Abstract

The condensation of 1,2,4-triazole and a pyrimidine ring gives rise to the formation of bicyclic heterocycles known as 1,2,4- triazolopyrimidines. Four different possibilities exist for the relative orientation of both rings, so four different isomeric families of compounds are defined. Among these, 1,2,4-triazolo[1,5-a]pyrimidine derivatives are the thermodynamically more stable and, thus, the most studied ones. Revisions surveying the synthesis, reactivity, spectroscopic characterization and crystallographic studies of 1,2,4-triazolo[1,5-c]pyrimidines, 1,2,4-triazolo[4,3-a]pyrimidine and 1,2,4-triazolo[4,3-c] pyrimidines have also been published.

The studies about the coordination chemistry of triazolopyrimidines have exclusively focused till now in the 1,5-a series. These compounds, which are structurally similar and may be regarded as mimic of isomeric purines, have displayed a rich coordination chemistry, a considerable number of new compounds with interesting structural features having been characterized, including simple mononuclear compounds with monodentately coordinated ligands and di or polynuclear compounds in which either the triazolopyrimidine ligand, or other auxiliary ligands bridge the metal atoms.

On the other hand, we have not found in the bibliography any reference for a coordination compound of any of the other arrangements (1,5-c, 4,3-a or 4,3- c), despite the fact that the different relative orientation of the nitrogen atoms inside the heterocycles could generate a wide number of new structure, specially if dimeric or polynuclear species are formed with bridging heterocycles. A difficulty that has to be taken into account in a study of this type is the lowest stability of these compounds if compared with the 1,5-a derivatives, isomerization processes (Dimroth rearrangement) may take place on heating, possibly catalyzed by acidic or basic pH.

This research and investigation of the coordination chemistry of triazolopyrimidine were the center of our thesis. Following this line of investigation a new derivative 7,8 dihydro-7-oxo-1,2,4-triazolo[4,3-a]pyrimidine was synthesized and characterized, In this thesis we chose the best method through the synthesis and modification to obtain maximum yield. The compound was characterized by usual methods and the results indicated that the most stable tautomer form is this when the acidic hydrogen was on N8 position, this result was supported by the theoretical study, ^{1}H-NMR and ^{13}C-NMR spectra. pka value was determined and it was more acidic than analogues purine bases, also from MO calculation there was no preference site of coordination.

This thesis is the first exploration in the coordination chemistry of 1,2,4-triazolo[4,3-a]pyrimidines. This compound comparing with the corresponding 1,5-a isomers, has the change in the position of one of the nitrogen atoms in the triazole ring which is now placed as separated as possible from the pyrimidine ring, with less steric hindrance and contiguous to the other external imidazole nitrogen. Synthesis of metal complexes of the first and second raw transition metals (Cu, Ni, and Ag) was carried out, some of these complexes were isolated in pure crystal form, others need further investigation, the complexes were characterize by X-ray crystallography showing that the ligand retain 4,3-a isomer which is less favored thermodynamically. With Cu the ligand form two complexes $CuL_2Cl_2(H2O)_3$, and $CuL_2Cl_2(H_2O)_5$ these complexes were not isolated in crystal form.

Also two nickel complexes were obtained $NiL_2(H_2O)_5$ and $Ni_9L_8(NO_3)_4(NH_3)_4(OH)_6(H_2O)_{16}$ cluster, for this complex cluster the ligand coordinated in its anionic form through N1, N2 and O without preference of one site over another, this cluster had showed ferromagnetic and antiferromagnetic interaction at lower temperature and also need further investigation since this type of compounds be could used in the field of electronics as data storage materials. Silver crystal complex $AgL_2(NO_3)_2(H_2O)_2$ were isolated and characterize by X-ray. The coordination mode in N1 and N2 atoms, the acidic hydrogen was situated on N8 the same as in the free ligand.

The most stable thermodynamic 1,5-a compound was also obtained during one of the reaction to prepare cobalt complex with the desired ligand an organic compound had precipitate and the isolated in the form of single crystal, product is in agreement with Dimroth rearrangement