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Sotaro Kusumoto, Yoshihiro Koide, Shinya Hayami, Yang Kim, Jack Harrowfield, et al.. Synthesis of crystalline uranyl ion coordination polymers with zwitterionic carboxylate ligands: comparing solvothermal and ambient conditions. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, 2024, 2024, pp.10.1007/s10847-024-01261-1. 10.1007/s10847-024-01261-1 . hal-04745844

HAL Id: hal-04745844

<https://hal.science/hal-04745844v1>

Submitted on 21 Oct 2024

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Synthesis of crystalline uranyl ion coordination polymers with zwitterionic carboxylate ligands: Comparing solvothermal and ambient conditions

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Dedicated to Dr. Jack M. Harrowfield on the occasion of his 80th birthday.

Abstract

Two neutral, dizwitterionic dicarboxylates, *N,N,N',N'*-tetramethylethane-1,2-diammonioacetate (L1) and biphenyl-4,4'-diyl-bis(4-carboxylatopyridiniomethylene) (L2), have been used as ligands in syntheses of uranyl ion complexes which exemplify the effect of different reaction conditions. $[\text{UO}_2(\text{L1})\text{Cl}_2]\cdot\text{H}_2\text{O}$ (**1**) has been crystallized at room temperature and is a simple monoperiodic coordination polymer. In contrast, $[(\text{UO}_2)_4(\text{O})_2(\text{OH})_2(\text{C}_2\text{O}_4)(\text{L1})_2]\cdot 4\text{H}_2\text{O}$ (**2**), obtained under solvo-hydrothermal conditions, contains a tetranuclear, bis(μ_3 -oxido)-bridged cluster resulting from uranyl hydrolysis, and additional oxalate coligands most likely due to oxidative degradation of L1, and it crystallizes as a diperiodic coordination polymer with tetranuclear nodes and the **sql** topology. The same arrangement is found in $[(\text{UO}_2)_4(\text{O})_2(\text{OH})_2(\text{L2})_3](\text{I}_3)_2\cdot 6\text{H}_2\text{O}$ (**3**), also synthesized under solvo-hydrothermal conditions, but here the more oxidation-resistant ligand does not generate oxalate, and replacement of the latter by neutral L2 bridges makes this complex cationic. The very large cells of the network in **3** ($\sim 22 \text{ \AA} \times 39 \text{ \AA}$) accommodate the triiodide anions formed *in situ*.

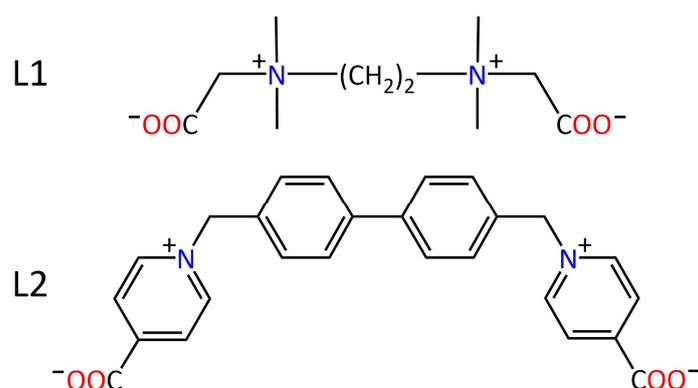
Keywords Uranyl ion · Zwitterionic ligands · Coordination polymer · Structure elucidation

Introduction

Solvothermal methods [1–4], very commonly involving reactions in mixed solvents under moderately elevated temperatures and pressures, have proved widely successful in generating crystalline forms of highly insoluble species such as coordination polymers and frameworks [5–7]. This success is partly due to their efficacy in forming initially homogeneous solutions from reactants with quite opposed solubility characteristics in any pure single solvent. Nonetheless, disadvantages arise from use of forcing conditions in that reactions other than coordination and crystallization may occur [1–4]. In our own work focussed on uranyl ion coordination polymers and frameworks, for example, we have encountered complications arising from organic cosolvent hydrolysis [8], intramolecular ligand reactions [9,10], ligand nitration [11], ligand decarboxylation [12], and ligand oxidation (partial [13] and degradative [11,14,15], formation of oxalate, in particular, having been investigated in some detail by others [16–18]). It is important to note, however, that these complications often allow the isolation of original, if unexpected, compounds, whether they provide additional ligands or counterions. The example of the formate ligand and the very common dimethylammonium counterion, both resulting from *N,N*-dimethylformamide hydrolysis, is a case in point. So, instead of being a mere drawback, these *in situ* reactions can be considered an asset, with the possibility of different species being obtained under modification of the experimental conditions. We describe here an illustration of this point with three uranyl ion complexes involving two neutral, dizwitterionic dicarboxylates pertaining to a family of ligands which has recently attracted some attention [11,12,15,19,20].

