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Uranyl–Nickel(II) Cation–Cation Interaction in a Triperiodic Framework with *cis*-1,2-Cyclohexanedicarboxylate and Isonicotinate Ligands

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Abstract

Uranyl and nickel(II) nitrates have been reacted with *cis*-1,2-cyclohexanedicarboxylic (H_2chdc) and isonicotinic (H-int) acids under solvo-hydrothermal conditions, giving the heterometallic, mixed-ligand complex $[(UO_2)_2Ni(chdc)_2(int)_2]\cdot CH_3CN$ (**1**). The uranyl cation is bound to carboxylate groups of both ligands while Ni^{II} is attached to two carboxylate and two nitrogen donors, with two strong additional interactions with uranyl oxo groups giving a nearly regular octahedral environment. The short Ni–O(oxo) bond length of 2.114(3) Å amounts to 67% of the sum of van der Waals radii. The trimetallic $(UO_2)_2Ni^{6+}$ clusters thus formed are assembled by $chdc^{2-}$ ligands into linear chains which are further bridged by int^- links to give a triperiodic framework with the **dia** topology, in which small channels encompass two rows of acetonitrile solvent molecules. Complex **1** does not display uranyl luminescence under excitation in the solid state.

Introduction

One expression of the oxophilicity of uranyl ion, UO_2^{2+}, is the fact that in heterometallic complexes involving transition metals where both aza-aromatic and pure carboxylate ligands are present, for example, uranyl ion is generally found in an environment exclusively made of carboxylate oxygen donors. Although homometallic uranyl ion complexes of aza-aromatic ligands are well known, their U–N bonds are relatively long, so that ambidentate ligands can be seen as a means of creating true heterometallic coordination polymers by extending homoleptic uranyl carboxylate species through bridging involving additional metal ions (most often d-block cations or Ag^I).[1–16] The family of pyridinecarboxylic acids is a case in point, and it nicely illustrates the importance of the relative position of both coordinating groups. While 2-carboxylatopyridine (picolinate) is often found to chelate the uranyl cation to form a five-membered ring,[17–21] such chelation is precluded and the nitrogen donor is thus available for bonding to the additional cation with 3-carboxylatopyridine (nicotinate)[22,23] and 4-carboxylatopyridine (isonicotinate, H-int),[24–26] although, in the absence of a second metal cation, nitrogen bridging interaction to uranyl has been observed.[27] Isonicotinic acid often bounds to uranyl in its neutral, zwitterionic form,[28–31] and in order to pursue our previous work on mixed-ligand uranyl ion complexes involving zwitterionic carboxylates,[32] we have first tried to synthesize such complexes involving H-int and diverse dicarboxylate ligands, but, although one case, with succinate, has previously been reported by another group,[31] our attempts proved disappointing. However, another approach consisting in adding the nickel(II) cation in order to generate a mixed-ligand, heterometallic complex proved successful in the case of *cis*-1,2-cyclohexanedicarboxylate ($chdc^{2-}$), a ligand known to give closed oligomers[33,34] and various polymeric species[35–37] with the uranyl cation. The complex actually formed does contain $(UO_2)_2Ni(chdc)_2^{2+}$

polymeric chains involving a “cation–cation” U=O–Ni interaction (a slightly misleading name since the interaction is *via* the partially negatively charged oxo group), with further bridging by int^- giving a triperiodic structure defining channels into which acetonitrile solvent molecules are included.

Results and Discussion

The asymmetric unit in the complex $[(UO_2)_2Ni(chdc)_2(int)_2]\cdot CH_3CN$ (**1**) contains one uranyl cation in general position and one nickel(II) cation located on a twofold rotation axis (Figure 1). The uranium atom is bound to one κ^2*O,O*′-chelating carboxylate group from one int^- ligand and to three more carboxylate oxygen donors pertaining to three $chdc^{2-}$ ligands, resulting in a pentagonal-bipyramidal coordination environment [U–O(oxo), 1.773(4) and 1.807(4) Å; U–O(carboxylato), 2.461(4) and 2.462(4) Å for the chelating group, 2.286(4)–2.340(4) Å for the others]. Ni^{II} is bound to two oxygen donors from two $chdc^{2-}$ ligands [Ni–O, 2.010(3) Å], two nitrogen donors from two int^- ligands [Ni–N, 2.060(4) Å] and, more unusually, to two *trans*-oxo groups from two uranyl cations [Ni–O, 2.114(3) Å], the *cis*-N_2O_4 octahedral donor sphere illustrating the anticipated donor atom distribution.

