

**P.07.04.13***Acta Cryst.* (2005). A61, C308**Inclusion Compounds of Plant Growth Regulators in Cyclodextrins**Athanassios Hountas, Kostas Bethanis, Frantzeska Tsorteki, Dimitris Mentzafos, *Physics Laboratory, Agricultural University of Athens, Greece*. E-mail: hount@aua.gr

As a part of a systematic investigation of the inclusion compounds of plant growth regulators in Cyclodextrins (CDs) we report here the crystal structures of the complexes of 4-chlorophenoxyacetic acid (4CPA) encapsulated in  $\beta$ -CD (4CPA/ $\beta$ -CD) and in heptakis(2,3,6-tri-*O*-methyl)- $\beta$ -CD (4CPA/TM $\beta$ CD). 4CPA is considered as a sufficiently safe plant growth regulator, exhibiting only slightly toxic quantities and it is fairly used in the food industry.

The 4CPA/ $\beta$ -CD complex crystallizes as a dimer in the space group  $C2$  in the Tetrad packing mode. A review on the packing modes of the dimeric  $\beta$ -CD inclusion compounds indicates that close correspondence of unit-cell dimensions is a necessary, but not a sufficient condition for isostructurality.

The 4CPA/TM $\beta$ CD inclusion complex crystallizes in the space group  $P2_1$  and its asymmetric unit contains two crystallographically independent complexes exhibiting different orientations. These complexes exhibit also different conformations related to the different orientation of the guests inside the cavities. It is noted that the complexation process induces striking differences between the hosts of the two complexes though the guest molecules retain the same conformation. Thus, we conclude that the same guest having the same conformation does not inevitably cause a definite conformation of the host.

[1] Tsorteki F., Bethanis K., Pinotsis N., Giastas P., Mentzafos D., *Acta Cryst. B.*, Accepted 7 February 2005.

**Keywords:**  $\beta$ -CD, TM $\beta$ CD, 4CPA**P.07.04.14***Acta Cryst.* (2005). A61, C308**X-ray Structures and Characterizations of Iron Complexes of Thiocalixarenetetrasulfonate**Haruo Akashi, Misato Ichikawa, *Research Institute of Natural Sciences, Okayama University of Science, Ridai-cho, Okayama 700-0005, Japan*. E-mail: akashi@high.ous.ac.jp

Recently, we have reported the structure of tetrasodium thiocalix[4]arenetetrasulfonate ( $H_4TCAS$ )[1]. Odo and co-workers found that some metal complexes of  $H_4TCAS$  attached on ion-exchangers showed peroxidase-like catalytic activity[2]. This prompted us to make single crystals of metal complexes of  $TCAS$  for the structure analyses. We succeeded in the preparation of micro crystals of Fe(III) complex of  $TCAS$ . A blue thin plate-like crystal of  $K_2[Fe(H_2O)_6](H_4TCAS) \cdot 8H_2O$ (1), selected for data collection, was mounted in the cold nitrogen stream (105 K) of RAXIS IV(Rigaku Corp.). The compound was found to crystallize in the orthorhombic space group  $Pcab$  with  $a = 18.552(1)$  Å,  $b = 18.7287(8)$  Å,  $c = 25.550(2)$  Å,  $V = 8863.1(9)$  Å<sup>3</sup>. The structure analysis of **1** revealed that the iron atom is located in a distorted octahedral site. The iron atom is bound to three oxygen atoms and one sulfur atom of the  $TCAS$ . This is the first example of the  $H_4TCAS$  ligand attached directly to the Fe(III) moiety. Second-sphere coordination compounds,  $K[Fe(H_2O)_6](H_4TCAS)$  and  $K_2[Fe(H_2O)_6](H_4TCAS)$ , will also be reported.

[1] Akashi H., et al., *Acta Cryst.*, 2003, E59, m336. [2] Odo J., et al., *Anal. Sci.*, 2004, 20, 707.

**Keywords:** thiocalixarene compound, catalytic activity, second-sphere coordination**P.07.04.15***Acta Cryst.* (2005). A61, C308**New Metal Carboxylates prepared at Room Temperature and by Hydrothermal Methods**Graciela Diaz de Delgado, Jines Contreras, Luis León, MarinoGutiérrez, José Miguel Delgado, *Laboratorio de Cristalografía-LNDRX, Universidad de Los Andes, Mérida, Venezuela*. E-mail: diaz@ula.ve

New alkaline-earth metal derivatives of nicotinic, isonicotinic, and *cis*-4-cyclohexene dicarboxylic (CDCA) acid have been prepared at room temperature and/or by hydrothermal methods. They have been characterized by spectroscopic, thermal, and X-ray diffraction techniques in polycrystalline and single crystal samples.

