Varying structure-directing anions in uranyl ion complexes with Ni(2,2 :6 ,2 -terpyridine-4 -carboxylate)2

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Varying Structure-Directing Anions in Uranyl Ion Complexes with Ni(2,2′:6′,2″-terpyridine-4′-carboxylate)$_2$

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Abstract

2,2′:6′,2″-Terpyridine-4′-carboxylic acid (tpycH) reacts with uranyl cations under solvo-hydrothermal conditions to give $[UO_2(tpyc)_2]\cdot 2H_2O$ (**1**), a monoperiodic polymer different from that previously reported. In the additional presence of Ni^{II} cations, the $Ni(tpyc)_2$ "expanded ligand" is formed and the structure of its complexes with the uranyl cation depends on the additional anions present. $[(UO_2)_2F_4(H_2O)_2Ni(tpyc)_2]\cdot 2H_2O$ (**2**) and $[UO_2(mds)(H_2O)Ni(tpyc)_2]$ (**3**), where mds^{2-} is methanedisulfonate, are monoperiodic polymers in which the fluoride anions are bridging and the mds^{2-} anions chelating. $[(UO_2)_4(NO_3)_2(H_2O)_4Ni_5(tpyc)_{10}](CF_3SO_3)_4(NO_3)_2\cdot 7H_2O$ (**4**) crystallizes as a wide and nearly planar monoperiodic ribbon. $[(UO_2)_2(NO_3)_2(chdc)Ni(tpyc)_2]\cdot chdcH_2\cdot 2CH_3CN$ (**5**), where $chdc^{2-}$ is *trans*-1,4-cyclohexanedicarboxylate, is a monoperiodic chain including both bridging $Ni(tpyc)_2$ and $chdc^{2-}$ ligands, the chains being further assembled into layers through hydrogen bonding to bridging $chdcH_2$ molecules. Finally, $[UO_2Ni_2(tpyc)_4](I_3)_2$ (**6**) crystallizes as a diperiodic network with **sql** topology. These results point to the possibility of modulating the structure of cationic uranyl ion complexes with $Ni(tpyc)_2$ through addition of a wide range of bonding or non-bonding anions.

Introduction

With two very different and divergent coordination sites, the anion derived from 2,2′:6′,2″-terpyridine-4′-carboxylic acid (tpycH) is a ligand particularly well suited to the synthesis of coordination polymers[1] and heterometallic complexes,[2] although examples are rare. In appropriately restricted quantities, metal cations M^{n+} having a preference for an octahedral N_6 environment can form with $tpyc^-$ the "expanded" dicarboxylate ligand $[M(tpyc)_2]^{(n-2)+}$,[3] which in its turn may coordinate two metal cations with a greater affinity for oxygen donors through its two divergent carboxylate groups, thus enabling the formation of heterometallic coordination polymers. We have recently applied this approach to the synthesis of two cationic uranyl ion complexes containing the neutral $Ni(tpyc)_2$ moiety, which crystallize as diperiodic coordination polymers with **sql** topology, one of them displaying twofold parallel interpenetration.[4] An analogous strategy using the larger 2,2′:6′,2″-terpyridine-4′-(phenyl-4-carboxylate) ligand was also recently reported to give access to heterometallic uranyl–M complexes (M = Fe, Co, Ni) which are mono- or diperiodic, the latter being polycatenated.[5] While uranyl–polycarboxylate coordination polymers are generally anionic,[6] thus allowing control of the structure through the use of varying structure-directing countercations, the cationic nature of the uranyl ion complexes based on the $Ni(tpyc)_2$ assembler suggests that their structure could be modulated through changes in the accompanying anions. The two complexes previously reported, $[UO_2(OH)(H_2O)Ni(tpyc)_2](NO_3)\cdot 1.5H_2O$ and $[(UO_2)_2(O)(H_2O)_4Ni_2(tpyc)_4](NO_3)_2\cdot 6H_2O$, contained nitrate counterions, which we have replaced in the present work by fluoride, iodide, carboxylate or sulfonate anions, thus generating different mono- and diperiodic structures, as expected. Some of the complexes formed retain their cationic nature while anion coordination in other cases gives neutral polymers, unlike the case with nitrates. While the homometallic complex

$[(UO_2)_2(tpyc)(HCOO)(OH)_2]$ previously reported contains formate coligands as a result of its synthesis in water/*N,N*-dimethylformamide, the organic cosolvent being hydrolyzed under solvo-hydrothermal conditions,[4] we describe herein a homometallic, homoleptic uranyl ion complex with $tpyc^-$.

Results and Discussion

Although synthesized in a mixture of water, *N,N*-dimethylformamide (DMF) and acetonitrile, the homometallic complex $[UO_2(tpyc)_2]\cdot 2H_2O$ (**1**) does not contain formate anions as its congener synthesized with only DMF as organic cosolvent, nor does it contain cesium cations, although these were added so as to possibly form a uranyl–cesium complex (see Experimental Section). The unique uranium atom is in a pentagonal-bipyramidal environment, being bound to the three nitrogen atoms of one ligand and to two carboxylate oxygen atoms from two different ligands [U–O(oxo), 1.7616(18) and 1.7827(18) Å; U–O(carboxylato), 2.2821(17) and 2.2984(17) Å; U–N, 2.551(2)–2.5957(19) Å] (Figure 1). One of the $tpyc^-$ ligands is coordinated through its two sites, although only one oxygen atom is involved, whereas the other is only bound through one oxygen atom, all three nitrogen atoms being uncoordinated and the two lateral rings being turned over so that the three nitrogen atoms do not point in the same direction. Uranyl ions and the bridging ligands form a simple monoperiodic polymer directed along [001], with the terminal ligands being projected sideways. Several parallel-displaced π-stacking interactions involving the two ligands may be present, as shown by the calculation of short contacts with PLATON[7] [centroid···centroid distances, 3.6219(14)–4.0124(15) Å; dihedral angles, 3.07(12)–10.33(13)°]. These interactions are both intrachain, the two ligands being roughly parallel and close to one another, and interchain. Examination of the Hirshfeld surface (HS)[8]

calculated with CrystalExplorer[9] shows however that the most prominent interactions are OH···O and CH···O hydrogen bonds, as usual. The packing contains no free space (Kitaigorodski packing index (KPI) calculated with PLATON, ~0.73, with disorder excluded).

