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Perrhenate anion encapsulation in a uranyl ion–zwitterionic dicarboxylate coordination polymer

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Abstract

The zwitterionic dicarboxylate 1,1'-[(2,3,5,6-tetramethylbenzene-1,4-diyl)bis(methylene)]bis(pyridin-1-ium-4-carboxylate) (L) has been reacted with uranyl nitrate under solvo-hydrothermal conditions and in the presence of KReO_4 to give the complex $[\text{UO}_2(\text{L})(\text{OH})(\text{H}_2\text{O})](\text{ReO}_4)$ (**1**). This compound crystallizes as a cationic, monoperiodic coordination polymer with ReO_4^- as a simple counterion. The daisy-chain polymer is based on dinuclear rings built by the convergent zwitterionic ligands, these rings being linked to one another by double hydroxide bridges. In addition to a Coulombic interaction with a pyridinium ring, ReO_4^- is involved in one $\text{OH}(\text{water})\cdots\text{O}$ and four $\text{CH}\cdots\text{O}$ interactions, and it is thus nestled in a cavity formed by three chains, seemingly with some selectivity over nitrate and chloride anions also present in the reaction mixture. This result illustrates the interest of zwitterionic dicarboxylates in building cationic assemblies able to trap ReO_4^- , a surrogate for the radioactive TcO_4^- , an anion of environmental relevance.

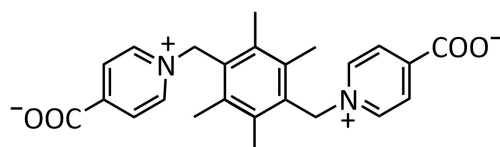
Keywords Uranyl ion · Perrhenate anion · Coordination polymer · Structure elucidation · Zwitterionic ligands

Introduction

Coordination polymers formed by uranyl ion with polycarboxylate ligands [1–5] very commonly have an anionic form and therefore can be regarded as potential cation exchange materials, a property which has in fact been demonstrated in several instances [6–12], if not always with evidence that the polymer form is retained in the process. Possible environmental remediation or nuclear waste treatment applications have nonetheless been foreshadowed [5,13]. Nuclear waste contains not only cationic radioactive species such as $^{137}\text{Cs}^+$ but also radioactive anions such as the long-lived (half-life, 2.13×10^5 yrs) $^{99}\text{TcO}_4^-$ (pertechnetate), and cationic polymers have been widely investigated as a means of removing this highly mobile anion from wastes, coordination polymer systems showing particular promise [14–21]. To optimize the design of cationic coordination polymers for this purpose, it is essential to understand the solid state interactions of the anion and an approach to this which avoids the difficulty of handling highly radioactive material consists of replacing pertechnetate by the structurally essentially identical but non-radioactive perrhenate anion ReO_4^- . Both are anions expected to have some parallel with ClO_4^- in being weak ligands in aqueous solution [22]. However, DFT molecular dynamics simulations of their binding to uranyl ion in particular [23,24] have indicated that this may be much stronger in non-aqueous solvents, and there is spectroscopic proof of TcO_4^- coordination to U^{VI} in CH_2Cl_2 [25]. In the solid state, structural proof of coordination is available for a wide range of metal ions [22] and, in the particular case of the uranyl ion, examples of coordination (most often monodentate) by both pertechnetate [26,27] and perrhenate [22,25,27–32] have been reported. ReO_4^- is, however, a simple counterion in the case of a monoprotic coordination polymer formed by the uranyl ion with cucurbit[7]uril [33], while several occurrences of its encapsulation within cucurbit[n]uril ($n = 6$ or 7) molecules associated with uranyl, thorium or lanthanide ions are known [30,31,34,35]. Examples of perrhenate and/or pertechnetate encapsulation in azacryptands, metallocages or

helicates have also been reported, these being examples of where the binding step must be accompanied by a further selective extraction step in order to isolate the anions [36–46].

