Uranyl–Organic Coordination Polymers with trans -1,2-, trans -1,4-, and cis -1,4-Cyclohexanedicarboxylates: Effects of Bulky PPh_4^+ and PPh_3Me$^+$ Counterions

Pierre Thuéry, Youssef Atoini, Jack Harrowfield

▶ **To cite this version:**

HAL Id: cea-01743230
https://cea.hal.science/cea-01743230

Submitted on 6 Apr 2018

Uranyl–Organic Coordination Polymers with

trans-1,2-, *trans*-1,4- and *cis*-1,4-Cyclohexanedicarboxylates:

Effects of Bulky PPh₄⁺ and PPh₃Me⁺ Counterions

Pierre Thuéry,*,† Youssef Atoini‡ 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: Three uranyl ion complexes with *trans*-1,2-cyclohexanedicarboxylic acid (*t*-1,2-chdcH$_2$) and six with *trans*- or *cis*-1,4-cyclohexanedicarboxylic acid (*t*- or *c*-1,4-chdcH$_2$) have been obtained under solvo-hydrothermal conditions in the presence of PPh$_4^+$ or PPh$_3$Me$^+$ counterions. The complex [PPh$_4$][UO$_2$(*R*-*t*-1,2-chdc)(HCOO)] (**1**) crystallized on use of the pure (1*R*,2*R*) enantiomer of the dicarboxylate ligand, while the isomorphous complex [PPh$_4$][UO$_2$(*S*-*t*-1,2-chdc)(HCOO)] (**2**), containing the (1*S*,2*S*) enantiomer, resulted from use of the racemic form through spontaneous resolution. Both contain the rare diaxial (*aa*) form of the ligand and are one-dimensional (1D) polymers. The complex [PPh$_3$Me][H$_2$NMe$_2$]$_3$[(UO$_2$)$_4$(*R*-*t*-1,2-chdc)$_6$]·H$_2$O (**3**), with the pure enantiomeric, diequatorial (*ee*) form of the ligand, is a two-dimensional (2D) species with hnb topology, which derives from the structure of tetranuclear clusters previously reported. Complexes [PPh$_4$][UO$_2$(*t*-1,4-chdc)(NO$_3$)]·2CH$_3$CN (**4**) and [PPh$_4$][UO$_2$(*c*-1,4-chdc)(NO$_3$)] (**5**) are 1D polymers, helical in the latter case due to the axial-equatorial (*ae*) form of the ligand. [PPh$_4$]$_2$[(UO$_2$)$_2$(*t*-1,4-chdc)$_3$]·4H$_2$O (**6**), [PPh$_3$Me]$_2$[(UO$_2$)$_2$(*t*-1,4-chdc)$_3$]·2H$_2$O (**7**), [PPh$_3$Me]$_2$[(UO$_2$)$_2$(*c*-1,4-chdc)$_3$]·2H$_2$O (**8**), and [PPh$_4$]$_2$[(UO$_2$)$_2$(*t*-1,4-chdc)$_2$(*c*-1,4-chdc)]·3H$_2$O (**9**) all crystallize as 2D networks with honeycomb topology, the shape of the rings and that of the layers varying due to the presence of *trans* isomers in both the *ee* and *aa* forms, and coexistence of *cis* and *trans* isomers in **9**; in all complexes **6–9**, large channels are formed, which contain the counterions. The uranyl emission spectra of compounds **1–4**, **6** and **9** in the solid state are in agreement with those usually found for tris-chelated carboxylate complexes, while that of complex **8**, containing a mixture of seven- and eight-coordinate uranium atoms, displays a superposition of ill-resolved maxima within a broad envelope. A quantum yield of 0.13 was measured for complex **6**.

INTRODUCTION

The topology of uranyl–organic coordination polymers,[1–5] when they are anionic, can easily be modulated through modifying the nature of the countercation. The latter is often an additional metallic species, which can be part of the polymer fabric itself or separate if associated with coligands such as nitrogen chelators.[5] It can also be an organic species, and, in particular, the very large range in size and geometry available in the family of ammonium cations has been extensively exploited, as evidenced by the 330 crystal structures of uranyl–containing polymers including such cations which are reported in the Cambridge Structural Database (CSD, Version 5.38).[6] In contrast, the quite common tetraphenylphosphonium and methyltriphenylphosphonium cations, PPh_4^+ and PPh_3Me^+, have never been used in the synthesis of uranyl–containing coordination polymers, and the former is only found in a handful of discrete, molecular uranyl complexes. The good solubility of these cations and their thermal stability make them well adapted to use in (solvo-)hydrothermal syntheses, and their bulkiness is likely to have a strong effect on the geometry of anionic uranyl–organic coordination polymers, comparable to that of the equally bulky $[ML_3]^{2+}$ cations, where M is a d-block metal cation and L is 2,2′-bipyridine or 1,10-phenanthroline.[5] Both PPh_4^+ and PPh_3Me^+ have been widely studied, in fact, for their structural influence resulting from "multiple phenyl embraces".[7–9] In the course of an investigation of the uranyl complexes formed with the different isomers of cyclohexanedicarboxylate ligands,[10–13] we have recently obtained the compound $[NH_4][PPh_4][(UO_2)_8(c\text{-}1,2\text{-chdc})_9(H_2O)_6]\cdot 3H_2O$ (where $c\text{-}1,2\text{-chdc}^{2-}$ is the dianion of *cis*-1,2-cyclohexanedicarboxylic acid), which contains an octanuclear cage of unique geometry, while crystallization in the absence of possible counterions gives simple two-dimensional (2D) neutral species.[14] In order to characterize more thoroughly the effect of PPh_4^+ and PPh_3Me^+ counterions on the dimensionality and geometry of uranyl complexes with cyclohexanedicarboxylate ligands,

we have now synthesized a series of complexes, three from *trans*-1,2-cyclohexanedicarboxylic acid (*t*-1,2-chdcH$_2$), either in its racemic or (1*R*,2*R*) pure enantiomeric form, and six from *trans*-1,4-cyclohexanedicarboxylic acid (*t*-1,4-chdcH$_2$) or a mixture of the *cis* and *trans* isomers (*c,t*-1,4-chdcH$_2$). These complexes have been characterized by their crystal structure and, in most cases, their emission spectrum in the solid state. The structures of the complexes of 1,4-chdc^{2-} in particular reflect the consequences of the variety of configurations and conformations possible for cyclohexanedicarboxylates, a feature known to lead to novel properties such as the "breathing" of 3D networks due to the accommodation of guests.[15]

EXPERIMENTAL SECTION

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

UO$_2$(NO$_3$)$_2 \cdot$6H$_2$O (depleted uranium, R. P. Normapur, 99%) was purchased from Prolabo, *rac-trans*-1,2-cyclohexanedicarboxylic acid (*rac-t*-1,2-chdcH$_2$) was from Lancaster, *trans*-1,4-cyclohexanedicarboxylic acid (*t*-1,4-chdcH$_2$) was from Alfa-Aesar, and 1,4-cyclohexanedicarboxylic acid (mixture of *cis* and *trans* isomers, *c,t*-1,4-chdcH$_2$) was from Aldrich. The (1*R*,2*R*) enantiomer of *t*-1,2-chdcH$_2$, denoted *R-t*-1,2-chdcH$_2$, was isolated through crystallization with (*R*)-1-phenylethylamine as a resolving agent, as in the literature,[16] although both the (1*R*,2*R*) and (1*S*,2*S*) enantiomers are also available commercially. Elemental analyses were performed by MEDAC Ltd. at Chobham, UK. For all syntheses, the mixtures in demineralized water were placed in 10 mL tightly closed glass vessels and heated at 140 °C under autogenous pressure.

[PPh₄][UO₂(R-t-1,2-chdc)(HCOO)] **(1)**. R-t-1,2-chdcH₂ (17 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and PPh₄Br (42 mg, 0.10 mmol) were dissolved in water (0.5 mL) and DMF (0.2 mL). Crystals of complex **1** were obtained overnight (22 mg, 38% yield based on U). Elemental analysis results indicate the probable presence of about one extra water molecule. Anal. Calcd for C₃₃H₃₁O₈PU + H₂O: C, 47.04; H, 3.92. Found: C, 47.20; H, 3.55%.

[PPh₄][UO₂(S-t-1,2-chdc)(HCOO)] **(2)**. rac-t-1,2-chdcH₂ (17 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and PPh₄Br (42 mg, 0.10 mmol) were dissolved in water (0.5 mL) and DMF (0.2 mL). Crystals of complex **2** were obtained in low yield within two days.

[PPh₃Me][H₂NMe₂]₃[(UO₂)₄(R-t-1,2-chdc)₆]·H₂O **(3)**. R-t-1,2-chdcH₂ (17 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and PPh₃MeBr (36 mg, 0.10 mmol) were dissolved in water (0.5 mL) and DMF (0.2 mL). Crystals of complex **3** were obtained within one week (24 mg, 57% yield based on the acid). Anal. Calcd for C₇₃H₁₀₄N₃O₃₃PU₄: C, 34.59; H, 4.14; N, 1.66. Found: C, 34.89; H, 4.17; N, 2.05%.

[PPh₄][UO₂(t-1,4-chdc)(NO₃)]·2CH₃CN **(4)**. t-1,4-chdcH₂ (17 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and PPh₄Br (42 mg, 0.10 mmol) were dissolved in water (0.5 mL) and acetonitrile (0.2 mL). Crystals of complex **4** were obtained in low yield within one week.

[PPh₄][UO₂(c-1,4-chdc)(NO₃)] **(5)**. c,t-1,4-chdcH₂ (17 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and PPh₄Br (42 mg, 0.10 mmol) were dissolved in water (0.7 mL) and N-methyl-2-pyrrolidone (0.3 mL). Crystals of complex **5** were obtained in low yield within one month.

[PPh₄]₂[(UO₂)₂(t-1,4-chdc)₃]·4H₂O **(6)**. t-1,4-chdcH₂ (17 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and PPh₄Br (42 mg, 0.10 mmol) were dissolved in water (0.7 mL) and DMF

4

(0.2 mL). Crystals of complex **6** were obtained overnight (47 mg, 78% yield based on the acid). Anal. Calcd for $C_{72}H_{78}O_{20}P_2U_2$: C, 48.01; H, 4.36. Found: C, 47.59; H, 3.95%. The same complex is obtained when DMF is replaced by acetonitrile.

[PPh₃Me]₂[(UO₂)₂(t-1,4-chdc)₃]·2H₂O **(7)**. t-1,4-chdcH₂ (17 mg, 0.10 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (35 mg, 0.07 mmol), and PPh₃MeBr (36 mg, 0.10 mmol) were dissolved in water (0.6 mL) and DMF (0.2 mL). Crystals of complex **7** were obtained within four days (7 mg, 13% yield based on the acid). Anal. Calcd for $C_{62}H_{70}O_{18}P_2U_2$: C, 45.37; H, 4.30. Found: C, 45.66; H, 4.34%.

