[Ni(cyclam)]²⁺ and [Ni(R,S-Me6cyclam)]²⁺ as Linkers or Counterions In Uranyl–Organic Species with cis-and trans-1,2-Cyclohexanedicarboxylate Ligands

Pierre Thuéry, Jack Harrowfield

► To cite this version:

Pierre Thuéry, Jack Harrowfield. [Ni(cyclam)]²⁺ and [Ni(R,S-Me6cyclam)]²⁺ as Linkers or Counterions In Uranyl–Organic Species with cis-and trans-1,2-Cyclohexanedicarboxylate Ligands. *Crystal Growth & Design*, 2018, 18, pp.5512-5520. 10.1021/acs.cgd.8b00834 . cea-01855343

HAL Id: cea-01855343

<https://hal-cea.archives-ouvertes.fr/cea-01855343>

Submitted on 7 Aug 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

[Ni(cyclam)]²⁺ and [Ni(*R,S*-Me₆cyclam)]²⁺ as Linkers or Counterions In Uranyl–Organic Species with *cis*- and *trans*-1,2-Cyclohexanedicarboxylate Ligands

Pierre Thuéry^{*,†} and Jack Harrowfield^{*,‡}

[†]NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France

[‡]ISIS, Université de Strasbourg, 8 allée Gaspard Monge, 67083 Strasbourg, France

ABSTRACT: The macrocyclic species [Ni(cyclam)]²⁺ and [Ni(*R,S*-Me₆cyclam)]²⁺ were used as additional cations in the solvo-hydrothermal synthesis of five uranyl ion complexes with *cis*- or *trans*-1,2-cyclohexanedicarboxylic acids (*c*-1,2-chdcH₂ and *t*-1,2-chdcH₂). In the complex [UO₂(*c*-chdc)₂Ni(cyclam)(H₂O)] (**1**), dimeric uranyl dicarboxylate subunits are assembled into a two-dimensional (2D) network through axial coordination of Ni^{II} to carboxylate groups. Although they involve different isomers, the complexes [(UO₂)₂(*c*-chdc)₂(*c*-chdcH)₂Ni(cyclam)] (**2**) and [(UO₂)₂(*t*-chdc)₂(*t*-chdcH)₂Ni(cyclam)] (**3**) are very similar, both containing uranyl-based one dimensional (1D) subunits which are assembled into 2D networks by bridging [Ni(cyclam)]²⁺ groups. The orientation of the uncoordinated carboxylic group is different in **2** and **3**, the layers in **2** being hydrogen bonded to each other through carboxylic acid dimer formation. Using the pure (*1R,2R*) enantiomer of *t*-1,2-chdcH₂ gives the complex [Ni(cyclam)][(UO₂)₅(*R-t*-chdc)₃(*R-t*-chdcH)(O)₂(CH₃COO)] (**4**), in which pentanuclear uranyl subunits are assembled into 1D chains by dicarboxylic/ate ligands in the usual bis(equatorial) chair conformation, another ligand in the divergent bis(axial) conformation uniting these chains into a 2D assembly; the [Ni(cyclam)]²⁺ ions are simple counterions and are stacked in parallel fashion between the layers. [Ni(*R,S*-Me₆cyclam)][Ni(*R,S*-Me₆cyclam)(H₂O)₂][(UO₂)₂(*t*-chdc)₂(O)]₂ (**5**), in which the (*1R,2R*) enantiomer used has undergone racemization, contains discrete bis(μ₃-oxo)-centered tetranuclear uranyl complexes, organized into columns and layers by extensive hydrogen bonding to the counterions. The discoidal shape, available axial coordination sites and hydrogen bond donor potential of these macrocyclic Ni^{II} complexes make them efficient assembling agents in uranyl–organic coordination polymers. As often observed in the presence of d-block metal cations, uranyl luminescence is either completely or partially quenched in complexes **1** and **3**, respectively.

INTRODUCTION

The formation of heterocationic complexes involving uranyl ion and multidentate ligands has proven to be a prolific means of generating uranyl ion clusters, rings, cages and one- to three-dimensional coordination polymers.¹⁻⁵ Both metallic and non-metallic cations have been used as the species to accompany uranyl ion but the former group has been the source of the greatest variety. This is in large part because a given metal ion can take different forms depending on its coligands, thus leading to functions varying from that of simple charge balance as an independent species interacting with the uranyl polymer through weak interactions (such as $\text{CH}\cdots\text{O}$ hydrogen bonds) only, through that of decoration of a uranyl polymer involving mostly only one or two coordination sites of the metal ion, to that of a bridging unit in a true heterometallic cluster or polymer. This last role is of particular interest because of the possibility of controlling the nature of the bridging by the use of coligands which limit the number and relative orientation of the coordination sites available for bridging, a possibility we have recently explored through the use of alkali metal ion complexes of crown ethers as cocations with uranyl ion.⁶ Greater opportunities, however, are offered by the use of transition metal ions, not only because of their varied spectroscopic, magnetic and redox properties but also because of the extensive nature of their known coordination chemistry with macrocyclic ligands,⁷⁻¹¹ ligands which provide exceptionally stable complexes with controlled location of remaining coordination sites. Thus, in the present work we have examined the influence of the cations $[\text{Ni}(\text{cyclam})]^{2+}$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane) and $[\text{Ni}(\text{R,S-Me}_6\text{cyclam})]^{2+}$ (*R,S*-Me₆cyclam (meso isomer) = 7(*R*),14(*S*)-5,5,7,12,12,14-hexamethylcyclam) on the crystal structures adopted by uranyl ion complexes of both *cis*- and *trans*-1,2-cyclohexanedicarboxylate, ligands known otherwise to give rise to a number of novel uranyl ion complexes.¹²⁻¹⁴ With the quadridentate macrocycles forming a square-planar N₄ array around Ni^{II}, these nickel complexes are known to form both diamagnetic and

paramagnetic species depending upon whether or not two extra axial donor atoms are present.^{7–10,15–17} In general, the presence of Ni^{II} in heterometallic uranyl ion complexes is known to influence the luminescence of the uranyl centres,^{18–20} so that various prospects, including that of thermally induced spin state changes possibly associated with changes in luminescence quantum yields, arise with the use of these materials.

