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Filling the equatorial garland of uranyl ion: its content and limitations

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Dedicated to the memory of Jacques Vicens, a man for whom chemistry was truly an art.

Abstract

Crystal structure determinations on the uranyl ion complexes $[H_2N(CH_3)_2]_2[UO_2(bpdc)_2]$, (**1**), (bpdc = 2,2'-bipyridine-3,3'-dicarboxylate), $[pyH]_2[UO_2(btfac)(NO_3)_2](NO_3)$, (**2**), (btfac = 1-phenyl-4,4,4-trifluorobutane-1,3-dionate), $[H_2dabco][UO_2(nta)]_2{\cdot}3H_2O$, (**3**), (dabco = 1,4-diazabicyclo[2.2.2]octane; nta = nitrilotriacetate) and $[Ni(cyclam)UO_2(edta)]{\cdot}2H_2O$, (**4**), (cyclam = 1,4,8,11-tetrazacyclotetradecane; edta = ethylenediaminetetraacetate) have provided further examples of U(VI) in tetragonal-, pentagonal and hexagonal-bipyramidal coordination environments. Consideration of each structure within the context of those of known relatives has been used to assess the influence of factors in addition to repulsions within the primary coordination sphere on the equatorial coordination number of U(VI).

Keywords Uranyl ion complexes · Structure determination · Hydrogen bonding

Declarations

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Availability of data and material All data generated or analysed during this study are included in this published article.
Code availability Not applicable.

Introduction

The high oxophilicity [1] of uranium(VI), reflected basically in the nature of its well-known form as that of uranyl ion, UO_2^{2+} [2], as well as in the difficulty of obtaining the simple aza-analogue of this cation [3], remains operative in the secondary coordination interactions which give rise to the array of donor atoms lying close to one plane perpendicular to the linear O-U-O unit and found almost universally in compounds regarded formally as containing the uranyl cation [2,4]. X-ray crystallographic studies, especially numerous in the case of carboxylate species [5,6,7], have shown that in the solid state this "equatorial garland" may contain different numbers of donor atoms varying between three (e.g. $[HNEt_3][UO_2$(hexahomotrioxacalix[3]arene – 3H)] and related species [8,9] and $[Na(thf)_2][UO_2\{N(SiMe_3)_2\}_3]$ [10]) and six (e.g. $Na[UO_2(OAc)_3]$ [11]), though with five or six being most frequent. The U(VI) aqua ion has been shown to have a pentagonal-bipyramidal form as $[UO_2(OH_2)_5]^{2+}$ in both the solid state and solution through XRD [12-14] and EXAFS measurements allied to computational studies [14-16] but what is very obvious in the crystal structure determinations is that this cation is involved in multiple H-bonding interactions with its environment, raising the question as to what influence such interactions may have on the equatorial coordination number. While H-bonding is certainly well-recognised as a factor influencing solid state structures of uranyl ion carboxylate complexes in particular [5,6,7], as well as in less abundant species (e.g. phosphonates [17]), it has not usually been assessed in terms of any influence upon the equatorial coordination sphere. To some extent, the use of terminology related to the idealised geometry of uranyl ion environments in describing them as, for example, pentagonal- or hexagonal-bipyramidal, disguises the fact that the equatorial donor atoms are rarely truly coplanar, and it should be noted that there are instances where deviations from this situation are quite dramatic [18,19]. Thus, in the present work we describe structural studies of a heterogeneous group of uranyl ion complexes with the specific objective of perceiving factors, not only H-bonding, which may influence equatorial coordination numbers and geometry.

Experimental

Synthesis

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

$[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (RP Normapur, 99%) was purchased from Prolabo. 2,2'-bipyridine-3,3'-dicarboxylic acid (H_2bpdc) and 1-phenyl-4,4,4-trifluorobutane-1,3-dione (benzoyltrifluoroacetone = Hbtfac) were obtained from Aldrich, nitrilotriacetic acid from Fluka and ethylenediaminetetraacetic acid disodium salt dihydrate from Sigma. $[Ni(cyclam)(NO_3)_2]$ was synthesized as previously described [20].

$[H_2N(CH_3)_2]_2[UO_2(bpdc)_2]$ (**1**). 2,2'-bipyridine-3,3'-dicarboxylic acid (24 mg, 0.10 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (35 mg, 0.07 mmol), and PPh_3MeBr (36 mg, 0.10 mmol) were dissolved in a mixture of water (0.8 mL) and DMF (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, giving a few yellow crystals of complex **1** within one month.

$[pyH]_2[UO_2(btfac)(NO_3)_2](NO_3)$ (**2**). 1-phenyl-4,4,4-trifluorobutane-1,3-dione (22 mg, 0.10 mmol) was added to a solution of $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (25 mg, 0.05 mmol) in pyridine (2 mL) and the orange solution formed was kept at 90 °C for 24 h before being allowed to slowly evaporate at room temperature to provide pale yellow crystals.

$[H_2dabco][UO_2(nta)]_2\cdot 3H_2O$ (**3**). Nitrilotriacetic acid (19 mg, 0.10 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (35 mg, 0.07 mmol), and dabco (22 mg, 0.20 mmol) were dissolved in a mixture of water (0.8 mL) and DMF (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, giving a few yellow crystals of complex **3** overnight.