These two ligands, shown in Scheme 1, are *N,N,N',N'*-tetramethylethane-1,2-diammonioacetate (L1) and biphenyl-4,4'-diyl-bis(4-carboxylatopyridiniummethylene) (L2). The “double betaine” L1 was first structurally investigated by Mak et al., both free and complexed to Na^+ or Hg^{2+} [21–23], and a series of uranyl ion complexes, most of them mixed-

ligand species involving diverse anionic polycarboxylate coligands, has been reported more recently [11]. No example of a uranyl ion complex with the pyridinium-based L2 is known, and the Cambridge Structural Database (CSD, Version 5.45) [24] reports only some complexes of transition metal cations [25–28]. Of the two uranyl ion complexes of L1 described here, one has been synthesized under ambient and the other under solvo-hydrothermal conditions, the latter displaying additional oxalate ligands and formation of a tetranuclear cluster through uranyl hydrolysis. An analogous cluster is found with ligand L2, but oxalate is absent in this case. All three complexes were characterized by their crystal structure.



Scheme 1 The dizwitterionic, dicarboxylate ligands L1 and L2.

Experimental section

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.

Dioxouranium(VI) nitrate hexahydrate, $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (RP Normapur, 99%), was purchased from Prolabo. *N,N,N',N'*-Tetramethylethane-1,2-diammonioacetic acid dichloride ($\text{L1H}_2\text{Cl}_2$) was prepared as previously reported [11,29], and its ^1H -NMR spectrum was measured by dissolving the product in D_2O (Figure S1, Supplementary Information).

Biphenyl-4,4'-diyl-bis(4-carboxypyridiniummethylene) dichloride (L2H₂Cl₂) was prepared by a slight modification of the reported method [25]. 4,4'-Bis(chloromethyl)biphenyl (1.25 g, 5 mmol) and isonicotinic acid (1.85 g, 15 mmol) were dissolved in acetonitrile (40 mL) and heated at 110 °C overnight. After cooling, the resulting precipitate was filtered and washed with acetonitrile before drying under vacuum to give a white powder (2.2 g, 89%). The ¹H-NMR spectrum of L2H₂Cl₂ was measured by dissolving the product in DMSO-*d*₆ (Figure S2, Supplementary Information).

[UO₂Cl₂(L1)]·H₂O (1). L1H₂Cl₂ (16 mg, 0.05 mmol) and Na₂CO₃ (5 mg, 0.05 mmol) were mixed with water (1 mL) to give a colourless solution after effervescence had subsided. Addition of [UO₂(NO₃)₂(H₂O)₂]·4H₂O (25 mg, 0.05 mmol) gave a pale yellow solution that was then allowed to evaporate slowly at room temperature, providing, at near dryness, pale yellow crystals of **1** that were separated manually from colourless crystals of NaNO₃.

[(UO₂)₄(O)₂(OH)₂(C₂O₄)(L1)₂]·4H₂O (2). L1H₂Cl₂ (16 mg, 0.05 mmol) and [UO₂(NO₃)₂(H₂O)₂]·4H₂O (25 mg, 0.05 mmol) were dissolved in a mixture of water (0.4 mL) and acetonitrile (0.2 mL). The solution was placed in a 10 mL tightly closed glass vessel and heated at 140 °C in a sand bath under autogenous pressure. A few yellow crystals of complex **2** were deposited under the reaction conditions (and not from subsequent cooling and depressurization) within three months.

[(UO₂)₄(O)₂(OH)₂(L2)₃](I₃)₂·6H₂O (3). L2H₂Cl₂ (25 mg, 0.05 mmol), [UO₂(NO₃)₂(H₂O)₂]·4H₂O (25 mg, 0.05 mmol), and CsI (26 mg, 0.10 mmol) were dissolved in a mixture of water (0.8 mL) and acetonitrile (0.2 mL). The solution was placed in a 10 mL tightly closed glass vessel and heated at 140 °C in a sand bath under autogenous pressure. A

few yellow crystals of complex **3** were deposited under the reaction conditions (and not from subsequent cooling and depressurization) within two days.

