Ni(2,2':6',2 -Terpyridine-4'-carboxylate) 2 zwitterions and carboxylate polyanions in mixed-ligand uranyl ion complexes with a wide range of topologies

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Ni(2,2′:6′,2″-terpyridine-4′-carboxylate)$_2$ Zwitterions and Carboxylate Polyanions in Mixed-Ligand Uranyl Ion Complexes with a Wide Range of Topologies

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ABSTRACT: The zwitterionic complex formed by Ni^{II} and 2,2′:6′,2″-terpyridine-4′-carboxylate, Ni(tpyc)$_2$, has been used as a coligand with a diverse group of polycarboxylates in uranyl ion complexes synthesized under solvo-hydrothermal conditions, thus giving a series of 14 mixed ligand, heterometallic compounds. Both [$(UO_2)_2$(*c*-1,2-chdc)Ni(tpyc)$_2$$(NO_3)_2$]$_2$·4$CH_3CN$ (**1**) and [$(UO_2)_2$(tdc)Ni(tpyc)$_2$$(NO_3)_2$]$_2$ (**2**), where *c*-1,2-chdc^{2-} is *cis*-1,2-cyclohexanedicarboxylate and tdc^{2-} is 2,5-thiophenedicarboxylate, display discrete U_4Ni_2 dinickelatetrauranacycles, a motif which is also found as part of a daisychain coordination polymer in [$(UO_2)_4$(bdc)$_3$$Ni_2$(tpyc)$_4$$(NO_3)_2$]·2$CH_3CN$·2$H_2O$ (**3**), where bdc^{2-} is 1,4-benzenedicarboxylate. Similar U_4Ni_2 rings associate to form a nanotubular polymer in [$(UO_2)_2$(tca)Ni(tpyc)$_2$$(NO_3)$]·2$CH_3CN$·2$H_2O$ (**4**), where tca^{3-} is tricarballylate. [$(UO_2)_2$(1,2-pda)(1,2-pdaH)Ni(tpyc)$_2$$(NO_3)$]·$CH_3CN$ (**5**), where 1,2-pda^{2-} is 1,2-phenylenediacetate, crystallizes as a meander-like chain in which each bent section can be seen as an open, semi-U_4Ni_2 ring. Oxalate (ox^{2-}) gives [$(UO_2)_2$(ox)$_2$Ni(tpyc)$_2$] (**6**), a monoperiodic polymer containing smaller U_4Ni rings, while 1,2,3-benzenetricarboxylate (1,2,3-btc^{3-}) and citrate (citH^{3-}) give [Ni(tpycH)$(H_2O)_3$][UO_2(1,2,3-btc)]$_2$·2H_2O (**7**) and [UO_2Ni_2(tpyc)$_4$][UO_2(citH)]$_2$ (**8**), two complexes with charge separation, the latter displaying 1D + 2D semi-interpenetration. [$(UO_2)_2$(btcH)Ni(tpyc)$_2$$(NO_3)$] (**9**) and [$(UO_2)_2$(cbtcH)Ni(tpyc)$_2$$(NO_3)$] (**10**), where btc^{4-} and cbtc^{4-} are 1,2,3,4-butanetetracarboxylate and *cis,trans,cis*-1,2,3,4-cyclobutanetetracarboxylate, respectively, are diperiodic networks with **hcb** topology, and [$(UO_2)_2$(ndc)Ni(tpyc)$_2$(OH)(NO_3)] (**11**), where ndc^{2-} is 2,6-naphthalenedicarboxylate, is a **sql** network containing dinuclear nodes and involving 100-membered $U_{10}Ni_4$ metallacyclic units. U_4Ni_2 rings are found in the diperiodic polymer formed in [$(UO_2)_4$(*t-R*-1,2-chdc)$_4$$Ni_2$(tpyc)$_4$] (**12**), where *t-R*-1,2-chdc^{2-} is *trans-R,R*-1,2-cyclohexanedicarboxylate, the heavily puckered sheets being interlocked. 1,3-Phenylenediacetate (1,3-pda^{2-}) gives a very thick diperiodic polymer with KIa topology, [$(UO_2)_4$(1,3-pda)$_4$$Ni_2$(tpyc)$_4$]·$CH_3CN$·2$H_2O$ (**13**). A triperiodic framework is formed with nitrilotriacetate (nta^{3-}) in [$(UO_2)_2$(nta)$_2$$Ni_2$(tpyc)$_2$] (**14**), where Ni^{II} is found in Ni(tpyc)$_2$ units as well as in Ni(nta)$_2^{4-}$ moieties which both act as 4-coordinated nodes.

INTRODUCTION

While mixed-ligand complexes of the uranyl ion UO_2^{2+} are abundant, in the majority of cases, as well exemplified with uranyl carboxylates,[1–4] they involve the association of a multidentate chelating or bridging ligand with rather simple anionic species such as oxide, hydroxide, fluoride, nitrate, formate or oxalate often arising inadvertently rather than as an intended component of the product. Simple neutral species such as H_2O, *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylpropyleneurea (DMPU) are known co-ligands derived from the solvents used for synthesis and neutral chelates such as 1,10-phenanthroline, 2,2′-bipyridine and 2,2′;6′,2″-terpyridine have, in a significant number of instances,[2,5–8] been used to block 2 or 3 equatorial coordination sites of the uranyl cation. None of these neutral species (4,4′-bipyridine dioxide providing an exception[9]), however, is known to have a significant capacity to bridge uranyl centres and thus to facilitate polymerization in the same way as anionic ligands such as polycarboxylates. Mixed-ligand polycarboxylate complexes are an intriguing prospect for the development of new coordination polymers with uranyl ion but there are only rare instances where use of a mixture of dicarboxylate ligands does provide a coordination polymer containing both, with some examples involving stereoisomeric species.[10,11] Nevertheless, what is well-known is that the neutral but zwitterionic ligand betaine (*N,N,N*-trimethylglycine) displays in the crystal structures of its uranyl ion complexes[12–15] all the characteristics of an anionic carboxylate, including the ability to bridge uranyl centres in a $\kappa^1O;\kappa^1O'$ manner. A variety of doubly- and triply-zwitterionic organic carboxylate ligands has also been shown to provide coordination polymers or frameworks with various metal ions other than uranyl where the ligand mimics the behaviour of analogous di- or tricarboxylate anions.[16–22] A particularly simple means of obtaining a dicarboxylato zwitterion is through the "expanded ligand" approach[23,24] involving the formation of $M^{II}L_2$ complexes where M is a transition metal and L

is a ditopic ligand such as 2,2′;6′,2″-terpyridine-4′-carboxylate (tpyc$^-$), which preferentially coordinates through the terpyridine unit. This is but one aspect of metalloligand chemistry,[25,26] which has been exploited for a considerable variety of carboxylato-substituted species (*e.g.* cationic[27] and anionic[28–30]) and which is recognized as a useful means of obtaining heterometallic coordination polymers and frameworks with varied functionality.[25,26,31]

As a charge-neutral species, any zwitterionic ligand must be accompanied by anions in its crystalline complexes with metal cations, giving rise to the possibility that polymerization due to binding of a multiple carboxylato-zwitterion could be reinforced or usefully modified by binding of a polycarboxylate anion. As part of our continuing exploration of the utility of tpyc$^-$ in uranyl ion coordination chemistry,[32,33] this has been found in the monoperiodic mixed ligand complex of uranyl ion formed with Ni(tpyc)$_2$ and *trans*-1,4-cyclohexane dicarboxylate (*t*-1,4-chdc^{2-}),[33] a result complementing the preceding characterization of the uranyl ion complex of Ni(cptpy)$_2$ (cptpy = 4′-(4‴-carboxylatophenyl)-2,2′;6′,2″-terpyridine) and 4,4′-biphenyl dicarboxylate,[34] where the greater size of both the zwitterion and the dicarboxylate species leads to a diperiodic coordination polymer with **hcb** topology exhibiting 2D + 2D → 3D polycatenation and remarkable catalytic properties. In the present work, we have focussed upon variation of the polycarboxylate accompanying the Ni(tpyc)$_2$ zwitterion in their uranyl ion complexes, and we have isolated a series of 14 mixed-ligand complexes which have been crystallographically characterized. It appears that under the solvo-hydrothermal conditions of crystallization employed, di- and tri-carboxylate entities are the favoured companions of the zwitterion, leading to complexes covering all the periodicity range, from polynuclear, discrete species to a three-periodic framework, and displaying a wide array of topologies, with the "terpyridine embrace" (TE)[35,36] involving both "face-to-face" and "edge-to-face" contacts of the aromatic units of the zwitterion units being a prominent feature of most of the structures.

EXPERIMENTAL SECTION

Syntheses. ***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%) and $Ni(NO_3)_2\cdot 6H_2O$ were purchased from Prolabo, and 2,2′:6′,2″-terpyridine-4′-carboxylic acid was from Alfa-Aesar. The carboxylic acids were from Aldrich, Fluka, or Alfa-Aesar, except for *rac-trans*-1,2-cyclohexanedicarboxylic acid which was from Lancaster and for which the (1*R*,2*R*) enantiomer was isolated through crystallization with (*R*)-1-phenylethylamine as a resolving agent, as in the literature.[37] For all syntheses, a mixture of $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (25 mg, 0.05 mmol), $Ni(NO_3)_2\cdot 6H_2O$ (10 mg, 0.03 mmol), tpycH (14 mg, 0.05 mmol), and the additional carboxylic acid (0.05 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL). The solutions were placed in 10 mL tightly closed glass vessels (Pyrex® culture tubes with SVL15 stoppers and teflon seals, provided by VWR) and heated at 140 °C in a sand bath. The crystals, of orange-yellow color, were grown in the hot, pressurized solutions (and not as a result of a final return to ambient conditions) and they were recovered after cooling down. A summary of the carboxylic acids used, represented in Scheme 1, and heating durations is given in Table 1. Elemental analyses were performed by MEDAC Ltd., and the results are given in Table 2, together with the yields. Only a few crystals were obtained for compounds **3**, **6** and **11**, so that no elemental analysis could be performed. Several compounds contain solvent molecules which were not found in the crystal structures but whose presence is in agreement with the existence of voids in the structures (see below), while in the case of compounds **1** and **5**, the acetonitrile molecules found from structure determination appear to have been lost during filtering and drying of the sample. In the case of compound **12**, the number of extra water molecules may

seem large, but it is in good agreement with the electron count for disordered solvent molecules determined from the crystal structure (316 electrons per formula unit). The solvent molecules indicated in Table 2 are in addition (or subtraction) to those indicated in the formulas.

Scheme 1. The Polycarboxylic Acids Used as Coligands.

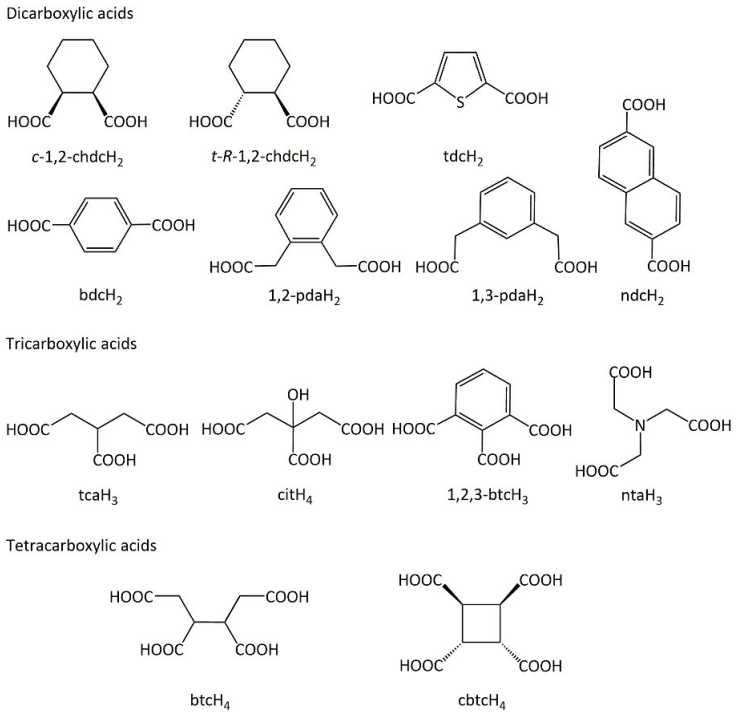

Table 1. Summary of the Synthesis Conditions

Compound	Additional carboxylic acid	Duration
$[(UO_2)_2(c\text{-}1,2\text{-chdc})Ni(tpyc)_2(NO_3)_2]_2{\cdot}4CH_3CN$ (**1**)	*cis*-1,2-cyclohexanedicarboxylic acid (*c*-1,2-chdcH_2)	1 w
$[(UO_2)_2(tdc)Ni(tpyc)_2(NO_3)_2]_2$ (**2**)	2,5-thiophenedicarboxylic acid (tdcH_2)	3 d
$[(UO_2)_4(bdc)_3Ni_2(tpyc)_4(NO_3)_2]{\cdot}2CH_3CN{\cdot}2H_2O$ (**3**)	1,4-benzenedicarboxylic acid (bdcH_2)	3 d
$[(UO_2)_2(tca)Ni(tpyc)_2(NO_3)]{\cdot}2CH_3CN{\cdot}2H_2O$ (**4**)	tricarballylic acid (tcaH_3)	3 d
$[(UO_2)_2(1,2\text{-pda})(1,2\text{-pdaH})Ni(tpyc)_2(NO_3)]{\cdot}CH_3CN$ (**5**)	1,2-phenylenediacetic acid (1,2-pdaH_2)	3 d
$[(UO_2)_2(ox)_2Ni(tpyc)_2]$ (**6**)	oxalic acid (oxH_2), generated *in situ* from malic acid	3 d
$[Ni(tpycH)(H_2O)_3][UO_2(1,2,3\text{-btc})]_2{\cdot}2H_2O$ (**7**)	1,2,3-benzenetricarboxylic acid (1,2,3-btcH_3)	2 w
$[UO_2Ni_2(tpyc)_4][UO_2(citH)]_2$ (**8**)	citric acid (citH_4)	3 w
$[(UO_2)_2(btcH)Ni(tpyc)_2(NO_3)]$ (**9**)	1,2,3,4-butanetetracarboxylic acid (btcH_4)	3 d
$[(UO_2)_2(cbtcH)Ni(tpyc)_2(NO_3)]$ (**10**)	*cis,trans,cis*-1,2,3,4-cyclobutanetetracarboxylic acid (cbtcH_4)	3 d
$[(UO_2)_2(ndc)Ni(tpyc)_2(OH)(NO_3)]$ (**11**)	2,6-naphthalenedicarboxylic acid (ndcH_2)	2 w
$[(UO_2)_4(t\text{-}R\text{-}1,2\text{-chdc})_4Ni_2(tpyc)_4]$ (**12**)	*trans-R,R*-1,2-cyclohexanedicarboxylic acid (*t*-*R*-1,2-chdcH_2)	3 w
$[(UO_2)_4(1,3\text{-pda})_4Ni_2(tpyc)_4]{\cdot}CH_3CN{\cdot}2H_2O$ (**13**)	1,3-phenylenediacetic acid (1,3-pdaH_2)	3 w
$[(UO_2)_2(nta)_2Ni_2(tpyc)_2]$ (**14**)	nitrilotriacetic acid (ntaH_3)	1 w

