Uranyl ion complexes with 2,2':6',2"-terpyridine-4'-carboxylate. Interpenetration of networks involving "expanded ligands"

Pierre Thuéry, Jack Harrowfield

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Interpenetration of networks involving "expanded ligands"†

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

2,2':6',2"-Terpyridine-4'-carboxylic acid (tpycH) has been used as a ligand in the synthesis of four uranyl ion complexes under solvo-hydrothermal conditions. The homometallic complex $[(UO_2)_2(tpyc)(HCOO)(OH)_2]$ (**1**) contains additional hydroxide and formate anions generated in situ and it crystallizes as a monoperiodic coordination polymer in which uranyl cations are bound to both the carboxylate group and the terpyridine N_3 site. Addition of Pb^{II} gives the heterometallic complex $[UO_2Pb(tpyc)(HCOO)_2(OH)(H_2O)_2]$ (**2**), in which uranyl is bound to the carboxylate group while lead(II) occupies the N_3 site, further hydroxide- and formate-bridging resulting in a diperiodic arrangement. Both complexes $[UO_2Ni(tpyc)_2(OH)(H_2O)]\cdot NO_3\cdot 1.5H_2O$ (**3**) and $[(UO_2)_2Ni_2(tpyc)_4(O)(H_2O)_4]\cdot(NO_3)_2\cdot 6H_2O$ (**4**) contain the neutral, octahedral $Ni(tpyc)_2$ "expanded ligand" unit, the uranyl cations being bound to the divergent carboxylate groups and to bridging hydroxo or oxo groups. Complex **3** crystallizes as a heavily corrugated diperiodic assembly in which hydroxo-bridged dinuclear secondary building units are the nodes of a network of **sql** topology. Diperiodic polymers with the same topology but a different shape are formed in **4**, which are involved in twofold parallel interpenetration.

Introduction

Heterofunctional, polytopic ligands displaying coordination sites of different hardness are an obvious choice for the design of heterometallic complexes involving metal cations with distinct chemical affinities. In the particular case in which the uranyl cation is one of the metal ions considered, its hardness and preference for oxygen donors are an asset since it will preferentially coordinate to carboxylate groups, for example, leaving softer coordination sites, such as those involving nitrogen donors, available for softer d-block metal cations. The first examples of such behaviour exploited ligands such as quinolinate,[1] 3,5-pyrazoledicarboxylate,[2] or 4,5-imidazoledicarboxylate,[3] many other cases of heterometallic complexes having since been reported in the ever-growing field of uranyl–organic coordination polymers and frameworks.[4] Geometrical differences between the *O*- and *N*-coordination sites were also taken advantage of in the synthesis of uranyl–lanthanide heterometallic complexes with 1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetate (deprotonated DOTA).[5]

As a divergently ditopic but unsymmetrical ligand, 2,2′:6′,2″-terpyridine-4′-carboxylic acid (tpycH, Scheme1) has obvious appeal as a complexant for the formation of coordination polymers[6] and oligomers[7] but has also been of interest as a terpyridine-type ligand with electronic properties usefully modified by the carboxylate substituent (and its derivatives)[8] or as one giving *N*-bound complexes where the carboxylate group can be used as an anchoring unit on supports.[9] An elegant extension of its applications as a complexant has been its use to form "expanded" dicarboxylate ligand species[10] where an $[M(tpyc)_2]^{(n-2)+}$ (n = charge on M) complex has the metal bound only to the nitrogen donors. Such a species can be regarded as zwitterionic and where $n = 2$ provides a divergent dicarboxylate ligand of overall neutral charge. This raises the prospect of their forming coordination polymers of cationic form due to the charge carried by bridging, carboxylate-bound metal ions.
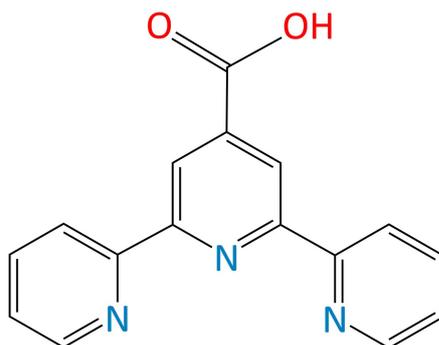
Scheme 1 2,2':6',2"-Terpyridine-4'-carboxylic acid (tpycH).

Carboxylate ligands are of major significance in uranyl ion coordination chemistry[4] but all interest, including our own, in uranyl polycarboxylate coordination polymers has been focussed on formally neutral or anionic species. Structures of the anionic polymers have proven to be fruitfully sensitive to the nature of their associated countercation, so that analogous sensitivity to counteranions might be expected in the case of cationic species. Although some examples of lanthanide ion complexes with tpyc$^-$ have been reported,[6] there has been no case of a characterized actinide complex reported up to now. Here, we report our preliminary structural investigations of the complexation of uranyl ion by tpyc$^-$ which establish that this ligand should indeed give rise to some novel solid state uranyl chemistry. Four uranyl ion complexes, either homo- or heterometallic, the latter including either Pb^{II} or Ni^{II} cations, have been crystallographically characterized. In the two complexes with Ni^{II} cations, the Ni(tpyc)$_2$ moiety plays the role of an "expanded ligand" for the carboxylate-bound uranyl cation. These four complexes crystallize as mono- or diperiodic coordination polymers, and one of the latter displays twofold parallel interpenetration, being thus an addition to the family of entangled uranyl–organic species.[11]

Experimental

Synthesis

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

$[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (RP Normapur, 99%), $Ni(NO_3)_2\cdot 6H_2O$ and $Pb(NO_3)_2$ were purchased from Prolabo, $Dy(NO_3)_3\cdot xH_2O$ was from Aldrich, and 2,2′:6′,2″-terpyridine-4′-carboxylic acid was from Alfa-Aesar. Elemental analyses were performed by MEDAC Ltd. For all syntheses, the mixtures of demineralized water and organic cosolvent were placed in 10 mL tightly closed glass vessels and heated at 140 °C in a sand bath, under autogenous pressure.

