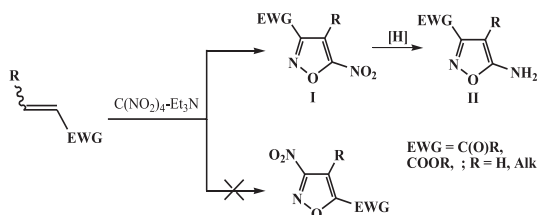


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Recently we have elaborated a new efficient method for the heterocyclization of electrophilic alkenes by the action of tetranitromethane (TNM) in the presence of triethylamine which afforded functionalized nitroisoxazoles [1]. The present investigation 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

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

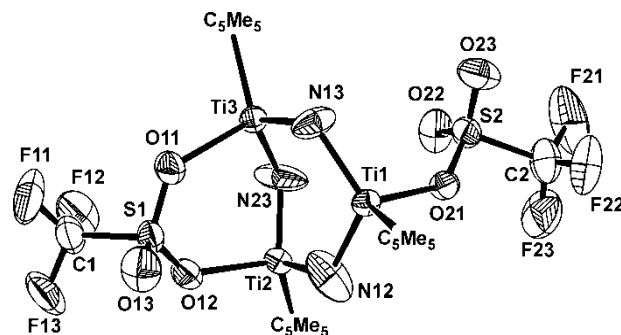
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Transition-metal nitrido complexes have been studied extensively in the past few decades. While nitrido complexes of Group 6-8 metals usually bear the nitrido ligands as a terminal functionality, the analogous derivatives of early transition metals exhibit polynuclear structures with μ_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 $[\{\text{TiCp}^*(\mu\text{-NH})_3(\mu_3\text{-N})\}]$ (A) ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) [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(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

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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_p,O_p) *cis*(Cl,Cl) octahedral configuration, while the other adopts a distorted trigonal bipyramidal geometry composed of two methyls, two chlorine atoms and carbonyl group.

There is also a very weak intermolecular Sn...O interaction in complex **4** between Sn2 and the uncoordinated oxygen atom of carbonyl group of a neighboring molecule and link the discrete molecular into a 1D chain with the Sn...Sn separation of 8.629 Å. Although the Sn–O distance [Sn2–O2 = 2.975 Å, (BO = 0.1)] is considerably longer than the normal Sn–O covalent bond, it lies in the range of Sn...O distances of 2.61–3.02 Å that have been reported to suggest Sn–O bonding [7]. However, such an elongation of Sn–O bond from the normal covalent bond distance point to a considerable ionic character associated with Sn–O bond.

Furthermore, the intermolecular NH...Cl hydrogen bonds produce two dimensional supramolecular structures in the lattice.

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Keywords: crystal structure, carbacylamidophosphate, hydrogen bond

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2-Chloro-N₄-[4-(dimethylamino)benzylidene]-N-[4-(3-methyl-3-phenylcyclobutyl)-1,3-thiazol-2-yl]acetohydrazide

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3- Substituted cyclobutane carboxylic acids exhibit anti-inflammatory and anti-depressant activity [1], as well as having liquid crystal properties [2]. Also, various thiazole derivatives have been shown to possess herbicidal [3], anti-inflammatory [4], anti-microbial [5], and anti-parasitic properties.

The molecular conformation of the title compound, C₂₅H₂₇ClN₄OS, is stabilized by an intramolecular benzylidene C—H...N_{thiazole} hydrogen bond. The thiazole ring makes dihedral angles of 12.0 (3)° and 20.4 (2)°, respectively, with the phenyl and benzene rings, while the phenyl and benzene rings make a dihedral angle of 22.6 (2)°. The crystal packing involves weak intermolecular thiazole C—H...O_{carbonyl} and methyl C—H...π hydrogen-bonding associations

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Keywords: crystallography, single crystal x-ray

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New Copper(I) Polymers Assembled by Dithioether Ligands

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During the last decade there is a spectacular increase of interest in the field of Cu(I)-based polymers due to their rich structural chemistry and photo-physical properties. The networks resulting from CuX/N,P,S-organic ligand self-assembly processes may adopt linear (1D), layered (2D) or three-dimensional (3D) topologies.[1] We present here some new structural features observed in CuX (X=I, Br, Cl) / RS(C)_nSR limited to n=4 systems. The C₄ spacer may be an n-butyl like (R-S-CH₂-CH₂-CH₂-CH₂-S-R) or 2-butylene (R-S-CH₂-CH=CH-CH₂-S-R) in both the Z- and E- geometries. The most largely studied copper(I) halide is CuI because it easily forms the cubane-like Cu₄I₄ motif as a secondary building unit (SBU) responsible for the intense luminescent properties.[2] However, other Cu_nX_m stoichiometries may also be reached, the most frequent is that of Cu₂X₂ rhomboid.

In C₄ spacer n-butyl-like series with Cu₄I₄ SBU the 2D structures are observed with R=tBu and nBu: (Cu₄I₄S₄, 2:1 CuX: ligand ratio). However, the layers therein are not planar, but undulating over the respective crystal lattice planes. The deviations of respective Cu₄I₄ centroids over these planes reaches ± 1.87 Å for R=tBu (Pbcn) and ± 1.81 Å for R=nBu (P21/c).[3] The 2D structure is obtained for R=tBu series with CuBr (P-1), but the SBU therein is rhomboidal Cu₂Br₂ with the overall ratio CuBr:ligand = 1:1. Going to the salt:ligand ratio of 2:1 a dramatic, but spectacular structure transformation is observed in R=tBu series from centrosymmetric P-1 to tetragonal chiral P₄, bearing the Cu₄Br₄(SC₄Slinker)Cu₄Br₄ helices. An overall 3D structure is reached therein through the strong Cu – S(spacer)S – Cu inter-helice interactions.

In the C₄ 2-butene spacer series the E-(trans) and Z-(cis) geometries of RSC₄SR dithioether influence on the composition and topology. E-(cis) isomers of PhSCH₂CH=CHCH₂SPh lead to 2D planar layers in triclinic (P-1) structures with Cu₂Br₂ and Cu₂I₂ SBU's, whereas the cis (Z) isomer gives with CuI a 2D monoclinic (C2/c) luminescent structure with Cu₄I₄ SBUs.

A steric effect of substitutions on Ph group (Me ortho, tBu meta) of dithioether in saturated R'S(nBu)SR' series has been also checked with CuI. The effect is evidenced by the formation of 1D linear ribbons with the coordination of solvent (NCMe) molecules on the copper atoms.

A particular attention will be paid for discussion of Cu-Cu distances. Variable temperature X-ray studies have been performed in several cases in order to find the structure/thermo-luminescent relationships.

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Keywords: copper(I), dithioethers, topology of the network