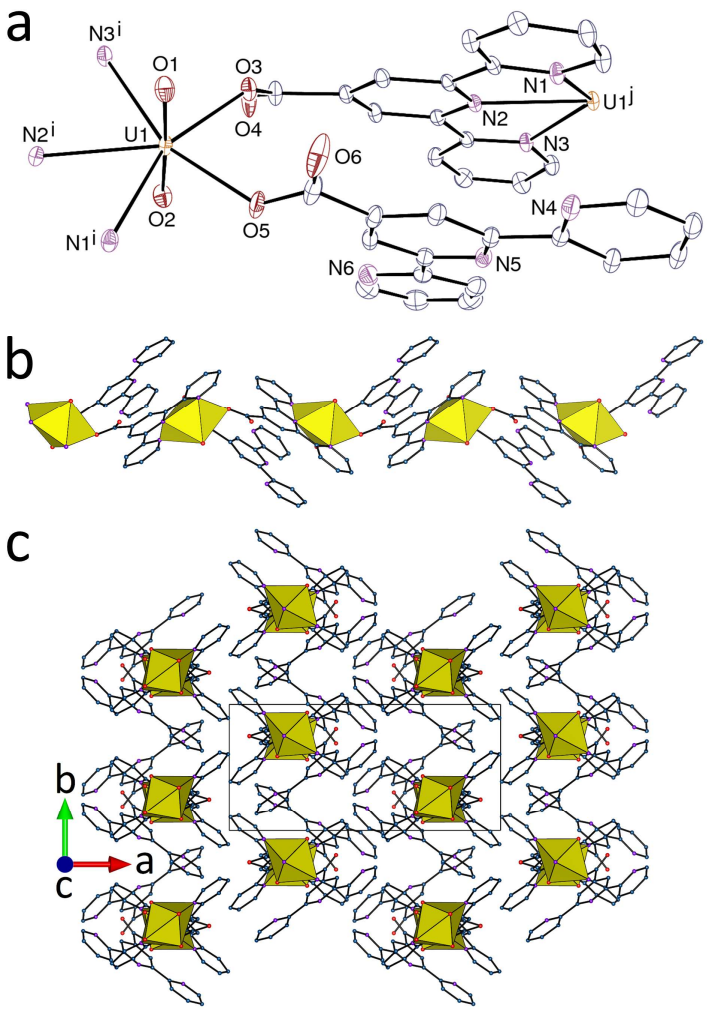

Figure 1. (a) View of complex **1**. Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = *x*, 3/2 – *y*, *z* + 1/2; j = *x*, 3/2 – *y*, *z* – 1/2. (b) View of the monoperiodic coordination polymer with uranium coordination polyhedra yellow. (c) Packing with chains viewed end-on.

The complex $[(UO_2)_2F_4(H_2O)_2Ni(tpyc)_2]\cdot 2H_2O$ (**2**), shown in Figure 2, is a neutral species in which fluoride groups play the same bridging role as hydroxide ions in $[UO_2(OH)(H_2O)Ni(tpyc)_2](NO_3)\cdot 1.5H_2O$,[4] the stoichiometry being however different. NBu_4BF_4

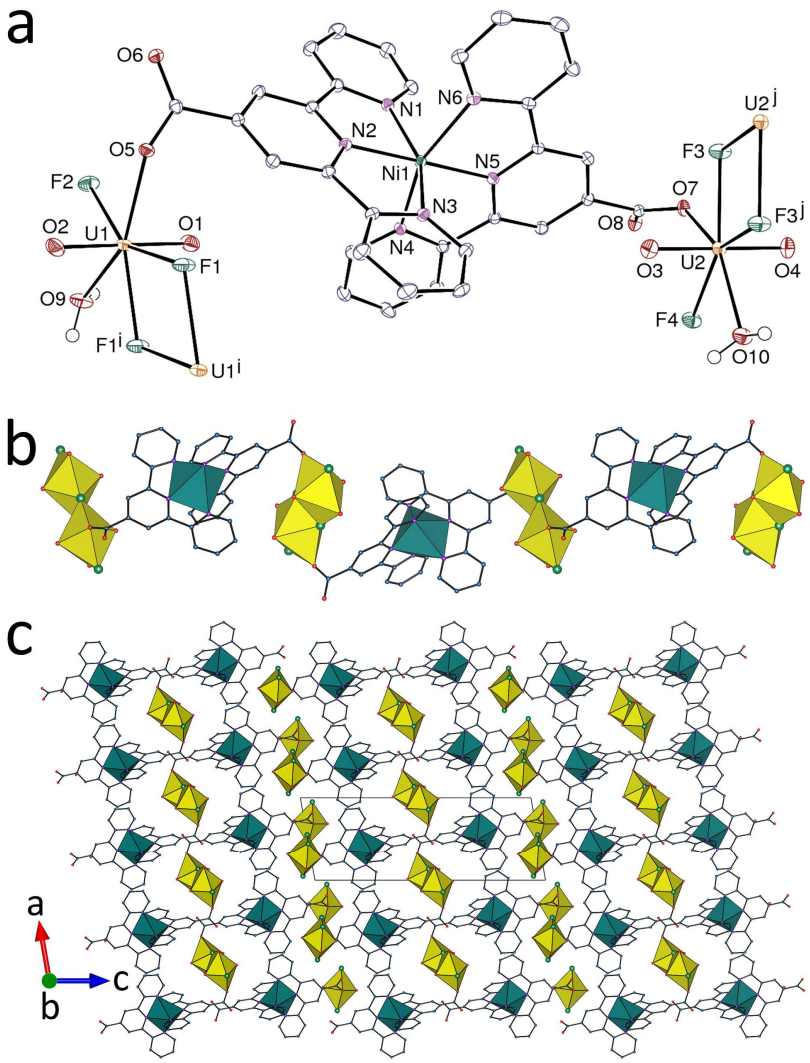

Figure 2. (a) View of complex **2**. Displacement ellipsoids are drawn at the 50% probability level. The solvent molecules and carbon-bound hydrogen atoms are omitted. Symmetry codes: i = 1 – *x*, 2 – *y*, –*z*; j = 2 – *x*, 1 – *y*, 1 – *z*. (b) View of the monoperiodic coordination polymer with uranium coordination polyhedra yellow and those of nickel green, and fluorine atoms shown as green spheres. (c) Packing with chains viewed obliquely.