$[(UO_2)_2(tpyc)(HCOO)(OH)_2]$ (1). tpycH (14 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (25 mg, 0.05 mmol), and $Dy(NO_3)_3\cdot xH_2O$ (25 mg, 0.07 mmol on an anhydrous basis), were dissolved in a mixture of water (0.8 mL) and N,N-dimethylformamide (DMF) (0.2 mL). A few yellow crystals of complex **1** were obtained overnight, the yield remaining very low even on prolonged heating.

$[UO_2Pb(tpyc)(HCOO)_2(OH)(H_2O)_2]$ (2). tpycH (14 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (25 mg, 0.05 mmol), and $Pb(NO_3)_2$ (17 mg, 0.05 mmol), were dissolved in a mixture of water (0.8 mL) and DMF (0.2 mL). Yellow crystals of complex **2** were obtained within one week (13 mg, 29% yield). Anal. Calcd for $C_{18}H_{17}N_3O_{11}PbU$: C, 24.11; H, 1.91; N, 4.69. Found: C, 24.82; H, 1.73; N, 4.81%.

$[UO_2Ni(tpyc)_2(OH)(H_2O)]\cdot NO_3\cdot 1.5H_2O$ (3). tpycH (14 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (15 mg, 0.03 mmol), $Ni(NO_3)_2\cdot 6H_2O$ (10 mg, 0.03 mmol), and 2,2′-bipyridine (16 mg, 0.10 mmol) were dissolved in a mixture of water (0.8 mL) and acetonitrile

(0.2 mL). Yellow-orange crystals of complex **3** were obtained in low yield within one week (~3 mg, 12% yield based on the acid). Elemental analysis results indicate the presence of about 8 water molecules in addition to those found in the crystal structure, in agreement with the presence of voids in the latter (see below). Anal. Calcd for $C_{32}H_{26}N_7NiO_{12.5}U$ + 8 H_2O: C, 33.44; H, 3.68; N, 8.53. Found: C, 33.40; H, 3.04; N, 8.51%.

[(UO₂)₂Ni₂(tpyc)₄(O)(H₂O)₄]·(NO₃)₂·6H₂O (4). tpycH (14 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot4H_2O$ (15 mg, 0.03 mmol), and $Ni(NO_3)_2\cdot6H_2O$ (10 mg, 0.03 mmol), were dissolved in a mixture of water (0.8 mL) and acetonitrile (0.2 mL). Dark yellow crystals of complex **4** were obtained within two weeks (11 mg, 42% yield based on the acid). Elemental analysis results indicate the presence of about 2 water molecules in addition to those found in the crystal structure, in agreement with the presence of voids in the latter (see below). Anal. Calcd for $C_{64}H_{60}N_{14}Ni_2O_{29}U_2$ + 2 H_2O: C, 36.28; H, 3.04; N, 9.26. Found: C, 35.92; H, 2.72; N, 9.81%.

Crystallography

Data collections were performed on a Bruker D8 Quest diffractometer using an Incoatec Microfocus Source (IμS 3.0 Mo) and a PHOTON III area detector, and operated with APEX3.[12] The data were processed with SAINT,[13] and empirical absorption corrections were made with SADABS.[14] The structures were solved by intrinsic phasing with SHELXT,[15] and refined by full-matrix least-squares on F^2 with SHELXL,[16] using the ShelXle interface.[17] When possible, hydrogen atoms bound to oxygen atoms were retrieved from residual electron density maps and they were refined with restraints; some of them were not found in complexes **2**–**4**. The other hydrogen atoms were introduced at calculated positions and treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Some water molecules in **2** and **3** were given occupancy parameters of 0.5 in order to retain acceptable displacement parameters. The SQUEEZE[18] software was used to subtract the contribution of

disordered solvent molecules to the structure factors for compounds **3** and **4**. The number of electrons found in the voids in the structure of **3** amounts to 77 per formula unit, which matches rather well the 80 corresponding to the eight water molecules deduced from elemental analysis (see above). In **4**, the extra 40 electrons per formula unit are in excess of those of the two water molecules from elemental analysis, possibly indicating loss of water during isolation of the sample. The Flack parameter for **4** was 0.027(5). Crystal data and structure refinement parameters are given in Table 1. Drawings were made with ORTEP-3[19] and VESTA,[20] and topological analyses with ToposPro.[21]

Table 1 Crystal data and structure refinement details

	1	2	3	4
Chemical formula	$C_{17}H_{13}N_3O_{10}U_2$	$C_{18}H_{17}N_3O_{11}PbU$	$C_{32}H_{26}N_7NiO_{12.5}U$	$C_{64}H_{60}N_{14}Ni_2O_{29}U_2$
M/g mol^{-1}	895.36	896.57	1005.34	2082.74
Crystal system	triclinic	triclinic	monoclinic	tetragonal
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P4_1$
a/Å	8.1750(4)	10.4295(5)	8.7682(2)	18.5799(5)
b/Å	11.2250(5)	10.5028(6)	16.9333(5)	18.5799(5)
c/Å	12.1741(5)	11.5621(6)	28.1757(7)	42.3462(13)
α/°	76.648(2)	63.375(2)	90	90
β/°	86.085(2)	74.261(2)	98.6612(13)	90
γ/°	70.908(2)	80.690(2)	90	90
V/Å^3	1027.13(8)	1088.56(10)	4135.67(19)	14618.4(9)
Z	2	2	4	8
T/K	293	100	100	100
Reflections collected	67332	74394	210879	318064
Independent reflections	3890	4133	10673	29878
Observed reflections [$I > 2\sigma(I)$]	3201	3998	9652	28728
R_{int}	0.067	0.051	0.087	0.070
Parameters refined	297	332	496	2012
R_1	0.025	0.020	0.034	0.036
wR_2	0.056	0.047	0.076	0.080
S	1.157	1.192	1.093	1.159
$\Delta\rho_{min}$/e Å^{-3}	−1.10	−1.05	−1.71	−1.09
$\Delta\rho_{max}$/e Å^{-3}	1.83	0.97	2.26	2.10

