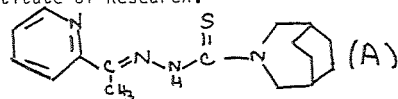


09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.4-6 2-ACETILPYRIDINE THIOSEMICARBAZONES: COMPLEXES WITH TRANSITION METALS Fe, Cu AND Co. By Judith L. Flippen-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 $R\bar{3}c$ along with $(FeCl_4)^-$. The Cu complex is square planar, complexing with one molecule of A and one thiocyanate anion in space group $P1$. The Co complex is octahedral and crystallizes with $[Co(SCN)_4]^{2-}$ in space group $P1$ with a ratio of 2 Co complexes to 1 $[Co(SCN)_4]$ moiety. Solvent molecules were also found in this system. The organic ligand crystallizes in the space group $P2_1/c$. Samples were provided by Major John Scovill of the Walter Reed Army Institute of Research.

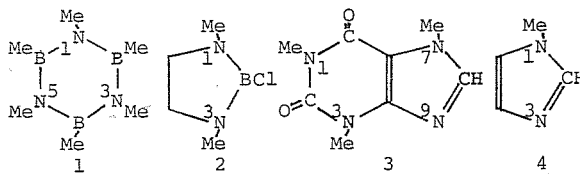


09.4-7 CRYSTAL STRUCTURE OF BIS(3,5-DIMETHYL-1-GUANYL PYRAZOLE) COPPER(II) NITRATE. By Aloka Podder & J.K. Dattagupta, Saha Institute of Nuclear Physics, Sector-I, Block-'AF', Bidhan Nagar, Calcutta-700064, INDIA and N. Saha, Department of Inorganic Chemistry, University College of Science, 92, A.P.C. Road, Calcutta-700009, INDIA.

Pyrazole derivatives are well known for their medicinal values. The crystal structure analysis of pyrazole derivative of Cu has been undertaken in order to investigate the coordinating properties of pyrazole derivative with transition metal ions. Bis(3,5-dimethyl-1-guanyl pyrazole) Cu(II) nitrate crystallizes in triclinic space group $P1$ with one molecule per unit cell. The cell dimensions are $a=9.708(3)$, $b=5.464(2)$, $c=9.367(3)$ Å, $\alpha=92.99(3)^\circ$, $\beta=101.24(3)^\circ$, $\gamma=108.54(3)^\circ$. 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 pyrazole ring and the two nitrogens of the guanyl 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 nitrate groups. The structure is stabilized by hydrogen bonds of the type $N-H...O$.

09.4-8 NEW ADDITION COMPOUNDS OF GALLIUM. By K. Anton (a,b), A. L. Beauchamp (a) and H. Nöth (b); (a): Université de Montréal, Département de Chimie, Montréal, Qué., H3C 3V1, CANADA; (b): Institut für Anorganische Chemie, 8 München 2, Meiserstr. 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 $GaCl_3$, 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 N1 (1,2) or N3(4) position, while a N9-protonated caffeine ion with a $GaCl_4^-$ counterion was isolated from the chloroform reaction solution (3). Ring system 1 and 2 are no longer planar in the complexes. The decrease of the N-Ga addition-bond distance is correlated with the increase of the corresponding nitrogen basicity of the ligands (1<2<4). The coordination sphere of the metal atom in solution is discussed in relation with the multinuclear NMR data of the addition compounds (1H , ^{11}B , ^{13}C , ^{14}N , ^{71}Ga).

09.4-9 NEUTRON DIFFRACTION ANALYSIS OF ISOMORPHOUS DIHYDRIDOBIS(TRIETHYLSILYL)PENTAMETHYLCYCLOPENTADIENYL-IRIDIUM(V) AND-RHODIUM(V) COMPLEXES AT 20K*. J.S. Ricci, Jr.† and T.F. Koetzle, Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973 USA; M. Fernandez and P.M. Maitlis, Department of Chemistry, The University, Sheffield S3 7HF England.

As a result of interest in catalytic hydrogenation reactions and in the geometries of transition metal hydrides, the low-temperature (20K) neutron diffraction analysis of the isomorphous species, $[n^5-C_5Me_5M(H)_2(SiEt_3)_2]$, where $M = Ir$ and Rh have been undertaken.

Initial coordinates for the nonhydrogen atoms were taken from the X ray results for the rhodium complex. The molecules show a "four-legged pianostool" geometry with the pentamethylcyclopentadienyl ring η^5 bonded to the metal from above and two triethylsilyl ligands trans in the basal plane. The two hydrides are trans to each other and are contained in the mirror plane bisecting the ring and reflecting the triethylsilyl ligands. The average Ir-H distance is 1.594(3) Å at $R(F^2) = 0.07$ while that for Rh-H is 1.581(3) Å at $R(F^2) = 0.07$. The latter is believed to be the shortest such distance reported thus far for a 4d or 5d transition metal based on neutron diffraction data. There are no abnormally short intermolecular contacts.

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