EXPERIMENTAL SECTION

Syntheses. *Caution!* *Uranium is a radioactive and chemically toxic element, and uranium-containing samples must be handled with suitable care and protection.*

UO₂(NO₃)₂·6H₂O (depleted uranium, R. P. Normapur, 99%) was purchased from Prolabo, *cis*-1,2-cyclohexanedicarboxylic acid (*c*-chdcH₂) was from Alfa Aesar, and *rac-trans*-1,2-cyclohexanedicarboxylic acid (*rac-t*-chdcH₂) was from Lancaster. The (1*R*,2*R*) enantiomer of *t*-chdcH₂, denoted *R-t*-chdcH₂, was isolated through crystallization with (*R*)-1-phenylethylamine as a resolving agent, as in the literature,²¹ although both the (1*R*,2*R*) and (1*S*,2*S*) enantiomers are also available commercially. *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.²² Elemental analyses were performed by MEDAC Ltd. at Chobham, UK. For all syntheses of uranyl ion complexes, the mixtures in demineralized water were placed in 10 mL tightly closed glass vessels and heated at 140 °C under autogenous pressure.

[Ni(cyclam)(NO₃)₂]. Separate solutions of cyclam (200 mg, 1.00 mmol) in CH₃OH (5 mL) and Ni(NO₃)₂·6H₂O (290 mg, 1.00 mmol) in CH₃OH (5 mL) were mixed to immediately provide a yellow-brown solution. A small amount of very insoluble yellow material was filtered out and the filtrate mixed with diethyl ether (10 mL) to cause precipitation of [Ni(cyclam)(NO₃)₂] as a pale violet solid which was collected by filtration and washed with ether (280 mg, 73% yield).

$[Ni(R,S\text{-}Me_6cyclam)(NO_3)_2]$. $Ni(NO_3)_2 \cdot 6H_2O$ (1.45 g, 5.00 mmol) was dissolved in dimethylsulfoxide (5 mL) by gentle warming and stirring to give a yellow-green solution. A solution of $R,S\text{-}Me_6cyclam$ (1.40 g, 4.90 mmol) in methanol (2 mL) was then added, the colour of the solution rapidly changing to a brownish-violet and precipitation of violet crystals commencing almost immediately. Ethanol (20 mL) was added to complete the precipitation and the product was finally collected by filtration, washed with ethanol, then diethyl ether and air dried (2.0 g, 85% yield).

$[UO_2(c\text{-}chdc)_2Ni(cyclam)(H_2O)]$ (**1**). $c\text{-}chdcH_2$ (17 mg, 0.10 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (35 mg, 0.07 mmol), and $[Ni(cyclam)(NO_3)_2]$ (40 mg, 0.10 mmol) were dissolved in water (0.7 mL) and DMF (0.2 mL). Crystals of complex **1** were obtained overnight (29 mg, 65% yield based on the acid). Anal. Calcd for $C_{26}H_{46}N_4NiO_{11}U$: C, 35.19; H, 5.22; N, 6.31. Found: C, 34.97; H, 5.08; N, 6.09%.

$[(UO_2)_2(c\text{-}chdc)_2(c\text{-}chdcH)_2Ni(cyclam)]$ (**2**). $c\text{-}chdcH_2$ (17 mg, 0.10 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (35 mg, 0.07 mmol), and $[Ni(cyclam)(NO_3)_2]$ (20 mg, 0.05 mmol) were dissolved in water (0.6 mL). Crystals of complex **2** were obtained in low yield within two weeks (2 mg, 5% yield based on the acid). Anal. Calcd for $C_{42}H_{66}N_4NiO_{20}U_2$: C, 34.05; H, 4.49; N, 3.78. Found: C, 34.07; H, 4.30; N, 3.98%.

$[(UO_2)_2(t\text{-}chdc)_2(t\text{-}chdcH)_2Ni(cyclam)]$ (**3**). $rac\text{-}t\text{-}chdcH_2$ (17 mg, 0.10 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (35 mg, 0.07 mmol), and $[Ni(cyclam)(NO_3)_2]$ (40 mg, 0.10 mmol) were dissolved in water (0.6 mL) and acetonitrile (0.2 mL). Crystals of complex **3** were obtained in low yield within two weeks (5 mg, 13% yield based on the acid). Anal. Calcd for $C_{42}H_{66}N_4NiO_{20}U_2$: C, 34.05; H, 4.49; N, 3.78. Found: C, 33.30; H, 4.15; N, 3.79%.

$[Ni(cyclam)][(UO_2)_5(R\text{-}t\text{-}chdc)_3(R\text{-}t\text{-}chdcH)(O)_2(CH_3COO)]$ (**4**). $R\text{-}t\text{-}chdcH_2$ (17 mg, 0.10 mmol), $UO_2(NO_3)_2 \cdot 6H_2O$ (35 mg, 0.07 mmol), and $[Ni(cyclam)(NO_3)_2]$ (40 mg, 0.10 mmol)

were dissolved in water (0.6 mL) and acetonitrile (0.2 mL). Crystals of complex **4** were obtained in very low yield within two weeks. Prolonged heating did not improve the yield.

$[Ni(R,S\text{-}Me_6cyclam)][Ni(R,S\text{-}Me_6cyclam)(H_2O)_2][(UO_2)_2(t\text{-}chdc)_2(O)]_2$ (**5**). *R*-*t*-chdcH₂ (17 mg, 0.10 mmol), UO₂(NO₃)₂·6H₂O (35 mg, 0.07 mmol), and [Ni(*R,S*-Me₆cyclam)(NO₃)₂] (23 mg, 0.05 mmol) were dissolved in water (0.6 mL), DMF (0.2 mL), and acetonitrile (0.2 mL). Crystals of complex **5** were obtained in low yield within four days (3 mg, 7% yield based on U). The elemental analysis results indicate that two acetonitrile molecules are probably retained, in keeping with the presence of voids containing unresolved solvent molecules in the crystal structure (see below). Anal. Calcd for C₆₄H₁₁₆N₈Ni₂O₂₈U₄ + 2CH₃CN: C, 31.45; H, 4.73; N, 5.39. Found: C, 31.53; H, 4.58; N, 5.29%.

