# Two protons masquerading as a metal ion? Anionic coordination polymers of uranyl ion and tetrahydrofurantetracarboxylate with protonated or metal-complexed azamacrocyclic cations

Pierre Thuéry, Jack Harrowfield

# Two protons masquerading as a metal ion ? Anionic coordination polymers of uranyl ion and tetrahydrofurantetracarboxylate with protonated or metal-complexed azamacrocyclic cations

Pierre Thuéry[a*], Jack Harrowfield[b*]

[a] *Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette, France*

[b] *ISIS, Université de Strasbourg, 8 allée Gaspard Monge, 67083 Strasbourg, France*

* Corresponding author. E-mail: pierre.thuery@cea.fr, harrowfield@unistra.fr

**Abstract**

The two complexes [*R,S*-Me$_6$cyclamH$_2$][(UO$_2$)$_3$(thftc)$_2$] (**1**) and [(UO$_2$)$_3$(thftc)$_2$Cu(*R,S*-Me$_6$cyclam)]·2H$_2$O (**2**) have been obtained from reaction of uranyl nitrate with (2*R**,3*R**,4*S**,5*S**)-tetrahydrofurantetracarboxylic acid (H$_4$thftc) under solvo-hydrothermal conditions, in the presence of either *R,S*-Me$_6$cyclam·4HNO$_3$ or [Cu(*R,S*-Me$_6$cyclam)(NO$_3$)$_2$] (*R,S*-Me$_6$cyclam = 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). Isomerization in situ results in both complexes involving the chiral 2*R**,3*R**,4*R**,5*S** form of the ligand. (UO$_2$)$_3$(thftc)$_2^{2-}$ diperiodic networks with the V$_2$O$_5$ topology are formed in both cases, which are separated by layers of hydrogen bonded counterions in **1**, or united into a triperiodic framework of 3,5T1 topology by bridging copper(II) cations in **2**. The packing of anionic sheets and azamacrocyclic moieties is however nearly identical in the two species, as a consequence of the similar stereochemistry of the otherwise different interactions linking the diperiodic polymer units.

*Keywords*: Uranyl ion, Tetrahydrofurantetracarboxylic acid, Azamacrocycles, Metal–organic frameworks

## 1. Introduction

The use of higher polycarboxylates, in particular tetracarboxylates, has been a successful ploy in the search for tridimensional uranyl ion coordination polymers, some of which have proven to show significant porosity [1]. One of the smallest tetracarboxylates, (2*R**,3*R**,4*S**,5*S**)-tetrahydrofurantetracarboxylate ($thftc^{4-}$) has been investigated as a possible extractant for separation of uranyl cations from transuranic and lanthanide cations during nuclear waste reprocessing [2], but its use as a ligand to synthesize uranyl ion complexes and coordination polymers has been rather limited, although it has shown rather unique behaviour. The first complexes reported were discrete tri- and tetranuclear metallamacrocycles formed under ambient conditions, which exist in equilibrium in solution but can be crystallized as pure individual species with the appropriate choice of countercation [3]. Mononuclear species are also known [2c], while syntheses under solvo-hydrothermal conditions mainly provided true coordination polymers, though ones of a periodicity no higher than two unless other metal ions are present [4]. The present work resulted from efforts to explore the hypothesis that solvothermal syntheses might show a sensitivity to countercations similar to that found for the oligonuclear species, but the exact opposite appears to apply in the two cases now characterized, in which the structure-directing cations are either the diprotonated azamacrocycle 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*R,S*-$Me_6cyclamH_2^{2+}$) or its copper(II) complex, Cu(*R,S*-$Me_6cyclam)^{2+}$.