Layered structures are obtained in all cases. However, it should be noted that the Ba derivative of CDCA prepared under hydrothermal conditions crystallizes in an orthorhombic unit cell, space group  $Cmc2_1$ , with  $a = 28.633(8)$ ,  $b = 9.036(3)$ ,  $c = 7.438(2)$  Å. This is a completely different structure from the one obtained previously at room temperature. The Sr and Ba complexes of isonicotinic acid are monoclinic,  $P2_1/c$ , with  $a = 6.1403(6)$ ,  $b = 43.976(4)$ ,  $c = 7.2170(7)$  Å,  $\beta = 118.72(1)^\circ$  for the Sr complex and  $a = 6.276(2)$ ,  $b = 44.334(8)$ ,  $c = 7.345(2)$  Å,  $\beta = 118.74(2)^\circ$  for the Ba complex.

The authors wish to thank Dr. Lee Daniels and Dr. Ron Benson from Rigaku MSC for data collection. We also thank FONACIT-Venezuela for support through grant LAB-97000821.

**Keywords:** carboxylates, hydrothermal synthesis, coordination compounds**P.07.04.16***Acta Cryst.* (2005). A61, C308**Silver Coordination Polymers with Flexible Ligands. Effect of the Size of the Ligand and the Solvent on the Network Formation**François Brisse, Mohamed Osman Awaleh, Antonella Badia, *Département de chimie, Université de Montréal, Montréal, Canada*. E-mail: francois.brisse@umontreal.ca

In metal-organic crystal engineering, when flexible ligands are involved in the supramolecular networks, predicting the topology of the coordination polymer is more difficult since several factors such as the kind of solvent, the metal coordination, the counter-anion, the metal-to-ligand ratio and the degree of flexibility of the ligand affect the framework formation. In order to gain some insight into the influence of those factors, we report here the effect of the size of the ligand, its symmetry and degree of flexibility, as well as the influence of the anion, upon the supramolecular architecture when diarylthioether ligands are used as building blocks in silver(I) complexes. Only ligands with an even number of methylene groups will be discussed here. The *non-coordinating anions* favor the formation of cationic three-dimensional networks. As the anions, which are usually located within the channel, are relatively free to move, the anion-exchange properties of those complexes will be examined. The *weakly coordinating anions* give rise to 1D-coordination polymers. As these anions serve as terminal ligands, the formation of two or three dimensional networks is ruled out. The *more strongly coordinating acetate anions* yield 2 or 3-dimensional networks. Weak silver-silver interactions are noted. In some cases, those interactions are retained in the 2D-network. The details of these 2D, 3D-networks and the silver-silver interactions will be described and illustrated. A rationalization of the influence of the various parameters upon the topologies of the supramolecular architectures will be presented.

**Keywords:** silver, flexible ligand, coordination polymer**P.07.04.17***Acta Cryst.* (2005). A61, C308-C309**Structural Relationships in the Coordination Complexes of Bis(phenylthio)methane (L1) and Bis(phenylthio)propane (L3) with Silver(I) Salts**Mohamed Osman Awaleh, Antonella Badia, François Brisse. *Département de chimie, Université de Montréal, Montréal, Canada*. E-mail: francois.brisse@umontreal.ca.

The structures adopted by coordination polymers formed with flexible ligands are difficult to predict. The factors affecting the framework formation of coordination polymers, such as the ligand length, the stoichiometry, the role of the anion and the solvent were

examined. We undertook the systematic synthesis and structural study of a large number of complexes. These were obtained with the above-named ligands, with an odd number of methylene groups, and combined with ten different silver salts. The counter-anions belong to three distinct classes: A = weakly coordinating anions, B = sulfonates such as p-tosylate and trifluorosulfonate, and C = fluorocarboxylates.

All complexes form extended networks of either 1D or 2D. Both the length of the ligand and the choice of the anion have a marked influence on the resulting crystal structures. For example, with complexes of L1, whatever the anion used, the 1D-coordination polymer is always observed. With type A anions, the ligand and Ag form a single chain and the anions are coordinated to the silver ions. With type B and C anions, the chains incorporate the anions in a double-bridge coordination mode. The chains are of the double-stranded type. For complexes of L3, type A anions give rise to host-guest compounds. The Ag and the ligands form 2D cationic sheets. The anions and the solvent are inserted within the sheets. Most complexes with B and C anions form 2D-coordination networks. The details of these 1D and 2D networks will be described and illustrated.

**Keywords:** silver, flexible ligand, coordination polymer

#### P.07.04.18

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#### Supramolecular Interactions as Determining Factors of the Primary Geometry of Metallic Building Blocks

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Notwithstanding the richness of Mn-carboxylate chemistry, tetracarboxylate-dimanganese species with a copper-acetate-like core have been characterized only recently [1]. Compound [Mn(tda)(bipy)]<sub>n</sub>, the first fully documented example of such a species, displays a supramolecular structure generated by an efficient  $\pi$ -stacking of bipy ligands between adjacent polymeric chains. The comparison of this structure and those of related compounds with 4,4'-Me<sub>2</sub>bipy and 5,5'-Me<sub>2</sub>bipy ligands allow us to confirm this assertion. Moreover, DFT calculations for isolated binuclear units provide evidence that the non-covalent interactions between coordination polymers in a supramolecular system can ultimately affect the primary structure of the metallic building blocks [2]. In general, metallic building blocks are used in supramolecular chemistry to generate specific directional patterns, while the present case reverses such a paradigm. In fact, the geometry of the building block adapts to support the most stabilized supramolecular architecture.

