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Multiple aspects of chirality in coordination polymers formed by the uranyl ion with (1*R*,3*S*)-(+)-camphorate ligands

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Abstract

Following previous work on complexes of the anions of (1*R*,3*S*)-(+)-camphoric acid (H$_2$cam) with the uranyl cation, three novel species have been synthesized under solvo-hydrothermal conditions. [UO$_2$(Hcam)$_2$(4,4′-bipy)] (**1**), where 4,4′-bipy is 4,4′-bipyridine, crystallizes as a monoperiodic polymer with bridging 4,4′-bipy molecules and chelating, terminal Hcam$^-$ anions, hydrogen bonding between carboxylic and carboxylate groups in adjacent chains giving diperiodic networks. [UO$_2$(cam)(2,2′-bipy)] (**2**), where 2,2′-bipy is 2,2′-bipyridine, crystallizes also as a monoperiodic polymer, but bis-chelating cam^{2-} anions are here bridging and the chelating 2,2′-bipy ligands induce chirality at the uranium centres; the chains are helical, left- or right-handed depending on the chirality of the associated uranium centres. [Zn(phen)$_3$][(UO$_2$)$_2$(cam)$_3$] (**3**), where phen is 1,10-phenanthroline, is an anionic diperiodic network with **hcb** topology displaying a grooved shape. In all three instances, the enantiomeric purity of the camphorate ligands does not produce significant enantioselectivity in regard to other aspects of the structural chirality.

Keywords: Uranyl Ion, Camphoric acid, Chiral coordination polymers

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1. Introduction

The synthesis of homochiral coordination polymers, a class of compounds with possible use in enantioselective catalysis in particular, among many other conceivable applications, can be achieved along several pathways, the use of pure enantiomorphic ligands being the most obvious [1]. $(1R,3S)$-(+)-Camphoric acid (H_2cam) is one such ligand, easily accessible, possessing two stereocentres and endowed with a suitable geometry to act as a bridge between metal centres, and its utility in metal–organic framework design has recently been reviewed [2]. Notably, $(1R,3S)$-(+)-camphorate is stable and does not racemize under the solvo- or hydrothermal conditions most often used to synthesize coordination polymers or frameworks, in contrast to other enantiopure ligands such as α-amino acids. In the field of uranyl-based coordination polymers or closed oligomeric species [3], which is our particular interest, $(1R,3S)$-(+)-camphorate is known to give complexes with a periodicity of zero to three under solvo-hydrothermal conditions, the most notable species being discrete, hexanuclear and octanuclear cages incorporating nine or twelve ligands, respectively [4]. Some of these complexes are heterometallic and include K^+, Ba^{2+} or Cu^{2+} cations. Different anionic complexes were obtained through variation of the structure-directing counterions, these being either organic (NH_4^+, PPh_3Me^+, PPh_4^+) or metal-containing [$M(R,S$-$Me_6cyclam)^{2+}$ where M is Ni or Cu and $Me_6cyclam$ is $7(R),14(S)$-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; $Co(en)_3^{3+}$, where en is ethylenediamine]. In some other cases, the organic solvent or cosolvent is coordinated and thus acts also as a structure-directing species (pyridine, methanol, N-methyl-2-pyrrolidone). We have now synthesized three novel complexes, all involving nitrogen chelators, 2,2′-bipyridine (2,2′-bipy) and 4,4′-bipyridine (4,4′-bipy), which are both bound to the uranyl ion and give neutral coordination polymers, and 1,10-phenanthroline (phen), which is part of $[Zn(phen)_3]^{2+}$ counterions to an anionic uranyl camphorate network. The applications envisaged for such chiral materials depend upon their