So-called cation–cation interactions due to bonding of one uranyl oxo group to a second metal cation (typically another uranium centre, in the +V or +VI oxidation state, an alkali or a d-block metal cation, Pb^{II} or Ag^{I}) have been known for long,[38–43] and several in-depth studies have recently been published.[44–46] Three examples involving U^{VI} and Ni^{II} have been reported;[47–49] in two of them, the Ni–O(oxo) bond lengths of 2.516(4) and 2.607(3) Å are much longer than in **1**, while the U=O–Ni angles of 157.5(2) and 178.20(16)° are also larger than that in **1**, 136.15(19)°.[47,48] In the third example, Ni^{II} is bound to only one oxo group, the other axial position being occupied by a water molecule, and the Ni–O(oxo) bond

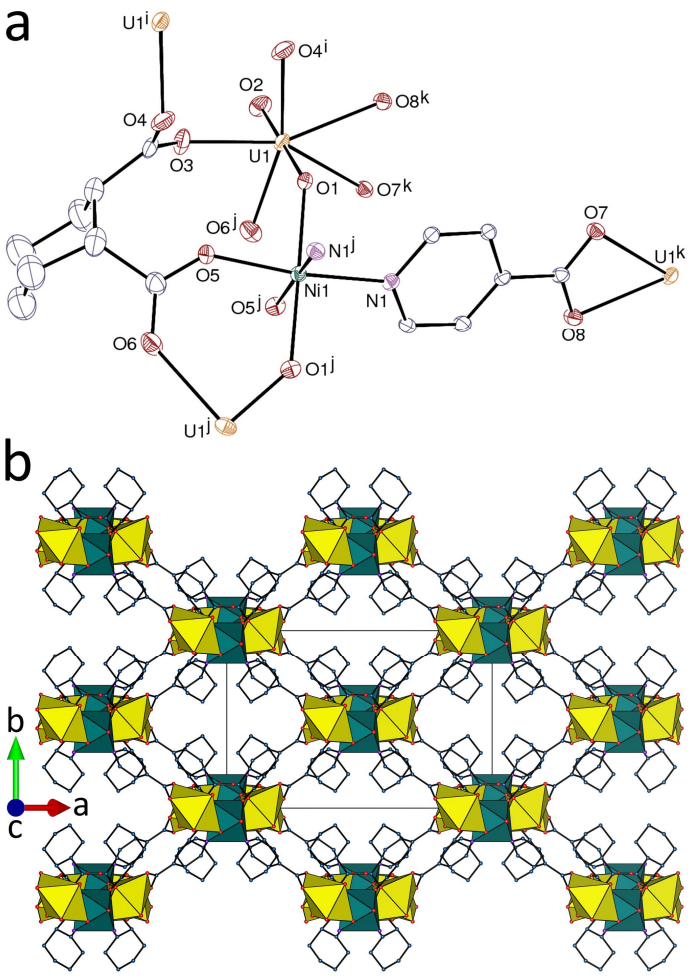

Figure 1. (a) View of complex **1**. Displacement ellipsoids are drawn at the 30% probability level. The solvent molecule and hydrogen atoms are omitted. Symmetry codes: i = 1 – *x*, 1 – *y*, 1 – *z*; j = 1 – *x*, *y*, 3/2 – *z*; k = 1/2 – *x*, 1/2 – *y*, 1 – *z*. (b) View of the triperiodic framework with uranium coordination polyhedra yellow and those of nickel(II) green.

length of 2.189(4) Å is closer to that in **1**, the U=O–Ni angle of 158(3)° being however larger.[49] The coordination environment is distorted octahedral in all cases, but in the three previous examples Ni^{II} is at the centre of an azamacrocycle, and the oxo donors occupy the axial sites, an environment quite different from the present one. A Ni–O(oxo) bond length comparable to that in **1**, 2.05(2) Å, has also been reported for a complex involving U^{V}.[50] Considering the very close Cu^{II} cation, the Cu–O(oxo) bond lengths and U=O–Cu angles in the 14 structures reported in the Cambridge Structural Database (CSD, Version 5.45)[51] vary in

the ranges of 2.27–2.74 Å and 121.6–174.2°, while bond lengths close to that in **1** (2.14–2.20 Å) are found in some U^{VI}/Co^{II} complexes.[52,53] As a result of this strong interaction in **1**, the two U=O bonds are clearly asymmetric, with a distinct and statistically significant lengthening of that with the bridging oxygen atom [1.807(4) *vs* 1.773(4) Å]. The interaction of the van der Waals spheres of Ni and the oxo atom O1 can be evaluated as %vdW = 100 × d(Ni–O)/(r_{Ni} + r_O),[44–46] where d is the interatomic distance and r is the van der Waals radius of the atom (1.63 for Ni, 1.52 for O[54]), which gives a particularly low value of 67%, indicative of a quite strong interaction. Bond valence[55] analysis with PLATON[56] provides another

