Novel Cu coordination compounds of three 1,2,4-triazole-3-thione derivatives have been synthesized applying two methods: solvent free mecanosynthesis 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. The activity of molecules containing S=C-N-N fragment such as triazole-3-thione Shift bases enhanced on complexation with metal ions. 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 pyridyl 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 CuCl₂ with ligands as well as through the second synthesis method were fine crystallites. The X-ray crystal structure analysis revealed formation of hexanuclear cyclic core with N₅S₃ 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.


Keywords: copper, complex, crystallochemistry
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-nitrosobstituted 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.

We thank the Russian Foundation for Basic Research (Project 11-03-01040-a) and Presidium of RAS for financial support of this work.

Keywords: small organic molecules, nitroisoxazoles, aminoisoxazoles

MS61.P28

New titanium nitrido complexes from [[TiCp*(μ-NH)]$_2$][μ-N] and methyltriflate
Adrián Pérez-Redondo, Jorge Caballo, Miguel Mena, Carlos Yélamos, Departamento de Química Inorgánica, Universidad de Alcalá, Alcalá de Henares-Madrid (Spain). E-mail: adrian.perez@uah.es

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 μ-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*(μ-NH)]$_2$][μ-N] (A) (Cp* = η$^5$-C$_5$Me$_5$)[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(v) nitrido complexes by treatment of compound A with an electrophilic chemical such as methyltrifluoromethanesulphonate (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.

We are grateful to the Spanish MEC (Grant CTQ2008-00061/BQU), Comunidad de Madrid-Universidad de Alcalá (Grant CCG10-UAM-PPQ-5935) and Factoría de Cristalización (CONSOLIDER-INGENIO 2010) for support of this research. J. C. thanks the MEC for a doctoral fellowship.

Keywords: titanium, nitrido ligand, methyltriflate

MS61.P29

Crystal structure of a carbacylamidophosphate organotin compound
Sedigheh Farshadian, Khodayar Gholivand, Forough Molaei, Zahra Hosseini, Department of Chemistry, Faculty of Science, Tarbiat Modares University, Tehran, (Iran). E-mail: sfarshadian@yahoo.com

Organotin compounds continue to attract significant attention, owing to their applications in agriculture, biology, catalysis, organic synthesis, etc [1-3]. Besides, carbacylamidophosphates, which have N(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$_2$Me$_2$ 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 $P1$. 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$_2$) cis(O$_2$O$_2$) cis(ClCl) octahedral configuration, while the other adopts a distorted trigonal bipyramidal geometry composed of two methyls, two chlorine atoms and carbonyl group.