A simple way of generating cationic uranyl-based coordination polymers suitable for the inclusion of TcO_4^- or ReO_4^- anions consists of using neutral, zwitterionic polycarboxylate ligands [47]. Some of the monomeric uranyl ion complexes known to trap these anions involve zwitterionic, monocarboxylate donors [27,32], and an example of a polymeric system involving a uranyl ion complex with a zwitterionic dicarboxylate ligand threading cucurbit[6]uril molecules is also known [48]. Some coordination polymers based on other metal ions also involve zwitterionic ligands [18]. This approach is not unlike that using zwitterionic molecular capsules for sequestering of anions, although the host is neutral in these cases [49–51]. There is also a novel example of an anionic uranyl ion polymer where the counteranion is a protonated trizwitterion encapsulating a bromide ion [52]. We have thus extended our studies of uranyl ion coordination polymers incorporating zwitterionic ligands to the complex formed in the presence of perrhenate anions by 1,1'-[(2,3,5,6-tetramethylbenzene-1,4-diyl)bis(methylene)]bis(pyridin-1-ium-4-carboxylate) (L, Scheme 1), which has been characterized by its crystal structure. This ligand has previously been shown to give uranyl ion complexes of periodicity varying from 0 to 3 when associated with other anionic donors [52,53].



Scheme 1 The zwitterionic dicarboxylate ligand L.

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 and KReO_4 was from Aldrich. 1,1'-[(2,3,5,6-Tetramethylbenzene-1,4-diyl)bis(methylene)]bis(pyridin-1-ium-4-carboxylic) acid dichloride (LH_2Cl_2) was synthesized as previously described [52].

$[\text{UO}_2(\text{L})(\text{OH})(\text{H}_2\text{O})](\text{ReO}_4)$ (1). LH_2Cl_2 (24 mg, 0.05 mmol), $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (25 mg, 0.05 mmol), and KReO_4 (29 mg, 0.10 mmol) were dissolved in a mixture of water (0.6 mL) and *N,N*-dimethylacetamide (DMA, 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 **1** 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 APEX3 software [54]. The data were processed with SAINT [55], and absorption effects were corrected for empirically with SADABS [56,57]. The structure was solved by intrinsic phasing with SHELXT [58] and refined by full-matrix least-squares on F^2 with SHELXL [59], using the ShelXle interface [60]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on residual electron density maps and they were refined with geometrical restraints. 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). Drawings were made with ORTEP-3 [61,62] and VESTA [63].

Crystal data for **1**: C₂₄H₂₇N₂O₁₂ReU, *M* = 959.70, triclinic, space group *P* $\bar{1}$, *a* = 9.7130(4), *b* = 11.3658(5), *c* = 13.3665(6) Å, α = 97.6896(15), β = 91.2930(14), γ = 111.4858(12)°, *V* = 1356.61(10) Å³, *Z* = 2. Refinement of 377 parameters on 8261 independent reflections out of 72060 measured reflections (*R*_{int} = 0.043, θ_{\max} = 30°) led to *R*1 = 0.027, *wR*2 = 0.066, $\Delta\rho_{\min}$ = -1.85, $\Delta\rho_{\max}$ = 1.96 e Å⁻³.

Results and discussion

The complex [UO₂(L)(OH)(H₂O)](ReO₄) (**1**), a product of partial hydrolysis of the uranyl cation, was obtained by reacting uranyl nitrate, LH₂Cl₂ and KReO₄ under solvo-hydrothermal conditions. The unique uranium atom is bound to two carboxylate donors from two different ligands, two hydroxide anions and one water molecule (Fig. 1), and its environment is thus pentagonal-bipyramidal [U–O(oxo), 1.779(3) and 1.794(3) Å; U–O(carboxylato), 2.367(3) and 2.419(3) Å; U–O(hydroxo), 2.287(3) and 2.320(3) Å; U–O(water), 2.513(3) Å]. The ligand L is bridging with both carboxylate groups monodentate, a coordinating mode quite frequent with this and other zwitterionic dicarboxylates [52,53,64–66], and a possible indication of a decrease of donor strength with respect to anionic dicarboxylates which is also suggested by photoluminescence properties [67]. The coordination polymer formed is monophasic and directed along [011], and it has the shape of a daisy chain where the zwitterion has a convergent conformation supporting the formation of diuranacyclic units linked by dihydroxido bridges. Despite the presence of one aqua ligand on uranium which might be considered susceptible to substitution, the perrhenate anion is not coordinated. It does, however, exclude the presence of other anions (nitrate, chloride, or hydrolysis products) in the deposited crystals. This selective trapping of perrhenate over nitrate or chloride is possibly related to the reduced hydration of the former due to its larger radius and lower charge density [14,38] (“Hofmeister bias” [68–

70]), although the different weak interactions formed by these anions in the solid state may have an effect too.

