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Protic oligozwitterions as a means of introducing strong hydrogen bonding interactions in uranyl ion coordination polymers

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Abstract

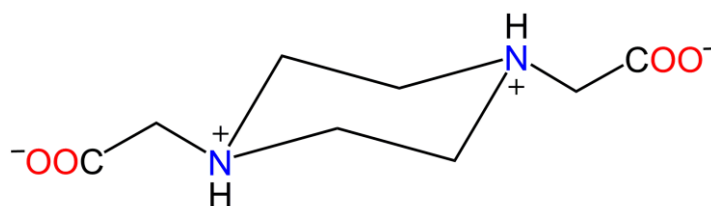
The neutral, dizwitterionic dicarboxylate 1,4-bis(carboxylatomethyl)piperazine (cmpip) was used in the solvo-hydrothermal synthesis of three uranyl ion complexes. Both $[(\text{UO}_2)_2\text{Cl}_2(\text{pda})(\text{cmpip})_2] \cdot 2\text{H}_2\text{O}$ (**1**) and $[(\text{UO}_2)_2\text{Cl}_2(\text{chdc})(\text{cmpip})_2]$ (**2**) are mixed-ligand complexes involving additional dianionic dicarboxylates, 1,4-phenylenediacetate (pda^{2-}) or *trans*-1,4-cyclohexanedicarboxylate (chdc^{2-}), respectively, which crystallize as two-stranded, ladder-like monoperiodic coordination polymers. The chains in **1** and **2** are arranged into thick layers, adjacent chains being associated through strong $\text{NH}\cdots\text{O}$ reciprocal hydrogen bonding of cmpip ligands. The complex $[\text{UO}_2(\text{cmpip})_2(\text{H}_2\text{O})](\text{NO}_3)\text{Cl} \cdot 2\text{H}_2\text{O}$ (**3**) involves only cmpip as a carboxylate donor, and it crystallizes as a diperiodic assembly with the **sql** topology. The four cmpip ligands bound to uranyl are located on the same side of it so as to form a deep cavity, resulting in the heavily puckered geometry of the layers. The cmpip ligands in **3** are involved in extended hydrogen bonding with other cmpip ligands, and chlorine and nitrate anions. Compound **2** is non-emissive, but **1** and **3** have a photoluminescence quantum yield of 7% in the solid state, with an emission spectrum showing the usual vibronic fine structure.

Introduction

Oligozwitterions with carboxylate donor groups and quaternary ammonium centres have proven to be useful in expanding the connectivity within oligocarboxylate coordination polymers based on uranyl ion, though they have not provided cavity-containing solids and, in some cases, have not formed the expected true mixed-ligand polymers where both neutral oligozwitterions and anionic oligocarboxylates are bound in the one polymer chain.^[1] In general, the quaternary ammonium centres do not appear to be involved in strong interactions determining the crystal structures. In contrast, simple (mono) protic carboxylate zwitterions, although commonly limited to a decorative role on uranyl ion coordination polymers,^[2-7] can be involved in multiple hydrogen bonding interactions with a clear structural influence. Their capacity to undergo deprotonation to give anionic carboxylate donors can, however, be a complication of their use in synthesis. Thus, although isonicotinic acid, H-int, under relatively mild, acidic solvothermal reaction conditions, with crystallization at room temperature, provides uranyl ion complexes of its zwitterionic form,^[2] reaction under more vigorous solvothermal conditions, with crystallization under those conditions, gives a complex of its conjugate anion (int⁻).^[8] This is perhaps a reflection of the fact that H-int crystallizes in its neutral, non-zwitterionic form^[9] but is largely zwitterionic in aqueous solution,^[10,11] indicating that the two forms are of similar energy and enabling the neutral acid to undergo deprotonation as seen generally with carboxylic acids under solvothermal conditions. Consistent with this argument is the fact that 4-(aminomethyl)benzoic acid, with a more basic N-centre, is known to adopt its zwitterionic form in the solid state^[12] and readily forms uranyl ion complexes of this form^[3] under solvothermal conditions similar to those we have applied with H-int,^[8] although mixed species are also known.^[13] Hence, in extending our studies to protic oligozwitterions, we have chosen to commence with an

investigation of 1,4-bis(carboxylatomethyl)piperazine (cmpip, Scheme 1), a species involving saturated tertiary amine centres and being one where a single proton can be attached to each centre, thus simplifying its potential hydrogen bonding interactions.