Results and discussion

Although the structures of the crystals obtained in the present work, as discussed ahead, are certainly informative in regard to how tpyc⁻ may interact with uranyl ion in the presence and absence of other metal ions, these results must be regarded as preliminary for several reasons,

the most obvious perhaps being that of the relation between the characterized crystals isolated and the conditions of their synthesis. All four complexes **1**–**4** were synthesized under solvo-hydrothermal conditions, the organic cosolvent being either *N,N*-dimethylformamide (DMF, **1** and **2**) or acetonitrile (**3** and **4**). Two of the syntheses (giving complexes **1** and **2**) were designed with the objective of obtaining heterometallic coordination polymers and two others (giving complexes **3** and **4**) with the objective of exploring "expanded ligand" effects. Complex **1** crystallizes without incorporation of the added Dy^{III} cation, though this is not to say that the lanthanide has no influence on the nature of **1**, since its ability to compete with uranyl ion for tpyc$^-$, its likely assistance as a catalyst in the hydrolysis of DMF to give the formate ligand found in **1** and the acidity of the [Dy(H$_2$O)$_8$]$^{3+}$ cation, for example, are all factors which could influence the solubility of **1**. Thus, the coordination chemistry of uranyl ion alone with tpyc$^-$ in DMF and in solvents which do not undergo hydrolytic scission remains to be established. Complex **2** is a true heterometallic polymer but, like complex **1**, incorporates both formate and hydroxo ligands, features which are difficult to predict, though formate binding could be excluded by the use of a cosolvent such as *N*-methyl-2-pyrrolidone (NMP), which is resistant to hydrolysis, and the presence of hydroxide may simply be a reflection of the basicity of tpyc$^-$ and could possibly be eliminated by the inclusion of some HNO$_3$ in the reaction mixture, although then in competition with a reduction in yield of any species binding the tpyc$^-$ anion. However, no exploitable crystals have been obtained up to now along these lines. Complexes **3** and **4** contain neither of the products of acetonitrile hydrolysis, nor does complex **3** contain the 2,2′-bipyridine included in the reaction mixture, although the presence of this component gives rise to a different crystalline product, somewhat surprisingly, given the basicity of 2,2′-bipyridine, containing the weaker base hydroxide rather than the oxide found in complex **4**. Both do contain the anticipated "expanded" dicarboxylate Ni(tpyc)$_2$ and nitrate counteranions

but these aspects, coupled to the quite different stoichiometry of the two complexes, indicate again that there are factors requiring further investigation.

[(UO$_2$)$_2$(tpyc)(HCOO)(OH)$_2$] (**1**) is the only homometallic complex in the series and, as expected, both oxygen and nitrogen donors are coordinated to uranyl ions. The structure of **1** provides confirmation that the ligand tpyc$^-$ can act as a bridge between uranyl ions and thus give rise to coordination polymers. The composition defined by the structure is not the simplest that might have been anticipated (even ignoring the absence of Dy^{III}), as the polymer is a neutral species due to the presence of the additional anionic ligands hydroxide and formate, the latter presumably arising from the hydrolysis of DMF under the reaction conditions, the former being of less certain origin. The two crystallographically independent uranyl ions are in different environments, with U1 bound to one monodentate carboxylate group of tpyc$^-$, one oxygen atom of the bridging formate, and three hydroxide groups, while U2 is bound to one formate, one hydroxide, and the three nitrogen atoms of another tpyc$^-$ anion (Fig. 1), the metal–ligand bond lengths being unexceptional [U–O(oxo), 1.767(5)–1.780(5) Å; U–O(carboxylato), 2.355(6)–2.457(6) Å; U–O(hydroxido), 2.244(5)–2.421(5) Å; U–N, 2.552(6)–2.601(6) Å]. The terpyridine (terpy) moiety is slightly domed, with a dihedral angle of 22.2(4)° between the two lateral aromatic rings, and U2 is displaced by 0.674(9) Å from the N$_3$ plane. As a result, U2 and the five equatorially coordinated atoms define a mean plane with a large root-mean-square (rms) deviation of 0.21 Å; however, U2 and the four atoms O8, O9, N1 and N3 define a mean plane with an rms of 0.018 Å, atom N2 (which is the most distant from U2) being displaced from this plane by 0.730(9) Å and the terpy moiety being markedly inclined with respect to the uranyl axis as a consequence. Such a distortion of the uranium equatorial donor atoms array is found in most uranyl ion complexes with terpy derivatives reported in the Cambridge Structural
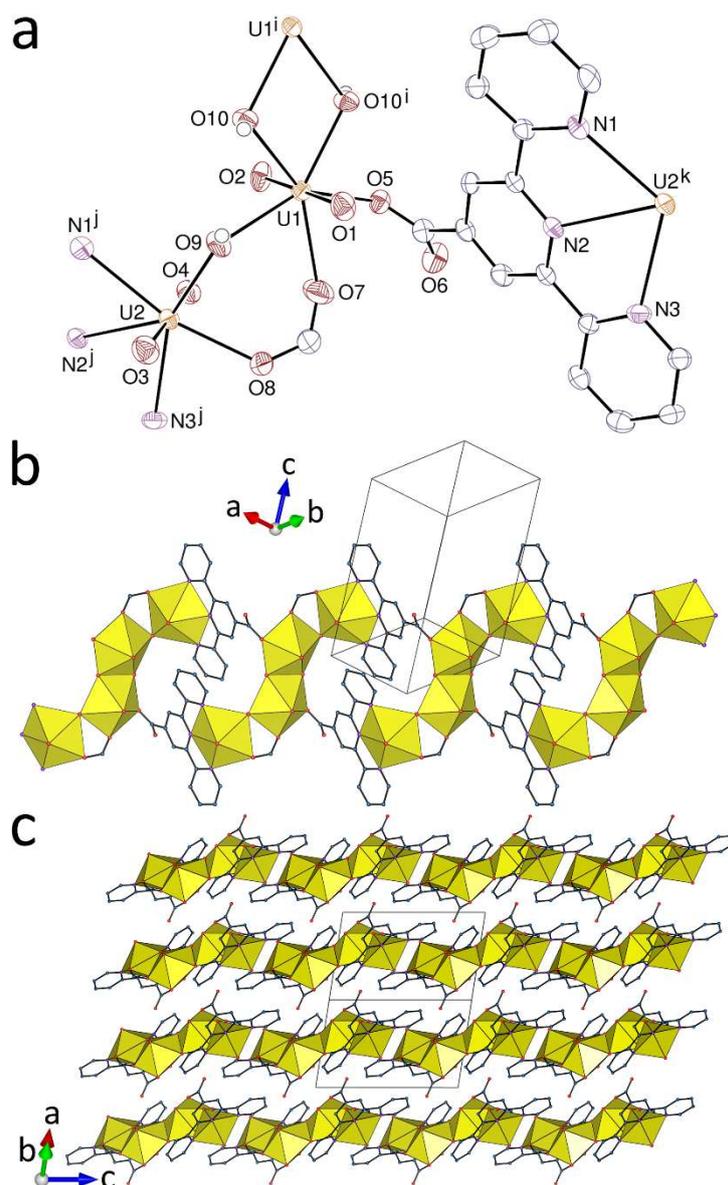
Fig. 1 (a) View of complex **1** with displacement ellipsoids shown at the 50% probability level. Symmetry codes: i = 2 − x, 1 − y, 2 − z; j = x + 1, y − 1, z; k = x − 1, y + 1, z. (b) View of the monoperiodic assembly showing uranium coordination polyhedra. (c) Packing with chains viewed end-on. Hydrogen atoms are omitted in all views.