capacity to discriminate between enantiomers and in this regard the induction of any enantioselectivity within the complete crystal structure of a given material as a consequence of the presence of (1R,3S)-(+)-camphorate units provides an indication of the utility it may have in substrate discrimination. In the case of the Zn^{II} complex formed in the presence of triethanolamine [5], for example, the chirality of the ligands appears to control not only the helicity of the structure but also the chirality about labile Zn^{II}, so that use of racemic (1R*,3S*)-camphorate results in crystallization of a conglomerate where mirror-image crystals contain either (1R,3S)-camphorate units in a right-handed helical polymer in which the two chelate rings formed by triethanolamine coordination both have a λ conformation or (1S,3R)-camphorate units in a left-handed helical polymer in which they have a δ conformation, *viz.* enantioselectivity appears to be complete. In the cases of the uranyl ion complexes of (1R,3S)-(+)-camphorate reported in the present work, however, chirality induction by the dicarboxylate appears to be considerably less effective.

2. Experimental part

2.1. *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.

[UO$_2$(NO$_3$)$_2$(H$_2$O)$_2$]·4H$_2$O (RP Normapur, 99%) was purchased from Prolabo, (1R,3S)-(+)-camphoric acid and Zn(NO$_3$)$_2$·6H$_2$O were from Aldrich, 2,2′- and 4,4′-bipyridine were from Fluka, and 1,10-phenanthroline was from Alfa-Aesar. All reagents were used as received. The elemental analysis of complex **2** was performed by the Service de Microanalyse, ICSN, CNRS, Gif-sur-Yvette. For all syntheses, the mixtures in demineralized water/organic solvent were

placed in 10 mL tightly closed glass vessels and heated at 140 °C in a sand bath, under autogenous pressure. The crystals characterized were those deposited under the reaction conditions and not from subsequent cooling and depressurization.

2.1.1. [UO$_2$(Hcam)$_2$(4,4'-bipy)] (1)

(1R,3S)-(+)-Camphoric acid (20 mg, 0.10 mmol), [UO$_2$(NO$_3$)$_2$(H$_2$O)$_2$]·4H$_2$O (50 mg, 0.10 mmol), and 4,4′-bipyridine (16 mg, 0.10 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL). A few yellow crystals of complex **1** were obtained within one week.

2.1.2. [UO$_2$(cam)(2,2'-bipy)] (2)

(1R,3S)-(+)-Camphoric acid (20 mg, 0.10 mmol), [UO$_2$(NO$_3$)$_2$(H$_2$O)$_2$]·4H$_2$O (50 mg, 0.10 mmol), and 2,2′-bipyridine (16 mg, 0.10 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL). Yellow crystals of complex **2** were obtained within one week (36 mg, 58% yield). *Anal.* Calc. for C$_{20}$H$_{22}$N$_2$O$_6$U: C, 38.47; H, 3.55; N, 4.49. Found: C, 38.60; H, 3.54; N, 4.44%.

2.1.3. [Zn(phen)$_3$][(UO$_2$)$_2$(cam)$_3$] (3)

(1R,3S)-(+)-Camphoric acid (20 mg, 0.10 mmol), [UO$_2$(NO$_3$)$_2$(H$_2$O)$_2$]·4H$_2$O (35 mg, 0.07 mmol), Zn(NO$_3$)$_2$·6H$_2$O (15 mg, 0.05 mmol), and 1,10-phenanthroline (18 mg, 0.10 mmol) were dissolved in a mixture of water (0.7 mL) and N,N-dimethylformamide (0.2 mL). A few yellow crystals of complex **3** were obtained within one week.

2.2. Crystallography

The data were collected at 100(2) K either on a Nonius Kappa-CCD area detector diffractometer [6] using graphite-monochromated Mo Kα radiation (complexes **1** and **2**), 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 [7] (complex **3**). The data for complexes **1** and **2** were processed with HKL2000 [8] and those for **3** with SAINT

[9], and absorption effects were corrected for empirically with SCALEPACK [8] or SADABS [10], respectively. The structures were solved by intrinsic phasing with SHELXT, [11] and refined by full-matrix least-squares on F^2 with SHELXL [12], using the ShelXle interface [13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms in **1** were found on a residual electron density map and they were refined with restraints on bond lengths and angles, and with an isotropic displacement parameter equal to 1.2 times that of the parent oxygen atom. The carbon-bound hydrogen atoms were introduced at calculated positions and treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3). The SQUEEZE software [14] was used to subtract the contribution of disordered solvent molecules to the structure factors for compound **3**. Crystal data and structure refinement parameters are given in Table 1. Drawings were made with ORTEP-3 [15] and VESTA [16].