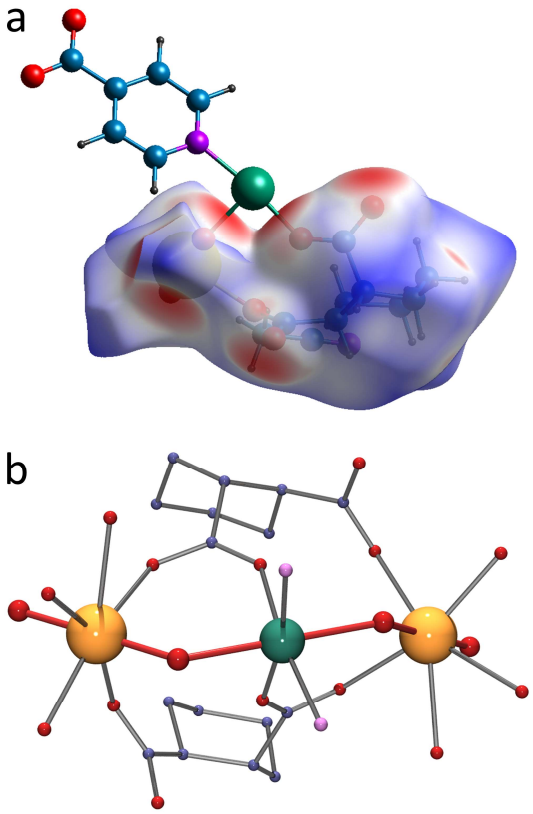

Figure 2. (a) Hirshfeld surface mapped with d_{norm} of the UO_2(chdc) fragment in **1** showing the Ni–O(oxo) interaction. Some of the other red spots are due to polymer truncation. (b) The $(UO_2)_2Ni^{6+}$ cluster and its environment (U, yellow; Ni, green; O, red; N, purple; C, blue).

measure of this, with values of 1.614 and 1.725 for U–O1 and U–O2, respectively, and 0.289 for Ni–O1 (to be compared with 0.381 for Ni–O5 and 0.378 for Ni–N1). The Hirshfeld surface[57,58] calculated for the UO_2(chdc) fragment clearly shows this interaction too (Figure 2a). The $(UO_2)_2Ni^{6+}$ cluster, with its internal bonds and subtended by the two $chdc^{2-}$ ligands (Figure 2b), can thus be considered as the elementary brick from which the structure is built. Similar oxo-bridged trinuclear moieties have previously been found, for example with Ni^{II} and Co^{II},[47,52] but this arrangement differs from the infinite chain found in another Ni^{II} complex, with both uranium and nickel atoms located on inversion centres (with however much weaker interactions).[48]

While the int^- ligand acts as a simple κ^2O,O' carboxylate chelate on U^{VI} and a κ^1N ligand on Ni^{II}, and is thus a simple edge, the $chdc^{2-}$ ligand has a far more complicated role, with both carboxylate groups acting as μ_2-κ^1O:κ^1O' bridges, one between uranyl centres 5.2703(4) Å apart (8-membered ring) and the other between uranyl and nickel 3.6392(4) Å apart (6-membered ring including the oxo bridge), with overall formation by two $chdc^{2-}$ ligands of a 14-membered ring between uranium atoms 6.9286(5) Å apart. The whole $(UO_2)_2Ni^{6+}$ cluster can naturally be chosen as a single node, which is 4-coordinated (4-c), with all links being double however, and both ligands are simple edges (Figure 3). The resulting uninodal, triperiodic framework has the point symbol $\{6^6\}$ and the **dia** (diamond) topological type from the RCSR database.[59] Double-stranded $(UO_2)_2Ni(chdc)_2^{2+}$ polymeric chains run down the *c* axis, and are connected to one another by the int^- anions. The structure has a Kitaigorodsky packing index (KPI, calculated with PLATON[56]) of 0.58 with solvent excluded. The acetonitrile molecules are arranged into double rows in the small channels running along the *c* axis. The aromatic rings of the int^- ligands are too far apart for any π–π interaction to be present (centroid···centroid distances larger than 4.8 Å).