Table 2. Elemental Analysis Results and Yields

Compound	Solvent molecules	Yield (%)	Calculated (%)			Found (%)		
			C	H	N	C	H	N
1	$-4CH_3CN$, $+10H_2O$	65	31.29	2.63	7.30	31.54	2.56	6.84
2	$+10H_2O$	57	29.73	2.10	7.30	29.76	2.04	6.95
3		< 1						
4		56	33.53	2.34	8.38	32.50	2.13	7.79
5	$-CH_3CN$, $+10H_2O$	58	35.11	3.23	5.51	34.41	2.68	6.01
6		< 1						
7		84	29.63	1.83	3.05	29.62	1.94	3.01
8	$+CH_3CN$, $+5H_2O$	35	36.86	2.50	7.16	36.12	2.49	7.55
9	$+5H_2O$	80	31.31	2.43	6.39	31.74	2.36	6.91
10		71	32.90	1.86	6.71	32.95	2.11	7.30
11		< 1						
12	$+30H_2O$	39	32.73	4.00	4.77	32.28	3.92	4.67
13	$+10H_2O$	24	38.25	3.00	5.47	38.52	2.83	6.04
14	$+10H_2O$	14	29.92	2.97	6.34	30.09	2.45	6.66

Crystallography. The data were collected at 100(2) K on a Bruker D8 Quest diffractometer equipped with an Incoatec microfocus source (IμS 3.0 Mo, $\lambda = 0.71073$ Å) and a PHOTON III area detector, and operated through the APEX3 software.[38] The crystals were mounted on Mitegen micromounts with a protective coating of Paratone-N oil (Hampton Research). The data were processed with SAINT[39] and absorption corrections, either empirical (multi-scan) or based on crystal shape, were made with SADABS.[40,41] All structures were solved by intrinsic phasing with SHELXT,[42] and refined by full-matrix least-squares on F^2 with SHELXL,[43] using the ShelXle interface.[44] All non-hydrogen atoms were refined with anisotropic displacement parameters. When possible, the hydrogen atoms bound to oxygen atoms were retrieved from residual electron density maps, and they were either refined with restraints or treated as riding atoms. 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, with optimized geometry). Some voids in the structures of compounds **1**–**3**, **5**, **6**, and **8**–**14** contain disordered solvent molecules (water or acetonitrile, as indicated also by elemental analysis results) which could not be modelled

satisfactorily, and the SQUEEZE software[45] was used to subtract their contribution to the structure factors. Crystal data and structure refinement parameters are given in Table 3. The molecular plots were drawn with ORTEP-3,[46,47] and the polyhedral representations with VESTA.[48] The topological analyses and nodal representations were made with ToposPro.[49] Special details for some of the structures are as follows.

*Compound **8**.* The uranyl cation containing U2 is disordered over two very close positions related by an inversion centre. One complete cation has been refined with an occupancy parameter of 0.5. The associated disorder affecting the carboxylate groups bound to this cation has only been partially resolved; two positions have been found for O12, O13 and the attached atom C22, which were refined with occupancy parameters constrained to sum to unity, but notwithstanding the large and very anisotropic displacement parameters of O14, O15, and some of the carbon atoms of the aromatic ring bearing O12 and O13, the modelling of the disorder could not be extended further satisfactorily.

*Compound **10**.* The uncoordinated carboxylic group is rotationally disordered over two positions which were refined with occupancy parameters constrained to sum to unity and restraints on displacement parameters and one bond length, and the associated hydrogen atoms were not found.

*Compound **12**.* One cyclohexanedicarboxylate ligand is disordered over two positions with one common oxygen atom, which have been refined with occupancy parameters constrained to sum to unity. Other parts of the structure are seemingly affected by unresolved disorder, particularly those bound to this ligand. Restraints on some bond lengths and displacement parameters have been applied for the disordered atoms and other parts of the structure. The value of the refined Flack parameter is 0.006(5).

*Compound **13**.* Large residual electron density peaks are located close to atoms U2 and U4 (at less than 1 Å) in all the six experiments made with six different crystals of different

sizes, and they remain whatever absorption correction method is applied. These peaks have been interpreted as due to minor components of disordered uranium atoms (U2A and U4A), the corresponding disorder on oxo atoms and ligands being unresolved but suggested by the rather large and anisotropic displacement parameters of many atoms. Restraints on several bond lengths and displacement parameters had to be applied. Checkcif suggests the possible space group $Pca2_1$, but, in addition to the large R_{int} value in the orthorhombic system, no satisfying refinement could be obtained in this space group, and the structure was refined as a 2-component inversion twin in space group Pc, with a Flack parameter 0.422(13).

Table 3. Crystal Data and Structure Refinement Details

	1	**2**	**3**	**4**	**5**	**6**	**7**
chemical formula	$C_{88}H_{72}N_{20}Ni_2O_{36}U_4$	$C_{76}H_{44}N_{16}Ni_2O_{36}S_2U_4$	$C_{92}H_{62}N_{16}Ni_2O_{36}U_4$	$C_{42}H_{35}N_9NiO_{19}U_2$	$C_{54}H_{40}N_8NiO_{19}U_2$	$C_{36}H_{20}N_6NiO_{16}U_2$	$C_{34}H_{25}N_3NiO_{23}U_2$
M (g mol^{-1})	3055.19	2890.93	3037.11	1504.56	1639.71	1327.35	1378.34
cryst syst	triclinic	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$	$Pnna$	$P\bar{1}$
a (Å)	8.9573(3)	8.6617(3)	8.9799(2)	41.1941(15)	12.4860(6)	21.6394(5)	10.6595(6)
b (Å)	17.0031(6)	15.9578(6)	15.2271(4)	8.6477(3)	15.7774(6)	14.7440(4)	12.4260(7)
c (Å)	18.7001(7)	19.1458(7)	19.7173(5)	32.6050(11)	28.6893(11)	13.1652(3)	15.6728(8)
α (deg)	76.7798(14)	104.8474(15)	72.1899(11)	90	90	90	78.465(3)
β (deg)	79.6445(17)	90.2832(16)	84.8226(10)	123.2887(15)	101.992(2)	90	82.089(3)
γ (deg)	75.3637(14)	105.7054(15)	74.3191(11)	90	90	90	70.078(3)
V (Å^3)	2660.02(17)	2454.64(16)	2471.27(11)	9709.2(6)	5528.3(4)	4200.38(18)	1906.84(19)
Z	1	1	1	8	4	4	2
reflns collcd	214106	165265	155118	83642	108336	119365	151309
indep reflns	13691	9329	12775	9218	10496	3990	9844
obsd reflns [$I > 2\sigma(I)$]	12749	8822	11447	7580	8499	3375	9007
R_{int}	0.050	0.045	0.057	0.068	0.090	0.088	0.057
params refined	678	613	685	672	758	277	596
R_1	0.021	0.017	0.022	0.046	0.043	0.029	0.024
wR_2	0.054	0.041	0.046	0.110	0.084	0.055	0.056
S	1.057	1.060	1.061	1.057	1.099	1.117	1.086
$\Delta\rho_{min}$ (e Å^{-3})	–0.88	–0.85	–1.68	–2.09	–1.72	–1.22	–1.43
$\Delta\rho_{max}$ (e Å^{-3})	1.26	1.65	1.48	3.16	1.72	1.22	1.50

	8	**9**	**10**	**11**	**12**	**13**	**14**
chemical formula	$C_{76}H_{50}N_{12}Ni_2O_{28}U_3$	$C_{40}H_{27}N_7NiO_{19}U_2$	$C_{40}H_{27}N_7NiO_{20}U_2$	$C_{44}H_{27}N_7NiO_{16}U_2$	$C_{96}H_{80}N_{12}Ni_2O_{32}U_4$	$C_{106}H_{79}N_{13}Ni_2O_{34}U_4$	$C_{44}H_{32}N_8Ni_2O_{20}U_2$
M (g mol^{-1})	2410.79	1444.45	1460.45	1444.49	2983.26	3148.36	1586.25
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$	$P\bar{1}$	$C222_1$	Pc	$C2/c$
a (Å)	8.4733(2)	23.3610(6)	24.0260(14)	8.7884(6)	20.8462(4)	24.3722(16)	9.9829(3)
b (Å)	30.4417(6)	9.1845(2)	8.8432(5)	15.6675(11)	28.1089(5)	16.0289(9)	25.1302(8)
c (Å)	16.7942(4)	46.5096(12)	25.4240(14)	19.8850(16)	45.8716(10)	14.2623(8)	21.9789(7)
α (deg)	90	90	90	78.414(3)	90	90	90
β (deg)	95.3601(12)	92.1370(13)	116.9437(16)	82.109(3)	90	90.626(2)	97.9405(18)
γ (deg)	90	90	90	80.438(2)	90	90	90
V (Å^3)	4312.98(17)	9972.1(4)	4815.4(5)	2629.6(3)	26879.1(9)	5571.4(6)	5461.0(3)
Z	2	8	4	2	8	2	4
reflns collcd	131445	96649	114065	22340	386454	133574	124005
indep reflns	8202	9469	9132	9635	25507	21134	5192
obsd reflns [$I > 2\sigma(I)$]	7319	8726	8114	5992	21708	18950	5020
R_{int}	0.076	0.093	0.062	0.084	0.090	0.080	0.043
params refined	590	622	658	631	1416	1442	345
R_1	0.030	0.049	0.029	0.055	0.034	0.069	0.022
wR_2	0.064	0.095	0.066	0.113	0.074	0.180	0.049
S	1.071	1.268	1.085	0.965	1.058	1.058	1.159
$\Delta\rho_{min}$ (e Å^{-3})	–1.07	–2.68	–1.33	–1.42	–1.20	–1.43	–0.71
$\Delta\rho_{max}$ (e Å^{-3})	2.63	1.59	1.46	1.61	1.47	3.79	1.92

RESULTS AND DISCUSSION

Prior to a description of each structure, it may be noted that, in all 14 compounds, the uranium coordination environment does not deviate significantly from its usual features. Uranium is either seven- or eight-coordinated, the coordination geometry being thus pentagonal- or hexagonal-bipyramidal in complexes **6**–**8**, **14** and **1**–**5**, **9**, **12**, **13**, respectively, with two instances (**10** and **11**) in which both geometries coexist. Uranium atoms are only bound to oxygen atoms from carboxylate or nitrate ligands, plus one instance of hydroxide anion in complex **11**, and the bond lengths do not deviate in any remarkable way from their usual values [U–O(oxo), 1.713(8)–1.795(17) Å, U–O(carboxylato), 2.379(13)–2.57(3) Å for κ^2O,O'-chelating groups, 2.240(5)–2.430(4) Å for the other groups; U–O(nitrato), 2.483(2)–2.536(4) Å; U–O(hydroxido), 2.311(7) and 2.336(7) Å]. The nickel(II) cations in the $Ni(tpyc)_2$ moieties are in the usual slightly distorted octahedral environment which will not be further described. The complexes will be discussed in the order of increasing periodicity.

It is also notable that in no case is either of the hydrolysis products from the acetonitrile cosolvent (NH_4^+ and $CH_3CO_2^-$) found as part of the isolated crystals, quite unlike numerous systems where the use of DMF as the co-solvent results rather frequently in the incorporation of $(CH_3)_2NH_2^+$ and/or HCO_2^-. Such hydrolytic "interference" in the syntheses of uranyl ion coordination polymers can be avoided by the use of NMP but an advantage in the use of solvents such as acetonitrile and DMF may well be that their hydrolysis results in buffering of the reaction medium at a higher pH than its initial value.

Polynuclear ring-shaped complexes. Two of the complexes in this series crystallize as discrete polynuclear complexes with analogous geometries, $[(UO_2)_2(c\text{-}1,2\text{-chdc})Ni(tpyc)_2(NO_3)_2]_2\cdot 4CH_3CN$ (**1**) and $[(UO_2)_2(tdc)Ni(tpyc)_2(NO_3)_2]_2$ (**2**), which include *cis*-1,2-cyclohexanedicarboxylate and 2,5-thiophenedicarboxylate, respectively. In the previously

reported structure of $[(UO_2)_2(t\text{-}1,4\text{-chdc})Ni(tpyc)_2(NO_3)_2]\cdot(t\text{-}1,4\text{-chdcH}_2)\cdot 2CH_3CN$,[33] involving *trans*-1,4-cyclohexanedicarboxylate, the positional isomer of *c*-1,2-chdc^{2-} found in complex **1**, the dicarboxylate and zwitterion units are present in perhaps the simplest form of coordination polymer that might be anticipated in that they act alternately as bridges between uranyl ions in a monoperiodic chain. Chelating nitrate ligands on each U^{VI} centre appear to block dicarboxylate or zwitterion coordination which could produce extension into a second direction. One or the other of these features is seen in most of the presently studied structures, though none shows the feature of the presence of the uncoordinated parent acid of the dicarboxylate acting as an hydrogen bonding bridge between polymer strands. Replacement of the divergent *t*-1,4-chdc^{2-} by the convergent and similarly bis-κ^2O,O'-chelated *c*-1,2-chdc^{2-} ligand has a conspicuous effect on the structure since, in complex **1**, two curved $(UO_2)_2(c\text{-}1,2\text{-chdc})^{2+}$ strands are connected by linear $Ni(tpyc)_2$ units to form a centrosymmetric, hexanuclear metallacyclic assembly, with four chelating nitrate anions completing the coordination spheres of the four uranium atoms and preventing further polymerization (Figure 1). While *c*-1,2-chdc^{2-} can adopt a chiral conformation, the two units in each macrocycle are enantiomeric. The dinickelatetrauranacycle (denoted U_4Ni_2 ring in the following) is 42-membered and it has an elongated shape with the terpyridine (terpy) motifs protruding inside, so that the internal space is separated into two small apertures (Figure 1b). The rings stack into columns parallel to [100] (Figure 1c), the packing containing some free spaces (see Experimental Section), as indicated by the Kitaigorodski packing index (KPI, calculated with PLATON[50]) of 0.64. TE interactions are apparent both within the macrocycles [Ni···Ni separation 8.6760(7) Å] and between those within the stacks down [100] [Ni···Ni separation 8.9573(3) Å], with formation of two parallel-displaced π-stacking interactions [centroid···centroid distances, 3.6449(17) and 3.7821(16) Å; dihedral angles, 0.03(14) and 6.45(13)°] and three edge-to-face CH···π interactions [H···centroid distances, 2.54–2.99 Å; C–H···centroid angles, 134–170°]. The macrocycle stacks

define channels that are occupied by the acetonitrile molecules, located close to the macrocycle cavity portal and involved in both CH(aromatic)···N and CH···O(carboxylate) hydrogen bonds, while adjacent stacks are closely packed as a result of both CH(aromatic)···O(carboxylate) and CH(aromatic)···O(nitrate) interactions as well as stacking of the nitrates with terpyridine rings.