Database (CSD, Version 5.42; 56 hits).[22] The carboxylate group is slightly rotated with respect to the attached aromatic ring, with a dihedral angle of 26.5(7)°. The two hydroxide anions are bridging, with U–O–U angles of 130.7(2) and 111.5(2)° for O9 and O10, respectively. Both uranium atoms are in pentagonal-bipyramidal environments, and since U1 shares a common edge with its bis-hydroxide-bridged image by inversion and only one vertex with U2, an S-

shaped tetranuclear secondary building unit (SBU) is formed (Fig. 1b), which does not pertain to one of the geometrical types usually found.[4c] The neutral coordination polymer formed is monoperiodic and parallel to [1$\bar{1}$0], each SBU being connected to each of its two neighbours by two tpyc$^-$ ligands, resulting in centrosymmetric hexa-uranacyclic rings. The structure can be considered as layered, with sheets parallel to (110) being composed of side-by-side monoperiodic units. The hydroxide ions are hydrogen bonded to the same uncomplexed carboxylate oxygen atom (O6) pertaining to an adjacent chain along the [100] axis [O···O distances, 2.802(7) and 2.901(8) Å; O–H···O angles, 155(8) and 148(9)°], thus forming a ring with the graph set descriptor[23] $R_2^1(6)$. Several parallel-displaced π-stacking interactions may associate terpy moieties pertaining to the same chain or to adjacent chains [centroid···centroid distances, 3.572(5)–4.295(4) Å; dihedral angles, 0–22.2(4)°]. Analysis of the Hirshfeld surface (HS)[24] with CrystalExplorer (ver. 3.1)[25] indicates however that only those between adjacent chains may involve energies greater than those of dispersion, and also that CH···O hydrogen bonds[26] are present, as usual in such complexes. The packing displays no significant free space and has a Kitaigorodski packing index (KPI, evaluated with PLATON[27]) of 0.71.

Addition of lead(II) cations gives the complex [UO$_2$Pb(tpyc)(HCOO)$_2$(OH)(H$_2$O)$_2$] (**2**) which, as complex **1**, also includes formate and hydroxide anions (Fig. 2). The structure of **2** is closely related to that of **1**, the most obvious difference being the replacement of U2 by Pb, so that it is now two Pb(tpyc) units which serve to bridge hydroxo-uranyl dimers and thus create a heterometallic polymer. Pb^{II} occupies here the N$_3$ coordination site, while uranyl is bound to one carboxylate oxygen atom from tpyc$^-$. The uranium centre is also bound to two formate anions, both bridging U and Pb atoms, and to two hydroxide anions related by inversion, and its environment is thus pentagonal-bipyramidal, the two cations in the dinuclear SBU sharing a
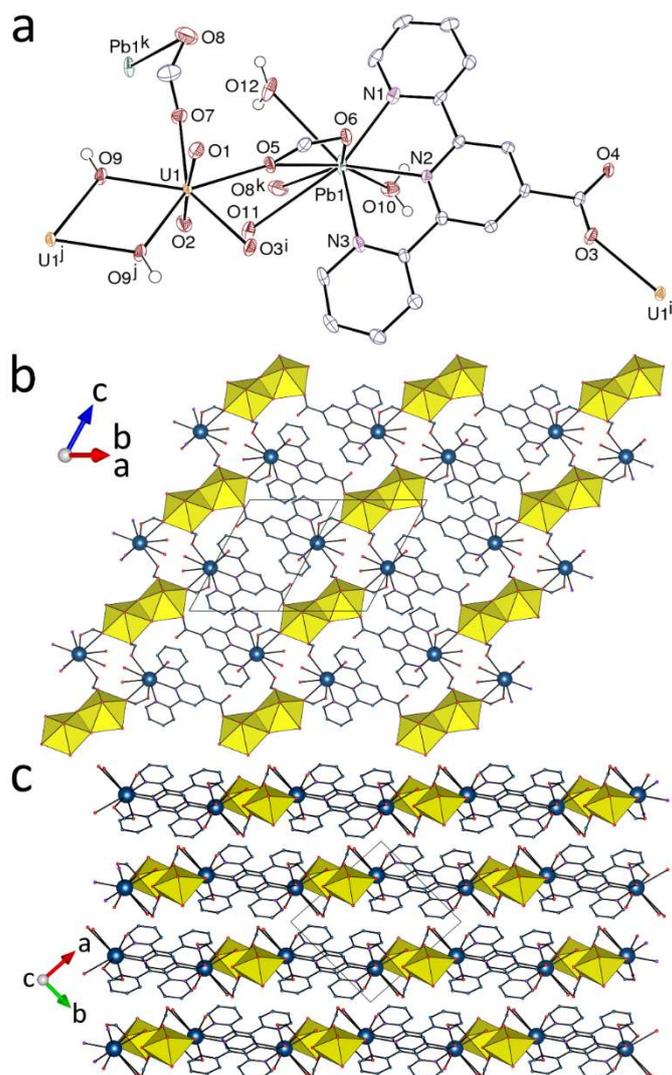
Fig. 2 (a) View of compound **2** with displacement ellipsoids shown at the 50% probability level and carbon-bound hydrogen atoms omitted. Symmetry codes: i = –x, 1 – y, 2 – z; j = 1 – x, 2 – y, 2 – z; k = 1 – x, 2 – y, 1 – z. View of the diperiodic assembly with uranium coordination polyhedra yellow and lead atoms shown as blue spheres. (c) Packing with layers viewed edge-on.