Table 1

Crystal data and structure refinement details.

	1	2	3
Chemical formula	$C_{30}H_{38}N_2O_{10}U$	$C_{20}H_{22}N_2O_6U$	$C_{66}H_{66}N_6O_{16}U_2Zn$
M_r	824.65	624.42	1740.67
Crystal system	monoclinic	triclinic	monoclinic
Space group	$C2$	$P1$	$P2_1$
a (Å)	22.3689(14)	12.8391(7)	16.5483(7)
b (Å)	12.3268(7)	13.3643(7)	25.2397(10)
c (Å)	12.3001(7)	13.9627(8)	18.5725(7)
α (°)	90	72.205(4)	90
β (°)	117.537(4)	68.578(3)	104.2928(19)
γ (°)	90	75.873(4)	90
V (Å^3)	3007.4(3)	2099.7(2)	7517.1(5)
Z	4	4	4
No. of reflections collected	42379	98641	443264
No. of independent reflections	5710	15591	28548
No. of observed reflections [$I > 2\sigma(I)$]	5225	11914	23900
R_{int}	0.067	0.070	0.107
No. of parameters refined	406	1058	1657
R_1	0.043	0.055	0.044
wR_2	0.111	0.124	0.100
S	1.069	1.029	1.054
$\Delta\rho_{min}$ (e Å^{-3})	−1.63	−2.35	−1.35
$\Delta\rho_{max}$ (e Å^{-3})	1.48	1.10	1.89
Flack parameter	0.03(2)	0.04(2)	0.058(7)

3. Results and discussion

The complex [UO$_2$(Hcam)$_2$(4,4′-bipy)] (**1**), shown in Fig. 1, crystallizes in the Sohncke space group $C2$, and there are two independent, but similar motifs in the asymmetric unit. The two uranium atoms, located on twofold rotation axes, are in hexagonal-bipyramidal environments, being bound to two chelating carboxylate groups in trans positions, and two
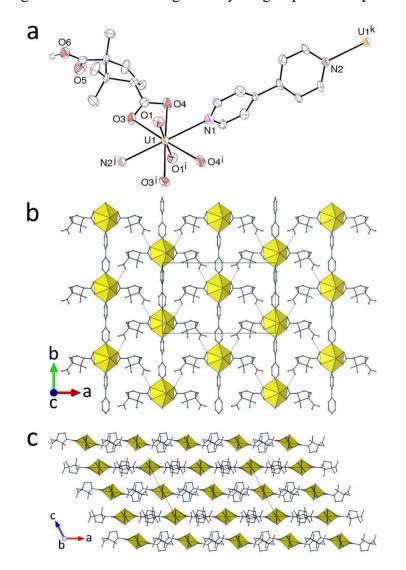

Fig. 1. (a) View of one of the two independent units in complex **1** with displacement ellipsoids shown at the 50% probability level and carbon-bound hydrogen atoms omitted. Symmetry codes: i = 2 − x, y, 2 − z; j = x, y − 1, z; k = x, y + 1, z. (b) View of the hydrogen bonding assembly of monoperiodic coordination polymers. Uranium coordination polyhedra are yellow and hydrogen bonds are shown as dotted blue lines. (c) Packing with chains viewed end-on.

