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(*R,R*)-Tartrate as a polytopic ligand for UO_2^{2+} : mono- and diperiodic coordination polymers including di- and tetranuclear subunits

Pierre Thuéry^{a*}, Jack Harrowfield^{b*}

^a *Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette, France*

^b *ISIS, Université de Strasbourg, 8 allée Gaspard Monge, 67083 Strasbourg, France*

* Corresponding author. E-mail: pierre.thuery@cea.fr, harrowfield@unistra.fr

Abstract

(*R,R*)-Tartaric acid (H_4tart) has been reacted with uranyl nitrate hexahydrate under solvo-hydrothermal conditions, in the presence of either $[\text{Ni}(\text{R,S-Me}_6\text{cyclam})]^{2+}$ (*R,S*- Me_6cyclam = 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), quinH^+ (quinuclidinium), or $[\text{Ni}(\text{bipy})_3]^{2+}$ (*bipy* = 2,2'-bipyridine), to give three complexes characterized by their crystal structure. $[\text{H}_2\text{NMe}_2]_2[(\text{UO}_2)_2(\text{Htart})_2(\text{HCOO})_2\text{Ni}(\text{R,S-Me}_6\text{cyclam})] \cdot 2\text{H}_2\text{O}$ (**1**) crystallizes as a monoperiodic coordination polymer in which dimeric $[\text{UO}_2(\text{Htart})]_2^{2-}$ subunits are linked by nickel(II) cations. The structure of the dimers matches that expected from solution experiments but not previously found in the solid state. Both $[\text{Hquin}][(\text{UO}_2)_2(\text{tart})(\text{CH}_3\text{COO})]$ (**2**) and $[\text{Ni}(\text{bipy})_3][(\text{UO}_2)_2(\text{tart})(\text{CH}_3\text{COO})]_2$ (**3**) crystallize as diperiodic networks based on tetranuclear $[(\text{UO}_2)_2(\text{tart})(\text{CH}_3\text{COO})]_2^{2-}$ subunits which contain a central U_2O_2 ring involving μ_2 -bridging alkoxide groups. Further chelation of the two lateral uranyl cations by the carboxylate groups of adjacent subunits yields a **sql**-type network. Due to the different bulk of the counterions, the layers are quasi-planar in **2** and corrugated in **3**. Comparison of these polynuclear subunits with those formed by the related ligands citrate, *R,S*-malate and *R*-citramalate shows that while the dimeric form is common to all, the tetranuclear subunit is specific to the tartrate ligand.

Keywords: Uranyl ion, Metal–organic networks, (*R,R*)-Tartaric acid, Structure elucidation

1. Introduction

Although it is a naturally occurring and very common ligand, the uranyl-complexing properties of tartrate in its pure enantiomer (*R,R* or *L, S,S* or *D*), racemic or meso forms have been the subject of only a few investigations, both in solution [1,2] and in the solid state [3]. Early studies suggested the existence of complexes with different, pH-dependent metal/ligand stoichiometries in solution, with possible formation of dimers and trimers involving both carboxylate and hydroxyl/alkoxide donors [1]. The structure of the 2:2 dimer was established by EXAFS spectroscopy [2], while the crystal structure of a diperiodic polymer synthesized under hydrothermal conditions, $[\text{UO}_2(\text{H}_2\text{tart})](\text{H}_2\text{O})$ ($\text{H}_4\text{tart} = (R,R)\text{-tartaric acid}$), in which only the carboxylic groups are deprotonated, confirmed the multidentate coordinating character of tartrate towards the uranyl ion, although with a connectivity quite different from those proposed to exist in solution at ambient temperature [3].

The use of an enantiomerically pure, multidentate, bridging ligand such as tartrate is considered the simplest means of obtaining a chiral coordination polymer and recent interest in such materials has been considerable [4,5]. Chiral uranyl ion coordination polymers in particular have potential uses not only based on their photo-oxidation capacity [4] but also on their circularly polarised luminescence (CPL) [6]. Crystallization of uranyl tartrates under different conditions and/or incorporating additional ligands or counterions has proven however to be difficult, and only two species other than $[\text{UO}_2(\text{H}_2\text{tart})](\text{H}_2\text{O})$ have been reported in the Cambridge Structural Database (CSD, version 5.43 [7]), these being $[\text{Co}(\text{en})_3][(\text{UO}_2)_4(\text{cam})(\text{tart})_2(\text{OH})]\cdot 3\text{H}_2\text{O}$ ($\text{en} = \text{ethylenediamine}$; $\text{cam}^{2-} = (1R,3S)\text{-}(+)\text{-camphorate}$), which is also a diperiodic polymer with tartrate bound to four uranyl cations through formation of three five-membered and one seven-membered chelate rings [8], and $(\text{H}_3\text{O})(\text{UO}_2)_3[\text{Cd}_7\text{Sb}_{24}\text{O}_{24}(\text{tart})_9(\text{Htart})_3(\text{H}_2\text{O})_6]\cdot 48\text{H}_2\text{O}$, a complex resulting from uranyl capture from aqueous solution by ion exchange with an insoluble polyoxometallate [9]. In

contrast to the related ligands citrate, malate or citramalate, whose uranyl ion complexes in the solid state have been the subject of several studies [10], the behaviour of citrate in solution having also attracted considerable interest [11], the structural chemistry of uranyl tartrates remains poorly developed. In order to gain more insight on the coordination preferences of (*R,R*)-tartrate toward the uranyl ion in complexes formed under solvo-hydrothermal conditions, we have now synthesized three new complexes which include additional cations as structure-directing species and determined their crystal structures. The cationic species used were $[\text{Ni}(\text{R,S-Me}_6\text{cyclam})]^{2+}$ (*R,S*-Me₆cyclam = 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), quinuclidinium (quinH⁺), and $[\text{Ni}(\text{bipy})_3]^{2+}$ (bipy = 2,2'-bipyridine), all of them having previously been found to be suitable for the modulation of the structures of uranyl ion complexes formed with diverse polycarboxylates [12].