Three crystalline uranyl ion complexes involving cmpip in its dizwitterionic form could be obtained. Two of them are neutral, mixed-ligand complexes, the other ligands being 1,4-phenylenediacetate (pda^{2-}) and *trans*-1,4-cyclohexanedicarboxylate (chdc^{2-}), both species having previously demonstrated their interest for the synthesis of mixed-ligand complexes with anionic and zwitterionic carboxylates.^[14–18] Both compounds crystallize as monophasic coordination polymers. In contrast, the cationic complex with cmpip alone is a diphasic assembly. All three compounds were characterized by their crystal structure and their emission properties in the solid state.



Scheme 1. The dizwitterionic dicarboxylate ligand cmpip.

Results and Discussion

Crystal structures

Given the known tendency of 1,4-phenylenediacetate (pda^{2-}) to form coordination polymers involving, notably, nanotubular arrays and diuranacyclic units behaving as small cavities,^[14,19,20] the synthesis of its uranyl ion complex with cmpip as a co-ligand was investigated in the hope of obtaining a complex with enlarged cavities. The complex $[(\text{UO}_2)_2\text{Cl}_2(\text{pda})(\text{cmpip})_2]\cdot 2\text{H}_2\text{O}$ (**1**), shown in Figure 1, proved to be a true mixed-ligand coordination polymer, in which the centrosymmetric pda^{2-} ligand is bis(κ^2O,O' -chelating)

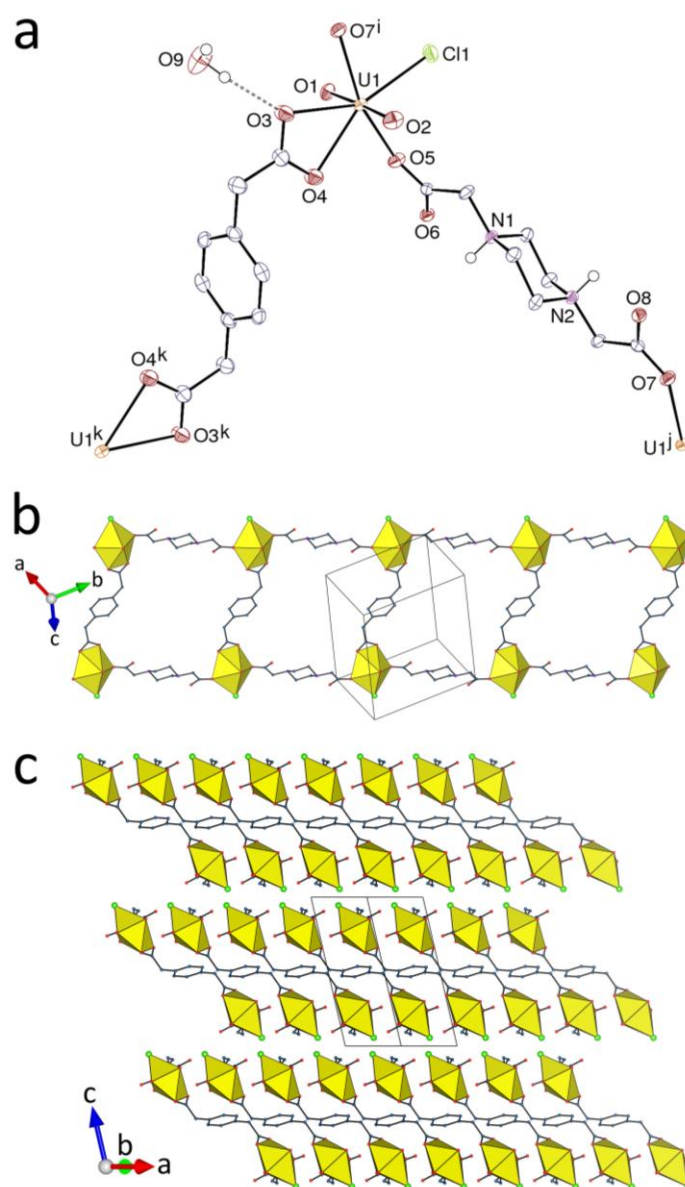


Figure 1. (a) View of complex 1. Displacement ellipsoids are drawn at the 50% probability level. The carbon-bound hydrogen atoms are omitted, and the hydrogen bond is shown as a dashed line. Symmetry codes: $i = x - 1, y + 1, z$; $j = x + 1, y - 1, z$; $k = -x, 1 - y, 1 - z$. (b) View of the ladderlike, monoperiodic coordination polymer with uranium coordination polyhedra in yellow. (c) View of the packing with chains viewed end-on.