$[Ni(cyclam)UO_2(edta)]\cdot 2H_2O$ (**4**). Ethylenediaminetetraacetic acid disodium salt dihydrate (37 mg, 0.10 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (35 mg, 0.07 mmol), and $[Ni(cyclam)(NO_3)_2]$ (20 mg, 0.05 mmol) were dissolved in a mixture of water (1.3 mL)

and DMF (0.4 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, giving a few yellow crystals of complex **4** within ten days.

Crystallography

The data were collected at 100(2) K (180(2) K for **1**) either on a Nonius Kappa-CCD area detector diffractometer [21] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (complexes **1** and **4**), or on a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source (IμS 3.0 Mo) and a PHOTON III area detector, and operated through the APEX3 software [22] (complexes **2** and **3**). The crystals were mounted into glass capillaries or on Mitegen micromounts with a protective coating of Paratone-N oil (Hampton Research). The data were processed with HKL2000 [23] or SAINT [24], and absorption effects were corrected for empirically with SCALEPACK [23] or SADABS [25]. All structures were solved by intrinsic phasing with SHELXT [26], expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL [27], using the ShelXle interface [28]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The CF_3 group in **2** is rotationally disordered over two sites which were refined with occupancy parameters constrained to sum to unity and with restraints on bond lengths and displacement parameters. The H_2dabco cation in **3** is disordered over two positions sharing one nitrogen atom located on a twofold rotation axis, which were refined with restraints on bond lengths and displacement parameters. When present, the hydrogen atoms bound to oxygen and nitrogen atoms were retrieved from difference electron density maps, except in **3**, in which they were introduced at calculated positions, and they were either treated as riding atoms (**1**, **3** and **4**) or refined (**2**). 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). Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3 [29] and the polyhedral representations with VESTA [30]. The topological analyses were made with ToposPro [31].

Table 1 Crystal data and structure refinement details

Complex	**1**	**2**	**3**	**4**
chemical formula	$C_{28}H_{28}N_6O_{10}U$	$C_{20}H_{18}F_3N_5O_{13}U$	$C_{18}H_{32}N_4O_{19}U_2$	$C_{20}H_{40}N_6NiO_{12}U$
M (g mol^{-1})	846.59	831.42	1075.53	853.32
crystal system	triclinic	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	*Pbcn*	$P\bar{1}$
a (Å)	8.9493(5)	9.8827(10)	19.5372(6)	8.6919(7)
b (Å)	9.3209(4)	11.6479(12)	13.2256(4)	8.7086(7)
c (Å)	9.5887(5)	11.9803(12)	11.1800(3)	11.5053(6)
α (°)	82.526(3)	73.140(5)	90	80.459(5)
β (°)	75.729(3)	85.557(5)	90	86.449(5)
γ (°)	75.748(3)	83.148(5)	90	61.767(4)
V (Å^3)	749.25(7)	1309.0(2)	2888.81(15)	756.53(10)
Z	1	2	4	1
reflections collected	35204	116001	130802	32125
independent reflections	2844	6762	2743	2869
observed reflections [$I > 2\sigma(I)$]	2805	6288	2421	2524
R_{int}	0.063	0.069	0.068	0.051
parameters refined	207	415	240	184
R_1	0.026	0.033	0.030	0.034
wR_2	0.062	0.102	0.063	0.066
S	1.055	1.105	1.066	0.993
$\Delta\rho_{min}$ (e Å^{-3})	−1.68	−1.50	−3.91	−1.05
$\Delta\rho_{max}$ (e Å^{-3})	1.23	3.62	2.89	0.92
CCDC reference number	2046316	2046317	2046318	2046319

Results and discussion

The syntheses of all the presently described materials are all trivial and do not warrant discussion other than to note that they exemplify extremes of common currently adopted procedures in that complex **2** was obtained by simple evaporation of an appropriate mixture of reagents (intended to provide the bis(diketonate) complex) under ambient conditions, whereas complexes **1**, **3** and **4** were obtained by solvo-hydrothermal methods and were crystallised under conditions of elevated pressure and temperature. The composition of the isolated materials is no doubt a reflection of the conditions of synthesis but our interest was focussed upon an analysis of their structures only.

The ligand 2,2'-bipyridine-3,3'-dicarboxylate (bpdc^{2-}) is found in complex **1** as a simple O,O-chelate involving unidentate-O coordination of both carboxylate groups in a centrosymmetric, mononuclear, bis(ligand), anionic species (Fig. 1). The U–O(oxo) bond

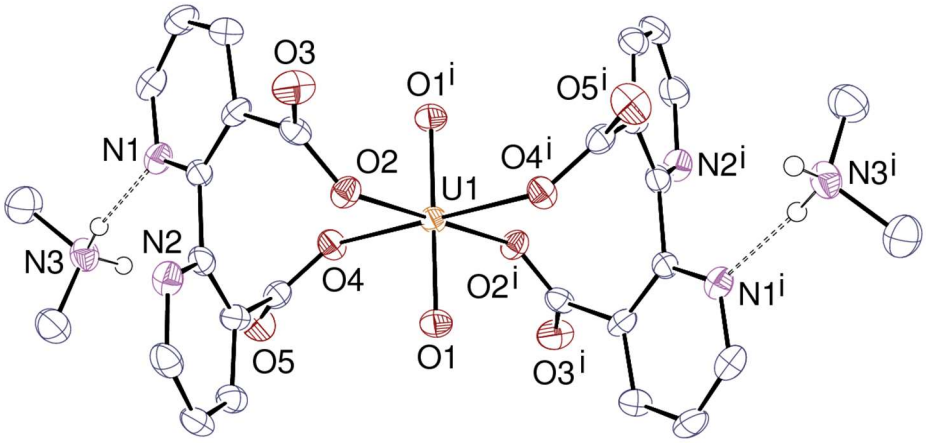


Fig. 1 View of $[H_2N(CH_3)_2]_2[UO_2(bpdc)_2]$ (**1**). Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry code: i = 1 – *x*, 1 – *y*, 1 – *z*.

