

with $\beta = 92.602(2)^\circ$. The final R value is 0.0258 for 2795 reflection measured. The X-ray analysis shows that benzene-1,3-diamine fragment in proton transfer compound is not contribute in the molecular structure of complex. The molecular structure consists of two metal fragments linked *via* the central four membered Sn_2O_2 ring. Each of two Sn atoms is coordinated by the chelate $(\text{pydc})^{2-}$ ligand, one bridging oxygen atom of carboxylate group, two terminal methyl group and as well as by one terminal ethoxy group. Therefore, the coordination number is seven for each central atom and distorted pentagonal bipyramid geometry is observed around the tin atoms.

Keywords: crystal structures, supramolecular chemistry, weak interactions

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A structural study of metal complexes of bisphosphonate partial ester derivatives

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The chemistry of metal bisphosphonates (BPs) is a growing area of interest due to the unique properties of these compounds, including chemical and thermal stability and the possibility to manipulate their structure. Metal BPs also exhibit a variety of open frameworks such as layered and microporous structures offering a diversity of practical applications in the areas of ion-exchange, catalysis, and sorption. Clodronate, (dichloromethylene)bisphosphonate, Cl_2MBP , is one of the best-documented BPs since it is effectively used in therapeutics. We have focused on studying the complexing properties of ester derivatives of clodronate with the divalent metal cations [1-3]. We present here the crystal structures and characterization of three novel Cd complexes of phenyl esters and alkyl ester derivatives of Cl_2MBP . The structures of the complex crystals were determined by X-ray single-crystal diffraction. All three compounds are coordination polymers with a layered structure. In the case of the Cd complex of the asymmetrical alkyl ester derivative of Cl_2MBP , the layers are connected into a 3D framework through hydrogen bonds. The Cd^{2+} cations of all compounds are in an octahedral environment. However, these layered architectures are different due to the different metal/ligand ratio and different protonation degree and coordination mode of the BP anions.

[1] J. Jokiniemi, M. Ahlgrén and J. J. Vepsäläinen, *Lett. Org. Chem.*, 2006, 3, 898. [2] J. Jokiniemi, E. Vuokila-Laine, S. Peräniemi, J. J. Vepsäläinen and M. Ahlgrén, *CrystEngComm.*, 2007, 9, 158. [3] J. Jokiniemi, S. Peräniemi, J. J. Vepsäläinen and M. Ahlgrén, A structural study of alkaline earth metal complexes of (dichloromethylene)bisphosphonic acid P-morpholinium- and P-pyrrolidinium- P^{\prime} -methyl esters, submitted

Keywords: bisphosphonate, metal complexes, crystal structures

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High pressure synthesis and analysis of new yellow emission Sr_2ZnS_3 : Eu visible-light driven phosphor

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Yellow emission phosphors, which can be excited by blue light, are actively sought for the applications in the LED based lighting. In this work we report synthesis and crystal structure of the new compound Sr_2ZnS_3 , which demonstrates strong yellow fluorescence when activated with Eu^{2+} . Mn doped Ba_2ZnS_3 material is a well-known important green emission phosphor. Recently, the Eu^{2+} activated compound also attracted much attention as a prospective red phosphor for the LED-based applications. Nevertheless, no successful report on synthesis of Sr_2ZnS_3 could be found in literature although in analogy with Ba_2ZnS_3 such a compound should have a remarkable potential as a host for development of new fluorescent materials. In this work Sr_2ZnS_3 was prepared for the first time from the individual metals sulfides under 5GPa pressure at 1000C. The composition of the material was confirmed by EDS. It has tetragonal unit cell (space group $Pbn2_1$) with $a=16.41\text{Å}$, $b=8.464\text{Å}$ and $c=4.071\text{Å}$. The crystal structure was solved *ab initio* using powder diffraction data. A series of Eu^{2+} activated phosphors was prepared from $\text{Sr}_{1-x}\text{Eu}_x\text{S}$ ($0.01 < x < 0.06$) precursors. In order to achieve homogeneous distribution of the activator, the precursors were synthesized by polymerizable complex method combined with conversion of the intermediate carbonate into sulfide by H_2S . The obtained Sr_2ZnS_3 :Eu materials demonstrated strong yellow emission, which can be excited by the near-UV and visible light, and it makes Sr_2ZnS_3 :Eu sulfide an appealing yellow phosphor for LED-based applications. Currently available samples demonstrate fluorescence intensity of 43% compared to one of the best commercial Ce^{3+} doped yttrium-aluminum garnet (YAG-P46) phosphor. The support of this work by Kakenhi grant 20900106 is acknowledged.

