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Variations on the Honeycomb Topology: from Triangular- and Square-Grooved Networks to Tubular Assemblies in Uranyl Tricarboxylate Complexes

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Supporting Information Placeholder

ABSTRACT: Depending on the counterion, uranyl tricarboxylate, UO₂(tca)⁻², is shown to crystallize either as two-dimensional nets or as one-dimensional tubules, all with honeycomb topology and united into higher dimensional assemblies when additional metal cations (Ag⁺, Pb²⁺) are present. A regular geometric progression involving ligands reorientation is apparent in the series, with triangular furrows in [H₂NMe₂][UO₂(tca)·H₂O] (1) followed by deepening square grooves in [UO₂Ag(tca)(H₂O)·0.5H₂O] (2) and full closure of square tubules in [NH₄][UO₂₂Pb(tca)₂(NO₃)(bipy)].

Since the first reports of uranyl-based nanotubular structures in phosphonate complexes by Clearfield et al. more than 20 years ago,¹⁻⁵ the number of such species has steadily increased and, although they are still uncommon, as expected for this linear cation, they appear to be accessible from a variety of ligand classes. While most examples are still found among phosphonates,¹⁻⁶ notable inorganic tubular arrangements have been found in uranyl selenates,⁹⁻¹¹ and polycarboxylates, prevalent in the design of uranyl–organic coordination polymers,¹²⁻¹⁴ have also provided several cases in recent years.¹⁵⁻¹⁹ Among the latter, phthalate (1,2-benzenedicarboxylate) gives tubular species through connection of hexanuclear rings¹⁶ (an analogous complex with neptunyl has also been reported²⁰); Kemp's tricarboxylate (cis,cis-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylate) yields uranyl–nickel(II) heterometallic tubules or uranyl octanuclear cages depending on whether Ni⁴⁺-bound 2,2'-bipyridine molecules are present or not,¹⁷ and the related cis,cis-1,3,5-cyclohexanetricarboxylate gives either two-dimensional (2D) honeycomb networks or a tubular assembly retaining the same topology, depending on the choice of counterions.¹⁸ Apart from coordination bonds, supramolecular interactions may also be summoned to create such species, and tubular channels are formed through hydrogen bonding of corrugated hexanuclear uranyl–iminodiacetate rings.¹⁹ Due to its curved shape, tricarboxylic acid (1,2,3-propanetricarboxylic acid, H₃tca) is of potential interest to generate uranyl-containing polymers with curved architectures, but the only complex reported so far, [UO₂Na(tca)(H₂O)₂], crystallizes as a 2D network with honeycomb topology.²¹ By varying the experimental conditions, we have now obtained three novel uranyl tricarboxylate complexes, two of which are heterometallic and include Ag⁺ or Pb²⁺ cations, that were synthesized solvothermally and have been characterized by their crystal structure.²² One of these complexes provides a new example of a tubular arrangement, deriving from a regular progression of geometric features in the series.

The asymmetric unit in [H₂NMe₂][UO₂(tca)·H₂O] (1) contains a unique uranyl ion located on a mirror plane and chelated by three carboxylate groups from three tca⁻² ligands (Fig. 1). The U–O(oxo) bond lengths of 1.757(8) and 1.758(7) Å, and the U–O(carboxylate) bond lengths of 2.462(5)–2.468(5) Å are unexceptional. Both metal and ligand are threefold nodes and they generate a 2D network parallel to (1 0 0), with the point (Schläfli) symbol {6¹} (honeycomb topology). This assembly is similar to that in the previously reported complex [UO₂Na(tca)(H₂O)₄] (4),²¹ both displaying triangular grooves. In both cases, grooves from adjacent layers are facing one another so as to form channels that are occupied by carboxylate- and oxo-bound Na(H₂O)₄⁺ cations in complex 4, and by disordered, hydrogen bonded H₂NMe₂⁺ cations in 1, the latter cations being formed in situ from DMF hydrolysis; the Kitaigorodsky packing index (KPI) for 1 is ~0.69. This peculiar geometry of the sheets results from the 1,3-carboxylate groups being in a common plane approximately perpendicular to that of the 2-carboxylate group [dihedral angle θ = 86.8(8)°], the equatorial planes of the uranyl ions bound to these groups retaining approximately the same geometrical relationship.