length of 1.780(3) Å and the U–O(carboxylato) bond lengths of 2.263(3) and 2.338(2) Å do not depart from their usual values. In particular, the mean U–O(carboxylato) bond length for the structures of six-coordinated U(VI) cations involving four equatorial carboxylate groups reported in the Cambridge Structural Database (CSD, Version 5.41) [32], is 2.30(2) Å. The mode of coordination is unusual for the ligand, which is known to adopt N,N-chelation [33] or N,N-chelation plus O-coordination of one carboxylate [34] with Cu(II), bridging by coordination of one oxygen of each carboxylate with Mn(II) [35], association by further bridging-coordination of one oxygen of each carboxylate to two cations with Na(I) and K(I) [36], and bridging by an even more complicated mode involving both N,O- and O,O'-chelation with Rb(I) and Cs(I) [36], although the mode seen in complex **1** has recently been identified, along with others, in heterometallic uranyl ion complexes involving 2,2';2",6'-terpyridine as a co-ligand [37]. It could also be considered as an unusual coordination mode on the basis of the expected preference of a large metal cation for chelation by a small- rather than a large-bite ligand [38], *i.e.* by the bipyridine rather than the dicarboxylate unit, and by the fact that repulsive interactions around the biaryl link place the O-donors rather far apart, although in fact the separation of the coordinated O atoms of bound $bpdc^{2-}$ (3.334(8) Å) is only slightly shorter than the minimum O···O separation in the parent acid H_2bpdc (3.457(9) Å) [33] and O- rather than N-coordination is of course consistent with the oxophilicity of uranyl ion.

Thus, perhaps the most unusual feature of the structure of **1** is the square bipyramidal (octahedral) coordination of the mononuclear U(VI) centre, this being so for two reasons. One is simply that such coordination is rare in uranyl ion complexes generally other than with very simple ligands such as hydroxide [5,6,15] and another is that for carboxylato complexes in particular it is best known for uranyl centres forming part of neutral, infinite polymer chains where the equatorial coordination is due to four μ_2-κ^1O,κ^1O' bridging carboxylate units [6,39-43], although, as noted above, there are precedents [37] for the present observation of a mononuclear species. As well, U(VI) in both six- (octahedral) and seven- (pentagonal bipyramidal) coordination is found in the structures of two heterometallic uranyl ion coordination polymer complexes of 2,2'-bipyridine-3,3';6,6'-tetracarboxylate ($bptc^{4-}$) [43] where, possibly as a result of crowding around the six-coordinate centre, distortions from a regular octahedral geometry are considerably greater than in any other cases. For example, in the structure of $[Cd(UO_2)_3(bptc)_2(H_2O)_2]$, the two U2-O(carboxylate) bond lengths are 2.262(4) and 2.343(4) Å, with (carboxylate)O-U-O(carboxylate) bond angles of 80.0 and 100.0 °, while in $[UO_2(benzoate)_2]$ [39], the corresponding values are 2.38(1) Å (4 equivalent bonds), and 90.8 and 89.2 °.

A significant comparison results from recognition that the ligand 2,2'-bipyridine-3,3'-dicarboxylate is a diaza-analogue of diphenate (1,1'-biphenyl-2,2'-dicarboxylate = dip^{2-}) and while the latter is known to form a variety of uranyl ion complexes with different coordination modes [44], it does form one anionic complex very similar to that in **1**. The complex $[Ni(R,S\text{-}Me_6cyclam)(H_2O)_2][UO_2(dip)_2]$ contains centrosymmetric $[UO_2(dip)_2]^{2-}$ anions (chelating O···O 3.192(6) Å) linked into infinite chains through H-bonding to the coordinated water molecules of the countercation (Fig. 2a). More pertinent to the