Complex **1** is non-emissive under excitation at 420 nm in the solid state, which is probably due either to energy transfer to Ni^{II} followed by non-radiative relaxation,[6,12,13,24,60] or to preferential absorption by Ni^{II}.

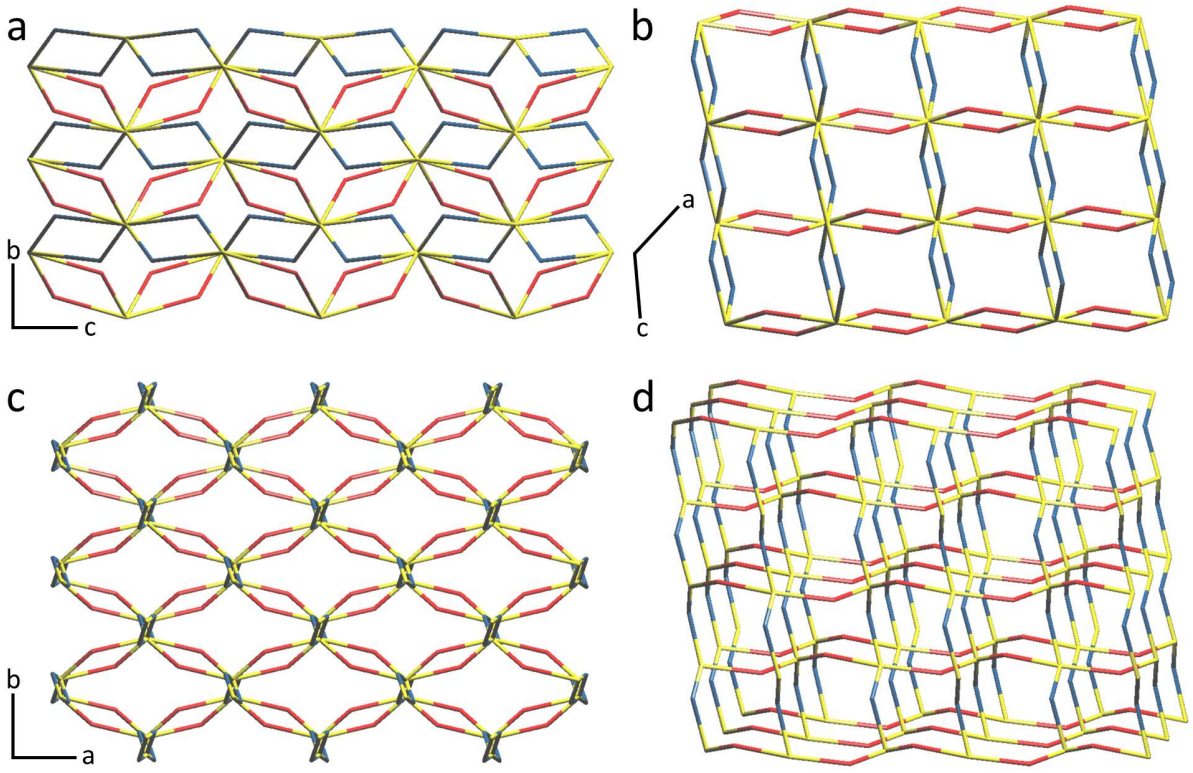

Figure 3. (a, b, c) Nodal representation of the framework in **1**, down the *a*, *b* and *c* axes. (d) View down *b* slightly rotated, with a single edge represented for each connection. $(UO_2)_2Ni^{6+}$ nodes, yellow; $chdc^{2-}$ edges, blue; int^{-} edges, red.

Conclusions

We have reported the synthesis and crystal structure of a uranyl–nickel(II) complex which is both a heterometallic and a mixed-ligand species involving *cis*-1,2-cyclohexanedicarboxylate and isonicotinate. As expected, the nitrogen donor of the latter ligand is bound to Ni^{II}, while uranyl is only bound to carboxylate groups. A particularly strong interaction between nickel and two uranyl oxo groups ("cation–cation interaction") results in the formation of the $(UO_2)_2Ni^{6+}$ cluster. Double bridging of the clusters by $chdc^{2-}$ generates linear chains which

are further assembled by double int^- links to give a triperiodic framework with the **dia** topology. Although the outcome of self-assembly processes involving so many components and possible interactions is hard to predict, the synthesis of heterometallic, mixed-ligand uranyl-based complexes appears as a promising strategy to get original structures and, in particular, to investigate the formation of bridging interactions of the uranyl oxo groups. While in the present instance the proximity of Ni^{II} to the uranyl centres appears to quench emission and raises the need for a better understanding of the electronic structure of the system, the facile synthesis of the complex should be readily adaptable to the substitution of Ni^{II} by other M^{II} species and thus to a detailed study of factors limiting uranyl luminescence behaviour.