nitrogen donors [U–O(oxo), 1.736(10) and 1.779(10) Å; U–O(carboxylato), 2.434(12)–2.521(13) Å; U–N, 2.51(2)–2.71(3) Å]. The Hcam⁻ ligand is coordinated through the carboxylate group only and it is thus a terminal ligand, while 4,4′-bipy is bridging. There are only six examples of 4,4′-bipy-bridged uranyl ion complexes in the Cambridge Structural Database (CSD, version 5.43 [17]), which are either binuclear or polymeric and in which the U–N bond lengths span the range of 2.54–2.66 Å [18], and only two examples of monodentate 4,4′-bipy coordination, with U–N bond lengths of 2.57 and 2.61 Å [18a,19]. The $UO_2(4,4′$-bipy)$^{2+}$ chains here are linear and directed along [010] and the Hcam⁻ ligands project from the two sides of the planar, ribbon-like polymer. The chains are assembled into layers parallel to (001) by hydrogen bonding of the carboxylic groups of one chain to carboxylate oxygen atoms of the two neighboring chains [O⋯O, 2.710(18) and 2.697(19) Å; O–H⋯O, 179(9) and 164(12)°] (Fig. 1b). There are two types of sheets which lie in alternation, incorporating either U1 or U2, with a slightly different orientation of the Hcam⁻ ligands but otherwise of very similar form except for the chirality associated with the 4,4′-bipy units. As a biaryl, 4,4′-bipy has a chiral form unless the dihedral angle formed by the two rings is 0 or 90°. This angle is 41.5(5)° in the 4,4′-bipy bound to U1, which has *R* chirality, while it is 26.7(6)° in that bound to U2, which has *S* chirality, meaning that the inequivalent sheets are diastereomeric. While the chains within a hydrogen-bonded sheet have the same chirality, CH(4,4′-bipy)⋯O bonding between sheets [C⋯O, 3.12(2)–3.19(2) Å; C–H⋯O, 122–128°] appears to be the reason for alternation of the bipyridine unit chirality, indicating that the diastereomeric interactions of Hcam⁻ with the enantiomeric forms of 4,4′-bipy must be of very similar energy. The 4,4′-bipy molecules being not only twisted but also far away from each other, no π-stacking interaction is present. The hydrogen-bonded layers are packed so that sheets of uranyl cations and Hcam⁻ ligands lie parallel to (100), as shown in Fig. 1c, and the Kitaigorodski packing index (KPI, evaluated with PLATON [20]) of 0.70 indicates that there is no significant free space.

The crystal structure of $[UO_2(cam)(2,2'\text{-bipy})]$ (**2**) is in a sense the inverse of that of **1** in that although again a monoperiodic coordination polymer is present, here it is the camphorate unit which functions as a bis($\kappa^2 O,O'$) bridge and the bipyridine as a simple chelate. This complex, shown in Fig. 2, crystallizes in the space group $P1$ and the asymmetric unit contains
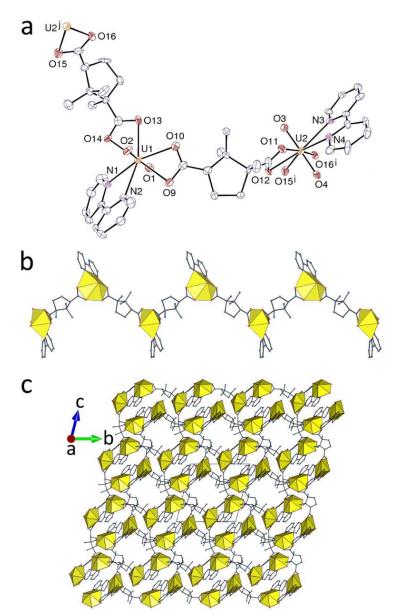

Fig. 2. (a) View of one of the two independent units in compound **2** with displacement ellipsoids shown at the 30% probability level and hydrogen atoms omitted. Symmetry codes: i = x, y + 1, z − 1; j = x, y − 1, z + 1. (b) View of the helical monoperiodic assembly. (c) Packing with chains viewed obliquely.