Crystallography

The data were collected at 100(2) K on a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source ($I\mu\text{S}$ 3.0 Mo) and a PHOTON III area detector and operated through the APEX4 software [30]. The data were processed with SAINT [31], and absorption effects were empirically corrected with SADABS [32,33]. The structures were solved by intrinsic phasing with SHELXT [34] and refined by full-matrix least-squares on F^2 with SHELXL [35], using the ShelXle interface [36]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on residual electron density maps (except for those of one water molecule in **3**), and they were refined either freely (**1**) or with geometrical restraints (**2** and **3**). All other 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). The I_3^- anion in **3** is disordered over two positions which have been refined with occupancy parameters constrained to sum to unity and restraints on displacement parameters. Some voids in the structures of compounds **2** and **3** contain disordered solvent molecules which could not be modeled satisfactorily, and the SQUEEZE software [37] was used to subtract their contribution to the structure factors; 14 and 30 electrons were added per formula unit in **2** and **3**, respectively, amounting to about 1.5 and 3 H_2O molecules. Crystal data and structure refinement parameters are given in Table 1. Drawings were made with ORTEP-3 [38,39] and VESTA [40].

Table 1 Crystal data and structure refinement details

Complex	1	2	3
Chemical formula	C ₁₀ H ₂₂ Cl ₂ N ₂ O ₇ U	C ₂₂ H ₅₀ N ₄ O ₂₈ U ₄	C ₇₈ H ₇₄ I ₆ N ₆ O ₃₀ U ₄
<i>M</i> (g mol ⁻¹)	591.22	1770.78	3288.95
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.2457(4)	9.0005(3)	10.0860(3)
<i>b</i> (Å)	11.9752(4)	9.9276(3)	15.7831(5)
<i>c</i> (Å)	15.8329(6)	12.4804(4)	17.1230(5)
α (°)	90	72.2167(11)	103.9954(17)
β (°)	105.0981(16)	83.2707(11)	103.9056(17)
γ (°)	90	84.2863(11)	106.4189(17)
<i>V</i> (Å ³)	1692.49(11)	1052.17(6)	2393.42(13)
<i>Z</i>	4	1	1
Reflections collected	106334	27312	124064
Independent reflections	8233	6418	9092
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	7858	6004	7896
<i>R</i> _{int}	0.045	0.037	0.060
Parameters refined	211	270	602
<i>R</i> ₁	0.014	0.016	0.042
w <i>R</i> ₂	0.032	0.038	0.124
<i>S</i>	1.103	1.056	1.122
$\Delta\rho_{\min}$ (e Å ⁻³)	-1.13	-1.35	-2.46
$\Delta\rho_{\max}$ (e Å ⁻³)	1.04	0.91	4.08
CCDC number	2379148	2379149	2379150

Results and discussion

Synthesis

The cationic nature of the protonated precursors to the zwitterions L1 and L2 renders them of appreciable solubility in water, and in neither case does their neutralization result in precipitation of the zwitterion so that, in principle, water alone could be used for the synthesis of their uranyl ion complexes. This is so for L1, but the addition of a solution of uranyl nitrate to one of L2 produces an immediate precipitate of amorphous material which remains insoluble on heating. This is a much more usual observation with such ligands, so that reaction with the zwitterion precursor under solvothermal conditions proved necessary to obtain a crystalline product in this case. With L1, neutralization of L1H₂Cl₂ in water by addition of an equimolar quantity of Na₂CO₃ produced, after the subsidence of effervescence, a colourless solution to which [UO₂(NO₃)₂(H₂O)₂]·4H₂O could be added without immediate formation of a precipitate. Only after allowing the pale yellow solution produced to evaporate slowly at room temperature