and cmpip is bound in bis(monodentate) fashion. As previously remarked for other mixed-ligand complexes,^[4] the connectivity of the zwitterionic ligand is lower than that of the accompanying anionic ligand. With one additional chlorine ligand located between the two

monodentate groups, the uranium atom is in a pentagonal-bipyramidal environment [U–O(oxo), 1.769(4) and 1.773(4) Å; U–O(carboxylato), 2.346(4) and 2.348(4) Å for the monodentate groups, 2.466(5) and 2.469(5) Å for the chelating group; U–Cl, 2.6869(15) Å]. The assembly formed is a relatively simple double-stranded monoperoiodic coordination polymer directed along $[1\bar{1}0]$, which has the $\{4^2.6\}$ point symbol and the (4,4)(0,2) topological type. The chains have a rather gently undulating profile where strands involving just the dizwitterion are cross-linked by pda^{2-} units. Both ligands adopt conformations with divergent arrays of their carboxylate units, which are equatorial in *cmpip*. These polymer units stack one upon the other to form thick sheets parallel to (001), which, when viewed down $[100]$, define channels enclosing the water molecules. This stacking of the polymer units involves both *cmpip* NH groups in reciprocal, inter-dizwitterion $\text{NH}\cdots\text{O}$ hydrogen bonding involving the uncomplexed carboxylate oxygen atoms O6 and O8 [$\text{N}\cdots\text{O}$, 2.702(6) and 2.826(6) Å; $\text{N}-\text{H}\cdots\text{O}$, 166(7) and 165(7)°], thus building a distinctive ring with the graph set descriptor^[21] $R_2^2(10)$ (Figure 2). These interactions are reinforced by the hydrogen bonding of the water molecule with the coordinated atom O3 in two different chains [$\text{O}\cdots\text{O}$, 2.820(8) and 3.142(8) Å; $\text{O}-\text{H}\cdots\text{O}$, 172 and 137°]. Once again, hydrogen bonding by the dizwitterion has a significant influence, especially in the formation of the channels, inviting some optimism as to the possibility of exchanging the water molecules for other species without disrupting the channel structure. Aside from dispersion force interactions, the structure also involves weak $\text{CH}\cdots\text{O}$ hydrogen bonds that link adjacent thick sheets. The chains are tightly packed, as shown by the Kitaigorodsky packing index (KPI, calculated with PLATON^[22]) of 0.75.

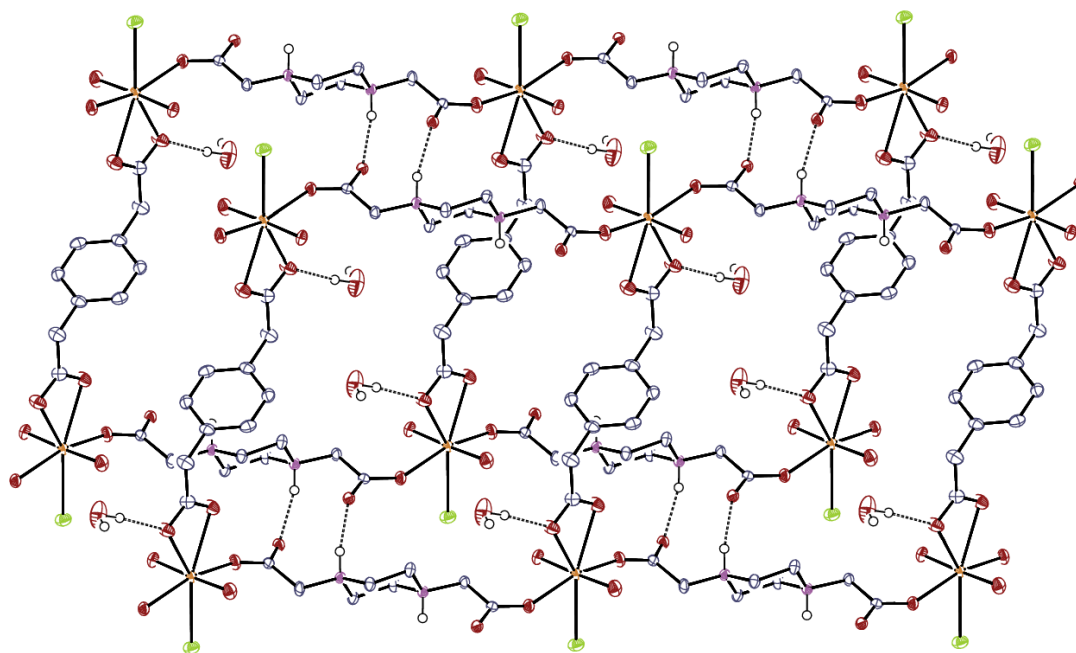


Figure 2. Hydrogen bonding (dashed lines) between two chains in complex **1** (U, yellow; Cl, green; O, red; N, purple; C, blue).