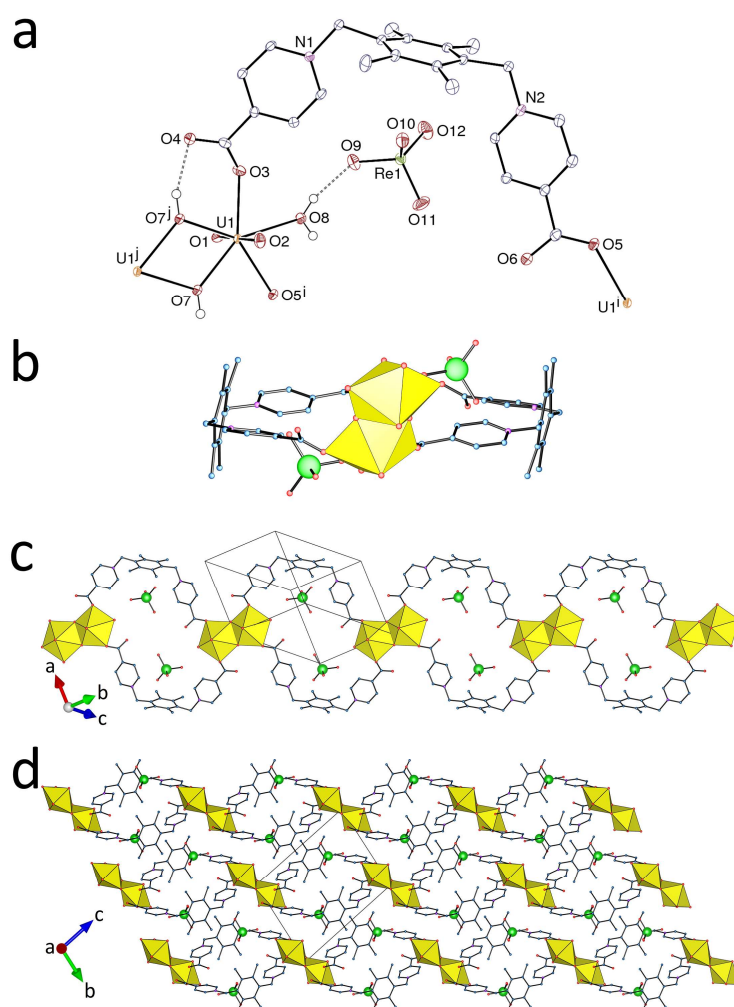


Fig. 1 (a) View of complex **1** with displacement ellipsoids shown at the 50% probability level. Carbon-bound hydrogen atoms are omitted and the hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 2 - x, 1 - y, 1 - z$; $j = 2 - x, 2 - y, 2 - z$. (b) View of the monoperiodic polymer down the chain axis with included perhenate anions; uranium coordination polyhedra are in yellow and rhenium atoms are shown as green spheres. (c) The chain viewed side-on. (d) Packing with chains viewed sideways.

The hydroxide anion forms an intrachain hydrogen bond with the uncoordinated carboxylate oxygen atom O4 [O...O, 2.745(5) Å; O–H...O, 159(6)°], thus forming a ring with the graph set descriptor $R_1^1(6)$ [71,72]. The coordinated water molecule is hydrogen bonded to the other uncoordinated carboxylate atom O6 [2.629(5) Å, 164(7)°] in another $R_1^1(6)$ ring, and

to the perrhenate oxygen atom O9 [2.760(5) Å, 165(6)°]. No solvent molecule is present and the packing of chains leaves no significant free space (Kitaigorodsky packing index evaluated with PLATON [73], 0.72). The aromatic rings are not involved in π -stacking interactions, all centroid \cdots centroid distances being larger than 4.3 Å, but, as usual, several CH \cdots O hydrogen bonds are present, which involve oxygen atoms from the uranyl and perrhenate ions [C \cdots O, 3.184(6)–3.238(6) Å; C–H \cdots O, 124–156°].