## 2. Experimental part

### *2.1. Synthesis*

**Caution!** Uranium is a radioactive and chemically toxic element, and uranium-containing samples, although depleted in $^{235}U$, still contain α-emitting $^{238}U$ and must be handled with

suitable care and protection. Experiments with radioactive substances should be performed by trained personnel in authorized laboratories only, and radioactive waste must be disposed of according to national rules. 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, $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$, was purchased from Prolabo and (2*R**,3*R**,4*S**,5*S**)-tetrahydrofurantetracarboxylic acid ($H_4$thftc) was from Aldrich. *R,S*-$Me_6$cyclam·$4HNO_3$ was obtained by treating 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (*R,S*-$Me_6$cyclam) with excess 2M $HNO_3$, slow evaporation of the solution at room temperature giving large colorless tablets of the salt. (7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) dinitrate, [Cu(*R,S*-$Me_6$cyclam)$(NO_3)_2$], was synthesized as previously reported [5]. Elemental analyses were performed by MEDAC Ltd..

*2.1.1. [R,S-$Me_6$cyclam$H_2$][$(UO_2)_3$(thftc)$_2$] (**1**).*

$H_4$thftc (25 mg, 0.10 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (50 mg, 0.10 mmol), and *R,S*-$Me_6$cyclam·$4HNO_3$ (54 mg, 0.10 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL). The solution was placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving light yellow crystals of 1,11-diaza-4,8-diazonia-7(*R**),14(*S**)-5,5,7,12,12,14-hexamethyl-cyclotetradecanium catena-[di((2*R**,3*R**,4*R**,5*S**)-tetrahydrofurantetracarboxylato)tri(dioxouranium(VI))] (**1**) within ten days (43 mg, 81% yield based on U). $C_{32}H_{46}N_4O_{24}U_3$ (1584.82): calcd. C 24.25, H 2.93, N 3.54; found C 24.52, H 2.83, N 3.99.

*2.1.2. [$(UO_2)_3$(thftc)$_2$Cu(R,S-$Me_6$cyclam)]·2$H_2O$ (**2**).*

$H_4$thftc (25 mg, 0.10 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (50 mg, 0.10 mmol), and [Cu(*R,S*-$Me_6$cyclam)$(NO_3)_2$] (24 mg, 0.05 mmol) were dissolved in a mixture of water (0.6 mL) and *N*-methyl-2-pyrrolidone (0.2 mL). The solution was placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving a few light purple crystals of complex catena-[(7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) di((2*R**,3*R**,4*R**,5*S**)-tetrahydrofurantetracarboxylato)ter(dioxouranium(VI))] dihydrate (**2**) within five days (~4 mg, 7% yield based on U).

### *2.2. Crystallography*

Crystallographic data were collected at 100(2) K either on a Nonius Kappa-CCD area-detector diffractometer [6] for complex **1**, or on a Bruker D8 Quest diffractometer using an Incoatec Microfocus Source (IμS 3.0 Mo) and a PHOTON III area detector and operated through the APEX3 software [7] for complex **2**, both operating with Mo radiation (λ = 0.71073 Å). The data were processed with HKL2000 [8] for **1** and with SAINT [9] for **2**, and absorption effects were corrected empirically with the programs SCALEPACK [8] or SADABS [10], respectively. The structures were solved with SHELXT [11] and refined with SHELXL [12] using the ShelXle interface [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to nitrogen atoms were retrieved from a residual electron density map for **1** and introduced at calculated positions for **2**, and they were treated as riding atoms. In compound **2**, the water solvent molecule is disordered over two positions which have been given occupancy parameters of 0.5 and whose hydrogen atoms were not found, and SQUEEZE [14] was used to subtract the contribution of other disordered solvent molecules to the structure factors. The molecular plots were drawn with ORTEP-3 [15] and the polyhedral representations with VESTA [16]. The topological analyses and nodal representations were made with ToposPro [17].

Crystal data for **1**: $C_{32}H_{46}N_4O_{24}U_3$, $M$ = 1584.82, triclinic, space group $P\bar{1}$, $a$ = 9.2377(7), $b$ = 10.3341(8), $c$ = 12.2342(10) Å, α = 99.300(6), β = 107.991(6), γ = 97.613(5)°, $V$ = 1075.31(16) Å$^3$, $Z$ = 1. Refinement of 289 parameters on 3998 independent reflections out of 41013 measured reflections ($R_{int}$ = 0.091) led to $R1$ = 0.067, $wR2$ = 0.146, $S$ = 1.031, $\Delta\rho_{min}$ = –2.88, $\Delta\rho_{max}$ = 2.84 e Å$^{-3}$.

