MIXED LIGAND CHELATES OF COBALT (II), NICKEL (II) AND COPPER (II) AND THERMAL DECOMPOSITION OF SOME MIXED LIGAND COMPLEXES OF METALS

By

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C E R T I F I C A T E

This is to certify that the thesis entitled "Mixed ligand chelates of cobalt(II), nickel(II) and copper(II) and thermal decomposition of some mixed ligand complexes of metals" being submitted by Mr. C.S.R. Murthy to the Indian Institute of Technology for the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. Murthy has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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A C K N O W L E D G E M E N T

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LIST OF FIGURES

CHAPTER-III

CHAPTER-V

A B S T R A C T

Schiff base ligands have been prepared from pyrazolones (4-amino-2,3-dimethyl-1-phenyl-pyrazol-5-one and 4-benzoyl-3-methyl-1-phenyl-pyrazol-5-one), 1,3-diaminopropan-2-ol and pyridine-2-aldehyde. They were characterized by elemental analysis and spectral data. Complexes of Co(II), Ni(II) and Cu(II) with the Schiff bases 2,3-dimethyl-4-iminopyridyl-1-phenyl-pyrazol-5-one (PA.AP), (4-benzoyl-3-methyl-1-phenyl-5-iminopyrazolyl) aminobenzene(BMPP.pd), 2,3-dimethyl-4-benzil-imino-1-phenyl-pyrazol-5-one (AP.B), 1,3-bis(4-amino-2,3-dimethyl-1-phenyl-5-iminopyrazolyl) propan-2-ol(AP_2.dap) and 1,3-bis(iminopyridyl)propan-2-ol (PA_2.dap) have been synthesised and characterized by elemental analysis, ultraviolet and visible spectroscopy, infrared spectroscopy and room temperature magnetic suceptibility measurements. While the tridentate neutral ligands PA.AP, BMPP.pd and AP.B formed mainly six-coordinate complexes with Co(II), Ni(II) and Cu(II) ions, PA_2.dap and AP_2.dap (which are pentadentate monobasic Schiff bases) mainly formed five-coordinate complexes with perchlorates and nitrates. Exceptions are $Co(PA_2.dap)'NO_3$, $Ni(PA_2.dap)'NO_3$, $Cu(PA_2.dap)'NO_3$ and $Cu(AP_2.dap)'NO_3$ which were found to be six-coordinate.

Mixed ligand complexes of Co(II), Ni(II) and Cu(II) containing a bulky bidentate ligand N,N,N',N'-tetramethyl-ethylenediamine (tmen) and tridentate neutral ligand[N-

hydroxyethylethylenediamine(heen), N-hydroxyethyl-propylenediamine(hepn) or triethanolamine(tea)] were prepared. All these complexes were found to be six-coordinate even with anions having weak coordinating capacity such as perchlorate and nitrate. Five-coordinate complexes of Ni(II) and Cu(II) (in some cases) were obtained when tridentate dibasic Schiff base ligands like salicylideneaminophenol, salicylideneaminobenzenethiol, naphthalideneaminophenol and 4-benzoyl-3-methyl-1-phenyl-5-pyrazolyliminophenol (BMPP.ap) along with bidentate neutral ligands (ethylenediamine, bipyridyl and tmen) were used. Ligand field parameters from the electronic spectral data of octahedral Co(II) and Ni(II) complexes were calculated.

Mixed ligand complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) containing 'heen', 'dap', 'tea' or diethylenetriamine(dien) and oxalate were prepared and characterized. Thermal decomposition of these complexes has been studied using TG and DSC techniques. Intermediate products of thermal decomposition have been isolated and characterized wherever possible. While 'heen' complexes of Mn(II), Cu(II), Zn(II) and Cd(II); 'dap' complexes of Co(II), Ni(II), Zn(II) and Cd(II) and 'tea' complexes of Mn(II), Co(II), Ni(II), Zn(II) and Cd(II) showed a distinct loss of one molecule of amine ligand, all the complexes of 'dien' showed a partial break up of the ligand, in the first step. Values of activation energy for the thermal decomposition reactions (where there was a distinct

loss of one ligand molecule) were calculated from TG curve using Coats and Redfern equation and modified Horowitz and Metzger equation. From DSC curve the data was obtained using Swarin and Wims equation. The values obtained from DSC technique were slightly higher than the values obtained from the TG methods. The trends observed in the values of activation energy were correlated to the corresponding thermal stabilities of the complexes.

C O N T E N T S