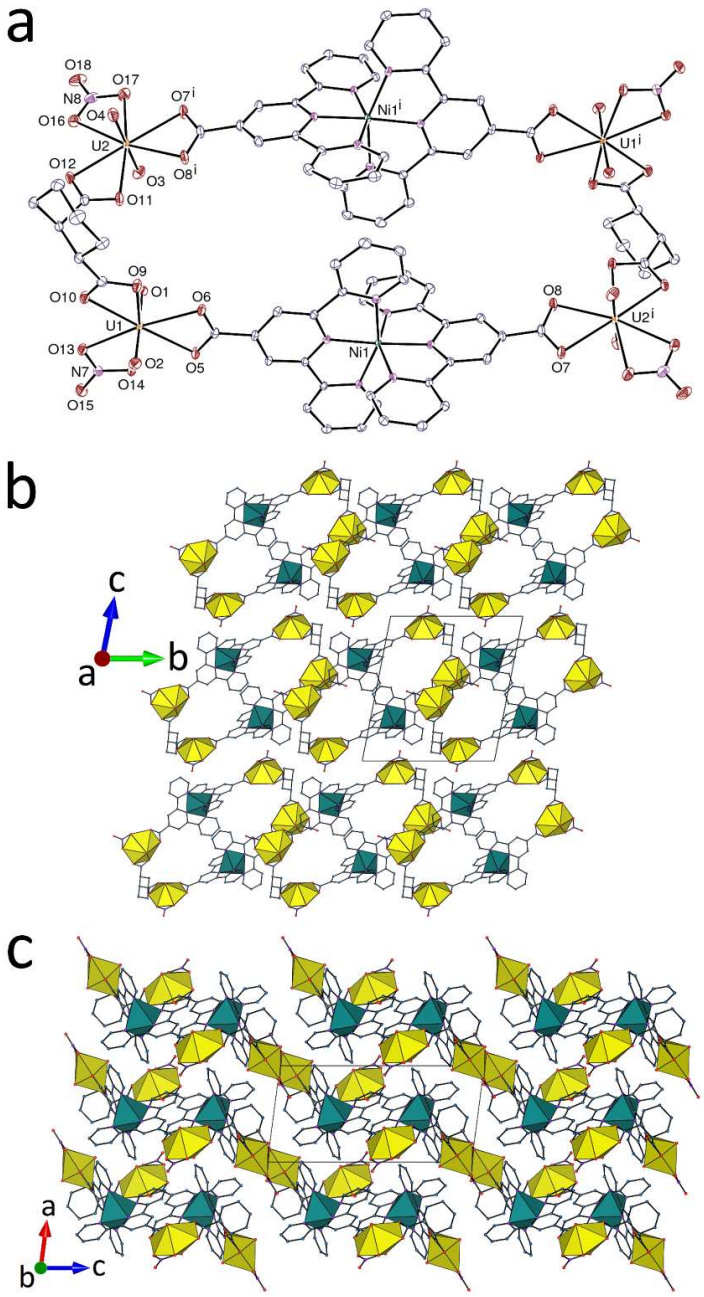

Figure 1. (a) View of compound **1**. Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules and hydrogen atoms are omitted. Symmetry code: i = 1 – *x*, 2 – *y*, 1 – *z*. (b, c) Two views of the packing with uranium coordination polyhedra yellow and those of nickel green.

With tdc^{2-}, a ligand of rather limited flexibility and a bent form with regard to its donor group orientations, complex **2** has a structure very similar to that of complex **1**, apart from the absence of any well-ordered solvent. Again, the complex unit present, shown in Figure 2, is a

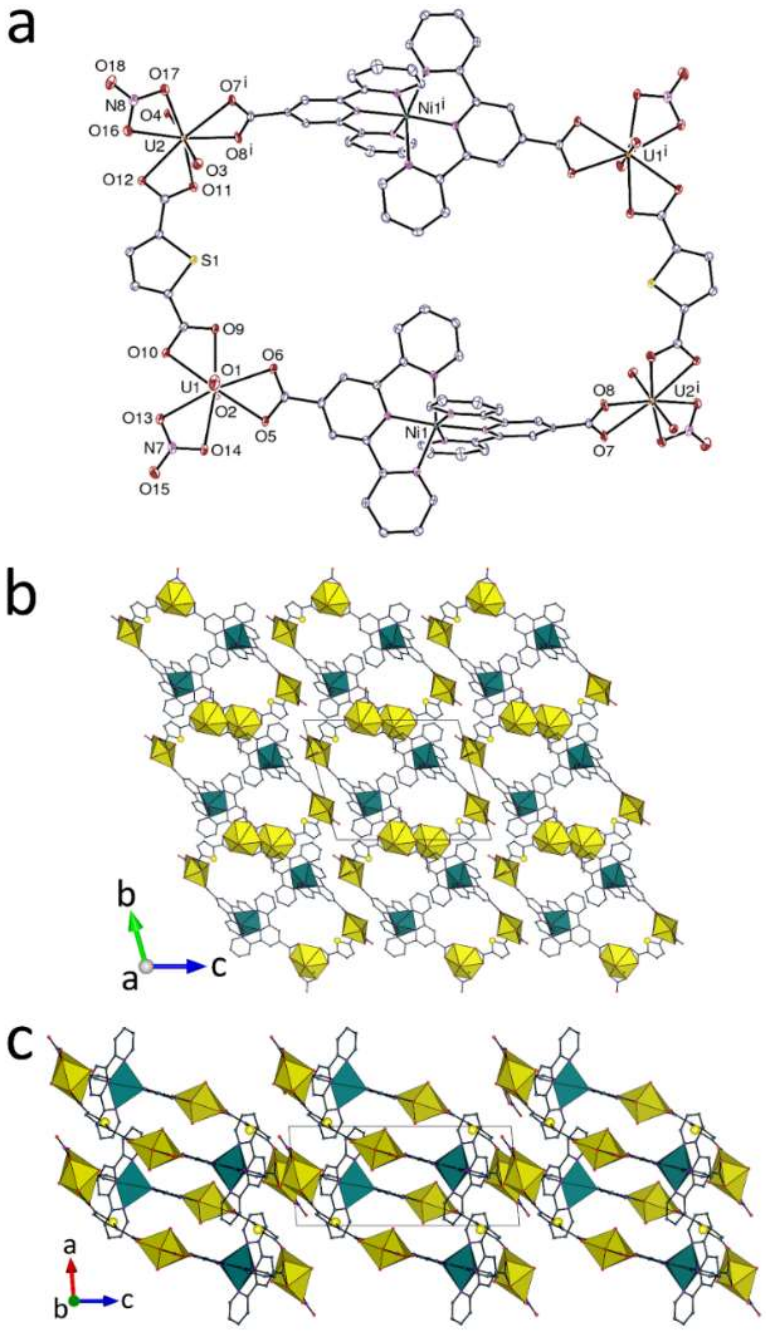

Figure 2. (a) View of compound **2**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted. Symmetry code: i = 2 – *x*, 1 – *y*, 1 – *z*. (b, c) Two views of the packing with uranium coordination polyhedra yellow and those of nickel green.

centrosymmetric, uncharged U_4Ni_2 ring which is now 44-membered. The intra-annular Ni···Ni separation in **2**, 12.5892(7) Å, is too great to produce a significant TE.[35,36] Instead, there is such a fourfold embrace [Ni···Ni 8.6617(3) Å] between terpy moieties in separate rings which form stacked arrays running down [100], with two parallel-displaced π-stacking interactions [centroid···centroid distances, 3.8112(17) and 3.6357(18) Å; dihedral angles, 0 and 5.07(14)°] and two CH···π interactions [H···centroid distances, 2.77 and 2.83 Å; C–H···centroid angles, 140 and 142°]. These interactions result in the columns being held together by two rows of TE interactions along their length. There is also a partial stacking overlap of terpy and thiophene rings pertaining to adjacent ring columns, [centroid···centroid distance, 3.9175(17) Å; dihedral angle, 18.95(14)°] and a clear CH(terpy)···O(nitrate) interaction extending the association of the metallacycles. Here also, the KPI of 0.60 indicates the presence of voids occupied by disordered solvent molecules.

Complexes **1** and **2** belong to the rather restricted family of uranyl-based metallacycles, with known examples involving (2*R*,3*R*,4*S*,5*S*)-tetrahydrofurantetracarboxylate,[51] Kemp's tricarboxylate,[52,53] 1,3-adamantanediacetate,[54] or iminodiacetate,[55] with further organization into nanotubules in the latter case. As shown in Figure 3, complex **2** appears as an expanded version of complex **1**, the distances between the inequivalent U^{VI} centres bridged by *c*-1,2-chdc^{2-} or tdc^{2-} ligands being 6.7726(2) and 10.2046(3) Å, respectively, resulting in distances between diametrically opposed, inversion-related uranium atom pairs of 18.7413(7)/19.4840(6) Å and 19.1363(6)/21.7885(7) Å, respectively. The overall shape is also closer to planarity in **2**, since the cyclohexyl groups in **1** protrude on either side of the complex. The intracyclic spaces are slightly wider in **2** and, possibly as a consequence, the solvent molecules are heavily disordered in this case, while well-ordered acetonitrile molecules are located close to the cavities in **1**. In both cases, the packing of the rings generates tube-like architectures, with however only two extremely narrow channels running inside.

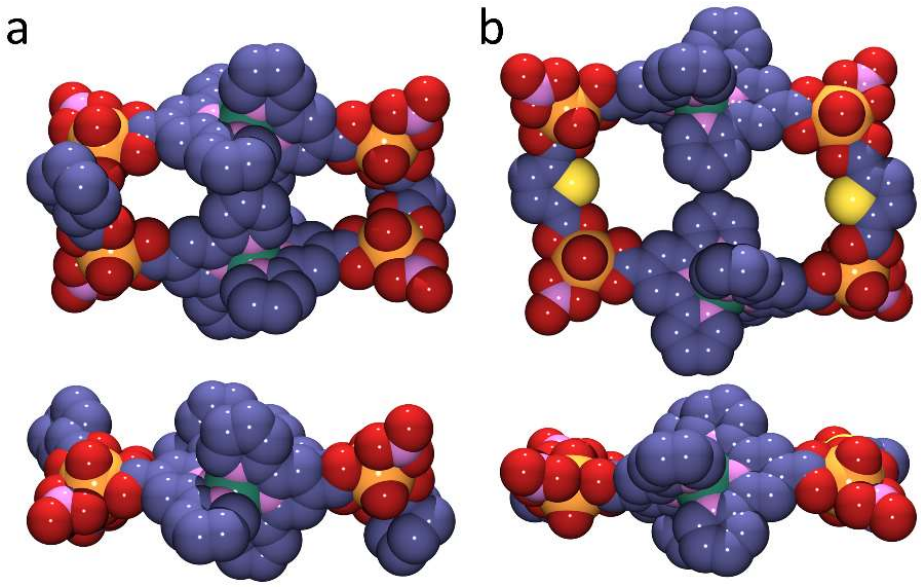

Figure 3. Space-filling representations of the rings in complexes **1** (a) and **2** (b) viewed down two orthogonal directions (uranium, orange; nickel, green; sulfur, yellow; oxygen, red; nitrogen, purple; carbon, blue; hydrogen atoms are omitted).

Monoperiodic coordination polymers. With another aromatic dicarboxylate of limited flexibility but a truly divergent orientation of its carboxylate groups, 1,4-benzenedicarboxylate (terephthalate, bdc^{2-}), a partial displacement of coordinated nitrate gives a complex of composition $[(UO_2)_4(bdc)_3Ni_2(tpyc)_4(NO_3)_2]\cdot 2CH_3CN\cdot 2H_2O$ (**3**), shown in Figure 4. Each of the two independent uranium atoms is chelated in the κ^2O,O' mode by one carboxylate group from the zwitterionic moiety, but U1 is further chelated by one carboxylate group from bdc^{2-} and one nitrate anion, whereas U2 is chelated by two carboxylate groups from two bdc^{2-} ligands. Centrosymmetric U_4Ni_2 rings, here 46-membered, are still present but they are linked into a daisy chain running along [111] by bridging bdc^{2-} units. Within the rings, the distance between the bdc^{2-}-bridged uranium centres is 10.7859(3) Å, and the diagonal distances between inversion-related centres are 18.6364(5) and 22.4796(5) Å, i.e. the size of the ring is not far

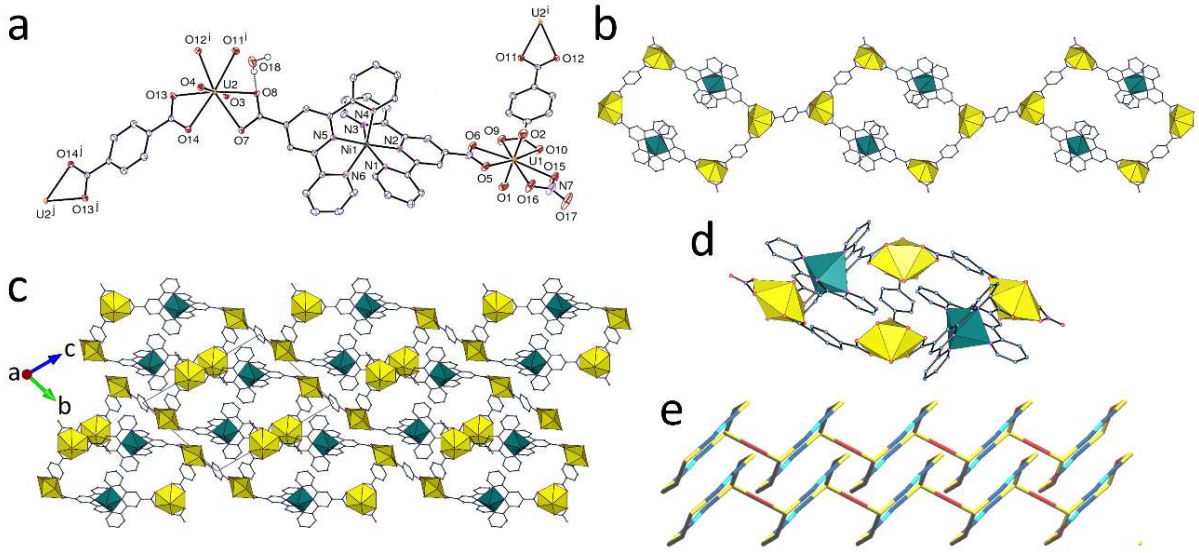

Figure 4. (a) View of compound **3**. Displacement ellipsoids are drawn at the 50% probability level. The acetonitrile molecule and carbon-bound hydrogen atoms are omitted, and the hydrogen bond to a water molecule is shown as a dashed line. Symmetry codes: i = 2 – *x*, 1 – *y*, 1 – *z*; j = 1 – *x*, –*y*, –*z*. (b) View of the monoperiodic coordination polymer with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with chains viewed sideways. (d) chain viewed down its axis. (e) Simplified representation showing the arrangement of chains (view down [101] with [010] horizontal; uranium, yellow; nickel, light blue; $tpyc^{-}$ ligands, dark blue; bdc^{2-}, red).

from that in **2**. Here also, the $Ni(tpyc)_2$ units are too distant from one another for intra-ring TE interactions to be present [Ni···Ni, 13.3909(7) Å]. As in **2**, the rings can be considered to form stacks down [100]; twofold TE is found here also, with inter-ring Ni···Ni separations of 8.9799(2) and 9.1077(7) Å and displaying two parallel-displaced π-stacking interactions [centroid···centroid distances, 3.7907(18) and 3.9233(18) Å; dihedral angles, 0 and 2.46(15)°] and two CH···π interactions [H···centroid distances, 2.87 and 2.88 Å; C–H···centroid angles, 135 and 147°]. One bdc^{2-} proton is also involved in intra- and inter-column CH···π interactions with both terpy and bdc^{2-} rings [H···centroid distances, 2.84 and 2.90 Å; C–H···centroid angles, 128 and 110°]. The well-resolved acetonitrile molecules are located within the columns, and here also disordered solvent molecules are present (KPI, 0.67; see Experimental Section).

