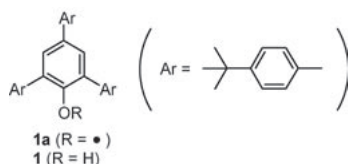


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While 2,4,6-tris(4-tert-butylphenyl)phenoxy radical (1a) itself gave an amorphous solid (A), in the presence of 2,4,6-tris(4-tert-butylphenyl)phenol (1) it yielded mixed crystals B (1a:1 = 60:40) and C (1a:1 = 30:70) from solution. Unlike C, B was apparently heterogeneous: it had purple inside and colorless outside, indicating that 1a was significantly concentrated at inside and virtually absent at outside. The thermal behavior of B and C was not identical but close to that of A and 1, respectively. Single-crystal X-ray diffraction study revealed crystal structures of B, C, and 1 were almost identical. In spite of the higher 1a content, C-O bond distances in B were found to be essentially longer than those of C and a little shorter than those of 1. These observations likely indicate that B was composed of three layers: amorphous 1a (inside), mixed crystal of 1a and 1 (boundary) and 1 (outside).



Keywords: mixed crystals, thermal properties, isomorphous replacement

P06.10.56

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Crystal structure of connatin, a strong radical scavenger from *Lyophyllum connatum*

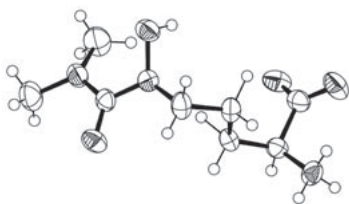
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In our continuing search for free radical scavengers from mushroom, we have isolated ergothioneine, β -hydroxyergothioneine, N-hydroxy-N',N'-dimethylurea, and connatin (N-hydroxy-N',N'-dimethylcitrulline) from the mushroom *Lyophyllum connatum*. We determined the crystal structure of β -hydroxyergothioneine [1], and report here the crystal structure of connatin (Figure 1). All the compounds displayed the ability to scavenge free radicals, based on a 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging assay. We found that ergothioneine and β -hydroxyergothioneine scavenged the radical in very fast manner (reaction almost completed less than 10 min in a UV-cell), therefore they can be classified as fast-reacting scavengers. On the other hand, N-hydroxy-N',N'-dimethylurea and connatin were slow reacting scavengers (for completion of the reaction required 2h). Furthermore, we also isolated N,N-dimethylcitrulline which is considered to be a plausible precursor of connatin. Crystallization of N,N-dimethylcitrulline is under progress.

[1] C. Kimura et al., *Biosci. Biotechnol. Biochem.* 69, 37(2005).

Keywords: connatin, radical scavenger, *Lyophyllum connatum*



P07.01.01

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Metal complexes of di(thiophenyl)ethenes: Synthesis, structure and bonding

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Di(thiophenyl)ethene ligands are of interest as prototypes for 'molecular switches' in future molecular electronic applications [1,2]. In this contribution we describe the synthesis of metal complexes of a di(thiophenyl)ethene ligand in the 'open' form, photolysis of which reversibly gives the 'closed' form (see Figure). Both open and closed forms have been characterised using single crystal X-ray diffraction, in addition to density functional theory and a variety of spectroscopic techniques.

Keywords: molecular electronics, photochemistry, thiophenes

P07.01.02

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Recent results from a long-term academic collaboration

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Several industrial and academic collaborations are underway at Newcastle Crystallography. Among the latter, the most fruitful has so far been the one with the group of Prof. R. E. Mulvey at the University of Strathclyde. About 70 crystal structures of air-sensitive, organometallic compounds were determined in Newcastle within the last 14 months, as part of this collaboration, with a good turnout of high-impact publications. The highlights from the published work, presented in this poster, show the systematic contribution of the structural investigation, not only as the ultimate means towards the identification of expected and unexpected products, but also as an effective tool for underpinning reaction pathways and intermediates.

Keywords: crystallography, metallorganic complexation, structural investigations

P07.01.03

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Structural study of an iron oxalate and a copper rubeanate layer on an ultra-smooth sapphire c-face

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The conductivity by proton in bulk such as a copper rubeanate complex has been studied [1]. Such complexes which consist of thin layers can be useful for a part of a fuel cell. Our purpose in this study

is to reveal the crystallinity of those metal complex layers which has not been studied yet. We made structural analysis on a metal complex ultra-thin film grown on a substrate using synchrotron x-ray reflectivity and grazing angle x-ray diffraction (GAXD). An iron oxalate layer and a copper rubeanate layer grown on an ultra-smooth sapphire (0001) substrate by wet method were measured. The ultra-smooth sapphire substrate was used to make an interface as smooth as possible [2]. The wavelength of incident x-rays used was 0.1 nm. The measurements were performed at BL13XU, SPring-8. The fitted result to x-ray reflectivity data from an iron oxalate layer on sapphire using a single layer model showed that the layer thickness is 0.41 nm. Two peaks were observed in the out-of-plane GAXD measurement profiles. The peaks correspond to periodic planes with the periods of 0.340 nm and 0.142 nm, respectively. No peaks were observed in the in-plane GAXD profiles. The structure of the layer in-plane direction would be random [3]. The results from a copper rubeanate layer showed that the layer formed a large crystal since the reflectivity profile showed peaks correspond to periodic planes with the periods of 0.69 nm and 0.344 nm. In-plane GAXD profiles had many peaks. We obtained the conclusion that both complex layers formed crystals, but the crystallinity of two layers were in different level.