Crystallography. The data were collected at 150(2) K (complexes **1–4**) or 100(2) K (**5**) on a Nonius Kappa-CCD area detector diffractometer²³ using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of ϕ - and ω -scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.²⁴ Absorption effects were corrected empirically with the program SCALEPACK.²⁴ The structures were solved by intrinsic phasing with SHELXT,²⁵ expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL-2014.²⁶ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen and nitrogen atoms were retrieved from difference Fourier maps when possible (see details below), and the carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH₃, with optimized

geometry). Crystal data and structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP-3,²⁷ and the polyhedral representations with VESTA.²⁸ The topological analyses were conducted with TOPOS.²⁹ Special details are as follows.

Complex 3. The cyclohexyl group C9–C14 and the uncoordinated carboxylic group containing O9 and O10 attached to it are affected by disorder, but the minor component could not be modelled properly, so that only the major one was refined with restraints on bond lengths, angles and displacement parameters. The hydrogen atom bound to this carboxylic group was not found.

Complex 4. The carboxylic oxygen atoms O27 and O28 are disordered over two positions which were refined with occupancy parameters constrained to sum to unity; the hydrogen atom attached to this group was not found. Restraints on bond lengths, angles and displacement parameters were applied in several parts of the structure which behaved badly probably because of unresolved disorder. The value of the refined Flack parameter is –0.023(19).

Complex 5. The two dicarboxylate ligands are partly disordered, and the two components were refined with occupancy parameters constrained to sum to unity and restraints on displacement parameters. The hydrogen atoms bound to N1, N2 and O14 were found on a difference Fourier map, but those bound to N3 and N4 were introduced at calculated positions. Some voids in the lattice indicate the presence of solvent molecules which could not be located properly; their contribution to the structure factors was taken into account with PLATON/SQUEEZE.³⁰

Table 1. Crystal Data and Structure Refinement Details

	1	2	3	4	5
chemical formula	C ₂₆ H ₄₆ N ₄ NiO ₁₁ U	C ₄₂ H ₆₆ N ₄ NiO ₂₀ U ₂	C ₄₂ H ₆₆ N ₄ NiO ₂₀ U ₂	C ₄₄ H ₆₈ N ₄ NiO ₃₀ U ₅	C ₆₄ H ₁₁₆ N ₈ Ni ₂ O ₂₈ U ₄
<i>M</i> (g mol ⁻¹)	887.41	1481.75	1481.75	2381.88	2515.18
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 1	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.7611(4)	9.3317(4)	9.3911(6)	9.6855(6)	10.2533(7)
<i>b</i> (Å)	11.2164(7)	11.0000(10)	12.2631(11)	11.9568(9)	14.2295(16)
<i>c</i> (Å)	13.6773(10)	12.5430(9)	12.3275(10)	14.8911(8)	16.1034(16)
α (deg)	88.724(3)	103.790(4)	105.199(4)	98.105(4)	113.337(4)
β (deg)	87.706(4)	90.068(4)	91.205(5)	103.738(4)	92.289(6)
γ (deg)	73.978(3)	93.812(5)	104.363(5)	98.106(5)	100.698(6)
<i>V</i> (Å ³)	1585.36(17)	1247.45(16)	1321.57(19)	1630.91(19)	2102.9(4)
<i>Z</i>	2	1	1	1	1
reflns colld	84530	60087	60304	72370	92202
indep reflns	6008	4745	5002	12239	7982
obsd reflns [<i>I</i> > 2 σ (<i>I</i>)]	5287	4077	4483	11041	5492
<i>R</i> _{int}	0.054	0.094	0.044	0.040	0.087
params refined	391	313	313	778	570
<i>R</i> ₁	0.042	0.048	0.048	0.055	0.072
<i>wR</i> ₂	0.106	0.145	0.137	0.143	0.188
<i>S</i>	1.112	1.049	1.166	1.108	1.058
$\Delta\rho_{\min}$ (e Å ⁻³)	-1.30	-1.72	-1.65	-2.83	-3.08
$\Delta\rho_{\max}$ (e Å ⁻³)	2.53	2.54	1.31	1.24	4.16

Luminescence Measurements. Emission spectra were recorded on solid samples using a Horiba-Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation and emission monochromator (2.1 nm mm⁻¹ of dispersion; 1200 grooves mm⁻¹) and a TBX-04 single photon-counting detector. The powdered compound was pressed between two silica plates which were mounted such that the faces were oriented vertically and at 45° to the incident excitation radiation. An excitation wavelength of 420 nm, a commonly used point although only part of a broad manifold, was used in all cases and the emission was monitored between 450 and 650 nm.

RESULTS AND DISCUSSION

Synthesis. The crystalline complexes **1–5** were obtained under purely hydrothermal (**2**) or solvo-hydrothermal conditions (all other complexes) at a temperature of 140 °C, the organic cosolvent being *N,N*-dimethylformamide (DMF) for complex **1**, acetonitrile for **3** and **4**, or a mixture of both for **5**. The 7:10 uranium/ligand stoichiometry was used in all cases, so as to

favour the formation of an anionic species; this ratio is 1:2 in **1–3**, 5:4 in **4**, and 1:1 in **5**, Ni^{II} providing extra positive charge in all cases, and the charge equilibrium in **4** and **5** being ensured by extra oxo and acetato anions. The presence of the latter anion in **4** results from acetonitrile hydrolysis possibly catalyzed by the metal cations, with acetamide as an intermediate species. The other product of this reaction, NH₄⁺, is also frequently found in uranyl ion complexes formed under similar conditions in the presence of acetonitrile.^{13,14,18,31} Oligomerization through bridging oxo anions, as observed in **4** and **5**, is a very common phenomenon in uranyl chemistry leading to a great variety of secondary building units.³ The presence of oxo ligands in complexes **4** and **5** is an indication that the reaction mixtures may have become significantly basic, possibly due to kinetically slow partial dissociation of the tetramine macrocycles from Ni^{II} under the reaction conditions. Such dissociation may also explain the rather poor yields of the crystals incorporating the intact macrocyclic complexes.