The flexible tricarballylate (1,2,3-propanetricarboxylate, tca^{3-}) ligand gives the complex $[(UO_2)_2(tca)Ni(tpyc)_2(NO_3)]\cdot 2CH_3CN\cdot 2H_2O$ (**4**) shown in Figure 5. The two independent

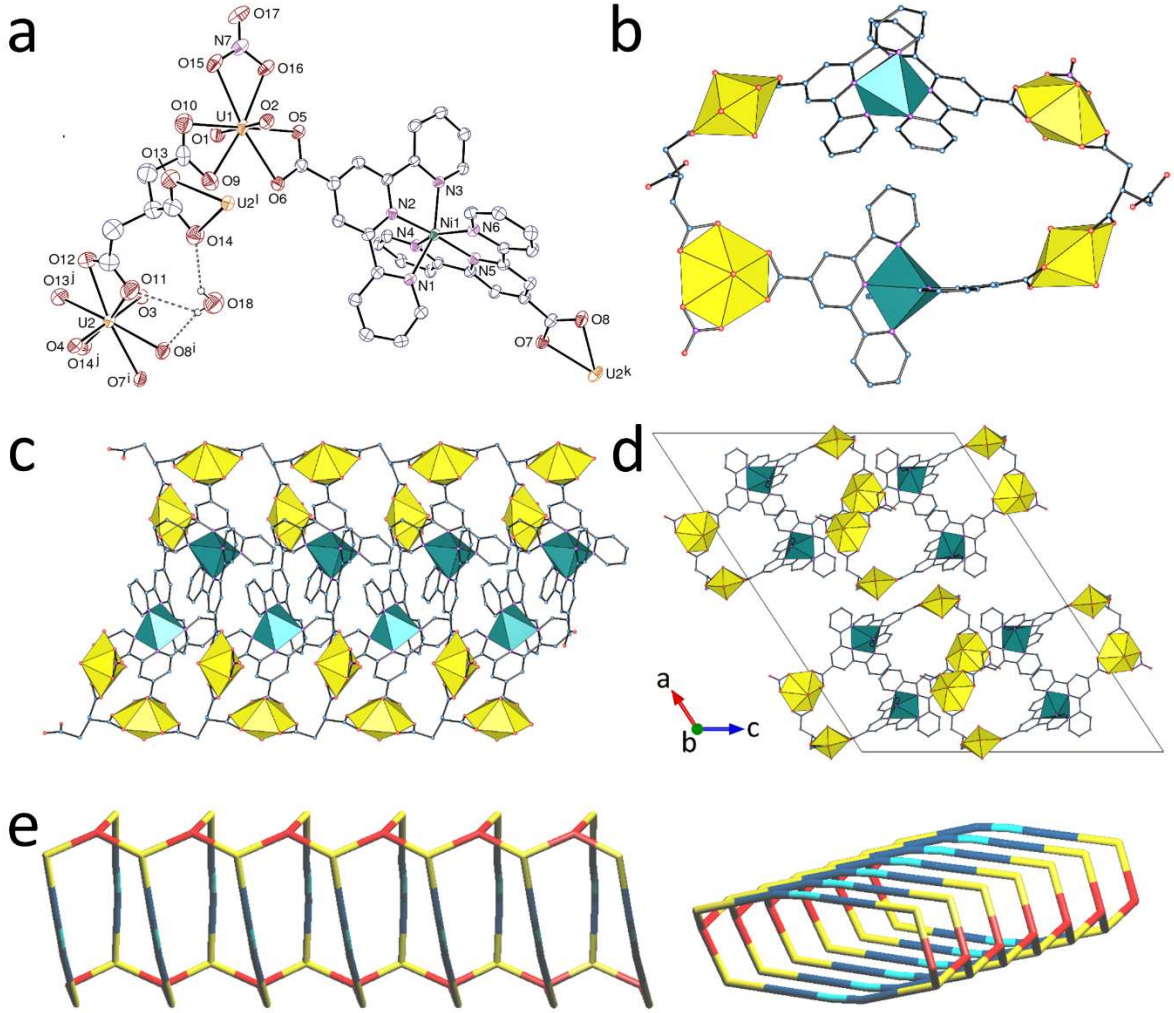

Figure 5. (a) View of compound **4**. Displacement ellipsoids are drawn at the 30% probability level. The acetonitrile molecules and carbon-bound hydrogen atoms are omitted, and hydrogen bonds are shown as dashed lines. Symmetry codes: i = 1/2 – *x*, *y* – 1/2, 1/2 – *z*; j = *x*, *y* – 1, *z*; k = 1/2 – *x*, *y* + 1/2, 1/2 – *z*; l = *x*, *y* + 1, *z*. (b) View of the U_4Ni_2 ring with uranium coordination polyhedra yellow and those of nickel green. (c) View of the monoperiodic coordination polymer. (d) Packing viewed down the nanotube axis. (e) Two views of the simplified representation of the nanotube (uranium, yellow; nickel, light blue; $tpyc^-$ ligands, dark blue; tca^{3-} ligands, red).

uranium atoms are tris-κ^2*O*,*O*′-chelated, U1 by one carboxylate group from $tpyc^-$, one from tca^{3-}, and one nitrate anion, and U2 by one carboxylate from $tpyc^-$ and two from two tca^{3-} anions, U2 and tca^{3-} being thus three-coordinated (3-c) nodes. Hexanuclear rings are found here

also, but they are 43-membered due to the different lengths of the carboxylate arms of the tca^{3-} ligand involved (Figure 5b). Each tricarboxylate pertains to two such rings, as seen in Figure 5e, and the concatenation of these rings gives rise to the formation of a nanotubular polymer directed along [010]. The projection of the tube along its axis looks rather similar to the ring in **1**, although two uranyl cations are strongly tilted with respect to the ring plane. The relatively small size of the tca^{3-} bridge brings U1 and U2 of one ring within 8.5105(5) Å of one another, a significantly longer distance than the corresponding separation in complex **1**, but the trans-annular U···U distances of 18.8136(9) and 19.8134(9) Å are not far from those in the latter complex, the shape of the rings being somewhat distorted in **4**. The intra-ring Ni···Ni separation of 9.6747(17) Å does not allow for very significant intra-ring TE interactions, with however a possible CH···π contact [H···centroid distance, 2.83 Å; C–H···centroid angle, 120°], but one parallel-displaced π-stacking interaction is found between adjoining rings with a Ni···Ni separation of 8.6477(3) Å [centroid···centroid distance, 3.580(5) Å; dihedral angle, 5.0(4)°] as well as two CH···π interactions [H···centroid distances, 2.83 and 2.93 Å; C–H···centroid angles, 143 and 137°]. The tubes, having large apertures on their sides, pack in a slightly interdigitated fashion so as to give layers parallel to (100), as shown in Figure 5d (KPI, 0.68), and the acetonitrile molecules are located within the tubes. Complex **4** belongs to the group of uranyl-based nanotubular species, which includes several complexes with carboxylates[55–62] and phosphonates.[63–66] Although nanotubular complexes involving only tricarballylate ligands are known,[60,62] which show the potential of this three-pronged and curved ligand to build closed species, the shape of complex **4** is more reminiscent of the nanotubes obtained with 1,3- and 1,4-phenylenediacetates,[61] in which the ligands adopt either a divergent, *trans* conformation and thus play a role analogous to $Ni(tpyc)_2$ here, or a convergent *cis* conformation providing the required curvature, as tca^{3-} here (notwithstanding a different denticity). It is also notable that the topology of these two species is the same, both being 3-c, uninodal nets with the point

symbol $\{4^2.6\}$, but while **4** contains uranium and tca^{3-} nodes, only uranium nodes are found in the phenylenediacetate complexes. Both species display an elongated, oblong section and wide side apertures, the $[M(bipy)_3]^{2+}$ (M = Co, Ni, Zn, Ru; bipy = 2,2′-bipyridine) counterions inserted within these spaces in the previous, anionic complexes being replaced by solvent molecules in the neutral complex **4**.

Another flexible aromatic dicarboxylic acid, 1,2-phenylenediacetate (1,2-pdaH$_2$), gives the complex $[(UO_2)_2(1,2\text{-pda})(1,2\text{-pdaH})Ni(tpyc)_2(NO_3)]\cdot CH_3CN$ (**5**) shown in Figure 6. The

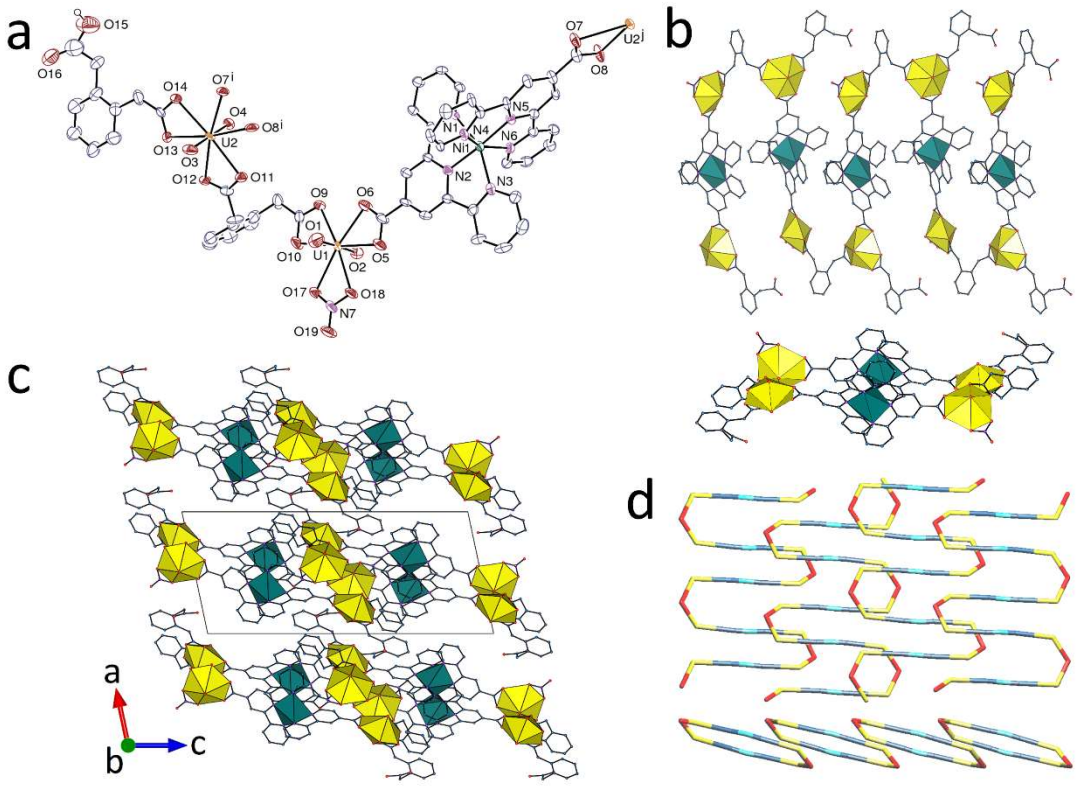

Figure 6. (a) View of compound **5**. Displacement ellipsoids are drawn at the 50% probability level. The solvent molecule and carbon-bound hydrogen atoms are omitted. Symmetry codes: i = 1 – *x*, *y* + 1/2, 1/2 – *z*; j = 1 – *x*, *y* – 1/2, 1/2 – *z*. (b) Two views of the zigzag monoperiodic coordination polymer face-on or end-on, with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with chains viewed end-on. (d) Simplified views showing the arrangement of chains, face-on or end-on (uranium, yellow; nickel, light blue; $tpyc^-$ ligands, dark blue; bridging 1,2-pda^{2-} ligands, red).

coordination environment of the two independent uranium atoms is the same as in **4**, but here two ligands, nitrate and 1,2-pdaH^{-}, are terminal instead of only one in **4**, the carboxylic group of the latter ligand being uncoordinated. As a consequence, no ring subunit is present, although the monoperiodic polymer formed, parallel to [010], has a meander-like shape with each section containing four uranium and two nickel atoms having a geometric arrangement very close to that in the rings, closure being prevented only by the presence of the terminal ligands, as shown in Figure 6b. The uncoordinated carboxylic group, in fact involved in hydrogen bonding to a carboxylate oxygen atom of an adjacent polymer chain [O···O distance, 2.753(10) Å; O–H···O angle, 155°], is located quite close to the coordinated nitrate group and its deprotonation with a slight displacement to dislodge the nitrate would generate the hexanuclear ring. The U···U distance between atoms separated by 1,2-pda^{2-} is 8.1242(5) Å and the distances between diagonally located atoms in the pseudo-ring are 18.9812(8) and 20.6903(8) Å, these values being close to those in **4**. The chain is in fact a severely flattened helix of short pitch (Figure 6d) where the Ni(tpyc)$_2$ units, with a Ni···Ni distance of 8.5251(7) Å, are involved in an infinite chain of TEs with one parallel-displaced π-stacking interaction [centroid···centroid distance, 3.819(4) Å; dihedral angle, 23.0(3)°] and one CH···π interaction [H···centroid distance, 2.66 Å; C–H···centroid angle, 145°]. There are also two possibly significant parallel-displaced π-stacking interactions between terpy and 1,2-pda^{2-} or 1,2-pdaH^{-} rings in adjacent chains [centroid···centroid distances, 3.965(6) and 4.295(5) Å; dihedral angles, 8.6(4) and 10.2(4)°]. Here also, some voids in the structure contain disordered solvent molecules (KPI, 0.68).