2. Experimental section

2.1. 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%) and (*R,R*)-tartaric acid were purchased from Prolabo. *R,S*-Me₆cyclam (meso isomer of 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) was prepared as described in the literature [13], and (7(*R*),14(*S*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) dinitrate, $[\text{Ni}(\text{R,S-Me}_6\text{cyclam})](\text{NO}_3)_2$, was synthesized as previously reported [14]. Quinuclidinium trifluoromethanesulfonate (HquinOTf) was obtained by adding a slight excess of trifluoromethanesulfonic acid to a solution of quinuclidine in

ethanol, then precipitating the salt by the addition of diethyl ether. Tris(2,2'-bipyridine)nickel(II) nitrate, $[\text{Ni}(\text{bipy})_3](\text{NO}_3)_2$, was obtained by adding 2,2'-bipyridine (bipy) to an ethanol solution of $[\text{Ni}(\text{NO}_3)_2] \cdot 6\text{H}_2\text{O}$ following a long-known procedure [15]. For all syntheses, the mixtures in demineralized water/organic cosolvent were placed in 10 mL tightly closed glass vessels and heated at 140 °C in a sand bath, under autogenous pressure. The crystals characterized were those deposited under the reaction conditions and not from subsequent cooling and depressurization.

2.1.1. $[\text{H}_2\text{NMe}_2]_2[(\text{UO}_2)_2(\text{Htart})_2(\text{HCOO})_2\text{Ni}(\text{R,S-Me}_6\text{cyclam})] \cdot 2\text{H}_2\text{O}$ (**1**)

(*R,R*)-tartaric acid (15 mg, 0.10 mmol), $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (35 mg, 0.07 mmol), and $[\text{Ni}(\text{R,S-Me}_6\text{cyclam})](\text{NO}_3)_2$ (23 mg, 0.05 mmol) were dissolved in a mixture of water (0.8 mL) and *N,N*-dimethylformamide (0.2 mL). A few yellow crystals of complex **1** were obtained within two months.

2.1.2. $[\text{Hquin}][(\text{UO}_2)_2(\text{tart})(\text{CH}_3\text{COO})]$ (**2**)

(*R,R*)-tartaric acid (15 mg, 0.10 mmol), $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (35 mg, 0.07 mmol), and HquinOTf (26 mg, 0.10 mmol) were dissolved in a mixture of water (0.7 mL) and acetonitrile (0.2 mL). A few yellow crystals of complex **2** were obtained within three months.

2.1.3. $[\text{Ni}(\text{bipy})_3][(\text{UO}_2)_2(\text{tart})(\text{CH}_3\text{COO})]_2$ (**3**)

(*R,R*)-tartaric acid (15 mg, 0.10 mmol), $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (35 mg, 0.07 mmol), and $[\text{Ni}(\text{bipy})_3](\text{NO}_3)_2$ (32 mg, 0.05 mmol) were dissolved in a mixture of water (0.7 mL) and *N,N*-dimethylacetamide (0.2 mL). A few yellow crystals of complex **3** were obtained within ten days.

2.2. 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 APEX3 software [16]. The data were processed with SAINT [17], and absorption effects were corrected for empirically with SADABS [18]. The structures were solved by intrinsic phasing with SHELXT [19] and refined by full-matrix least-squares on F^2 with SHELXL, using the ShelXle interface [20]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen and nitrogen atoms in complex **1** were found on a residual electron density map and they were refined with restraints on bond lengths. The hydrogen atoms bound to nitrogen atoms in **2** and all 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). The two quinuclidinium cations in **2** are extremely badly resolved, and the disorder probably present could not be modelled properly. Both were refined with restraints on bond lengths, angles and displacement parameters, and restraints on displacement parameters were also applied for several atoms in the anionic part of the structure. Voids in the structures of **2** and **3** are probably occupied by very disordered and unresolved solvent molecules, and the SQUEEZE software [21] was used to subtract the contribution of these solvent molecules to the structure factors. Crystal data and structure refinement parameters are given in Table 1. Drawings were made with ORTEP-3 [22] and VESTA [23].

Table 1

Crystal data and structure refinement details.