common edge [U–O(oxo), 1.794(3) and 1.802(3) Å; U–O(carboxylato), 2.405(3)–2.430(3) Å; U–O(hydroxido), 2.301(3) and 2.327(3) Å]. The U–O–U angle around the hydroxide donor is 113.69(13)°. In addition to the three nitrogen atoms, the lead atom is bound to one asymmetrically chelating formate anion, one other formate donor, and three water molecules, two of them being however affected with half-occupancy, so that the coordination number is somewhat uncertain, but probably of eight [Pb–O(carboxylato), 2.451(3)–3.397(5) Å; Pb–

O(aquo), 2.650(4)–3.339(7) Å; Pb–N, 2.498(4)–2.528(4) Å]. Some of the Pb–O bond lengths are however rather long and their consideration as indicative of true bonds may be questionable,[28] but the HS provides indications of weak interactions there, particularly with the formate atom O8. But for the two disordered water molecules, the Pb^{II} environment would be hemidirected.[29] The terpy moiety is here close to planarity, with an rms deviation of 0.037 Å, and the lead centre is displaced by 0.137(2) Å from the mean plane. The carboxylate group is also close to the mean plane of the attached ring, with a dihedral angle of 13.7(7)°. The coordination polymer formed is diperiodic and parallel to ($1\bar{1}0$), but is reduced to monoperiodic and parallel to [110] if the longest Pb–O contact, with atom O8, is not considered as true bonding. The hydroxo-bridges between equivalent uranyl centres serve to link diurana-diplumbacycles, so that this polymer chain subunit consists of alternating 4- and 18-membered rings. The hydroxide anion makes an intralayer (or intrachain) hydrogen bond with the uncomplexed carboxylate atom O4 [O···O distance, 2.809(4) Å; O–H···O angle, 152(6)°], and the water ligands are hydrogen bonded to carboxylate and water acceptors. One intra- and one interlayer parallel-displaced π-stacking interactions may associate terpy moieties [centroid···centroid distances, 3.967(3) and 3.757(3) Å; dihedral angles, 0 and 1.8(2)°], and one interlayer CH···π interaction possibly links one formate hydrogen atom to one terpy ring [H···centroid distance, 2.67 Å; C–H···centroid angle, 164°]. In particular, the two terpyridine units in each of the larger rings lie close to parallel and strongly overlap in projection, the HS showing reciprocal C···C interactions beyond dispersion. This enhanced intra-annular interaction may be due to both the ring size being smaller than that in **1** and to the much closer to truly planar conformation of the Pb^{II}-bound terpy unit. The resulting packing is quite compact (KPI 0.74).

Both complexes $[UO_2Ni(tpyc)_2(OH)(H_2O)]\cdot NO_3\cdot 1.5H_2O$ (**3**) and $[(UO_2)_2Ni_2(tpyc)_4(O)(H_2O)_4]\cdot(NO_3)_2\cdot 6H_2O$ (**4**) contain Ni^{II} cations bound to the N_3 sites of two

tpyc⁻ ligands, thus making up the neutral Ni(tpyc)$_2$ "expanded ligand". The syntheses of these two complexes differ only by the presence of 2,2′-bipyridine in the case of **3**, which is not present in the isolated complex but had sufficient influence, possibly as a basic agent, for the two compounds to have strikingly different structures. The unique Ni^{II} cation in **3** and the four independent Ni^{II} cations in **4** are in a distorted octahedral environment [Ni–N, 1.966(9)–2.126(9) Å], and the terpy moieties are close to planarity (rms deviations 0.060–0.139 Å) and make dihedral angles of 76.48(6)–89.41(3)° with one another in each unit, the geometry being thus similar to that in the structure of [Ni(tpyc)$_2$]·4H$_2$O previously reported.[6]