Complex **6**, [(UO$_2$)$_2$(ox)$_2$Ni(tpyc)$_2$], was obtained from malic acid, oxalate (ox^{2-}) being generated *in situ*, a frequent occurrence when solvo- or hydrothermal synthetic procedures are used, the formation mechanism involved having been elucidated in some particular cases only.[67,68] The absence of any nitrate and the presence of the particularly rigid and strongly coordinating oxalate ligand are notable features of the structure of complex **6**. The unique

uranyl cation is chelated by two oxalate ligands, one of them centrosymmetric and the other having twofold rotation symmetry, and it is also bound to one carboxylate oxygen atom from $tpyc^-$ (Figure 7). The $Ni(tpyc)_2$ moiety has also twofold rotation symmetry. Bridging of uranyl centres through the formation of two 5-membered chelate rings, leaving one coordination site

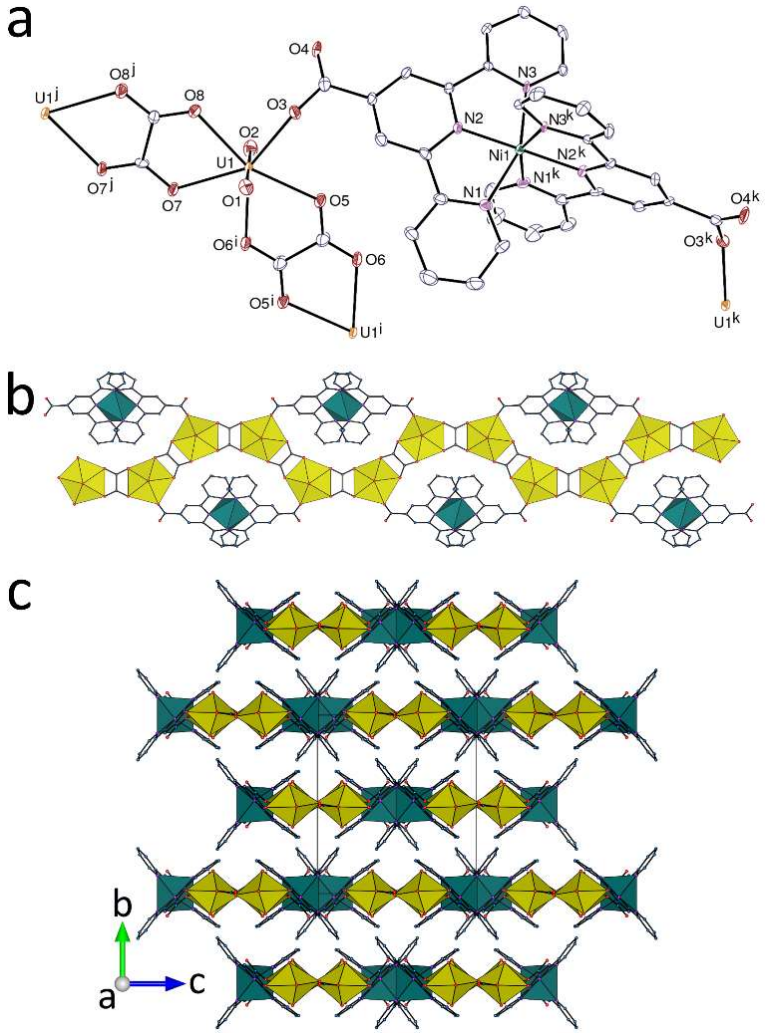

Figure 7. (a) View of compound **6**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted. Symmetry codes: i = 1 – *x*, 1 – *y*, –*z*; j = 3/2 – *x*, 1 – *y*, *z*; k = 1/2 – *x*, 1 – *y*, *z*. (b) View of the monoperiodic coordination polymer with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with chains viewed end-on.

available for an additional donor, is usual with the oxalate ligand,[69–72] and it leads here to the formation of a serpentine monoperiodic polymer running along [100] where the $Ni(tpyc)_2$ units

act as bridges between uranium centres separated by two others, thus filling the undulations of the polymer on both sides and defining U_4Ni rings. The presence of the two oxalate chelate rings limits further coordination to that of a single donor from $Ni(tpyc)_2$. This bis(κ^1O) coordination mode of $Ni(tpyc)_2$ has been frequently observed[32,33] (an analogous behaviour is known for the $Ni(cptpy)_2$ species[34]) but this is the first occurrence in the present series. The terpy moieties do not interact with one another within the polymer chain but the packing (KPI, 0.62) results in TE interactions between chains adjacent along [010] (Ni···Ni distance, 8.3154(8) Å), with one parallel-displaced π-stacking interaction [centroid···centroid distance, 3.611(3) Å; dihedral angle, 8.4(3)°] and one CH···π interaction [H···centroid distance, 2.63 Å; C–H···centroid angle, 149°].

With the quite rigid 1,2,3-benzenetricarboxylate (1,2,3-btc^{3-}) ligand, a rather dramatic change in the nature of the product occurs, the complex $[Ni(tpycH)(H_2O)_3][UO_2(1,2,3\text{-}btc)]_2{\cdot}2H_2O$ (**7**) (Figure 8) having an ionic composition. The two independent uranyl ions are in similar environments, each being chelated by two carboxylate groups from two 1,2,3-btc^{3-} ligands forming two seven-membered rings and bound to a fifth carboxylate oxygen donor from a third ligand, thus giving a monoperiodic coordination polymer parallel to [10$\bar{1}$] of a form essentially identical to that known in association with various counterions or decorating cations.[73] This indication of a particular stability of the polymer may explain its resistance to incorporation of $Ni(tpyc)_2$ and its crystallization in association with a cation of dipositive charge involving the undeprotonated form of tpycH. The polymeric anion chain has a step profile, such that the chains lie side by side in sheets parallel to (010) where aromatic ring stacking is involved to both sides. The cations form stacked pairs with significant overlap in projection of the terpy sections and reciprocal hydrogen bonding interactions of coordinated water with the tpycH carbonyl oxygen atom [O···O, 2.711(4) Å; O–H···O 152(5)°]. These pairs lie in sheets

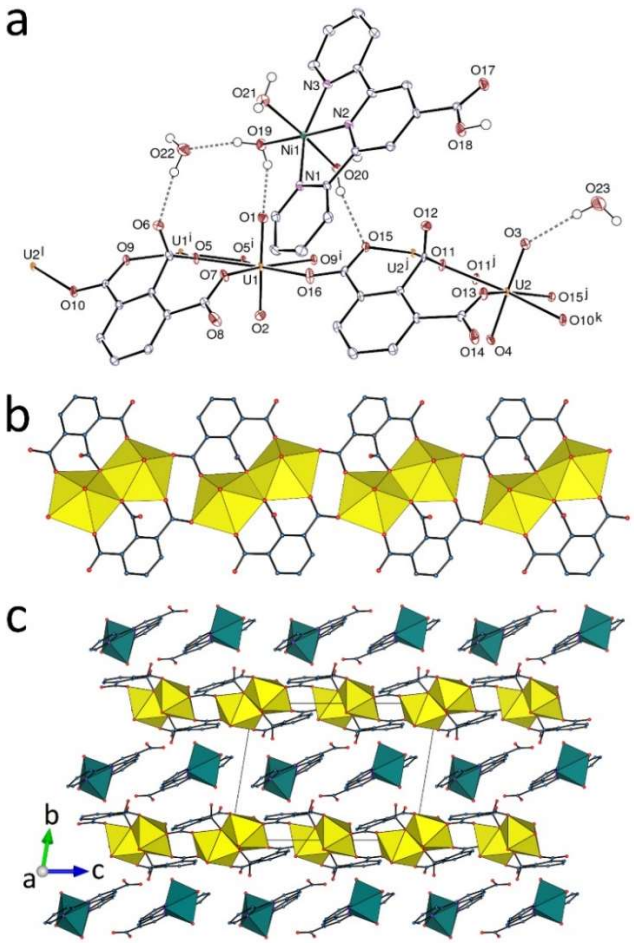

Figure 8. (a) View of compound **7**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: i = 1 – *x*, –*y*, –*z*; j = –*x*, –*y*, 1 – *z*; k = *x* – 1, *y*, *z* + 1; l = *x* + 1, *y*, *z* – 1. (b) View of the monoperiodic coordination polymer. (c) Packing with uranium coordination polyhedra yellow and those of nickel green.

between those of the anions, with the coordinated water molecules involved in additional hydrogen bonding interactions with uranyl oxo groups, carboxylate oxygen atoms of the anions and uncoordinated water molecules. The carboxylic group is hydrogen bonded to an uncoordinated carboxylate oxygen atom of the anion [O···O, 2.512(4) Å; O–H···O 166(7)°]. Two parallel-displaced π-stacking interactions associate 1,2,3-btc^{3-} ligands with one another or with a tpycH ligand [centroid···centroid distances, 3.783(2) and 3.941(2) Å; dihedral angles, 10.51(17) and 5.28(16)°]. With a KPI of 0.72, the packing does not display free spaces.

Diperiodic coordination polymers. The presence of the citrate ligand $Hcit^{3-}$, in which the hydroxyl group has been deprotonated but one carboxylate group retains a proton, has consequences somewhat similar to that of $123btc^{3-}$ in that an anionic uranyl citrate polymer is associated with a cationic polymer involving $Ni(tpyc)_2$ only as ligand, giving the complex $[UO_2Ni_2(tpyc)_4][UO_2(citH)]_2$ (**8**) shown in Figure 9. Again, the monoperiodic polymer chains, directed along [100], are of a familiar form, closely related to that of those known in various other uranyl citrate complexes.[74,75] The uranium atom bound to $Ni(tpyc)_2$ is disordered and its environment somewhat uncertain, but it appears to be chelated by one carboxylate group of $tpyc^-$ and bound to three more carboxylate donors from three other ligands, and it is thus a 4-c node in the diperiodic cationic polymer formed, which is parallel to (100). This network has the point symbol $\{4^4.6^2\}$ and the common **sql** topological type, as previously found in the complex $[UO_2Ni_2(tpyc)_4](I_3)_2$.[33] Due to the protruding terpyridine moieties, the size of the free space within the rings is however small, at ~8 × 15 $Å^2$, the elongated rings being arranged in herringbone fashion. The novelty of complex **8** is that it displays 1D + 2D semi-interpenetration (i.e. the two components can in principle be separated without the breakage of bonds) of the anionic polymers through the packed diperiodic networks (Figures 9b and 9c). The uranyl citrate ribbons in adjacent rows along [010] are tilted with respect to one another so as to accommodate the elongated shape of the spaces in the herringbone arrangement. The two components are tethered to each other through hydrogen bonding of the carboxylic group of $Hcit^{3-}$ to the uncoordinated carboxylate oxygen atom of $tpyc^-$ [O···O, 2.619(5) Å; O–H···O 160(6)°]. The $Ni(tpyc)_2$ units form undulating chains directed along [001] within the cationic sheets, in which TE interactions are found (Ni···Ni distance, 8.7590(3) Å), as well as between units in different sheets (Ni···Ni, 8.4733(2) Å) with in both cases one parallel-displaced π-stacking interaction [centroid···centroid distances, 3.906(3) and 3.495(2) Å; dihedral angles,

10.4(2) and 7.8(2)°] and one CH···π interaction [H···centroid distances, 2.76 and 2.84 Å; C–H···centroid angles, 147 and 145°]. Some voids are present in the packing (KPI, 0.61).

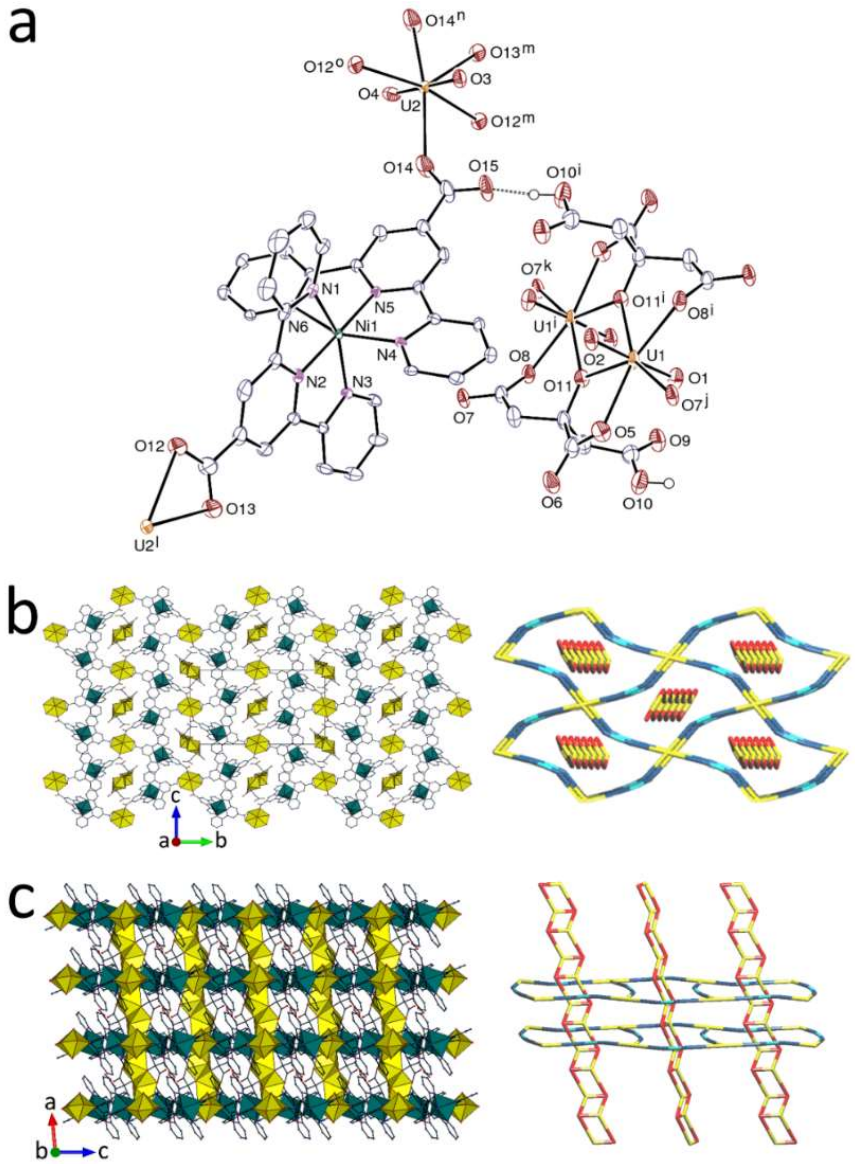

Figure 9. (a) View of compound **8**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and the hydrogen bond is shown as a dashed line. Only one position of the disordered atoms is shown. Symmetry codes: i = 1 – *x*, 1 – *y*, 1 – *z*; j = *x* + 1, *y*, *z*; k = –*x*, 1 – *y*, 1 – *z*; l = –*x*, *y* – 1/2, 3/2 – *z*; m = –*x*, *y* + 1/2, 3/2 – *z*; n = –*x*, 1 – *y*, 2 – *z*; o = *x*, 1/2 – *y*, *z* + 1/2. (b) Diperiodic network viewed side-on and monoperiodic chains viewed end-on, with uranium coordination polyhedra yellow and those of nickel green (left), and slightly rotated simplified view (right; uranium, yellow; nickel, light blue; tpyc^{-} ligands, dark blue; citH^{3-} ligands, red). (c) Packing with sheets viewed edge-on (left), and simplified view of the two assembled coordination polymers (right).