two independent motifs, each with two uranium atoms in similar, hexagonal-bipyramidal environments. Each uranium centre is chelated by two carboxylate groups from two cam^{2-} ligands and by one 2,2′-bipy molecule [U–O(oxo), 1.72(2)–1.81(2) Å; U–O(carboxylato), 2.415(19)–2.51(2) Å; U–N, 2.62(2)–2.65(2) Å]. As usual in the case of uranyl chelation by 2,2′-bipy, the latter molecule is strongly tilted with respect to the uranyl equatorial plane defined by the two carboxylate groups, by 46.8(5), 40.6(7), 44.9(6) and 43.5(6)° for U1–U4, respectively, these values being in the highest part of the usual range or even above [21], and the displacement of the nitrogen atoms out of this plane is in the range of 0.49(4)–1.06(4) Å. A search in the CSD of uranyl complexes with chelating 2,2′-bipy molecules and O_4N_2 equatorial environments (disregarding the structures involving peroxo ligands) gives dihedral angles in the range of 21.6–42.5°. The monoperiodic polymer formed, parallel to [01$\bar{1}$], is now helical and the U^{VI} centres are chiral due to the tilting of 2,2′-bipy, differences which render the stereochemistry of the complete structure considerably more complicated, though again showing that the cam^{2-} ligand does not engender stereospecificity. The helical structure of the coordination polymer is similar to that found in one case in a family of complexes of the same stoichiometry involving long-chain aliphatic α,ω-dicarboxylates in place of cam^{2-} and either 2,2′-bipy or phen co-ligands [21], where again the 8-coordinate U^{VI} centre is chiral. In the presence of cam^{2-}, the enantiomeric uranium centres should not be of identical energy but the discrimination in **2** appears to be negligible. Of the four inequivalent uranium sites within the structure, two have a Δ absolute configuration and two Λ (as defined in terms of the projection of the N···N vector of the 2,2′-bipy chelate on the uranyl OUO vector). Centres of the Λ configuration (U1 and U2) belong to coordination polymer units of left-handed (*S*) helicity, while those of Δ configuration (U3 and U4) belong to polymer strands of right-handed (*R*) helicity. There are two inequivalent cam^{2-} units in each polymer strand, differing only in torsion angles about the C–CO_2 bonds but even just this limited degree of flexibility appears sufficient

to accommodate variations in other aspects of the crystal chirality. The inequivalence of uranium centres within the polymer units is a reflection of the stacking (also observed in the aliphatic dicarboxylate structures) of 2,2′-bipy units. Among the several possible parallel-displaced π-stacking interactions revealed by short contact analysis with PLATON, the most conspicuous is that between the 2,2′-bipy ligands bound to U2 and U4, leading effectively to the formation of interchain racemic uranyl pairs [centroid···centroid distances, 3.73(2) Å (twice); dihedral angles, 13 and 14°; slippage 1.10 and 1.43 Å]. Examination of the Hirshfeld surface (HS) [22] calculated with CrystalExplorer [23], shows the presence of several interchain CH···O hydrogen bonds. The packing is quite intricate and it does not display significant free space (KPI, 0.67).

The complex [Zn(phen)$_3$][(UO$_2$)$_2$(cam)$_3$] (**3**), shown in Fig. 3, crystallizes in the space group $P2_1$ and it possesses a large asymmetric unit containing four uranyl ions, six cam^{2-} ligands and two [Zn(phen)$_3$]$^{2+}$ counterions. The four uranium centres are in similar, hexagonal-bipyramidal achiral environments, being $\kappa^2 O,O'$-chelated by three carboxylate groups [U–O(oxo), 1.682(14)–1.783(10) Å; U–O(carboxylato), 2.414(9)–2.510(11) Å]. The six cam^{2-} ligands, which differ only slightly with respect to C–CO$_2$ torsions, are bis-chelated bridges. As commonly observed in anionic uranyl ion complexes with dicarboxylate ligands with the 2:3 U/ligand stoichiometry, the coordination polymer formed is diperiodic and has the {6^3} point symbol and the **hcb** topological type (Fig. 3b). However, as shown in Fig. 3c, the layers, parallel to (100), are not planar but they display an alternation along [010] of groups of uranyl ions with their mean equatorial plane parallel to the layer plane and groups of uranyl ions displaced on the same side of the layer plane and tilted with respect to it, thus giving the assembly the shape of a planar layer with well-separated grooves, all on the same side. Successive planes along [100] are related by twofold screw axes and every group of two adjacent layers has the two sets of grooves facing alternately inside or outside the paired layers. The counterions are located