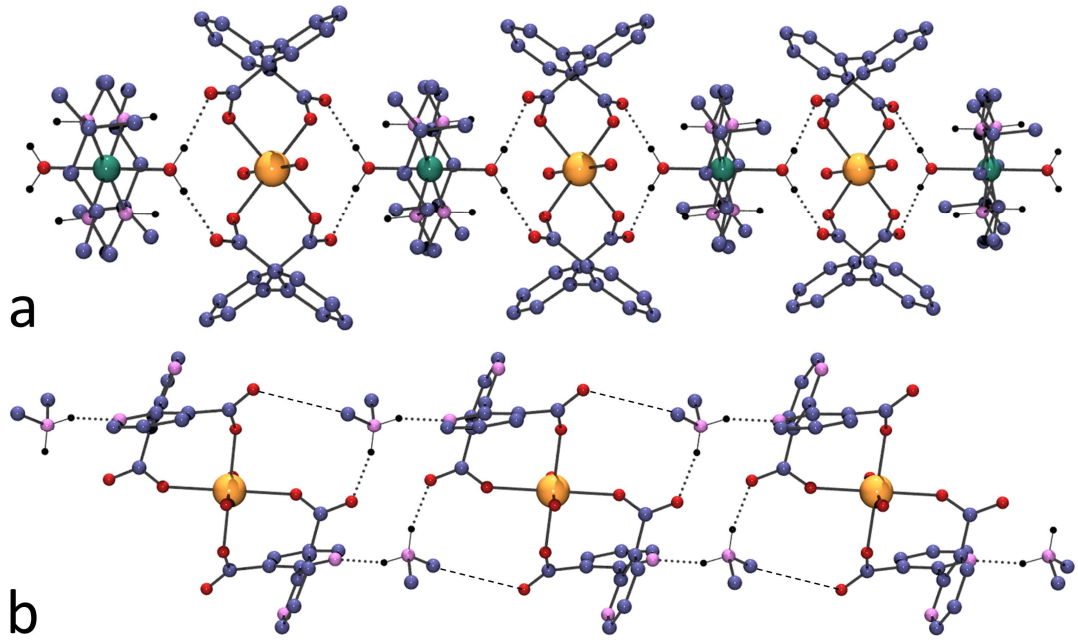


Fig. 2 Hydrogen-bonded chains in [Ni(*R,S*-Me$_6$cyclam)(H$_2$O)$_2$][UO$_2$(dip)$_2$] (a) and in **1** (b). Carbon-bound hydrogen atoms are omitted; OH···O and NH···O/N hydrogen bonds are shown as dotted lines and CH···O bonds as dashed lines.

present work is the observation of exactly this mode of bridging by water in the isomorphous complexes [M(terpy)$_2$][UO$_2$(bpdc)$_2$]·3H$_2$O (M = Ni, Cu) [37]. Here, the water molecules are not coordinated to either metal ion but the dimensions of the dianion, in particular the O···O separation within the chelate rings of 3.299(4) Å (M = Ni) and 3.307(6) Å (M = Cu) are virtually identical and very close to those of complex **1** (see above). Variations in the separation of the carboxylate groups are possible by changes in the degree of twisting about the aromatic ring link and the NCCN dihedral angles of 115 ° in the structures of the [M(terpy)$_2$][UO$_2$(bpdc)$_2$]·3H$_2$O complexes are again close to that of complex **1** (118°) but quite different to that (105°) of the complex [UO$_2$(bpdc)(terpy)]·H$_2$O [37], where the O···O (chelate) separation is 3.009(4) Å. Here, the N$_3$O$_2$ equatorial garland is significantly nonplanar, consistent with repulsive interaction between the two ligands being accommodated in at least two ways and certainly with changes in the O-chelate dimensions being associated with rotational barriers which must be close to minimal.

In complex **1**, interactions of the dimethylammonium countercation with the anion are more complicated than in the earlier examples due the ability of the countercation to act (as is evident on examining the Hirshfeld surface [45,46]) as both

an NH and CH donor in interacting with the O- and N-atoms of the bound ligands. In part, this leads to the formation of H-bonded polymer chains involving NH···O/N interactions of the cation with carboxylate groups and the pyridine rings (Fig. 2a) [N3···N1 2.880(5) Å, N3–H···N1 161°; N3···O5^{j} 2.800(5) Å, N3–H···O5^{j} 160°; symmetry code: j = –*x*, 1 – *y*, 2 – *z*] but there is also a CH···O interaction (C14···O3 3.376(9) Å; H14A···O3 2.48 Å) which results in the cation spanning the two ligands on one uranyl centre and blocking potential additional coordination sites in the same way as free or coordinated water as in the examples cited above (Fig. 2b). In all known cases, therefore, it appears possible that the low coordination number of the U(VI) centres may be a consequence of the blockage of additional coordination sites by the close association of the anionic complex either with its countercation or with solvent.

Complex **2**, $[pyH]_2[UO_2(btfac)(NO_3)_2](NO_3)$, is an analogue of structurally characterised species [47,48] containing anions with acetylacetonate ($acac^-$) in place of $btfac^-$ and in which the uranium(VI) is also in a hexagonal-bipyramidal environment as seen in **2** (Fig. 3). The uranyl cation is chelated by the $btfac^-$ ligand and by two nitrate anions, with U–O bond lengths in the usual ranges [U–O(oxo) 1.764(4) and 1.768(4) Å, U–O(diketonato) 2.361(4) and 2.359(4) Å, U–O(nitrato) 2.512(4)–2.529(4)]. Significantly, bis(diketonato)uranyl ion species appear to be resistant to accepting a

