Preface

This thesis deals with solid state spectroscopic study of hydrogen bonded one-dimensional complexes of organic and organometallic materials. Here we have tried hard to come out the physics from the organometallic conductors.

In the introduction of the thesis, we have tried to follow the Little’s model which was suggested by W.A.Little in 1964 Phy.Rev.134.1416. In which Little suggested that it might be possible to synthesize a room temperature superconductor using organic materials in which the electron traveled along certain kinds of chains, effectively confined to one dimensional. Little’s idea was that the build up of positive charge by a passing electron could be speeded up dramatically if instead of having to move ions, it need only rearrange other electrons.

It is now possible to verify some of the conclusion of one-dimensional models directly in low-dimensional solids having highly anisotropic structural and physical properties. A set of new phenomena peculiar to low-dimensional nature has opened a distant possibility of high temperature superconductivity.

We explain on the basis of exciton mechanism. An exciton is a bound state of an electron and hole which are attracted to each other by the electrostatic coulomb force. It is an electrically neutral quasi particle that exists in insulator,
semiconductors and some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.

We have hydrogen bonded copper, nickel, α-cyclodextrin, β-cyclodextrin and amylose compounds with polyanilines like emeraldine, nigraniline & pernigraniline and also with dyes like Para red, Congo red, Direct red, Bismark brown, Trypan blue & Evans blue. In this case we referring the book of Lloyd N. Ferguson “The modern structural theory of organic chemistry”. Physical properties like electrical & optical properties of inclusion compounds of iodine have also became popular because of its quasi-one-dimensional conducting nature.

**In Chapter 2** of the thesis the inclusion compounds of iodine such as α-cyclodextrin-KI-I₂-4H₂O, β-cyclodextrin-KI-I₂-H₂O and amylose-iodine are hydrogen bonded with dyes such as Para red, Congo red, Direct red, Bismark brown, Trypan blue & Evans blue. Hydrogen bonding of these O-H and N-H containing dyes seen to occur at glucosidic oxygen atoms or O-H groups of the polysaccharides. Excitons are emitted and absorbed by the electrons along the iodine chains as revealed by analysis, which reduces band gap along the polyiodine chains.

**Chapter 3** In the present work, we have prepared new materials by forming hydrogen bonding of emeraldine, nigraniline and pernigraniline with copper
chelates based on R-substituted salicylaldiminate where R=hydrogen, methyl, ethyl and phenyl. As a method of initial characterization, we have obtained FTIR spectra since these spectra provide information of electron-phonon coupling and hydrogen bonding. Hydrogen bonds of polyanilines with salicylaldiminate ligand at free groups as well as with π-clouds are verified with IR spectroscopy. Nature of transitions, line shapes of absorption of envelopes and fine-structures due to elementary excitations reveal that the intermolecular interactions are of different type than normal charge transfer interaction.

Chapter 4 Some of bis(N-R-Salicylaldiminato)Cu$^{II}$ where R=H$_1$,CH$_3$,C$_2$H$_5$ and C$_6$H$_5$ are found to have copper chains in one direction of the crystals. These 1-d systems are hydrogen bonded with six highly polarizable dyes namely Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue. The FTIR spectra reveal infrared absorption edge and its modification with exciton-phonon coupling. Threshold energies for the formation of excitons with phonon emissions are observed. When exciton-phonon coupling is weak, large number of phonon bands are observed in the edge spectrum. Free excitons are strongly bound and bound excitons are weakly bound to phonons.

Chapter 5 Some of bis(N-R-salicylaldiminoto)Ni$^{II}$ where R=H, CH$_3$, C$_2$H$_5$ and C$_6$H$_5$ are likely to have nickel chains in one direction of the crystals. These 1-d systems are hydrogen bonded with polyanilines namely emeraldine, nigraniline
and pernigraniline. The FTIR spectra reveal hydrogen bonding as well as modification of absorption edge with exciton-phonon coupling. Threshold energies for the formation of excitons with phonon emissions are observed. Theories of both direct and indirect excitons are discussed. Phonon-assisted recombination of electron-hole pairs is discussed which gives rise to infrared luminescence.

Chapter 6 Some of bis(N-R-salicylaldiminato)Ni^{II}, where R=CH_{3},C_{2}H_{5} are likely to have metal chains in one direction of crystals. These 1-D systems are hydrogen bonded with six highly polarizable dyes such as Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue in the present work. The FTIR spectra reveal hydrogen bonding as well as modification of absorption edge due to exciton-phonon coupling. Threshold energies of excitons with phonon emissions are observed. There is possibility of electron hole droplet formation at low temperatures as well as infrared luminescence.

Chapter 7 Lead phthalocyanine is a one-dimensional conductor having lead chains in one direction of the crystals. In the present study, hydrogen bonding of polyanilines namely emeraldine, nigraniline and pernigraniline has been carried out and studied with FTIR spectroscopy. Hydrogen bonding is verified with infrared spectra. These hydrogen bonded systems show threshold energies for the formation of excitons with phonon emission in the infrared absorption edges.
There is possibility of the formation of electron-hole liquid (EHL) at low
temperature because of high exciton density media. Also there is possibility of
recombination of electrons and holes across small band gap. EHL can be formed
when the band gap is somewhat large.

**Chapter 8** Lead Phthalocyanine, a well-known one-dimensional conductor is
hydrogen bonded with six highly polarizable, dyes namely Bismark brown, Congo
red, Para red, Direct red, Evans blue and Trypan blue in the present work. The
hydrogen bonding is verified with FTIR spectroscopy. FTIR spectra also gives
further information about phonon-assisted creation of free excitons and electron
hole pairs. Intrinsic absorption edge spectrum is modified by exciton-phonon
coupling. There are threshold energies for the formation of excitons with phonon
emission. Also noise in absorption spectrum is found due to localization near the
band edges. This is an infrared analogy of what is observed in gallium phosphide
and other ionic semiconductors.

**Chapter 9** Bis(dimethylglyoximato)Ni^{II} is a one-dimensional system having
nickel chains in one direction of crystal. Here the hydrogen bonding of
polyanilines, namely emeraldine, nigraniline and perigraniline with Ni(Hdmg)₂ is
carried out and studied with FTIR spectroscopy. Hydrogen bonding is verified
with infrared spectra. Moreover, the H-bonded systems show threshold energies of
excitons with phonon emission in the infrared absorption edges. There is
possibility of condensation of such infrared excitons at low temperatures leading to electron-hole droplets. Also there is possibility of infrared luminescence because of recombinations of electron-hole pairs.

Chapter 10 Here the one-dimensional semiconductor namely bis(dimethylglyoximato)Ni\textsuperscript{II} is hydrogen bonded with six highly polarizable dyes namely Para red, Congo red, Direct red, Bismark brown, Evans blue and Trypan blue. The hydrogen bonding was verified with FTIR spectroscopy. FTIR spectra also reveal modification of absorption edges by exciton-phonon coupling. There are threshold energies for the formation of free excitons and electron-hole pairs with phonon emissions in the intrinsic absorption edge spectrum. The remainder absorption at the value of the band gap is proportional to the exciton ionization energy in both direct and indirect excitons. This remainder absorption increases with the increase in the number of phonon bands in the absorption edge.