was added during the synthesis, tetrafluoroborate being a commonly used anion in metal ion salts, but one known to be susceptible to hydrolysis,[10] and it appears that at least under solvo-hydrothermal conditions U^{VI} is efficient at extracting F^- from this anion. The two crystallographically independent uranium atoms are in similar, pentagonal-bipyramidal

environments, being bound to three fluorine atoms, two bridging and one terminal, one monodentate carboxylate group and one water molecule [U–O(oxo), 1.7794(17)–1.7835(17) Å; U–O(carboxylato), 2.3527(15) and 2.3593(15) Å; U–F, 2.2353(14)–2.3339(13) Å; U–O(aquo), 2.4516(17) and 2.4467(17) Å]. Centrosymmetric, bis-fluoride-bridged binuclear secondary building units (SBUs) are formed, with U···U distances of 3.9043(2) and 3.8869(2) Å for U1 and U2, respectively. In contrast with the diperiodic nature of the coordination polymer formed by the hydroxide derivative, the assembly here is monoperiodic and directed along [1$\bar{1}$1]. Two interchain parallel-displaced π-stacking interactions involving the two ligands are apparent [centroid···centroid distances, 3.7530(12) and 3.7109(12) Å; dihedral angles, 4.76(10) and 4.81(10)°], as well as two CH···π interactions [H···centroid, 2.97 and 2.95 Å; C–H···centroid, 135 and 139°]. The directions of the π-stacking interactions being roughly orthogonal to one another, formation of a triperiodic assembly ensues. Here also, the HS evidences the predominance of hydrogen bonds, of the OH···O, OH···F, CH···O and CH···F type. Each of the four water molecules, two coordinated and two free, makes one hydrogen bond with either a carboxylate oxygen atom or a uranyl oxo group [O···O, 2.672(2)–2.903(3) Å; O–H···O, 143(3)–169(4)°] and one with one of the terminal fluoride ions F2 or F4 [O···F, 2.631(2)–2.817(3) Å; O–H···F, 113(4)–176(3)°], all of these bonds building bridges between chains, either direct or mediated by uncoordinated water molecules. The resulting packing is devoid of free spaces (KPI, 0.70).

The complex $[UO_2(mds)(H_2O)Ni(tpyc)_2]$ (**3**) was obtained with methanedisulfonate (mds^{2-}) as additional anion. Here also, complexation of this anion produces a neutral coordination polymer (Figure 3). The uranium atom, in a pentagonal-bipyramidal environment, is bound to two carboxylate oxygen atoms from two $tpyc^-$ ligands, one

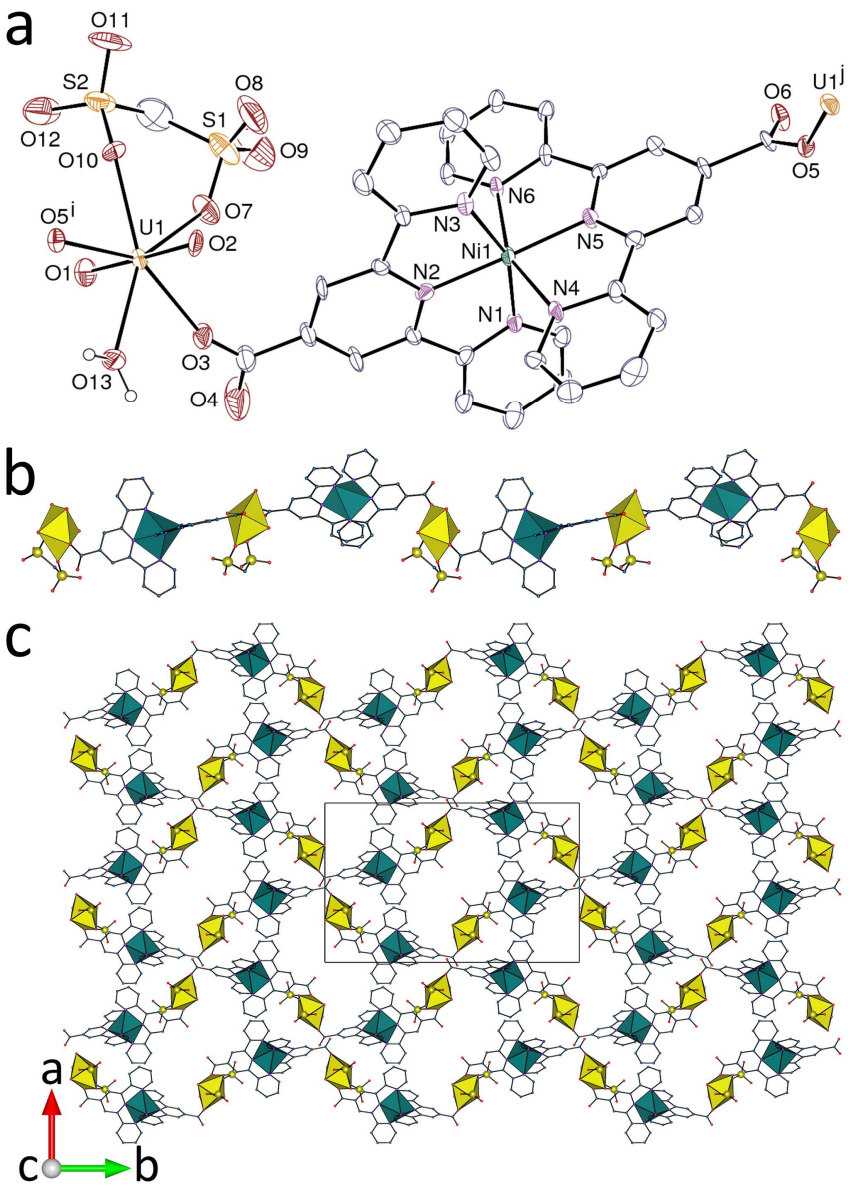

Figure 3. (a) View of complex **3** with displacement ellipsoids drawn at the 30% probability level. Carbon-bound hydrogen atoms are omitted. Symmetry codes: i = 3/2 – *x*, *y* + 1/2, *z* – 1/2; j = 3/2 – *x*, *y* – 1/2, *z* + 1/2. (b) View of the monoperiodic coordination polymer with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with chains viewed side-on.