	1	2	3
Chemical formula	C ₃₀ H ₆₄ N ₆ NiO ₂₂ U ₂	C ₂₆ H ₃₈ N ₂ O ₂₄ U ₄	C ₄₂ H ₃₄ N ₆ NiO ₂₄ U ₄
<i>M_r</i>	1395.64	1714.70	2017.58
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 1	<i>P</i> 2 ₁	<i>P</i> 2 ₁
<i>a</i> (Å)	8.8931(6)	13.4885(6)	13.9220(5)
<i>b</i> (Å)	11.1230(7)	11.9470(5)	12.9635(4)
<i>c</i> (Å)	12.4269(8)	14.0289(5)	15.2783(6)
α (°)	111.951(2)	90	90
β (°)	90.973(3)	102.0695(19)	95.3923(15)
γ (°)	103.786(3)	90	90
<i>V</i> (Å ³)	1099.58(13)	2210.74(16)	2745.19(17)
<i>Z</i>	1	2	2
No. of reflections collected	159177	90751	109356
No. of independent reflections	11292	8372	10417
No. of observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	11172	8022	9850
<i>R</i> _{int}	0.048	0.044	0.077
No. of parameters refined	591	508	697
<i>R</i> ₁	0.013	0.030	0.027
w <i>R</i> ₂	0.033	0.075	0.060
<i>S</i>	1.071	1.029	1.052
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.56	-1.08	-1.01
$\Delta\rho_{\max}$ (e Å ⁻³)	2.47	1.59	1.92
Flack parameter	0.045(4)	0.102(17)	-0.002(9)

3. Results and discussion

All three complexes crystallized after long reaction periods and all included components derived from hydrolysis reactions of the organic cosolvents used. These cosolvents appeared to eliminate the problem found in the simple hydrothermal synthesis of uranyl tartrate [3] where the yield was limited by the oxidation of tartrate to oxalate, possibly through their action as sacrificial reductants. Nonetheless, the yields of all three products were low, indicating that the rarity of crystal structure determinations on uranyl tartrate species may be simply due to the high solubility of these materials. The formation of mixed-ligand species with simple monocarboxylates such as formate and acetate, and indeed with another chiral dicarboxylate, 1*R*,3*S*-camphorate [8], appears to be a way of reducing this solubility. Although luminescence measurements have not been made, all three complexes have a pale yellow colour, indicating that their photoluminescence quantum yields must be low [24].

The complex $[\text{H}_2\text{NMe}_2]_2[(\text{UO}_2)_2(\text{Htart})_2(\text{HCOO})_2\text{Ni}(\text{R},\text{S}\text{-Me}_6\text{cyclam})]\cdot 2\text{H}_2\text{O}$ (**1**) was synthesized with *N,N*-dimethylformamide (DMF) as organic cosolvent and it includes formate coligands and dimethylammonium counterions formed *in situ* from DMF hydrolysis, a frequent occurrence [25]. The anionic complex is heterometallic, and the asymmetric unit contains two independent uranyl cations, one $\text{Ni}(\text{R},\text{S}\text{-Me}_6\text{cyclam})^{2+}$ cation, and two trianionic Htart^{3-} anions where one hydroxyl proton is retained (Fig. 1). The two uranium atoms are in similar environments, each being part of one five- and one six-membered chelate rings, each ring

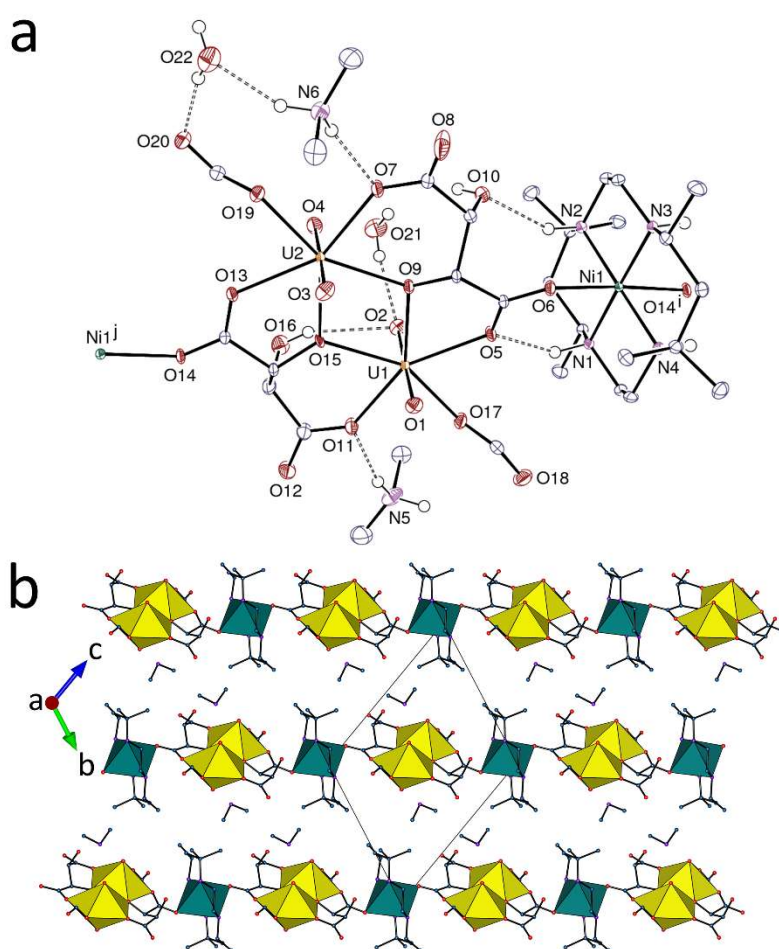


Fig. 1. (a) View of complex **1** with displacement ellipsoids shown at the 50% probability level. The labels of carbon atoms are omitted for clarity, as well as the carbon-bound hydrogen atoms. Hydrogen bonds are shown as dashed lines. Symmetry codes: $i = x, y + 1, z + 1$; $j = x, y - 1, z - 1$. (b) View of the packing with uranium coordination polyhedra colored yellow and those of nickel green.