[PPh₃Me]₂[(UO₂)₂(c-1,4-chdc)₃]·2H₂O **(8)**. c,t-1,4-chdcH₂ (17 mg, 0.10 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (35 mg, 0.07 mmol), and PPh₃MeBr (36 mg, 0.10 mmol) were dissolved in water (0.6 mL) and DMF (0.2 mL). Crystals of complex **8** were obtained within four days (7 mg, 13% yield based on the acid). Anal. Calcd for $C_{62}H_{70}O_{18}P_2U_2$: C, 45.37; H, 4.30. Found: C, 45.23; H, 4.27%.

[PPh₄]₂[(UO₂)₂(t-1,4-chdc)₂(c-1,4-chdc)]·3H₂O **(9)**. c,t-1,4-chdcH₂ (17 mg, 0.10 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (35 mg, 0.07 mmol), and PPh₄Br (42 mg, 0.10 mmol) were dissolved in water (0.6 mL) and DMF (0.2 mL). Crystals of complex **9** were obtained overnight (16 mg, 27% yield based on the acid). Anal. Calcd for $C_{72}H_{76}O_{19}P_2U_2$: C, 48.49; H, 4.30. Found: C, 49.17; H, 3.96%.

Crystallography. The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[17] using graphite-monochromated Mo Kα radiation (λ = 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 at least 4 for 90% of the

reflections) were processed with HKL2000.[18] Absorption effects were corrected empirically with the program SCALEPACK.[18] The structures were solved by intrinsic phasing with SHELXT,[19] expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL-2014.[20] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were retrieved from difference Fourier maps when possible, and the carbon-bound hydrogen atoms were introduced at calculated positions (as well as the ammonium hydrogen atoms in **3**). All hydrogen atoms 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, with optimized geometry). In compound **3**, the dimethylammonium counterion is disordered over two sites, one of them being itself disordered around a threefold rotation axis, and restraints were applied for bond lengths, angles and displacement parameters in the disordered parts. One lattice water molecule in complex **6** is disordered over two positions which have been refined with occupancy parameters constrained to sum to unity, and the corresponding hydrogen atoms were not found. In the case of compound **9**, restraints on bond lengths and displacement parameters were applied in several parts of the structure; the highest residual electron density peaks are located near the uranium atoms, probably as a result of imperfect absorption corrections. The Flack parameter values are –0.012(8), –0.008(10) and 0.002(10) for the three enantiomerically pure complexes **1**–**3**, respectively. Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3,[21] and the polyhedral representations with VESTA.[22] The topological analyses were conducted with TOPOS.[23]

Table 1. Crystal Data and Structure Refinement Details

	1	2	3	4	5
chemical formula	$C_{33}H_{31}O_8PU$	$C_{33}H_{31}O_8PU$	$C_{73}H_{104}N_3O_{33}PU_4$	$C_{36}H_{36}N_3O_9PU$	$C_{32}H_{30}NO_9PU$
M (g mol^{-1})	824.58	824.58	2534.68	923.68	841.57
cryst syst	monoclinic	monoclinic	trigonal	orthorhombic	monoclinic
space group	$P2_1$	$P2_1$	$R3$	$Pbcn$	$P2_1/n$
a (Å)	7.7964(3)	7.7955(4)	13.6231(3)	20.5334(8)	14.2044(5)
b (Å)	14.9394(4)	14.9391(4)	13.6231(3)	14.7720(5)	14.6258(6)
c (Å)	13.2101(5)	13.2114(7)	42.3397(12)	23.7294(11)	15.1949(4)
α (deg)	90	90	90	90	90
β (deg)	101.558(2)	101.563(3)	90	90	99.312(2)
γ (deg)	90	90	120	90	90
V (Å^3)	1507.43(9)	1507.35(12)	6805.0(4)	7197.6(5)	3115.15(19)
Z	2	2	3	8	4
D_{calcd} (g cm^{-3})	1.817	1.817	1.856	1.705	1.794
μ(Mo Kα) (mm^{-1})	5.489	5.489	7.214	4.612	5.317
$F(000)$	800	800	3630	3616	1632
reflns collcd	59027	47434	69249	161672	91403
indep reflns	7755	7762	5744	6823	5909
obsd reflns [$I > 2\sigma(I)$]	7017	6232	5668	4459	5116
R_{int}	0.032	0.041	0.017	0.053	0.030
params refined	389	389	374	454	397
R_1	0.031	0.040	0.024	0.037	0.026
wR_2	0.078	0.084	0.066	0.085	0.069
S	1.023	1.054	1.075	0.921	1.042
$\Delta\rho_{min}$ (e Å^{-3})	−1.30	−1.35	−0.93	−0.92	−1.07
$\Delta\rho_{max}$ (e Å^{-3})	1.15	1.79	1.30	1.34	0.60

	6	7	8	9
chemical formula	$C_{72}H_{78}O_{20}P_2U_2$	$C_{62}H_{70}O_{18}P_2U_2$	$C_{62}H_{70}O_{18}P_2U_2$	$C_{72}H_{76}O_{19}P_2U_2$
M (g mol^{-1})	1801.34	1641.18	1641.18	1783.32
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	10.0284(4)	8.7748(4)	28.3178(6)	28.1368(9)
b (Å)	13.5216(6)	25.8721(7)	13.1707(3)	19.3550(4)
c (Å)	14.0662(6)	13.6877(7)	16.3855(3)	40.1254(12)
α (deg)	102.635(3)	90	90	90
β (deg)	95.694(3)	97.150(2)	91.0988(13)	106.988(2)
γ (deg)	106.678(3)	90	90	90
V (Å^3)	1755.91(14)	3083.3(2)	6110.1(2)	20898.3(10)
Z	1	2	4	12
D_{calcd} (g cm^{-3})	1.703	1.768	1.784	1.700
μ(Mo Kα) (mm^{-1})	4.724	5.368	5.418	4.761
$F(000)$	884	1600	3200	10488
reflns collcd	99165	74279	192267	383533
indep reflns	6667	5850	11568	39092
obsd reflns [$I > 2\sigma(I)$]	6062	4809	10274	23869
R_{int}	0.042	0.040	0.022	0.071
params refined	443	380	759	2554
R_1	0.022	0.030	0.021	0.064
wR_2	0.053	0.069	0.049	0.161
S	1.024	1.030	1.020	1.034
$\Delta\rho_{min}$ (e Å^{-3})	−1.16	−1.36	−0.79	−3.31
$\Delta\rho_{max}$ (e Å^{-3})	0.49	0.81	0.38	4.92

Luminescence Measurements. Emission spectra were recorded on solid samples using a Horiba-Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation, and emission monochromators (2.1 nm mm^{-1} of dispersion; 1200 grooves mm^{-1}) and a TBX-04 single photon-counting detector. The powdered compound 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, a commonly used point although only part of a broad manifold, was used in all cases and the emission was monitored between 450 and 650 nm. The quantum yield measurement was performed by using an absolute photoluminescence quantum yield spectrometer Hamamatsu Quantaurus C11347 and exciting the sample between 300 and 400 nm.

RESULTS AND DISCUSSION

Synthesis. Complexes **1**–**9**, as crystalline solids, were synthesized under solvo-hydrothermal conditions at a temperature of 140 °C, the organic cosolvent being *N*,*N*-dimethylformamide (DMF) for complexes **1**–**3** and **6**–**9**, acetonitrile for **4** and *N*-methyl-2-pyrrolidone (NMP) for **5**. In all cases, the uranium/ligand stoichiometry used was 7:10, in the expectation that it would favour the formation of an anionic species. All complexes are indeed anionic, notwithstanding some variations in uranium/chdc^{2-} stoichiometry. This ratio is 1:1 in **1** and **2**, in which an extra negative charge is provided by one formate anion formed *in situ* from DMF hydrolysis, as previously documented,[24] and also in **4** and **5** which include a nitrate anion, while it assumes the expected value of 2:3 in complexes **3** and **6**–**9**. The PPh$_4^+$ or PPh$_3$Me$^+$ counterions are present in all cases (as well as dimethylammonium cations resulting from DMF hydrolysis in complex **3**), indicating that, notwithstanding many other attempts with different ligand/cosolvent combinations which failed to provide any crystalline material, association of

these large counterions with uranyl-containing polymers gives systems fairly amenable to crystallization and to a degree controllable with respect to their stoichiometry. The effect of the organic cosolvent, other than on the solubility of the initial reaction mixture, is difficult to predict in cases where it, too, undergoes reaction, the present structures providing examples where DMF hydrolysis may provide either an anion (formate) or a cation (dimethylammonium) incorporated in the complex finally obtained. The formation of mixed carboxylato complexes of uranyl ion, though rarely a direct objective of the syntheses, has proven to be a relatively common and useful pathway to formation of crystalline coordination polymers, especially where oxalate is the "unintentional" additional carboxylate.[25–27] As is commonly the case with chiral ligands used in their racemic form, crystallisation can involve the formation of conglomerate solids where separate crystals contain only one or the other of the enantiomeric ligand forms and this is illustrated here by complex **2**, which has the same structure as complex **1** except for the fact that by chance a crystal was selected containing the ($1S,2S$) rather than the ($1R,2R$) form of the enantiomerically pure ligand used to prepare complex **1**.