within the bilayers with the grooves facing inside (Fig. 3d), with only two possible parallel-displaced π-stacking interactions [centroid···centroid distances, 4.1110(2) and 4.1323(2) Å; dihedral angles, 6 and 7°; slippage 2.15 and 1.74 Å]. Numerous CH···O hydrogen bonds link the cations to the anionic polymer, and they are apparent on the HS (Fig. 4). The KPI of 0.57
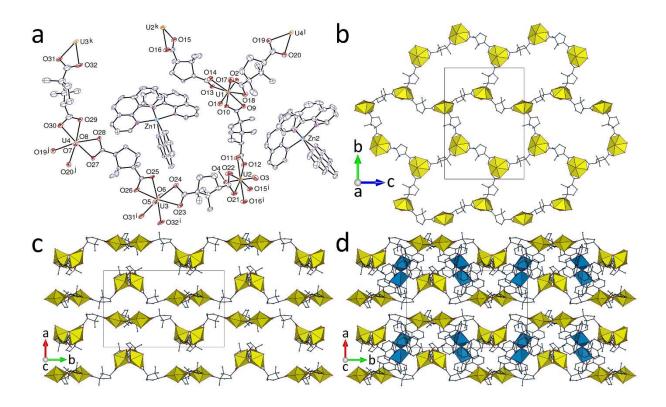

Fig. 3 (a) View of compound **3** with displacement ellipsoids shown at the 30% probability level and hydrogen atoms omitted. Symmetry codes: i = *x*, *y*, *z* − 1; j = *x*, *y* − 1, *z*; k = *x*, *y*, *z* + 1; l = *x*, *y* + 1, *z*. (b) View of the diperiodic assembly. (c) and (d) Two views of the packing with layers edge-on, without and with counterions, respectively. Uranium coordination polyhedra are yellow and those of zinc blue.

indicates the presence of voids probably occupied by disordered solvent molecules (see Experimental part). Complex **3** is unlike the Zn^{II} complex of cam^{2-} and triethanolamine [5] in that the labile Zn^{II} centre is not part of the coordination polymer and this has significant consequences in regard to the chiral influence of the cam^{2-} units. There is no apparent selectivity with respect to the enantiomers of the $[Zn(phen)_3]^{2+}$ countercations, as the structure is racemic

in this regard. These enantiomers have similar environments, each lying close to the centre of a hexanuclear ring in one or the other of the two paired layers. There is a parallel here with the complexes Δ-[Co(en)$_3$][Ln(dipic)$_3$] (Ln = lanthanide(III); dipic = pyridine-2,6-dicarboxylate) [24], where the anticipated chiral resolution of the anions was not achieved, despite the chiral nature of the crystals due to the configurational stability of Δ-[Co(en)$_3$]$^{3+}$.
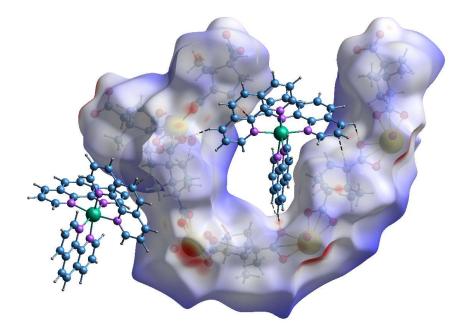

Fig. 4 Hirshfeld surface of the anion in compound **3** mapped with d_{norm} showing some of the CH···O hydrogen bonds formed by the [Zn(phen)$_3$]$^{2+}$ cations. Hydrogen bonds are shown as dashed lines. The large red spots at the bottom of the HS are due to truncation of the polymeric chain.