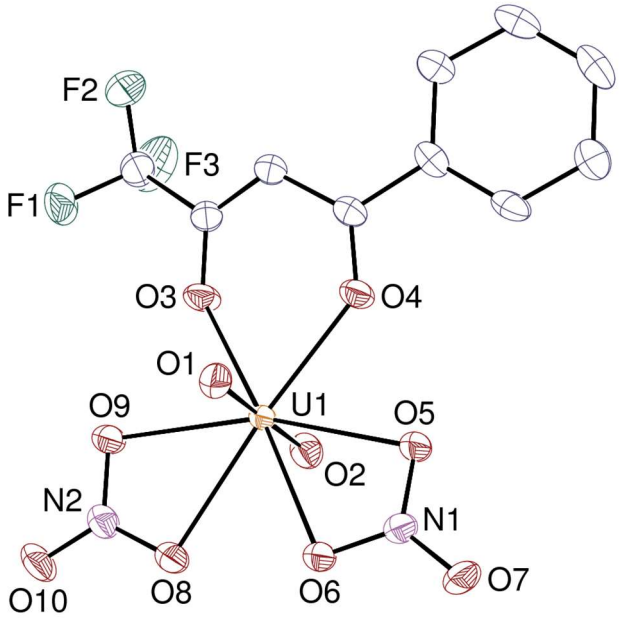


Fig. 3 View of the $[UO_2(tfbzac)(NO_3)_2]^-$ anion in **2**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted and the rotational disorder of the CF_3 group is not shown.

bidentate ligand [48-50] but will accept one extra donor atom in forming a variety of pentagonal-bipyramidal species, two such having been structurally characterised with btfac$^-$ [51,52] and even the simple dimer of anhydrous $UO_2(acac)_2$ being one example [53], this behaviour being taken conventionally to mean that it is the small bite and thus the reduced repulsive interactions of nitrate that enable $[UO_2(diketonate)(NO_3)_2]^-$ anions to form. It has of course been argued that chelating nitrate could well be considered as occupying a single coordination site on a metal ion [54], meaning that in this sense the $[UO_2(btfac)(NO_3)_2]^-$ anion could be regarded as containing again U(VI) in square pyramidal coordination. More significant may be the fact that known structurally characterised $[UO_2(diketonate)(NO_3)_2]^-$ anions all involve protonated aza-aromatic countercations which are involved in multiple CH···O interactions with both nitrate ligands (Fig. 4), again raising the possibility that it is not just interactions within the equatorial coordination sphere that determine its occupancy. Additionally, the uncoordinated nitrate anion in **2** is hydrogen bonded to the two pyridinium cations, both interactions being bifurcated [N···O 2.725(6)–3.064(7) Å, N–H···O 125(7)– 176(8)°].

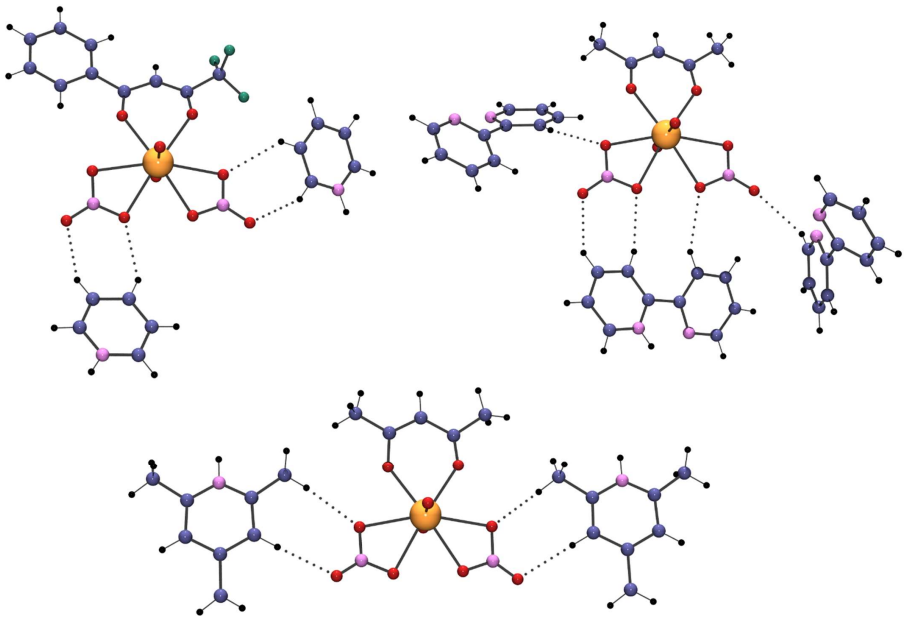


Fig. 4 CH···O interactions (dotted lines) in $[UO_2(diketonate)(NO_3)_2]^-$ anions. (NH···O and NH···N interactions not shown).

The unique uranyl cation in the complex $[H_2dabco][UO_2(nta)]_2{\cdot}3H_2O$ (**3**) is O,N,O-chelated by one nta^{3-} ligand and it is further bound to two carboxylate donors from two more ligands, the uranium environment being thus pentagonal-bipyramidal, as shown in Fig. 5 [U–O(oxo) 1.773(5) and 1.774(5) Å, U–O(carboxylato) 2.313(5)–2.390(4) Å, U–N