Crystal data for **2**: $C_{32}H_{48}CuN_4O_{26}U_3$, $M$ = 1682.37, triclinic, space group $P\bar{1}$, $a$ = 9.2646(3), $b$ = 10.2713(4), $c$ = 14.0243(5) Å, α = 107.5874(17), β = 99.2739(14), γ = 98.9441(15)°, $V$ = 1225.61(8) Å$^3$, $Z$ = 1. Refinement of 313 parameters on 4648 independent reflections out of 66685 measured reflections ($R_{int}$ = 0.047) led to $R1$ = 0.028, $wR2$ = 0.070, $S$ = 1.054, $\Delta\rho_{min}$ = –1.99, $\Delta\rho_{max}$ = 2.18 e Å$^{-3}$.

## 3. Results and discussion

As a functionalized tetracarboxylate, thftc$^{4-}$ (and its variously protonated forms) can act as an oxygen donor not only through carboxylate but in principle also through the neutral furan group. Despite its oxophilic nature, U$^{VI}$ does not appear to bind very strongly to ether donors, with U–O(ether) bond lengths in the 113 crystal structures reported in the Cambridge Structural Database (CSD, version 5.43 [18]) being in the range of 2.31–2.95 Å, with a mean value of 2.50(11) Å. Nonetheless, in all known homometallic uranyl ion complexes of H$_n$thftc$^{(4-n)-}$, where the mean U–O(ether) distances are 2.546(2) and 2.67(4) Å for pentagonal- and hexagonal-bipyramidal coordination, respectively (the latter including one unusually large value of 2.746(5) Å [4b]), it has been assumed that a true coordinate bond exists. Bond lengths for the associated U–O(carboxylate) interactions are consistent with the assigned coordination numbers, although it may be noted that broader considerations of structures

involving related ligands [19] indicate that the U–O(ether) bonds must indeed be rather weak, as shown also by their lability in a family of oxacalixarenes [20].

The two presently characterized complexes, [*R,S*-$Me_6$cyclam$H_2$][$(UO_2)_3$(thftc)$_2$] (**1**) and [$(UO_2)_3$(thftc)$_2$Cu(*R,S*-$Me_6$cyclam)]·2$H_2O$ (**2**), crystallize in the same space group with unit cell parameters which are not widely different and, although they are not strictly isomorphous, their structures are closely related (Figures 1 and 2). In both, there are two inequivalent uranium atoms, one (U1) located on an inversion centre and bound to the $O_3$ site of two ligands (hexagonal-bipyramidal environment), and the other (U2) twice chelated by two carboxylate groups pertaining to the same ligand (two seven-membered rings) and bound to one additional carboxylate donor (pentagonal-bipyramidal environment). The U–O(oxo) and U–O(carboxylato) bond lengths have usual ranges, 1.680(12)–1.773(5) Å and 2.328(13)–2.431(5) Å, respectively. The U–O(ether) bond lengths, expected, for the reasons given above to be the weakest bonds and therefore most susceptible to subtle differences in the structures, are 2.727(10) and 2.636(4) Å in **1** and **2**, respectively. In both cases, the location of the axially directed NH bonds corresponds to the usual trans-III conformation of the azamacrocycle [21]. The thftc$^{4-}$ ligands are in the chiral *R*,R*,R*,S** (*trans,trans,cis*) form generated in situ from the achiral *R*,R*,S*,S** (*trans,cis,trans*) form, an isomerization probably involving an ene-diol intermediate and previously found to occur in a family of zinc(II) complexes [22], as well as in a silver(I) complex [4b], and they connect four uranium centres, one $O_3$-chelated, two $O_2$-chelated and one bound in the simple monodentate mode. The two carboxylate groups adjacent

