with uranium coordination polyhedra colored yellow.

which crystallizes in the $P2_12_12_1$ space group at room temperature, and the various forms of tdc^{2-} coordination possible, as seen in the fact that $[UO_2(tdc)(dmf)]$ crystallizes as a double-stranded chain, with one carboxylate group of tdc^{2-} bridging as in **1** and the other κ^2O,O'-chelating, thus reducing the overall connectivity of the ligand, with both U and tdc^{2-} becoming 3-c nodes. Nonetheless, the molar volume of dmf (90 Å^3) is smaller than that of dma or nmp,

and the juxtapositioning of the double-stranded chains can be seen as defining again approximately rectangular profile channels in which, in projection, dmf molecules lie side-by-side. There are similarities here to the solvent dispositioning in the structure of the room temperature form of $[UO_2(tdc)(nmp)]$.

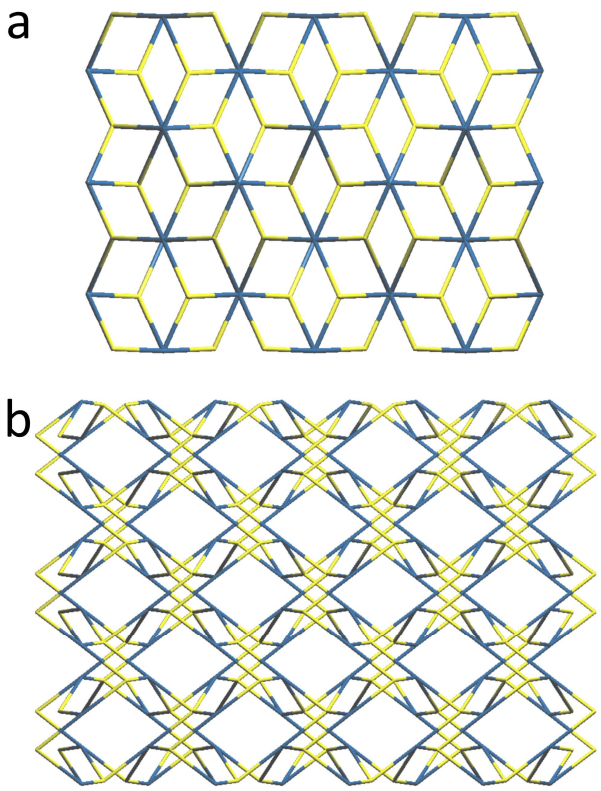

Fig. 2. Nodal representation of the framework in **1**, down [010] with [100] horizontal (a) or down [001] with [100] horizontal (b). U nodes, yellow; tdc^{2-} nodes, blue.

The complex $[UO_2(tdc)(OPPh_3)]$ (**2**), obtained in the presence of $[Ni(PPh_3)_2Br_2]$, crystallizes with six uranyl cations and six of each of both ligands in the asymmetric unit, thus giving a large assembly affected by some disorder (see Experimental section). All six uranium atoms are in similar pentagonal-bipyramidal environments, with one κ^2O,O'-chelating and two monodentate carboxylate groups and one $OPPh_3$ ligand in the equatorial plane [U–O(oxo), 1.724(11)–1.782(10) Å; U–O(carboxylato), 2.433(9)–2.507(10) Å for the chelating groups and 2.321(10)–2.403(9) Å for the other groups; U–$OPPh_3$, 2.293(10)–2.380(10) Å] (Fig. 3). The