to near dryness were yellow crystals of $[\text{UO}_2(\text{L1})\text{Cl}_2]\cdot\text{H}_2\text{O}$ (**1**) obtained. These were accompanied by colourless crystals of NaNO_3 , and a superior synthesis subsequently developed was based on the reaction of $[\text{UO}_2(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ with $\text{L1H}_2\text{Cl}_2$ in water. It was also possible to conduct the reaction of the zwitterion precursor with uranyl nitrate in a water/acetonitrile mixture under solvo-hydrothermal conditions to obtain the product $[(\text{UO}_2)_4(\text{O})_2(\text{OH})_2(\text{C}_2\text{O}_4)(\text{L1})_2]\cdot 4\text{H}_2\text{O}$ (**2**). The oxalate present in **2** is most likely due to oxidative degradation of L1, since although it could also be produced by oxidation of the cosolvent, it is not present in all products obtained from other syntheses using this, and the fact that oxalate is known to be an excellent ligand for actinides [41] indicates that it should be present in all if produced in this way. Here, the solvothermal conditions have led to partial hydrolysis of the uranyl ion, possibly due to the cosolvent hydrolysis leading to buffering at a raised pH, although it is also known that the acidity of $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ increases with temperature [42]. The reaction between $\text{L2H}_2\text{Cl}_2$ and $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ in a water/acetonitrile mixture under solvothermal conditions produced $[(\text{UO}_2)_4(\text{O})_2(\text{OH})_2(\text{L2})_3](\text{I}_3)_2\cdot 6\text{H}_2\text{O}$ (**3**), containing a tetrauranate cluster similar to that of **2** but in a cationic species lacking oxalate and counterbalanced by triiodide anions produced by oxidation of added iodide. That oxalate is not present in **3** could simply be due to L2 being more resistant to oxidation than L1 but may also be a consequence of the (unintended) action of iodide, added to the initial reaction mixture as CsI and found to act as a sacrificial reductant to consume nitrate, a reaction for which there is some precedent [43].

Crystal structures

Complex **1**, shown in Fig. 1, is a simple species in which the uranyl cation is bound to one κ^2O,O' -chelating carboxylate group, one monodentate carboxylate from another ligand and two

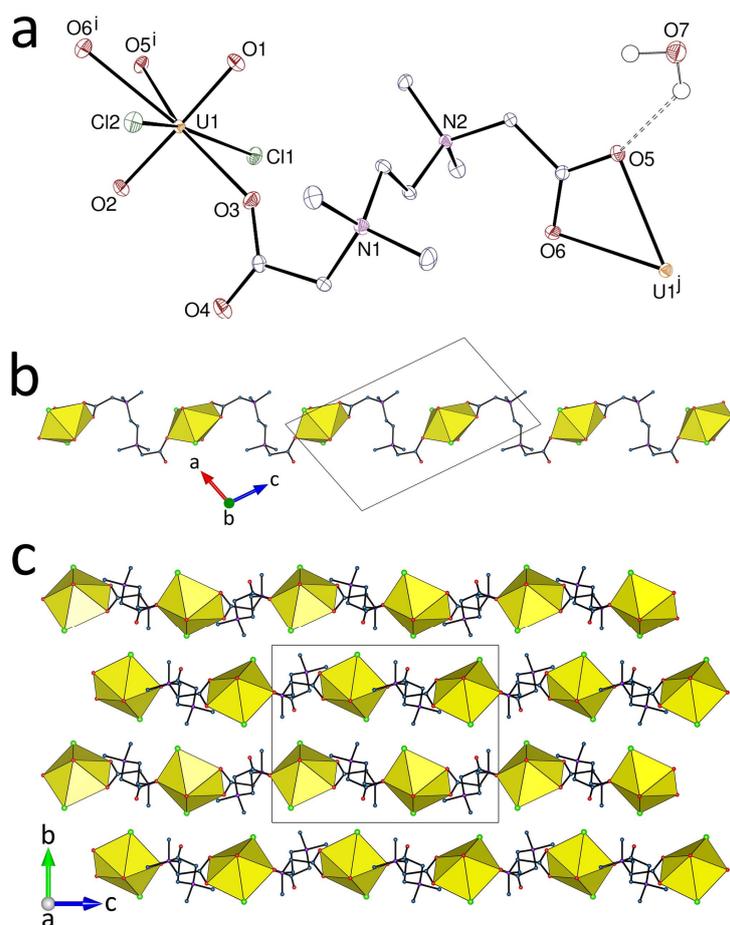


Fig. 1 **a** View of complex **1** with displacement ellipsoids shown at the 50% probability level. Carbon-bound hydrogen atoms are omitted and the hydrogen bond is shown as a dashed line. Symmetry codes: $i = x + 1/2, 3/2 - y, z - 1/2$; $j = x - 1/2, 3/2 - y, z + 1/2$. **b** View of the monoperiodic polymer with uranium coordination polyhedra in yellow. **c** Packing with chains viewed sideways.