In passing to 1,2,3,4-butanetetracarboxylate (btc^{4-}), the complex formed, $[(UO_2)_2(btcH)Ni(tpyc)_2(NO_3)]$ (**9**), contains this ligand in its monoprotonated form and shows a return to the involvement of nitrate coordination (Figure 10). One of the two independent

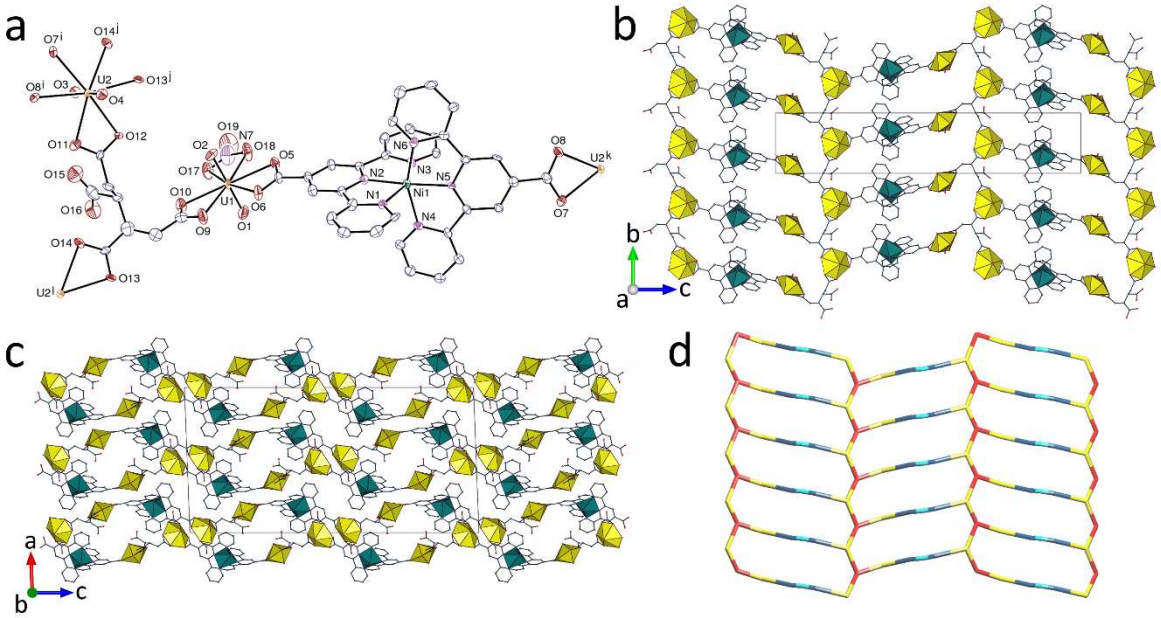

Figure 10. (a) View of compound **9**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted. Symmetry codes: i = *x*, 2 – *y*, *z* – 1/2; j = *x*, *y* + 1, *z*; k = *x*, 2 – *y*, *z* + 1/2; l = *x*, *y* – 1, *z*. (b) View of the diperiodic network with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with layers viewed edge-on. (d) Simplified view of the network (uranium, yellow; nickel, light blue; $tpyc^-$ ligands, dark blue; $btcH^{3-}$ ligands, red).

uranium atoms is chelated by one nitrate anion and two carboxylate groups from the two different ligands, and the other is chelated by two groups from two $btcH^{3-}$ ligands and one from $tpyc^-$, a situation analogous to that found in complexes **3**–**5**. Atom U2 and the $btcH^{3-}$ ligand are thus 3-c nodes in the diperiodic network formed, which is parallel to (100) and has the $\{6^3\}$ point symbol and the very common **hcb** topological type. The 48-membered cells of the honeycomb geometry are very elongated due to the presence of the U–(tpyc)–Ni–(tpyc) links, their length being ~23 Å. They differ from the rings in complexes **1**–**4** by one dicarboxylate

link being replaced by a (btcH)U(btcH) motif, so that the ring is here a dinickelapentauranacycle. The $Ni(tpyc)_2$ units are arranged in columns along [010], with the presence of intra-ring TE interactions (Ni···Ni distance, 9.1845(2) Å) involving one parallel-displaced π-stacking interaction [centroid···centroid distance, 4.135(5) Å; dihedral angle, 9.6(4)°], and the KPI of 0.60 indicates the presence of solvent-accessible voids.

Passing to the related system based on the corresponding cyclic, monoprotonated *cis,trans,cis*-1,2,3,4-cyclobutanetetracarboxylate ligand ($cbtcH^{3-}$), the complex isolated, $[(UO_2)_2(cbtcH)Ni(tpyc)_2(NO_3)]$ (**10**), has the same stoichiometry as **9**, and a structure only slightly different. The coordination mode is different from that in **9** only in that two of the carboxylate groups bound to U1 are here monodentate instead of chelating, and a water molecule completes the coordination sphere (Figure 11). The carboxylic group of $cbtcH^{3-}$ is

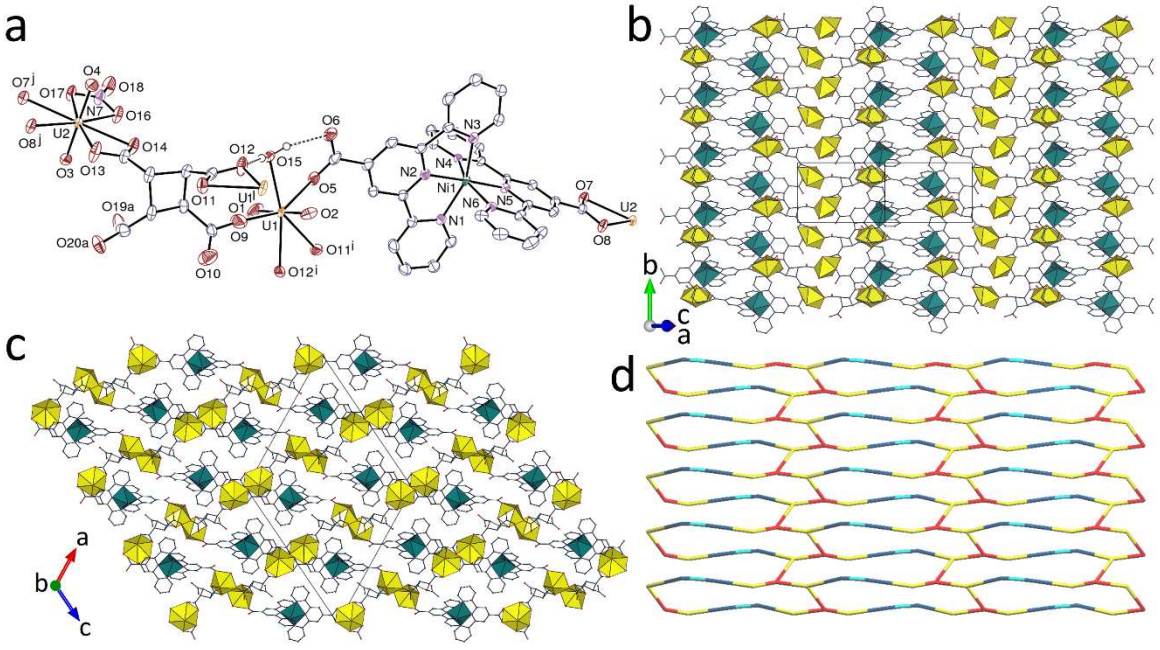

Figure 11. (a) View of compound **10**. Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Only one position of the disordered atoms is shown. Symmetry codes: i = 1 – *x*, *y* + 1/2, 3/2 – *z*; j = *x* + 1, *y*, *z* + 1; k = *x* – 1, *y*, *z* – 1; l = 1 – *x*, *y* – 1/2, 3/2 – *z*. (b) View of the diperiodic network with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with layers viewed edge-on. (d) Simplified view of the network (uranium, yellow; nickel, light blue; $tpyc^-$ ligands, dark blue; $cbtcH^{3-}$ ligands, red).

uncoordinated, so that both this ligand and atom U1 are 3-c nodes in the diperiodic polymer formed, which is parallel to (10$\bar{1}$) and has the same $\{6^3\}$ point symbol and **hcb** topological type as that in **9**. Here also, the rings are very elongated (~26 Å) and they include five uranium and two nickel atoms. Whereas the $Ni(tpyc)_2$ units are arranged into linear rows in **9**, they form zigzag arrangements along [010] in **10**. There is no twofold TE here, but only one parallel-displaced π-stacking interaction between ligands adjacent along [010] [centroid···centroid distance, 3.961(3) Å; dihedral angle, 0.3(3)°], and the KPI of 0.63 indicates the presence of significant voids.

In the structure of the complex $[(UO_2)_2(ndc)Ni(tpyc)_2(OH)(NO_3)]$ (**11**) obtained with the large, rigid aromatic 2,6-naphthalenedicarboxylate (ndc^{2-}), features seen in the previous complexes are augmented by the presence of bridging hydroxido ligands leading to the formation of dinuclear secondary building units (SBUs), which coexist with isolated uranyl moities. Both independent uranium atoms are chelated by one carboxylate group from one of the two centrosymmetric ndc^{2-} ligands, but U1 is further chelated by one carboxylate group from $tpyc^-$ and one nitrate anion, while U2 is bound to one monodentate carboxylate from $tpyc^-$ and two hydroxido anions, 7- and 8-coordination thus coexisting in the structure (Figure 12). If the dinuclear SBUs are considered as single, 4-c nodes, the diperiodic network formed, parallel to (10$\bar{1}$), has the **sql** topological type, with very elongated cells (~50 Å between outermost SBUs). The cyclic units are 100-membered tetranickeladecauranacycles. Equally elongated decauranacycles (~53 Å in length) have been found in a complex with sebacic acid,[7] but, to the best of our knowledge, cycles containing as many as 14 metal cations do not appear to have been reported in uranyl-based complexes. When viewed down [010], the sheets are sawtooth-shaped and terpy moieties pertaining to adjacent sheets are involved in a parallel-displaced π-stacking interaction [centroid···centroid distance, 3.632(6) Å; dihedral angle, 2.1(5)°], as well

as a CH···π interaction [H···centroid distance, 2.80 Å; C–H···centroid angle, 146°], the distance between the nickel centres being 8.7884(6) Å. There are also intra-sheet double π-stacking interactions between ndc^{2-} and two $tpyc^{-}$ moieties located on either side of it [centroid···centroid distances, 3.636(6) and 3.695(6) Å; dihedral angle, 11.0(5)° for both]. The KPI of 0.58 indicates the presence of large solvent-accessible voids.

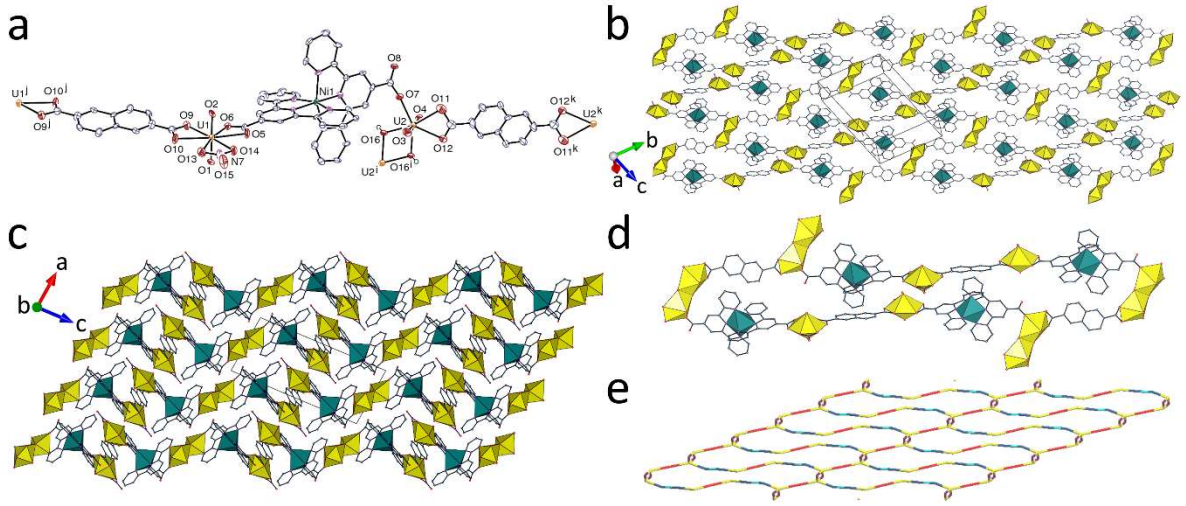

Figure 12. (a) View of compound **11**. Displacement ellipsoids are drawn at the 50% probability level and carbon-bound hydrogen atoms are omitted. Symmetry codes: i = 1 – *x*, 1 – *y*, –*z*; j = 2 – *x*, 3 – *y*, 1 – *z*; k = 1 – *x*, –*y*, –*z*. (b) View of the diperiodic network with uranium coordination polyhedra yellow and those of nickel green. (c) Packing with layers viewed edge-on. (d) View of one 14-nuclear ring. (e) Simplified view of the network (uranium, yellow; nickel, light blue; $tpyc^{-}$ ligands, dark blue; 2,6-ndc^{2-} ligands, red; hydroxide groups, orange).