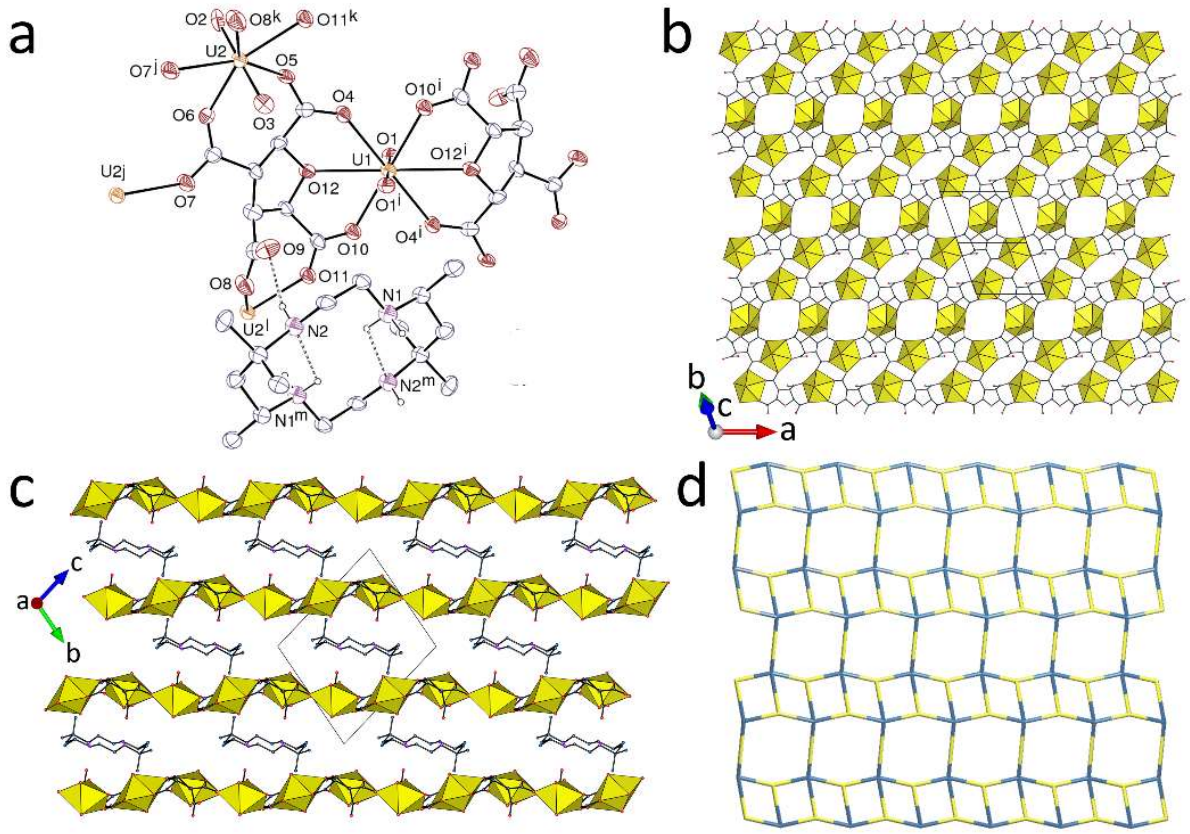


**Fig. 1.** (a) View of complex **1** with displacement ellipsoids shown at the 20% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: i = 1 – *x*, –*y*, 1 – *z*; j = 1 – *x*, 1 – *y*, 2 – *z*; k = *x* – 1, *y*, *z*; l = *x* + 1, *y*, *z*; m = 2 – *x*, 1 – *y*, 1 – *z*. (b) View of the diperiodic coordination polymer showing uranium coordination polyhedra. (c) Packing with layers viewed edge-on. (d) Nodal representation of the network (uranium nodes and edges, yellow; $thftc^{4-}$ nodes, blue; same orientation as in b).