Crystal Structures. The complex [UO₂(*c*-chdc)₂Ni(cyclam)(H₂O)] (**1**) pertains to the still limited family of uranyl complexes with *c*-chdc²⁻, the other examples being an octanuclear cage obtained in the presence of PPh₄⁺ and NH₄⁺ cations,¹⁴ and two complexes, two- and three-dimensional (2D and 3D) including alkali metal ions complexed by crown ethers.⁶ The unique uranyl cation in **1** is chelated by one $\kappa^2 O, O'$ carboxylate group, and bound to two more carboxylate groups from two different ligands and a water molecule, the uranium atom being thus in a pentagonal bipyramidal environment (Figure 1). The two *c*-chdc²⁻ ligands are in the chair conformation, with one carboxylate group axial and the other equatorial (*ae*). One of them chelates the uranyl cation with one carboxylate group and is bound in a monodentate fashion to one Ni^{II} cation with the other, while the other is bound to one uranyl ion through each of its carboxylate groups, one of them being also bound to one Ni^{II} cation (μ_2 - $\kappa^1 O$: $\kappa^1 O'$ mode).

Figure 1. (a) View of compound **1**. Displacement ellipsoids are drawn at the 30% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 1 - x, 1 - y, -z$; $j = -x, 1 - y, 1 - z$; $k = 1 - x, -y, -z$. (b) View of the dimeric motif with uranium coordination polyhedra colored yellow and those of nickel(II) green, and hydrogen atoms omitted. For clarity, only two of the four surrounding Ni^{II} cations are shown.

Centrosymmetric uranyl dinuclear subunits displaying a 14-membered ring are thus formed, which are bound to four Ni^{II} cations, all located on inversion centers, and thus fused into much larger (50-membered) cyclic structures. The cyclam macrocycle adopts the usual *trans*-III conformation with *R,S,R,S* configurations of the *N*-donors,³² and the two inequivalent Ni^{II} centres are six-coordinate, therefore paramagnetic, with two axial carboxylate oxygen donors

Figure 2. (a) View of the 2D network in compound **1**. (b) Representation of the 2D network (yellow: uranium nodes; blue: centroids of the dicarboxylate ligand nodes or links; green: nickel links). (c) View of the packing with layers viewed edge-on.

[Ni–O 2.156(5) and 2.136(5) Å]. As in all the complexes reported here, the U–O and the Ni–N bond lengths are unexceptional and will not be further commented upon. The presence of ammonium protons in the cyclam moieties results in formation of numerous hydrogen bonds,

particularly between NH and carboxylate groups bound to the same Ni^{II} centre; the water ligand also forms hydrogen bonds with carboxylate oxygen atoms. The polymeric assembly formed is 2D and parallel to (1 0 1), and, since one of the *c*-chdc²⁻ ligands and the Ni^{II} cations are simple links which are transformed into edges in the simplified net used for topology determination, it has the point (Schläfli) symbol {4.8²} and the common fes topological type (Figure 2).

The two complexes [(UO₂)₂(*c*-chdc)₂(*c*-chdcH)₂Ni(cyclam)] (**2**) and [(UO₂)₂(*t*-chdc)₂(*t*-chdcH)₂Ni(cyclam)] (**3**), involving either the *cis* or the racemic *trans* form of the carboxylate ligand, respectively, have the same composition and they crystallize in the same space group and with unit cell parameters which, if not very close, are not widely different. The rotational freedom about the C–CO₂⁻ bonds enables the *cis* and *trans* isomers of the ligand to adopt very similar dispositions of their donor atoms, although the former assumes the (*ae*) and the latter the (*ee*) conformation. Although most commonly it is found that solvo-hydrothermal syntheses involving weak acids such as carboxylic acids result in isolation of complexes of the fully deprotonated acid without the need to add a base, partial deprotonation is not unknown,^{20,33} and these complexes provide other examples in which the consequences of this partial retention of the protons are quite dramatic. The unique uranyl cation is chelated by one carboxylate group and bound to three carboxylate oxygen atoms from three more ligands, the uranium environment being here also pentagonal bipyramidal (Figures 3 and 4). The dicarboxylate ligand is chelating and bridging bidentate (μ_2 - $\kappa^1 O$: $\kappa^1 O'$), thus connecting two uranyl and one Ni^{II} cations, the latter located on an inversion centre, while the mono-deprotonated ligand is bridging two uranyl ions through the μ_2 - $\kappa^1 O$: $\kappa^1 O'$ -carboxylate group, the carboxylic one being uncoordinated. Chains of doubly bridged uranyl cations run along the *c* axis (with alternate *c*-chdc²⁻ and *c*-chdcH⁻ bridges), which are cross-linked by the Ni^{II} centres to form a 2D network parallel to (0 1 0). The polymer has the same point symbol {4.8²} and the same topology (fes) as that in **1**, with the nickel(II) cations simplified as edges, and the two two-fold ligands bridging

two uranyl cations making a double edge. There is however a marked difference related to hydrogen bond formation between the two complexes **2** and **3**. In complex **2**, the sheets are linked down the *b* axis by classical carboxylic acid dimer formation [$\text{O}\cdots\text{O}$ 2.626(12) Å, $\text{O}-\text{H}\cdots\text{O}$ 153°], thus giving a 3D network. In contrast, in complex **3**, the carboxylic groups (which are badly resolved and upon which the proton could not be located, see Experimental Section) do not form hydrogen bonded pairs and they are instead directed toward the centre of the layers, a difference which may partly account for the largest difference in unit cell parameters between **2** and **3** being on the *b* axis.

Figure 3. (a) View of compound **2**. Displacement ellipsoids are drawn at the 20% probability level. Carbon-bound hydrogen atoms are omitted and the hydrogen bond is shown as a dashed line. Symmetry codes: $i = 1 - x, 1 - y, 1 - z$; $j = 1 - x, 1 - y, 2 - z$; $k = 2 - x, 1 - y, 1 - z$. (b) View of the 2D network. (c) Packing with sheets viewed edge-on. (d) Representation of the 2D network (yellow: uranium nodes; blue: centroids of the dicarboxylate ligand nodes or edges; green: nickel links).

