Abstract

Coordination polymers (CPs) are the group of compounds builds from metal ions and organic ligand via coordination bonds. A careful design and architecture of coordination polymers can leads to a number of properties such as porosity, chirality, catalysis, luminescence, magnetism, electrical conductivity, sensors, non-linear optics (NLO) and multifunctional materials. A single material designed to exhibit more than one physical properties is designated as multifunctional materials.

The coordination polymers of $\pi$ – conjugated ligands are good source of multifunctional materials. Nobel laureate (2000) Heegar et al. reported that $\pi$ – conjugated polymer having integer oxidation states on different atoms are insulator or high band gap semiconductor materials however, they become highly conductive upon redox treatment to make some of the atoms of coordination polymers involved in conjugation to exhibit fractional oxidation state. In order to get fractional oxidation state in monometallic coordination polymers a partial redox treatment is required which introduces impurities and other complications. As two different metal ions possess different standard electrode potential therefore, it is possible to obtain fractional oxidation state without redox treatment i.e. by incorporating hetero-metals in the conjugated coordination polymers it is capable to exhibit electronic communication between different metal centers and complications of redox treatment can be avoided. It is reported that the bridging $\pi$ – conjugated ligand allows the electronic communication between two metal centers in the conjugated coordination polymers therefore, they are expected to exhibit good electrical conductivity as a consequence of fractional oxidation state at the metal centers arising by electronic communication in a coordination polymers. In going from monometallic to heterobimetallic conjugated coordination polymers, it is expected to exhibit higher conductivity as each metal ion would exhibit fractional oxidation states provided they are bridged by $\pi$ – conjugated ligand. In general organic ligand molecules possess paired electron consequently they are diamagnetic. The metal ions particularly transition metal ions exhibit unpaired electrons therefore, their complexes exhibit magnetic properties. Depending upon interelectron interaction in the polymer/complexes they exhibit various magnetic properties such as antiferromagnetism, ferromagnetism and/ ferrimagnetism. Therefore, incorporation of
transition metal ions in the conjugated coordination polymer leads to different magnetic behavior. Thus, complexes of $\pi$–conjugated ligand with transition metal ions may exhibit good electrical and magnetic properties.

As discussed above, the heterobimetallic conjugated coordination polymers with transition metal ions having unpaired electrons are expected to possess good magnetic and conducting properties. 2,5-Dichloro-3,6-bis(ethylamino)-1,4-benzoquinone ($\text{H}_2\text{dedb}$) is a $\pi$–conjugated ligand possessing two donor atoms at each opposite ends of the molecule, therefore, it is capable to form 1–D coordination polymers on coordination with metal ions. Heterobimetallic coordination polymer having at least one of the transition metal ion with $\pi$–conjugated bridging ligand 2,5-dichloro-3,6-bis(ethylamino)-1,4-benzoquinone ($\text{H}_2\text{dedb}$) is expected to meet all the requirements for good conducting and magnetic material. To the best of our knowledge, metal complexes/coordination polymers of $\text{H}_2\text{dedb}$ are not known in the literature, therefore, the present work involving the synthesis and characterization of $\pi$-conjugated ligand 2,5-dichloro-3,6-bis(ethylamino)-1,4-benzoquinone ($\text{H}_2\text{dedb}$) and its coordination polymers was undertaken. The present thesis has been divided into six chapters. Chapter 1 deals introduction and chapter 2 includes general methods of synthesis and physico-chemical measurements. Characterization of the ligand has been described in chapter 3, whereas synthesis, characterization and determination of solid state electrical conductivity of heterobimetallic coordination polymers of Cu(II) and Zn(II) have been presented in the chapter 4. Chapters 5 and 6 include synthesis, characterization and solid state electrical conductivity and magnetic properties of heterobimetallic coordination polymers of the type $[\text{Cu},\text{Ni}_{1-x},\text{(dedb)},x\text{H}_2\text{O}]_n$ $[\text{Cu},\text{Fe}_y,\text{(dedb)},2\text{H}_2\text{O}]_n$, respectively.

**Experimental**

The ligand was synthesized by modifying the reported literature methods as follows.

![Scheme 1 Synthesis of $\text{H}_2\text{dedb}$.](image-url)
The monometallic and heterobimetallic coordination polymers were synthesized by following sequence of reactions.