The nearly planar, dinuclear ring has a large size (\sim 15 Å between facing tetramethylbenzene rings and \sim 10 Å in the transverse direction), and one perrhenate anion is located in each half of it. Examination of short contacts with PLATON and of the Hirshfeld surface (HS) [74,75] of the anion clearly shows the involvement of O9 as a bridge through one OH \cdots O and one CH \cdots O hydrogen bond, that of O10 also as a bridge through two CH \cdots O bonds with the same chain, and of O11 in only one CH \cdots O bond with another chain, while O12 acts as a donor to a CN bond of a pyridinium unit in a third chain [O \cdots N, 2.913(6) Å; O \cdots C, 2.947(6) Å] (Fig. 2). Since the latter contact is between two charged species, its origin is Coulombic (ion pair), so that it does not strictly qualify as a so-called anion $\cdots\pi$ interaction, these generally involving neutral electron-depleted aromatic rings [76–83]. However, the anion-binding ability of nitrogen-containing heterocycles has been shown to be strongly increased by protonation [84,85], which produces a situation comparable to that observed here. Overall, each perrhenate ion is thus involved in weak interactions with three polymeric chains, forming a weakly bonded triperiodic array. Hydrogen bonding interactions are largely dominant and represent 89.4% of the fingerprint plot of the HS (bulk and peak associated with the shortest distances in Fig. 2d), whereas the O \cdots C and O \cdots N interactions account for only 5 and 1.3%, respectively (secondary peak in Fig. 2d). Out of the six weak interactions formed by ReO $_4^-$, four involve the same polymeric chain, with one of the curved zwitterionic ligands encircling the anion (at bottom right in Fig. 2a). The two other chains fill most of the remaining space, the

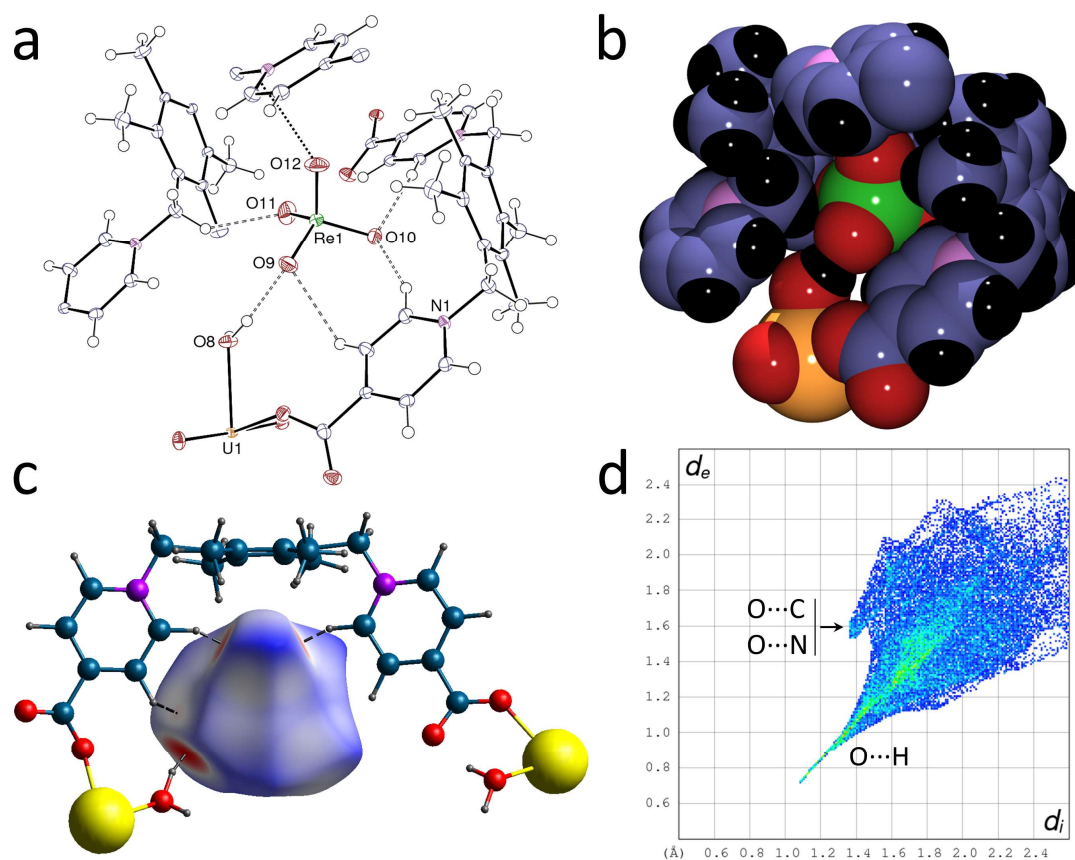


Fig. 2 (a) Interactions of ReO_4^- with three polymeric chains (only part of the L ligand is shown for two of them for clarity); $\text{OH}\cdots\text{O}$ and $\text{CH}\cdots\text{O}$ hydrogen bonds are shown as dashed lines and the $\text{O}\cdots\text{C/N}$ interaction as a dotted line. (b) Space-filling representation of the same motif with the same orientation (U, yellow; Re, green; O, red; N, purple; C, blue; H, black). (c) HS of ReO_4^- mapped with d_{norm} showing four of the hydrogen bonds. (d) Fingerprint plot of the HS.

