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Keywords: Host, guest, inclusion

MS61.P23

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Layer-type Supramolecular Networks from Rosette Ribbons and Bridging Connectors

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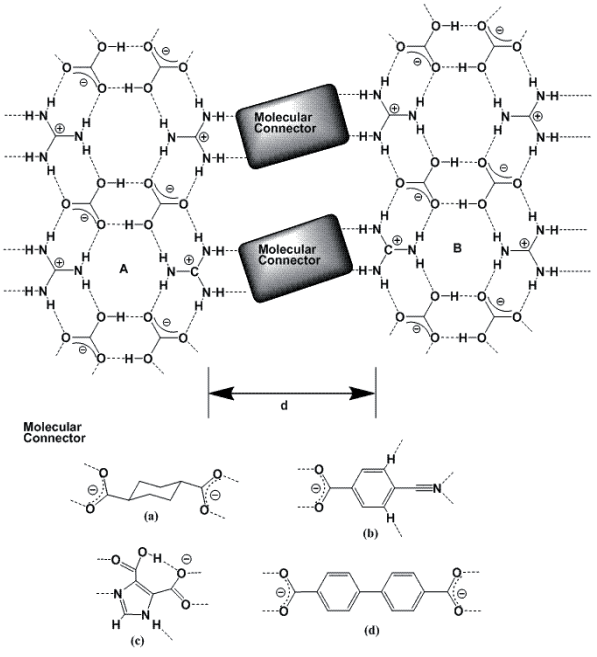
Over the years, chemical systems bearing a rosette motif (often described as hexagonal honeycomb unit or grid) have attracted considerable interest in connection with supramolecular self-assembly.[1] A rosette ribbon consists of a linear arrangement of hexagonal structural units that share fused opposite sides, and a sheet-like network can be generated by bridging an array of parallel ribbons with molecular connectors.[2]

We report the synthesis and X-ray analysis of a family of robust layer-type supramolecular networks featuring an uncharged, linear $GM^+HCO_3^-$ (GM^+ = guanidinium cation) fused-rosette ribbon hemmed with multiple N-H hydrogen-bond donor sites. Bridging of such parallel rosette ribbons by hydrogen-bond acceptors (1,4-cyclohexanedicarboxylate, 1,4-benzenedicarboxylate, 4-cyanobenzate and 1H-imidazole-4,5-dicarboxylate) as anionic molecular connectors is tolerant to a wide inter-ribbon separation ranging from 10.00 to 19.42 Å. Various tetraalkylammonium cations serve as guest templates to construct this series of four inclusion compounds.



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Keywords: hydrogen bonding, inclusion compound, supramolecular assembly

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Crystal structures of hydrazinecarbothioamide derivatives

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Thiosemicarbazide compounds exhibit various biological activities such as anti-bacterial, anti-fungal and especially antituberculosis. Besides, thiosemicarbazide derivatives offer special affinity to inhibit corrosion of metals in acidic solutions [1, 2]. In order to search for new thiosemicarbazides, the compounds **I**-**III** have been synthesized and their crystal structures are reported here:

I: *N*-(4-chlorophenyl)-2-[(4-methyl-1,3-thiazol-5-yl)carbonyl]hydrazinecarbothioamide,

II: 2-(2-methyl-3-furoyl)-*N*-(4-methylphenyl)hydrazinecarbothioamide,

III: *N*-{[2-(1*H*-pyrrol-2-ylcarbonyl)hydrazino]carbonothioyl}benzamide hemihydrate.

	I	**II**	**III**
crystal system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	P-1	$P2/c$
a [Å]	9.899(2)	9.441(3)	14.494(5)
b [Å]	8.059(1)	11.883(4)	4.835(2)
c [Å]	17.702(2)	14.463(6)	19.915(6)
α [º]		74.46(4)	
β [º]	97.51(1)	69.56(3)	96.51(3)
γ [º]		73.93(3)	

In the crystal lattice of **I**, inversion related molcules are joined by chelated N–H···O hydrogen bonds forming the cyclic dimer. The interactions are thioamide···carbonyl and hydrazine···carbonyl, and within this dimer they could be described by the cyclic first-level $R^2_2(10)$ and $R^2_2(14)$ motifs. Moreover, in this crystal, second type of cyclic dimer is observed; molecules are linked by C–H···S (chlorophenyl··· thioamide) interactions – $R^2_2(12)$ graph set. Additionaly, the molecular structure is stabilized by intramolecular N–H···O (hydrazine···carbonyl) hydrogen bond.

Crystals of **II** are triclinic (*P*-1) with Z = 4. Two symmetrically independent V-shaped molecules are linked by N–H···O (thioamide···carbonyl), C–H···O (methyl-furoyl···carbonyl and methylphenyl···carbonyl) and N–H···S (hydrazine···thioamide) hydrogen bonds to form a ribbon.

As in **I**, dimeric arrangement is also observed in the crystal structure of hemihydrate **III**. Nearly planar molecules are associated by inversion-related N–H···O (pyrrol···carbonyl) hydrogen bonds, the dimer is denoted by the cyclic $R^2_2(10)$ graph set. Further, the dimers connected by N–H···O (hydrazine···carbonyl) and π···π interactions built the three-dimensional crystal net. There is second kind of N–H···O hydrogen bond – an intramolecular (hydrazine···carbonyl) which stabilized the molecular structure. In addition to these interactions water···**III** hydrogen bonds are observed, they are N–H···O (thioamide···water) and O–H···S (water···thioamide).

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Keywords: thiosemicarbazide, dimer, hydrazinecarbothioamide

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Synthesis and Conformational Analysis of a Dcp-containing Homooligopeptides

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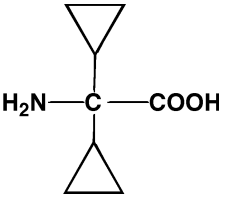
Various α,α-disubstituted amino acids have an influence on the peptide conformation, and the incorporation of these amino acids into the oligopeptides restrict their conformational freedom. For example, it is well known that α,α-dimethylglycine (Aib) makes the folded 3_{10}-helical or α-helical structure more stable than the extended structure, whereas α,α-diethylglycine (Deg) or α,α-dipropylglycine (Dpg) leads to the extended C_5-conformation rather than the helical structure [1]. Therefore, α,α-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 α,α-disubstituted glycine, namely α,α-dicyclopropylglycine (Dcp), we investigated the conformations of a series of Dcp-containing homooligopeptides by X-ray crystal and NMR solution analyses. Z-$(Dcp)_n$-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 homo-oligopeptides 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^3-NH, Dcp^4-NH and Dcp^5-NH are insensitive to the addition of DMSO-d_6 into the $CDCl_3$ 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-oligopepide, 310-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 mechanosynthesis and direct synthesis starting from *zero-valent* metal.

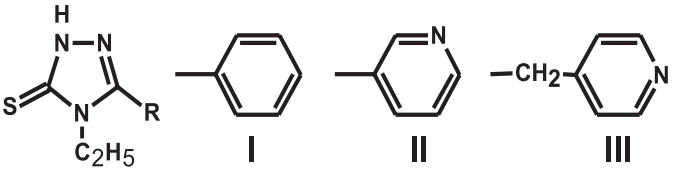
The studied ligands (**I-III**) are investigated due to their biological activity including antitumor, antibacterial, antifungal, antiviral *etc*. Some 1,2,4-triazoles are potent inhibitors of enzymes such as methionine aminopeptidase-2 and farnesyltransferase [1-2]. The activity of molecules containing S=C-N-N fragment such as triazole-3-thione Shiff 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 pirydynyl 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 $CuCl_2$ 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

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