Crystal Structures. The two complexes [PPh$_4$][UO$_2$(R-t-1,2-chdc)(HCOO)] (**1**) and [PPh$_4$][UO$_2$(S-t-1,2-chdc)(HCOO)] (**2**), in which R-t-1,2-chdc^{2-} and S-t-1,2-chdc^{2-} are the ($1R,2R$) and ($1S,2S$) enantiomers of t-1,2-chdc^{2-}, respectively, are isomorphous and crystallize in the monoclinic Sohncke group $P2_1$. While **1** was obtained from the pure ($1R,2R$) enantiomer of the ligand, **2** was synthesized from the racemic form, which indicates that resolution occurred during crystallization, the particular crystal subjected to analysis containing the pure ($1S,2S$) enantiomer. The asymmetric unit in both cases contains one uranyl cation chelated by two carboxylate groups from two dicarboxylate ligands, and one formate anion, the uranium coordination environment being thus hexagonal bipyramidal, with unexceptional U–O bond lengths (Figures 1 and 2). The t-1,2-chdc^{2-} ligand is in the chair conformation with both
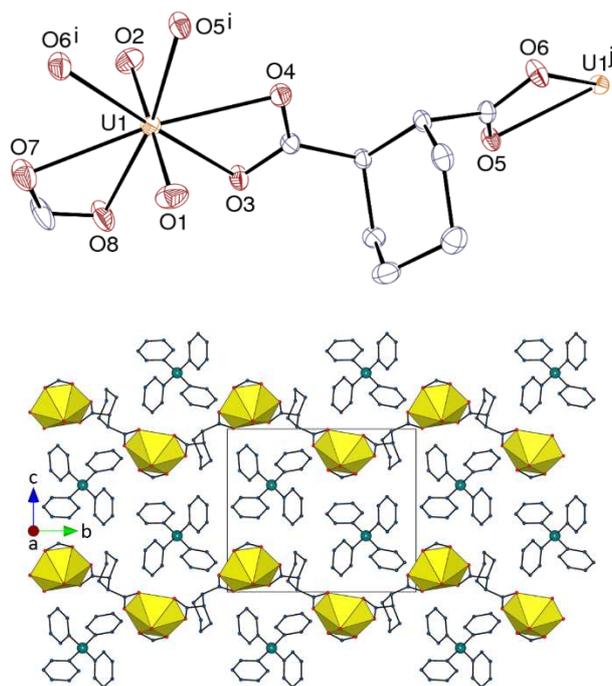
9

Figure 1. Top: View of compound **1**. Displacement ellipsoids are drawn at the 30% probability level. Counterions and hydrogen atoms are omitted. Symmetry codes: i = 1 – x, y – 1/2, –z; j = 1 – x, y + 1/2, –z. Bottom: Packing with uranium coordination polyhedra colored yellow and hydrogen atoms omitted.
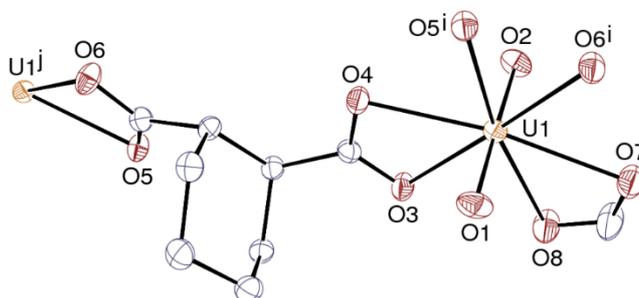

Figure 2. View of compound **2**. Displacement ellipsoids are drawn at the 20% probability level. Counterions and hydrogen atoms are omitted. Symmetry codes: i = 1 – x, y + 1/2, 2 – z; j = 1 – x, y – 1/2, 2 – z. The packing is similar to that in **1**.

carboxylate groups axial (*aa*), so that the cyclohexyl ring is roughly perpendicular to the mean plane defined by the two carboxylate groups and the attached uranium atoms. In all the uranyl complexes with *t*-1,2-chdc²⁻ previously reported,[11,12] the ligand assumes the more common chair conformation with the two carboxylate groups equatorial (*ee*). A search of the CSD reveals only two metal ion complexes with the *aa* conformation,[28,29] with in both cases

10

coexistence of the *ee* and *aa* forms in the lattice. However, a study of the conformational preferences of *t*-1,2-chdcH$_2$ and its mono- and dianion in solution by NMR spectroscopy revealed that, depending on the medium, the *aa* population could be significant, representing as much as 57% for the dianion in DMSO.[30] In contrast to the *ee* form, the *aa* form is a distinctly divergent ligand and a zigzag one-dimensional (1D) polymer directed along the *b* axis is formed, in which the directions of the cyclohexyl ring and formate ligand alternate from one unit to the next. Extension of the 1D chains into a 2D network is prevented by the presence of the terminal formate ligands. It is notable that, when similarly *bis*-chelating, the *ee* form of the ligand readily gives tetrahedral uranyl clusters,[11,12] thus showing that its geometry is much better adapted than that of the *aa* form to the formation of closed species. The undulating chains lie parallel to one another in sheets parallel to (0 0 1). The PPh$_4^+$ cations lie in undulating sheets parallel to those of the anionic polymers, forming arrays essentially identical to those considered to define "multiple phenyl embraces" in a wide variety of simpler derivatives.[7–9] PPh$_4^+$ cations related to one another by translations along the *a* axis are involved in fourfold, "O4PE",[8] embraces [P···P distances 7.7964(3) and 7.7955(4) Å in complexes **1** and **2**, respectively]. However, the corresponding interactions are no stronger than dispersion, and no significant π-stacking or CH···π interaction is present in the lattice. Only some weak CH(cation)···O(carboxylate) hydrogen bonds may be present [C···O 3.115(10) and 3.280(9) Å for the shortest ones], which appear to be stronger than dispersion from examination of the Hirshfeld surfaces[31] calculated with CrystalExplorer.[32] With a Kitaigorodski packing index (KPI, estimated with PLATON[33]) of 0.70, the packing has no solvent-accessible spaces. Complexes isomorphous to **1** and **2** are obtained when DMF is replaced by acetonitrile or NMP, in which the formate anions are replaced by nitrate anions, but, in the absence of crystals suitable for a satisfactory structure refinement, these complexes will not be further described.

Changing PPh_4^+ for PPh_3Me^+ results in a profound structural modification in the case of R-t-1,2-chdc^{2-}, which gives the complex $[PPh_3Me][H_2NMe_2]_3[(UO_2)_4(R\text{-}t\text{-}1,2\text{-chdc})_6]\cdot H_2O$ (**3**). The same experiment performed with rac-t-1,2-chdcH$_2$ gave the same complex, indicating that resolution of the two enantiomers occurred during crystallization here also. Instead of including formate coligands as **1** and **2**, **3** contains the other product of DMF hydrolysis, dimethylammonium cations. **3** crystallizes in the trigonal Sohncke group $R3$; the asymmetric unit contains two uranyl cations, one of them (U1) located on a threefold rotation axis (Wyckoff position 3a), and the other (U2) in general position, two R-t-1,2-chdc^{2-} ligands, one highly disordered $H_2NMe_2^+$ cation (see Experimental Section), and one PPh_3Me^+ cation located on a threefold rotation axis (Figure 3). Both uranium atoms are chelated by three carboxylate groups from three R-t-1,2-chdc^{2-} ligands and they are thus in hexagonal bipyramidal environments. The *bis*-chelating ligands are in the usual chair conformation with both carboxylate groups equatorial (*ee*), which results in the formation of a binodal 2D network parallel to (0 0 1). The point (Schläfli) symbol is $\{3.9^2\}_3\{9^3\}$ and the topological type is hnb, which, with its nine-node rings, is an unusual one for nets based on threefold nodes (Figure 4). It is interesting to note that, if the local environment of the uranyl ion located on the rotation axis is considered, it can be seen to assume the shape of a half-closed tetranuclear cluster, thus appearing as an intermediate step (from a geometric, not mechanistic, point of view) toward the formation of closed, discrete tetrahedral species[11,12] (Figure 3). Each of the three tilted uranyl ions attached to the central one is part of a three-node ring which is also analogous to part of the tetrahedral cluster. The network thus appears to be derived from the cluster through breaking of two of the three links around one uranyl group, rotating this group and forming two new links with two different three-node rings derived from adjacent clusters. While the anionic tetrahedral molecular species can be readily obtained in the presence of NH_4^+, alkali or alkaline-earth,
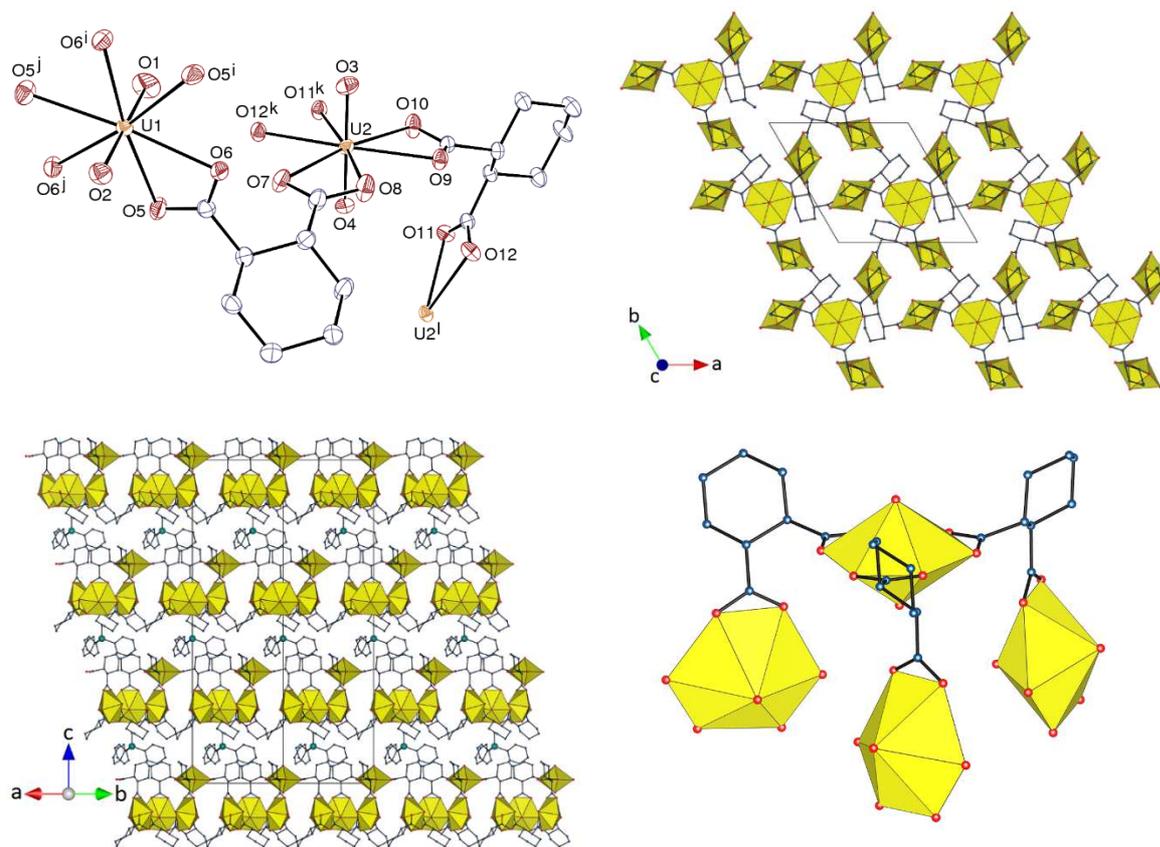
Figure 3. Top left: View of compound **3**. Displacement ellipsoids are drawn at the 30% probability level. Counterions, solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = 1 – *y*, *x* – *y* + 1, *z*; j = *y* – *x*, 1 – *x*, *z*; k = –*y*, *x* – *y*, *z*; l = *y* – *x*, –*x*, *z*. Top right: View of the uranyl-based 2D network. Bottom left: Packing with sheets viewed edge-on, and solvent molecules and hydrogen atoms omitted. Bottom right: Local arrangement of uranyl ions and dicarboxylate ligands around the threefold rotation axis.
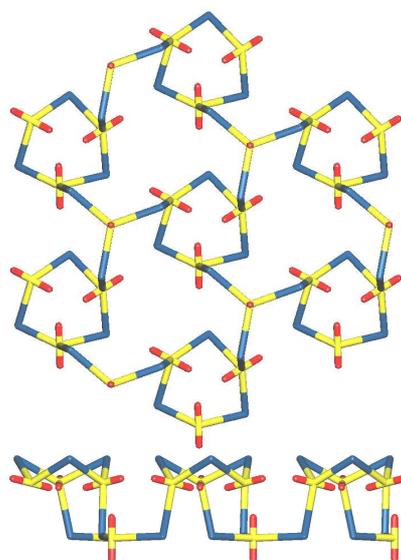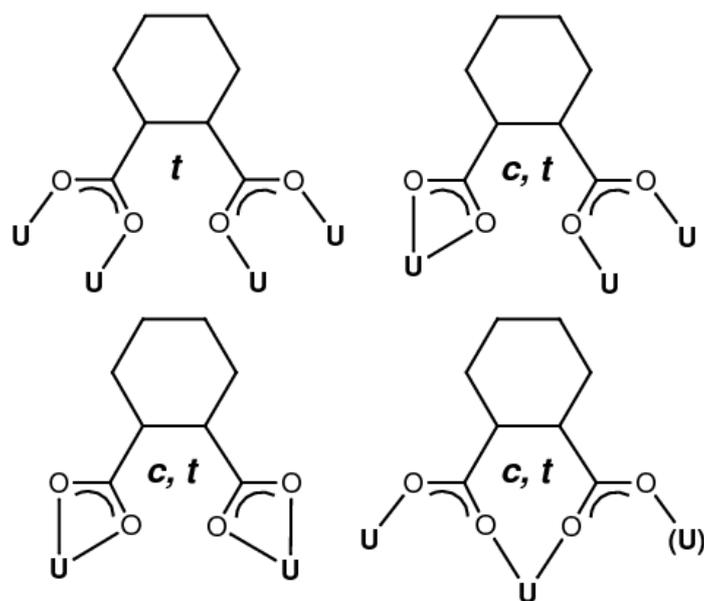

