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Little is known regarding the structure and properties of technetium oxides. This is mainly due to the absence of any naturally occurring Tc isotopes and the radioactivity of those available [1]. Tc oxides are important since <sup>99</sup>Tc is found in nuclear waste and has a long half-life ( $2.13 \times 10^5$  yr). Tc is a 4d element, and like its lighter analogue Mn a 3d element it can adopt a number of oxidation states. 3d oxides are generally, but not always magnetic, while 4d and 5d oxides, with their more spatially extended d-orbitals tend not to be magnetic although SrRuO<sub>3</sub> [2] is a notable exception.

Here we have combined synchrotron X-ray and neutron diffraction to examine the structure of CaTcO<sub>3</sub>, SrTcO<sub>3</sub> and Pb<sub>2</sub>Tc<sub>2</sub>O<sub>7-d</sub>. The only previous report on these materials was by Muller, White and Roy in 1964 [3]. They reported the existence of these materials and suggested the CaTcO<sub>3</sub> and SrTcO<sub>3</sub> were orthorhombic whereas the Pb<sub>2</sub>Tc<sub>2</sub>O<sub>7-d</sub> was reported as being pyrochlore. This earlier work concentrated on synthesis hence little is known about these three compounds and there has been no study of their structures or magnetic properties.

We found that CaTcO<sub>3</sub> and SrTcO<sub>3</sub> both adopt a distorted perovskite structure with G-type antiferromagnetic ordering with surprisingly high Neel temperatures, ~ 800 K for CaTcO<sub>3</sub> [4] and ~1000K for SrTcO<sub>3</sub> [5]. The Pb<sub>2</sub>Tc<sub>2</sub>O<sub>7-d</sub> was found to be a pyrochlore of stoichiometry of Pb<sub>2</sub>Tc<sub>2</sub>O<sub>6.86</sub> and did not exhibit any magnetic properties. Variable temperature diffraction results indicated that the CaTcO<sub>3</sub> does not undergo any structural transitions below 1000 K though magnetostriction was observed. SrTcO<sub>3</sub> underwent the following structural transitions *Pnma* -390K- *Imma* -625K- *I4/mcm* -800K- *Pm3m*. Rietveld refinements demonstrated that the magnetism in SrTcO<sub>3</sub> persisted to the cubic phase. The Pb<sub>2</sub>Tc<sub>2</sub>O<sub>6.86</sub> sample did not undergo any structural transitions and is similar to Pb<sub>2</sub>Re<sub>2</sub>O<sub>7-d</sub> rather than the analogous ruthenates which display oxygen vacancy ordering. Displacive disorder of the Pb cations was evident from the Rietveld refinements with X-ray absorption measurements indicating the the valence of the Tc is greater than 4.0.

The discovery of these unexpectedly high magnetic ordering temperatures could open new frontiers in the relation of magnetism and properties of heavy transition metal systems.

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### The "organic fluorine" in action in the construction of organometallic molecular materials

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Fluorine containing organic substituents are currently used to gain control on the solid state supramolecular organization of both organic and inorganic materials [1]. The introduction of CF<sub>3</sub> groups adequately positioned on the rigid core of a molecule, could be sufficient to provide fluorine-fluorine interactions able to modify, in absence of other strong interactions like hydrogen bonding, the packing motifs in the structure of crystalline materials. Moreover, segregation effects of fluoroaliphatic groups, in terms of micro-segregation of hydrophilic versus hydrophobic parts of molecules, is a specific tool for the generation of layered and/or columnar structures, which are tailored solid state organizations able to generate specific properties in molecular materials [2]. We have recently used this approach in the generation of new cyclometalated complexes, molecular materials of great interest as a result of their photophysical and mesogenic properties [3]. In particular, fluorine substitution proves to be a useful strategy in the promotion of different and enhanced photophysical properties as well as phase-segregated structures favorable for the appearance of columnar mesomorphism, due to the delicate balance between incompatible parts of the molecules, in acetylacetonate and hexafluoro-acetylacetonate cyclopalladated and cycloplatinated complexes [4, 5].

In this communication, the use of fluoroaliphatic groups on both the cyclometalated and the ancillary ligands in novel palladium(II) and platinum(II and IV) complexes, is illustrated with the intention of providing evidence that the 'organic fluorine' can be used to drive the solid state supramolecular organization of new crystalline molecular materials and their thermal and photophysical properties. In the case of the Pt(IV) derivatives, bearing as C<sup>N</sup> cyclometallating species the 2-phenylpyridine ligand, the effects of the variation between aliphatic and fluoroaliphatic ancillary ligands, and the intermolecular interactions eventually introduced by the fluorine atoms, will be discussed in relation with other possible halogen bonding due to the presence of the halides axially coordinated to the metal centre.

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### Addressing structure solution challenges from light-atom clathrates with very large Z'

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Inflexible small molecules with strong structure-directing groups, such as carboxylic acids, provide many examples of clathrate assemblies with large unit cells, low space group symmetry and disordered inclusion molecules. Similar to porous coordination frameworks, but lacking metals with higher electron density, these samples provide significant contemporary challenges for chemical crystallography.

