Tetrahydrofuran-tetracarboxylic Acid: an Isomerizable Framework-Forming Ligand in Homo- and Heterometallic Complexes with UO_2^{2+} , Ag^+ and Pb^{2+}

Pierre Thuéry^{*,†} and Jack Harrowfield^{*,‡}

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

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

ABSTRACT: ($2R^*,3R^*,4S^*,5S^*$)-Tetrahydrofuran-tetracarboxylic acid (H_4thftc) has been used as a ligand to synthesize five uranyl ion complexes, three of them including additional silver(I) or lead(II) metal cations. The complex $[\text{C}(\text{NH}_2)_3]_2[\text{UO}_2(\text{H}_2\text{thftc})_2]$ (**1**), obtained in water at room temperature, is a discrete mononuclear species in which the uranyl cation is bound to the tridentate coordination site (involving the ether oxygen atom and the two adjoining carboxylate groups) of two ligands, and extensive hydrogen bonding is present. All the other complexes were obtained under (solvo)-hydrothermal conditions giving rise to higher degrees of ligand deprotonation. $[(\text{UO}_2)_3(\text{Hthftc})_2(\text{H}_2\text{O})_2] \cdot 2\text{CH}_3\text{CN}$ (**2**) crystallizes as a two-dimensional (2D) network with the V_2O_5 topological type, whereas in the heterometallic complex $[(\text{UO}_2)_3\text{Ag}_2(\text{thftc})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**3**), similar 2D layers are assembled into a three-dimensional (3D) framework by bridging Ag_2 moieties. Lead(II) replaces uranyl in the tridentate coordination site in the two complexes $[\text{UO}_2\text{Pb}(\text{thftc})(\text{H}_2\text{O})]$ (**4**) and $[\text{UO}_2\text{Pb}(\text{thftc})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**5**), and the high connectivity of the ligand, bound to seven metal cations through diverse chelating and bridging interactions, ensures that both are 3D frameworks. Bonding of a uranyl oxo group to either silver(I) or lead(II) is apparent in complexes **3** and **5**. The homometallic complexes $[\text{Ag}_3(\text{Hthftc})]$ (**6**) and $[\text{Pb}_2(\text{thftc})(\text{H}_2\text{O})]$ (**7**), devoid of uranyl cations, are both 3D frameworks in which the ligand is bound to 11 or 9 metal cations, respectively. Complex **6** is the single instance in this series in which the ligand, originally in the *trans,cis,trans* form, has undergone isomerization into the chiral *cis,trans,trans* ($2R^*,3S^*,4S^*,5S^*$) form through a process probably involving an ene-diol intermediate. Only complexes **1**, **2** and **4** display intense and well-resolved emission bands under excitation at 420 nm in the solid state, the uranyl emission of complexes **3** and **5** being largely quenched.

INTRODUCTION

An appealing ligand with a somewhat flexible conformation and four possible degrees of deprotonation, tetrahydrofuran tetracarboxylic acid (H₄thftc) has not been widely used till now, and virtually all the crystal structures reported for its salts or complexes contain alkali, alkaline-earth,^{1,2} or d-block metal cations.^{3–13} In the f-element series, the complexation of lanthanide ions by H₄thftc was investigated in solution,^{14,15} and the complexes formed were shown to be stronger than those with uranyl ion;¹⁵ the weak complexation of the latter cation compared with that of transuranic elements was put to use in a solvent extraction process for nuclear waste reprocessing.¹⁶ However, no crystal structure of a lanthanide or transuranic cation complex with H₄thftc has ever been reported, and, apart from the complexes of the cations cited above, the only crystallographically characterized species are three uranyl ion complexes.^{17,18}

In the overwhelming majority of the known structures containing H₄thftc or its anions, either free or complexed, the molecule retains the achiral *trans,cis,trans* (2*R**,3*R**,4*S**,5*S**) isomeric form of the single species shown to be present in the commercially available acid.¹⁴ In principle, six diastereomeric forms are possible and in some early publications^{3,19} evidence for the presence of more than one has been noted. More significantly, in a recent study of zinc(II) complexes, mainly mixed-ligand species, obtained by solvothermal syntheses, clear evidence was obtained for the isomerization of the achiral acid to the chiral (2*R**,3*S**,4*S**,5*S**) form, isolated in good yield in several complexes.⁸ An acid-dependent inversion process, relatively rapid at the temperature of solvothermal methods and involving an ene-diol intermediate, was suggested to be the cause of this isomerization and such a mechanism could also explain the observation of related isomerization processes in other alicyclic polycarboxylic acids used to prepare metal ion complexes by solvothermal methods.^{20–25} Thus, under acidic solvothermal conditions, H₄thftc can be regarded

as being in a dynamic equilibrium involving possibly up to 6 diastereomeric species and thus can be considered as a single-molecule dynamic covalent library,²⁶ open potentially to selective coordination and amplification of a given isomer depending upon the metal and, as shown in the case of crystalline Zn^{II} complexes,⁸ any co-ligands. The present work provides one further example of this selective coordination within a precipitated solid, this resulting from our continuing efforts to characterise the influence of the presence of other heavy metal ions on the structure of uranyl ion/polycarboxylate coordination polymers.

Of the known uranyl ion complexes of H₄thfc, which all contain the (2*R**,3*R**,4*S**,5*S**) isomer, [Hpip]₆[UO₂(thfc)]₃·9H₂O (where pip is *N*-ethylpiperidine) and [HNEt₃]₈[UO₂(thfc)]₄·2MeOH·2H₂O were synthesized in organic solvents (methanol or dimethylsulfoxide) at room temperature, in the presence of an organic base;¹⁷ both are metallamacrocycles, with three and four metal centres, respectively, in which one uranyl ion is chelated by the two carboxylate groups in the positions 2 and 5 and is also bound to the ether oxygen donor in between (a tridentate coordination site analogous to that of oxydiacetate), and another one is chelated by the carboxylate groups in the positions 3 and 4 (analogous to succinate). Under mild conditions, isomerization of the ligand would not be anticipated but the (2*R**,3*R**,4*S**,5*S**) configuration is also found in the heterometallic complex [UO₂Cu(thfc)(bipy)(H₂O)]·2H₂O (bipy = 2,2'-bipyridine), where the tetracarboxylic acid is again fully deprotonated, which was obtained under hydrothermal conditions at a temperature of 180 °C.¹⁸ This compound crystallizes as a two-dimensional (2D) array with the {4⁴.6²} point symbol, in which the [Cu(bipy)(H₂O)]²⁺ cations have no topological role. The coordination mode here is different from that in the homometallic, molecular species since the copper(II) cation occupies the tridentate coordination site. Such differences between homo- and heterometallic complexes of a given ligand are well-known in general and have been explored in the field of uranyl complexes,^{27–}