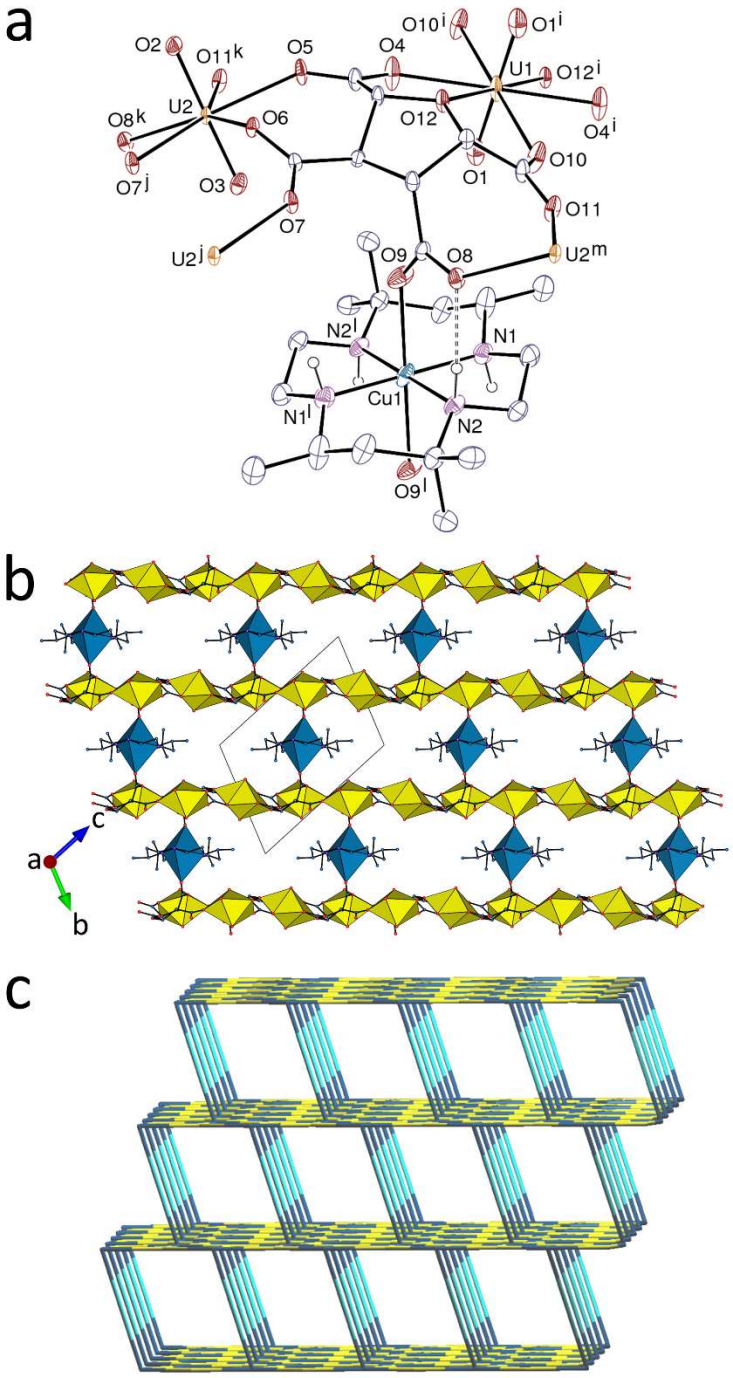


**Fig. 2.** (a) View of complex **2** with displacement ellipsoids shown at the 30% probability level. Solvent molecules and carbon-bound hydrogen atoms are omitted and the hydrogen bond is shown as a dashed line. Symmetry codes: i = 1 – *x*, 1 – *y*, 2 – *z*; j = –*x*, –*y*, 1 – *z*; k = *x* – 1, *y*, *z*; l = 1 – *x*, 1 – *y*, 1 – *z*; m = *x* + 1, *y*, *z*. (b) View of the triperiodic framework with uranium coordination polyhedra yellow and those of copper blue. (c) Nodal representation of the framework (uranium nodes and edges, yellow; copper edges, light blue; $thftc^{4-}$ nodes, dark blue).