involving one carboxylate and one alkoxide donors, a monodentate formate anion completing the coordination sphere to give the common pentagonal-bipyramidal uranium environment [U–O(oxo), 1.778(4)–1.807(4) Å; U–O(carboxylato), 2.321(4)–2.410(4) Å; U–O(alkoxido), 2.364(4)–2.392(4) Å]. A 2:2 [UO₂(Htart)]₂ dimeric secondary building unit (SBU) is thus formed, which is connected through one carboxylate donor in each ligand to two Ni(*R,S*-Me₆cyclam)²⁺ moieties, the nickel atom being in a slightly elongated octahedral environment [Ni–N, 2.066(3)–2.096(3) Å; Ni–O, 2.155(3) and 2.177(3) Å]. Both Htart³⁻ ligands are bound to three metal atoms, with one carboxylate group bridging in the *syn/anti* μ_2 - $\kappa^1 O:\kappa^1 O'$ mode, the other monodentate, and the alkoxide group μ_2 -bridging. A monophasic polymer parallel to [011] is thus formed, the chains being arranged in layers parallel to (0 $\bar{1}$ 1). The hydroxylic protons are involved either in an interchain hydrogen bond with an uncoordinated formate oxygen atom, or in an intrachain one with a uranyl oxo group [O10...O18^k, 2.634(5) Å; O10–H...O18^k, 164(5)°; O16...O2, 3.168(6) Å; O16–H...O2, 156(5)°; symmetry code: $k = x + 1, y, z$]. The amino groups of *R,S*-Me₆cyclam form intrachain hydrogen bonds with carboxylate and alkoxide oxygen atoms [N...O, 2.778(4)–3.172(4) Å; N–H...O, 111(3)–169(4)°], while the H₂NMe₂⁺ counterions, located between the layers, are hydrogen bonded to oxo and carboxylato groups in the same layer, with additional bonds to water molecules [N...O, 2.785(7)–3.098(7) Å; N–H...O, 110(3)–157(5)°]. The counterions and water molecules make links between chains in a layer so that, as shown in Fig. 1(a), the resulting intralayer hydrogen bond network is rather intricate, with in particular formation of uranium-containing rings with the graph set descriptors $R_1^1(7)$ and $R_3^3(10)$ and nickel-containing $R_1^1(6)$ and $R_1^1(8)$ rings [26]. The structure has a Kitaigorodski packing index (KPI, evaluated with PLATON [27]) of 0.72.

Complete tartrate deprotonation is achieved in the complex [Hquin][(UO₂)₂(tart)(CH₃COO)] (**2**), shown in Fig. 2. Acetate anions are present, which have been generated *in situ* from hydrolysis of the acetonitrile cosolvent [28] and result in the

formation of a mixed-ligand complex. Incorporation of products resulting from acetonitrile hydrolysis (acetate and ammonium ions) in uranyl ion complexes synthesized under solvo-hydrothermal reactions is far from being as frequent as that of residues from *N,N*-dimethylformamide hydrolysis, and only in rare cases has the presence of ammonium counteranions been observed [10]. The long reaction time of three months necessary to