Another ligand known for its conformational flexibility and capacity to provide structures of various dimensionalities, *trans*-1,4-cyclohexanedicarboxylate (chdc^{2-}),^[23–25] was chosen to accompany cmpip in the synthesis of complex **2**, shown from its structure determination to have the composition $[(\text{UO}_2)_2\text{Cl}_2(\text{chdc})(\text{cmpip})_2]$ (Figure 3), differing from that of complex **1** in the absence of ordered water of crystallization, although disordered solvent molecules are probably present (see Experimental Section). In all other respects, however, the complex has a remarkably similar structure to that of complex **1**, the bonding mode of both ligands and uranium environment being identical [U–O(oxo), 1.769(4) and 1.783(4) Å; U–O(carboxylato), 2.297(4) and 2.315(3) Å for the monodentate groups, 2.459(4) and 2.476(4) Å for the chelating group; U–Cl, 2.7117(12) Å]. The coordination polymer formed is monophasic, with two families of chains parallel to either [130] or $[1\bar{1}30]$. Here

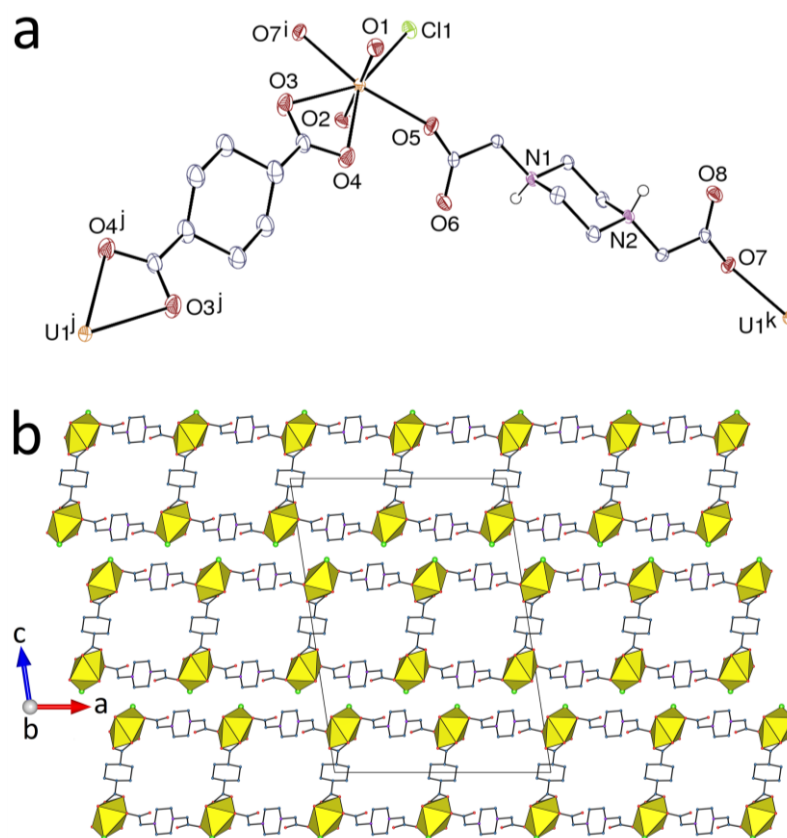


Figure 3. (a) View of complex **2**. Displacement ellipsoids are drawn at the 50% probability level. The carbon-bound hydrogen atoms are omitted. Symmetry codes: $i = x - 1/2, y - 3/2, z$; $j = 1 - x, -1 - y, 1 - z$; $k = x + 1/2, y + 3/2, z$. (b) View of the packing of ladderlike monoperic coordination polymers.

also, parallel double-stranded chains are stacked into sheets with a thickness of ~ 13.3 Å between the planes defined by the outermost chlorine atoms, compared to ~ 12.5 Å in complex **1**. As in **1** also, this stacking involves reciprocal hydrogen bonding interactions of the flanking cmpip units [$N \cdots O$, 2.720(5) and 2.816(5) Å; $N-H \cdots O$, 151 and 163°], reinforced by cyclohexane- $CH \cdots O$ (uranyl) interactions. The presence of disordered water molecules prevents a more detailed analysis of hydrogen bonding interactions. The KPI of 0.63 only indicates the presence of voids occupied by the unresolved solvent molecules.