to the ether group are bridging in the *anti/anti* $\mu_2$-$\kappa^1O$:$\kappa^1O'$ mode, one of the other two groups bridges two uranyl cations in the *syn/anti* $\mu_2$-$\kappa^1O$:$\kappa^1O'$ mode, and the last is either monodentate in **1** or bridging uranyl and copper in the *syn/anti* $\mu_2$-$\kappa^1O$:$\kappa^1O'$ mode in **2**. If only uranium metal cations are considered, the ligand is thus a 4-coordinated (4-c) node, while U2 is a 3-c node and U1 a simple edge in the diperiodic networks formed, which are parallel to $(01\bar{1})$ and have the $\{4^2.6^3.8\}\{4^2.6\}$ point symbol and the $V_2O_5$ topological type, previously found in a neutral uranyl complex with $Hthftc^{3-}$, albeit with a slightly different coordination mode [4b]. Alternatively, if the $UO_2(thftc)_2^{6-}$ centrosymmetric units are considered as single nodes, the arrangement simplifies to a 3,6-c binodal network with the point symbol $\{4^3\}_2\{4^6.6^6.8^3\}$ and the **kgd** topological type (rhombic geometry). The difference between **1** and **2** does arise in the manner whereby the diperiodic sheets are linked to one another.

In complex **1**, sheets of centrosymmetric *R,S*-$Me_6cyclamH_2^{2+}$ counterions separate the coordination polymer layers, to which they are associated through hydrogen bonding. The diprotonated atom N1 forms one intramolecular bond with N2 and one with the uranyl oxo atom O3, while N2 is hydrogen bonded to the single uncoordinated carboxylate atom O9 [N···O/N distances, 2.784(19)–2.948(17) Å; N–H···O/N angles, 119–156°], thus giving rise to the formation of a weakly bonded triperiodic assembly. In complex **2**, the copper centre is bound to the same atom O9, with a Cu–O bond length of 2.493(5) Å, and it is thus in an axially elongated octahedral environment [Cu–N, 2.022(6) and 2.035(5) Å]. The diperiodic subunits are thus assembled into a binodal 3,5-c triperiodic framework with the $\{4^2.6^5.8^3\}\{4^2.6\}$ point symbol and the 3,5T1 topological type. Simplification through equating $UO_2(thftc)_2^{6-}$ to a single node gives a 3,8-c binodal net with the point symbol $\{4^3\}_2\{4^6.6^{18}.8^4\}$ and the topological type **tfz-d**. Copper coordination is accompanied by hydrogen bonding of N2 to the carboxylate atom O8 [N···O, 3.084(7) Å; N–H···O, 168°], thus forming a ring with the graph set descriptor [23] $R_1^1(6)$, a recurrent motif when metal-complexed azamacrocycles

are associated with uranyl coordination polymers [24]. The interesting point is that the arrangement of anionic diperiodic subunits and azamacrocycles is analogous irrespective of whether the latter is diprotonated or complexed to $Cu^{II}$, as shown in Figure 3. The diperiodic array appears to be sufficiently stable

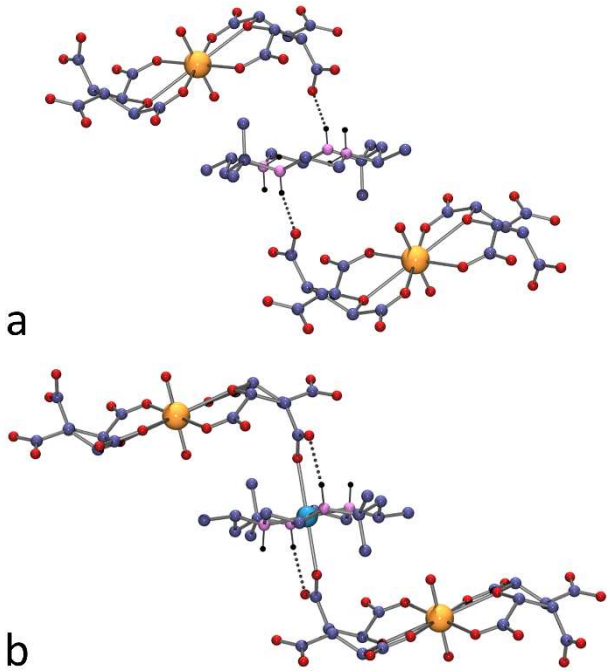


**Fig. 3.** Arrangement of the diprotonated azamacrocycle in **1** (a) and the $Cu^{II}$-complexed azamacrocycle in **2** (b) with respect to the $UO_2(thftc)_2^{6-}$ units from two polymeric layers. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dotted lines.