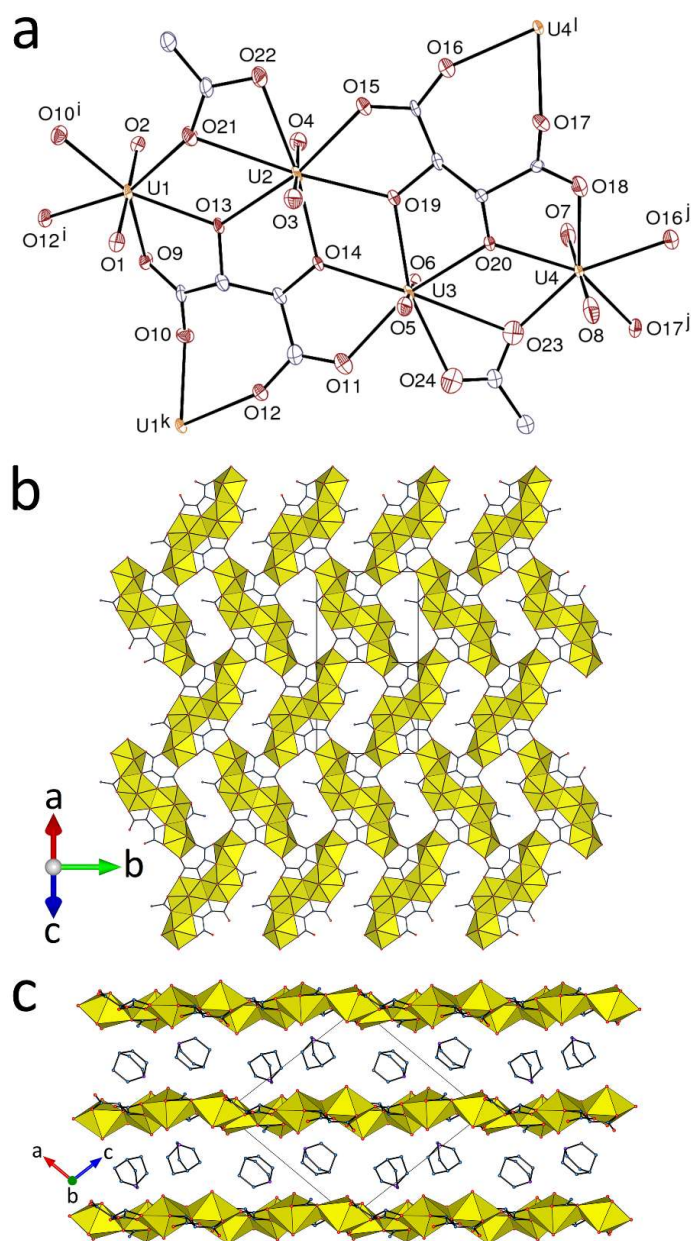


Fig. 2. (a) View of compound **2** with displacement ellipsoids shown at the 30% probability level. The labels of carbon atoms are omitted for clarity, as well as the counterions and hydrogen atoms. Symmetry codes: $i = -x, y + 1/2, 2 - z$; $j = 1 - x, y - 1/2, 1 - z$; $k = -x, y - 1/2, 2 - z$; $l = 1 - x, y + 1/2, 1 - z$. (b) View of the diperiodic network with uranium coordination polyhedra colored yellow. (c) Packing with layers viewed edge-on.

obtain crystals of **2** is possibly related to the slow kinetics of the reaction. The asymmetric unit contains four independent uranyl cations and two tart⁴⁻ ligands. U1 and U4 are in similar environments, being twice chelated, by the two carboxylate groups of one ligand (seven-membered ring) and by one carboxylate and one alkoxide groups of another ligand (five-membered ring); one acetate oxygen atom completes the uranium pentagonal-bipyramidal environment. U2 and U3 are in similar hexagonal bipyramidal environments, with threefold chelation by the carboxylate and alkoxide groups of one ligand, the two alkoxide groups of another ligand (five-membered ring) and an acetate anion. All bond lengths are as usual, with however a large dispersion of those with the acetate anions [U–O(oxo), 1.684(14)–1.769(14) Å; U–O(carboxylato), 2.328(16)–2.879(16) Å; U–O(alkoxido), 2.354(10)–2.438(11) Å]. The four uranium coordination polyhedra thus share three edges, two of them containing one alkoxide and one acetate donors, and the third two alkoxide groups, and the tetranuclear SBU has thus the shape of a sinuous chain in which no adjacent uranium atoms share more than one edge. This geometry is not among the most common for the tetranuclear SBUs [29], and it is also slightly different from that in [Co(en)₃][(UO₂)₄(cam)(tart)₂(OH)]·3H₂O [8], in which the bonding mode of the camphorate ligand, which replaces acetate, can best be described as bis(μ_2 - $\kappa^1 O:\kappa^1 O'$)-bridging, so that the lateral uranium atoms share a single vertex with the central ones. The tart⁴⁻ ligand in **2** is bound to three uranium atoms of one SBU arranged in semi-circular fashion on the side on which the alkoxide groups are located, and to one uranium atom from a second SBU chelated by the two carboxylate groups on the other side, while, in the former compound, only one ligand adopts the same bonding mode, the other giving no seven-membered chelate ring. Overall, both tart⁴⁻ ligands are bound to four metal atoms, with the two carboxylate groups bridging in the anti/anti μ_2 - $\kappa^1 O:\kappa^1 O'$ mode and the alkoxide groups μ_2 -bridging. If the SBUs are considered as 4-coordinated (4-c) nodes and the tart⁴⁻ ligands as

edges, the diperiodic network formed, which is parallel to (101) has the **sql** topology. The elongated SBUs are however arranged in herringbone fashion, having the same orientation within rows parallel to [010]. The layers are quasi-planar and the interlayer space is occupied by the badly resolved counterions (see Experimental Part), which form hydrogen bonds with carboxylate oxygen atoms. As indicated by the low KPI of 0.60, the interlayer spaces contain voids which are probably occupied by disordered water molecules.

The complex $[\text{Ni}(\text{bipy})_3][(\text{UO}_2)_2(\text{tart})(\text{CH}_3\text{COO})_2]$ (**3**), in which acetate results from hydrolysis of *N,N*-dimethylacetamide, crystallizes in the same Sohncke group ($P2_1$) as **2**. The connectivity in the anionic, diperiodic coordination polymer is the same as in **2** [U–O(oxo), 1.753(9)–1.791(9) Å; U–O(carboxylato), 2.333(8)–2.671(9) Å; U–O(alkoxido), 2.356(8)–2.431(7) Å] (Fig. 3). The diperiodic network, parallel to (10 $\bar{1}$), has the same topology as that in

