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**Keywords:** thiosemicarbazide, dimer, hydrazinecarbothioamide

## MS61.P25

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### Synthesis and Conformational Analysis of a Dcp-containing Homooligopeptides

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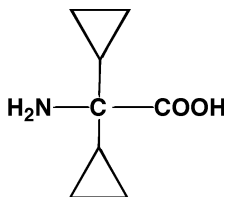
Various  $\alpha,\alpha$ -disubstituted amino acids have an influence on the peptide conformation, and the incorporation of these amino acids into the oligopeptides restrict their conformational freedom. For example, it is well known that  $\alpha,\alpha$ -dimethylglycine (Aib) makes the folded  $3_{10}$ -helical or  $\alpha$ -helical structure more stable than the extended structure, whereas  $\alpha,\alpha$ -diethylglycine (Deg) or  $\alpha,\alpha$ -dipropylglycine (Dpg) leads to the extended  $C_5$ -conformation rather than the helical structure [1]. Therefore,  $\alpha,\alpha$ -disubstituted glycine could be a useful tool to restrict the peptide backbone conformation to a well-defined secondary structure [2].

In order to clarify the conformational preference of a novel  $\alpha,\alpha$ -disubstituted glycine, namely  $\alpha,\alpha$ -dicyclopropylglycine (Dcp), we investigated the conformations of a series of Dcp-containing homooligopeptides by X-ray crystal and NMR solution analyses. Z-(Dcp)<sub>n</sub>-OMe (n=3-5) were synthesized using the CMPT-AC9M/DIEA/DMF coupling method and their peptide yields were 41%, 9% and 11%, respectively.

The three-dimensional crystal structures of these homooligopeptides were determined by the X-ray analysis and were refined accurately. The results revealed that the tri-, tetra- and pentapeptides adopted  $3_{10}$ -helical structures stabilized by one, two and three intramolecular hydrogen bonds of Dcp-NH protons, respectively. Because these peptides lack any chiral amino acid, the right-handed and left-handed  $3_{10}$ -helices with the opposite conformation were both presented in the crystal.

On the other hand, the NMR analysis showed that the chemical shifts of Dcp<sup>3</sup>-NH, Dcp<sup>4</sup>-NH and Dcp<sup>5</sup>-NH are insensitive to the addition of DMSO-*d*<sub>6</sub> into the CDCl<sub>3</sub> solution. This indicates that these amide protons participate in the intramolecular hydrogen bonds to form a  $3_{10}$ -helical conformation in the same way as those in the crystal structure.

In conclusion, the Dcp residue has moderate reactivity and the propensity to adopt the folded conformation, and thus it may be one of the promising conformationally constrained building blocks.



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**Keywords:** homo-oligopeptide,  $3_{10}$ -helices, conformation analysis,

## MS61.P26

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### Novel Cu complexes of 1,2,4-triazole-3-thione derivatives

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Novel Cu coordination compounds of three 1,2,4-triazole-3-thione derivatives have been synthesized applying two methods: solvent free mechanochemistry and direct synthesis starting from zero-valent metal.

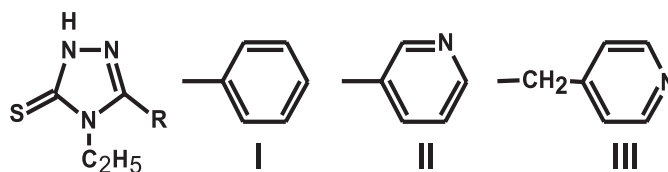
The studied ligands (**I-III**) are investigated due to their biological activity including antitumor, antibacterial, antifungal, antiviral etc. Some 1,2,4-triazoles are potent inhibitors of enzymes such as methionine aminopeptidase-2 and farnesyltransferase [1-2]. The activity of molecules containing S=C-N-N fragment such as triazole-3-thione Schiff bases enhanced on complexation with metal ions [3]. This phenomenon is not clear but frequently explained by the ability of ligands to chelate metal ions by S and N atoms. Multinuclear copper centres are also present in some oxidases, oxidoreductases, and oxygen-transporting proteins. Copper ions in such clusters are coordinated by histidine residues and often are bridged by S atom.

We have undertaken study on binding copper ions by 1,2,4-triazole-3-thione derivatives in order to simulate such environment. The studied ligands possess ability to bind metal ions through S and N atoms.

In the crystal structure of ligands the association mode depends on substituent type. The molecules with pyridinyl N atom (**II** and **III**) form chains through N-H...N hydrogen bonds. The lack of additional N acceptor atom in **I** enable interaction with S atom resulting in centrosymmetric dimer.

Most of the new complexes obtained by grinding CuCl<sub>2</sub> with ligands as well as through the second synthesis method were fine crystallites and have been characterized by PXRD and FTIR methods.

Only Cu complex of **I**, synthesized through direct synthesis from zero valence metal, gave good quality single crystals. The X-ray crystal structure analysis revealed formation of hexanuclear cyclic core with N,S bridging triazole ligands forming discrete complexes. Distances between Cu ions in the core are slightly shorter than sum of van der Waals radii viz. 2.7776(3) and 2.7970(3)Å.