chloride anions, resulting in a pentagonal-bipyramidal uranium environment [U–O(oxo), 1.7767(9) and 1.7780(9) Å; U–O(carboxylato), 2.4757(9) and 2.5019(9) Å for the chelating group, 2.2989(9) Å for the monodentate; U–Cl, 2.7018(3) and 2.7327(3) Å]. Topologically, both metal and ligand are thus 2-coordinated only, and the coordination polymer formed is a simple, zigzag chain directed along $[10\bar{1}]$. L1 assumes a divergent conformation with an S-shape, with the two carboxylate groups bound differently to U^{VI} , one being κ^2O,O' -chelating and the other κ^1O -monodentate. Within each polymer chain, the conformation of L1 units is close to centrosymmetric, so that the whole polymer chain has no overall helicity. Polymer

chains lie side-by-side in sheets parallel to (010), with the water molecule forming three hydrogen bonds with O5 and the two chlorine atoms, thus bridging three chains. The Kitaigorodsky packing index (KPI) evaluated with PLATON [44], 0.73, indicates that no further solvent-accessible space is present. It is notable that another uranyl ion complex with ligand L1 and chloride anions, crystallized under solvo-hydrothermal conditions, has been previously described, which has the formula $[(\text{UO}_2)_2(\text{L1})_3\text{Cl}_2][(\text{UO}_2\text{Cl}_3)_2(\text{L1})]$ and contains a cationic, diperiodic coordination polymer with the honeycomb topology, the cells of which are crossed by dinuclear anions [11].

Complex **2** provides a very different picture, as shown in Fig. 2. The asymmetric unit contains two independent uranyl cations, one of them (U1) bound to two oxo and one hydroxo anions, and two carboxylate donors from two L1 molecules, and the other (U2) bound to one oxo and one hydroxo group, one chelating oxalate ligand, and one carboxylate donor from L1. Both uranium atoms are thus in pentagonal-bipyramidal environments [U–O(oxo), 1.7929(18)–1.8002(18) Å; U–O(carboxylato), 2.4939(17) and 2.5075(17) Å for oxalate, 2.3953(18)–2.5048(18) Å for L1; U–O²⁻, 2.2391(16)–2.3278(16) Å; U–OH⁻, 2.2745(17) and 2.3661(17) Å]. The zwitterion coordination is again unsymmetrical, but here it involves $\kappa^1\text{O}$ and bridging *syn/syn* $\mu_2\text{-}\kappa^1\text{O}:\kappa^1\text{O}'$ modes. The $\kappa^1\text{O}$ mode may be enforced by hydrogen bonding of the uncoordinated oxygen atom to the bridging hydroxido ligand and a water molecule. $(\text{UO}_2)_4(\text{O})_2^{4+}$ units involving μ_3 -oxido ligands are quite commonly encountered in U^{VI} coordination complexes [45], though most involve both hexagonal- and pentagonal-bipyramidal coordination, as often seen, for example, in phthalate complexes [46], rather than the exclusive pentagonal-bipyramidal coordination found in **2** (also observed with phthalate [46]). In addition to the hydrogen atom of the hydroxido anion having been found, the difference in nature of the oxido and hydroxido bridges is confirmed by the corresponding bond