chelating mds^{2-} ligand and one water molecule [U–O(oxo), 1.750(7) and 1.765(7) Å; U–O(carboxylato), 2.321(8) and 2.324(6) Å; U–O(sulfonato), 2.362(7) and 2.406(8) Å; U–O(aquo), 2.433(7) Å]. There is only one other example of uranyl chelation by mds^{2-}, in a complex involving also cucurbit[6]uril,[11] with U–O bond lengths of 2.393(3) and 2.413(3) Å.

Due to the terminal nature of the chelating ligand, no dinuclear SBU is formed here and the monoperiodic coordination polymer formed is a simple chain with isolated metal centres running along [011]. The chains are connected by hydrogen bonds involving the water molecule and carboxylate or sulfonate oxygen atoms [O···O 2.675(10) and 2.761(14) Å; O–H···O, 158(10) and 145(13)°], but large voids in the structure (KPI, 0.56) indicate the presence of disordered solvent molecules (see Experimental Section). Two interchain parallel-displaced π-stacking interactions involving each $tpyc^-$ ligand with its own image by symmetry are apparent [centroid···centroid distances, 3.800(6) and 3.676(6) Å; dihedral angles, 4.0(5) and 5.1(5)°], leading to the formation of a triperiodic assembly.

The nitrate anions are accompanied by trifluoromethanesulfonate anions in the complex $[(UO_2)_4(NO_3)_2(H_2O)_4Ni_5(tpyc)_{10}](CF_3SO_3)_4(NO_3)_2\cdot 7H_2O$ (**4**), and two are coordinated, in contrast to what was observed in $[UO_2(OH)(H_2O)Ni(tpyc)_2](NO_3)\cdot 1.5H_2O$ and $[(UO_2)_2(O)(H_2O)_4Ni_2(tpyc)_4](NO_3)_2\cdot 6H_2O$.[4] The large asymmetric unit in this complex contains four independent uranium atoms and five $Ni(tpyc)_2$ moieties (Figure 4). The uranium atoms divide into two groups of two, the metal environment being similar within each group. U1 and U2 form a doubly carboxylate-bridged binuclear SBU, with further bonding of each metal centre to two more carboxylate groups, one κ^2O,O'-chelating and the other monodentate [U–O(oxo), 1.718(14)–1.775(11) Å; U–O(carboxylato), 2.472(9)–2.516(10) Å for chelating groups and 2.269(10)–2.371(9) Å for the others]. U3 and U4, also in pentagonal-bipyramidal environments, are bound to two monodentate carboxylate groups, one monodentate nitrate anion and two water molecules [U–O(oxo), 1.728(12)–1.753(11) Å; U–O(carboxylato), 2.306(10)–2.337(11) Å; U–O(nitrato), 2.534(12) and 2.503(17) Å; U–O(aquo), 2.401(11)–2.500(13) Å]. U1 and U2 are thus four-coordinated (4-c) nodes, whereas U3 and

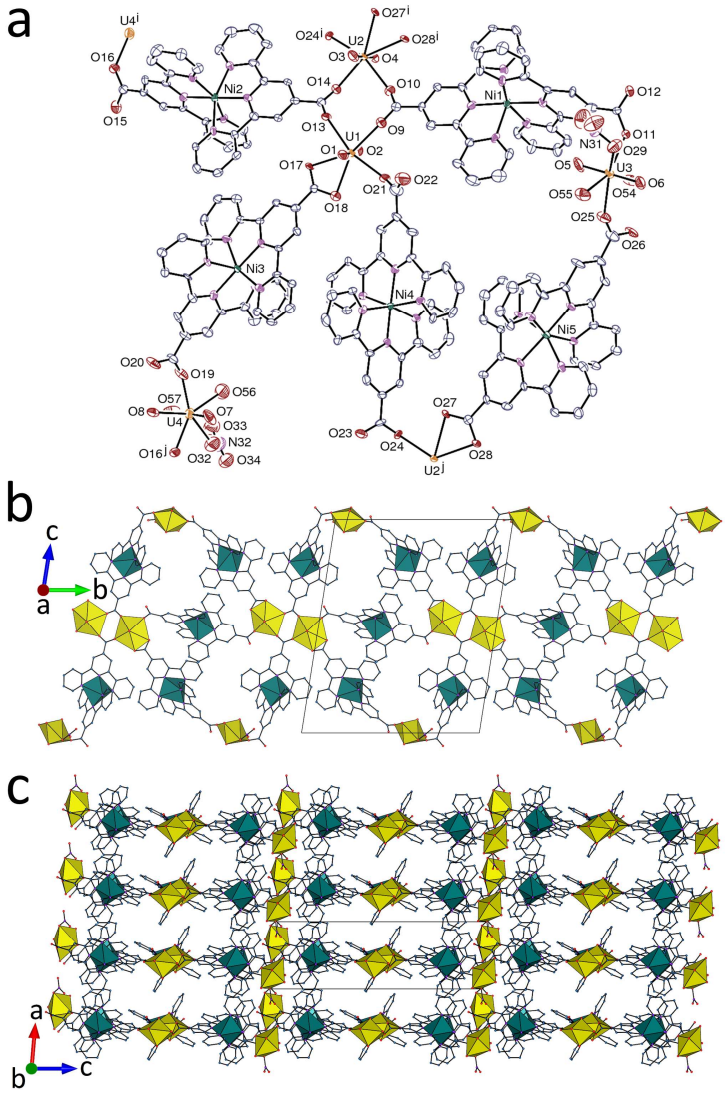

Figure 4. (a) View of complex **4** with displacement ellipsoids drawn at the 50% probability level. The counterions, solvent molecules and hydrogen atoms are omitted. Symmetry codes: i = *x*, *y* + 1, *z*; j = *x*, *y* – 1, *z*. (b) View of the monoperiodic coordination polymer with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with chains viewed end-on.