³⁵ although principally with the objective there of increasing the dimensionality of the lattice to generate uranyl–organic frameworks (UOFs^{36–39}) and not for the purpose of selecting different ligand isomers. To explore both issues and in continuation of our recent work on heterometallic complexes of 1,3,5-benzenetriacetic acid involving metal ions with very different coordination preferences,⁴⁰ we have now examined the complexes formed by uranyl cations with H₄thftc, mainly in the presence of silver(I) or lead(II) cations under (solvo)-hydrothermal conditions, and we report herein the crystal structures and emission spectra in the solid state of three heterometallic complexes, all of them three-dimensional (3D) frameworks, as well as those of four homometallic complexes, containing either uranyl, silver or lead alone, for comparison purposes. The homometallic Ag^I complex provides the second example of crystallization of the (2*R**,3*S**,4*S**,5*S**) isomer of the ligand.

EXPERIMENTAL SECTION

Syntheses. Caution! *Uranium is a radioactive and chemically toxic element, and uranium-containing samples must be handled with suitable care and protection.*

UO₂(NO₃)₂·6H₂O (depleted uranium, R. P. Normapur, 99%), AgNO₃, Pb(NO₃)₂ and [C(NH₂)₃]NO₃ were purchased from Prolabo, and (2*R**,3*R**,4*S**,5*S**)-tetrahydrofuran-tetracarboxylic acid (H₄thftc) was from Aldrich. Elemental analyses were performed by MEDAC Ltd. at Chobham, UK and the Service de Microanalyse of the CNRS at Gif-sur-Yvette, France.

[C(NH₂)₃]₂[UO₂(H₂thftc)₂] (**1**). H₄thftc (25 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (50 mg, 0.10 mmol) and guanidinium nitrate (24 mg, 0.20 mmol) were dissolved in demineralized water (0.6 mL). The solution was left to evaporate slowly at room temperature, giving light yellow

crystals of complex **1** within ten days (22 mg, 50% yield based on H₄thftc). Anal. calcd for C₁₈H₂₄N₆O₂₀U: C, 24.50; H, 2.74; N, 9.52. Found: C, 24.39; H, 2.71; N, 9.45%.

$[(UO_2)_3(Hthftc)_2(H_2O)_2] \cdot 2CH_3CN$ (**2**). H₄thftc (25 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (50 mg, 0.10 mmol), Cd(NO₃)₂·4H₂O (31 mg, 0.10 mmol), 2,2'-bipyridine (16 mg, 0.10 mmol), acetonitrile (0.4 mL), and demineralized water (0.6 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving light yellow crystals of complex **2** overnight (11 mg, 23% yield based on U). Anal. calcd for C₂₀H₂₀N₂O₂₆U₃: C, 16.94; H, 1.42; N, 1.97. Found: C, 17.31; H, 1.45; N, 1.92%.

$[(UO_2)_3Ag_2(thftc)_2(H_2O)_2] \cdot 2H_2O$ (**3**). H₄thftc (25 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (50 mg, 0.10 mmol), AgNO₃ (34 mg, 0.20 mmol), and demineralized water (1.0 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving light yellow crystals of complex **3** within two weeks (6 mg, 11% yield based on U). Anal. calcd for C₁₆H₁₆Ag₂O₂₈U₃: C, 12.12; H, 1.02. Found: C, 12.44; H, 1.48%.

$[UO_2Pb(thftc)(H_2O)]$ (**4**). H₄thftc (25 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (50 mg, 0.10 mmol), Pb(NO₃)₂ (33 mg, 0.10 mmol), AgNO₃ (17 mg, 0.10 mmol), and demineralized water (1.0 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving light yellow crystals of complex **4** within two days (13 mg, 18% yield). Anal. calcd for C₈H₆O₁₂PbU: C, 13.00; H, 0.82. Found: C, 12.87; H, 1.07%.

$[UO_2Pb(thftc)(H_2O)_2] \cdot H_2O$ (**5**). H₄thftc (25 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (50 mg, 0.10 mmol), Pb(NO₃)₂ (33 mg, 0.10 mmol), and demineralized water (1.0 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving light yellow crystals of complex **5** overnight (12 mg, 15% yield). Anal. calcd for C₈H₁₀O₁₄PbU: C, 12.39; H, 1.30. Found: C, 12.97; H, 1.15%.

$[Ag_3(Hthftc)]$ (**6**). H_4thftc (25 mg, 0.10 mmol), $AgNO_3$ (34 mg, 0.20 mmol), acetonitrile (0.2 mL), and demineralized water (0.8 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving colourless crystals of complex **6** within two weeks (6 mg, 16% yield based on Ag). Anal. calcd for $C_8H_5Ag_3O_9$: C, 16.90; H, 0.89. Found: C, 17.23; H, 0.99%.

$[Pb_2(thftc)(H_2O)]$ (**7**). H_4thftc (13 mg, 0.05 mmol), $Pb(NO_3)_2$ (33 mg, 0.10 mmol), acetonitrile (0.3 mL), and demineralized water (0.6 mL) were placed in a 10 mL tightly closed glass vessel and heated at 140 °C under autogenous pressure, giving colourless crystals of complex **7** overnight (13 mg, 38% yield). Anal. calcd for $C_8H_6O_{10}Pb_2$: C, 14.20; H, 0.89. Found: C, 14.13; H, 0.94%.

Crystallography. The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer⁴¹ using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of φ - and ω -scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.⁴² Absorption effects were corrected empirically with the program SCALEPACK.⁴² The structures were solved by intrinsic phasing with SHELXT,⁴³ expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL-2014.⁴⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen and nitrogen atoms were retrieved from difference Fourier maps, and the carbon-bound hydrogen atoms were introduced at calculated positions; all hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. In the case of complex **6**, 3-component twinning was detected with

PLATON/TwinRotMat⁴⁵ and taken into account; atom Ag3 is further disordered over two positions (one of them located on an inversion centre), which have been refined with occupancy parameters constrained to sum to unity.

Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3⁴⁶ and the polyhedral representations with VESTA.⁴⁷ The topological analyses were conducted with TOPOS.⁴⁸

Luminescence Measurements. Emission spectra were recorded on solid samples using a Horiba-Jobin-Yvon Fluorolog spectrofluorometer. The powdered complex was pressed between two silica plates which were mounted such that the faces were oriented vertically and at 45° to the incident excitation radiation. An excitation wavelength of 420 nm was used in all cases and the emissions monitored between 450 and 650 nm.