Figure 4. (a) View of compound 3. Displacement ellipsoids are drawn at the 20% probability level. Carbon-bound hydrogen atoms are omitted and the hydrogen bond is shown as a dashed line. Symmetry codes: $i = 1 - x, 1 - y, 1 - z$; $j = 1 - x, 1 - y, 2 - z$; $k = 2 - x, 1 - y, 1 - z$. (b) View of the 2D network. (c) Packing with sheets viewed edge-on.

Given that the polymer sheets of compound **3** are heterochiral, it is unsurprising that the complex derived from the resolved ligand, $[\text{Ni}(\text{cyclam})][(\text{UO}_2)_5(R\text{-}t\text{-chdc})_3(R\text{-}t\text{-chdcH})(\text{O})_2(\text{CH}_3\text{COO})]$ (**4**), has a different structure but indeed the differences are quite dramatic. This complex crystallizes in the Sohncke group *P*1, with five independent uranium cations in slightly different environments, all of them pentagonal bipyramidal, one $[\text{Ni}(\text{cyclam})]^{2+}$ counterion, three fully deprotonated and one mono-deprotonated $R\text{-}t\text{-chdc}^{2-}$ ligands, two μ_3 -oxo anions, and one acetato anion formed *in situ* from acetonitrile hydrolysis (Figure 5). Atoms U1 to U4 are arranged into a tetranuclear cluster around the two μ_3 -oxo anions O11 and O12, a very common motif in uranyl chemistry.³ The coordination polyhedra of U1 and U2 share two edges with those of adjacent uranium atoms, while those of U3 and U4 share only one edge. Atom U5 is linked to this cluster through apex-sharing with atom U4, thus generating a pentanuclear subunit. Atoms U1 and U2 are chelated by one carboxylate group and bound to two oxo and one more carboxylate donor, U5 is also chelated by one carboxylate and bound to three more carboxylate donors, while U3 and U4 are chelated through both carboxylate groups of one ligand, and bound to one oxo and two more carboxylate groups. Within the cluster, the $\text{U}_4(\text{O})_2$ unit involves nearest $\text{U}\cdots\text{U}$ separations ranging from 3.6042(11) to 4.0985(11) Å, while the fifth uranium centre is more distant [$\text{U4}\cdots\text{U5}$ 4.5657(14) Å]. The shortest $\text{U}\cdots\text{U}$ separation between clusters is between U3 and U5, at 5.1791(13) Å. All these distances are in fact shorter than any of the minimum $\text{U}\cdots\text{U}$ distances in **1** [6.6947(7) Å], **2** [5.5764(7) Å], and **3** [5.6107(7) Å]. The coordinative roles of the $R\text{-}t\text{-chdc}^{2-}/R\text{-}t\text{-chdcH}^-$ ligands are remarkably varied, one of the dianionic ones being bound to four uranium atoms through its two bridging bidentate $\mu_2\text{-}\kappa^1\text{O}:\kappa^1\text{O}'$ -carboxylate groups, and the other two to three metal centres through a mixture of $\kappa^2\text{O},\text{O}'$ -chelation, chelation between the two carboxylate groups

Figure 5. (a) View of compound **4**. Displacement ellipsoids are drawn at the 30% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = x, y + 1, z$; $j = x - 1, y, z - 1$; $k = x + 1, y, z + 1$; $l = x, y - 1, z$. (b) View of the uranium-based 2D network. (c) Packing with layers viewed edge-on. Only one position of the disordered atoms is shown in all views.

and monodentate bonding, while the monoanionic ligand is bound to two metal atoms in the $\mu_2\text{-}\kappa^1\text{O}:\kappa^1\text{O}'$ mode, as is also the acetate anion. The pentanuclear clusters are linked to one another to form chains directed along the $[1\ 0\ 1]$ axis, these being united into a 2D network parallel to $(1\ 0\ \bar{1})$ through the unique ligand to be in the (*aa*) conformation instead of the more usual (*ee*) one, which is the ligand bound to four metal centres and containing atoms O17 to O20. The (*aa*) form was previously encountered in other complexes of *t*-chdc²⁻ with uranyl³⁴ or other metal cations,^{35,36} and a study of the conformational preferences of *t*-chdcH₂ and its mono- and dianion in solution by NMR spectroscopy revealed that, depending on the medium, the (*aa*) population could be significant, representing as much as 57% for the dianion in DMSO.³⁷ From a geometrical point of view, while the (*ee*) form is a convergent ligand, the (*aa*) form is divergent, as befits the connection of chains into a planar layer. In contrast to the previous complexes, the Ni^{II} cation here is not axially bound to two oxygen atoms, the shortest axial contact, with only the uranyl oxo atom O1, being at 2.736(17) Å. Although this is long and comparable to distances to various donor atoms in simpler complexes where the Ni^{II} is described as four-coordinate,³⁸ an interaction beyond dispersion is apparent on the Hirshfeld surface³⁹ for the cation, calculated with CrystalExplorer.⁴⁰ Five-coordination is certainly known in closely related Ni^{II} macrocycle complexes.⁴¹ Whether or not the interaction here has a significant structural influence, the [Ni(cyclam)]²⁺ counterions, with their mean plane approximately parallel to that of the proximal parts of the layers, are located in channels directed along the *b* axis, and they are hydrogen bonded to both neighbouring layers, thus forming a 3D assembly.

The substitution of *meso* Me₆cyclam as the ligand bound to Ni^{II} has also important consequences, possibly again in part due to some hydrolysis, resulting in free base release, the room temperature stability of [Ni(Me₆cyclam)]²⁺ being known to be significantly less than that of [Ni(cyclam)]²⁺.¹⁷ Although the synthesis of complex **5**, [Ni(*R,S*-Me₆cyclam)][Ni(*R,S*-

$\text{Me}_6\text{cyclam})(\text{H}_2\text{O})_2][(\text{UO}_2)_2(t\text{-chdc})_2(\text{O})]_2$, was conducted using resolved *R*-*t*-chdcH₂, the chirality was lost in the isolated product, again a possible consequence of a relatively basic reaction medium due to tetramine release. Although *c*-chdcH₂ must be an intermediate in the conversion of *R,R*- to *S,S*-*t*-chdcH₂, it is not present in the crystal, possibly indicative of the equilibrium between *cis* and *trans* isomers being in favour of the latter. As seen in other species