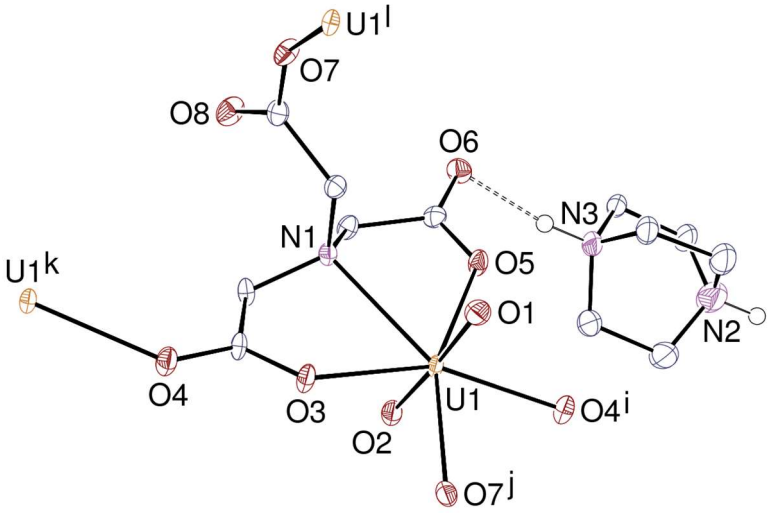


Fig. 5 View of the cation-anion association in $[H_2dabco][UO_2(nta)]_2 \cdot 3H_2O$ (**3**). Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and the hydrogen bond is shown as a dashed line. Only one position of the disordered H_2dabco^{2+} cation is shown. Symmetry codes: i = 3/2 – *x*, *y* – 1/2, *z*; j = 3/2 – *x*, 3/2 – *y*, *z* + 1/2; k = 3/2 – *x*, *y* + 1/2, *z*; l = 3/2 – *x*, 3/2 – *y*, *z* – 1/2.

2.625(5) Å]. The nta^{3-} ligand is thus bound to three metal cations, with one carboxylate group bridging in the anti/anti μ_2-κ^1O:κ^1O' mode and the other two monodentate. Both metal and ligand are thus 3-coordinated (3-c) nodes in the uninodal diperiodic coordination polymer formed, which is parallel to (100) and has the vertex symbol $\{6^3\}$ and the **hcb** topological type (Fig. 6). The disordered H_2dabco^{2+} cations, located between

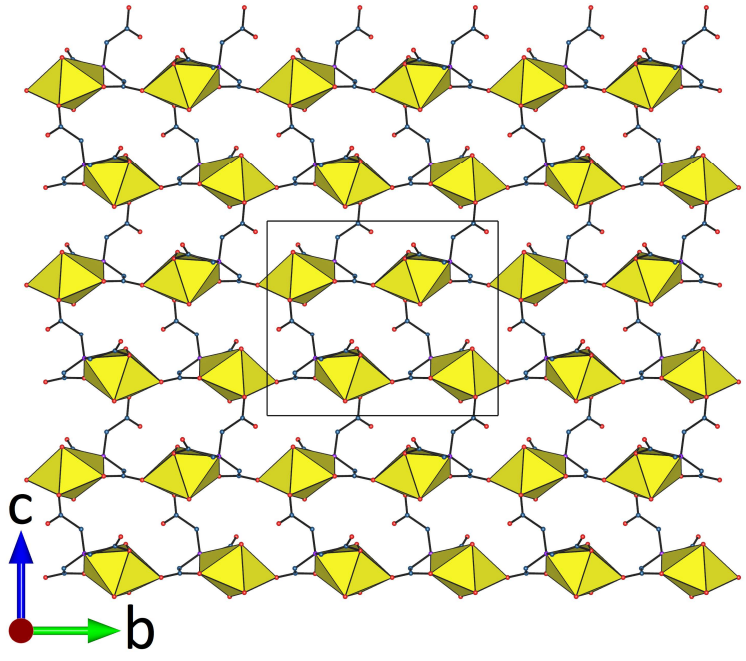


Fig. 6 View of the honeycomb-type network in **3**.

the sheets, are hydrogen bonded to carboxylate groups and water molecules [N···O 2.710(14)–3.041(11) Å, N–H···O 122–172°]. Few uranyl ion complexes involving nitrilotriacetate are known, none involving U–N coordination; where the central nitrogen atom is protonated, the three carboxylate groups are monodentate and a monoperiodic ribbon-like coordination polymer is formed [55,56] while, in the presence of additional Ni(II) cations, a triperiodic framework is obtained [57] in which the nta^{3-} is bound in a tridentate ONO manner to Ni(II) and interactions with the uranyl ions involve carboxylate groups only through monodentate and μ_2-κ^1O:κ^1O' coordination. Interestingly, the difference between Ni–N and Ni–O bond lengths (mean values 2.08 and 2.03 Å, respectively) to the bound nta^{3-} is only 0.05 Å. The principal features worthy of note in the present case are: (i) that it appears that the essentially planar nature of the equatorial uranyl coordination sphere prevents tripodal coordination of the nitrilotriacetate ligand to a single centre, thus leaving one carboxylate free for interaction with a separate uranyl ion, even though this still results in only a di- rather than a tri-periodic coordination polymer; (ii) that in the tridentate unit the U–N bond length is considerably greater, by ~0.27 Å, than that of the U–O, although it is similar to, if slightly shorter than, values known for 2,2'-bipyridine and 1,10-phenanthroline complexes, see e.g. [58].