Figure 4. Simplified side-on and edge-on representations of the uranyl-based 2D network with hnb topology in compound **3** (yellow: uranium; red: oxygen; blue: centroid of the dicarboxylate ligand).

silver(I) or lead(II) cations (with formation of heterometallic cuboidal clusters with Cs^+ and Rb^+), the much bulkier PPh_3Me^+ cation promotes a rearrangement which, even if geometrically minor, yields a 2D coordination polymer. The PPh_3Me^+ cation is located so that the methyl group points towards the centre of the three-node ring, and is probably involved in three weak CH⋯O hydrogen bonds with three carboxylate oxygen atoms from the ring [C⋯O 3.349(8) Å, C–H⋯O 161°], an interaction clearly apparent on the Hirshfeld surface. Although coulombic interactions are largely dominant in the packing,[34] such weak interactions may play a local role on the finest details of the arrangement. When viewed sideways, the 2D sheets have a corrugated aspect, with a thickness of ~11 Å, one of the faces being lined by the trinuclear rings, while the uranyl cations located on the rotation axes are located on the other face, and the sheets are separated from one another by layers of PPh_3Me^+ counterions. Possibly because of the dominance of the interactions of the methyl groups with carboxylate oxygen atoms, the counterions are well spaced [shortest P⋯P distance 13.6231(3) Å] within their sheets and do not appear to be involved in "phenyl embraces". As entities with a 3-bladed propeller form, they are chiral and the chirality of the lattice is reflected in the fact that all define right-handed helices.

It appears that, among all the coordination modes found up to now in uranyl ion complexes with the *cis* and *trans* isomers of 1,2-chdc^{2-}, which are shown in Scheme 1, the only one observed in the present complexes with the *trans* form is the bis-chelating mode. However, an extra level of variety is introduced by the possible axial or equatorial positioning of the carboxylate groups.

Scheme 1. Coordination modes of *c*- and *t*-1,2-chdc^{2-} in uranyl ion complexes.

Complexes [PPh$_4$][UO$_2$(*t*-1,4-chdc)(NO$_3$)]·2CH$_3$CN (**4**) and [PPh$_4$][UO$_2$(*c*-1,4-chdc)(NO$_3$)] (**5**), synthesized from *t*-1,4-chdcH$_2$ and *c,t*-1,4-chdcH$_2$ (mixture of *cis* and *trans* isomers), respectively, have the same overall formula (except for the solvent), but different structures. In both cases, the asymmetric unit contains one uranyl cation which is chelated by two carboxylate groups and one nitrate anion, one 1,4-chdc^{2-} ligand in the chair conformation, and two PPh$_4^+$ cations with twofold rotation symmetry (Figures 5 and 6). The two carboxylate groups of the *trans* isomer in **4** are equatorial, and the ligand is thus a divergent, linear linker which forms a zigzag 1D polymer running along the *a* axis (a linear chain was previously observed in [UO$_2$(*t*-1,4-chdc)(H$_2$O)$_2$], in which the water ligands occupy *trans* positions in the uranyl equatorial plane[13]). These ribbon-like chains are packed in an oblique fashion to form sheets parallel to (0 0 1), which are separated by large spaces (> 6 Å) containing the counterions and solvent molecules (KPI 0.69). The counterions are stacked into columns along the *b* axis, with an alternation of P···P distances of 7.253(3) and 7.519(3) Å, in which two parallel-displaced π-stacking interactions are present within each cation pair [centroid···centroid distances 4.000(3) and 4.181(4) Å, dihedral angles 15.8(3) and 16.2(3)°]. One CH···π
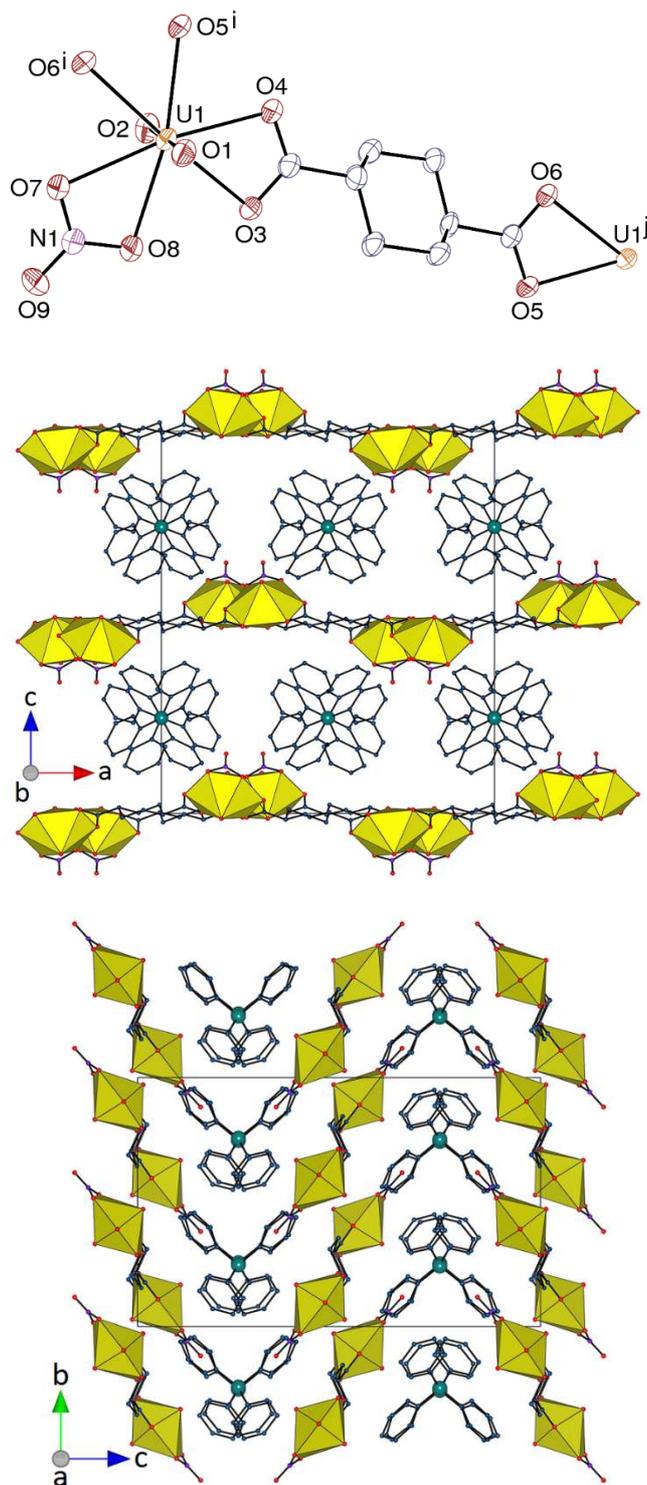
Figure 5. Top: View of compound **4**. Displacement ellipsoids are drawn at the 50% probability level. Counterions, solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = $x - 1/2$, $1/2 - y$, $1 - z$; j = $x + 1/2$, $1/2 - y$, $1 - z$. Middle and bottom: Packing with chains viewed side-on or end-on, respectively, and solvent molecules and hydrogen atoms omitted.

interaction involving a proton from the ligand is also possibly present [H···centroid 2.80 Å, C–H···centroid 138°]. Examination of the Hirshfeld surface reveals also several CH···O/N hydrogen bonds between protons of the counterions and solvent molecules and oxo or carboxylato oxygen atoms, or acetonitrile nitrogen atoms.