RESULTS AND DISCUSSION

Synthesis. Complex **1** only was synthesized at room temperature, while the other complexes were obtained under purely hydrothermal (**3–5**) or solvo-hydrothermal (**2**, **6** and **7**) conditions, the latter with acetonitrile as a co-solvent, in which cases the crystalline materials deposited during the heating phase (140 °C). All the uranyl complexes with variously deprotonated H₄thfc ligands crystallized at room temperature, either in pure water or in organic solvents, in the present and previous studies¹⁷ are molecular species, whereas all those synthesized by (solvo)-hydrothermal methods are coordination polymers (even in the absence of additional metal cations in the final compound, as in the case of complex **2**), thus providing a nice illustration of the specific interest of the latter methods for constructing polymeric species.

An interesting feature of the series is the variable degree of deprotonation, the lower corresponding to the room temperature synthesis, in which two carboxylic protons are retained, while one proton is found in complexes **2** and **6**, full deprotonation being reached in the other cases (full deprotonation was also achieved in the metallamacrocyclic structures, obtained at room temperature in the presence of organic bases¹⁷). It is notable that the protons retained are located on the carboxylic groups at positions 3 and 4 (see below). The reported pK_{ai} ($i = 1-4$) values determined by titration for H₄thfc are 0.95, 3.40, 5.55 and 6.42,⁴⁹ or in the ranges 1.57–2.08, 2.86–3.68, 4.08–5.40 and 5.61–7.26,^{14,19} depending largely on the ionic strength. The low value of pK_{a1} indicates that the electron-withdrawing inductive effects associated with carboxylic and ether groups strongly favour the departure of the first proton. While the most acidic proton is most probably one of either of the two carboxylic groups in the α position with respect to the ether,¹ there is some uncertainty as to the subsequent deprotonation order, with either the protons at positions 2 and 5 being the more acidic,¹ or a 2, 4, 5, 3 deprotonation sequence.¹⁴ However, esterification of H₄thfc in methanol gave the 2,5-diester, thus showing that the carboxylic groups at those positions are possibly the most acidic.⁵⁰ This does not necessarily mean that these sites must be the ones where a metal ion would most readily replace the proton and it should be noted that coordination to the tetrahydrofuran-O may be an important factor favouring binding to the two adjacent carboxylate units.

Crystal Structures. The complex $[C(NH_2)_3]_2[UO_2(H_2thfc)_2]$ (**1**), represented in Figure 1, contains a mononuclear dianionic species in which the unique hexagonal bipyramidal uranium atom, located on an inversion centre, is bound to the tridentate, oxydiacetate-like site of two ligands, both carboxylic groups at the 3 and 4 positions retaining their proton. Formation of two five-membered chelate rings within the tridentate unit must be favoured over that of one seven-

membered ring that would result from chelation by the groups in the 3 and 4 positions.¹⁵ The U–O(carboxylate) [2.399(3) and 2.447(3) Å] and U–O(ether) [2.640(3) Å] bond lengths are unexceptional, and they are larger by ~0.09 Å than those in the metallamacrocycles previously reported¹⁷ as a consequence of the different coordination number, seven in the latter complexes and eight in **1**; in particular, these bond lengths are very close to those measured in eight-coordinate uranyl complexes with oxydiacetate (2.36–2.46 Å and 2.62–2.72 Å, respectively).^{51–54} The six equatorial donors define a regularly puckered plane with a root mean square (rms) deviation of 0.27 Å. The H₂thfc^{2–} anion is, as expected given the mild preparative conditions, in the achiral *trans,cis,trans* (2*R**,3*R**,4*S**,5*S**) form and the complex crystallizes in a centrosymmetric space group. The ligand adopts an envelope conformation with the carbon atom C1, next to O10, being displaced by 0.555(6) Å from the average plane defined by the four other atoms of the ring (rms deviation 0.015 Å). This is at variance with the conformation possessing mirror symmetry found in the cyclic polynuclear species, in which the ether group is out of the plane defined by the four carbon atoms.¹⁷ Due to the presence of carboxylic groups and proton-rich C(NH₂)₃⁺ guanidinium counterions, extensive hydrogen bonding interactions are present. The carboxylic groups are hydrogen bonded to the uncoordinated oxygen atoms of the carboxylate groups from neighbouring complexes [O6...O5^j 2.557(5) Å, O6–H...O5^j 134°; O8...O3^k 2.629(5) Å, O8–H...O3^k 164°; symmetry codes: *j* = 1 – *x*, 2 – *y*, 1 – *z* and *k* = 1 – *x*, 1 – *y*, 2 – *z*], which gives rise to the formation of sheets parallel to (1 –1 –1) with alternating cations and anions arranged into staggered rows, as shown in Figure 1. The guanidinium counterion is involved in five intra-sheet hydrogen bonds, all with carboxylate oxygen atoms, with one of the protons involved in a bifurcated bond, while two protons bound to different nitrogen atoms are hydrogen bonded to the same oxygen atom. The other two hydrogen bonds formed by the counterion involve carboxylic oxygen atoms (O7 and O9)

from an adjacent sheet, so that a 3D network is formed. Overall, the hydrogen bonds with guanidinium are significantly longer than those involving carboxylic donors [N $\cdots$ O 2.877(6)–3.204(6) Å, N–H $\cdots$ O 132–162°]. A weak inter-sheet interaction between a carbon-bound proton of the ligand and the oxo atom O1, with a H $\cdots$ O distance of 2.27 Å, may also be present. With a Kitaigorodski packing index (KPI, estimated with PLATON⁴⁵) of 0.73, the packing displays no free space.