Figure 6. (a) View of compound **5**. Displacement ellipsoids are drawn at the 20% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines. Symmetry codes: $i = 1 - x, 1 - y, 1 - z$; $j = -x, 1 - y, -z$; $k = -x, 1 - y, 1 - z$. (b) View of the anionic tetranuclear uranyl complex. (c) View of the packing. Only one position of the disordered atoms is shown in all views.

isolated from both racemic and resolved *t*-1,2-chdcH₂,^{12,13} it appears that the ligand stereochemistry is not an important influence on the form of the complex. Here also, an oxo anion is present, and the two independent uranium cations and their image through inversion form a bis-(μ₃-oxo)-bridged cluster analogous to that found in **4** (Figure 6). However, while the four uranium atoms in the cluster in **4** have pentagonal bipyramidal environments, there is in **5** a mixture of pentagonal (U1) and hexagonal (U2) bipyramidal environments. As a result, the cluster is more compact, with the maximum number of possible shared edges between adjacent polyhedra being achieved. Atom U1 is twice chelated between the two carboxylate groups of a ligand, the fifth position being occupied by the oxo anion, while U2 is chelated in the κ²O,O' mode by two carboxylate groups, and bound to two oxo bridges. Overall, the cluster is surrounded by four ligands in the chair, (*ee*) conformation, and it is present in the lattice as an isolated species not involved in higher degrees of coordinative aggregation. The Ni^{II} cations are not involved in coordination to carboxylate groups, but instead are present as (presumably) paramagnetic, octahedral [Ni(*R,S*-Me₆cyclam)(H₂O)₂]²⁺ and square planar [Ni(*R,S*-Me₆cyclam)]²⁺ species, both centrosymmetric, formally with just a charge-balancing role. The tetranuclear anions and the [Ni(*R,S*-Me₆cyclam)]²⁺ counterions parallel to them are stacked into alternate columns directed along the *a* axis, while the [Ni(*R,S*-Me₆cyclam)(H₂O)₂]²⁺ cations are perpendicular and located between the columns. Within the columns, the [Ni(*R,S*-Me₆cyclam)]²⁺ counterions are linked to the two adjoining uranyl clusters by four hydrogen bonds involving uranyl oxo groups as acceptors [N...O 3.23(2) and 3.02(2) Å, N–H...O 153 and 161°]. The [Ni(*R,S*-Me₆cyclam)(H₂O)₂]²⁺ cations are hydrogen bonded to two clusters in different columns, with both ammonium and water as donors and the uncoordinated carboxylate atoms O8 and O12 as acceptors [N...O 3.176(16) and 3.316(15) Å, N–H...O 150 and 146°; O...O 2.821(15) and 2.834(15) Å, O–H...O 167 and 145°], resulting in the formation of hydrogen bonded layers parallel to (0 1 0).

Luminescence properties. A frequent drawback of the use of d-block transition metal counterions in uranyl-containing polymers is the quenching of uranyl luminescence, probably due to the transition metal cation providing a nonradiative relaxation pathway.⁴² Indeed, the emission spectra recorded for compounds **1** and **3**, the only ones to have been synthesized pure in sufficient quantity, show complete quenching for **1**, and only weak emission for **3** (Figure 7). The usual series of peaks associated with the vibronic progression corresponding to the $S_{11} \rightarrow S_{00}$ and $S_{10} \rightarrow S_{0\nu} (\nu = 0-4)$ electronic transitions⁴³ is apparent, with the main maxima at 502, 524 and 548 nm for the latter group of electronic transitions being typical of five-coordinate uranyl carboxylate complexes.⁴⁴

Figure 7. Emission spectrum of compound **3** in the solid state at room temperature, under excitation at a wavelength of 420 nm.

CONCLUSIONS

Although d-block metal cations complexed by nitrogen chelators such as 2,2'-bipyridine or 1,10-phenanthroline have often been used as structure-directing counterions in uranyl-containing coordination polymers or frameworks,⁵ the use of macrocyclic complexes of these cations is much more unusual. Only a uranyl complex with *R*-citramalate including [Ni(cyclam)]²⁺ moieties has been reported previous to the present work, in which uranyl dicarboxylate chains are bridged by Ni^{II} cations axially bound to two carboxylate groups to form a 2D assembly.²⁰ In three out of the five complexes reported here, the centrosymmetric [Ni(cyclam)]²⁺ moiety is also bound to two carboxylate donors and it thus assembles uranyl dimers (complex **1**) or chains (**2** and **3**) into 2D networks. In contrast, [Ni(cyclam)]²⁺ in the 2D compound **4** and [Ni(Me₆cyclam)(H₂O)_{*x*}]²⁺ (*x* = 0 or 2) in the discrete, tetranuclear complex **5** are mere counterions and, apart from a long contact between Ni^{II} and a uranyl oxo atom in **4** possibly indicating bonding as a decorating group, their interaction with the anions involve a number of hydrogen bonds between ammonium groups (and also water ligands in **5**) and either carboxylate or uranyl oxo acceptors which probably play a major role in their structure-directing effect. We have recently investigated the role of crown ethers (12-crown-4, 15-crown-5 and 18-crown-6) and their Na⁺ or K⁺ ion complexes as assembler groups in uranyl ion complexes with, in particular, *c*- and *t*-chdc²⁻,⁶ and they appear to behave in a way comparable to that of the present Ni^{II} macrocyclic complexes, notwithstanding the charge difference. In both cases, the complex assumes an essentially discoidal shape which is well suited to stacking with the often planar uranyl-containing subunits, as illustrated here by complexes **4** and **5**, and by most cases with crown ethers. The two axial positions on Ni^{II} in the cyclam complex are well adapted for bridging through bonding to carboxylate groups, whereas the quasi-planar K(18-crown-6)⁺ cation displays a marked propensity to be axially bound to two uranyl oxo groups. An important difference however is that ammonium groups are hydrogen bond donors

while ether oxygen atoms are potential acceptors. The former are thus well adapted to hydrogen bonding to uranyl carboxylate subunits, which are rich in acceptor groups, but the latter may at best be hydrogen bonded to water coligands. A drawback related to crown ether use is the systematic formation of oxalate coligands under hydrothermal conditions, which is absent here. Partial dissociation of the tetramine macrocycles from Ni^{II} and the consequent increase in basicity of the solutions may explain the presence of oxo anions in complexes **4** and **5**. Finally, although these Ni^{II} macrocyclic complexes turn out to be efficient assemblers in uranyl carboxylate coordination polymers (better for example than the coordinatively saturated tris(ethylenediamine)cobalt(III) complex, which can only form hydrogen bonds¹⁸), they offer little prospect in relation to luminescence properties, since complete or substantial quenching of uranyl emission occurs for complexes **1** and **3**, as is often the case in uranyl species containing d-block cations. Whether the quenching effect is determined by the electronic state of the metal ion, both diamagnetic and paramagnetic ground states being available to Ni^{II} , remains to be established.