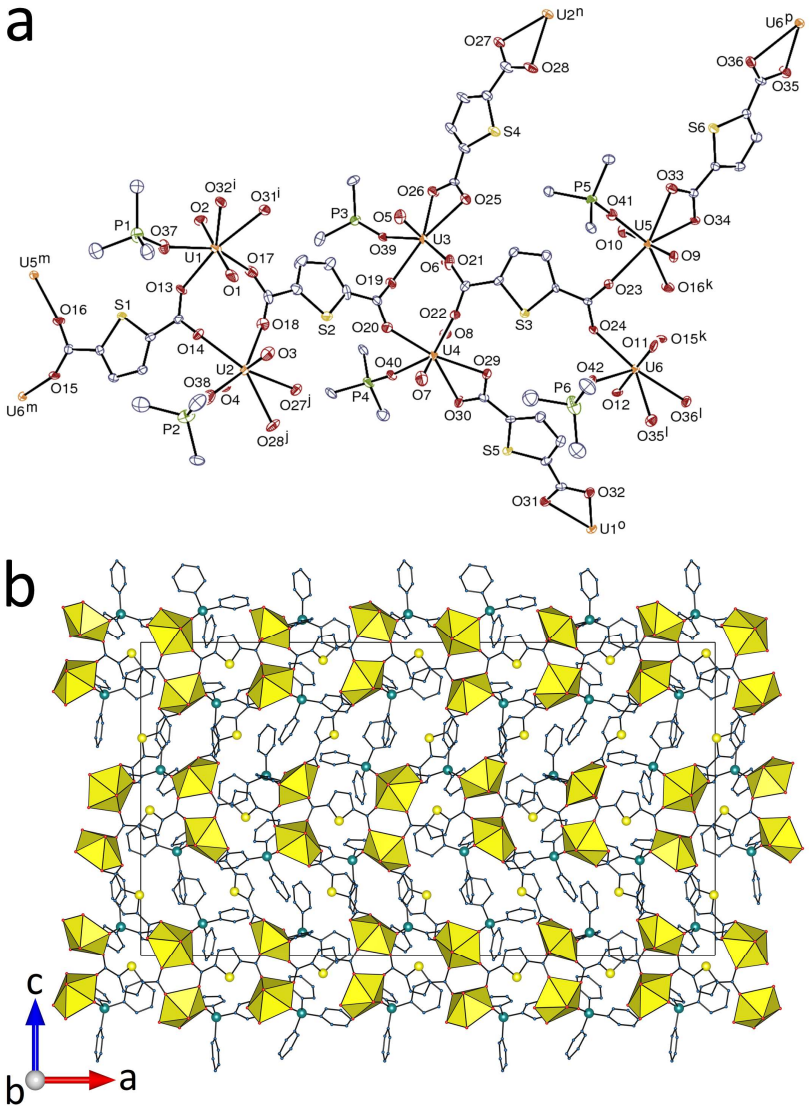

Fig. 3. (a) View of complex **2** with displacement ellipsoids shown at the 30% probability level and hydrogen atoms omitted. For clarity, only the carbon atom attached to phosphorus in the aromatic rings is shown. Symmetry codes: i = 3/2 – *x*, *y* – 1/2, *z* + 1/2; j = 3/2 – *x*, *y* – 1/2, *z* – 1/2; k = *x* + 1/2, 3/2 – *y*, *z*; l = 2 – *x*, 1 – *y*, *z* – 1/2; m = *x* – 1/2, 3/2 – *y*, *z*; n = 3/2 – *x*, *y* + 1/2, *z* + 1/2; o = 3/2 – *x*, *y* + 1/2, *z* – 1/2; p = 2 – *x*, 1 – *y*, *z* + 1/2. (b) View of the triperiodic framework with uranium coordination polyhedra colored yellow. Only one position of the disordered aromatic rings is shown.

CSD contains 36 crystal structures displaying uranyl bonding to $OPPh_3$, with bond lengths in the range of 2.283–2.456 Å [mean value, 2.35(4) Å], in perfect agreement with the present observed range. While all uranium atoms are 3-c nodes, tdc^{2-} ligands are separated into two

groups, with three of them bis(μ_2-κ^1O:κ^1O')-bridging and thus 4-c nodes, and the three others bis(κ^2O,O')-chelating and thus simple edges.

The binodal (3-c)$_2$(4-c) coordination polymer formed is here also triperiodic, and it has the point symbol $\{4.10^2\}_2\{4^2.10^4\}$ and the **dmd** topological type, as defined in the RCSR [33,34] (Fig. 4), which derives from **pts** through splitting of a 4-c vertex into two 3-c vertices