Although it was synthesized in the presence of cadmium(II) nitrate and 2,2'-bipyridine, complex **2**, [(UO₂)₃(Hthftc)₂(H₂O)₂] $\cdot$ 2CH₃CN, does not contain these additional species and is a unique case of a polymeric homometallic uranyl complex obtained from H₄thftc. The additional species in the reaction mixture could influence the solution equilibria both through nitrate and 2,2'-bipyridine complexation of uranyl and pH effects, though the acidity of the aqua-Cd(II) cation would presumably counter the basicity of 2,2'-bipyridine and it can only be said that the overall consequence is to enhance the degree of deprotonation of H₄thftc. Note that in only three of the present seven cases does the stoichiometry of the isolated solid reflect that of the reaction mixture. The asymmetric unit of **2** includes two independent uranium atoms, one of them (U1) located on an inversion centre, and one Hthftc³⁻ anion (Figure 2). Atom U1 is in the same environment as its counterpart in complex **1**, with similar U–O(carboxylate) [2.386(3) and 2.447(4) Å] and U–O(ether) [2.660(3) Å] bond lengths. Atom U2 is chelated by two carboxylic groups in the positions 2 and 3 (atoms O7 and O8) to give a 7-membered ring, and it is also bound to two more carboxylate oxygen atoms from two different ligands and a water molecule, its environment being thus pentagonal bipyramidal with unexceptional U–O(carboxylate) bond lengths [2.321(4)–2.432(4) Å]. The ligand retains the *trans,cis,trans* (2*R**,3*R**,4*S**,5*S**) form, with an envelope conformation, the carbon atom C2, next to O12, being at 0.613(8) Å from the average plane defined by the other

four atoms of the ring (rms deviation 0.013 Å). Each ligand is bound to four metal atoms, its three carboxylate groups being bridging bidentate ($\mu_2\text{-}\eta^1\text{:}\eta^1$ coordination mode) and the carboxylic acid group being uncoordinated (Scheme 1). Only U2 and Hthftc³⁻ are nodes (three- and four-fold, respectively) in the 2D polymeric assembly parallel to (1 1 0), with the point (Schläfli) symbol $\{4^2.6^3.8\}\{4^2.6\}$ (topological type V₂O₅). As shown in Figure 2, this arrangement can be viewed as formed of an alternation of rows of differently sized parallelograms and it is different from the $\{4^4.6^2\}$ network found in the uranyl/copper(II) heterometallic complex of thftc⁴⁻, in which the copper cations have no topological role.¹⁸ The carboxylic proton is hydrogen bonded to the acetonitrile solvent molecule [O11...N1 2.720(6) Å, O11-H...N1 153°], and those of the water molecule are bonded to either a carboxylate or a carboxylic oxygen atom pertaining to the same or an adjacent layer, respectively [O13...O6ⁱ 2.779(5) Å, O13-H...O6ⁱ 168°; O13...O10ⁱⁱ 2.748(6) Å, O13-H...O10ⁱⁱ 146°; symmetry codes: i = 1 - x, 2 - y, 2 - z and ii = 1 - x, 1 - y, 2 - z]. The oxo atoms O2 and O3 may be involved in weak interactions with carbon-bound hydrogen atoms from a ligand of the neighbouring sheet (H...O 2.45 Å) and the acetonitrile molecule (2.69–2.79 Å). The KPI of 0.71 indicates a compact arrangement devoid of free spaces.

The asymmetric unit in the heterometallic complex [(UO₂)₃Ag₂(thftc)₂(H₂O)₂].2H₂O (**3**) contains two uranium atoms, one of them (U2) located on an inversion centre, one silver(I) cation and one fully deprotonated thftc⁴⁻ ligand (Figure 3). Like U1 in complexes **1** and **2**, atom U2 is bound to the tridentate site of two ligands, with unexceptional U–O(carboxylate) [2.373(4) and 2.407(5) Å] bond lengths and a U–O(ether) bond length of 2.746(5) Å slightly longer than usual. Atom U1 is chelated by two carboxylate groups in the 2 and 3 positions of one ligand and it is bound to two more carboxylate donors from two more ligands [U–O(carboxylate) bond lengths 2.315(2)–2.453(4) Å] and to a water molecule, as for U2 in complex **2**. A centrosymmetric pair of

silver atoms connected through a strong argentophilic interaction [2.7773(13) Å] is trapped between two $\mu_2\text{-}\eta^1\text{:}\eta^1$ carboxylate groups, which is a usual motif, with more than 60 comparable examples reported in the Cambridge Structural Database (CSD, Version 5.37),^{55,56} giving an average Ag...Ag distance of 2.89(10) Å. The Ag–O(carboxylate) bond lengths of 2.169(5) and 2.186(5) Å are unexceptional [average 2.25(9) Å from the CSD]. Ag1 is involved in three longer contacts, one with the carboxylate atom O7^I [2.706(5) Å; symmetry code: $1 = x - 1, y, z$] and the others with the uranyl oxo atoms O3^I [2.899(5) Å] and O1^{II} [2.974(5) Å; symmetry code: $11 = x, y + 1, z$]. The Ag–O bond lengths reported in the CSD range approximately from 2.0 to 3.1 Å [average 2.45(16) Å], so that the latter interactions with the oxo groups may be considered as weak interactions at best, as confirmed by the absence of significant lengthening of the U=O bond lengths [1.760(5)–1.776(5) Å]; only the bond with O3^I is shown in Figure 3. Much stronger Ag–O(uranyl) bonds, with distances as short as 2.38–2.58 Å, have been reported.^{57–59} Here again, the ligand is in the *trans,cis,trans* (2*R**,3*R**,4*S**,5*S**) form, and the envelope conformation brings atom C1, next to O12, to 0.612(9) Å from the mean plane defined by the other four atoms of the ring (rms deviation 0.006 Å). The ligand is bound to four uranyl ions, in a similar way as that found in complex **2**, the difference arising from replacement of the uncomplexed carboxylic group by a silver-bound carboxylate (Scheme 1). Considering only uranyl cations, a 2D assembly analogous to that in **2** is thus formed, with the V₂O₅ topological type and parallel to (1 $\bar{1}$ 1). Instead of being hydrogen bonded to one another, the layers are united into a 3D coordination polymer by the bridging Ag₂ moieties. The coordinated and lattice water molecules are hydrogen bonded to oxo and carboxylato groups, and to one another. The KPI of 0.73 (0.68 with solvent excluded) indicates that no spaces or channels of significant size are present.