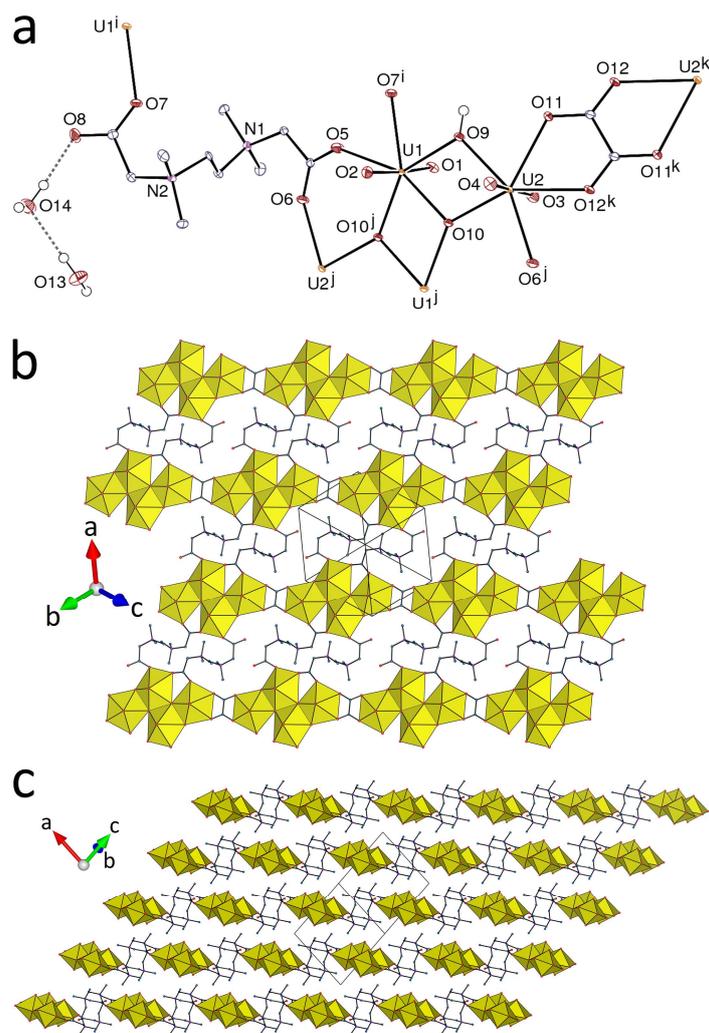


Fig. 2 **a** View of complex **2** with displacement ellipsoids shown at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 1 - x, -y - 1, 1 - z$; $j = -x, -y, 1 - z$; $k = -x, 1 - y, -z$. **b** View of the diperiodic polymer with uranium coordination polyhedra in yellow. **c** Packing with layers viewed edge-on.

valence parameters calculated using PLATON, 1.91 and 1.18, respectively. The tetranuclear clusters are assembled into linear chains by the oxalate bridges, these chains being further double-linked by L1 ligands to produce a diperiodic network parallel to (111). If the clusters are considered single nodes, both ligands are edges, and the assembly has the topology of a square lattice (**sql**), with however double L2 edges. The KPI is 0.71, with possibly a small quantity of disordered water solvent present, in excess of the four molecules found (see

Experimental section). Another complex with a mixture of L1 and oxalate ligands has previously been reported, $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_2(\text{L1})]$, which crystallizes as a diperiodic polymer with the honeycomb topology and isolated uranyl centres; formation of oxo and hydroxo bridges did not occur in this case, for which the synthesis conditions were somewhat different, the crystals being deposited under solvo-hydrothermal conditions with acetonitrile as organic cosolvent, in the presence of either *cis*-muconic or 4-ketopimelic acids (in attempts to form mixed-ligand complexes) [11].

In contrast to complexes **1** and **2**, which are neutral complexes, **3** contains a cationic uranyl complex associated with I_3^- anions formed *in situ* from the iodide anions present. The two independent uranyl ions are part of a centrosymmetric, bis(μ_3 -oxo-bridged) tetranuclear cluster similar to that in **2** [U–O(oxo), 1.779(7)–1.811(7) Å; U–O(carboxylato), 2.483(7) and 2.588(6) Å for the chelating group, 2.418(6)–2.474(6) Å for the others; U–O²⁻, 2.189(6)–2.319(6) Å; U–OH⁻, 2.252(6) and 2.336(6) Å] (Fig. 3). The centrosymmetric oxalate ligand in **2** is replaced here by a centrosymmetric, bis($\kappa^2\text{O},\text{O}'$ -chelating) L2 ligand, the other L2 ligand being bound, as in **2**, in the mixed $\kappa^1\text{O}/\mu_2\text{-}\kappa^1\text{O}:\kappa^1\text{O}'$ mode. The diperiodic network formed is parallel to (1–34), and it has the same topology as that in **2**. Both ligand units can be considered to have divergent carboxylate groups but the much greater length of L2 in comparison to L1 means that the uranate clusters are well separated, the elongated cells having a size of $\sim 22 \text{ \AA} \times 39 \text{ \AA}$. The packing of the undulating polymer sheets is such as to define quite large spaces occupied by the triiodide anions and water molecules, the presence of the large counterions possibly preventing network entanglement (polycatenation is allowed for example by the equally large cells in a neutral In^{3+} complex [26]). One possible parallel-displaced π – π interaction exists between the phenyl ring proximal to N2 and its image by inversion within the double edge [centroid···centroid distance, 3.923(7) Å; dihedral angle, 0°; slippage, 0.37 Å]. The