Rather similar differences in U–N and U–O bond lengths to those in **3** are seen in complexes of the related ligand, iminodiacetate (ida^{2-}) [59,60]. In a series of remarkable nanotube-forming, hexanuclear metallacycle species where the ligand takes an ONO tridentate form as the dianion but is also bidentate-bridging in a zwitterionic monoprotonated form as $(^{-}O_2CCH_2)_2NH_2^{+}$, the mean U–N and U–O values are close to 2.58 and 2.36 Å, respectively, with no systematic differences between the U–O distances for the chelating and bridging groups [59]. The bridging role for the ligand, where it acts simply as an O-donor, is possibly just another reflection of the oxophilicity of uranyl ion but may also indicate that a U–N separation ~2.6 Å is close to the limit of what may be considered a bonding distance. In the simpler complex $[H_2Q][(UO_2)_2(OH)_2(ida)_2]$ (Q = quinuclidine) [60], essentially identical values of r_{U-N} and r_{U-O} apply. That dicarboxylate chelation might enforce coordination of weaker donors held between the carboxylates is also implicit in what is seen in complexes of 2,2'-bipyridine-3,3';6,6'-tetracarboxylate ($bptc^{4-}$) [43], where chelation of the bipyridine unit between two carboxylates is associated with significantly shorter U-N bond lengths than in simple bipyridine

complexes [58] where the coordination number and coordination sphere composition are the same.

Somewhat surprisingly, given the supposed oxophilicity of U(VI), when the N of ida^{2-} is changed to O of oxydiacetate (oda^{2-}), a uranyl complex, $[H_2tmen][UO_2(oda)_2]$ (tmen = tetramethylethylenediamine) can be isolated [60] in which one ligand is bound in a tridentate manner with U–O(carboxylate) 2.352(7) Å and U–O(ether) 2.564(10) Å but the other is bound in a bidentate manner through the carboxylate donors only, with U–O(carboxylate) 2.376(8) Å and (nonbonding) U···O(ether) 3.111(12) Å. The Hirshfeld surface of the complex provides no evidence for interactions beyond dispersion with the uncoordinated ether-O, so it does not appear that there is an external cause of its detachment, implying that the energy of the U–O(ether) bond must be rather small, with its involvement leading to a barely significant decrease in the U–O(carboxylate) bond length associated with a change in the bound ligand conformation, implying that the U–O(ether) bond energy may be comparable to the conformational barrier. When the O of oxydiacetate is changed to the poorer Lewis base S in thiodiglycolate (tdg^{2-}) [61], the ligand behaves solely as a bis(κ^1O,κ^1O') chelate bridging ligand, with no U···S interaction, very much showing the same uranyl ion coordination chemistry as its analogue glutarate where CH_2 replaces S [62].

Similar basic features to those of **3** can be discerned in the structure of complex **4**, $[Ni(cyclam)UO_2(edta)]\cdot 2H_2O$, where the $edta^{4-}$ ligand acts as a bis(tridentate) bridging unit. The unique uranium atom, located on an inversion centre, is O,N,O-chelated by two ligands and is thus in a hexagonal-bipyramidal environment [U–O(oxo) 1.785(3) Å, U–O(carboxylato) 2.364(3) and 2.397(3) Å, U–N 2.788(3) Å] (Fig. 7). The U–N bond length here is significantly longer than that in complex **3**, which is probably due to the pressure of the greater number of equatorial donors in **4**, and indeed somewhat longer also than in the mixed-ligand, $(H^+)edta^{4-}$ containing complexes $[K_4[(UO_2)_4(O_2)_2(Hedta)_2(IO_3)_2]\cdot 16H_2O$ and $LiK_3[(UO_2)_4(O_2)_2(edta)_2(H_2O)_2]\cdot 18H_2O$ [63] which include small-bite peroxo bridges and in which the U–N bond lengths range between 2.665(6) and 2.758(6) Å. The Ni(II) cation in **4** is bound to the four nitrogen atoms of the cyclam macrocycle and it makes two longer axial contacts with two carboxylate oxygen atoms, being thus in a slightly elongated octahedral environment

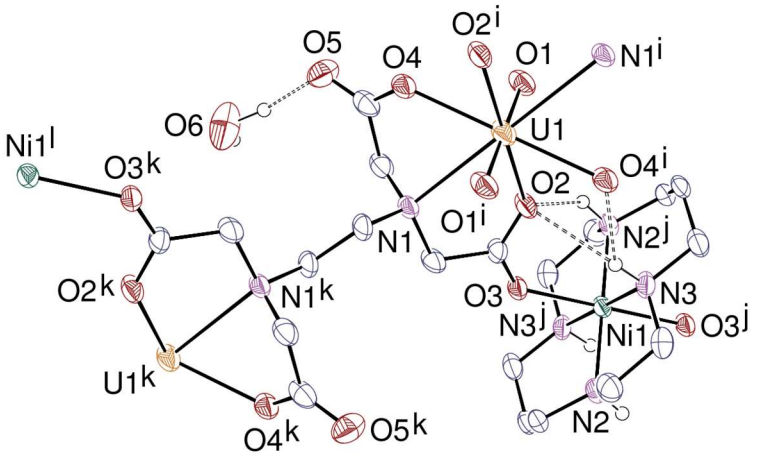


Fig. 7 View of [Ni(cyclam)UO_2(edta)]·2H_2O (**4**). Displacement ellipsoids are drawn at the 50% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: i = 1 – *x*, 1 – *y*, 1 – *z*; j = 1 – *x*, 1 – *y*, 2 – *z*; k = 2 – *x*, 1 – *y*, 1 – *z*; l = *x* + 1, *y*, *z* – 1.