Two crystalline complexes combining uranyl and lead(II) cations have been obtained, $[\text{UO}_2\text{Pb}(\text{thftc})(\text{H}_2\text{O})]$ (**4**) and $[\text{UO}_2\text{Pb}(\text{thftc})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**5**), their syntheses differing by the additional presence of silver nitrate in that of compound **4**. The asymmetric unit in **4** contains one uranyl and one lead(II) cation, and one fully deprotonated thftc^{4-} ligand (Figure 4). The most prominent difference with the previous cases is that the tridentate coordination site is now occupied by lead(II) (as it was by copper(II) in the previously reported heterometallic complex¹⁸), and U(VI) is found exclusively in a pentagonal bipyramidal environment. The uranium atom is chelated by two carboxylate groups from the 2 and 3 positions, as in complexes **2** and **3**, but here this happens twice and involves two ligands; one more carboxylate oxygen atom from a third ligand completes the pentagonal bipyramidal environment [U–O(carboxylate) bond lengths in the range 2.333(9)–2.453(9) Å]. The lead(II) cation is bound to the ether atom O11 [2.859(8) Å; the average Pb–O(ether) bond length from the CSD is 2.75(11) Å], to seven carboxylate oxygen atoms [2.553(9)–3.108(9) Å], among which four pertain to two chelating groups, and to a water molecule [2.439(9) Å], which gives a nine-coordinate environment of very irregular geometry possibly influenced by the presence of a stereochemically active lone pair.^{60–62} Holodirected bonding should be favoured in the present case,⁶⁰ but it should be noted that all the Pb–O(carboxylate) bond lengths are somewhat long and several of them may correspond to rather weak bonds only, a situation commonly encountered in Pb^{II} complexes.⁶² The thftc^{4-} ligand is in the same form as in the previous complexes, with atom C2, next to O11, deviating by 0.56(2) Å from the average plane defined by the four other atoms of the ring (rms deviation 0.010 Å). The ligand is bound to seven (four lead(II) and three uranyl) metal cations (Scheme 1), and this high connectivity gives rise to the formation of a 3D framework, a situation different from that in the copper(II)-containing complex previously reported, in which the terminal nature of the bipy and water ligands bound to Cu^{II} limited the

polymer propagation.¹⁸ Planar sheets parallel to (1 1 0) are apparent, that are connected to one another through lead–carboxylate bonds, a feature reminiscent of that found in complex **3**. However, the sheets here are heterometallic, with alternating rows of uranyl dimers (with double carboxylate bridges) and lead cations directed along the *c* axis (Figure 4). The KPI of 0.81 is indicative of a very compact arrangement.

With respect to that in **4**, the asymmetric unit in **5** contains two additional water molecules, one coordinated and one free, but the connectivity is different. The uranium atom is once more chelated by two carboxylate groups in 2 and 3 positions, and is bound to two more carboxylate donors from two different ligands and one water molecule [U–O(carboxylate) bond lengths in the range 2.283(4)–2.417(3) Å]. The tridentate coordination site is here again occupied by the lead(II) cation, with a Pb–O(ether) bond length [2.675(4) Å] shorter than that in **4**. The lead(II) cation is bound to six carboxylate oxygen atoms [2.580(4)–2.759(4) Å, with a longer contact at 3.031(5) Å with the bridging atom O9, part of an unsymmetrical chelating group] and to a water molecule [2.502(4) Å]. It is also possibly bonded to the uranyl oxo atom O1, at 2.999(4) Å, a value significantly lower than that of 3.176(5) Å found in a complex with 1,3,5-benzenetriacetate.⁴⁰ Distances for such oxo–cation interactions involving lanthanides are 2.822(4) Å for Ce(III) and 2.792(6) Å for Nd(III);⁶³ the ionic radius of Pb^{II} being about 0.1 Å larger than that of Ce(III), the present distance seems compatible with the existence of such an interaction, but the absence of significant U=O bond lengthening [U1–O1 1.774(4), U1–O2 1.763(4) Å] indicates however that it is not a very strong one. Pb1 is thus in an irregular nine-coordinate environment that would have a hemidirected character but for the contact with the oxo group. The ligand is in the same form as in the other compounds, but the envelope conformation has atom C4 (in the succinate-like part) displaced by 0.653(8) Å from the mean plane defined by the four other atoms of the ring (rms deviation 0.019 Å), a conformation previously found, for example, in the cesium or calcium salts

of partially or fully deprotonated H₄thftc,¹ or in the heterometallic uranyl/copper(II) complex of the latter.¹⁸ As in complex **4**, the ligand is bound to seven (four lead(II) and three uranyl) metal cations, although they are differently arranged in both compounds (Scheme 1), and this high degree of connectivity results here also in the formation of a 3D framework (KPI 0.78), in which thick layers parallel to (0 0 1) can be discerned (Figure 5). The water molecules are hydrogen bonded to one another and to carboxylate and oxo groups.

Since no structure of a homometallic complex formed by H₄thftc with either silver(I) or lead(II) has been reported, it appeared worthwhile to synthesize such compounds so as to compare the coordination modes observed to those in the heterometallic complexes. In the event, this also proved interesting in regard to the selection of isomers of H₄thftc apparently present in the solvothermal reaction mixtures. The asymmetric unit in [Ag₃(Hthftc)] (**6**) contains three independent silver cations, one of them (Ag3) being disordered over two positions (one of them located on an inversion centre), and one Hthftc³⁻ ligand (Figure 6). The tridentate site is occupied by one silver(I) cation (Ag1), but the Ag1–O9 bond length of 2.772(7) Å indicates that the interaction is not a strong one [Ag–O(ether) bond lengths reported in the CSD vary widely in the 2.15–3.16 Å range, with a maximum around 2.55 Å, large values being often associated to constrained ligands, as is the case here]. The Ag–O(carboxylic/ate) bond lengths in **6** are in the range 2.239(7)–2.765(6) Å [average 2.45(15) Å], and the coordination environments are very irregular (even when only the shorter contacts are considered). The most unusual feature of this structure concerns the Hthftc³⁻ ligand, which is in the chiral *cis,trans,trans* (2*R**,3*S**,4*S**,5*S**) form, with the three carboxylate groups located on one side of the ring and the carboxylic group on the other side. As noted previously, inversion of the ring carbon atoms of H₄thftc has been observed in a family of zinc(II) complexes,⁸ and the same phenomenon arises with 1,2,3,4-cyclobutanetetracarboxylic acid (*cis,trans,cis* and *trans,trans,trans* isomers)^{18,21,23,24} and with

1,2,3,4,5,6-cyclohexanhexacarboxylic acid (*all-cis* and *all-trans* isomers).^{20,22,25} The cyclopentane ring is here once more in an envelope conformation, albeit somewhat more distorted than in complexes **1–5**, with atom C1, next to O9, displaced by 0.547(12) Å from the mean plane defined by the four other atoms (rms deviation 0.051 Å). With about 11 silver(I) cations bound to the ligand (the value may vary due to the disorder affecting Ag3; only one possible arrangement is shown in Scheme 1), it is unsurprising that the polymer generated is 3D and extremely intricate. The cations appear to be concentrated into layers parallel to (1 0 0), these layers containing cylindrical channels with a diameter of ~5 Å running along the *c* axis (Figure 6). Notwithstanding these narrow free spaces, the KPI value of 0.79 (calculated for only one position of Ag3) indicates that this compound cannot be considered as really porous, at least for any practical purpose.