In contrast, one of the two carboxylate groups of the *cis* isomer of the ligand in **5** is equatorial and the other is axial, thus conferring a kinked shape to the ligand. A 1D polymeric chain, directed along the *b* axis, is formed here also, but it has a distinctly helical shape as a
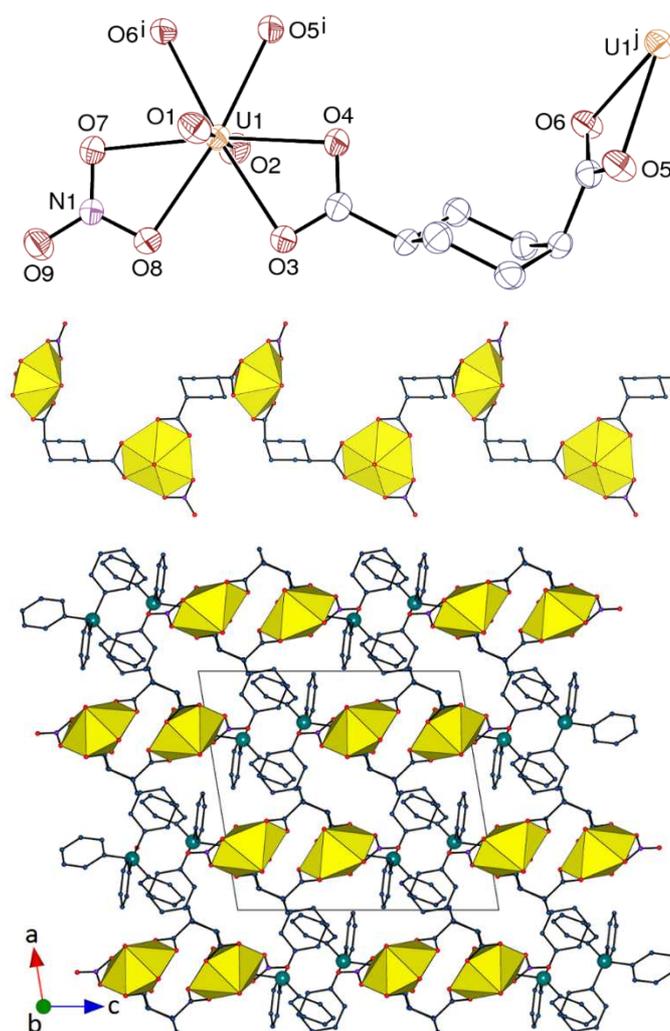

Figure 6. Top: View of compound **5**. Displacement ellipsoids are drawn at the 50% probability level. Counterions and hydrogen atoms are omitted. Symmetry codes: i = 3/2 – *x*, *y* – 1/2, 3/2 – *z*; j = 3/2 – *x*, *y* + 1/2, 3/2 – *z*. Middle: View of the 1D helical polymer. Bottom: Packing with chains viewed end-on. Hydrogen atoms are omitted in the last two views.

result of the ligand geometry and is akin to the chain in the neutral complex [UO$_2$(c-1,4-chdc)(bipy)], in which bipy is chelating and replaces nitrate.[13] The space group being centrosymmetric, both left- and right-handed helices are present in the lattice. The chains are arranged so as to form layers parallel to (1 0 $\bar{1}$), separated from one another by the counterions (KPI 0.68). Centrosymmetric pairs of cations with a P···P distance of 6.7433(18) Å are formed, and can be considered as a case of sextuple phenyl embrace.[7] However, no short contact indicative of significant π-stacking interaction is present here, but three CH(cyclohexyl)···π interactions are possibly significant [H···centroid 2.85–2.99 Å, C–H···centroid 151–170°], as well as one CH···O hydrogen bond involving a proton from the counterion and a carboxylate oxygen atom [C···O 3.113(5) Å, C–H···O 133°], these contacts being apparent on the Hirshfeld surfaces.

The two complexes [PPh$_4$]$_2$[(UO$_2$)$_2$(t-1,4-chdc)$_3$]·4H$_2$O (**6**) and [PPh$_3$Me]$_2$[(UO$_2$)$_2$(t-1,4-chdc)$_3$]·2H$_2$O (**7**) differ by the counterion and the number of lattice water molecules, but, as in complex **3**, the absence of a coligand such as formate or nitrate results in the expected uranium/ligand ratio of 2:3. The asymmetric unit in **6** contains a unique uranium atom chelated by three carboxylate groups, three centrosymmetric t-1,4-chdc^{2-} ligands and one PPh$_4^+$ cation (Figure 7). All ligands are in the chair conformation, but two are in the *ee* and one in the less usual *aa* geometry. Examples of coexistence of these two forms are known,[28] one of them in a uranyl–lead(II) complex.[13] Uranyl ions are three-fold nodes in the 2D network formed parallel to (1 –2 1), which has the {6^3} point symbol of the honeycomb (hcb) topological type. The same topology was previously encountered in [H$_2$NMe$_2$]$_2$[(UO$_2$)$_2$(c-1,4-chdc)(t-1,4-chdc)$_2$]·2H$_2$O, which crystallizes as a threefold 2D parallel interpenetrated network;[13] the bulkiness of the counterions in **6** may prevent a similar entanglement. Due to the presence of the ligand in the *aa* conformation, the layers are not planar, but display a sawtooth-shaped
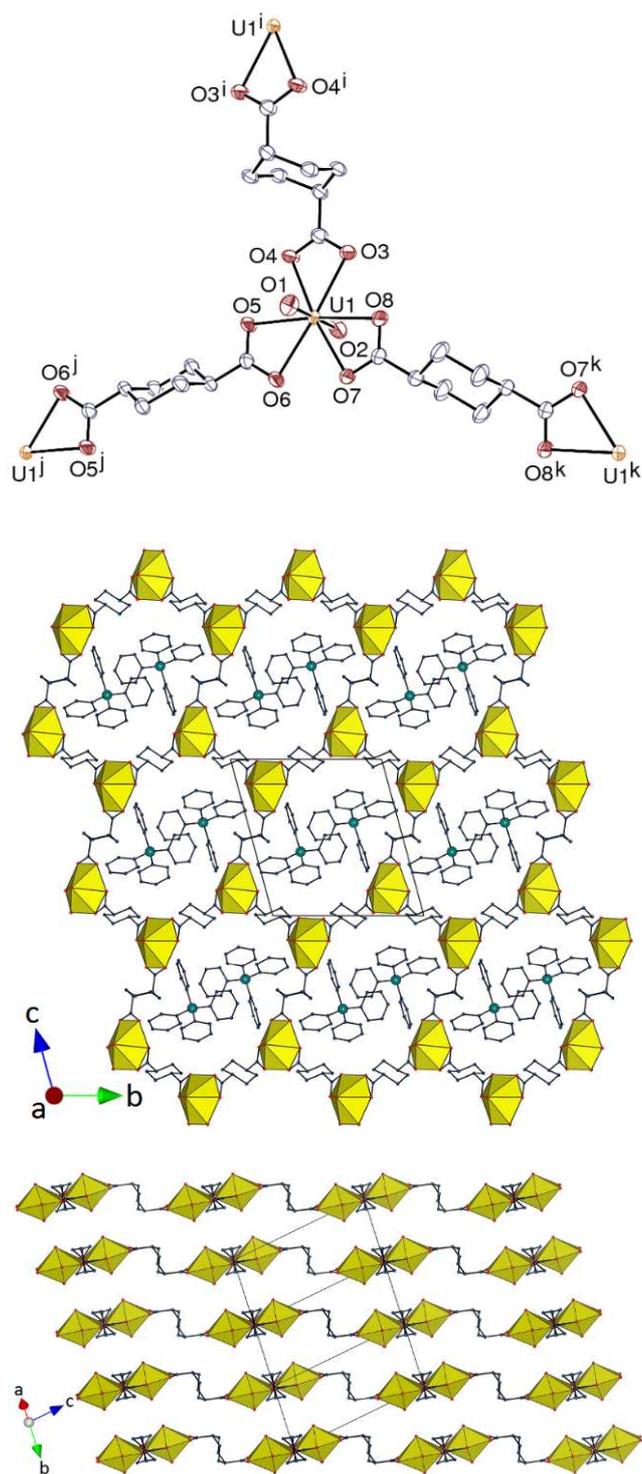
Figure 7. Top: View of compound **6**. Displacement ellipsoids are drawn at the 50% probability level. Counterions, solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = 1 − x, −y, 1 − z; j = 2 − x, 1 − y, 2 − z; k = −x, −y, 2 − z. Middle: View of the uranyl-based 2D network and the counterions. Bottom: Packing of the sheets with counterions and solvent molecules omitted.

section. The counterions occupy the channels formed parallel to the *a* axis, which have a section of ~15 × 10 Å^2, and within these channels form centrosymmetric pairs involved in sextuple phenyl embraces with a short P···P separation of 6.1587(16) Å. One parallel-displaced π-stacking interaction is particularly obvious [centroid···centroid distance 4.027(2) Å, dihedral angle 0°], and also one CH···π interaction involving a proton from one ligand [H···centroid 2.69 Å, C–H···centroid 154°] and two CH(counterion)···O(carboxylate) hydrogen bonds [C···O 3.091(5) and 3.234(5) Å, C–H···O 124 and 130°].

The asymmetric unit in **7** contains one tris-chelated uranyl cation, one ligand in the *ee* conformation, and a second, centrosymmetric one in the *aa* conformation, and one PPh$_3$Me$^+$ cation (Figure 8). The connectivity is identical to that in **6** and, here also, a 2D network with hcb topology is formed, parallel to (1 0 –2). The layers have here a square wave-shaped section, and the counterions are located within the channels (~15 × 11 Å^2) directed along the *a* axis (KPI 0.68). Once again, the cations in the channels can be considered to contain centrosymmetric close pairs [P···P 6.680(2) Å] involved in sextuple phenyl embraces, but the Hirshfeld surface only provides evidence that this embrace involves dispersion interactions and that cation interactions beyond dispersion are predominantly of the CH···O type involving oxygen atoms of the anionic polymer. One CH···π interaction involving a proton from the *aa* ligand appears to be present [H···centroid 2.79 Å, C–H···centroid 136°] along with four CH(counterion)···O(oxo/carboxylate) hydrogen bonds, two of them involving the methyl group [C···O 3.132(5)–3.346(5) Å, C–H···O 115–176°].
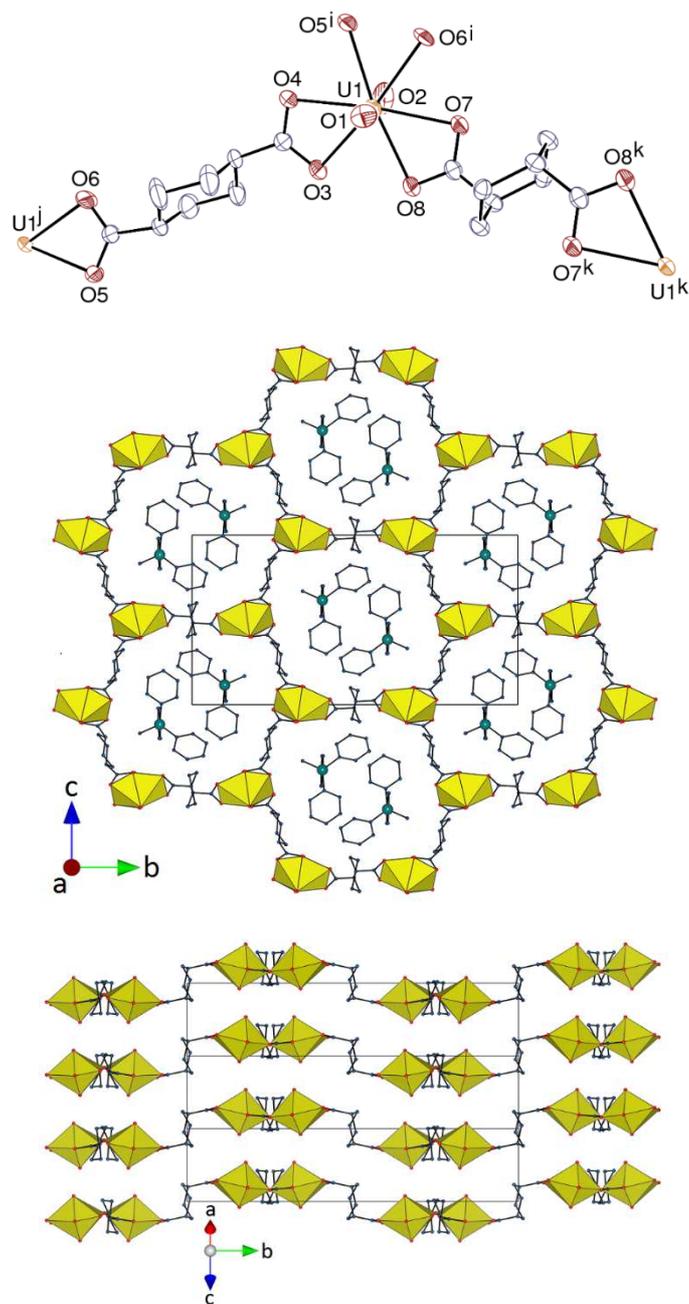
Figure 8. Top: View of compound **7**. Displacement ellipsoids are drawn at the 50% probability level. Counterions, solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = $x + 1$, $3/2 - y$, $z + 1/2$; j = $x - 1$, $3/2 - y$, $z - 1/2$; k = $2 - x$, $2 - y$, $1 - z$. Middle: View of the uranyl-based 2D network and the counterions. Bottom: Packing of the sheets with counterions and solvent molecules omitted.