The unique uranyl cation in **3** is bound to two carboxylate oxygen atoms from two different tpyc⁻ ligands, two hydroxide anions related by inversion, and one water molecule, the uranium atom environment being here also pentagonal-bipyramidal [U–O(oxo), 1.778(3) and 1.787(3) Å; U–O(carboxylato), 2.348(3) and 2.353(3) Å; U–O(hydroxido), 2.324(3) and 2.326(3) Å; U–O(aquo), 2.478(4) Å] (Fig. 3). The two carboxylate groups are very differently tilted with respect to the aromatic rings, by 2.4(3) and 37.5(3)°. A corrugated diperiodic network parallel to (101) is formed, which can be viewed as having the **sql** (square lattice) topological type if the dinuclear SBUs are considered as single nodes. The basic unit of the polymer is a 60-membered hexa-urana-tetra-nickelacycle, the dimeric uranyl units serving as points of fusion of the rings. A major feature of the structure is the "terpyridine embrace" which however, from consideration of the HS, involves largely dispersive interactions, with only one C···H contact at 2.79 Å exceeding this limit; the zig-zag profile of the polymer sheets when viewed down [10$\bar{1}$] offers a means of optimizing the embraces of the neutral complex units. Only one, interlayer parallel-displaced π-stacking interaction may be present [centroid···centroid distance,
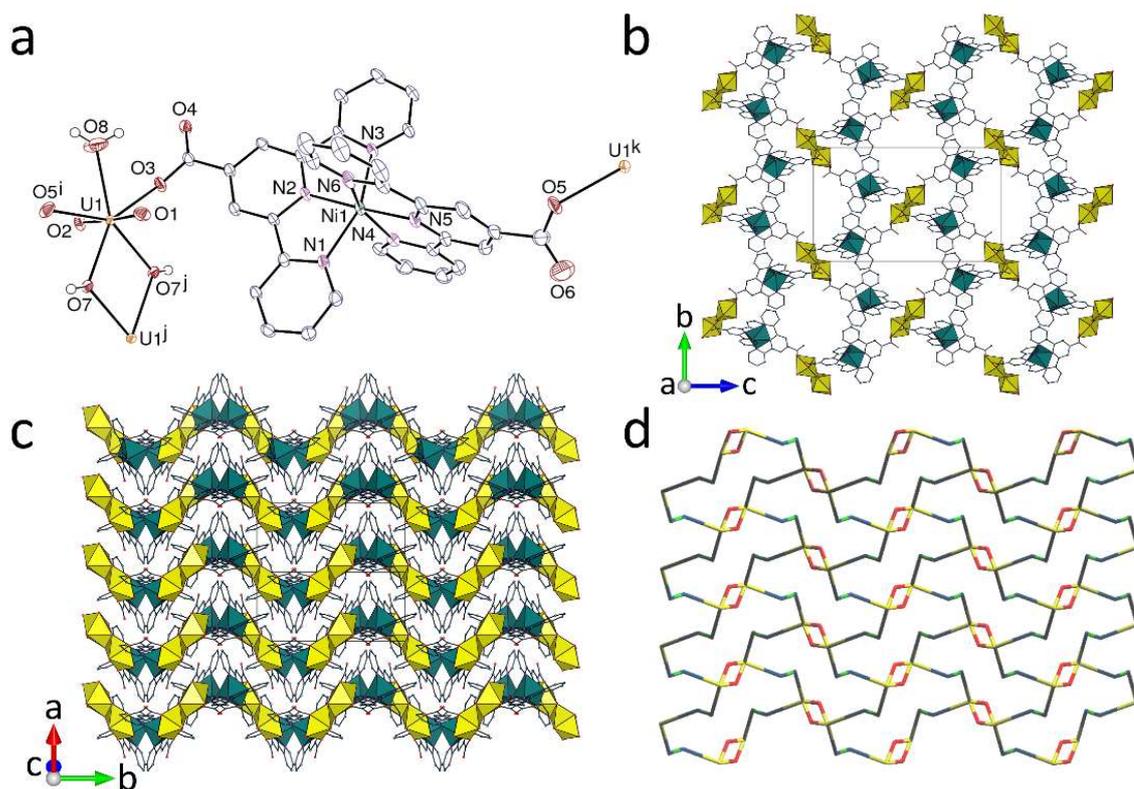
Fig. 3 (a) View of compound **3** with displacement ellipsoids shown at the 50% probability level. Counterions, solvent molecules and carbon-bound hydrogen atoms are omitted. Symmetry codes: i = $x + 1/2$, $1/2 - y$, $z - 1/2$; j = $1 - x$, $1 - y$, $1 - z$; k = $x - 1/2$, $1/2 - y$, $z + 1/2$. (b) The diperiodic assembly with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with layers viewed edge-on. (d) Simplified representation of the network (yellow, uranium; red, oxygen; green, nickel; dark blue, tpyc⁻).

3.718(2) Å; dihedral angle, 6.9(2)°; slippage 1.18 Å], but several CH···π interactions are apparent [H···centroid distances, 2.84–2.97 Å; C–H···centroid angles, 124–145°]. The hydroxide anion (O7) forms a hydrogen bond with the uncomplexed carboxylate oxygen atom (O4) pertaining to a neighbouring sheet, while the coordinated water molecule (O8) is bound to one nitrate oxygen atom and one solvent water molecule [O···O distances, 2.751(7)–2.957(9) Å; O–H···O angles, 139–170°]. The packing displays voids occupied by disordered solvent molecules (see Experimental), leading to a KPI of 0.58 only.