The complex $[UO_2(cmpip)_2(H_2O)](NO_3)Cl \cdot 2H_2O$ (**3**) is a coordination polymer where cmpip is the only bridging ligand since the pimelate dianion present during the synthesis is

not retained in the final product. The unique U^{VI} centre has a pentagonal-bipyramidal coordination geometry, with its equatorial environment provided by four κ^1O carboxylate donors from four separate cmpip ligands and one water molecule, both nitrate and chloride anions being uncoordinated [U–O(oxo), 1.779(2) Å (twice); U–O(carboxylato), 2.329(2)–2.406(2) Å; U–O(water), 2.386(2) Å] (Figure 4). Two cmpip ligands are centrosymmetric,

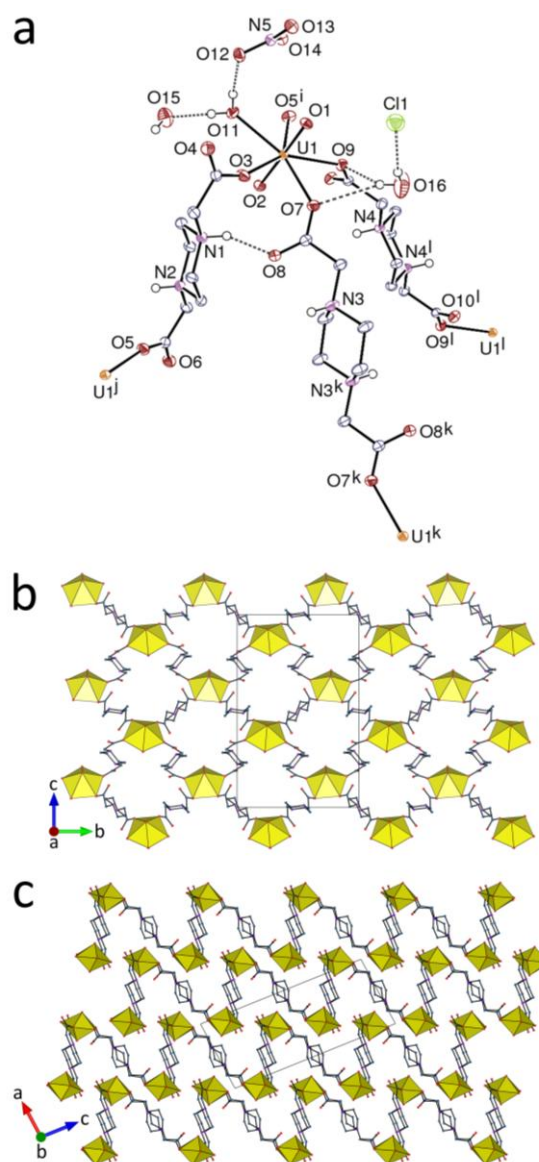


Figure 4. (a) View of complex **3**. Displacement ellipsoids are drawn at the 50% probability level. The carbon-bound hydrogen atoms are omitted, and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 1/2 - x, y - 1/2, 1/2 - z$; $j = 1/2 - x, y + 1/2, 1/2 - z$; $k = -x, 1 - y, 1 - z$; $l = -x, -y, 1 - z$. (b) View of the diperiodic **sqI** network. (c) Packing with layers viewed edge-on.

while the other has only pseudo-inversion symmetry. The disposition of these ligands is somewhat unusual in that all four lie to one side of the uranyl equatorial plane, thus defining a cavity lying to one side of the uranyl unit. The uranium atom is a 4-coordinated node, and all cmpip ligands are simple edges in the diperiodic network formed, parallel to (101), which has the point symbol $\{4^4.6^2\}$ and the very common **sql** topology. The sheets are very strongly puckered, the four uranium centres of the cell being the apexes of a distorted tetrahedron, and they have a width of ~ 11.3 Å. The chloride ion lies close to the centroid of the U_4 unit and it is involved in hydrogen bonding interactions with the N3H group [N \cdots Cl, 3.219(3) Å; N–H \cdots Cl, 165(4)°] and two uncoordinated water molecules [O \cdots Cl, 3.174(4) and 3.180(4) Å; O–H \cdots Cl, 161 and 162°] (Figure 5). Although, like chloride, the nitrate ion lies close to the

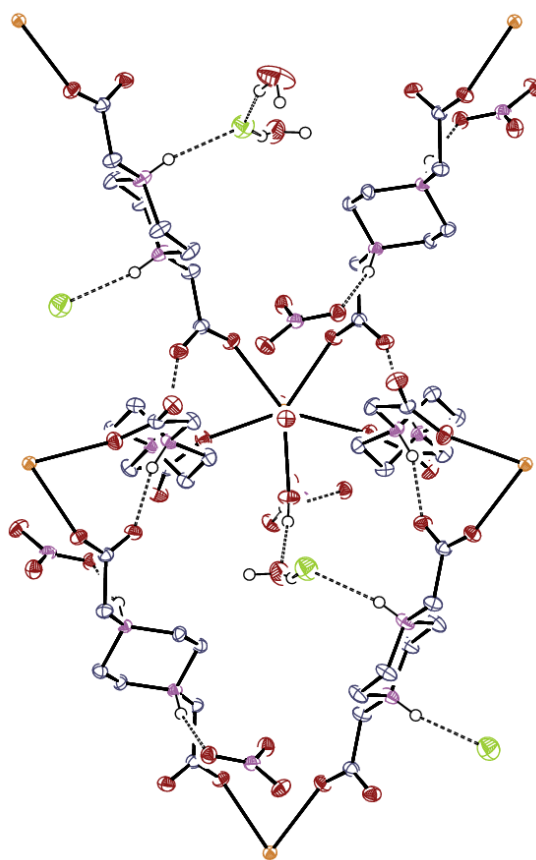


Figure 5. Hydrogen bonding (dashed lines) in complex **3** (U, yellow; Cl, green; O, red; N, purple; C, blue).