4. Conclusions

We have reported the synthesis and crystal structure of three new complexes formed by the uranyl ion and the enantiopure (1R,3S)-(+)-camphorate ligand. When 4,4′-bipy was used as a coligand, camphoric acid was only half-deprotonated and assumed the role of a terminal, chelating ligand on uranyl, the formation of monoperiodic polymers being due to uranyl bridging by 4,4′-bipy. Further hydrogen bonding between chains resulted in formation of planar diperiodic networks. In contrast, 2,2′-bipy was a terminal, chelating ligand in a monoperiodic

polymer with bridging, bis-chelating cam^{2-} ligands which displayed a helical shape, the handedness depending on the chirality at the uranium centers induced by the tilting of 2,2′-bipy with respect to the uranyl equatorial plane. An anionic, diperiodic network with honeycomb topology was formed with bis-chelating cam^{2-} ligands in the presence of $[Zn(phen)_3]^{2+}$ counterions. These structures are cases where a configurationally stable chiral species of very limited flexibility forms crystals in which it is associated with one or two other sources of chirality but has no discernible influence on their enantiomer distribution. The complexes formed can be regarded as examples of the failure of Pasteur's second method of resolution, examples which are probably in underestimated numbers simply because they are failures and thus not reported. They show that diastereomeric interactions may well be of equal energy, though the structures also show that this may not be simply a matter of proximal interactions that can occur in solution but also of multiple such interactions between extended substructures in the solid state. The extended substructure interactions observed here appear to favour enantiomer pair formation and may possibly be a reflection of the fact that racemates are usually less soluble than pure enantiomers, a feature which is nonetheless open to change [25].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

CCDC 2141926–2141928 contains the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1]   H.M. Tay, N. Kyratzis, S. Thoonen, S.A. Boer, D.R. Turner, C. Hua, Coord. Chem. Rev. 435 (2021) 213763.

[2]   Z.G. Gu, C. Zhan, J. Zhang, X. Bu, Chem. Soc. Rev. 45 (2016) 3122–3144.

[3]   (a) K.X. Wang, J.S. Chen, Acc. Chem. Res. 44 (2011) 531–540;

        (b) M.B. Andrews, C.L. Cahill, Chem. Rev. 113 (2013) 1121–1136;

        (c) T. Loiseau, I. Mihalcea, N. Henry, C. Volkringer, Coord. Chem. Rev. 266–267 (2014) 69–109;

        (d) J. Su, J.S. Chen, Struct. Bond. 163 (2015) 265–296;

        (e) P. Thuéry, J. Harrowfield, Dalton Trans. 46 (2017) 13660–13667;

        (f) K. Lv, S. Fichter, M. Gu, J. März, M. Schmidt, Coord. Chem. Rev. 446 (2021) 214011.

[4]   (a) P. Thuéry, Eur. J. Inorg. Chem. (2006) 3646–3651;

        (b) P. Thuéry, Cryst. Growth Des. 9 (2009) 4592–4594;

        (c) P. Thuéry, J. Harrowfield, CrystEngComm 16 (2014) 2996–3004;

        (d) P. Thuéry, Y. Atoini, J. Harrowfield, Inorg. Chem. 58 (2019) 870–880.

[5]   S. Chen, J. Zhang, X. Bu, Inorg. Chem. 48 (2009) 6356–6358.

[6]   R.W.W. Hooft, COLLECT, Nonius BV: Delft, The Netherlands, 1998.

[7]   APEX3, ver. 2019.1-0, Bruker AXS, Madison, WI, 2019.