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The structure of complex **4** differs significantly from that of **3**, although there are some common features. Complex **4** crystallizes in the chiral space group $P4_1$, and the four independent uranyl cations are each bound to two carboxylate oxygen atoms from two different ligands, one bridging oxo group, and two water molecules, the uranium environment being here also pentagonal-bipyramidal [U–O(oxo), 1.758(8)–1.786(8) Å; U–O(carboxylato), 2.330(8)–2.394(7) Å; U–O(bridging oxo), 2.280(7)–2.317(7) Å; U–O(aquo), 2.417(8)–2.519(9) Å] (Fig. 4). The U–O–U angles around the bridging oxo groups are 131.4(3) and 130.1(3)°. The dihedral angles between the carboxylate groups and the attached aromatic rings are in the range of 2.1(7)–11.4(9)°, all tpyc⁻ ligands being thus close to planarity. The four inequivalent "expanded ligand" Ni(tpyc)₂ bind to dimeric uranyl units to form two separate tetranuclear units, each of which generates a uninodal diperiodic coordination polymer parallel to (001), which has the $\{6^3\}$ point symbol and the **hcb** topological type, with uranium atoms as 3-coordinated (3-c) nodes, four long edges corresponding to the "expanded ligands" and two very short edges defined by the oxo bridges. Here also, considering the dinuclear uranyl subunits as single nodes reduces the topological type to **sql**, which better describes the general shape involving rings which appear to be nearly square when projected down [001] (the layers are in fact heavily corrugated, with a thickness of ~13 Å). These rings are again 60-membered hexa-urana-tetra-nickelacycle units, and they now have approximate C_2 symmetry, with the axis containing both bridging oxo anions, and not inversion symmetry as in **3**, the assembly being chiral. The two inequivalent diperiodic networks are associated through twofold, parallel 2D + 2D → 2D interpenetration (Fig. 5). Parallel entanglement is allowed by the corrugation of the sheets and the large size of the rings, with a distance of ~17 Å between opposite coordinated water molecules and ~11 Å between opposite terpy moieties, these values being however moderate when compared to those found in other uranyl-containing interpenetrated or polycatenated
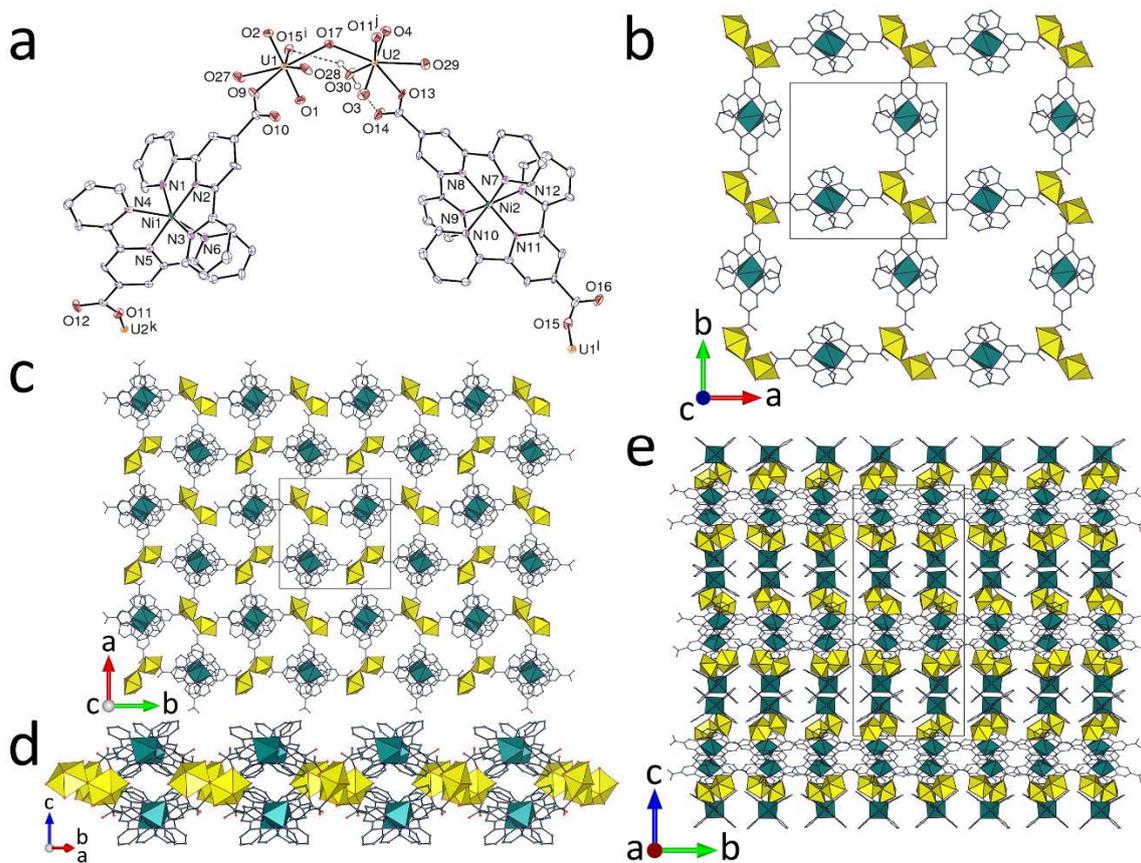
Fig. 4 (a) View of one of the two independent units in compound **4** with displacement ellipsoids shown at the 50% probability level. Counterions, solvent molecules and carbon-bound hydrogen atoms are omitted, and hydrogen bonds are shown as dashed lines. Symmetry codes: i = $x - 1$, y, z; j = x, $y + 1$, z; k = x, $y - 1$, z; l = $x + 1$, y, z. (b) View of a single diperiodic coordination polymer with uranium coordination polyhedra yellow and those of nickel green. (c) and (d) Two views of the interpenetrated diperiodic assembly, side-on or edge-on. (d) Packing with sheets viewed edge-on.
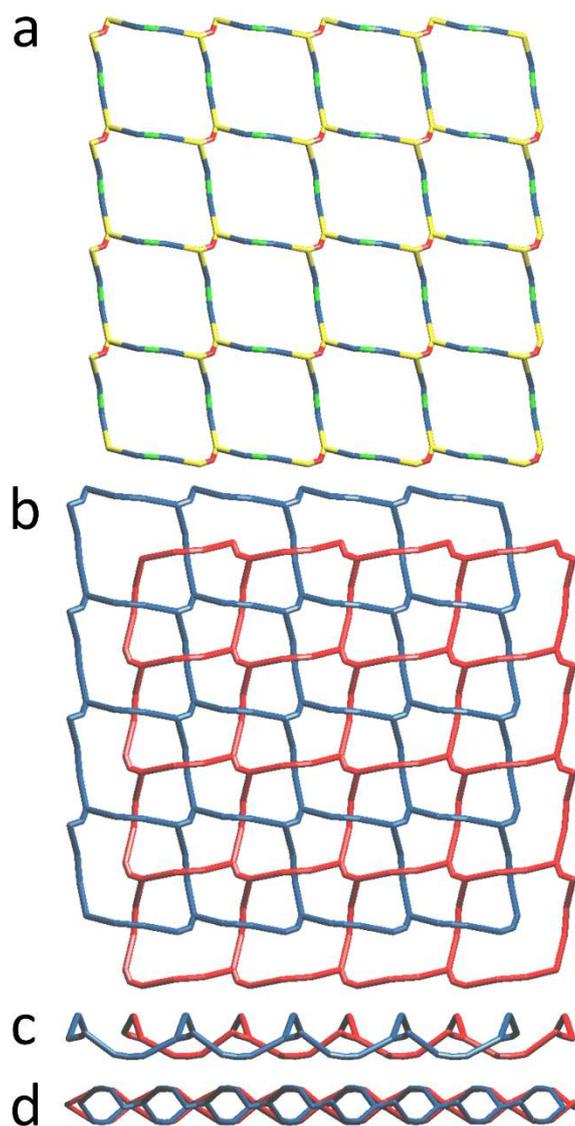
Fig. 5 Simplified view of one diperiodic network in compound **4** (yellow, uranium; red, oxygen; green, nickel; dark blue, tpyc⁻) (a). Twofold interpenetration of diperiodic networks viewed down [001] (b), [010] (c), and [1$\bar{1}$0] (d).