U4 are simple links. Two of the Ni(tpyc)$_2$, containing Ni3 and Ni5, have one carboxylate group κ^2O,O'-chelating and the other monodentate, two others, containing Ni1 and Ni2, have one group bridging in the μ_2-κ^1O:κ^1O' mode and the other monodentate, and finally that containing Ni4 is bis(monodentate), so that they are simple links but for those associated with Ni1 and Ni2 which are 3-c nodes. The monoperiodic coordination polymer

formed, parallel to [010], has the shape of a nearly planar ribbon with the binuclear SBUs U1/U2 in a central row and U3/U4 located at the two edges. Large rings containing three uranium and three $Ni(tpyc)_2$ units are arranged in groups of two around a common U–$[Ni(tpyc)_2]$–U edge, separated from the neighbouring groups by the binuclear SBUs. The width of the ribbon, ~30 Å, is slightly larger than the *c* unit cell parameter and the ribbons are packed in wide layers parallel to (001) with slight interdigitation between neighbouring layers. The cohesion of the layers is possibly reinforced by five interchain parallel-displaced π-stacking interactions (in addition to two intrachain ones) [centroid···centroid distances, 3.605(8)–4.262(8) Å; dihedral angles, 4.5(7)–18.3(7)°], as well as several CH···π interactions [H···centroid, 2.72–2.99 Å; C–H···centroid, 133–152°]. Considering that there are four bound and at least seven free water molecules (the presence of others is suggested by the low KPI of 0.62 indicating the presence of voids in the structure; see Experimental Section), a large number of hydrogen bonds is expected but, the hydrogen atoms not having been located, a more specific discussion of this point would be questionable.

Although our past experience has shown that reacting mixtures of different polycarboxylates with the uranyl ion does not generally give a complex including the different ligands, this strategy was successful when using $tpyc^-$ and *trans*-1,4-cyclohexanedicarboxylate ($chdc^{2-}$), chosen for its two divergent coordination sites, giving the complex $[(UO_2)_2(NO_3)_2(chdc)Ni(tpyc)_2]\cdot chdcH_2\cdot 2CH_3CN$ (**5**) shown in Figure 5. Replacement of nitrate is however only partial, and two independent, centrosymmetric uncoordinated $chdcH_2$ molecules are also included in the structure. The asymmetric unit contains two uranium atoms in the same hexagonal-bipyramidal environment comprising two κ^2O,O'-chelating carboxylate groups and one chelating nitrate [U–O(oxo), 1.7665(15)–1.7710(15) Å; U–O(carboxylato), 2.4329(14)–2.4827(14) Å; U–O(nitrato), 2.5045(15)–2.5150(15) Å]. All

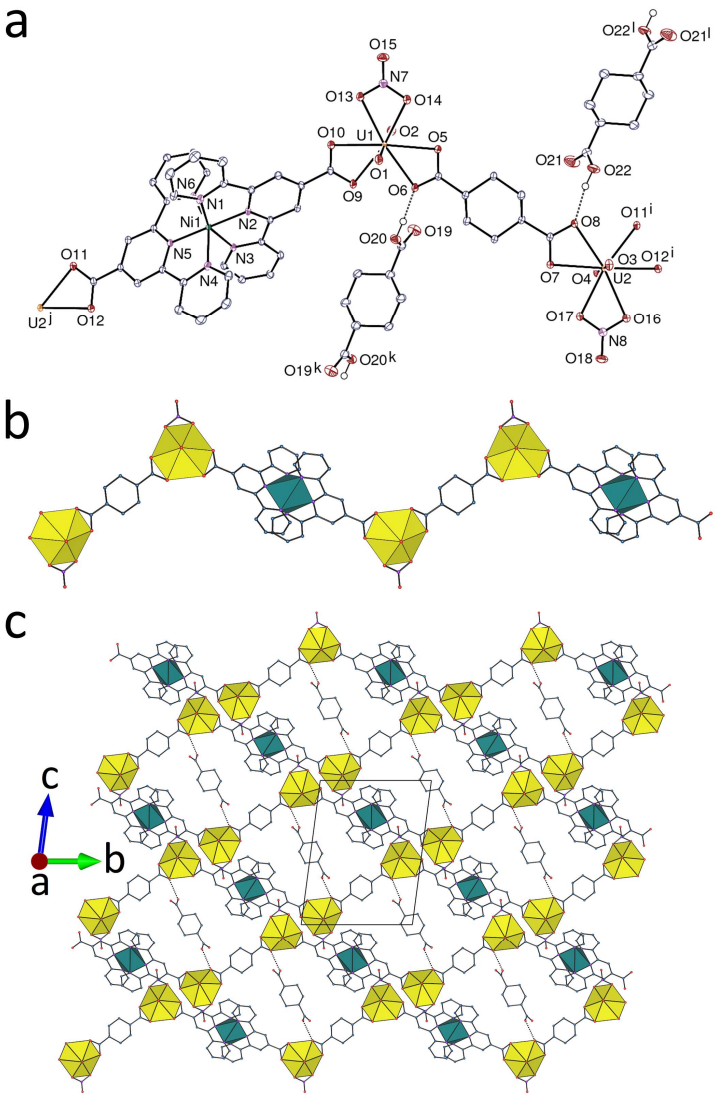

Figure 5. (a) View of complex **5**. Displacement ellipsoids are drawn at the 50% probability level. The solvent molecules and carbon-bound hydrogen atoms are omitted, and the hydrogen bonds are shown as dashed lines. Symmetry codes: i = *x* – 1, *y* + 2, *z*; j = *x* + 1, *y* – 2, *z*; k = 2 – *x*, –*y*, 1 – *z*; l = 1 – *x*, 2 – *y*, –*z*. (b) View of the monoperiodic coordination polymer with uranium coordination polyhedra yellow and those of nickel green. (c) Formation of layers through hydrogen bonding of chains by chdcH_2 molecules.

metal cations and ligands are thus simple links in the monoperiodic coordination polymer formed, which has a zigzag shape and runs along [1–20]. Adjacent chains stack so as to form what can be seen as a pseudo-square lattice parallel to (210), each rhombus-shaped space

defined by the concave part of two chains being occupied by one $chdcH_2$ molecule hydrogen bonded to carboxylate oxygen atoms of the two chains [O···O 2.652(2) and 2.651(2) Å; O–H···O, 169(4)° for both]. Two interlayer parallel-displaced π-stacking interactions are apparent [centroid···centroid distances, 3.8425(13) and 3.7431(12); dihedral angle, 0° for both], which associate the hydrogen-bonded layers into a compact triperiodic assembly (KPI, 0.70). CH···O as well as CH···N hydrogen bonds, the latter involving the acetonitrile molecules, are present as well.