mean plane of the puckered sheet, it is well away from the centroid of the U_4 unit, seemingly because of a strong hydrogen bonding interaction with the coordinated water molecule [$O\cdots O$, 2.755(4) Å; $O-H\cdots O$, 172(4)°], and of a bifurcated (but highly asymmetric) bond with the N4H group [$N\cdots O$, 2.831(3) and 2.949(3) Å; $N-H\cdots O$, 166(4) and 113(3)°], along with several weaker $CH\cdots O$ interactions. The N1H and N2H groups of the cmpip ligand with no symmetry are hydrogen bonded to the uncoordinated carboxylate oxygen atoms O8 and O10 pertaining to the same sheet [$N\cdots O$, 2.690(3) and 2.704(3) Å; $N-H\cdots O$, 154(4) and 160(5)°]. The KPI of 0.76 indicates a compact packing with no free space present. The full interactions of the protic zwitterions have a clear overall structural influence, with the effective encapsulation of chloride ions indicating some prospects for their use in forming porous coordination polymers.

Luminescence properties

The emission spectra of complexes **1–3** in the solid state under excitation at 420 nm have been recorded (Figure 6). Complex **2** appears to be nearly non-emissive, but the spectra of **1** and **3**, which have both a photoluminescence quantum yield (PLQY) of 7%, display the typical vibronic progression due to the $S_{10} \rightarrow S_{0\nu}$ ($\nu = 0-4$) transitions of the uranyl ion.^[26,27] The four main peaks are located at 497, 519, 542, and 569 nm for **1** and 495, 517, 540, and 566 nm for **3**, these values being in the range usually observed for uranium centres in a pentagonal-bipyramidal environment with an O_5 equatorial donor set.^[23] The low intensity “hot-band” ($S_{11} \rightarrow S_{00}$) due to electron-phonon coupling^[28] is observed as a shoulder at ~485 nm (**1**) or a very small peak at ~478 nm (**3**).

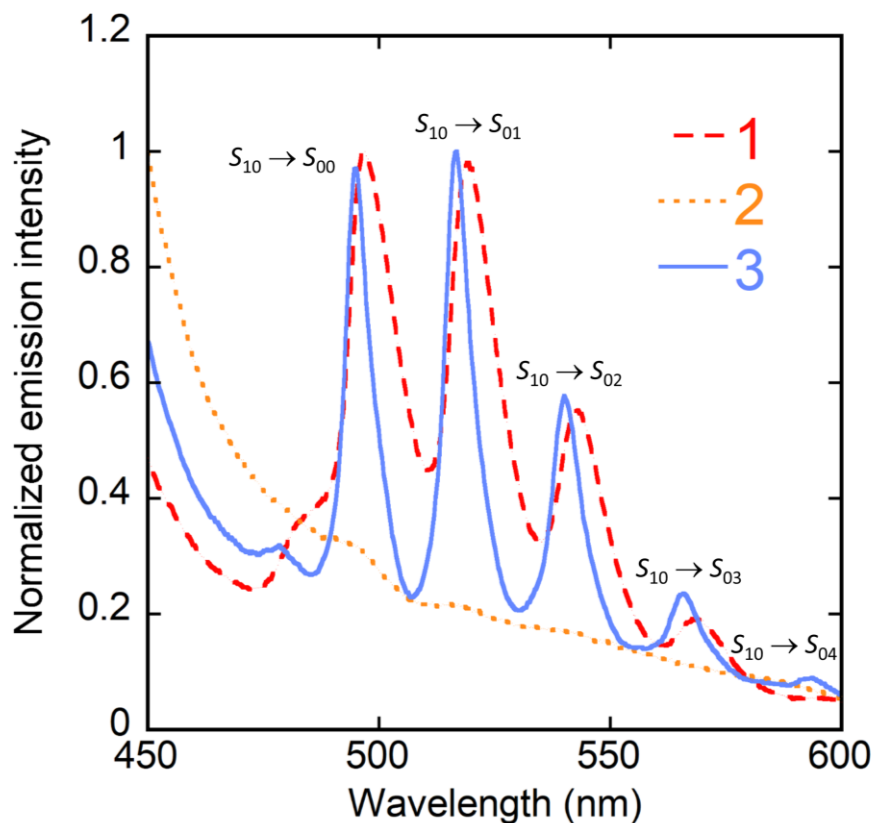


Figure 6. Emission spectra of complexes **1–3** in the solid state, under excitation at 420 nm.