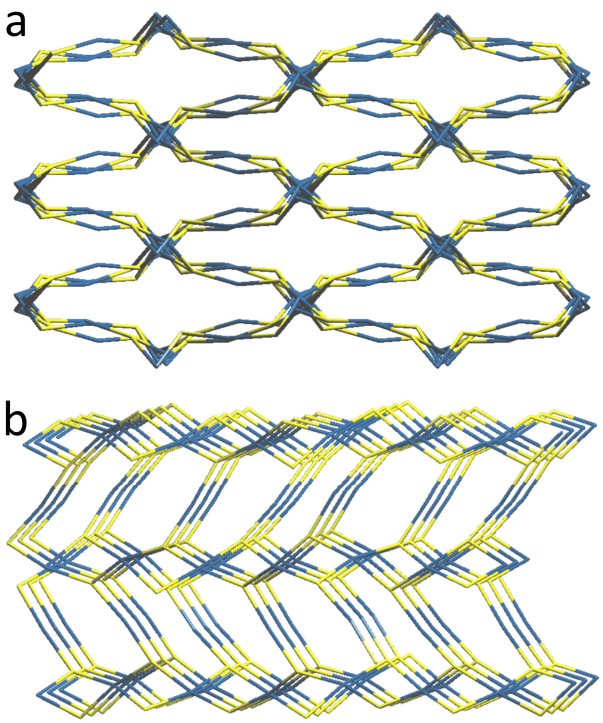

Fig. 4. Nodal representation of the **dmd** framework in **2**, down [100] with [001] horizontal (a) or down [010] (slightly rotated) with [100] horizontal (b). U nodes, yellow; tdc^{2-} nodes and edges, blue.

[35]. Some other examples of this topology, somewhat uncommon in coordination chemistry, have been reported [35–38]. The framework is built from rows of $[UO_2(tdc)]_2$ units connected one to the other through the shared 4-c ligand nodes, these rows, directed along [100], being further assembled into the triperiodic polymer through the 2-c ligand edges. The KPI of ~0.65 (disorder excluded) indicates the presence of small solvent-accessible voids (see Experimental section).

The $OPPh_3$ ligand here has a much larger molar volume (~360 $Å^3$, estimated as for the solvent ligands) than nmp, dma or dmf and the structure of **2**, when viewed down [100], defines large channels of elongated profile (Fig. 4a) which accommodate these units. Although disorder of three phenyl groups renders the analysis of weak interactions somewhat imprecise, no consequential parallel-displaced π–π interaction appears to be present, the shortest centroid···centroid distances of 4.166(10) and 4.199(12) Å being between tdc^{2-} and $OPPh_3$ rings, with corresponding dihedral angles of 31 and 28°. $OPPh_3$ can be considered as a structure-inducing species in the formation of this structure which is very unusual among all those known for uranyl–tdc^{2-} complexes. A different way to get a triperiodic framework in this system consists, not in using an additional ligand, but an additional metal ion complex unit, $Cu(phen)^{2+}$ (phen = 1,10-phenanthroline), whose bridging nature results in the formation of a complex with the **cds** topological type [11].

3.3. Luminescence

The emission spectrum of complex **2** in the solid state under excitation at 420 nm has been recorded. While that of **1** could not be measured due to lack of a sufficient quantity of the pure compound, the spectrum of the isomorphous complex $[UO_2(tdc)(nmp)]$ has been previously published [16]. The spectrum of **2**, shown in Fig. 5, displays the typical vibronic progression due to the $S_{10} \rightarrow S_{0\nu}$ (ν = 0–4) transitions of the uranyl ion [39,40]. The peaks are located at 492, 513, 537, 563 and 590 nm, these values being in the range usually observed for uranium centres in a pentagonal-bipyramidal environment with an O_5 equatorial donor set [41]. The low intensity "hot-band" ($S_{11} \rightarrow S_{00}$) due to electron-phonon coupling [42] is observed as a shoulder at ~480 nm, as confirmed by the disappearance of this signal in the spectrum recorded at 77 K. The low temperature spectrum shows changes in the relative intensity of the main, narrower

peaks, but no modification of the peak locations. The photoluminescence quantum yield (PLQY) of **2** is 3%, and this complex is thus only weakly emissive.