An acidic medium exposed to the light containing both uranyl and nitrate ions is clearly one to be considered oxidizing and this character was exhibited in a further experiment intended to test whether a cationic complex of uranyl ion with $Ni(tpyc)_2$ could be isolated as the iodide. Indeed, the product of the synthesis can be regarded as containing a cationic polymer associated with a simple anion but this anion proved to be the oxidation product triodide, I_3^-. The asymmetric unit in complex **6**, $[UO_2Ni_2(tpyc)_4](I_3)_2$, shown in Figure 6, contains a single uranium atom located on an inversion centre and bound to four monodentate carboxylate groups, thus having a square bipyramidal (compressed octahedral) environment, a relatively rare situation with carboxylate donors,[6c] showing how sensitive the equatorial environment of U^{VI} can be to seemingly rather remote influences [U–O(oxo), 1.776(2) Å; U–O(carboxylato), 2.2749(19) and 2.3019(18) Å]. The uranium centre is thus a 4-c node and the $Ni(tpyc)_2$ unit a simple link in the diperiodic polymer formed, which is parallel to (101) and has the point symbol $\{4^4.6^2\}$ and the **sql** topological type. The U_4 rings are however not square, but oblong and arranged in herringbone fashion. The layers are gently undulating and two disordered I_3^- anions are located within the concave parts, directly above or below the U_4 rings. Only one parallel-displaced π-stacking interaction links ligands pertaining to different layers [centroid···centroid distance, 3.6442(16) Å; dihedral

angle, 3.31(14)°], associated with the usual intra- and interlayer CH···O hydrogen bonds, the packing displaying no very significant free space (KPI, 0.66, with disorder excluded).

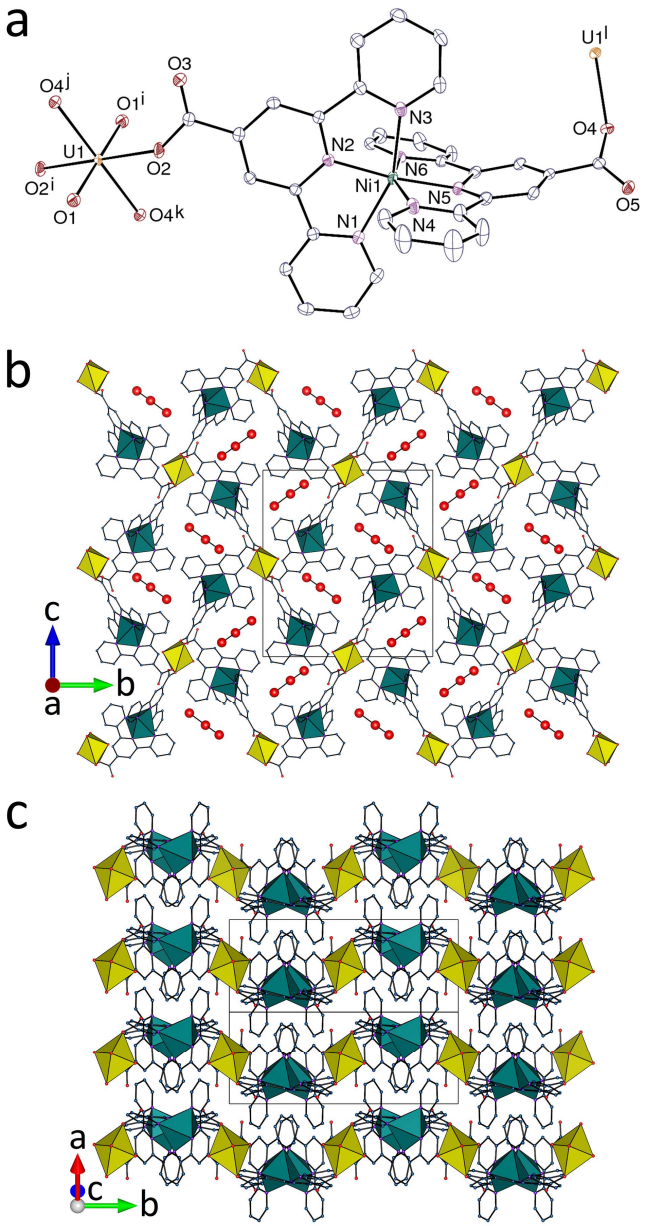

Figure 6. (a) View of complex **6** with displacement ellipsoids drawn at the 50% probability level. Counterions and hydrogen atoms are omitted. Symmetry codes: i = 1 – *x*, 1 – *y*, –*z*; j = 1/2 – *x*, *y* – 1/2, 1/2 – *z*; k = *x* + 1/2, 3/2 – *y*, *z* – 1/2; l = 1/2 – *x*, *y* + 1/2, 1/2 – *z*. (b) View of the diperiodic network with uranium coordination polyhedra yellow and those of nickel green, and with the iodine atoms of the I_3^- counterions shown as red spheres (only one position of the disordered atoms is represented). (c) Packing with layers viewed edge-on and counterions omitted.