Unlike the homometallic Ag^I complex but like all other complexes in the present study, the homometallic Pb^{II} complex, [Pb₂(thftc)(H₂O)] (**7**), contains the ligand in its *trans,cis,trans* (2*R**,3*R**,4*S**,5*S**) form. There are two inequivalent metal atoms, with Pb1 bound to the tridentate site of the ligand, and an 8-membered chelate ring formed on Pb2 through binding of just the carboxylate-O donors on ring positions 2 and 5 (O1 and O3) and not of their intervening ether-O atom. Pb1 is also bound to four more carboxylate oxygen atoms (among which O7 and O8 pertain to a chelating group), and to two water molecules [Pb1–O(water) bond lengths 2.813(5) and 2.962(5) Å]. Pb2 has no water ligand, and it is bound to nine carboxylate oxygen donors, all but O2 being involved in chelation through either one or two carboxylate groups. All the chelating interactions are quite unsymmetrical, and both Pb1 and Pb2 are 9-coordinate with an irregular geometry, probably best described as holodirected. The Pb1–O9(ether) bond length of 2.729(4) Å lies between those found in complexes **4** and **5**. The Pb–O(carboxylate) bond distances vary considerably [2.451(5)–3.000(5) Å for Pb1, 2.369(4)–3.089(5) Å for Pb2] but over a similar range

to that found in the heterometallic complexes. The ligand ring conformation is here again of the envelope type and an atom in the succinate-like part (as in complex **5**), C3, is at 0.623(9) Å from the average plane defined by the four other atoms (rms deviation 0.040 Å). All nine O-donors of the ligand are involved in coordination, through chelating and bridging interactions (with in particular a regular $\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1$ coordination mode for the two carboxylate groups of the succinate-like part), to nine Pb^{II} centres (Scheme 1). The water molecule is hydrogen bonded to carboxylate oxygen atoms [O...O distances 2.903(6) and 2.738(6) Å, O–H...O angles 151 and 168°]. The complex is a 3D coordination polymer in which layers of ligand molecules parallel to (0 1 0) can be considered to be linked within and bridged by layers containing both Pb1 and Pb2. The high KPI value of 0.86 is indicative of a dense arrangement.

Luminescence properties. Solid state emission spectra have been recorded under excitation at a wavelength of 420 nm, a value suitable for excitation of uranyl,⁶⁴ for compounds **1–7**, and those for the uranium-containing complexes **1–5** are shown in Figure 8. The spectra of the uranyl-only complexes **1** and **2**, and that of the uranyl/lead(II) complex **4** show intense and well-resolved uranyl emission displaying the vibronic progression corresponding to the $S_{11} \rightarrow S_{00}$ and $S_{10} \rightarrow S_{0\nu}$ ($\nu = 0\text{--}4$) states.⁶⁵ The maxima are at 496, 518, 542, 568 and 596 nm for complex **1**, while they are blue-shifted by 2 nm in **2**, and red-shifted by 2 nm in **4**; some changes in the relative intensities of the peaks are also observed, which could be due at least partly to a very broad single peak seemingly convoluted with the uranyl spectrum in the case of **1** and **4**. Weak bands at ~477 and ~482 nm in the spectra of **2** and **4**, respectively, correspond to a shoulder of the first intense band in the spectrum of **1**. The positions of the main maxima are very close to those recently measured in an 8-coordinate uranium(VI) complex with 2,5-thiophenedicarboxylate ligands and

Ag(bipy)₂⁺ counterions,⁶⁶ and also to those in several 7-coordinate complexes, with 4,4'-(1,1,1,3,3,3-hexafluoroisopropylidene)diphthalate,⁶⁷ 1,1'-biphenyl-2,2',6,6'-tetracarboxylate,⁶⁸ terephthalate,^{69,70} and 2,5-thiophenedicarboxylate,⁷⁰ irrespective of the different uranium coordination numbers present here (8 in **1**, 7 in **4** and a mixture of both in **2**), and they are all red-shifted, by ~10–20 nm, with respect to the values, measured under identical experimental conditions, generally reported for 8-coordinate uranium(VI) carboxylate complexes.^{25,40,70–76} Spectra that are nearly identical for 7- and 8-coordinate complexes have also been reported in 4,4'-biphenyldicarboxylate complexes, with maxima positions blue-shifted by ~6 nm with respect to those for **1**.⁷⁷ The slightly unsymmetrical shape of the main peaks for complex **2** may be due to the convolution of signals corresponding to these two coordination numbers. Clearly, if the coordination number is a known factor governing the uranyl emission spectra, other factors such as the ligand strength are also at play.^{78,79} The spectra of the silver- and lead-containing heterometallic complexes **3** and **5** show strong quenching of uranyl luminescence, attributed to the additional metal cations providing nonradiative relaxation pathways.⁸⁰ Such quenching is not general with silver(I),^{66,81,82} although it has been previously observed to occur.^{40,80} In the spectrum of complex **3**, in which 7- and 8-coordination of uranium coexist, only three very weak peaks at ~481, 502 and 521 nm are apparent, these values being identical to those measured for several 8-coordinate uranyl complexes with carboxylates.^{25,40,70–76} These three peaks are superimposed upon a broad emission centred near 490 nm; given that the homometallic Ag^I complex **6** displays a broad, weak emission centred near 550 nm (Figure S1, Supporting Information), it is assumed that the emission at 490 nm in complex **3** is due to the Ag–carboxylate entity. In a previous study with 1,3,5-benzenetriacetate, lead(II) evinced no major quenching effect,⁴⁰ as shown here also by complex **4**, but in contrast to what is observed for complex **5**. The emission in the latter complex

is again extremely weak, with maxima at 483, 499, 521, 545 and 572 nm, very close to those for complex **4** (it is notable that the lead(II) complex **7** is non-emissive, see Supporting Information). The origin of the emission intensity difference between **4** and **5** may be subtle, since the coordination environment of uranium(VI) is very similar in the two cases, although somewhat more irregular in complex **5**, but the bound water molecule in the latter offers an obvious pathway for non-radiative energy loss from uranium(VI) which is not available in complex **4** (although one coordinated water is also present in the strongly emitting complex **2**). Assuming that energy loss from excited uranium(VI) could occur by transfer to a nearby metal ion, it is of interest that in the two structures each lead(II) cation is within 5 Å of two uranium(VI), and each uranium(VI) within 5 Å of two lead(II) centres, thus comprising PbUPbU parallelograms with sides of 4.6335(7) and 4.9402(8) Å in complex **4** and 4.6837(5) and 4.7089(5) Å in complex **5**, the difference in the minimum separation being clearly rather slight. The average vibronic splitting energies for the $S_{10} \rightarrow S_{0v}$ transitions are in the range of 852–859 cm⁻¹ for complexes **1**, **2**, **4** and **5**, these values being comparable to that of 852 cm⁻¹ measured in uranyl malonates,⁶⁵ as well as to those in uranyl complexes with other polycarboxylates.^{66,70,75}

