

**PHYSICAL STABILITY VERSUS CHEMICAL LABILITY IN
MICROPOROUS METAL COORDINATION POLYMERS: CASE OF
[Cu(OH)(INA)] AND [Cu(INA)₂]**

S. M-F Lo¹ C. Z-J Lin¹ S. S-Y Chui¹ F. L-Y Shek¹ I. D. Williams¹ K. Suwinska² J. Lipkowski²

¹Department of Chemistry, Hong Kong University of Science and Technology, Clear Water Bay KOWLOON NA HONG KONG ²Institute of Physical Chemistry (PAN), Polish Academy of Sciences, Warszawa, Poland

A critical feature in the crystal engineering of microporous metal coordination polymer zeotypes is the stability of the open frameworks. Two microporous copper isonicotinate polymers [Cu(OH)(INA)] (left) and [Cu(INA)₂] (right) have been formed hydrothermally in good yield and purity. Each has 1-D channels of ca. 4 x 6 Å dimension, but with quite different hydrophilicities. The frameworks retain structural integrity to 225°C and 250°C respectively, however whilst [Cu(OH)(INA)] is also chemically stable, the [Cu(INA)₂] is highly labile and readily transforms to the molecular complex [Cu(INA)₂(H₂O)₄] in water at room temperature.

We are grateful to the RGC (grant HKUST 6128/01P) for financial support of this work.

**Keywords: METAL COORDINATION POLYMERS MICROPOROUS
SOLID STRUCTURAL STABILITY**

**SUPRAMOLECULAR ARRANGEMENT IN DIMETHYL THALLIUM
COMPLEXES THROUGH TI-S**

S. Santos-Jr¹ E.E. Castellano¹ J. Ellena¹ M. Toma³ J.S. Casas² M.S. Garcia-Tasende² A. Sanchez² J. Sordo²

¹Departamento de Física e Informática, Instituto De Física De Sao Carlos Rua Trabalhador Saocarlene, CP369 SAO CARLOS SP 13560-970 BRAZIL

²Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain.

³Department of Inorganic Chemistry, Al. I. Cuza University, Iasi, Rumania.

The determination of the three-dimensional structures of heavy-metal chelates and of some potentially useful chelating agents is a very important tool in the study of complexes that may act as antidotes against poisoning by ingestion of heavy metals. A detailed knowledge of these complexes is expected to assist in the design of molecular structures and procedures that are more effective in counteracting the life threatening processes inevitably developed by individuals with chronic heavy-metal intoxication. Within this framework a series of dimethylthallium(III) complexes were studied. Here we present complexes of the type [TlMe₂L], where L=2-mercapto-3-pyridine carboxylic acid(I), 6-mercapto-3-pyridine-methoxycarboxylate(II), 2-mercapto-3-pyridine-methoxycarboxylate(III), 6-mercapto-3-pyridine-ethoxycarboxylate(IV) and 2-mercapto-3-pyridine-ethoxycarboxylate(V). The study of the supramolecular arrangement of these complexes shows that, in spite of the differences in space group symmetry and substituents in the ligand, the crystals packing are remarkably similar. The complexes form infinite polymers in one, two and three dimensions, based upon TI-S covalent bonds and intermolecular secondary interactions. The complexes also present strong hydrogen bond intermolecular interactions. Compounds (IV) and (V) form two-dimensional nets while (I) forms a three-dimensional one, the three of them stabilized by hydrogen bonds. Compounds (II) and (III) form one- and three-dimensional nets, respectively, generated only by covalent bonds and intermolecular TI...S and TI...O secondary interactions.

We gratefully acknowledges support from Agencia Espanola de Cooperacion Internacional, Fapesp(Brazil) and CNPq(Brazil).