[Ni–N 2.060(4) and 2.071(4) Å, Ni–O 2.120(3) Å]. The cyclam NH groups are hydrogen bonded to carboxylate oxygen atoms [N···O 3.180(5)–3.289(5) Å, N–H···O 136–143°], as usual in such complexes [20], the longer of these interactions causing the $[Ni(cyclam)]^{2+}$ unit to bridge and thus block the gap between ligand units on uranyl ion, just as in complex **3** and its analogues. Two carboxylate groups of the ligand bridge uranium and nickel ions in the syn/anti μ_2-κ^1O:κ^1O' mode, and the other two are monodentate. The ligands link uranyl centres into chains running down [100], these being assembled by the Ni(II) cations into a diperiodic polymeric assembly parallel to (010). Both metal cations are simple links and $edta^{4-}$ is a 4-c node, the uninodal network having the $\{4^4.6^2\}$ vertex symbol and the **sql** topological type (Fig. 8). The water molecules bridge the layers through hydrogen bonding to carboxylato and oxo groups [O···O 2.745(5) and 2.953(5) Å, O–H···O 162 and 165°]. The considerable variations in U–N bond lengths seen in these complexes are consistent with a weak U–N interaction compared to U–O being more subject to significant influence by otherwise subtle differences in structural factors.

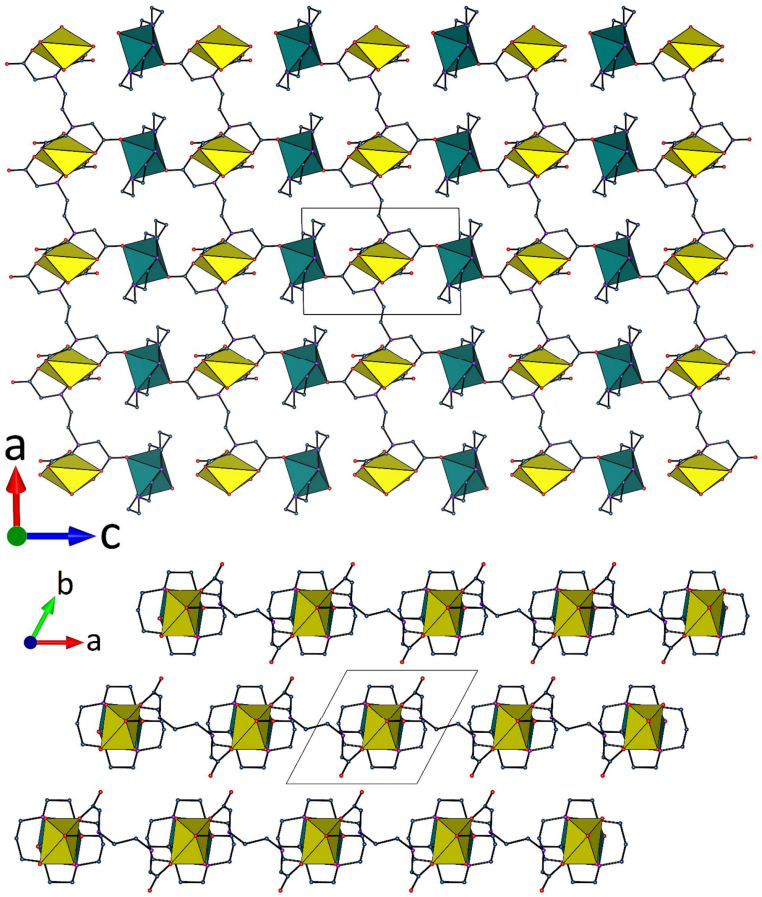


Fig. 8 Views of the diperiodic network (top) and of the packing of layers (bottom) in **4**. Hydrogen atoms and solvent molecules are omitted.

Conclusions

The four structures discussed herein can be placed in a context of numerous similar ones which show the same influences on the overall structure arising from interactions outside the primary coordination sphere of the uranyl ion. It is of course accepted on the basis of theoretical work that both repulsive and attractive interactions within this coordination sphere and its immediately adjacent atoms are important and can have a major effect on individual bond energies [64] but the fact that estimates of UO_2–(donor atom)$_{equatorial}$ bond energies [64,65] are not necessarily much greater than the energy of interactions such as H-bonding justifies the hypothesis that what is observed in the solid state regarding the coordination number of uranyl ion may indeed be a feature of that state only. In addition, structures of the uranyl ion complexes of aliphatic ligands where two carboxylate groups are linked by H_2CXCH_2 (X = NR, O, S) units are interesting in that they show that detachment of the central atom from U(VI) can be associated with a relatively minor conformational change, indicating that the bond energy must be small,

although it is also important to note that even with chelating nitrate, where U···N ~2.9 Å, theory [64] indicates that the U···N interaction makes a significant contribution to the ligand binding. Here again it is plausible that the strong U-O interaction enforces this U-N contact just as it may do in complexes of iminodiacetate, nitrilotriacetate and 2,2'-bipyridine-3,3';6,6'-tetracarboxylate ($bptc^{4-}$).

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