diperiodic assemblies[11,30] due to the very small length of the oxo bridges. Uranium atoms separated by the "expanded ligand" are at distances of ~16 Å, which provides ample scope for the synthesis of entangled systems. Threefold parallel interpenetration of **hcb** networks has been found in a uranyl complex with 1,4-cyclohexanedicarboxylate in which the rings have dimensions comparable to those in **4** (~22 × 12 Å),[31] but the Ni(tpyc)$_2$ ligands here are much too cumbersome to allow for more than twofold entanglement. Only one possible parallel-

displaced π-stacking interaction links terpy moieties from different interpenetrated sheets [centroid···centroid distance, 4.114(6) Å; dihedral angle, 3.1(6)°; slippage 2.28 Å], and there is no CH···π interaction. Although only some of their hydrogen atoms were found, the coordinated water molecules do not appear to form interlayer links. The packing contains some voids, in agreement with the presence of unresolved solvent molecules (see Experimental), and the KPI is 0.68.

Conclusions

The four uranyl ion complexes described herein show that the ligand 2,2′:6′,2″-terpyridine-4′-carboxylate can clearly function as a heterotopic, divergent ligand capable of forming coordination polymers with the uranyl ion. The latter appears to be readily dislodged from the N_3 coordination site by metal ions such as Pb^{II} and Ni^{II}, thus rendering this ligand well suited to the synthesis of heterometallic species. Where this competition involves 1:1 complexation, as with Pb^{II} in the case of complex **2** presently, this could be expected to block polymerization reactions but the presence of adventitious formate in the reaction mixture providing this complex enables linkage of Pb and U centres and thus the retention of a polymeric form. Where a 1:2 complex can form, as seen with Ni^{II}, this has the more interesting consequence of generating a divergent, ditopic, "expanded" dicarboxylate ligand that, depending on subtle influences yet to be fully defined, can give cationic uranyl ion-containing coordination polymers of quite different nature but of forms in which embracing interactions of the Ni(tpyc)$_2$ units are prominent. The commercial availability of uranyl nitrate as a reactant in syntheses as developed in the present work renders it somewhat inconvenient to contemplate variations in the counteranion for uranyl-M(tpyc)$_n$ complexes but it must be presumed that nitrate does to some extent determine the structures of complexes **3** and **4**, though perhaps not as much as does formate in the cases of complexes **1** and **2**. A notable point in all these complexes is the rather

unusual monodentate coordination mode of the carboxylate group, a somewhat unfortunate trend since, although this mode is topologically equivalent to the very common $\kappa^2 O,O'$-chelating mode, it limits the ligand connectivity with respect to the equally common bridging bidentate mode. One of the complexes containing the Ni(tpyc)$_2$ "expanded ligand" displays twofold, parallel interpenetration of diperiodic networks, providing a novel example of an entangled uranyl-based species, a member of a diverse and rapidly growing family of complexes, and also suggesting that other original arrangements may be obtained with this versatile ligand upon modification of the synthesis conditions.

Conflicts of interest

There are no conflicts of interest to declare.

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Uranyl ion complexes with 2,2′:6′,2″-terpyridine-4′-carboxylate.

Interpenetration of networks involving "expanded ligands"

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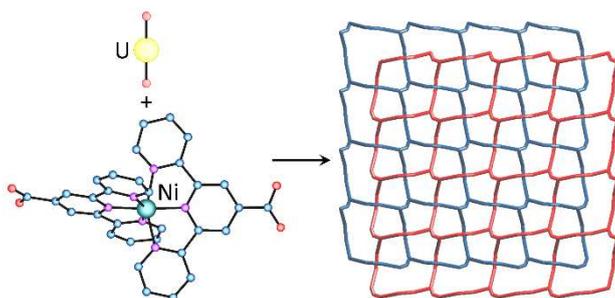
2,2′:6′,2″-Terpyridine-4′-carboxylate (tpyc⁻) gives mono- or diperiodic uranyl ion complexes. With additional Ni^{II} cations, uranyl is bound to the divergent carboxylate groups of the "expanded ligand" $Ni(tpyc)_2$, giving corrugated layers with, in one case, twofold interpenetration.