Keywords: SUPRAMOLECULAR THALLIUM ORGANOMETALLICS

**SOLID-STATE TRANSFORMATIONS IN COORDINATION POLYMERS
INFLUENCED BY THE LOSS OR ADDITION OF WATER MOLECULES**

A. Neels H. Stoeckli-Evans

University of Neuchatel Institut of Chemistry Avenue De Bellevaux 51
NEUCHATEL 2007 SWITZERLAND

Coordination complexes often contain coordinated solvent molecules and molecules of crystallization in their crystal structure. The three-dimensional structure of such compounds can be obtained by using low-temperature single crystal X-ray analysis, so avoiding the decomposition initiated by solvent loss. What happens to the main structure of the coordination compound on drying? X-ray powder diffraction methods can be used to evaluate eventual structural changes.

Here we present the solid state transformation of some copper(II) coordination complexes. Complex Ia was formed by the reaction of copper(II) chloride with 2,3,5,6-tetraminomethylpyrazine. A ladder-like 1-D polymer was formed, containing water molecules of crystallization situated between the rungs of the ladder. During the drying process the polymer changes into a binuclear complex, Ib. The original octahedral coordination sphere of the copper atoms undergoes a Berry pseudorotation mechanism. The elongated square bipyramidal conformation of the copper atoms in Ia change to that of a distorted square pyramidal geometry in Ib. Complex IIa, obtained by the reaction of copper(II) bromide with methyl-5,6-bis(2-pyridyl)pyrazine-2,3-dicarboxylate, is a 1-D chain polymer. Here, loss of the coordinated and solvent molecules of crystallization results in the formation of a 2-D polymer, IIb. Neighbouring chains are now linked by carboxylate groups coordinated to the copper atoms.

Complex IIIa, first synthesized by Noro et al., [1], is a 3-D metal-organic framework structure containing copper(II) ions linked by 4,4-bipyridyl and hexafluorosilicate anions. When the compound is exposed to air, i.e. humidity, the hexafluorosilicate anions migrate into the cavities in the structure so liberating two copper coordination sites for water molecules. This results in the formation of an interpenetrating 2-D network, IIIb.

[1] S. Noro, S. Kitagawa, M. Kondo, K. Seki, Angew. Chem. Int. Ed. 39 (2000) 2082.

**Keywords: COORDINATION POLYMERS POWDER DIFFRACTION
SOLID STATE TRANSFORMATION**

**SUPRAMOLECULAR STRUCTURE OF 1,10-PHENANTHROLIN-1-
IUM CATION WITH A TIN(IV) ANION**

W. Somphon¹ K.J. Haller¹ S.W. Ng²

¹Suranaree University of Technology School of Chemistry 111 University Avenue NAKHON RATCHASIMA 30000 THAILAND ²Institute of Postgraduate Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia

Single crystals of the 1,10-phenanthroline-1-ium salt of the [SnC₁₂(CH₂CH₂CO₂H)(CH₂CH₂CO₂)] complex monoanion was investigated as part of a study of pseudo symmetric structures. The six coordinate tin exhibits pseudo octahedral coordination by two *cis* Cl atoms, two *trans* C atoms, and two O atoms *trans* to the Cl atoms. One proton has been transferred from the originally neutral tin dicarboxylic acid complex to form the complex anion and a phenanthroline-1-ium monocation. The Sn-O distances for the chemically distinct oxygen atoms of the five member chelate rings of the carboxylate and carboxylic acid groups thus formed differ by more than 0.2 Å (2.306(2) and 2.519(2) Å) leading to large differences in the Cl atoms coordinated *trans* to the two O atoms (Sn-Cl distances are 2.404(1) and 2.486(1) Å). One nitrogen atom of the 1,10-phenanthroline is protonated (d[N-H] = 0.78 Å) while the other nitrogen is not. Protonation of the N causes the C-N-C angle to increase (122.14° in the protonated ring vs 116.51° in the unprotonated ring). The protonated ring exhibits increased Lewis acidity and links into a network with the anions using an N-H...O (2.688 Å), a C-H...O (3.155 Å), and two C-H...Cl (3.578 and 3.876 Å) bonds. The remaining rings also participate in hydrogen bonding by forming significantly weaker C-H...O and C-H...Cl interactions. These layers are joined into a 3-dimensional network of interactions by two distinct alternating face-to-face (η-η) interactions along the a axis.

**Keywords: SUPRAMOLECULAR STRUCTURE PHENANTHROLIN-1-
IUM TIN COMPLEX**