The complex [PPh$_3$Me]$_2$[(UO$_2$)$_2$(c-1,4-chdc)$_3$]·2H$_2$O (**8**) was synthesized from the mixture of *cis* and *trans* isomers of the ligand, but, as complex **5**, it contains only the *cis* form. The stoichiometry is the same as in **6** and **7**, and the asymmetric unit contains two uranyl ions

in different environments, three ligands in the chair *ae* conformation and two PPh$_3$Me$^+$ cations (Figure 9). Atom U1 is chelated by three carboxylate groups, whereas U2 is chelated by two
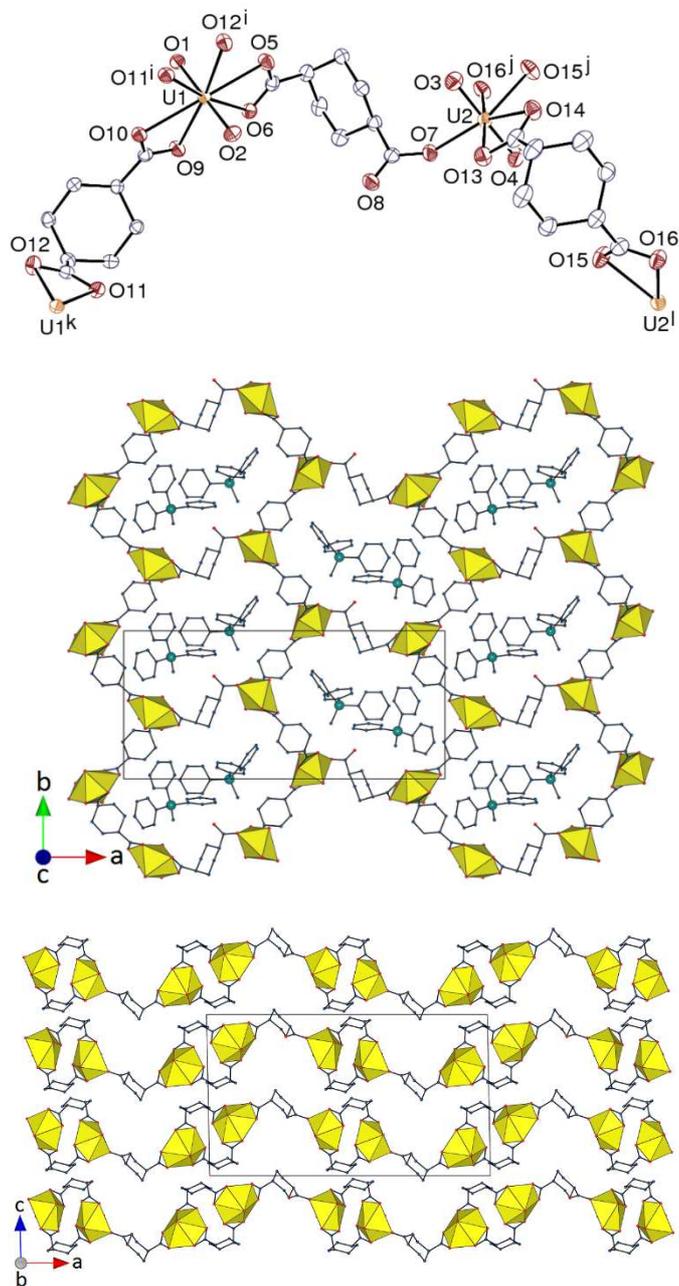

Figure 9. Top: View of compound **8**. Displacement ellipsoids are drawn at the 50% probability level. Counterions, solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = –*x*, *y* – 1/2, 1/2 – *z*; j = 1 – *x*, *y* – 1/2, 1/2 – *z*; k = –*x*, *y* + 1/2, 1/2 – *z*; l = 1 – *x*, *y* + 1/2, 1/2 – *z*. Middle: View of the uranyl-based 2D network and the counterions. Bottom: Packing of the sheets with counterions and solvent molecules omitted.

groups only and bound to one oxygen atom from a third ligand, and it is thus in a pentagonal bipyramidal environment. This minor difference has no effect on the nature of the polymeric arrangement, which is here also 2D with the hcb topology, and parallel to (0 0 1). When viewed sideways, the layers display a triangular wave-shaped or undulating section; the irregular channels containing the counterions run along the [0 1 1] axis (~9 × 6 Å^2, while the hexagonal rings have a size of ~15 × 9 Å^2), the overall packing leaving no significant space apart from that occupied by the water molecules (KPI 0.69). Here, it is the inequivalent cations which appear to be involved in forming pairs through a phenyl embrace analogous to that found in complex **4**, but that is tighter [P···P 6.5100(10) Å], and two parallel-displaced π-stacking interactions are possibly present [centroid···centroid distances 3.9206(18) and 4.3484(19) Å, dihedral angles 25.12(15) and 13.60(15)°], along with two CH(cyclohexyl)···π interactions [H···centroid 2.91 and 2.92 Å, C–H···centroid 137 and 123°] and six CH(counterion)···O(carboxylate/water) hydrogen bonds [C···O 3.260(4)–3.412(4) Å, C–H···O 143–170°]. The latter interactions involving hydrogen atoms appear prominently on the Hirshfeld surfaces.

The complex [PPh$_4$]$_2$[(UO$_2$)$_2$(t-1,4-chdc)$_2$(c-1,4-chdc)]·3H$_2$O (**9**) is the only one in the present series to include both *cis* and *trans* isomers of the 1,4-chdc^{2-} ligand, but other cases, with varying *cis/trans* ratios, have previously been described.[13] Complex **9** crystallizes in the monoclinic space group *P*2$_1$/*n* with a large asymmetric unit containing six tris-chelated uranyl cations, three *c*-1,4-chdc^{2-} and seven (two of them centrosymmetric) *t*-1,4-chdc^{2-} ligands, all in the chair conformation, and six PPh$_4^+$ cations (Figure 10). While all the *cis* ligands are of the *ae* form, five (one of them centrosymmetric) of the *trans* ligands are of the extended *ee* form and two (one of them centrosymmetric) of the kinked *aa* form. The 2D network formed, parallel to (1 0 –5), has here also the hcb topology. The layers are strongly corrugated, with a triangular wave-shaped section and slight interdigitation of adjacent layers, and the channels that run
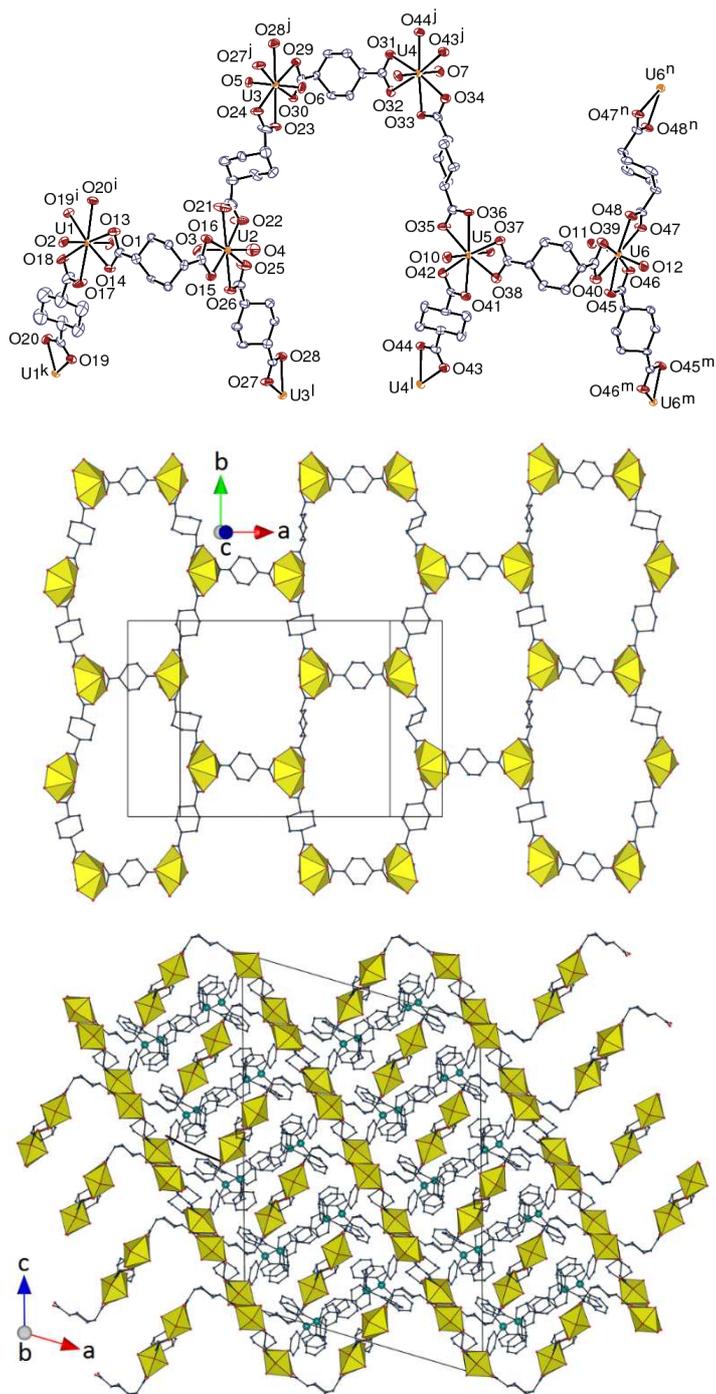
Figure 10. Top: View of compound **9**. Displacement ellipsoids are drawn at the 40% probability level. Counterions, solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = –x – 1/2, y – 1/2, 1/2 – z; j = x, y – 1, z; k = –x – 1/2, y + 1/2, 1/2 – z; l = x, y + 1, z; m = 2 – x, 2 – y, 1 – z; n = 2 – x, 1 – y, 1 – z. Middle: View of the uranyl-based 2D network. Bottom: Packing with sheets viewed edge-on and solvent molecules omitted.