The complex incorporating enantiomerically pure *trans-R,R*-1,2-cyclohexanedicarboxylate (*t-R*-1,2-$chdc^{2-}$), $[(UO_2)_4(t\text{-}R\text{-}1,2\text{-}chdc)_4Ni_2(tpyc)_4]$ (**12**), has some points in common with complex **1** involving *c*-1,2-$chdc^{2-}$, but the stoichiometry is different and the absence of terminal nitrate anions leads to an increased periodicity. Complex **12** crystallizes in the Sohncke group $C222_1$, and the four independent uranyl cations are all in similar environments, being κ^2O,O'-chelated by two carboxylate groups from *t-R*-1,2-$chdc^{2-}$ ligands and one from $tpyc^{-}$ (Figure 13). Hexanuclear, 42-membered rings analogous to those in **1** are

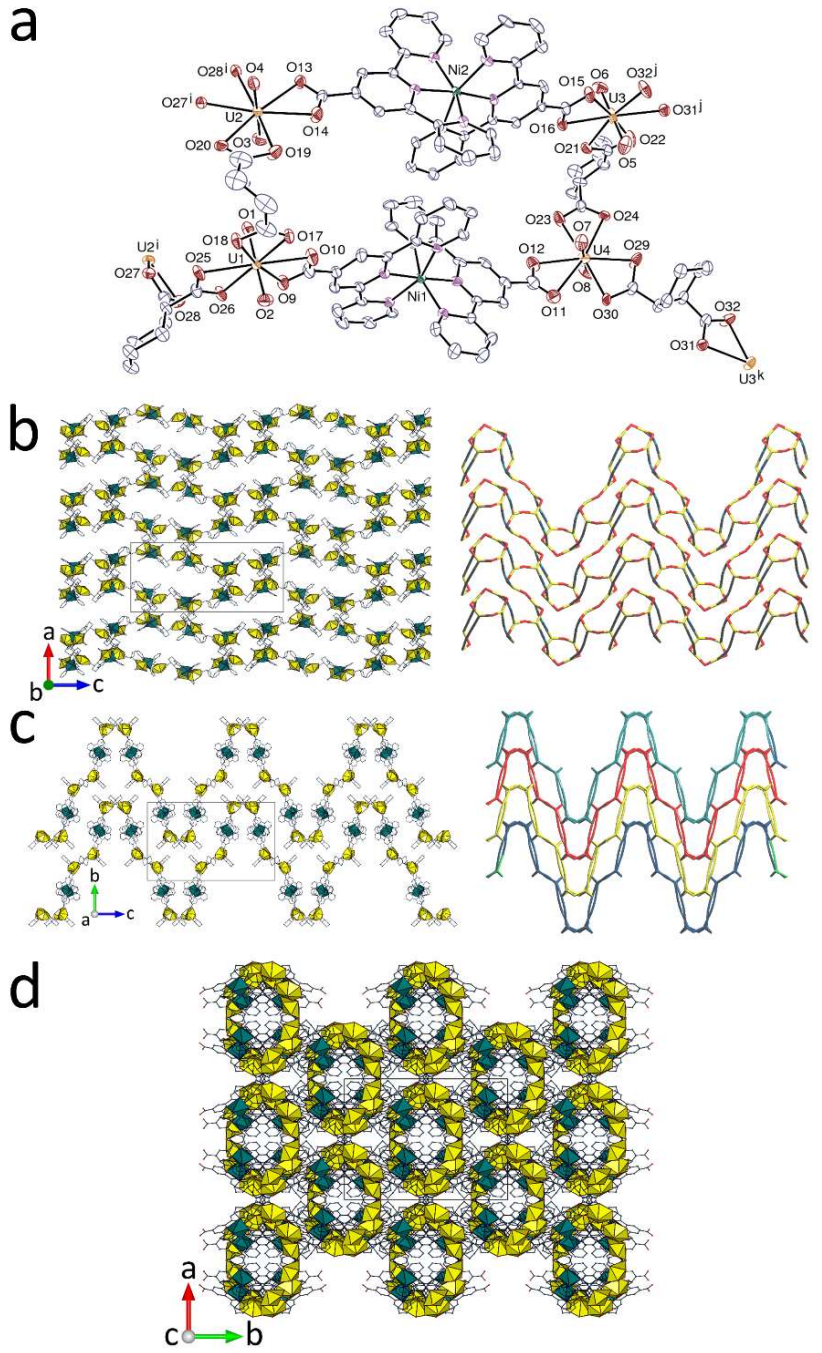

Figure 13. (a) View of compound **12**. Displacement ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted. Only one position of the disordered atoms is shown. Symmetry codes: i = 1 – *x*, *y*, 3/2 – *z*; j = *x* – 1/2, 1/2 – *y*, 1 – *z*; k = *x* + 1/2, 1/2 – *y*, 1 – *z*. (b) View of the diperiodic network with uranium coordination polyhedra yellow and those of nickel green (left), and slightly rotated simplified view (right; uranium, yellow; nickel, light blue; tpyc^{-} ligands, dark blue; *t*-*R*-1,2-chdc^{2-} ligands, red). (c) Two layers viewed edge-on, with one intermediate layer omitted for clarity (left), and simplified view of four interlocked layers (right). (d) Another view of the packing with layers viewed edge-on.

formed, but instead of being isolated, they are part of a 2-nodal diperiodic network parallel to (010), in which the uranium atoms are separated into two kinds of 3-c nodes, and which has the point symbol $\{4.12^2\}\{4^2.6\}$. Apart from the hexanuclear rings, tetrauranacycles with twofold rotation symmetry are present, which involve atoms U1 and U2 and their symmetry equivalents and *t*-*R*-1,2-chdc^{2-} bridges only, as well as larger, saddle-shaped rings containing twelve uranium and four nickel centres. The *t*-*R*-1,2-chdc^{2-} ligands in the tetrauranacyclic units are in a chair conformation with the carboxylate groups equatorial. The assembly can be seen as built from somewhat sinusoidal chains directed along [001] and containing both carboxylate ligands, cross-linked to one another in the [100] direction by *t*-*R*-1,2-chdc^{2-} ligands only. In the central, mean plane of the polymer, U3 and U4 and their symmetry equivalents are linked into an infinite right-handed helical array intersecting the sinusoidal chains by *t*-*R*-1,2-chdc^{2-} units which alternate in conformation between diequatorial and (disordered) diaxial. The sheets are thus very strongly puckered, the outermost points corresponding to the tetrauranacyclic units being separated by ~41 Å, and they pack with pronounced interlocking, each layer encompassing part of its two neighbours on each side along [010]. In projection down [001], the packing displays an annular-like arrangement of the metal atoms. TE interactions with a Ni···Ni distance of 8.9028(15) Å are found within the hexanuclear rings [centroid···centroid distance, 3.682(5) Å; dihedral angle, 2.4(5)°], as well as CH···π interactions [H···centroid distances, 2.80 and 2.41 Å; C–H···centroid angles, 177 and 169°]. The KPI of 0.49 indicates the presence of large voids occupied by disordered water molecules, in agreement with elemental analysis results (see Experimental Section).

The complex $[(UO_2)_4(1,3\text{-pda})_4Ni_2(tpyc)_4]\cdot CH_3CN\cdot 2H_2O$ (**13**) involves 1,3-phenylenediacetate (1,3-pda^{2-}), an isomer of 1,2-pda^{2-} giving the monoperiodic complex **5**, of quite different composition; nitrate is no longer present here and the structure is considerably more complicated than that of **5**. Complex **13** crystallizes in the Sohncke group *Pc* with four

independent uranium atoms in the asymmetric unit, all of them $\kappa^2 O,O'$-chelated by two carboxylate groups from two 1,3-pda^{2-} ligands and one from tpyc^{-} (Figure 14). The uranium

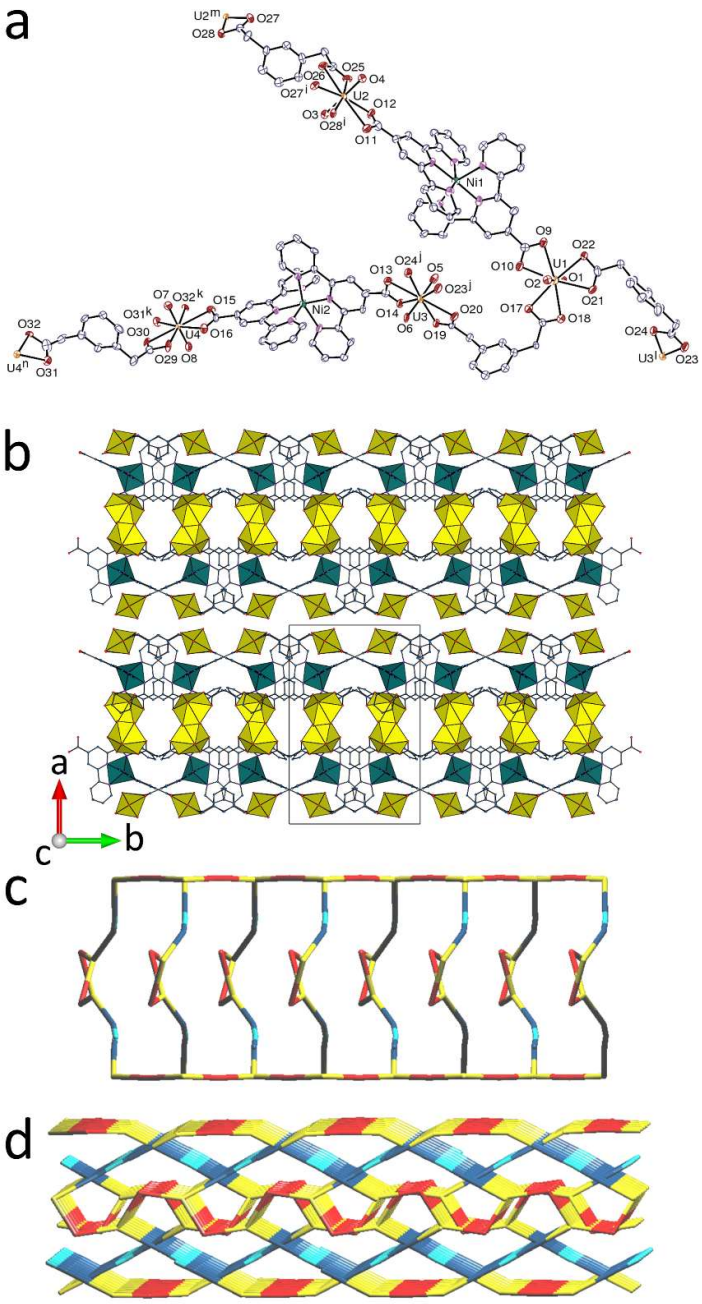

Figure 14. (a) View of compound **13**. Displacement ellipsoids are drawn at the 30% probability level. Solvent molecules and hydrogen atoms are omitted. Only one position of the disordered atoms is shown. Symmetry codes: i = *x*, –*y*, *z* – 1/2; j = *x*, *y* – 1, *z*; k = *x*, –*y* – 1, *z* + 1/2; l = *x*, *y* + 1, *z*; m = *x*, –*y*, *z* + 1/2; n = *x*, –*y* – 1, *z* – 1/2. (b) Packing with two layers viewed edge-on. Uranium coordination polyhedra are yellow and those of nickel green. (c) and (d) Simplified views of the diperiodic assembly down [010] with [001] horizontal, and down a direction slightly rotated from that in b (uranium, yellow; nickel, light blue; tpyc^{-} ligands, dark blue; 1,3-pda^{2-} ligands, red).

atoms are thus 3-c nodes while all the other components are simple links. The uninodal coordination polymer formed is diperiodic and parallel to (100), and it has the $\{8^2.10\}$ point symbol and the KIa topological type. The same topology has previously been found in other uranyl ion complexes with elongated ligands such as glutarate,[76] 1,13-tridecanedioate,[77] and 1,15-pentadecanedioate.[78] The layers are very thick (~22 Å) and they display two sets of UO_2(1,3-pda) polymers on both surfaces, another set of such a polymer in the centre, and the bridging $Ni(tpyc)_2$ units in between. The outermost UO_2(1,3-pda) polymers, which include atoms U2, U4 and their symmetry equivalents, are chains with a square-wave profile running along [001], while the central polymers are zigzag or flattened helical chains directed along [010] and including U1 and U3. These two families of chains, with the lateral ones orthogonal to the central ones, are connected to one another by the $Ni(tpyc)_2$ pillars, thus generating the diperiodic network. The KPI of 0.64 indicates that solvent molecules in excess of those found in the structure determination must be present (see Experimental Section), so that the role of hydrogen bonding interactions in the formation of the network is uncertain. There are no TE interactions here, the only parallel-displaced π-stacking and CH···π interactions being between 1,3-pda^{2-} and $tpyc^-$ [centroid···centroid distances, 3.615(12)–3.855(14) Å; dihedral angles, 4–11°; H···centroid distances, 2.90–2.97 Å; C–H···centroid angles, 167–169°]. The π-stacking interactions are simply pairwise for the central chains but they extend along [001] for the lateral chains, with the terpy aromatic rings involved inserted within the square wave part of the chains.

Triperiodic framework. While the oxophilicity of U^{VI} results in its strong bonding to carboxylato donors, the azophilicity of Ni^{II} may explain the particular nature of the complex isolated when nitrilotriacetate (nta^{3-}) was used as another functionalized tricarboxylate. Thus, the asymmetric unit in the complex $[(UO_2)_2(nta)_2Ni_2(tpyc)_2]$ (**14**) contains one uranyl cation,

one $Ni(tpyc)_2$ moiety with twofold rotation symmetry, and one nta^{3-} anion, as expected, plus a second Ni^{II} cation located on an inversion centre and bound to two nta^{3-} anions (Figure 15).