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**Keywords:** copper, complex, crystallochemistry

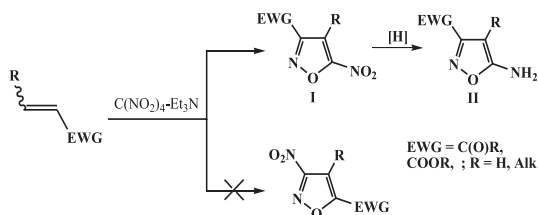
## MS61.P27

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### X-Ray study of structure of nitrosubstituted isoxazoles from the reaction of electrophilic alkenes and tetranitromethane-triethylamine.

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Recently we have elaborated a new efficient method for the heterocyclization of electrophilic alkenes by the action of tetranitromethane (TNM) in the presence of triethylamine which afforded functionalized nitroisoxazoles [1]. The present investigation deals with X-ray analysis of thus obtained nitroisoxazoles and corresponding products of their reduction, aminoisoxazoles, for a reliable confirmation of their structure. X-ray analysis established that nitro- and amino-groups were located at position 5 of the isoxazole cycle. Thus, a new heterocyclization of electrophilic alkenes under TNM in the presence of triethylamine afforded 5-nitrosubstituted isoxazoles. In present time, X-ray study for first step of this reaction was made for five nitroisoxazoles I (see scheme). Second step of reaction was studied only for aminoisoxazole II (R = H, EWG = C(O)Et). The crystal structures of all nitroisoxazoles are formed only by Van der Waals force – no any non-classical hydrogen bonds found. Classical hydrogen (with amino-group as donor) bonds are found in crystal structure of aminoisoxazole.



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**Keywords:** small organic molecules, nitroisoxazoles, aminoisoxazoles

## MS61.P28

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### New titanium nitrido complexes from $\{[TiCp^*(\mu-NH)]_3(\mu_3-N)\}$ and methyltriflate

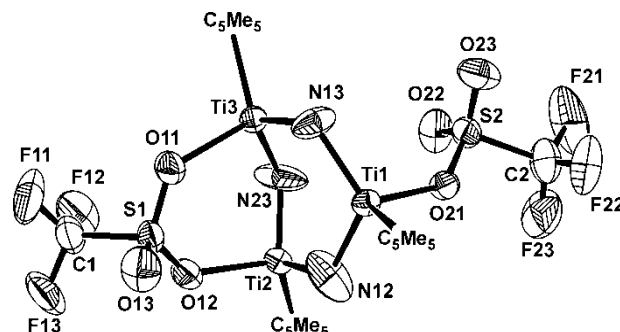
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Transition-metal nitrido complexes have been studied extensively in the past few decades. While nitrido complexes of Group 6-8 metals usually bear the nitrido ligands as a terminal functionality, the analogous derivatives of early transition metals exhibit polynuclear structures with  $\mu_n$ -nitrido ligands bridging two or more metal centers. In many cases, the nitrido group is accompanied by amido or imido ligands, like those found in the imido-nitrido titanium complex  $[\{TiCp^*(\mu-NH)\}_3(\mu_3-N)]$  (A) ( $Cp^* = \eta^5-C_5Me_5$ ) [1]. Over the last few years we have been studying the capability of compound A to act as a tridentate ligand, as well as the reactivity of the nitrido group towards nucleophilic reagents [2] or Lewis acids [3].

In this communication, we will present the synthesis of new titanium(IV) nitrido complexes by treatment of compound A with an electrophilic chemical such as methyltrifluoromethanesulfonate (methyltriflate) in different molar ratios. The X-ray crystal structures determined for these compounds will be discussed. For instance, we show in figure the molecular structure of the singular trinuclear

imido-nitrido titanium complex obtained through reaction of A with 4 equivalents of methyltriflate. This compound presents nitrido, imido and triflate groups bridging the titanium centers.

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**Keywords:** titanium, nitrido ligand, methyltriflate

## MS61.P29

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### Crystal structure of a carbacylamidophosphate organotin compound

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Organotin compounds continue to attract significant attention, owing to their applications in agriculture, biology, catalysis, organic synthesis, etc [1-3]. Besides, carbacylamidophosphates, which have  $-C(O)NHP(O)-$  in their molecular core units are potential bidentate O,O-donor chelating ligands for metal ions, particularly for lanthanides [4]. Previously, diorganotin(IV) compounds of the N-benzoyl derivatives of carbacylamidophosphates [5,6] were synthesized, in which the coordination of the ligands were only through the oxygen atom of the phosphoryl group. The solid state results showed the monomeric *all-trans* octahedral complexes due to the fewer steric hindrance in the *trans* geometry. However, to our knowledge no organotin complexes of N-acetyl derivatives of carbacylamidophosphates are known.

In this work, N-monochloroacetyl, N', N''-bis(isopropyl) phosphoric triamide and its complex with  $SnCl_2Me_2$  have been synthesized and characterized. The structure of complex has been determined by X-ray crystallography. Colorless crystals were obtained from a concentrated toluene solution at room temperature. The compound crystallizes in the triclinic system with space group  $P\bar{1}$ . Coordination of the ligand to tin (IV) occurs through both oxygen atoms of phosphoryl and carbonyl groups. This complex is binuclear structure with two non-equivalent Sn atoms. One adopts a distorted *trans*(C,C) *cis*(O<sub>p</sub>,O<sub>p</sub>) *cis*(Cl,Cl) octahedral configuration, while the other adopts a distorted trigonal bipyramidal geometry composed of two methyls, two chlorine atoms and carbonyl group.