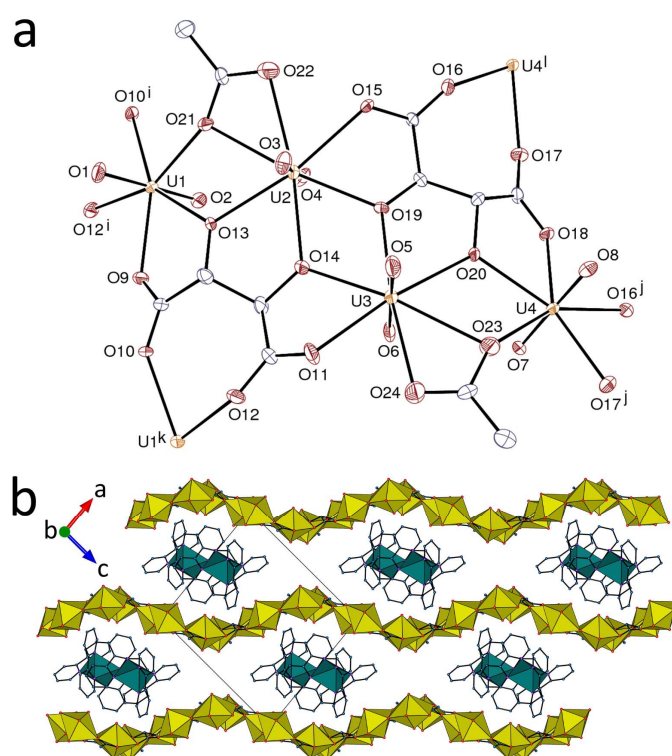


Fig. 3 (a) View of compound **3** with displacement ellipsoids shown at the 50% probability level. The labels of carbon atoms are omitted for clarity, as well as the counterions and hydrogen atoms. Symmetry codes: $i = -x, y + 1/2, -z$; $j = 1 - x, y - 1/2, 1 - z$; $k = -x, y - 1/2, -z$; $l = 1 - x, y + 1/2, 1 - z$. (b) Packing with layers viewed edge-on. Uranium coordination polyhedra are colored yellow and those of nickel green.

2, but a slightly different shape. Instead of being quasi-planar, the sheets are here corrugated, with facing hollows of the corrugation giving rise to channels ($\sim 10 \times 14 \text{ \AA}$) containing the bulky counterions. The tetranuclear SBU itself assumes a curved shape contrasting with its near-planarity in **2** (Fig. 4), due to slight reorientation of tart^{4-} ligands with respect to the uranyl ion

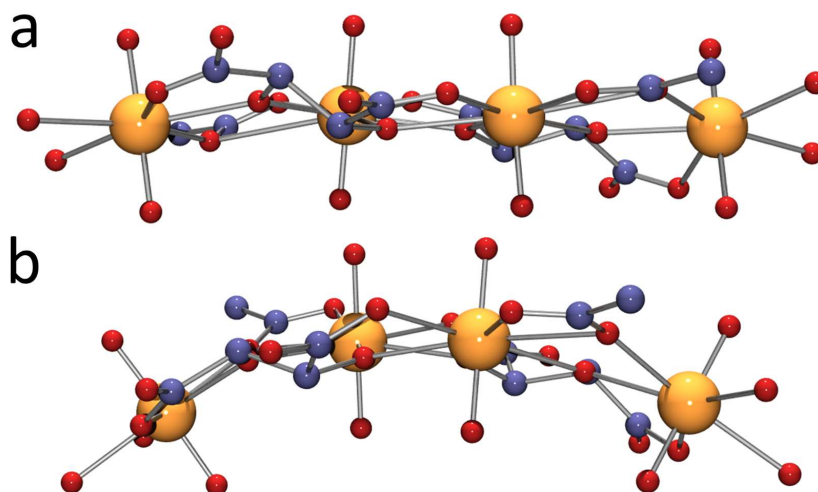
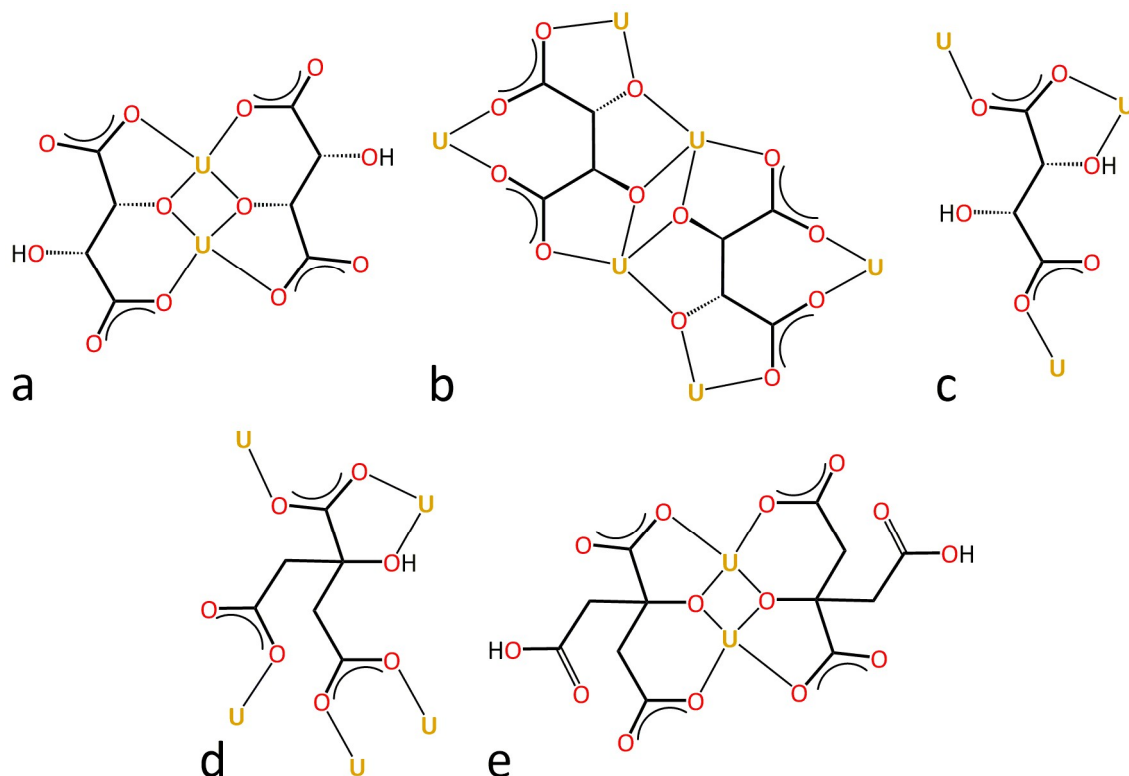