Conclusions

We have reported the synthesis, crystal structure, and luminescence properties of three uranyl ion complexes involving the neutral, dizwitterionic ligand cmpip, either as sole carboxylate donor or associated with the anionic carboxylates pda^{2-} or chdc^{2-} . The coordination polymers formed are monophasic and ladder-like in the two latter cases, while the complex with only cmpip links crystallizes as a diphasic network with **sql** topology. In this case, formation of cavities lined by the four cmpip ligands bound to a single uranyl cation results in a heavily puckered layer shape.

The use of a protic dizwitterion such as cmpip as a ligand in uranyl ion coordination polymers does indeed produce complexes with structures involving spaces potentially suited to guest incorporation, though the promise seen in the structure of the complex of this

ligand in the absence of other carboxylate donors (complex **3**) that mixed-ligand, closed (cage) discrete species might be generated has not been realised in the two instances (complexes **1** and **2**) presently studied. The utility of hydrogen bonding possible with protic zwitterions as a major structural influence is clearly evident even in these cases where a single proton is available at each site. Complex **2** is a relatively novel case in our studies of mixed-ligand, zwitterionic plus anionic carboxylate species in that the co-ligands are both aliphatic in nature. In the numerous previously characterised crystalline complexes of this type involving aromatic ligands, interaction involving the aromatic cores have often appeared to have a structural influence but the fact that, here, complexes **1** and **2** have virtually identical structures implies that any such interactions are readily overwhelmed by zwitterion NH bonding. Novel structures have in fact been observed in several instances for simple complexes of aliphatic dicarboxylates, indicating that further exploration of aliphatic-aliphatic zwitterion-anion combinations may be worthwhile.

Experimental Section

General: $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (RP Normapur, 99%) was purchased from Prolabo. 1,4-Phenylenediacetic acid (H_2pda) was from Aldrich and *trans*-1,4-cyclohexanedicarboxylic acid (H_2chdc) was from Alfa Aesar. The ^1H NMR spectrum of $\text{H}_2\text{cmpipCl}_2$ was recorded on a Bruker AVANCE III HD 400 (400.13 MHz) spectrometer at ambient temperature.

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.

1,4-bis(carboxymethyl)piperazine (cmpip): $\text{H}_2\text{cmpipCl}_2$ was prepared upon slight modifications of previously reported methods.^[29,30] Piperazine (2.0 g, 23.8 mmol) was dissolved in an aqueous solution of 10% NaOH (10 mL, 62.5 mmol). Chloroacetic acid (4.8 g, 50.8 mmol) was then gradually added to the solution. After stirring the mixture at ambient temperature overnight, it was acidified with conc-HCl, forming a white precipitate. The turbid solution was stirred for 3 hours at ambient temperature, filtered, washed with water, and dried in an oven to yield the product (2.9 g, 60% yield). ^1H NMR (D_2O): δ 3.55 (s, 4H), 3.36 ppm(s, 8H) (Figure S1, Supplementary Information).

$[(\text{UO}_2)_2\text{Cl}_2(\text{pda})(\text{cmpip})_2]\cdot 2\text{H}_2\text{O}$ (1): $\text{H}_2\text{cmpipCl}_2$ (14 mg, 0.05 mmol), H_2pda (10 mg, 0.05 mmol), and $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ (25 mg, 0.05 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL). The mixture 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 **1** formed within three weeks.

$[(\text{UO}_2)_2\text{Cl}_2(\text{chdc})(\text{cmpip})_2]$ (2): $\text{H}_2\text{cmpipCl}_2$ (14 mg, 0.05 mmol), H_2chdc (9 mg, 0.05 mmol), and $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ (25 mg, 0.05 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL). The mixture 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 **2** formed overnight.

$[\text{UO}_2(\text{cmpip})_2(\text{H}_2\text{O})](\text{NO}_3)\text{Cl}\cdot 2\text{H}_2\text{O}$ (3): $\text{H}_2\text{cmpipCl}_2$ (14 mg, 0.05 mmol), pimelic acid (8 mg, 0.05 mmol), and $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ (25 mg, 0.05 mmol) were dissolved in a mixture of

water (0.6 mL) and acetonitrile (0.2 mL). The mixture 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 **3** formed within three weeks.