CONCLUSIONS

The present work provides further illustration of the fact that the solid-state coordination chemistry of uranyl ion can be radically modified by the presence of other metal ions. Silver(I) and lead(II) provide important examples of this effect in that the origins of their influence appear to be quite different. Thus, Pb^{II}, like Cu^{II}, prevents uranyl ion adopting certain coordination modes, in particular, tridentate coordination involving the ether-O, by preferentially binding in the same manner. Silver(I), in contrast, has a coordination chemistry which is quite different to that of uranyl

ion (and Pb^{II}) and while this does not prevent uranyl ion adopting tridentate coordination of thftc^{4-} anions and thus may be a reason why the ligand is found still in its *trans,cis,trans* ($2R^*,3R^*,4S^*,5S^*$) form, binding of Ag_2 dimers to the ligand creates an “exotic” unit within the lattice which modifies the way the uranyl entities are connected. The effects of Ag^{I} and Pb^{II} in uranyl–organic coordination polymers are however much dependent on the nature of the ligand, as indicated by recent findings that, in a series of complexes with 1,3,5-benzenetriacetate, Pb^{II} generates less marked changes in the uranyl coordination mode than Ag^{I} ,⁴⁰ an outcome at variance with that observed here and which seems related to the peculiar nature of the tridentate coordination site of thftc^{4-} , for the occupation of which uranyl and Pb^{II} are in competition.

The specific coordination preferences of silver(I) may also explain its deposition as the complex of the ($2R^*,3S^*,4S^*,5S^*$) isomer of the ligand when no other metal ion is present. That this is the only isomer so far found in the two cases where isomerization of the starting species can be confirmed may mean that the “library” of equilibrated isomers consists of only two members (R^*,R^*,S^*,S^* and R^*,S^*,S^*,S^*), or that an unfavourable equilibrium is displaced by precipitation, or that the isolated complexes are simply the least soluble materials (when crystallised at room temperature). Further work is required to characterize the equilibrium achieved under hydrothermal conditions with the acid alone and an interesting further experiment would be to search for a metal precipitating the ($2R^*,3S^*,4S^*,5S^*$) isomer as a racemic mixture (“spontaneous resolution”) rather than as a racemic compound.

From a crystal engineering viewpoint, it is notable that the homometallic uranyl complexes obtained up to now are either discrete, molecular species when synthesized at room temperature, as complex **1** in the present study or the metallamacrocycles previously reported,¹⁷ or a 2D coordination polymer when isolated from a solvo-hydrothermally treated solution (complex **2**). In contrast to the 2D network observed in the uranyl/copper(II) complex

$[\text{UO}_2\text{Cu}(\text{thftc})(\text{bipy})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$,¹⁸ in which the terminal bipy ligand plays a role in restricting the dimensionality, all the heterometallic complexes reported here, with silver(I) and lead(II) additional cations, crystallize as 3D frameworks as a result of the high connectivity of the ligand which is bound to seven metal atoms in all cases, and the bridging nature of all cations (the high coordination number of lead(II) cations in particular being conducive to the formation of intricate arrangements). 3D frameworks are also found in the homometallic silver(I) and lead(II) complexes, and the ligand connectivity achieved in these cases is even higher, with 9 (Cu) or 11 (Ag) cations bound to the ligand. The $\text{UO}_2/\text{Pb}/\text{Ag}/\text{H}_4\text{thftc}$ system has obviously a rich potential for the building of 3D assemblies, none of those described here presenting significant porosity however. Intense and well resolved solid state emission in the 470–600 nm range showing the vibronic fine structure typical of the uranyl cation is displayed by the homometallic complexes **1** and **2**, and the uranyl/lead(II) heterometallic complex **4**, while uranyl emission in the silver(I)- and lead(II)-containing complexes **3** and **5** is largely quenched.

ASSOCIATED CONTENT

Accession Codes

CCDC 1500859–1500865 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: .
Emission spectra of complexes **6** and **7**. (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: pierre.thuery@cea.fr (P. T.)

*E-mail: harrowfield@unistra.fr (J. H.)

Notes

The authors declare no competing financial interest.

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Table 1. Crystal Data and Structure Refinement Details

	1	2	3	4	5	6	7
chemical formula	C ₁₈ H ₂₄ N ₆ O ₂₀ U	C ₂₀ H ₂₀ N ₂ O ₂₆ U ₃	C ₁₆ H ₁₆ Ag ₂ O ₂₈ U ₃	C ₈ H ₆ O ₁₂ PbU	C ₈ H ₁₀ O ₁₄ PbU	C ₈ H ₅ Ag ₃ O ₉	C ₈ H ₆ O ₁₀ Pb ₂
<i>M</i> (g mol ^{−1})	882.46	1418.47	1586.12	739.35	775.38	568.73	676.51
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	6.2002(3)	8.7169(7)	8.7147(5)	8.8187(7)	8.8496(7)	23.2795(14)	7.4504(4)
<i>b</i> (Å)	10.6342(6)	9.3205(7)	10.2265(7)	8.8607(7)	9.0520(5)	15.6544(10)	14.8246(7)
<i>c</i> (Å)	11.3736(7)	10.6388(8)	10.4323(6)	9.0395(5)	10.1130(8)	6.0326(3)	9.8755(3)
α (deg)	65.659(3)	72.033(4)	113.368(4)	105.947(5)	67.789(5)	90	90
β (deg)	86.674(4)	80.405(5)	99.416(4)	109.384(5)	86.077(4)	96.116(4)	101.315(3)
γ (deg)	78.118(4)	82.241(5)	110.693(4)	103.226(4)	71.439(5)	90	90
<i>V</i> (Å ³)	668.31(7)	807.48(11)	746.80(9)	599.47(9)	709.75(10)	2185.9(2)	1069.54(8)
<i>Z</i>	1	1	1	2	2	8	4
<i>D</i> _{calcd} (g cm ^{−3})	2.193	2.917	3.527	4.096	3.628	3.456	4.201
μ (Mo K α) (mm ^{−1})	6.178	15.112	17.612	27.586	23.319	5.368	31.498
<i>F</i> (000)	426	638	706	648	688	2128	1192
reflns collcd	27613	38948	42152	26089	41540	35228	37176
indep reflns	2539	3067	2832	2258	2688	2074	2029
obsd reflns [<i>I</i> > 2 σ (<i>I</i>)]	2539	2676	2619	2078	2386	1849	1873
<i>R</i> _{int}	0.021	0.072	0.065	0.026	0.079	0.031	0.047
params refined	205	233	223	199	217	191	181
<i>R</i> ₁	0.028	0.027	0.029	0.047	0.027	0.048	0.025
<i>wR</i> ₂	0.072	0.055	0.071	0.134	0.055	0.129	0.065
<i>S</i>	1.051	1.024	1.059	1.109	1.063	1.043	1.129
$\Delta\rho_{\min}$ (e Å ^{−3})	−1.48	−1.61	−2.01	−2.46	−2.05	−3.41	−2.53
$\Delta\rho_{\max}$ (e Å ^{−3})	1.01	1.40	2.13	2.80	1.20	2.08	1.08