[1] H. Kitagawa et al, *Inorg. Chem. Commun.* 6 (2003) 346.

[2] M. Yoshimoto et al, *Appl. Phys. Lett.* 67 (1995) 2615.

[3] R. Haruki et al. *Trans. Mat. Res. Soc. Jpn.* accepted.

Keywords: iron oxalate, copper rubeanate, sapphire substrate

P07.01.04

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Crystal structures of two homotetranuclear oxovanadium complexes

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The self-assembly reactions between $\text{VO}(\text{acac})_2$ and hydrazone(SFH) with similar condition give two cyclic homotetranuclear complexes 1 and 2. There are two common structural features in the two oxovanadium complexes. First, the two complexes are with same chemical formula $[(\text{VO}_2)(\text{VO})(\text{CH}_3\text{O})(\text{C}_{12}\text{H}_7\text{N}_2\text{O}_4)(\text{C}_5\text{H}_5\text{N})]_2$. Second, the two title complexes are centrosymmetrically cyclic tetranuclear oxovanadium complexes and each complex molecule in the two complexes has a (V-N-N-V-O)₂ core. Third, the coordination geometry around the V(1) atom is a distorted octahedron, while the coordination polyhedron of V(2) atom is between the square-pyramid and the trigonal bi pyramid. The two title complexes crystallize as two different polymorphs with different dihedral angle between benzene ring and furfuran ring in the same hydrazone ligand.

Keywords: oxovanadium complex, cyclic tetranuclear complex, crystal structure

P07.01.05

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Cleavage of Ti_3E_3 (E= O, N) rings by aluminum derivatives

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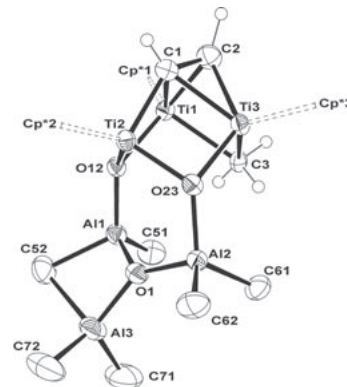
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During the last years our group has studied the chemistry of the organometallic complexes $[\{\text{TiCp}^*(\mu_3\text{-O})\}_3(\mu_3\text{-CR})]$ [R = H (**1**), Me (**2**)] and $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (**3**) [$\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$]. These complexes are able to act as neutral ligands towards different alkyl and halide group 13 and 14 derivatives, to give the corresponding adducts via oxo or imido coordination.¹ Although sometimes the reactions evolve to give very interesting organometallic compounds as $[\{\text{MeAl}\}\{(\mu\text{-OH})(\mu_3\text{-O})\}_2\{(\mu\text{-O})_2(\text{TiCp}^*)_3(\mu_3\text{-CH})\}_2]$, obtained by addition of AlMe_3 to a solution of complex **1**.² We will show how the addition of different aluminum derivatives to complexes **2** and **3** lets to open the Ti_3E_3 rings removing one oxygen or nitrogen atoms and leads to the formation of several singular structures (see figure). We thank the Spanish MEC (CTQ2005-00238) and Factoria de Cristalizacion (CONSOLIDER-INGENIO 2010) for financial support.

¹ M. Garcia-Castro, A. Martin, M. Mena, C. Yelamos, *Organometallics* **2007**, 26, 408-416

² O. Gonzalez-del Moral, A. Hernan-Gomez, A. Martin, M. Mena, C. Santamaria, *Dalton Trans.* **2008**, 44-46.



Keywords: titanium compounds, nitrides, oxides

P07.01.06

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Formation of alkylated di-cation by weak hydrogen bonds in the crystal of $\text{Ni}(\text{dmit})_2$ salts

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The Crystals of $[\text{Ni}(\text{dmit})_2]^+$ (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) salts with two kinds of counter di-cations (1,1-Cn-dipyridinium (dPyr) or 1,1-Cn-di-3-acetylpyridinium (dAce); Cn alkylene chain length; n = 4, 6, 8, 10), were prepared and characterized by single crystal X-ray analysis. The effects of both weak hydrogen bond that connects the cations and alkylene chain that adjust the length of cation have been investigated by X-ray crystallographic analysis. dPyr cations in their complex salts were linked by C-H \cdots π interactions to form one-dimensional structure. On the other hand, dAce cations formed one-dimensional structure linked by C-H \cdots O hydrogen bonds. Furthermore, the type of linkage depended on the length of the alkylene chain. Cations with short (n = 4) and long (n = 10) alkylene chain were linked by C-H \cdots O hydrogen bond with A type of linkage. For those with medium (n = 6, 8), however, the cations adopted B type of linkage. These results indicate that the crystal packing as a whole is controlled by the Coulomb interaction, but the C-H \cdots O hydrogen bonds were found to function superior to the C-H \cdots π interactions on the formation of cation domain.