[1] Grirrane A., Pastor A., Galindo A., Ienco A., Mealli C., *Chem. Commun.*, 2003, 512. [2] Grirrane A., Pastor A., Galindo A., del Río D., Orlandini A., Mealli C., Ienco A., Caneschi A., Sanz J. F., *Angew. Chem.*, accepted for publication.

**Keywords:** supramolecular, thiodiacetate, crystal structures

#### P.07.05.1

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#### New Stable Ge(II) and Sn(II) Organic Derivatives: an X-ray Diffraction Study

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New types of stable Ge(II) and Sn(II) organic derivatives have been studied by X-ray diffraction analysis.

1. It has been established for the first time that Ge(II) and Sn(II) compounds can be stabilized in the monomeric form solely by the electronic effects, viz., intramolecular M(II)←N coordination and  $\sigma$ -acceptor ability of the oxygen atoms, without substantial steric shielding of the central metal atoms.

2. It has been shown that very interesting Ge(II) and Sn(II) species (for example, azides, carboxylates, etc.) can be isolated as thermally

stable solids owing to the electronic effects described above.

3. It has been found that the substituent effects responsible for the stabilization of divalent Group 14 derivatives in the monomeric form are drastically different for homoleptic and heteroleptic compounds and thus do not follow the simple "building block" principle.

4. It has been revealed that the bidentate ligands in the Ge(II) carboxylates (both in neutral and in anionic complexes) are not chelating, and the Ge(II) atoms have the most favorable trigonal-pyramidal configuration.

The stereochemistry and polymorphism of the investigated compounds are discussed.

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**Keywords:** low-coordinated germanium and tin compounds, intramolecular interactions, X-ray crystal structure analysis

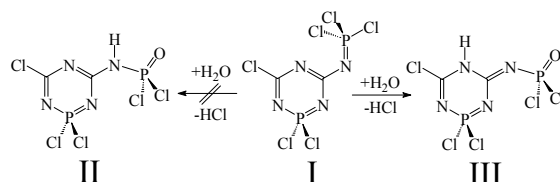
#### P.07.05.2

*Acta Cryst.* (2005). A61, C309

#### Gentle Hydrolysis of a Trichlorophosphazeno-1,3,5,2 $\lambda$ <sup>5</sup>-triazaphosphorine

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The reaction product of dicyandiamide with PCl<sub>5</sub> (1:2) was determined to have structure **I** [1]. By a gentle hydrolysis of **I** not the expected aromatic compound **II**, but the hitherto unknown compound **III** was obtained.



The crystal structure determination of compound **III** was performed at 100K and shows unambiguously that the H atom is bonded to the ring N atom at position 5 and not to the exocyclic N atom: at first by the isotropic refinement of the H atom, then by the observed bonding distances [for example N<sub>exocyclic</sub>-C = 1.361(3)Å in **I** and 1.310(4)Å in **III**, resp.], and finally by the packing of the molecules: two molecules lying around a center of symmetry are held together by two presumably strong N-H...O hydrogen bonds [N...O 2.732(4)Å, N-H...O 166.5(2)°].

The single crystal X-ray refinement of the structure of compound **III** reported here is the first for a member of this hydrogenated 1,3,5,2 $\lambda$ <sup>5</sup>-triazaphosphorine ring system.

[1] Belaj F., *Z. Naturforsch.*, 1996, **51b**, 1428.

**Keywords:** phosphazene, triazaphosphorine, aromaticity

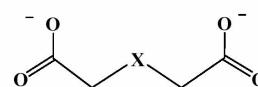
#### P.07.05.3

*Acta Cryst.* (2005). A61, C309-C310

#### Structural Features of Oxydiacetate and Thiodiacetate Complexes and Crystal Structures of Magnesium Derivatives

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In this communication we will review the structural features of oxydiacetate (oda) and thiodiacetate (tda) compounds, illustrating the similarity and differences between the ample diversity of coordination modes that exhibits this type of ligands.



X = O, oda; S, tda

Additionally, we will report novel magnesium oxydiacetate and thiodiacetate complexes, [Mg(oda)(H<sub>2</sub>O)<sub>2</sub>·H<sub>2</sub>O]<sub>n</sub> (**1**) and [Mg(tda)(H<sub>2</sub>O)<sub>3</sub>·H<sub>2</sub>O] (**2**), which were synthesized from the reaction of aqueous solutions of magnesium dichloride with a 1:1 mixture of