Crystallography: The data were collected on a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source ($I\mu S$ 3.0 Mo) and a PHOTON III area detector, and operated through the APEX4 software.^[31] The data were processed with SAINT,^[32] and absorption effects were corrected empirically with SADABS.^[33,34] The structure was solved by intrinsic phasing with SHELXT^[35] and refined by full-matrix least-squares on F^2 with SHELXL,^[36] using the ShelXle interface.^[37] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to nitrogen atoms were found and either refined with geometric restraints (**1** and **3**) or treated as riding atoms (**2**). The hydrogen atoms of water molecules were found and treated as riding atoms (**1**) or refined with geometric restraints (**3**). The 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. Some voids in the structure of **2** indicate the presence of unresolved solvent molecules whose contribution to the structure factors was removed with SQUEEZE; 62 electrons were added per formula unit, possibly corresponding to about 6 water molecules. Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3^[38,39] and the polyhedral representations with VESTA.^[40] The topological analyses were done with ToposPro.^[41]

Deposition Numbers 2404713 (for **1**), 2404714 (for **2**), and 2404715 (for **3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Table 1. Crystal data and structure refinement details.

	1	2	3
Empirical formula	C ₂₆ H ₄₀ Cl ₂ N ₄ O ₁₈ U ₂	C ₂₄ H ₃₈ Cl ₂ N ₄ O ₁₆ U ₂	C ₁₆ H ₃₄ ClN ₅ O ₁₆ U
<i>M</i> (g mol ⁻¹)	1243.58	1185.54	825.96
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	6.2295(3)	20.9354(8)	9.0251(3)
<i>b</i> (Å)	10.8549(6)	6.4170(2)	13.4278(4)
<i>c</i> (Å)	13.3728(7)	28.8204(12)	21.3729(6)
α (°)	93.298(2)	90	90
β (°)	101.902(2)	98.6186(12)	96.1470(13)
γ (°)	101.303(2)	90	90
<i>V</i> (Å ³)	863.14(8)	3828.1(2)	2575.23(14)
<i>Z</i>	1	4	4
Reflections collected	53130	27500	106054
Independent reflections	3255	3608	7837
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	3209	3532	7238
<i>R</i> _{int}	0.047	0.044	0.049
Parameters refined	241	217	382
<i>R</i> ₁	0.024	0.028	0.025
<i>wR</i> ₂	0.075	0.062	0.068
<i>S</i>	1.111	1.251	1.061
$\Delta\rho_{\min}$ (e Å ⁻³)	-1.38	-2.32	-1.78
$\Delta\rho_{\max}$ (e Å ⁻³)	1.71	1.63	2.30

Luminescence Measurements: Emission spectra were recorded on solid samples using an Edinburgh Instruments FS5 spectrofluorimeter equipped with a 150 W CW ozone-free xenon arc lamp, dual-grating excitation and emission monochromators (2.1 nm mm⁻¹ dispersion; 1200 grooves mm⁻¹) and an R928P photomultiplier detector. The powdered compounds were pressed to the wall of a quartz tube, and the measurements were performed using the right-angle mode in the SC-05 cassette. An excitation wavelength of 420 nm was used in all

cases, and the emission was monitored from 450 to 600 nm. The quantum yield measurements were performed using a Hamamatsu Quantaaurus C11347 absolute photoluminescence quantum yield spectrometer and exciting the samples between 300 and 400 nm.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Uranyl cation / Carboxylic acids / Zwitterionic ligands / Coordination polymers / Structure elucidation / Photoluminescence

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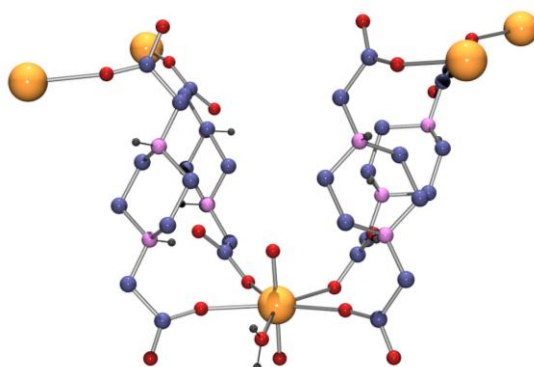
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Table of Contents Entry

Protic oligozwitterions as a means of introducing strong hydrogen bonding interactions in uranyl ion coordination polymers

Young Hoon Lee, Youssef Atoini, Sotaro Kusumoto, Shinya Hayami,
Yang Kim, Jack Harrowfield, and Pierre Thuéry

Key Topic: Uranyl complexes



A protic, dizwitterionic dicarboxylate has been used as a ligand for the uranyl ion, either alone or in association with anionic dicarboxylates, giving three complexes which crystallize as mono- or diperiodic coordination polymers and display extended hydrogen bonding interactions.