Keywords: phosphors, high-pressure high-temperature synthesis, *ab-initio* powder structure determination

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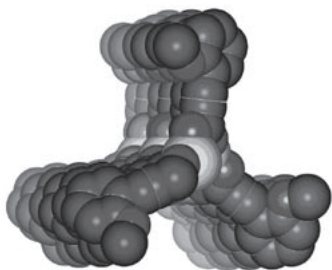
Designing Zn and Co based 1-D coordination polymers with possible magnetic and electronic properties

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Several coordination polymers composed of Zn and Co as metal ions and various aromatic carboxylates as ligands have been synthesized and their structures determined. Typical structures are composed of 1-D chains in which divalent metal ions (Zn or Co) form a polymeric chain surrounded by carboxylate ligands. In all cases the carboxylate ligands coordinate to two metal ions and as a consequence act as a bridge between them, with the coordination environment being tetrahedral in some structures, or a combination of tetrahedral and octahedral in others. Some examples containing oxygen as an additional bridging atom have also been synthesized. In all the structures, the neighboring chains interact with each other through C-H... π and π ... π interactions. All the structures are

composed of achiral building blocks resulting in most of the polymeric chains being aligned relative to each other in a centrosymmetric manner. There is however, one example in which an interesting high symmetry chiral structure has been formed. As is to be expected, the cobalt structure has been found to have magnetic properties.



Keywords: crystal engineering, coordination polymer, magnetism

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A single-crystal-to-single-crystal apical ligand exchange process in a 2D coordination network

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Crystal engineers are becoming more and more aware of the potential coordination chemistry holds. The successes in the design and synthesis of new functional materials, based on metal-organic complexes, are most noticeable in the continuously growing group of porous coordination compounds, with applications such as guest encapsulation, ion exchange and catalysis. As crystalline materials are the main focus of most preliminary studies, reports dealing with structural transformations in the solid state are presently more often, yet still rarely, encountered in the literature. In continuation of our studies on the development of new functional materials and our interest in solid-to-solid interconversions, we report a single-crystal-to-single-crystal ligand exchange process. The copper centers have been incorporated in corrugated square-grid coordination layers which provide big channels occupied by water and/or solvent molecules and chloride ions. The copper coordination geometry is square pyramidal with the chloride ion in the apical position and four ditopic imidazole type ligands at the equatorial positions. Upon immersion of crystals in a saturated methanolic solution of NaBr (3 h), a color change was noticed. X-ray analysis revealed that the apical chloride was substituted by a bromide ion. During the exchange process, the crystals didn't lose their crystallinity, as was monitored by atomic force microscopy (AFM). These results and the use of other anions for exchange will be presented, as well as supporting analyses.

Keywords: crystal engineering, single-crystal-to-single-crystal transformations, polymeric coordination compounds

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Boronic acids as hydrogen-bond bridges between metal coordinated carboxylates

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Boronic acids have been the subject of several recent papers describing their H-bonding ability in supramolecular chemistry. There have been papers on the functionalised acids (Pedireddi), calixarene derivatives (Atwood) and those linking metal complexes (Orpen, Braga) among others. Applications are varied for boronic acids and their derivatives and range from fluorescent sensors, to organic reagents to supramolecular assemblies and beyond. Our studies focus on the use of such acids to link metal carboxylate complexes together. Such complexes normally fail to link due to a lack of H-bond donors. Reaction of $(PPh_3)_2Cu(BH_4)$ with a pyridine or pyrazine carboxylate in a sealed reaction vessel results in hydrolysis of BH_3 to $B(OH)_3$. The $B(OH)_3$ is then available *in situ* and co-crystallises with the Cu(I) complex to form motifs as shown in fig.1. We have exploited this reaction and used a range of boronic acids to form a number of 0D, and 1D architectures. Some data sets have been collected with the use of SR. We note that the Etter graph set descriptions fail to distinguish between the central, head-to-tail and boronic acid-carboxylate double donor $R^2_2(8)$ motifs, yet they are different.

Keywords: hydrogen bonding recognition, boronic acids, supramolecular assemblies

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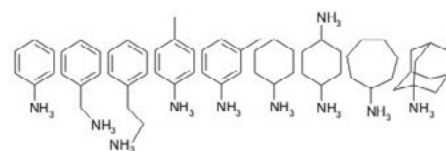
Noncovalent interactions in a family of cyclic ammonium nitrates

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The aim of crystal engineering is the design of crystal structures, and as a result, materials with desired properties. A fundamental requirement of crystal engineering is the understanding of the role of non-covalent interactions present in the solid-state structure. This study focuses on the identification of non-covalent interactions in a family of cyclic ammonium nitrate salts, as indicated below. All the compounds crystallize in layered structures, with the organic layer containing the cyclic ammonium moiety, while the ammonium groups and nitrate anions comprise the inorganic layer. Trans-1,4-diammonium nitrate exhibits polymorphism. Non-covalent interactions present in the structures include pi-pi interactions, nitrate...nitrate interactions and strong, charge assisted N⁺-H...O-interactions. The hydrogen bonding networks observed are compared, and trends relating to the interactions are identified. The effect of the bulkiness, saturation, charge, number of hydrogen bonding donors and directionality, ring-size and alkyl chain length of the cation

on the structure obtained, and on the non-covalent interactions present is highlighted.



Keywords: crystal engineering, nitrates, hydrogen-bond patterns