ASSOCIATED CONTENT

Accession Codes

CCDC 1845770–1845774 contain 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.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: pierre.thuery@cea.fr. (P.T.)

*E-mail: harrowfield@unistra.fr. (J.H.)

ORCID

Pierre Thuéry: [0000-0003-1683-570X](https://orcid.org/0000-0003-1683-570X)

Jack Harrowfield: [0000-0003-4005-740X](https://orcid.org/0000-0003-4005-740X)

Notes

The authors declare no competing financial interest.

REFERENCES

1. Wang, K. X.; Chen, J. S. Extended Structures and Physicochemical Properties of Uranyl–Organic Compounds. *Acc. Chem. Res.* **2011**, *44*, 531–540.
2. Andrews, M. B.; Cahill, C. L. Uranyl Bearing Hybrid Materials: Synthesis, Speciation, and Solid-State Structures. *Chem. Rev.* **2013**, *113*, 1121–1136.
3. Loiseau, T.; Mihalcea, I.; Henry, N.; Volkringer, C. The Crystal Chemistry of Uranium Carboxylates. *Coord. Chem. Rev.* **2014**, *266–267*, 69–109.
4. Su, J.; Chen, J. S. MOFs of Uranium and the Actinides. *Struct. Bond.* **2015**, *163*, 265–296.
5. Thuéry, P.; Harrowfield, J. Recent Advances in Structural Studies of Heterometallic Uranyl-Containing Coordination Polymers and Polynuclear Closed Species. *Dalton Trans.* **2017**, *46*, 13660–13667.
6. Thuéry, P.; Atoini, Y.; Harrowfield, J. Crown Ethers and Their Alkali Metal Ion Complexes as Assembler Groups in Uranyl–Organic Coordination Polymers with *cis*-1,3-, *cis*-1,2-, and *trans*-1,2-Cyclohexanedicarboxylates. *Cryst. Growth Des.* **2018**, *18*, 3167–3177.
7. Melson, G. A. Coordination Chemistry of Macrocyclic Compounds. Plenum Press: New York, 1979.

8. Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*. Cambridge University Press: Cambridge, 1989.
9. Dietrich, B.; Viout, P.; Lehn, J. M. *Macrocyclic Chemistry*. VCH: Weinheim, 1993.
10. Curtis, N. F. N-Macrocyclic Ligands. In: McCleverty, J. A.; Meyer, T. J. (Eds.), *Comprehensive Coordination Chemistry II*, Elsevier: Amsterdam, 2003, Vol. 1, Ch. 20, pp. 447–474.
11. Bernal, I. (Ed.), *Stereochemical and Stereophysical Behaviour of Macrocycles*. Elsevier: Amsterdam, 2012.
12. Thuéry, P.; Harrowfield, J. Coordination Polymers and Cage-Containing Frameworks in Uranyl Ion Complexes with *rac*- and (1*R*,2*R*)-*trans*-1,2-Cyclohexanedicarboxylates: Consequences of Chirality. *Inorg. Chem.* **2017**, *56*, 1455–1469.
13. Thuéry, P.; Harrowfield, J. Tetrahedral and Cuboidal Clusters in Complexes of Uranyl and Alkali or Alkaline-Earth Metal Ions with *rac*- and (1*R*,2*R*)-*trans*-1,2-Cyclohexanedicarboxylate. *Cryst. Growth Des.* **2017**, *17*, 2881–2892.
14. Thuéry, P.; Atoini, Y.; Harrowfield, J. Counterion-Controlled Formation of an Octanuclear Uranyl Cage with *cis*-1,2-Cyclohexanedicarboxylate Ligands. *Inorg. Chem.* DOI: 10.1021/acs.inorgchem.8b00147.
15. Curtis, N. F.; Curtis, Y. M. Some Nitrate–Amine Nickel(II) Compounds with Monodentate and Bidentate Nitrate Ions. *Inorg. Chem.* **1965**, *4*, 804–809.
16. Bosnich, B.; Tobe, M. L.; Webb, G. A. Complexes of Nickel(II) with a Cyclic Tetradentate Secondary Amine. *Inorg. Chem.* **1965**, *4*, 1109–1112.
17. Hinz, F. P.; Margerum, D. W. Ligand Solvation and the Macrocyclic Effect: A Study of Nickel(II) Tetramine Complexes. *Inorg. Chem.* **1974**, *13*, 2941–2949.
18. Thuéry, P.; Rivière, E., Harrowfield, J. Counterion-Induced Variations in the Dimensionality and Topology of Uranyl Pimelate Complexes. *Cryst. Growth Des.* **2016**, *16*, 2826–2835.