anion being encapsulated in the cavity thus formed (Fig. 2b). The formation of anionic uranacycles by convergent dicarboxylate donor ligands is rather common and well illustrated in the structures of complexes of phenylenediacetates [86–89], where in some instances diuranacycles are also assembled into daisy-chains and enclose counteranions held in place by hydrogen bonds. In the present structure, the two anions located in the ring are quite well separated, so that any selectivity in their binding does not seem to be associated with their pairwise presence.

The luminescence properties of **1** in the solid state have been investigated, but this complex proved to be non-emissive under excitation at 420 nm. The reasons for this quenching of uranyl luminescence are unclear, and may not be closely related to those invoked in the cases of fluorescent Re/TcO₄⁻ sensing systems of very different nature such as silver(I) or zirconium(IV) cationic coordination polymers [18,21] or cryptands [41]. Complete quenching of uranyl ion emission in coordination polymers is infrequent but certainly not exceptional, as is the observation of emission with the characteristics of an organic luminophore, and the two phenomena may both be a reflection of excitation energy transfer to ligand sites within the solid that themselves may either emit or undergo rapid deactivation.

Conclusions

We have reported the synthesis and crystal structure of a cationic uranyl ion complex with a zwitterionic dicarboxylate ligand crystallizing as a monophasic, daisy-chain polymer incorporating ReO₄⁻, a surrogate for the environmentally hazardous TcO₄⁻, as counteranion. The anions are held in cavities built by one diuranacyclic ring and parts of ligands pertaining to two additional chains by one OH...O and four CH...O hydrogen bonds, and one interaction with an N-C bond of a pyridinium ring. It is notable that perrhenate anions are sequestered selectively in the solid formed, in preference to the chloride and nitrate anions also present in the reaction medium. This result shows that, besides other methods used to generate cationic metal-organic frameworks [19], the use of a zwitterionic dicarboxylate with a large separation between the bonding sites allows for the building of a cationic coordination polymer able to encapsulate ReO₄⁻. In particular, compared with neutral nitrogen donors, these ligands are quite strong and well suited to the complexation of metal ions with a marked affinity for oxygen donors such as the uranyl cation. The cavity in complex **1** is formed from three polymeric chains which are assembled around the perrhenate anion, the latter probably acting as a structure-

directing agent. An obvious further step would be to devise a cationic uranyl-based triperiodic framework with zwitterionic ligands displaying built-in cavities with a size suitable for selective trapping of perrhenate anions, our observations with a trizwitterionic ligand [52] providing some prospect for success.

Supplementary Information

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2311986 (for **1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax (internet.) + 44-1223/336 – 033; E-mail: deposit@ccdc.cam.ac.uk].

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Declarations

Competing Interests The authors declare no competing interests.

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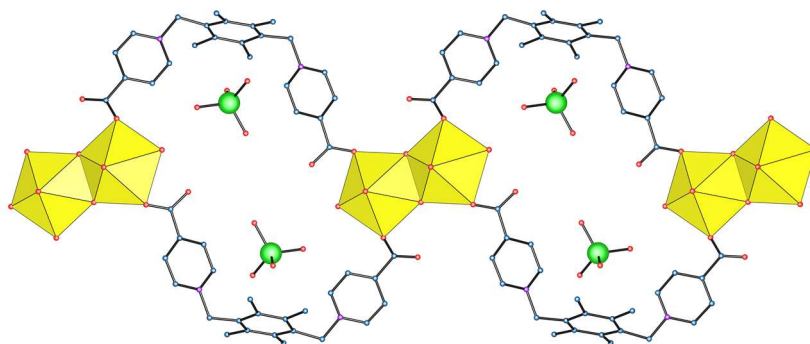
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Table of Contents Entry

Perrhenate anion encapsulation in a uranyl ion–zwitterionic dicarboxylate coordination polymer

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A zwitterionic dicarboxylate ligand was reacted with the uranyl ion to generate a cationic, daisy-chain coordination polymer including perrhenate as counterion. Examination of the Hirshfeld surface of the anion allows for an analysis of the weak interactions involved.