

(Australia). ^bSchool of Chemistry, The University of Sydney, Sydney, NSW 2006 (Australia). ^cBragg Institute, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, (Australia). E-mail: gjt@ansto.gov.au

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 ⁹⁹Tc is found in nuclear waste and has a long half-life (2.13×10^5 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 SrRuO₃ [2] is a notable exception.

Here we have combined synchrotron X-ray and neutron diffraction to examine the structure of CaTcO₃, SrTcO₃ and Pb₂Tc₂O_{7-d}. 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 CaTcO₃ and SrTcO₃ were orthorhombic whereas the Pb₂Tc₂O_{7-d} 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 CaTcO₃ and SrTcO₃ both adopt a distorted perovskite structure with G-type antiferromagnetic ordering with surprisingly high Neel temperatures, ~ 800 K for CaTcO₃ [4] and ~1000K for SrTcO₃ [5]. The Pb₂Tc₂O_{7-d} was found to be a pyrochlore of stoichiometry of Pb₂Tc₂O_{6.86} and did not exhibit any magnetic properties. Variable temperature diffraction results indicated that the CaTcO₃ does not undergo any structural transitions below 1000 K though magnetostriction was observed. SrTcO₃ underwent the following structural transitions *Pnma* -390K- *Imma* -625K- *I4/mcm* -800K- *Pm3m*. Rietveld refinements demonstrated that the magnetism in SrTcO₃ persisted to the cubic phase. The Pb₂Tc₂O_{6.86} sample did not undergo any structural transitions and is similar to Pb₂Re₂O_{7-d} 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

Alessandra Crispini,^a Iolinda Aiello, Mauro Ghedini, Teresa Mastropietro, Alessia Aprea, Daniela Pucci, Massimo La Deda, Mario Amati,^b Francesco Lelj^b ^aCentro di Eccellenza CEMIF. CAL - LASCAMM, Unità INSTM della Calabria - Dipartimento di Chimica, Università della Calabria, Arcavacata di Rende (CS), (Italy). ^bLASCAMM, CR-INSTM Unità della Basilicata and LaMI, Dipartimento di Chimica, Università degli Studi della Basilicata, I-85100, Potenza, (Italy). E-mail: a.crispini@unical.it

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 CF₃ 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 fluoro-aliphatic 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^N 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'

Jesse L. C. Rowsell,^a Matthias Zeller,^b and Charles F. Campana,^c ^aDepartment of Chemistry and Biochemistry, Oberlin College, 119 Woodland St., Oberlin, Ohio USA 44074, ^bDepartment of Chemistry, Youngstown State University, One University Plaza, Youngstown, Ohio, (USA) 44555, ^cBRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, Wisconsin, (USA) 53711. E-mail: jrowsell@oberlin.edu

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