In this research, a novel supramolecular proton transfer compound was synthesized from the reaction between pyridine-2,6-dicarboxylic acid, C₇H₅NO₄, and propane-1,3-diamine, C₃H₆N₂. According to the crystal structure, the resulting compound formulated as 2(C₇H₅NO₄)(C₇H₆N₂O₄)·(C₇H₆N₂O₄)·(C₇H₄NO₄)·(C₇H₃NO₄)·5H₂O. This compound crystallizes in the triclinic system and contains two molecules per unit cell. The unit cell dimensions are a=7.8355(4)Å, b=13.5296(6)Å, c=20.8930(6)Å, α=90.603(1)°, β=90.603(1)°, and γ=106.662(1)°. The final R value was 0.0427 for 9245 reflections. In anionic fragment, one of four hydrogen atoms of hydroxy groups is disordered. In cationic fragment, two carbon and nitrogen atoms, are disordered on two position with occupancies 0.88/0.12. Anion molecules form two independent hydrogen bonded zigzag-type chains. The hydrogen bonds as type O-H···O, N-H···O, and N-H···N play a role in the construction of supramolecular framework. Interactions between cationic and anionic fragments consist of ion-pairing, hydrogen bonds and π-π stacking. The reaction of the proton transfer compound with ZrCl₂ was carried out. This complex formulated as (C₇H₅N₂)[Zr(C₇H₆N₂O₄)]·4H₂O. The Zr⁴⁺ complex crystallizes in the space group P2₁/c of the monoclinic system with four molecules per unit cell. The unit cell dimensions are a=10.0246(6)Å, b=17.1883(10)Å, c=17.8643(10)Å, and β=97.2970(10)°. The metal atom is ninecoordinated by three pyridine-2,6-dicarboxylate as tridentate ligand. The Zr⁴⁺ atom is located in the center of a distorted tricapped trigonal prism arrangement. The crystal-packing diagram indicates the layered structure for this complex. This complex arises from ion pairing and the extensive hydrogen bonding.

Keywords: zirconium, supramolecular compounds, crystal structures

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Binuclear Sn⁶⁺ complex obtained from benzene-1,3-diaminobis(hydropyrone-2,6-carboxylate)

Jafar Attar Gharamaleki¹, Shabnam Sheshmani², Zahra Hassanpour³, Mohammad Ghadermazi², Hossein Aghabozorg³, Guido Kickelbick¹
¹Tarbiat Moallem University, Chemistry, Faculty of Chemistry, Tarbiat Moallem University, 49 Mofateh Ave., 15614, Tehran, Iran, Tehran, Iran, 15614, Iran, ²Department of Chemistry, Islamic Azad University, Shahr-e Rey Branch, Tehran, Iran, ³Department of Chemistry, Islamic Azad University, Shahr-e Rey Branch, Tehran, Iran, 4Department of Chemistry, Faculty of Science, Kurdistan University, Sanandaj, Iran, 5Faculty of Chemistry, Tarbiat Moallem University, Tehran, Iran, 6Institute of Materials Chemistry, Vienna University of Technology, Wien, Austria, E-mail:attar_jafar@yahoo.com

In recent years, our research group has studied and worked on several bi- or trivalent metal complexes with several proton transfer ion pairs containing pyridine-2,6-dicarboxylic acid, pydH₂. In resulting complexes, some fragments of ion pairs coordinate to metal ions and some other fragments act as counter ions in the structure. Here we wish to report the molecular structure of the Sn(IV) complex, which obtained from a novel proton transfer compound (bdaH₂)(pydH₂)·2H₂O. The proton transfer compound (bdaH₂)(pydH₂)·2H₂O, has been prepared from the reaction between benzene-1,3-diamine, bda, and pyridine-2,6-dicarboxylic acid, pydH₂. The reaction of this adduct with Sn(CH₃)₂Cl₂ gives complex with stoichiometry [Sn(pydCl)(OC₃H₄)(CH₃)₂H(OCl)]. This complex was characterized by IR, NMR spectroscopy and X-ray crystallography. This complex crystallizes in the monoclinic system, space group P2₁/c, with four molecules per unit cell. The unit cell dimensions are a=11.5924(14)Å, b=13.2674(17)Å, c=7.7566(10)Å
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 SnO$_2$ ring. Each of two Sn atoms is coordinated by the chelate (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

Jonna Jokiniemi$^1$, Harri Nätäniemi$^1$, Eija Vuokila-Laine$^1$, Jukou J Vepsäläinen$^2$, Sirpa Peräniemi$^2$, Markku Ahlgrén$^1$

$^1$University of Joensuu, Department of Chemistry, P.O. Box 111, Joensuu, 80101, Finland, $^2$Laboratory of Chemistry, Department of Biosciences, University of Kuopio, P.O. Box 1627, 70211 Kuopio, Finland, E-mail: jonna.jokiniemi@joensuu.fi

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$_2$MBP, 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$_2$MBP. 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$_2$MBP, 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.


Keywords: bisphosphonate, metal complexes, crystal structures

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High pressure synthesis and analysis of new yellow emission Sr$_2$Zn$_3$: Eu visible-light driven phosphor

Valery Petrykin$^1$, Maki Okube$^2$, Satoshi Sasaki$^2$, Masato Kakihana$^1$

$^1$Tohoku University, Institute of Multidisciplinary Research for Advanced Materials, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan, $^2$Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yohokoma 226-8503, Japan, E-mail: valery@agen.tohoku.ac.jp

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$_2$Zn$_3$:Eu, which demonstrates strong yellow fluorescence when activated with Eu$^{3+}$. Mn doped Ba$_2$ZnS$_3$:Eu material is a well-known important emission phosphor. Recently, the Eu$^{3+}$ activated compound also attracted much attention as a prospective red phosphor for the LED-based applications. Nevertheless, no successful report on synthesis of Sr$_2$Zn$_3$:Eu could be found in literature although in analogy with Ba$_2$ZnS$_3$ such a compound should have a remarkable potential as a host for development of new fluorescent materials. In this work Sr$_2$Zn$_3$:Eu was prepared for the first time from the individual metals sulfides under 5GPa pressure at 1000°C. The composition of the material was confirmed by EDS. It has tetragonal unit cell (space group Pbnm) with $a=16.41A$, $b=4.64A$ and $c=4.07A$. The crystal structure was solved ab initio using powder diffraction data. A series of Eu$^{3+}$ activated phosphors was prepared from Sr$_2$Eu$_2$S$_3$(0.01 < x < 0.06) precursors. In order to achieve homogeneous distribution of the activator, the precursors were synthesized by polymerizable complex metal combined with conversion of the intermediate carbonate into sulfide by H$_2$S. The obtained Sr$_2$Zn$_3$:Eu materials demonstrated strong yellow emission, which can be excited by the near-UV and visible light, and it makes Sr$_2$Zn$_3$: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

Manuel A. Fernandes

University of the Witwatersrand, School of Chemistry, Private Bag X3, 2050 Wits, Johannesburg, Gauteng, 2050, South Africa, E-mail: manuel.fernandes@wits.ac.za

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...