19. Thuéry, P.; Harrowfield, J. Complexes of Uranyl Ions with Aromatic Di- and Tetracarboxylates Involving $[\text{Ni}(\text{bipy})_n]^{2+}$ ($n = 2, 3$) Counterions. *Eur. J. Inorg. Chem.* **2017**, 5451–5460.
20. Thuéry, P.; Harrowfield, J. Uranyl Ion Complexes with Chiral Malic and Citramalic, and Prochiral Citric and Tricarballic Acids: Influence of Coligands and Additional Metal Cations. *Eur. J. Inorg. Chem.* **2018**, 1016–1027.
21. Kimura, K.; Watanabe, Y.; Suda, T.; Senda, H.; Hosoi, S.; Ohta, T.; Kunimoto, K. K. Crystal Structure of (1*R*,2*R*)-trans-1,2-Cyclohexanedicarboxylic Acid-(*R*)-1-Phenylethylamine Salt. *Anal. Sci.* **1999**, *15*, 609–610.
22. Tait, A. M.; Busch, D. H., in Douglas, B. E. (Volume Editor), *Inorganic Syntheses*, Volume 18, Ch. 1.2, p. 10, John Wiley & Sons: New York, 1978.
23. Hooft, R. W. W. *COLLECT*, Nonius BV: Delft, The Netherlands, 1998.
24. Otwinowski, Z.; Minor, W. Processing of X-Ray Diffraction Data Collected in Oscillation Mode. *Methods Enzymol.* **1997**, *276*, 307–326.
25. Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr., Sect. A* **2015**, *71*, 3–8.
26. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.
27. Farrugia, L. J. WinGX and ORTEP for Windows: an Update. *J. Appl. Crystallogr.* **2012**, *45*, 849–854.
28. Momma, K.; Izumi, F. VESTA: a Three-Dimensional Visualization System for Electronic and Structural Analysis. *J. Appl. Crystallogr.* **2008**, *41*, 653–658.
29. Blatov, V. A. *TOPOS*, Samara State University, Russia, 2004.
30. Spek, A. L. *PLATON SQUEEZE*: a Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. *Acta Crystallogr., Sect. C* **2015**, *71*, 9–18.

31. Thuéry, P.; Harrowfield, J. Variations on the Honeycomb Topology: From Triangular- and Square-Grooved Networks to Tubular Assemblies in Uranyl Tricarballylate Complexes. *Cryst. Growth Des.* **2017**, *17*, 963–966.
32. Bosnich, B.; Poon, C. K.; Tobe, M. L. Complexes of Cobalt(III) with a Cyclic Tetradentate Secondary Amine. *Inorg. Chem.* **1965**, *4*, 1102–1108.
33. Thuéry, P.; Harrowfield, J. Tetrahydrofuranetracarboxylic Acid: an Isomerizable Framework-Forming Ligand in Homo- and Heterometallic Complexes with UO_2^{2+} , Ag^+ , and Pb^{2+} . *Cryst. Growth Des.* **2016**, *16*, 7083–7093.
34. Thuéry, P.; Atoini, Y.; Harrowfield, J. Uranyl–Organic Coordination Polymers with *trans*-1,2-, *trans*-1,4-, and *cis*-1,4-Cyclohexanedicarboxylates: Effects of Bulky PPh_4^+ and PPh_3Me^+ Counterions. *Cryst. Growth Des.* **2018**, *18*, 2609–2619.
35. Hernández-Ahuactzi, I. F.; Höpfl, H.; Barba, V.; Román-Bravo, P.; Zamudio-Rivera, L. S.; Beltrán, H. I. Pore-Size Tuning in Double-Pillared Metal–Organic Frameworks Containing Cadmium Clusters. *Eur. J. Inorg. Chem.* **2008**, 2746–2755.
36. Yue, Q.; Huang, Q.; Gao, Y. Y.; Gao, E. Q. Homochiral Coordination Polymers from a Chiral Dicarboxylic Acid and Dipyridyl Ligands: Structural Diversity, Photoluminescence and Magnetic Properties. *Inorg. Chim. Acta* **2016**, *443*, 110–117.
37. Garza, A. J.; Nag, M.; Carroll, W. R.; Goddard, W. A. III; Roberts, J. D. Conformational Preferences of *trans*-1,2- and *cis*-1,3-Cyclohexanedicarboxylic Acids in Water and Dimethyl Sulfoxide as a Function of the Ionization State As Determined from NMR Spectroscopy and Density Functional Theory Quantum Mechanical Calculations. *J. Am. Chem. Soc.* **2012**, *134*, 14772–14780.
38. Curtis, N. F.; Wikaira, J.; Butcher, R. (3,5,7,7,12,14,14-Heptamethyl-1,4,8,11-tetraazacyclotetradec-4-11-diene)nickel(II) Revisited and some (2,5,5,7,12,12,14-

- Heptamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) Compounds. *Inorg. Chim. Acta* **2015**, *436*, 103–117.
39. Spackman, M. A.; Jayatilaka, D. Hirshfeld Surface Analysis. *CrystEngComm* **2009**, *11*, 19–32.
40. Wolff, S. K.; Grimwood, D. J.; McKinnon, J. J.; Turner, M. J.; Jayatilaka, D.; Spackman, M. A. *CrystalExplorer*, University of Western Australia, 2012.
41. Barefield, E. K.; Busch, D. H. Low-Spin Five-Coordinate Nickel(II) Complexes Containing a Macrocyclic Tetradentate Amine. *Inorg. Chem.* **1971**, *10*, 1216–1220.
42. Kerr, A. T.; Cahill, C. L. Postsynthetic Rearrangement/Metalation as a Route to Bimetallic Uranyl Coordination Polymers: Syntheses, Structures, and Luminescence. *Cryst. Growth Des.* **2014**, *14*, 1914–1921.
43. Brachmann, A.; Geipel, G.; Bernhard, G.; Nitsche, H. Study of Uranyl(VI) Malonate Complexation by Time Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS). *Radiochim. Acta* **2002**, *90*, 147–153.
44. Thuéry, P.; Harrowfield, J. Structural Consequences of 1,4-Cyclohexanedicarboxylate Cis/Trans Isomerism in Uranyl Ion Complexes: From Molecular Species to 2D and 3D Entangled Nets. *Inorg. Chem.* **2017**, *56*, 13464–13481.

For Table of Contents Use Only

**[Ni(cyclam)]²⁺ and [Ni(*R,S*-Me₆cyclam)]²⁺ as Linkers or
Counterions In Uranyl–Organic Species with
cis- and *trans*-1,2-Cyclohexanedicarboxylate Ligands**

Pierre Thuéry and Jack Harrowfield

Five uranyl complexes with *cis*- or *trans*-1,2-cyclohexanedicarboxylic acids, the latter in the racemic or (1*R*,2*R*) enantiomeric form, were synthesized in the presence of [Ni(cyclam)]²⁺ or [Ni(*R,S*-Me₆cyclam)]²⁺. The macrocyclic complexes are either hydrogen bonded counterions or assembling units through axial bonding of Ni^{II} to carboxylate groups.