

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

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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

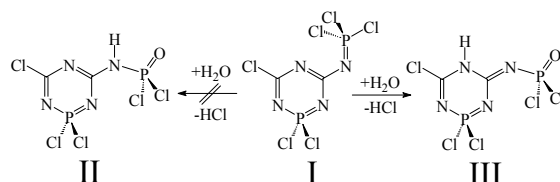
#### P.07.05.2

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#### Gentle Hydrolysis of a Trichlorophosphazeno-1,3,5,2 $\lambda^5$ -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 $\lambda^5$ -triazaphosphorine ring system.

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

**Keywords:** phosphazene, triazaphosphorine, aromaticity

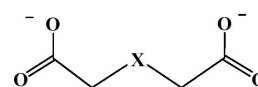
#### P.07.05.3

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#### 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