Experimental Section

General: $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (RP Normapur, 99%) and $Ni(NO_3)_2\cdot 6H_2O$ were purchased from Prolabo. *cis*-1,2-Cyclohexanedicarboxylic acid (H_2chdc) was from Alfa Aesar and isonicotinic acid (H-int) was from Aldrich. The elemental analysis was performed by MEDAC Ltd.

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.

$[(UO_2)_2Ni(chdc)_2(int)_2]\cdot CH_3CN$ (1): H_2chdc (17 mg, 0.10 mmol), H-int (12 mg, 0.10 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (50 mg, 0.10 mmol), and $Ni(NO_3)_2\cdot 6H_2O$ (15 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. The yellow crystals of **1** formed directly from the pressurized and heated reaction mixture within about one month and not as a result of subsequent cooling (14 mg, 23%), and they were recovered by filtration. Elemental analysis results indicate the presence of about one extra acetonitrile molecule with respect to the formula derived from crystal structure determination. $C_{30}H_{31}N_3NiO_{16}U_2$ + C_2H_3N (1265.4): calcd. C 30.37, H 2.71, N 4.43; found C 30.10, H 2.66, N 4.24.

Crystallography: The data were collected 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 APEX4 software.[61] The data were processed with SAINT[62] and absorption effects were corrected for empirically with SADABS.[63,64] The structure was solved by intrinsic phasing with SHELXT[65] and refined by full-matrix least-squares on F^2 with SHELXL,[66] using the ShelXle interface.[67] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3). The acetonitrile molecule was given an occupancy factor of 0.5 in order to retain acceptable displacement parameters. The large displacement parameters of some atoms of the cyclohexyl ring probably indicate that disorder is present, but attempts to separate two positions proved unsatisfactory. Restraints on displacement parameters were applied for the atoms of the cyclohexyl ring and the acetonitrile molecule. The molecular plot was drawn with ORTEP-3[68,69] and the polyhedral representation with VESTA.[70] The topological analysis was performed with ToposPro.[71]

*Crystal data for **1***. $C_{30}H_{31}N_3NiO_{16}U_2$, M = 1224.35, monoclinic, space group $C2/c$, a = 24.0814(9), b = 12.3683(5), c = 16.8998(7) Å, β = 130.0559(11)°, V = 3852.8(3) Å^3, Z = 4. Refinement of 250 parameters on 3662 independent reflections out of 69287 measured reflections (R_{int} = 0.042) led to R1 = 0.027, wR2 = 0.072, S = 1.136, $\Delta\rho_{min}$ = –1.35, $\Delta\rho_{max}$ = 1.72 e Å^{-3}.

Deposition Number 2376485 (for **1**) contains 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.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Carboxylic acids / Metal–organic frameworks / Cation–cation interaction / Structure elucidation / Uranyl cation

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Table of Contents Entry

Uranyl–Nickel(II) Cation–Cation Interaction in a Triperiodic Framework with *cis*-1,2-Cyclohexanedicarboxylate and Isonicotinate Ligands

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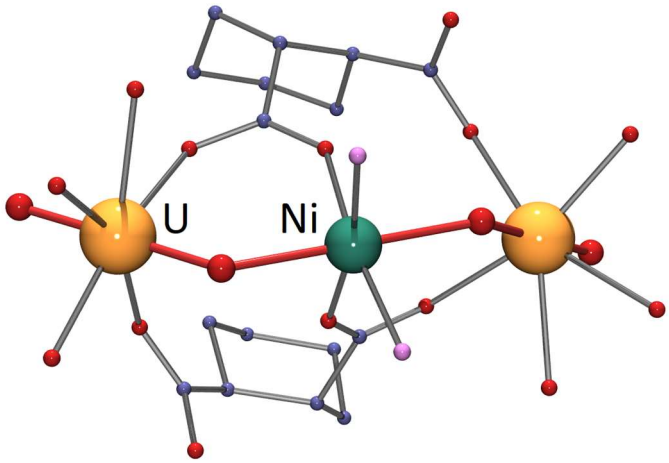
Key Topic: Uranyl complexes



A mixed-ligand, heterometallic uranyl–nickel(II) complex involving O- and O/N-donor ligands crystallizes as a triperiodic framework with the **dia** topology, with $(UO_2)_2Ni^{6+}$ clusters, formed by nickel bonding to uranyl oxo groups, as nodes.