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 (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: Host, guest, inclusion

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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, thiosemicarbazides 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-{1H-pyrryl-2-ylcarbonyl}hydrazino]carbonothioyl}benzamide hemihydrate.

In the crystal lattice of I, inversion related molecules 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 R2(10) and R2(14) motifs. Moreover, in this crystal, second type of cyclic dimer is observed; molecules are linked by C–H···S (chlorophenyl···thioamide) interactions – R3(2) graph set. Additionally, 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-furyl···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 R3(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···II hydrogen bonds are observed, they are N–H···O (thioamide···water) and O–H···S (water···thioamide).

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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 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 [1-2]. The activity of molecules containing S=C-N-N fragment such as triazole-3-thione Shift 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 pipyrdynyl 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 centroymmetric dimer.

Most of the new complexes obtained by grinding CuCl₂ 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.

Keywords: copper, complex, crystallochemistry.