09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.4-6 2-ACETYL-PYRIDINE THIOSEMICARBAZONES: COMPLEXES WITH TRANSITION METALS Fe, Cu AND Co. By Judith L. Flippin-Anderson, Richard Gilardi and Clifford George, Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D. C. 20375, U.S.A.

Thio- and selenosemicarbazones derived from 2-acetylpyridine, such as 3-azabicyclo[3.2.2]nonane-3-thiocarboxylic acid 2-[1-(2-pyridyl)ethylidene] hydrazide (A), have shown significant antimalarial and cytostatic properties. These compounds are also efficient transition metal chelators, coordinating with Mn, Fe, Co, Ni, Cu, Pd and Pt. Relative to the free ligands, some of these complexes exhibit reduced antimalarial activity, however, their antileukemic properties are enhanced. The metal ions coordinate with up to 2 organic ligands. The coordination of the metal ions in these compounds has been found to be square planar (Cu(II), Ni(II)), square-pyramidal (Fe(III)) and octahedral (Fe(II), Ni(II), Co(III)). The structures of several of these chelates are being studied as part of a project comparing the biological activities of this class of compounds. This paper will report on the structures of the coordination compounds of A with Fe, Cu and Co and on the structure of a non-thiol derivative of A. The Fe complex is octahedral and crystallizes in space group P6 3 along with [FeCl₄]⁻. The Cu complex is square planar, complexes with one molecule of A and one thioylate anion in space group PT. The Co complex is octahedral and crystallizes with [Co(SCN)₄]²⁻ in space group P1 with a ratio of 2 Cu complexes to 1 Co(SCN)₄ moiety. Solvent molecules were also found in this system. The organic ligand crystallizes in the space group P2₁/c. Samples were provided by Major John Scovill of the Walter Reed Army Institute of Research.

09.4-7 CRYSTAL STRUCTURE OF BIS(3,5-DIMETHYL-1-PYRIDINUM) COPPER(II) CHLORIDE. By Alok Poddar & J.K. Dattaquota, Baha Institute of Nuclear Physics, Sector-I, Block-'A', Bidhan Nagar, Calcutta-700064, INDIA and N. Saha, Department of Chemistry, Indian Institute of Technology, New Delhi, New Delhi, INDIA.

Pyrazyl derivatives are well known for their medicinal values. The crystal structure analysis of pyrazyl derivatives of Cu has been undertaken in order to investigate the coordinating properties of pyrazyl derivative with transition metal ions. Bis(3,5-dimethyl-1-pyrazyl) Cu(II) dihydrate crystallizes in triclinic space group PT with one molecule per unit cell. The cell dimensions are a=7.098(1), b=4.640(3), c=8.367(3)Å, α=92.99(3)°, β=101.26(3)°, γ=108.56(3)°. The structure has been solved by heavy atom method and was refined by block-diagonal least-squares method to a R value of 0.053. The structure is centrosymmetric about the Cu-atom. The two tertiary ring nitrogens of the pyrazyl ring and the two nitrogens of the quinolin moiety are the binding sites and these constitute the square plane around the Cu atom. The two apical sites of the octahedron are occupied by the two nitrogens of the centrosymmetrically related nitrogens. The structure is stabilized by hydrogen bonds of the type N-H...O.

09.4-8 NEW ADDITION COMPOUNDS OF GALLIUM. By R. Anton (a,b), A. L. Beauchamp (a) and H. W. Kisch (b); (a): Université de Montréal, Département de Chimie, Montréal, Québec, H3C 3V1, CANADA; (b): Institut für Anorganische Chemie, 8 München 2, Weizerstr. 1, F.R.G.

To gain information about the relative basicity of donor atoms in multifunctional heterocyclic molecules such as aminoborane, purine and imidazole, the ligands (1)-(4) were reacted with GaCl₃, which is known to be a very strong and sensitive Lewis acid.

Single-crystal X-ray structure determinations show that the new addition compounds contain a four-coordinated gallium atom bonded to the Nl (1,2) or N3(4)position, while a N9-protonated caffeinum ion with a GaCl₄ counterion was isolated from the chloroform reaction solution (3). The decrease of the N-Ga addition bond distance is correlated with the increase of the corresponding nitrogen basicity of the ligands (3 & 4). The coordination sphere of the metal atom in solution is discussed in relation with the multinuclear NMR data of the addition compounds (N₉, N₈, N₇, N₆, N₅, N₄).