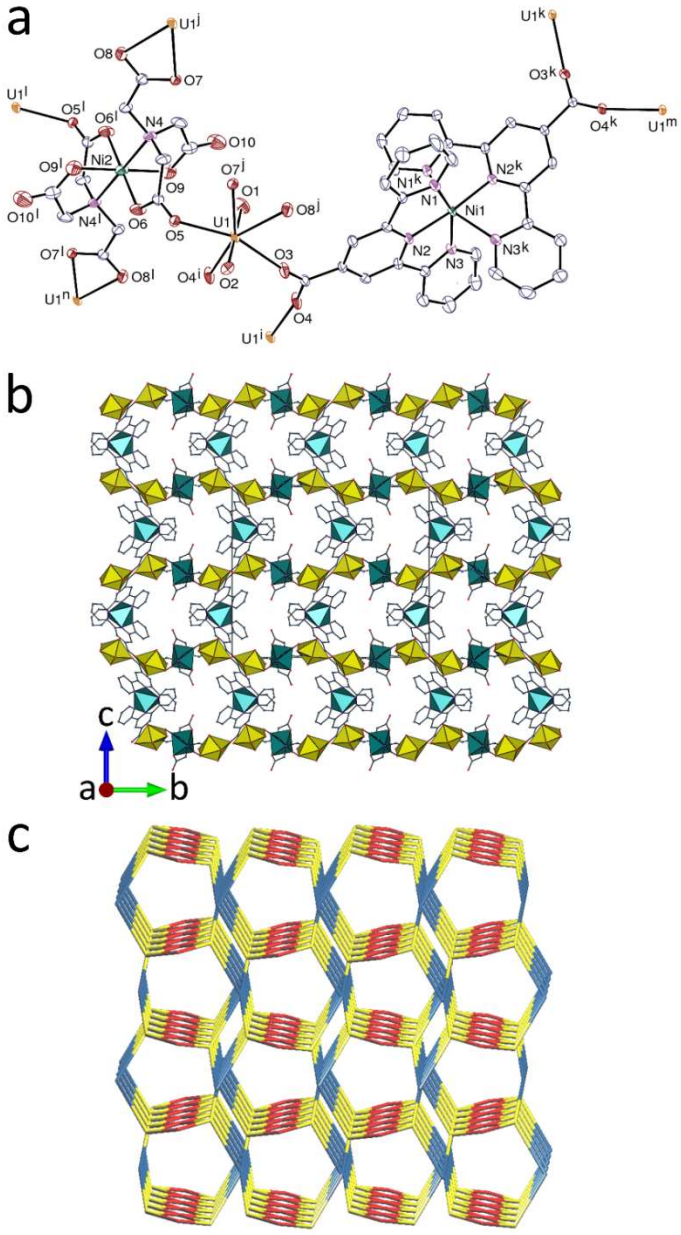

Figure 15. (a) View of compound **14**. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted. Symmetry codes: i = –*x*, 1 – *y*, 1 – *z*; j = 1/2 – *x*, 3/2 – *y*, 1 – *z*; k = 1 – *x*, *y*, 1/2 – *z*; l = –*x* – 1/2, 3/2 – *y*, 1 – *z*; m = *x* + 1, 1 – *y*, *z* – 1/2; n = *x* – 1, *y*, *z*. (b) View of the three-periodic framework with uranium coordination polyhedra yellow and those of nickel green. (c) Nodal representation of the framework, slightly rotated with respect to the orientation in b (uranium, yellow; $Ni(tpyc)_2$ nodes, dark blue; $Ni(nta)_2^{4-}$ nodes, red).

The uranium atom is chelated by one carboxylate group from nta^{3-} and bound to three more oxygen donors from two $tpyc^{-}$ and one nta^{3-} anions. Ni2 is in a *trans*-N_2O_4 octahedral environment [Ni–O, 2.021(3) and 2.039(3) Å, Ni–N, 2.096(3) Å]. Uranium and nickel bonding modes are thus in agreement with expectations based on the "soft" and "hard" characters of the donors.[79,80] The carboxylate group of $tpyc^{-}$ is bridging two uranium atoms in the μ_2-κ^1O:κ^1O' mode, while one carboxylate group of nta^{3-}, directed away from the nickel atom, is κ^2O,O'-chelating uranium, another is bridging uranium and nickel centres in the *anti/anti* μ_2-κ^1O:κ^1O' mode, and the last is monodentate on the same nickel atom, each nta^{3-} being thus bound to three metal cations. If $Ni(tpyc)_2$ and $Ni(nta)_2^{4-}$ are considered as 4-c nodes, together with uranium atoms which are also 4-c nodes, the framework is 3-nodal and it has the $\{4^2.8^3.10\}\{4^2.8^4\}_3$ point symbol. There are no TE interactions here, all distances between aromatic ring centroids being larger than 4.5 Å and Ni···Ni distances larger than 9.9 Å. An interaction between the uranyl oxo group O2 and one aromatic ring is notable [O···centroid distance, 3.062(6) Å; U=O···centroid angle, 133.97(13)°]. Chains of uranyl ions and $Ni(tpyc)_2$ ligands are arranged in sheets parallel to (010), the $Ni(nta)_2^{4-}$ units bridging these chains to form the triperiodic assembly. Small channels run along [100], and the KPI is 0.60, disordered solvent molecules being present.

Discussion of the structures. In 12 of the complexes reported here, the $Ni(tpyc)_2$ "expanded ligand" connects two uranyl cations, most often in the bis(κ^2O,O')-chelating mode, with rarer occurrences of monodentate ligation (Table 4), and it is thus a divergent, quasi-linear linker. Only in the unique triperiodic complex (**14**) does it display the bis(μ_2-κ^1O:κ^1O')-bridging mode, thus turning into a 4-c node. The quasi-linear (UO_2)–[$Ni(tpyc)_2$]–(UO_2) motif is thus nearly ubiquitous in this family of complexes. Due to the variety of their geometry,

Table 4. Principal Characteristics of the Complexes Reported

Compound	Polycarboxylate ligand (L)	Coordination mode of uranium by $Ni(tpyc)_2$	Topological connectivity U	L	Periodicity	Geometrical features
1	*c*-1,2-chdc^{2-}	bis(κ^2O,O')	2-c	2-c	0	discrete U_4Ni_2 ring
2	tdc^{2-}	bis(κ^2O,O')	2-c	2-c	0	discrete U_4Ni_2 ring
3	bdc^{2-}	bis(κ^2O,O')	2/3-c	2-c	1	U_4Ni_2 rings in daisychain
4	tca^{3-}	bis(κ^2O,O')	2/3-c	3-c	1	U_4Ni_2 ring-based nanotubes
5	1,2-pda^{2-}	bis(κ^2O,O')	2/3-c	2-c	1	semi-U_4Ni_2 rings in zigzag chain
6	ox^{2-}	bis(κ^1O)	3-c	2-c	1	chain with U_4Ni rings
7	1,2,3-btc^{3-}		3-c	3-c	1	anionic chain and separated cations
8	citH^{3-}	κ^1O; κ^2O,O'	3-c	3-c	1 + 2	semi-interpenetration
9	btcH^{3-}	bis(κ^2O,O')	2/3-c	3-c	2	**hcb** network with U_5Ni_2 rings
10	cbtcH^{3-}	κ^1O; κ^2O,O'	2/3-c	3-c	2	**hcb** network with U_5Ni_2 rings
11	ndc^{2-}	κ^1O; κ^2O,O'	2/4-c[a]	2-c	2	**sql** network with $U_{10}Ni_4$ rings
12	*t-R*-1,2-chdc^{2-}	bis(κ^2O,O')	3-c	2-c	2	network with U_4Ni_2 rings
13	1,3-pda^{2-}	bis(κ^2O,O')	3-c	2-c	2	KIa network
14	nta^{3-}	bis(μ_2-κ^1O:κ^1O')	4-c	4-c[b]	3	framework including $Ni(nta)_2^{4-}$ nodes

[a] 4-c refers to dinuclear nodes. [b] Connectivity of the $Ni(nta)_2^{4-}$ node.

number of coordination sites, and involvement in weak interactions, the roles of the polycarboxylate ligands are more diverse. The dicarboxylates *c*-1,2-chdc^{2-}, tdc^{2-}, bdc^{2-} and *t-R*-1,2-chdc^{2-} lead to the formation of U_4Ni_2 rings which are either discrete in the first two cases, or part of mono- or diperiodic coordination polymers in the two last cases, respectively. In these complexes, the dicarboxylate ligand is always 2-c, and thus a simple link, while uranium is 2-c if chelated by nitrate, or a 3-c node if not, which results in periodicity increase. Only in some of these cases are intra-ring TE interactions present, which shows that these are not required for ring stabilization. Similar rings are found with tca^{3-}, but this tricarboxylate ligand is a 3-c node, and a ring-based nanotubular assembly is formed. A closely related semi-cyclic arrangement is found with 1,2-pda^{2-}, which is part of a meander-like chain. That closed species are obtained with convergent ligands such as *c*-1,2-chdc^{2-}, *t-R*-1,2-chdc^{2-} and tca^{3-} is not particularly surprising since these ligands have previously been shown to give uranyl ion complexes crystallizing as polynuclear cage-like or nanotubular species,[60,62,81–84] the $Ni(tpyc)_2$ connector

introducing a larger separation between metal atoms. The formation of rings in the case of the divergent bdc^{2-} is more unusual since this ligand is akin to *t*-1,4-$chdc^{2-}$, which gives a simple chain under similar conditions;[33] the presence of CH···π interactions in the case of bdc^{2-} possibly plays a role here. The rigid 1,2,3-btc^{3-} ligand yields a complex in which uranium and nickel are in separated, charged entities. Separation of charges is also found with $citH^{3-}$, but here semi-interpenetration of monoperiodic, anionic uranyl citrate chains into a diperiodic, cationic **sql** network incorporating uranyl and $Ni(tpyc)_2$ is observed. The formation of rather similar uranyl-based monoperiodic polymers with 1,2,3-btc^{3-} and $citH^{3-}$ is in keeping with the previously noted relatedness of these two ligands in their uranyl ion complexes.[73] More usual **hcb** diperiodic networks are found with $btcH^{3-}$ and $cbtcH^{3-}$, in which these ligands are 3-c nodes only due to the carboxylic group being uncoordinated, which prevents formation of a triperiodic framework. Other diperiodic networks, with the **sql** or KIa topologies, are formed with the dicarboxylates ndc^{2-} and 1,3-pda^{2-} acting as simple links. Due to the length of the $Ni(tpyc)_2$ linkers, the rings formed in these species are generally very elongated, the maximum extent being found in the $U_{10}Ni_5$ rings in complex **11**. The tricarboxylate nta^{3-} coordinates both uranium and nickel atoms, and is part of a $Ni(nta)_2^{4-}$ 4-c node which, together with uranium and $Ni(tpyc)_2$ 4-c nodes, generates a triperiodic framework.

In all but two instances (complexes **13** and **14**), a degree of association or interlocking of $Ni(tpyc)_2$ units is apparent which resembles that described as the "terpyridine embrace" although here it does not extend beyond pairwise or extended linear arrays. In complex **13**, π-stacking does occur but it associates $tpyc^-$ and 1,3-pda^{2-} units, whereas in complex **14** the uranyl oxo interaction with $tpyc^-$ blocks the approach of other $tpyc^-$ units. In **5**, $tpyc^-$ units have a small degree of facial overlap accompanied by facial overlaps with both the 1,2-pda^{2-} and 1,2-$pdaH^-$ units in a structure which illustrates well how multiple weak interactions attain a unique balance in every crystal. The 4′-carboxylate group of course renders $tpyc^-$ a different stacking entity to

2,2;6′,2″-terpyridine itself and in all but two of the present structures (that of **13**, where $tpyc^-$ self-association is disrupted by that with 1,3-pda^{2-}, and that of **7**, where there are no $Ni(tpyc)_2$ units) the $O_2C\cdots Ni\cdots CO_2$ axes of the closest $Ni(tpyc)_2$ pairs lie close to parallel. While details of the crystal formation mechanism are unknown, an $[Ni(tpyc)_2]_2$ pair with parallel axes places carboxylate group pairs with a separation ~7–8 Å, a distance compatible with bridging by various U–(bridging ligand)–U units, which might suggest the involvement of an embracing $[Ni(tpyc)_2]_2$ pair in the initial steps of formation of cyclic units, but not necessarily in their final form, as shown by the existence of such units devoid of intra-ring TE interactions.

CONCLUSION

We have reported the synthesis and crystal structure of 14 uranyl ion complexes involving the $Ni(tpyc)_2$ zwitterionic assembler and a diverse set of polycarboxylate ligands intended to form neutral coordination polymers, an objective met in all but two cases in which separate charged species are obtained. The presence of the $Ni(tpyc)_2$ unit in all but one of the present structures shows that it can be used as a stable divergent dicarboxylate ligand, with a separation of ~13 Å between the oxygen atoms of the two bonding sites, in varied coordination polymer systems and in particular can be employed to add variety to anionic polycarboxylate structures. One of its most notable properties is to organize most often into parallel arrangements with frequent occurrences of TE interactions. The use of di-, tri- and tetracarboxylate ligands displaying a large range of geometries has allowed the isolation of complexes with periodicities varying from zero to three and various geometrical or topological features. Under the particular solvo-hydrothermal conditions of synthesis employed, a preferred arrangement in this system appears to be in the form of U_4Ni_2 metallacycles, these being either discrete or part of mono- or diperiodic coordination polymers. Other metallacycles, U_4Ni, U_5Ni_2 and $U_{10}Ni_4$, are also found

within mono- or diperiodic polymers, the last one displaying a high degree of elongation. While large heterometallacycles have been found in the structures of a variety of other uranyl ion coordination polymers,[3] the adoption of a roughly rectangular form is unique to the present species and may be a consequence of the long, rod-like nature of the $Ni(tpyc)_2$ links.

Although $Ni(tpyc)_2$ has proven to be useful in defining the prospects in combining a neutral, zwitterionic dicarboxylate with polycarboxylate anions for the formation of uranyl ion coordination polymers, it has the disadvantage that the strong absorption of $Ni(tpyc)_2$ at the wavelengths useful for uranyl ion excitation leads to the quenching of uranyl ion emission. Replacement of Ni^{II} by Zn^{II} may solve this problem but the fact that only a single triperiodic structure with rather small internal cavities has been found so far in the Ni^{II} systems indicates that either larger zwitterions or larger coligands must be found in order to generate solids with cavities present favouring potential applications as photo-oxidation catalysts.

ASSOCIATED CONTENT

Accession Codes

CCDC 2163681−2163686, 2163690−2163695, 2163697 and 2163698 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.

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Notes

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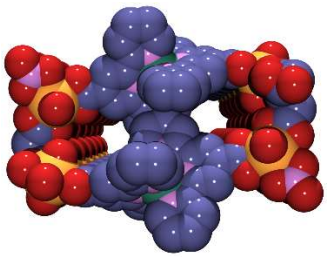
Ni(2,2′:6′,2″-terpyridine-4′-carboxylate)$_2$ Zwitterions and Carboxylate Polyanions in Mixed-Ligand Uranyl Ion Complexes with a Wide Range of Topologies

Pierre Thuéry and Jack Harrowfield



Ni(2,2′:6′,2″-terpyridine-4′-carboxylate)$_2$ has been used as a neutral, "expanded" coligand to generate a family of heterometallic, mixed ligand uranyl polycarboxylate complexes which display a variety of periodicities and geometries. Most notable is the formation of dinickelatetrauranacycles which are found in discrete as well as polymeric mono- and diperiodic species.