to resist any change due to the difference in the nature of the cations, and replacement of pure hydrogen bonding by complexation plus hydrogen bonding, the charge and macrocycle conformation being unchanged, involves only minor modifications in the packing. It is however notable that where uranyl ion coordination polymers of 1,2,3,4-cyclobutanetetracarboxylate have been crystallized with the same *R,S*-$Me_6cyclamH_2^{2+}$ and Cu(*R,S*-$Me_6cyclam)^{2+}$ moieties, the structures formed are quite different, being monoperiodic and triperiodic, respectively, the latter having the same topology as **2** [25].

## 4. Conclusions

We have reported the synthesis and crystal structure of two complexes formed by uranyl cations and thftc$^{4-}$ in the presence of either *R,S*-Me$_6$cyclamH$_2^{2+}$ (**1**) or Cu(*R,S*-Me$_6$cyclam)$^{2+}$ (**2**). Complex **1** crystallizes as a diperiodic network with the $V_2O_5$ topological type, which is also found as a subunit in the triperiodic framework formed in **2**. It appears that formation of networks with this topology is a frequent occurrence in the uranyl–H$_n$thftc$^{(4-n)-}$ system, and this regardless of whether the ligand is present in its *R*,R*,S*,S** or *R*,R*,R*,S** diastereomeric forms. In addition to complexes **1** and **2**, it is also observed in one homometallic and one uranyl–silver(I) heterometallic species described earlier [4b]. While the layers remain separate in the homometallic complexes, they are united into triperiodic species by copper(II) or silver(I) linkers in the heterometallic ones. Although complex **1** is diperiodic and **2** is triperiodic, the difference in the overall packing of anionic sheets and azamacrocyclic moieties is minimal, as a consequence of the similar stereochemistry of the otherwise different interactions linking the diperiodic polymer units. In this sense it can be said that, in the present system, doubly protonated *R,S*-Me$_6$cyclam has a structural influence equal to that of its complex with Cu$^{II}$.

### Appendix A. Supplementary material

CCDC 2204503 and 2204504 contain the supplementary crystallographic data for **1** and **2**. 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**

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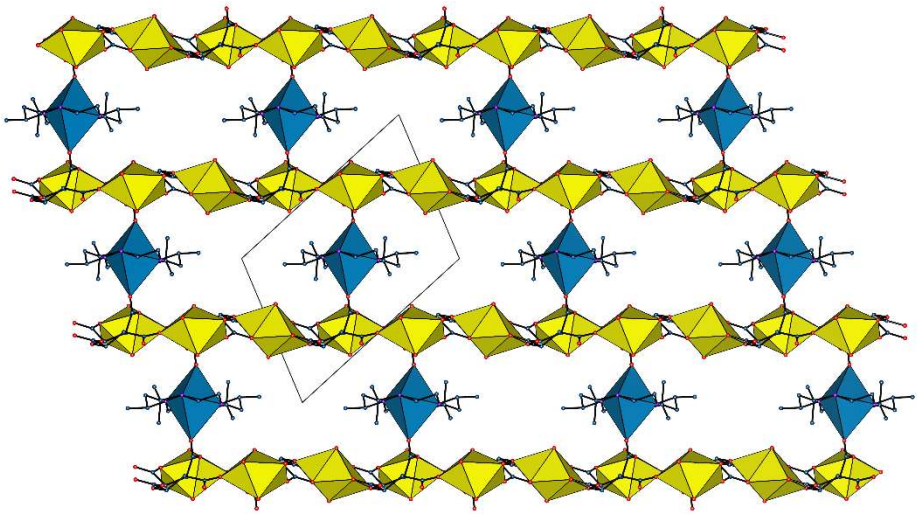

Although they have different periodicities, two uranyl ion complexes with tetrahydrofurantetracarboxylate involving a protonated or a metal-complexed azamacrocyclic cation display overall arrangements reflecting the similar stereochemistry of the interactions.