along the [1 0 $\bar{1}$] direction are more elongated and irregular than in **6** and **7** (~17 × 8 Å^2). It is possible to discern three relatively close cation pairs [P1···P4 7.687(4) Å; P2···P5 7.376(4) Å; P3···P6 7.712(4) Å] involving partial embraces but these only form part of more extended columnar arrays and the single instance of phenyl ring stacking must be considered rather distorted [centroid···centroid distance 4.390(6) Å, dihedral angle 35.6(5)°]. Five CH(cyclohexyl/phenyl)···π interactions [H···centroid 2.71–2.99 Å, C–H···centroid 134–151°] are apparent, along with a CH···O(water), but no CH···O(carboxylate) hydrogen bond. The KPI of 0.67 indicates that the packing is no more compact than the former ones.

Luminescence properties. The emission spectra of compounds **1**–**4**, **6**, **8** and **9** in the solid state were recorded at room temperature under excitation at a wavelength of 420 nm, a value suitable for excitation of the uranyl chromophore,[35] and they are shown in Figure 11. The spectra of **1**–**4**, **6** and **9** display the usual series of well-resolved maxima associated with the vibronic progression corresponding to the $S_{11} \rightarrow S_{00}$ and $S_{10} \rightarrow S_{0\nu}$ ($\nu = 0$–4) electronic transitions.[36] The maxima positions are very close for these six complexes, with the four main peaks [$S_{10} \rightarrow S_{0\nu}$ ($\nu = 0$–3)], at 480–482, 500–501, 521–524 and 545–548 nm. These values are typical of complexes in which uranyl is chelated by three carboxylate groups,[13] and they are significantly blue-shifted with respect to those generally measured in comparable complexes with five equatorial donors. It is thus unsurprising that complex **8**, in which half the uranyl centres have five and the other half six equatorial donors, gives a spectrum in which a broad envelope encompasses several unresolved maxima, the first intense one being at ~480 nm as expected for the component with six donors, and the second at ~509 nm, a value at the upper end of the range usual for complexes with five donors.[13] A photoluminescence quantum yield (PLQY) of 0.13 was measured for compound **6**, which could be obtained in sufficiently large quantity (in one batch), this value being twice that measured for the octanuclear complex

[NH$_4$][PPh$_4$][(UO$_2$)$_8$(*c*-1,2-chdc)$_9$(H$_2$O)$_6$]·3H$_2$O.[14] This value is relatively low, probably due to dynamic quenching induced by ambient oxygen, but also static quenching, as already described for other f-block compounds in their crystalline state.[37,38] It is however important to mention that it is still higher than that for other uranyl-based compounds previously reported.[39]
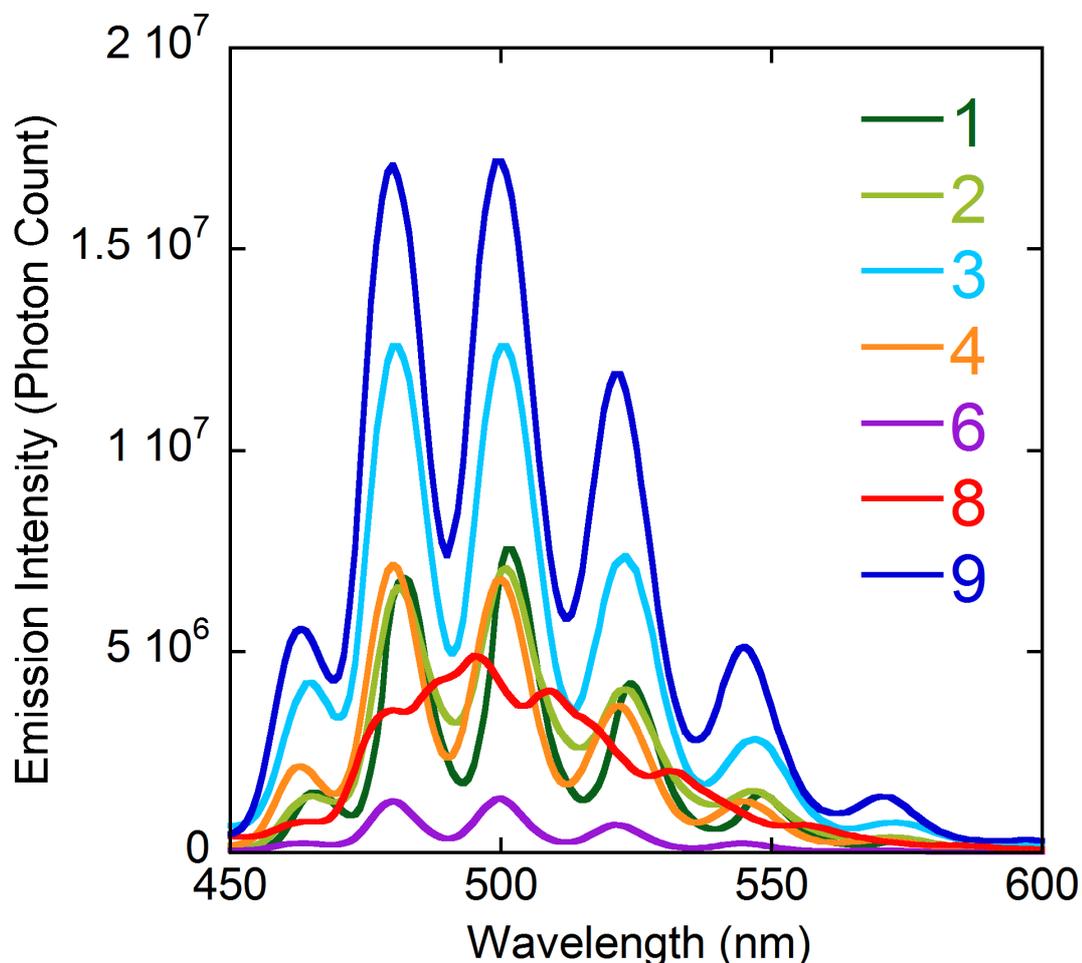

Figure 11. Emission spectra of compounds **1**–**4**, **6**, **8** and **9** in the solid state, under excitation at a wavelength of 420 nm.

CONCLUSIONS

Substitution on the cyclohexane ring has long been exploited to provide access to multidentate ligands and these are well-known to form metal ion complexes with properties significantly dependent upon the conformational preferences of the ring. We report herein a series of uranyl complexes with *trans*-1,2-, *trans*-1,4- and *cis*-1,4-cyclohexanedicarboxylates obtained under

solvo-hydrothermal conditions in the presence of PPh_4^+ or PPh_3Me^+ counterions and various organic cosolvents. The broader spectrum of systems now available with these ligands does reveal subtle differences in these structures associated with different counterions and also shows that, in the case of t-1,2-chdc^{2-}, the species obtained from the racemic ligand can display a degree of selectivity in their isomeric composition.

Although the formation of tetrahedral clusters with t-1,2-chdc^{2-} is frequently observed, in particular in the presence of NH_4^+ counterions,[12] it is not found with PPh_4^+ or PPh_3Me^+ cations. However, the local geometry in the hnb network of compound **3** appears to be derived from that of the tetrahedral cluster. The *cis* and *trans* isomers behave differently in the presence of the PPh_4^+ cation since the octanuclear cage which is formed with the former[14] is not observed with the latter. NH_4^+ cations formed *in situ* from acetonitrile decomposition probably play an essential role in the formation of this cage, in which they are included, but experiments performed with t-1,2-chdc^{2-} in acetonitrile only gave complexes isomorphous to **1** and **2** and including nitrate ions, and the $H_2NMe_2^+$ cations formed from DMF hydrolysis and present in complex **3** are too bulky to act in the same manner as NH_4^+ (and they cannot form four hydrogen bonds with oxo groups as the latter). These results suggest that the axial or equatorial positioning of the carboxylate groups on the cyclohexyl ring in the chair conformation, *ee* or *aa* in the *trans* isomer (the present results indicate that the difference in energy may be quite small), and *ae* in the *cis*, has a determinant effect on the geometry of the complex. It is notable that the racemic and pure (1*R*,2*S*) enantiomer are no different in the present complexes, due to resolution of the enantiomers during crystallization in the complexes synthesized from the racemic form.

The polymeric assemblies formed with bis(chelating) 1,4-chdc^{2-} ligands are either 1D (helical in one case) or 2D with the hcb topology (finer variations being provided by the coexistence of the *cis* and *trans* isomers in one case, and by the two possible geometries of the

trans isomer, linear *ee* or kinked *aa*). The prevalence of the hcb topology with both PPh_4^+ or PPh_3Me^+ as counterions, while it has been found only once in previous experiments in the absence of, or with different counterions,[13] points to a particular tendency of these large cations to induce the formation of species with large rings able to form channels sufficiently spacious to accommodate them. Probably as a consequence, the entanglement of networks, 2D or 3D, frequently observed in previous experiments, is absent here. The tendency of PPh_4^+ and PPh_3Me^+ to aggregate in the solid state through phenyl embraces means that they can in fact be considered to be able to generate exceptionally large cations but the present results show that this tendency can be disrupted by other weak interactions.

The seven complexes for which the photoluminescence properties were investigated show uranyl ion emission with the characteristic resolution of vibronic fine structure. The maxima positions for the six complexes in which the uranyl ion has six equatorial donors match the values usually found for tris-chelated carboxylate complexes, whereas the spectrum of the complex in which environments with five and six donors coexist gives a broad envelope masking a superposition of different series of peaks. A quantum yield of 0.13 was measured for complex **6**, a promising result since this compound is the least emissive in this series.