Conclusions

We have reported the synthesis and crystal structure of one homoleptic complex of uranyl ion with the tpyc$^-$ ligand and five heterometallic complexes with the "expanded ligand" Ni(tpyc)$_2$. The latter demonstrate the possibility of changing the structure of the complexes, generally cationic, through addition of different structure-directing anions. The use of acetonitrile as the only co-solvent in the syntheses (except that of complex **1**), rather than DMF as in previous work,[4] excludes the possible presence of formate but does not lead, via CH_3CN hydrolysis, to the presence of acetate in the products, even though other anions are readily included. Nitrate ions are always present during the synthesis from uranyl and nickel nitrates, but several additional anions readily displace them from the isolated crystals, either completely in the case of fluoride, iodide, and methanedisulfonate, or partly in the case of trifluoromethanesulfonate and *trans*-1,4-cyclohexanedicarboxylate. It is notable that, as in the previously reported complexes in this family,[4] the denticity of the carboxylate group of the tpyc$^-$ ligand is often low. Overall, among the 20 independent tpyc$^-$ carboxylate groups found in the present structures, 14 are κ^1O-monodentate, 4 are κ^2O,O'-chelating and only 2 are μ_2-κ^1O:κ^1O'-bridging. This is clearly a limitation as to the periodicity of the coordination polymers which can be generated, most being monoperiodic and only one diperiodic. The additional anions used assume different roles. Trifluoromethanesulfonate and triiodide are separate counterions, and they give either a monoperiodic polymer which has the shape of a very large ribbon, or a diperiodic network, respectively. Fluoride, *trans*-1,4-cyclohexanedicarboxylate, and methanedisulfonate are bound to uranium, the first two as bridging ligands and the third as a terminal one, but they do not increase the periodicity of the polymer. Generation of diperiodic networks or, desirably, triperiodic frameworks in this family thus seems to require either non-bonding anions of suitable bulkiness and shape, or

bridging anions able to act as three-coordinated nodes at least. Polycarboxylates may be suitable for the latter approach, and further work in this direction is in progress.

Experimental Section

General: $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (RP Normapur, 99%) and $Ni(NO_3)_2\cdot 6H_2O$ were purchased from Prolabo. 2,2′:6′,2″-Terpyridine-4′-carboxylic acid and *trans*-1,4-cyclohexanedicarboxylic acid ($chdcH_2$) were from Alfa-Aesar and methanedisulfonic acid dipotassium salt ($mdsK_2$) was from Aldrich. Only for compound **6** did the yield allow for elemental analysis, which was performed by MEDAC Ltd. For all syntheses, the mixtures in demineralized water were placed in 10 mL tightly closed glass vessels and heated at 140 °C in a sand bath, under autogenous pressure. The crystals formed directly from the pressurized and heated reaction mixtures and not as a result of subsequent cooling.

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

$[UO_2(tpyc)_2]\cdot 2H_2O$ (1): tpycH (14 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (13 mg, 0.026 mmol), and $CsNO_3$ (20 mg, 0.10 mmol) were dissolved in a mixture of water (0.8 mL), acetonitrile (0.2 mL), and *N,N*-dimethylformamide (0.2 mL), giving a few yellow crystals of complex **1** within two months. As frequently found in solvothermal synthesis involving

different metal cations,[12] the Cs^+ cations, added so as to possibly form a heterometallic complex, are not included in the final compound.

$[(UO_2)_2F_4(H_2O)_2Ni(tpyc)_2]\cdot 2H_2O$ (2): tpycH (14 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (25 mg, 0.05 mmol), $Ni(NO_3)_2\cdot 6H_2O$ (10 mg, 0.03 mmol), and NBu_4BF_4 (20 mg, 0.06 mmol) were dissolved in a mixture of water (0.9 mL) and acetonitrile (0.2 mL), giving a few orange crystals of complex **2** within one week.

$[UO_2(mds)(H_2O)Ni(tpyc)_2]$ (3): tpycH (14 mg, 0.05 mmol), $mdsK_2$ (13 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (25 mg, 0.05 mmol), and $Ni(NO_3)_2\cdot 6H_2O$ (10 mg, 0.03 mmol) were dissolved in a mixture of water (0.8 mL) and acetonitrile (0.2 mL), giving a few pale orange crystals of complex **3** within three days.

$[(UO_2)_4(NO_3)_2(H_2O)_4Ni_5(tpyc)_{10}](CF_3SO_3)_4(NO_3)_2\cdot 7H_2O$ (4): tpycH (14 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (13 mg, 0.026 mmol), $Ni(NO_3)_2\cdot 6H_2O$ (10 mg, 0.03 mmol), and $NBu_4CF_3SO_3$ (24 mg, 0.06 mmol) were dissolved in a mixture of water (0.9 mL) and acetonitrile (0.2 mL), giving a few orange crystals of complex **4** within one week.

$[(UO_2)_2(NO_3)_2(chdc)Ni(tpyc)_2]\cdot chdcH_2\cdot 2CH_3CN$ (5): tpycH (14 mg, 0.05 mmol), $chdcH_2$ (9 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (25 mg, 0.05 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (10 mg, 0.03 mmol) were dissolved in a mixture of water (0.8 mL) and acetonitrile (0.2 mL), giving a few orange crystals of complex **5** within one week.

$[UO_2Ni_2(tpyc)_4](I_3)_2$ (6): tpycH (14 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (25 mg, 0.05 mmol), $Ni(NO_3)_2\cdot 6H_2O$ (10 mg, 0.03 mmol), and NBu_4I (22 mg, 0.06 mmol) were dissolved in a mixture of water (0.9 mL) and acetonitrile (0.2 mL), giving dark orange crystals of complex **6** overnight (4 mg, 18% yield based on I). $C_{64}H_{40}I_6N_{12}Ni_2O_{10}U$ (2253.93): calcd. C 34.11, H 1.79, N 7.46; found C 34.01, H 2.03, N 7.30. The same complex is obtained when NBu_4I is replaced by an equimolar amount of CsI, but in this case it is mixed with crystals of the previously reported complex $[(UO_2)_2Ni_2(tpyc)_4(O)(H_2O)_4](NO_3)_2\cdot 6H_2O$.[4]

Crystallography: The data were collected on a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source (IμS 3.0 Mo) and a PHOTON III area detector, and operated through the APEX3 software.[13] The data were processed with SAINT[14] and absorption effects were corrected for empirically with SADABS.[15] The structures were solved by intrinsic phasing with SHELXT[16] and refined by full-matrix least-squares on F^2 with SHELXL,[17] using the ShelXle interface.[18] All non-hydrogen atoms were refined with anisotropic displacement parameters. The carbon-bound hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3). Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3[19] and the polyhedral representations with VESTA.[20] Special details are as follows.

