

INTRODUCTION

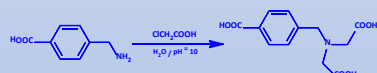
The study of the behavior of the UO_2^{2+} ion has been the subject of focused attention due to increasing global nuclear energy demand.¹ As a result, its presence in nature poses serious environmental concerns where it may come across a huge number of chemical, geochemical, biochemical, and environmental processes.²

Obviously, the knowledge of the behavior of cationic UO_2^{2+} species is essential for accurate monitoring, speciation, and furthermore estimation of their interactions during migration within terrestrial humic substances³ and certainly it is of relevance for nuclear waste management.

For several years, we have directed our synthetic efforts towards the construction of coordination polymers (CPs) by using symmetric ligands with increased flexibility. The ditopic ligand N-(4-carboxybenzyl)iminodiacetic acid (LH_3) is our first attempt to construct CPs from asymmetric ligands.⁴ The iminodiacetate moiety has been extensively studied as a ligand in coordination chemistry, and it can easily be coordinated in a bis-chelating fashion,⁵ while the 4-carboxybenzyl moiety can be utilized for coordination to other metals, since the carboxylate group at the fourth position of the ring does not allow the formation of an extra chelating ring. The methylene hinge provides enough flexibility for the system.

SYNTHETIC COMMENTS

The ligand N-(4-carboxybenzyl)iminodiacetic acid (LH_3) was prepared by the reaction of the corresponding amine and chloroacetic acid in aqueous alkaline media followed by acidification in accordance with the following equation:



Compound **1**, formulated as $[(\text{Me}_2\text{NH}_2)_2][(\text{UO}_2)_4\text{L}_3(\text{H}_2\text{O})_2] \cdot 3\text{DMF} \cdot 6\text{H}_2\text{O}$, prepared by the solvothermal reaction of a concentrated solution of commercial hydrated uranyl(IV) nitrate with LH_3 in aqueous DMF at 115 °C for 48 hrs. Rhombic yellow plate-like crystals were separated upon cooling and isolated by filtration, washed with DMF and dried in air.

Compound **2**, formulated as $[(\text{Mg}(\text{UO}_2)_2\text{L}_2(\text{H}_2\text{O}))_2 \cdot 3\text{DMF} \cdot 4\text{H}_2\text{O}]_n$ was prepared as **1**, with the exception that magnesium acetate was added in the reaction mixture.

STRUCTURAL COMMENTS (1)

- 4 symmetry independent UO_2^{2+} and 3 ligand anions constitute the asymmetric unit of compound **1**. (Fig. 1a)
- A dinuclear node is formed via *syn-syn* coordination of the benzoate carboxylate and a bridged water molecule. (Fig. 1b)
- The coordination sphere about the uranium atom can be characterized as pentagonal bipyramidal.
- One of the ligand molecules has different coordination mode (the iminodiacetate part) than the others leading to the formation of porous double honeycomb layers. (Fig. 3)
- The pores of the structure host the cations and solvated molecules of the structure (Fig. 2)
- A unique topological 2D net type is formed (Fig. 3)

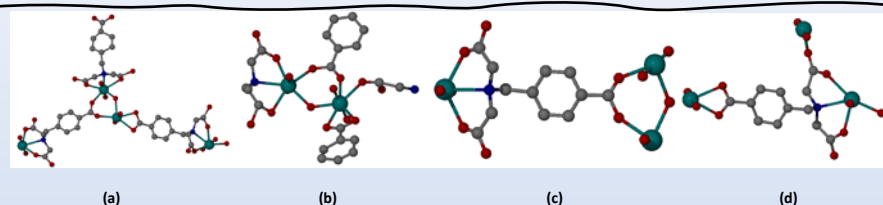


Figure 1. a) The asymmetric unit of the anionic polymer formed in compound **1** formulated as $[(\text{UO}_2)_4\text{L}_3(\text{H}_2\text{O})_2]$. The negative charge is counterbalanced by dimethylammonium cations produced by the hydrolysis of DMF solvent under hydrothermal conditions used for the preparation of the compound. b) The dinuclear oxo-carboxy bridged unit found in **1**. c and d) The two different coordination modes of the ditopic ligand L^{3-} found in **1**. Color code: U stone green, O red, N blue, C grey. H atoms omitted for clarity.