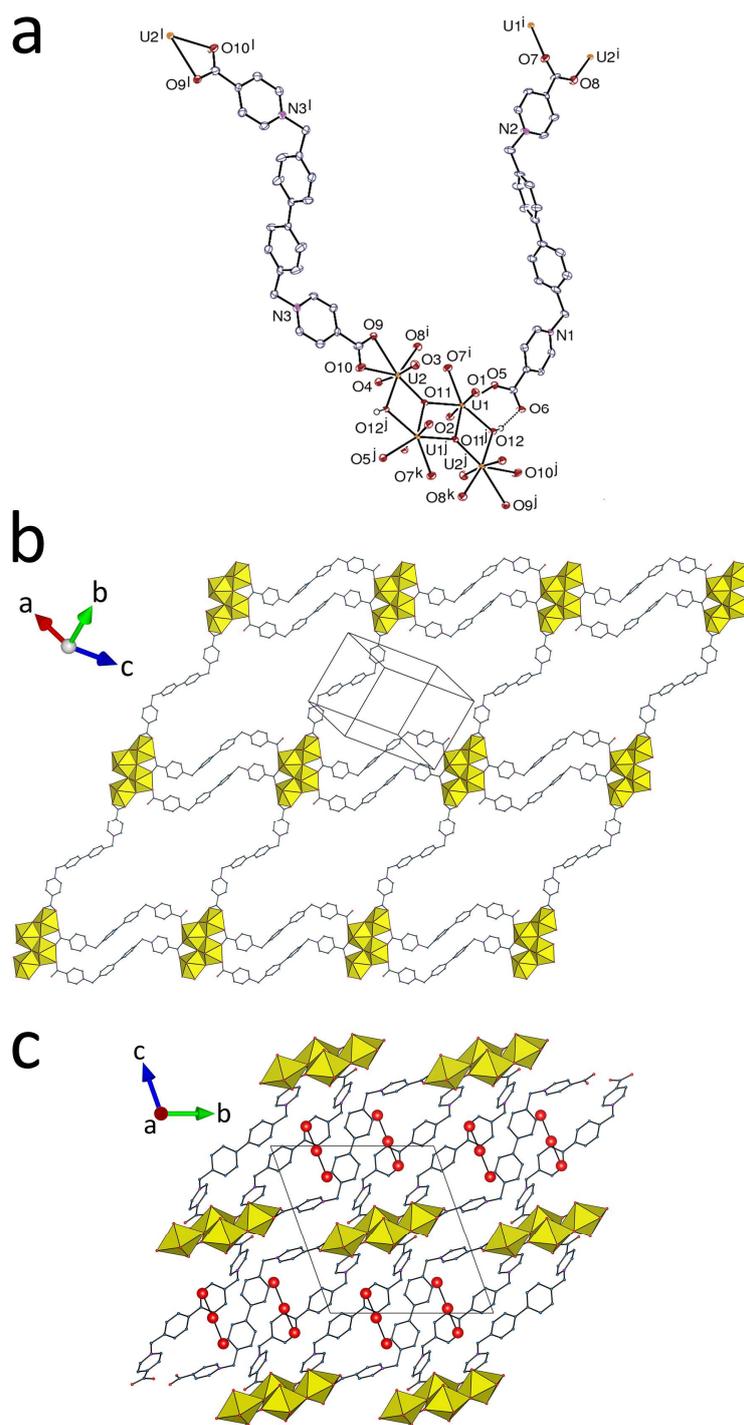


Fig. 3 **a** View of complex **3** with displacement ellipsoids shown at the 50% probability level. Counterions, solvent molecules, and carbon-bound hydrogen atoms are omitted. The hydrogen bond is shown as a dashed line. Symmetry codes: $i = 2 - x, -y, -z$; $j = 1 - x, 1 - y, 1 - z$; $k = x - 1, y + 1, z + 1$; $l = -x - 1, -y - 1, -z$. **b** View of the diperiodic polymer with uranium coordination polyhedra in yellow. **c** Packing with layers viewed sideways and iodine atoms in red (only one position of the disordered anion is shown).