The asymmetric unit in [UO₂Ag(tca)(H₂O)·0.5H₂O] (2) contains two uranyl and two silver(I) cations, and two tca⁻² ligands (Figs. 2 and S1, Supporting Information). Both uranyl cations are in similar environments with three chelating carboxylate groups from three ligands [U–O bond...
...lengths of 2.418(8)–2.499(8) Å, average 2.46(2) Å. In contrast, the two silver(I) cations are in different environments. Ag1 is chelated by atoms O14 and O15 from two carboxylate groups of the same ligand [bond lengths of 2.516(10) and 2.455(9) Å, respect]...n to either two or three Ag1 ions, the coordination modes of the carboxylate groups being κ²O,O', μ₂-κ¹'O:κ²O,O' or μ₂-κ¹'O:κ²O,O':κ¹'O. If only the uranyl cations and tca³⁻ ligands are considered, a 2D network parallel to (0 0 1) is generated, with the same honeycomb topology as that in 1 and 4; however, instead of displaying a triangular furrowing, this assembly is deeply corrugated and the grooves are square-shaped, a difference apparent in the nodal representations shown in Fig. 3. The difference between the geometries observed in 1/4 and 3/4 arises from the different number of ligand units defining each groove, two in the former case and three in the latter. Ag1 and its symmetry equivalents are located inside these layers and do not lead to a dimensionality increase, while Ag2 and its equivalents are located at the periphery of the sheets and, through formation of doubly water-bridged silver(I) dimers, unite the 2D subunits into a 3D framework. Roughly elliptical channels run along the a axis, due to the grooves facing each other as in 1, that do not exceed ~3 Å in their narrowest parts and are thus too small for any practical use. The framework is compact, as shown by its KPI of 0.77. The coordinated and free water molecules form an intricate network of rather weak simple, bifurcate or even trifurcate hydrogen bonds, the acceptors being uranyl oxo, carboxylate and water oxygen atoms [O⋯O 2.716(15)–3.298(14) Å, H⋯O 2.14–2.52 Å, O–H⋯O 108–164°].

Replacement of Ag¹ by the divalent Pb²⁺ results in a different stoichiometry in the complex [NH₄][[(UO₂)₂Pb(tca)₃(NO₃)₂(bipy)] (3) (bipy = 2,2'-bipyridine), in which the ammonium cations appear to have been generated in situ from acetonitrile hydrolysis possibly catalyzed by U⁶⁺, a similar phenomenon having previously
been encountered during the synthesis of a uranyl pimelate complex.\textsuperscript{23} The two crystallographically independent uranyl ions are both chelated by three carboxylate groups, with unexceptional U–O(oxo) \(1.758(4)–1.779(5)\ \text{Å}\), average \(1.771(8)\ \text{Å}\) and U–O(carboxylate) \(2.422(4)–2.498(5)\ \text{Å}\), average \(2.46(2)\ \text{Å}\) bond lengths (Figs. 4 and S2, Supporting Information). The unique lead(II) cation is chelated by the bipy molecule [Pb–N bond lengths 2.422(6) and 2.452(5)\ \text{Å}] and is bound to the carboxylate atom O6 at 2.722(4) \text{Å} and three oxygen atoms pertaining to two nitrate anions, two of them (O17 and O18) being chelating \(2.515(5)\) and \(2.723(6)\ \text{Å}\) and the third (O19) monodentate \(2.847(6)\ \text{Å}\). The nitrate ion is thus bound in a \(\mu_2\text{-}k'O:k'O',O''\) coordination mode. A longer contact exists between Pb1 and O14\textsuperscript{2+}, at 3.193(4) \text{Å}. Depending on whether this last contact is considered as a true bond or not, the coordination number is six or seven, but the environment is in both cases more hemi-than holodirected.\textsuperscript{24} The tca\textsuperscript{3–} ligand is here also in its right-angled shape, with dihedral angles \(\theta_{ka}\) of 87.8(5) and 88.2(7)\textsuperscript{o}, but, instead of generating a 2D lattice, the UO\textsubscript{2}(tca)\textsuperscript{–} assembly is folded so as to create a tubular 1D polymer directed along the \(a\) axis, while retaining the \{6\} topology. The cross-section of the tubules is square, with an edge length of ~6 \text{Å}, the uranium atoms on the four edges being offset along the \(a\) axis, so that sufficient inner space is available for inclusion of the NH\textsubscript{4}\textsuperscript{+} counterions. The latter are hydrogen bonded to two uranyl oxo and two carboxylate groups from opposite sides of the cavity \(\text{N}--\text{O} 2.971(8)–3.031(9)\ \text{Å}, \text{H}--\text{O} 2.16–2.35\ \text{Å}, \text{N}--\text{H}--\text{O} 134–175\text{o}\), so that it may be surmised that they exert a structure-directing role. The tubules are further assembled into a 2D lattice parallel to \((0 1 0)\) by centrosymmetric nitrate-bridged Pb\textsuperscript{2+} dimers (KPI 0.74), an arrangement reminiscent of the bridging of uranyl phosphonate tubules by Cu\textsuperscript{II} cations.\textsuperscript{8}