Figure Captions

Figure 1. Top: View of complex **1**. Displacement ellipsoids are drawn at the 50% probability level. Symmetry code: $i = -x, 1 - y, 1 - z$. Bottom: View of a hydrogen bonded sheet, with uranium coordination polyhedra colored yellow. The carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines in both views.

Figure 2. Top left: View of complex **2**. Displacement ellipsoids are drawn at the 50% probability level. The solvent molecule and carbon-bound hydrogen atoms are omitted. The hydrogen bond is shown as a dashed line. Symmetry codes: $i = 1 - x, 2 - y, 2 - z$; $j = x, y, z - 1$; $k = 2 - x, 1 - y, 2 - z$; $l = x, y, z + 1$. Top right: View of the 2D assembly with the uranium coordination polyhedra colored yellow. Bottom left: Packing with layers viewed edge-on. All hydrogen atoms are omitted in the last two views. Bottom right: Nodal representation of the 2D network (yellow: uranium, red: oxygen, blue: ligand centroid).

Figure 3. Top: View of complex **3**. Displacement ellipsoids are drawn at the 50% probability level. The solvent molecules and carbon-bound hydrogen atoms are omitted. Symmetry codes: $i = x - 1, y - 1, z$; $j = 1 - x, 1 - y, 2 - z$; $k = 2 - x, 1 - y, 1 - z$; $l = x - 1, y, z$; $m = 1 - x, 2 - y, 2 - z$; $n = x + 1, y, z$; $o = x + 1, y + 1, z$; $p = 1 - x, 1 - y, 1 - z$. Bottom: View of the 3D framework with uranium coordination polyhedra colored yellow and silver atoms shown as blue spheres. The uranium-containing layers are similar to those in complex **2**. Solvent molecules and hydrogen atoms are omitted.

Figure 4. Top: View of complex **4**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted. Symmetry codes: $i = x, y, z + 1$; $j = -x, 1 - y, 2 - z$; $k = 1 - x, -y, 2 - z$; $l = 1 - x, -y, 1 - z$; $m = x, y - 1, z$; $n = x, y, z - 1$; $o = x, y + 1, z$. Middle and bottom: Two views of the 3D framework with uranium coordination polyhedra colored yellow and lead atoms shown as blue spheres. All hydrogen atoms are omitted in the last two views.

Figure 5. Top: View of complex **5**. Displacement ellipsoids are drawn at the 50% probability level. The solvent molecule and carbon-bound hydrogen atoms are omitted. Symmetry codes: $i = x, y, z - 1$; $j = 1 - x, 1 - y, 1 - z$; $k = 2 - x, 2 - y, 1 - z$; $l = 1 - x, 2 - y, 1 - z$; $m = x, y + 1, z$; $n = x, y, z + 1$; $o = x, y - 1, z$. Bottom: View of the 3D framework with uranium coordination polyhedra colored yellow and lead atoms shown as blue spheres. Solvent molecules and hydrogen atoms are omitted.

Figure 6. Top: View of the silver-only complex **6**. Displacement ellipsoids are drawn at the 40% probability level. Carbon-bound hydrogen atoms are omitted. Symmetry codes: $i = x, y, z - 1$; $j = 1 - x, y, 1/2 - z$; $k = x, -y, z - 1/2$; $l = 1/2 - x, 1/2 - y, -z$; $m = 1 - x, 1 - y, -z$; $n = x, 1 - y, z - 1/2$; $o = x, 1 - y, z + 1/2$; $p = x, -y, z + 1/2$; $q = x, y, z + 1$. Middle and bottom: Two views of the 3D framework with all hydrogen atoms omitted. In all views, only one position (and its symmetry equivalents) of the disordered silver cation Ag_3 is represented.

Figure 7. Top: View of the lead-only complex **7**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted. Symmetry codes: $i = -x, y + 1/2, 3/2 - z$; $j = 1 - x, y + 1/2, 3/2 - z$; $k = x, 1/2 - y, z + 1/2$; $l = -x, 1 - y, 2 - z$; $m = 1 - x, 1 - y, 1 - z$; $n = x + 1, y, z$; $o = x, 1/2 - y, z - 1/2$; $p = x - 1, y, z$; $q = 1 - x, y - 1/2, 3/2 - z$; $r = -x, y - 1/2, 3/2 - z$. Bottom: View of the 3D framework with all hydrogen atoms omitted.

Figure 8. Solid state emission spectra of the homometallic uranyl complexes **1** and **2** and the uranyl/lead(II) heterometallic complex **4** (top), and of the heterometallic complexes **3** and **5** (bottom). The excitation wavelength was 420 nm.

Scheme 1. Coordination Mode of the thftc Ligand in the Polymeric Complexes 2–7

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

For Table of Contents Use Only

**Tetrahydrofuran tetracarboxylic Acid: an Isomerizable
Framework-Forming Ligand in Homo- and Heterometallic
Complexes with UO_2^{2+} , Ag^+ and Pb^{2+}**

Pierre Thuéry and Jack Harrowfield

Seven homo- and heterometallic complexes formed by tetrahydrofuran tetracarboxylic acid with either uranyl, silver(I) or lead(II) cations or mixtures thereof display arrangements of various dimensionality, among which three-dimensional frameworks are dominant. The ligand is found to have undergone isomerization into one of its chiral forms in the silver-only complex.