Complex **1**. The water solvent molecules (one of them disordered over two positions close to one another) were given partial occupancy parameters. The hydrogen atoms were only found for one of them, and refined with restraints on bond lengths and angle, and with an isotropic displacement parameter equal to 1.5 times that of the oxygen atom.

Complex **2**. The fact that fluoride, and not hydroxide, ions are present is indicated by the much too small displacement parameters obtained when oxygen atoms are considered instead of fluorine atoms. The hydrogen atoms bound to oxygen atoms were found and refined with geometrical restraints, and with isotropic displacement parameters either refined (O9, O10) or equal to 1.5 times that of the parent atom (O11, O12).

Complex **3**. The crystals were of low quality and, seemingly due to a phase transition, they deteriorated when cooled. The data collection was thus made at room temperature, with the consequence of large displacement parameters, possibly due also to unresolved disorder. The hydrogen atoms of the water molecule were found and refined with geometrical restraints and an isotropic displacement parameter equal to 1.5 times that of the oxygen atom. Some voids indicate the presence of unresolved solvent molecules, and the SQUEEZE software[21] was used to subtract their contribution to the structure factors. The refined Flack parameter was 0.039(9).

Complex **4**. Crystals of this complex were of rather low quality and the present refinement uses the best data out of three measured sets. The nitrate and triflate counterions are very badly resolved and were refined with restraints on bond lengths and displacement parameters. One CF_3 group is disordered over two positions, but the corresponding disorder on oxygen atoms could not be resolved. The hydrogen atoms bound to oxygen atoms were not found. Some voids indicate the presence of other solvent molecules, and SQUEEZE was used to subtract their contribution to the structure factors. The refined Flack parameter was 0.058(5).

Complex **5**. The hydrogen atoms bound to oxygen atoms were found and refined with no restraint.

Complex **6**. The two terminal atoms of the I_3^- anion are disordered over two positions which were refined with occupancy parameters constrained to sum to unity.

Deposition Numbers 2132894 (for **1**), 2132895 (for **2**), 2132896 (for **3**), 2132897 (for **4**), 2132898 (for **5**), and 2132899 (for **6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Table 1. Crystal data and structure refinement details.

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{32}H_{24}N_6O_8U$	$C_{32}H_{28}F_4N_6NiO_{12}U_2$	$C_{33}H_{24}N_6NiO_{13}S_2U$	$C_{164}H_{122}F_{12}N_{34}Ni_5O_{63}S_4U_4$	$C_{52}H_{48}N_{10}NiO_{22}U_2$	$C_{64}H_{40}I_6N_{12}Ni_2O_{10}U$
M (g mol^{-1})	858.60	1299.37	1073.44	5178.86	1699.77	2253.93
Crystal system	monoclinic	triclinic	orthorhombic	triclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$Pna2_1$	$P1$	$P\bar{1}$	$P2_1/n$
a (Å)	18.5200(6)	8.8236(5)	17.6006(11)	8.5540(5)	12.6601(5)	8.7629(3)
b (Å)	8.5232(3)	8.8330(4)	28.1831(18)	22.0032(12)	14.5132(6)	18.9136(6)
c (Å)	18.8765(6)	24.3817(9)	8.7873(5)	26.9125(15)	17.1818(7)	20.9498(7)
α (°)	90	98.738(2)	90	80.814(2)	82.552(2)	90
β (°)	100.4858(14)	99.782(2)	90	84.814(2)	88.625(2)	98.0363(16)
γ (°)	90	90.187(2)	90	87.378(2)	65.241(2)	90
V (Å^3)	2929.89(17)	1850.09(15)	4358.9(5)	4977.4(5)	2841.0(2)	3438.1(2)
Z	4	2	4	1	2	2
T (K)	100	100	293	100	100	100
Reflections collected	107818	121343	72574	221569	231596	119999
Independent reflections	7575	11292	8254	37810	17282	6536
Observed reflections [$I > 2\sigma(I)$]	6721	10919	7156	33408	16015	5992
R_{int}	0.057	0.038	0.101	0.085	0.048	0.051
Parameters refined	448	542	512	2612	794	449
R_1	0.020	0.018	0.039	0.050	0.019	0.020
wR_2	0.042	0.040	0.087	0.117	0.049	0.042
S	1.042	1.152	1.056	1.036	1.039	1.036
$\Delta\rho_{min}$ (e Å^{-3})	−0.76	−0.86	−1.29	−2.90	−1.13	−1.48
$\Delta\rho_{max}$ (e Å^{-3})	0.78	1.93	0.86	1.55	2.60	1.31

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carboxylic acids / Metal–organic networks / Structure elucidation / Terpyridine ligands / Uranyl cation

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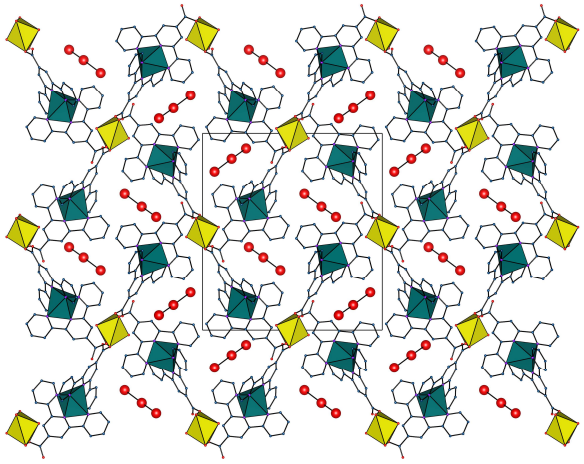
Table of Contents Entry

Varying Structure-Directing Anions in Uranyl Ion Complexes with Ni(2,2′:6′,2″-terpyridine-4′-carboxylate)$_2$

Pierre Thuéry, Jack Harrowfield

Key Topic: Uranyl complexes



Mono- or diperiodic coordination polymers with different geometries can be generated by reaction of uranyl and nickel(II) ions with 2,2′:6′,2″-terpyridine-4′-carboxylate through variation of the accompanying anions.