We have recently solved the structures of a series of pseudo-polymorphs (differing in degree of solvation) with large Z' values from an unassuming small molecule comprised of less than 40 carbon and oxygen atoms. These structures presented problems that were at last

addressed by collecting high quality data at low temperature using a microfocus Cu X-ray source and employing dual-space recycling (SHELXD) for structure solution. The very large numbers of independent molecules present good exercises for the RESI and BLOC commands during refinement. For example, one structure in space group *I2* has a unit cell volume of nearly 43 000 Å<sup>3</sup> and contains fourteen independent molecules. Despite a fascinating topological interweaving, more than one-third of the unit cell volume is occupied by solvent molecules that are disordered to the point of being impractical to model. Following application of the SQUEEZE routine in PLATON, the residual *R*<sub>i</sub> decreased from 8.4% to 4.5%.

**Keywords:** Z-prime, pseudosymmetry, porous

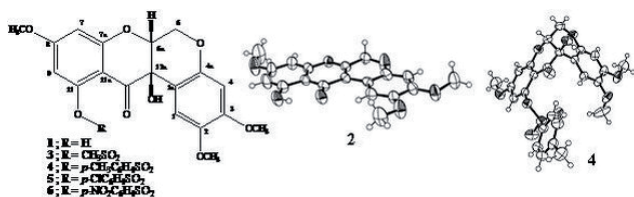
## MS61.P05

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### X-ray structure-cytotoxicity relationship of the 6-deoxyclitriacetals derivatives

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6-Deoxyclitriacetals (**1**) has been identified to have a good cytotoxic activity against various types of human carcinoma, possibly due to its ability to intercalate with DNA as evidenced *in vitro* assay [1]. The sulfonate derivatives of 6-deoxyclitriacetals were synthesized to enhance its cytotoxic activities as novel anticancers [2,3]. Screening of these compounds for cytotoxic activity has shown that tosylate derivative (**4**) was more potent and selective than commercial doxorubicin hydrochloride. X-ray structures and their cytotoxic activities have considerably revealed that not only a bent-shaped structure but also the suitable functional groups at C11 play an important role in increasing their cytotoxicities. Preliminarily, molecular docking of **4** with d(CGATCG)<sub>2</sub> revealed that this derivative with a bent shape structure can intercalate between CG base pair, like doxorubicin behavior. Additionally, the sulfonate derivatives were evaluated their ability to inhibit topoisomerase II activity. They had potentially inhibited the topoisomerase II more 70% inhibition. Finally, we studied the DNA-binding affinity, thermal denaturation of 6-deoxyclitriacetals and its sulfonate derivatives based on UV-Visible spectroscopic techniques [4].



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**Keywords:** 6-deoxyclitriacetal, X-ray structure-cytotoxicity, topoisomerase II

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### Synthesis, crystal structure and properties of [Be(H<sub>2</sub>O)<sub>4</sub>][UO<sub>2</sub>(C<sub>2</sub>H<sub>3</sub>COO)<sub>3</sub>]<sub>2</sub>

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A novel complex compound [Be(H<sub>2</sub>O)<sub>4</sub>][UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>3</sub>]<sub>2</sub> (**1**) was synthesized and studied by X-Ray diffraction, IR spectroscopy and thermal analysis. Yellow prismatic crystals of **1** were obtained by slow evaporation of aqueous solution containing equimolar amounts of beryllium and uranyl acetates. **1** crystallizes in tetragonal crystal system, unit cell parameters: *a* = 10.3647, *c* = 23.4127 Å, *V* = 2515.2 Å<sup>3</sup>, *Z* = 4, space group *I4<sub>1</sub>/a*, *R<sub>i</sub>* = 0.0194 (for 1436 reflections). Each beryllium atom in structure of **1** is tetrahedrally surrounded by four oxygen atoms of water molecules and forms [Be(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> complex. The crystal-chemical formula (CCF) of this complex is AM<sub>1</sub><sub>4</sub> (A = Be<sup>2+</sup>, M<sup>1</sup> = H<sub>2</sub>O). CCF is given in accordance with [1]. Uranyl cation forms mononuclear [UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>3</sub>]<sup>-</sup> complex with AB<sup>0</sup><sub>3</sub> (A = UO<sub>2</sub><sup>2+</sup>, B<sup>0</sup> = CH<sub>3</sub>COO<sup>-</sup>) CCF. Coordination polyhedron of uranium atom is in shape of hexagonal bipyramid. Six oxygen atoms that are located in equatorial plane belong to three acetate groups, which act as bidentate chelate ligands (the B<sup>0</sup> coordination type).

The [Be(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> and [UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>3</sub>]<sup>-</sup> in **1** are bound with each other by electrostatic interactions and hydrogen bonds. The hydrogen bonds are formed by atoms of water molecules and oxygen atoms of acetate groups. There are two crystallographically different H-bonds in **1**. According to Steiner classification [2], both of them are of moderate strength (the OH...O angles are equal to 175 and 170°, and the O...O distances are equal to 2.60 and 2.67 Å). Meanwhile Voronoi-Dirichlet polyhedron solid angles of the O...O face (expressed as a percentage of 4π steradian) calculated without hydrogen atoms equal 16.6 and 14.9% respectively. This result agrees with previously reported method [3] of H-bonds finding in structures which contain hydrogen atoms, but its coordinates have not been determined.

Thermal decomposition of **1** includes three stages. At the first stage (120-140°C) a removal of water molecules takes place. Further heating up to 220°C leads to sequential acetate anions decomposition. The product of decomposition is a black-colored mixture of BeO and U<sub>3</sub>O<sub>8</sub>.

IR spectrum of **1** contains uranyl, acetate and water absorption bands. It is in agreement with structure data obtained using single-crystal X-Ray diffraction experiment.

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### Synthesis and structure of uranyl complexes with *n*-butyrate and *n*-valerate ions

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