[8]   Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307–326.

[9]   SAINT, ver. 8.40A, Bruker Nano, Madison, WI, 2019.

[10]   (a) SADABS, ver. 2016/2, Bruker AXS, Madison, WI, 2016;

        (b) L. Krause, R. Herbst-Irmer, G.M. Sheldrick, D. Stalke, J. Appl. Crystallogr. 48 (2015) 3–10.

[11]   G.M. Sheldrick, Acta Crystallogr., Sect. A 71 (2015) 3–8.

[12]   G.M. Sheldrick, Acta Crystallogr., Sect. C 71 (2015) 3–8.

[13]   C.B. Hübschle, G.M. Sheldrick, B. Dittrich, J. Appl. Crystallogr. 44 (2011) 1281–1284.

[14]   A.L. Spek, Acta Crystallogr., Sect. C 71 (2015) 9–18.

[15]   L.J. Farrugia, J. Appl. Crystallogr. 45 (2012) 849–854.

[16]   K. Momma, F. Izumi, J. Appl. Crystallogr. 44 (2011) 1272–1276.

[17]   (a) C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, Acta Crystallogr., Sect. B 72 (2016) 171–179;

(b) R. Taylor, P.A. Wood, Chem. Rev. 119 (2019) 9427–9477.

[18]   (a) L.A. Borkowski, C.L. Cahill, Cryst. Growth Des. 6 (2006) 2248–2259;

(b) K. Takeshi, N. Tatsuru, K. Takafumi, Bull. Chem. Soc. Jpn. 83 (2010) 1528–1530;

(c) C. Wang, W. Xu, Y.N. Ren, H.L. Zhu, Y.Q. Zheng, Inorg. Chim. Acta 493 (2019) 29–37;

(d) S.P. Kelley, V. Smetana, S.D. Emerson, A.V. Mudring, R.D. Rogers, Chem. Commun. 56 (2020) 4232–4235.

[19]   P. Thuéry, Acta Crystallogr., Sect. C 63 (2007) m54–m56.

[20]   A. L. Spek, Acta Crystallogr., Sect. D 65 (2009) 148–155.

[21]   P. Thuéry, J. Harrowfield, CrystEngComm 18 (2016) 3905–3918.

[22]   P.R. Spackman, M.J. Turner, J.J. McKinnon, S.K. Wolff, D.J. Grimwood, D. Jayatilaka, M.A. Spackman, J. Appl. Cryst. 54 (2021) 1006–1011.

[23]   S.K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka, M.A. Spackman, CrystalExplorer 3.1, University of Western Australia, 2012.

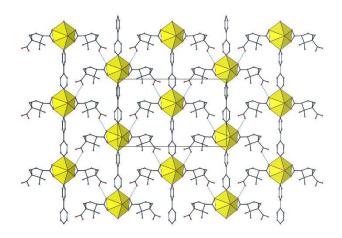[24]   J. Harrowfield, Y. Kim, B.W. Skelton, A.N. Sobolev, A.H. White, CrystEngComm 19 (2017) 2372–2379.

[25] H.K. Buchholz, R.K. Hylton, J.G. Brandenburg, A. Seidel-Morgenstern, H. Lorenz, M. Stein, S.L. Price, Cryst. Growth Des. 17 (2017) 4676–4686.

Multiple aspects of chirality in coordination polymers formed by the uranyl ion with (1*R*,3*S*)-(+)-camphorate ligands

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(1*R*,3*S*)-(+)-Camphorate was used to synthesize three enantiomerically pure, chiral uranyl ion complexes which crystallize as mono- (linear or helical) or diperiodic (honeycomb) coordination polymers depending on the role of additional *N*-donors, 4,4′-bipyridine, 2,2′-bipyridine or 1,10-phenanthroline, which are either bridging, chelating or part of a separate [Zn(phen)$_3$]$^{2+}$ counterion, respectively.