A regular geometric progression is thus apparent in this series, from triangular and square grooves defined by two and three ligands, respectively, to tubular shapes lined by four ligands. From a purely geometric point of view, this transformation involves reorientation of otherwise conformationally almost invariant ligands so that the direction of connection changes by 180\textdegree, the topology being unmodified (Fig. 3). A similar conversion of an undulated honeycomb 2D network into a tubular assembly has previously been encountered in uranyl ion complexes with cis,cis-1,3,5-cyclohexanetricarboxylate,\textsuperscript{16} but no intermediate step was found in this case. Of course, the mechanism of formation of the tubules in 3 is unknown and, although formation of nanotubes through folding of the corresponding sheets is a known mechanism,\textsuperscript{9,10} it most probably does not involve 2D intermediates analogous to
those in 1/4 and 2 since ligand reorientation would require the breaking of bonds. The nature of the counterions obviously plays a key-role in the choice of a particular outcome. In particular, the ammonium counterions may be essential in organizing the ligands, during polymer growth, in the best position for hydrogen bonding, thus favoring the formation of a closed assembly encircling the NH₄⁺ divergent, fourfold hydrogen bond donor. The aptitude of honeycomb nets to accommodate folding is particularly evident in carbon nanotubes. With respect to those, the size of the tubular species in 3 is limited by the fact that only four metal/ligand units are sufficient to ensure closure, which is related to one uranium node being markedly displaced from the mean plane of the five other nodes of the hexagonal honeycomb ring, thus giving the latter a pronounced angular shape well suited to define a square cross-section. Larger tubules are obtained when six uranyl/ligand units subtend the tube perimeter, a situation common with other polycarboxylates as well as phosphonates, although narrower tubes with four-membered cross-sections were also found in the latter case.

The emission spectra of complexes 1 and 3 in the solid state were measured at room temperature under excitation at 420 nm (Figure S3). The Supporting Information: no sufficient amount of pure 2 could be obtained. The usual vibronic fine structure is observed in both cases, with the maxima positions being redshifted by 3 nm in complex 3 with respect to those in 1. These positions (463, 480, 500, 522 and 545 nm in 1) are in good agreement with those for other complexes with uranyl ions chelated by three carboxylate groups.

In summary, it appears that, depending on the choice of counterion, uranyl tricarballylate crystallizes as 2D networks with variable degrees and shapes of corrugation, or as a tubular species in which closure is fully achieved. All these forms having a common honeycomb topology, a frequently encountered geometry in uranyl coordination polymers, this points to the possibility of generating other tubular structures, with a diameter depending on the ligand curvature and geometrical flexibility.

ASSOCIATED CONTENT

Accession Codes

CCDC 1529441–1529443 contains 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.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Experimental details, additional figures, emission and excitation spectra of compounds 1 and 3. (PDF)

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Notes

The authors declare no competing financial interest.

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22. Crystal data for 1: C₂H₂NO₄U, M = 507.24, orthorhombic, space group Pnma, a = 16.5103(11), b = 9.96305(5), c = 8.7565(6) Å, V = 1440.38(46) Å³, Z = 4. Refinement of 113 parameters on 1436 independent reflections out of 5357 measured reflections (Rₑ ≈ 0.019) led to R₁ = 0.036, wR₂ = 0.095, S = 1.144, ΔRmax = 2.24 e Å⁻³. Crystal data for 2: C₆H₆AgO₄U, M = 578.03, monoclinic, space group P2₁/c (a = 10.0331(2), b = 10.2446(3), c = 21.0228(6) Å, β = 92.267(2), V = 2160.44(10) Å³, Z = 8. Refinement of 317 parameters on 4107 independent reflections out of 121896 measured reflections (Rₑ ≈ 0.031) led to R₁ = 0.037, wR₂ = 0.110, S = 1.136, ΔRmax = 4.28, ΔRmax = 1.70 e Å⁻³. Crystal data for 3: C₆H₈₂N₂O₇PB₆U₃, M = 1329.68, triclinic, space group P1, a = 10.0187(5), b = 13.1772(10), c = 13.7467(10) Å, α = 62.229(3), β = 88.065(4), γ = 89.737(4), V = 1488.50(19) Å³, Z = 2. Refinement of 433 parameters on 5641 independent reflections out of 68981 measured reflections (Rₑ ≈ 0.080) led to R₁ = 0.030, wR₂ = 0.063, S = 1.096, ΔRmax = 1.69, ΔRmax = 1.32 e Å⁻³.
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The right-angled curvature of the tricarballylate ligand gives a corrugated shape to the two-dimensional honeycomb assemblies it forms with the uranyl cation. The shape of the furrows can be monitored through the choice of counterions, resulting in triangular or square geometries, and finally closure of the grooves to form tubules with square cross-section.