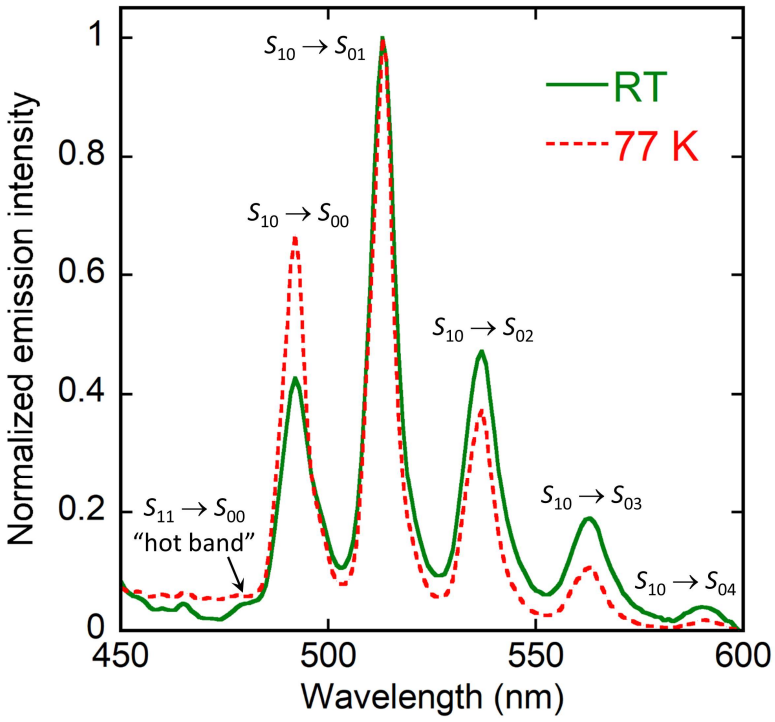

Fig. 5 Emission spectrum of complex **2** in the solid state, under excitation at 420 nm, measured at room temperature (green, solid line) and at 77 K (red, dashed line). The "hot band" appears only on the room temperature spectrum.

4. Conclusions

The five structures now known for crystals of the composition $[UO_2(tdc)(L)]$, where L is a unidentate ligand, show the remarkable adaptability of the $UO_2(tdc)$ component to the nature of L wherein despite considerable variations in the size and composition of L, it is localized within channels defined by various $UO_2(tdc)$ forms. This adaptability must arise both from the lability of carboxylate donors to uranyl ion equatorial coordination and the capacity of tdc^{2-} to adopt various coordination modes [7]. It has the consequence that solvent or neutral ligand exchange processes of any given $[UO_2(tdc)(L)]$ species would not be expected to show any selectivity. Even where the $UO_2(tdc)$ network has a triperiodic form, it would seem not to have sufficent rigidity to resist structural change associated with unidentate ligand exchange.

What is particularly notable in this and previous work [16] is that, while increasing the connectivity of the ligands or adding bridging species may be an efficient means of getting coordination polymers with higher periodicities, as often found with uranyl ion complexes, and particularly in the case of a heterometallic tdc^{2-} complex [11], occupation of one coordination site by a unidentate, terminal ligand, not necessarily bulky, has sometimes the somewhat paradoxical effect of promoting the formation of triperiodic structures. In the case of tdc^{2-}, which has a strong propensity to form diperiodic, often entangled networks with uranyl when bound in the bis(κ^2*O*,*O'*-chelating) mode, the uranyl cation being thus tris(chelated) [5–7], coordination of nmp, dma or $OPPh_3$ disrupts this most frequent binding mode and favours formation of triperiodic frameworks with cavities or channels accommodating stacks of unidentate ligands.

Appendix A. Supplementary data

CCDC 2375656 and 2375657 contain the supplementary crystallographic data for **1** and **2**, 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) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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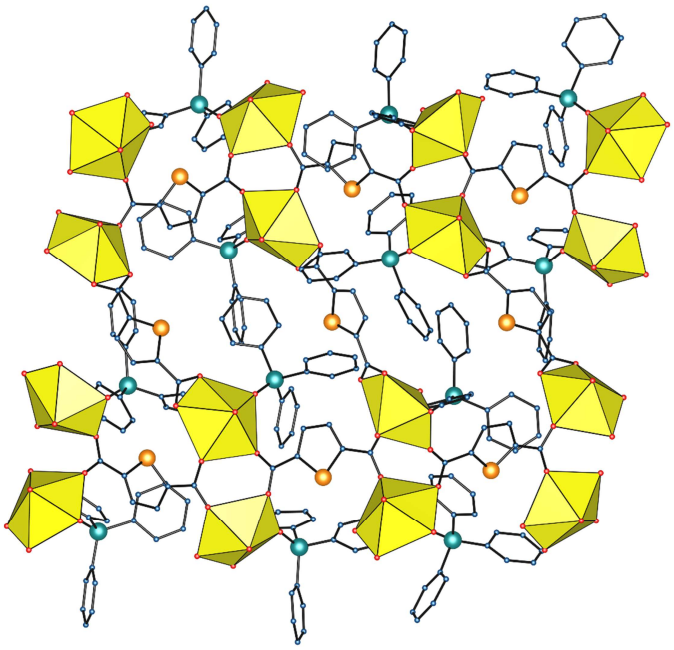
Table of Contents Entry

Triperiodic frameworks in the uranyl–2,5-thiophenedicarboxylate system: effect of unidentate auxiliary ligands

Pierre Thuéry, Youssef Atoini, Jack Harrowfield



Two triperiodic frameworks are formed when 2,5-thiophenedicarboxylate complexes the uranyl ion in the presence of *N,N*-dimethylacetamide or triphenylphosphine oxide as unidentate coligands. Both assemblies display channels accommodating the latter coligands.