Fig. 4. Edge-on views of the tetranuclear subunits in **2** (a) and **3** (b).

equatorial mean planes. This geometric variation results most probably from a structure-directing effect exerted by the $[\text{Ni}(\text{bipy})_3]^{2+}$ counterions which are arranged into columns directed along $[010]$. π -Stacking interactions are however not prominent within the columns, with only one short centroid...centroid distance of $3.974(7) \text{ \AA}$ associated to a dihedral angle of $35.1(6)^\circ$. Some voids in the interlayer spaces (KPI, 0.63) indicate the presence of unresolved solvent molecules (see Experimental section).

The present complexes thus show the existence of di- and tetranuclear, 2:2 and 4:2 uranyl/tartrate units which can be compared to the structures proposed from early solution experiments and EXAFS measurements, and to previous crystal structures on the one hand, and to the polynuclear units formed by related ligands, on the other hand. Of the two possible

models for 2:2 dimers in solution proposed by Rajan and Martell [1d], one, represented in Scheme 1(a), was shown by Allen et al. [2] to be the correct structure from EXAFS experiments,



Scheme 1. (a) The dimeric $[\text{UO}_2(\text{Htart})]_2^{2-}$ subunit as found from solution experiments [1d,2] and in complex **1**. (b) The tetranuclear subunit in complexes **2** and **3**, with further chelate bonding to two uranium atoms from other subunits. (c) Coordination mode of $\text{H}_2\text{tart}^{2-}$ in $[\text{UO}_2(\text{H}_2\text{tart})(\text{H}_2\text{O})]$ [3]. (d) Coordination mode of Hcit^{3-} in $[(\text{UO}_2)_3(\text{Hcit})_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ [10a]. (e) The dimeric $[\text{UO}_2(\text{Hcit})]_2^{2-}$ subunit as found from solution [11a] and solid state experiments [10b–e,g,h,j,l].

in particular from its agreement with the measured $\text{U}\cdots\text{U}$ distance of 3.95 Å. This distance is in very good agreement with that of 3.9211(3) Å measured for $\text{U1}\cdots\text{U2}$ in the dimeric unit of complex **1**, which displays the same structure as that found in solution. Each uranium atom in **1** is part of one five- and one six-membered chelate ring, and not of either two five- or two six-membered ones, an arrangement which could not be ruled out from previous experiments, and the two hydroxyl groups are thus located on the same side of the asymmetric dimer. The

existence of higher oligomers was considered in earlier work, with indications for trimer formation through dimer hydrolysis [1d], but the arrangement found in complexes **2** and **3** (Scheme 1(b)) does not seem to have been anticipated from solution experiments. In this 4:2 tetranuclear unit, the two alkoxide groups of each ligand are convergent and chelate one uranyl cation, one other cation being chelated by each carboxylate/alkoxide part of the ligand; two such units, shifted with respect to one another, are fused to form the tetranuclear moiety, which is further connected to two others through bis(carboxylate) chelation of the two ligands. Such a highly connected structure is of course typical of a solid state polymeric compound, but oligomeric parts of it could exist in solution. It is also notable that acetate anions play a role in its formation since they further bridge lateral and central uranium atoms in the tetranuclear unit. In the mixed-ligand complex $[\text{Co}(\text{en})_3][(\text{UO}_2)_4(\text{cam})(\text{tart})_2(\text{OH})]\cdot 3\text{H}_2\text{O}$, the tetranuclear subunit formed is essentially the same, the main difference being that one link with an adjoining subunit is monodentate instead of chelating. In contrast, the complex formed under hydrothermal conditions after the addition of KOH, $[\text{UO}_2(\text{H}_2\text{tart})(\text{H}_2\text{O})]$, has a quite different connectivity, with each ligand bound to three metal cations only and formation of only one chelate ring, possibly an effect of retention of the two hydroxyl protons and of the non-bridging character of the water ligand [3] (Scheme 1(c)).

In a similar manner, when reacted under hydrothermal conditions in the presence of NaOH, citric acid retains its hydroxylic proton and complexes the uranyl ion with formation of only one five-membered chelate ring in $[(\text{UO}_2)_3(\text{Hcit})_2(\text{H}_2\text{O})_3]\cdot 2\text{H}_2\text{O}$ [10a] (Scheme 1(d)). The presence of additional oxo/hydroxo bridging anions yields trinuclear 3:3 or 3:2 species [10j,11c], and a triperiodic framework containing monoprotic SBUs [10f], all involving formation of both five- and six-membered chelate rings with μ_2 -bridging alkoxide donors. However, by far the most common coordination mode found for citrate at acidic pH values is that giving 2:2 dimers shown in Scheme 1(d), first proposed from solution experiments [11a]

and which occurs under a wide range of experimental conditions and with diverse additional species (counterions, metal cations), with possible deprotonation of the two pendent carboxylic groups and further coordination of carboxylate donors leading to polymerization [10b–e,g,h,j,l]. The analogous arrangement is also found with *R,S*-malate [10h,k,l] and *R*-citramalate [10c,g,h,l] in which the pendent carboxylate groups are replaced by hydrogen or methyl substituents, respectively. Obviously, the structure of complex **1** confirms previous solution experiment results and shows that this dimeric motif is a common one for all this family of related ligands, and one that is easily retained upon further polymerization.