ASSOCIATED CONTENT

Accession Codes

CCDC 1822636−1822644 contain 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.

AUTHOR INFORMATION

Corresponding Authors

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

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

ORCID

Pierre Thuéry: 0000-0003-1683-570X

Youssef Atoini: 0000-0003-4851-3713

Jack Harrowfield: 0000-0003-4005-740X

Notes

The authors declare no competing financial interest.

REFERENCES

1. Wang, K. X.; Chen, J. S. Extended Structures and Physicochemical Properties of Uranyl–Organic Compounds. *Acc. Chem. Res*. **2011**, *44*, 531–540.

2. Andrews, M. B.; Cahill, C. L. Uranyl Bearing Hybrid Materials: Synthesis, Speciation, and Solid-State Structures. *Chem. Rev*. **2013**, *113*, 1121–1136.

3. Loiseau, T.; Mihalcea, I.; Henry, N.; Volkringer, C. The Crystal Chemistry of Uranium Carboxylates. *Coord. Chem. Rev*. **2014**, *266–267*, 69–109.

4. Su, J.; Chen, J. S. MOFs of Uranium and the Actinides. *Struct. Bond*. **2015**, *163*, 265–296.

5. Thuéry, P.; Harrowfield, J. Recent Advances in Structural Studies of Heterometallic Uranyl-Containing Coordination Polymers and Polynuclear Closed Species. *Dalton Trans.* **2017**, *46*, 13660–13667.

6. Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr., Sect. B* **2016**, *72*, 171–179.

7. Dance, I.; Scudder, M. Supramolecular Motifs: Concerted Multiple Phenyl Embraces between Ph$_4$P$^+$ Cations are Attractive and Ubiquitous. *Chem. Eur. J.* **1996**, *2*, 481–486.

8. Scudder, M.; Dance, I. Crystal Supramolecular Motifs. Ladders, Layers and Labyrinths of Ph$_4$P$^+$ Cations Engaged in Fourfold Phenyl Embraces. *J. Chem. Soc., Dalton Trans* **1998**, 3155–3165.

9. Scudder, M.; Dance, I. Crystal Supramolecular Motifs. Two- and Three-Dimensional Networks of Ph$_4$P$^+$ Cations Engaged in Sixfold Phenyl Embraces. *J. Chem. Soc., Dalton Trans* **1998**, 3167–3175.

10. Thuéry, P. Two Novel Uranyl–Organic Frameworks with Cyclohexane-1,3-Dicarboxylate Ligands. *CrystEngComm* **2009**, *11*, 232–234.

11. Thuéry, P.; Harrowfield, J. Coordination Polymers and Cage-Containing Frameworks in Uranyl Ion Complexes with *rac-* and (1*R*,2*R*)-*trans*-1,2-Cyclohexanedicarboxylates: Consequences of Chirality. *Inorg. Chem.* **2017**, *56*, 1455–1469.

12. Thuéry, P.; Harrowfield, J. Tetrahedral and Cuboidal Clusters in Complexes of Uranyl and Alkali or Alkaline-Earth Metal Ions with *rac-* and (1*R*,2*R*)-*trans*-1,2-Cyclohexanedicarboxylate. *Cryst. Growth Des*. **2017**, *17*, 2881–2892.

13. Thuéry, P.; Harrowfield, J. Structural Consequences of 1,4-Cyclohexanedicarboxylate Cis/Trans Isomerism in Uranyl Ion Complexes: From Molecular Species to 2D and 3D Entangled Nets. *Inorg. Chem.* **2017**, *56*, 13464–13481.

14. Thuéry, P.; Atoini, Y.; Harrowfield, J. Counterion-Controlled Formation of an Octanuclear Uranyl Cage with *cis*-1,2-Cyclohexanedicarboxylate Ligands. *Inorg. Chem*., submitted.

15. Niekiel, F.; Lannoeye, J.; Reinsch, H.; Munn, A. S.; Heerwig, A.; Zizak, I.; Kaskel, S.; Walton, R. I.; de Vos, D.; Llewellyn, P.; Lieb, A.; Maurin, G.; Stock, N. Conformation-Controlled

Sorption Properties and Breathing of the Aliphatic Al-MOF [Al(OH)(CDC)]. *Inorg. Chem.* **2014**, *53*, 4610–4620.

16. Kimura, K.; Watanabe, Y.; Suda, T.; Senda, H.; Hosoi, S.; Ohta, T.; Kunimoto, K. K. Crystal Structure of (1*R*,2*R*)-trans-1,2-Cyclohexanedicarboxylic Acid-(*R*)-1-Phenylethylamine Salt. *Anal. Sci.* **1999**, *15*, 609–610.

17. Hooft, R. W. W. *COLLECT*, Nonius BV: Delft, The Netherlands, 1998.

18. Otwinowski, Z.; Minor, W. Processing of X-Ray Diffraction Data Collected in Oscillation Mode. *Methods Enzymol.* **1997**, *276*, 307–326.

19. Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr., Sect. A* **2015**, *71*, 3–8.

20. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.

21. Farrugia, L. J. WinGX and ORTEP for Windows: an Update. *J. Appl. Crystallogr.* **2012**, *45,* 849–854.

22. Momma, K.; Izumi, F. VESTA: a Three-Dimensional Visualization System for Electronic and Structural Analysis. *J. Appl. Crystallogr.* **2008**, *41,* 653–658.

23. Blatov, V. A. *TOPOS*, Samara State University, Russia, 2004.

24. Thuéry, P.; Harrowfield, J. Modulation of the Structure and Properties of Uranyl Ion Coordination Polymers Derived from 1,3,5-Benzenetriacetate by Incorporation of Ag(I) or Pb(II). *Inorg. Chem.* **2016**, *55*, 6799–6816 and references therein.

25. Thuéry, P.; Harrowfield, J. Structural Variations in the Uranyl/4,4′-Biphenyldicarboxylate System. Rare Examples of 2D → 3D Polycatenated Uranyl–Organic Networks. *Inorg. Chem.* **2015**, *54*, 8093–8102 and references therein.

26. Andrews, M. B.; Cahill, C. L. *In Situ* Oxalate Formation During Hydrothermal Synthesis of Uranyl Hybrid Materials. *CrystEngComm* **2011**, *13*, 7068–7078.

27. Knope, K. E.; Kimura, H.; Yasaka, Y.; Nakahara, M.; Andrews, M. B.; Cahill, C. L. Investigation of in Situ Oxalate Formation from 2,3-Pyrazinedicarboxylate under Hydrothermal Conditions Using Nuclear Magnetic Resonance Spectroscopy. *Inorg. Chem.* **2012**, *51*, 3883–3890.

28. Hernández-Ahuactzi, I. F.; Höpfl, H.; Barba, V.; Román-Bravo, P.; Zamudio-Rivera, L. S.; Beltrán, H. I. Pore-Size Tuning in Double-Pillared Metal-Organic Frameworks Containing Cadmium Clusters. *Eur. J. Inorg. Chem.* **2008**, 2746–2755.

29. Yue, Q.; Huang, Q.; Gao, Y. Y.; Gao, E. Q. Homochiral Coordination Polymers from a Chiral Dicarboxylic Acid and Dipyridyl Ligands: Structural Diversity, Photoluminescence and Magnetic Properties. *Inorg. Chim. Acta* **2016**, *443*, 110–117.

30. Garza, A. J.; Nag, M.; Carroll, W. R.; Goddard, W. A. III; Roberts, J. D. Conformational Preferences of *trans*-1,2- and *cis*-1,3-Cyclohexanedicarboxylic Acids in Water and Dimethyl Sulfoxide as a Function of the Ionization State As Determined from NMR Spectroscopy and Density Functional Theory Quantum Mechanical Calculations. *J. Am. Chem. Soc.* **2012**, *134*, 14772–14780.

31. Spackman, M. A.; Jayatilaka, D. Hirshfeld Surface Analysis. *CrystEngComm* **2009**, *11*, 19–32.

32. Wolff, S. K.; Grimwood, D. J.; McKinnon, J. J.; Turner, M. J.; Jayatilaka, D.; Spackman, M. A. *CrystalExplorer*, University of Western Australia, 2012.

33. Spek, A. L. Structure Validation in Chemical Crystallography. *Acta Crystallogr., Sect. D* **2009**, *65*, 148–155.

34. Gavezzotti, A. The "Sceptical Chymist": Intermolecular Doubts and Paradoxes. *CrystEngComm* **2013**, *15*, 4027–4035.

35. Knope, K. E.; de Lill, D. T.; Rowland, C. E.; Cantos, P. M.; de Bettencourt-Dias, A.; Cahill, C. L. Uranyl Sensitization of Samarium(III) Luminescence in a Two-Dimensional Coordination Polymer. *Inorg. Chem.* **2012**, *51*, 201–206.

36. Brachmann, A.; Geipel, G.; Bernhard, G.; Nitsche, H. Study of Uranyl(VI) Malonate Complexation by Time Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS). *Radiochim. Acta* **2002**, *90*, 147–153.

37. Tkachuk, A. M.; Razumova, I. K.; Perlin, E. Y.; Joubert, M. F.; Moncorge, R. Luminescence Self-Quenching in Tm^{3+}: YLF Crystals: II. The Luminescence Decay and Macrorates of Energy Transfer. *Opt. Spectrosc*. **2001**, *90*, 78–88.

38. Tkachuk, A. M.; Ivanova, S. E.; Joubert, M. F. Guyot, Y.; Guy, S. Luminescence Self-Quenching from $^4F_{3/2}$, $^2P_{3/2}$ and $^4D_{3/2}$ Neodymium Levels in Double Sodium–Yttrium Fluoride Crystals. *J. Lumin*. **2001**, *94–95*, 343–347.

39. Natrajan, L. S. Developments in the Photophysics and Photochemistry of Actinide Ions and their Coordination Compounds. *Coord. Chem. Rev.* **2012**, *256*, 1583–1603.

Uranyl–Organic Coordination Polymers with *trans*-1,2-, *trans*-1,4- and *cis*-1,4-Cyclohexanedicarboxylates: Effects of Bulky PPh$_4^+$ and PPh$_3$Me$^+$ Counterions

Pierre Thuéry, Youssef Atoini and Jack Harrowfield

One- and two-dimensional uranyl-containing coordination polymers with *trans*-1,2-, *trans*-1,4- and *cis*-1,4-cyclohexanedicarboxylate ligands result from the use of PPh$_4^+$ or PPh$_3$Me$^+$ as counterions. Both the diequatorial and the unusual diaxial forms are found for the *trans* isomer of both ligands, resulting in geometric variations within series of related complexes.