two aromatic rings containing N1 and N2 form possible interactions with triiodide anions, with I...centroid distances of 3.491(6) and 3.756(5) Å for the main component of the disordered anion. The aromatic ring containing N1 is also possibly involved in an intersheet interaction with the uranyl oxo atom O2 [O2...centroid distance, 2.905(8) Å; U–O...centroid angle, 143.9(4)°], as previously observed in other uranyl ion complexes involving pyridinium groups [47]. The KPI of only 0.65 confirms that other, highly disordered solvent molecules are present (see Experimental section). The ligand related to L1 but with a longer central $-(\text{CH}_2)_3-$ bridge (L3) has been shown to give the complex $[(\text{UO}_2)_7(\text{O})_3(\text{OH})_{4.3}(\text{L3})_2\text{Cl}_{2.7}]\text{Cl}\cdot 7\text{H}_2\text{O}$ under solvo-hydrothermal conditions and in the presence of CsI, as **3**; in this case, however, triiodide is absent (as well as oxalate), and uranyl hydrolysis produces a monophasic chlorouranate polymer, with further bridging by L3 giving a triperiodic framework displaying 2-fold interpenetration [11].

Conclusions

Aside from precautions relating to radioactivity, the synthesis of uranyl ion complexes is generally amenable to methods developed for those of all other metal ions. There is specificity, however, relating to the commercial availability of starting materials in that there is very little choice other than hydrated uranyl nitrate (significantly, it has been shown that under solvothermal conditions, using uranyl triflate rather than nitrate can lead to entirely different reaction products [18]). The present syntheses of complexes **2** and **3** illustrate two different ways in which the presence of nitrate can influence the nature of the product. In contrast, the synthesis of complex **1** under mild ambient conditions indicates that interference due to nitrate oxidation of a ligand can be avoided, though, unfortunately, such conditions are not widely applicable to the preparation of crystalline coordination polymers.

The three complexes described, together with some of those previously reported

involving the same or related ligands [11] evidence the extreme sensitivity of the structures formed on the synthesis temperature and the presence of additional reagents, even when these are not present in the final product, as in the case of anionic dicarboxylates in some of the former complexes. Uranyl hydrolysis is very common when solvo-hydrothermal conditions are used, and it is found here in the two complexes so synthesized, leading, quite remarkably, to the same tetranuclear cluster in both cases. The difference in both the susceptibility to oxidation of the ligands and the presence of the additional CsI reagent in one case led to the replacement of oxalate by L2 in the otherwise similar diperiodic networks in **2** and **3**, thus transforming a neutral into a cationic species. The network in the latter displays very large cells which could be suitable for entanglement, this being prevented by the presence of the included triiodide anions. In contrast to the very simple species formed at room temperature, hydrothermal conditions appear to be conducive to forming very diverse polymeric species, which are highly dependent on the nature of the additional species present.

Supplementary Information The online version contains supplementary material available at...

Acknowledgements This work was supported by KAKENHI Grant-in-Aid for Early-Career Scientists JP22K14698 for S. Kusumoto, and JSPS KAKENHI Grant Number 20K21213 for S. Hayami.

Declarations

Competing Interests The authors declare no competing interests.

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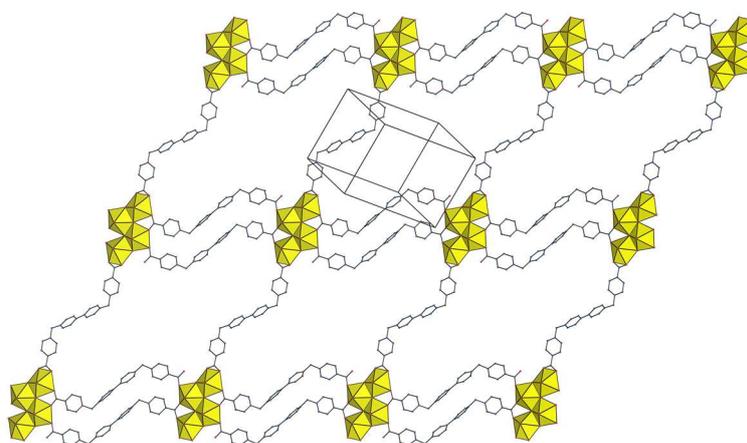
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Table of Contents Entry

Synthesis of crystalline uranyl ion coordination polymers with zwitterionic carboxylate ligands: Comparing solvothermal and ambient conditions

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Yang Kim · Jack Harrowfield · Pierre Thuéry



Three uranyl ion complexes involving neutral, dizwitterionic dicarboxylates illustrate the effect of different crystallization conditions, with a simple monoperiodic species obtained at room temperature and diperiodic assemblies including oxo/hydroxo-bridged tetranuclear clusters generated under solvothermal conditions.