The 4:2 tetranuclear motif found in complexes **2**, **3** and $[\text{Co}(\text{en})_3][(\text{UO}_2)_4(\text{cam})(\text{tart})_2(\text{OH})] \cdot 3\text{H}_2\text{O}$ is however more interesting in that it is specific to the tartrate anion and, to the best of our knowledge, it has not been described before. It results from the fusion of two fan-like arrangements of three cations bound to each ligand and it shares with the dimeric motif the presence of a central U_2O_2 ring built with the alkoxide donors. With respect to the dimeric unit, a second alkoxide replaces here one carboxylate donor, resulting in the central U_2O_2 ring being encircled by four five-membered chelate rings, instead of two five- and two six-membered rings in the dimers. In comparison with citrate, malate and citramalate, tartrate has thus the ability to form three adjoining chelate rings when it is in the conformation bringing the two alkoxide groups in convergent positions. This conformation results in the tetranuclear unit not being far from planarity, with only slight curvature observed in **2**, and only diperiodic networks are formed, at least in the present experiments. This can be seen as a drawback when compared to the possible incorporation of the uranyl citrate dimers into triperiodic frameworks through bonding of the pendent and divergent carboxylate groups [10e], but this is seldom achieved [10l] and the triperiodic uranyl citrate frameworks are mostly based on different coordination modes [10a,f].

4. Conclusions

In order to improve the characterization of (*R,R*)-tartrate as a multidentate ligand for uranyl ion in the solid state, we have synthesized three complexes under solvo-hydrothermal conditions and in the presence of different cationic structure-directing species, $[\text{Ni}(\text{R,S-Me}_6\text{cyclam})]^{2+}$, Hquin^+ , or $[\text{Ni}(\text{bipy})_3]^{2+}$, which doubles the number of known structures. Countercations and/or anionic coligands resulting from hydrolysis of the organic cosolvent are present in all cases, HNEt_3^+ and HCOO^- in **1**, and CH_3COO^- in **2** and **3**, signifying a particular solvent effect in the syntheses. In complex **1**, $[\text{Ni}(\text{R,S-Me}_6\text{cyclam})]^{2+}$ moieties are part of the monophasic coordination polymer since they bridge dimeric $[\text{UO}_2(\text{Htart})]_2^{2-}$ subunits while Hquin^+ and $[\text{Ni}(\text{bipy})_3]^{2+}$ are simple counterions to anionic, diphasic networks in **2** and **3**, the influence of their different size being notable in the planar and corrugated shape of the layers, respectively. These diphasic networks have as nodes tetranuclear SBUs, $[(\text{UO}_2)_2(\text{tart})(\text{CH}_3\text{COO})]_2^{2-}$, in which the convergent position of the two alkoxide groups results in formation of three adjoining five-membered chelate rings by each ligand. Whereas the dimeric units, whose existence was initially inferred from solution experiments, are analogous to those found with citrate, *R,S*-malate and *R*-citramalate ligands, the tetranuclear units result from a convergent arrangement of the two alkoxide groups and they are peculiar to tartrate. While these results have been obtained on solid state species, they may provide some clues as to the nature of complexes present in solution.

Appendix A. Supplementary data

CCDC 2237343–2237345 contains the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>,

or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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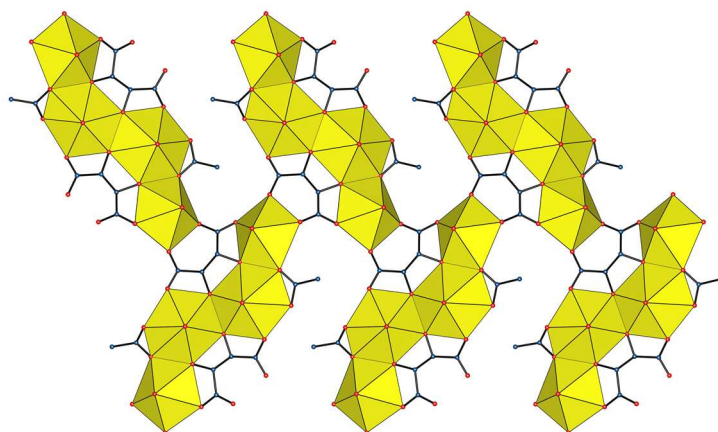
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Table of Contents Entry

(*R,R*)-Tartrate as a polytopic ligand for UO_2^{2+} : mono- and dimeric coordination polymers including di- and tetranuclear subunits

Pierre Thuéry, Jack Harrowfield



(*R,R*)-Tartrate, in its ter- or tetradeprotonated forms, gives mono- or dimeric polymers with uranyl cations, depending on the structure-directing species used. The former contains dimeric subunits analogous to those formed by citrate and related ligands, whereas tetranuclear subunits specific to tartrate are found in the latter.