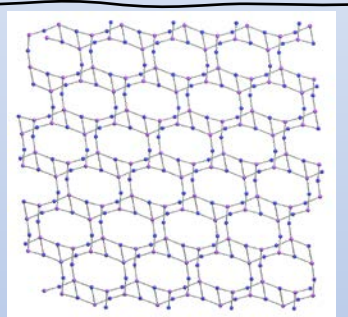


Figure 3. Topological representation of the thick 2D layer formed in **1**. Blue spheres represent the ligand while purple spheres represent the uranyl(VI) dinuclear units. A 3-nodal network is formed with stoichiometry $(3c)_2(4c)$ and point symbol $(4.6.8)(4.6^2.8^3)(6^2.8)$.

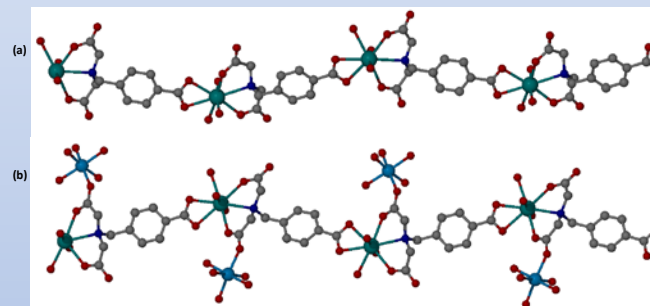


Figure 4. The anionic (a) and the cationic (b) chains present in the crystal structure of **2**. H atoms omitted for clarity.

STRUCTURAL COMMENTS (2)

- 2 symmetry independent UO_2^{2+} , 2 ligand anions, 1 Mg^{2+} , and 7 coordinated water molecules constitute the asymmetric unit of compound **2**.
- While uranium atoms have the same coordination spheres the ligands have different coordination modes. (Fig. 4)
- The coordination sphere about the uranium atom can be characterized as hexagonal bipyramidal
- The compound can be realized as a 'salt' with both the anion and the cation being 1D polymers.
- The difference in coordination mode of the ligands and charge of the 1D chains is due to the magnesium atom which is coordinated to the anti position of a iminodiacetate oxygen.

CONCLUDING REMARKS

- Two unique uranium coordination polymers have been synthesized with solvothermal procedures that may serve as models for the interaction of uranyl cations with polycarboxylate ligands bearing both bridging and chelating groups.
- Both of them possess unique structural characteristics.
- Preliminary results suggest that the cations of **1** can be exchanged with metal ions. When Pb^{2+} was used to replace dimethylammonium cations in the structure, a quenching of the radioactive emission of uranium was observed, and further experiments to quantify this property and check the possibility of using compound one for lead sensing are in progress.

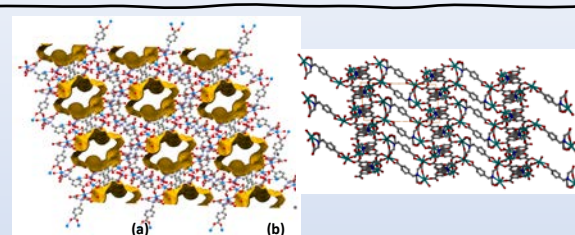


Figure 2. Two packing diagrams of the 2D polymeric anion in **1** down to the crystallographic axes *a* and *b*, respectively. In (a) the solvent accessible volume in form of channels parallel to *a* is also depicted in yellow. This is the space where the disordered cations and lattice solvents are located.

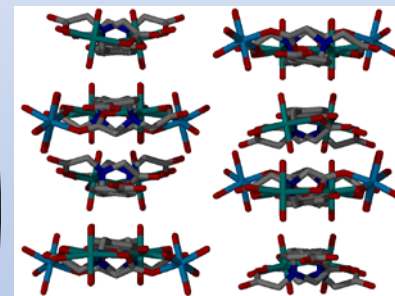


Figure 5. A packing diagram of **2** showing pairs of 1D cations and anions in the lattice, which interact with each other with H-bonds. The space between the pairs is filled with solvated molecules H-bonded to the polymeric pairs

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