

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.

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

Keywords: iron oxalate, copper rubeanate, sapphire substrate

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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

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

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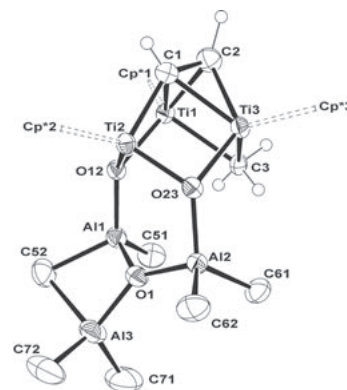
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During the last years our group has studied the chemistry of the organometallic complexes $[\{\text{TiCp}^*(\mu_3\text{-O})\}_3(\mu_3\text{-CR})]$ [R = H (1), Me (2)] and $[\{\text{TiCp}^*(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ (3) [$\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$]. 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.

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



Keywords: titanium compounds, nitrides, oxides

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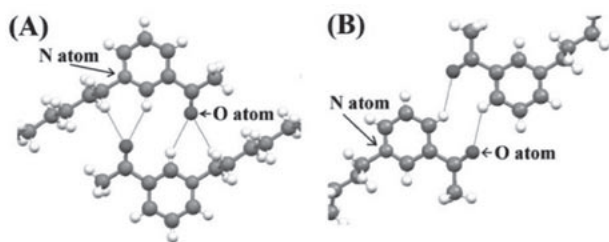
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Formation of alkylated di-cation by weak hydrogen bonds in the crystal of $\text{Ni}(\text{dmit})_2$ salts

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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.



Keywords: dmit complex, weak hydrogen bond, alkylated di-cation

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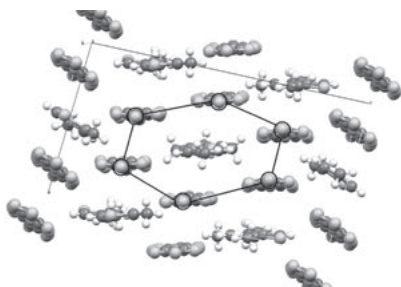
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Honeycomb-like structures in the crystals of Ni(dmit)₂ salts with di- and tri-alkylthiazole cations

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In the crystal structure of 2,3-diethylthiazolium [Ni(dmit)₂] (dmit = 1,3-dithiole-2-thione-4,5-dithiolate) previously reported,^[1] anions formed a distorted honeycomb-like structure. In relation to this compound, two thiazolium derived cations (3,5-dimethyl-, and 3,4,5-trimethylthiazolium) were synthesized and the crystal of their [Ni(dmit)₂] salt were characterized by single crystal X-ray analysis. In dialkylthiazolium salts, anions also formed similar honeycomb-like structures and took cations inside the honeycomb cavities by S...S interactions. On the other hand, in trimethylthiazolium salts, no honeycomb structures were constructed but the layers of cations and anions piled up alternately. These results indicate that the difference in the crystal packing between dialkyl- and trimethyl-thiazolium cations is caused by the steric hindrance of the methyl group. Figure Honeycomb-like structure of [Ni(dmit)₂] in 3,5-dimethylthiazolium salt.



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Keywords: honeycomb-like structure, dmit complex, sulfur compounds

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Structural investigations of the nickel mediated coupling products of CO₂ and isoprene

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The nickel mediated coupling with unsaturated substrates is an efficient way to use CO₂ as a carbon source. By using 1,3-dienes in this reaction, nickelacyclic carboxylates with an allyl group are

obtained.[1] Several ligands can be used in this reaction, among them tetramethylethylenediamine (tmeda) and 2,2'-bipyridine (bipy). During our investigations of the coupling reaction of 2,3-dimethyl-1,3-butadiene (dmbd) and CO₂, the related isoprene coupling products were obtained as side products, formed from traces of isoprene in dmbd. The X-ray structure determination shows, that with bipy the usual regioisomere **A** [2] is formed, while with pyridine (derived from the tmeda complexes by ligand exchange) the opposite regioisomere **B** is observed. The formation of the unexpected isomere **B** encouraged us to further investigate the regioselectivity of the isoprene/CO₂ coupling with tmeda as supporting ligand. The formed products are characterized by X-ray structure determination and the results are presented.

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[2] H. Hoberg, D. Schaefer, B.W. Oster *J. Organomet. Chem.* **266** (1984) 313-320.

Keywords: carbon dioxide, nickel, coupling reaction

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Hydrothermal synthesis and crystal structure of a new copper coordination polymer

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Hydrothermal method provides a powerful tool for the construction of materials containing unique structures and special properties. It also a route to synthesis of complexes of transition metals and the molecular structures of complexes obtained by this method are unexpected compared to those obtained by the common solution method. We have recently reported hydrothermal synthesis of binuclear Co(II) complex under hydrothermal condition. Here we wish to report the hydrothermal synthesis of a new Cu(II) coordination polymer containing bridged oxalate ions and 2,2'-bipyridine ligand. The complex has been prepared from the reaction of bis(1,5 cyclohexanone) oxal dihydrazone and 2,2' - bipyridine with Cu(NO₃)₂ in basic solution under hydrothermal condition. The characterization was performed using IR, NMR spectroscopy and X-ray crystallography. The result showed that the bis(1,5 cyclohexanone) oxal dihydrazone was changed to oxalate ion under heating and basic pH. This complex is crystallized in triclinic system, space group *P*-1, with two molecules per unit cell. The unit cell parameters are $a = 8.9298(18)\text{\AA}$, $b = 9.1011(18)\text{\AA}$, $c = 9.7112(19)\text{\AA}$, $\alpha = 97.61(3)^\circ$, $\beta = 92.602(2)^\circ$ and $\gamma = 105.80(3)^\circ$. Complex is a coordination polymer. Each metal ion center is in a distorted octahedral geometry and coordinated by four O atoms from two bridged oxalate ions and two N atoms of 2,2' - bipyridine. Two uncoordinated water molecules occupy general positions in the cell. In the crystal structure, some H-bonds and π - π interaction cause formation of a 3D network.

Keywords: coordination polymers, crystal structure determination, hydrothermal method