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\begin{align*}
H_2\text{dedb} + 2\text{KOH} & \rightarrow K_2\text{dedb} + 2\text{H}_2\text{O} \\
K_2\text{dedb} + M^{2+}(\text{aq}) & \rightarrow [M(\text{dedb}).y\text{H}_2\text{O}]_n \\
K_2\text{dedb} + x\text{Cu}^{2+}(\text{aq}) + (1-x) M^{2+}(\text{aq}) & \rightarrow [\text{Cu}_xM_{1-x}(\text{dedb}).y\text{H}_2\text{O}]_n \\
(M = \text{Zn(II) and Ni(II) and } x = 1.0, 0.5, 0.25, 0.125 \text{ and } 0.0625) \\
K_2\text{dedb} + x\text{Cu}^{2+}(\text{aq}) + (1-x) \text{Fe}^{2+}(\text{aq}) & \rightarrow [\text{Cu}_x\text{Fe}_y(\text{dedb}).y\text{H}_2\text{O}]_n \\
(x = 1, y = 0; 0, 0.67; 0.5, 0.33; 0.25, 0.5; 0.125, 0.583; 0.0625, 0.625 \text{ and } n = \text{degree of polymerization})
\end{align*}
\]

**Results and Discussion**

**Characterization, DFT level calculations and electrical conductivity of the ligand**

Ligand \(H_2\text{dedb}\) was characterized by elemental analysis, FAB mass, IR, \(^1\text{H}\) & \(^{13}\text{C}\) NMR, UV-visible spectroscopic techniques and single crystal X – ray.

Positive ion FAB mass spectrum of \(H_2\text{dedb}\) in the matrix of \(m–\text{nitrobenzyl alcohol (NBA)}\) shows molecular \([M]^+\) as well as pseudo molecular \([M + H]^+\) ion peaks at \(m/z\) 262 and 263, respectively. Peaks corresponding to isotope distribution at \(m/z\) value 265 and 267 corresponds to \([M+2+H]^+\) and \([M+4+H]^+\) corroborates the presence of two Cl atoms in the molecule. The \(^1\text{H}\) NMR of \(H_2\text{dedb}\) exhibits three peaks corresponding to N-H, CH$_2$, and CH$_3$ in order of decreasing chemical shift values. \(^{13}\text{C}\) NMR spectrum shows five peaks corresponding carbon atoms designated as C=O, C-NH, C-Cl, CH$_2$, and CH$_3$ in decreasing order of chemical shift values which match with proposed chemical structure of \(H_2\text{dedb}\). Further, the ligand \(H_2\text{dedb}\) was characterized by UV-Visible and cyclic voltammogram. Single crystal X – ray data of \(H_2\text{dedb}\) crystal shows that it crystallizes in triclinic crystal system with space group P-1, unit cell parameter \(a = 4.7129, b = 7.5434, c = 8.3452, \alpha = 99.642, \beta = 92.298, \gamma = 106.41^\circ\) and one molecules per unit cell.

Geometrical optimization at DFT level with Gaussian 03 software shows \(C_i\) point group symmetry. Optimized structure of ligand exhibits two parallel sets of \(\pi\) – conjugated strands capable to conduct charges across the molecule. Computed APT charges on carbonyl carbon (atoms 3 and 6) of \(H_2\text{dedb}\) possess highest positive charges whereas carbon attached to chlorine (atom 1 and 4) acquire negative charges. The assignments of all the normal modes of vibration have been done on the basis of
potential energy distributions (PED) analysis by using GAR2PED software. The observed IR frequencies corresponding to the fundamental modes have been correlated to the calculated fundamental frequencies. Variable temperature solid state conductivity of $H_2$dedb shows semiconductor behavior.

**Characterization of the Coordination Polymers of $[\text{Cu}_x\text{M}_{1-x}(\text{dedb}).y\text{H}_2\text{O}]_n$**

$[\text{Cu}_x\text{Fe}_y(\text{dedb}).2\text{H}_2\text{O}]_n$ [M = Zn$^{2+}$, Ni$^{2+}$; x =1.0, 0.5, 0.25, 0.125, 0.0625 and y = 0.33, 0.58, 0.5, 0.625 and n = degree of polymerization]

All the coordination polymers are stable in air upto 195 °C, however, they are weakly hygroscopic. They are insoluble in almost all the common organic solvents.

**IR Spectra**

IR spectra of coordination polymers do not exhibit $\nu_{as}(\text{N-H})$ vibrational mode indicating deprotonation of N-H protons. This indicates the involvement of nitrogen donor atoms in bonding/coordination. Asymmetric ($\text{C = O}$) stretching mode of vibration in the coordination polymers are observed at lower frequency (1636 – 1651 cm$^{-1}$) as compared to that of the ligand $H_2$dedb (1659 cm$^{-1}$) indicating involvement of quinonic oxygen in coordination. Appearance of broad $\nu(\text{O - H})$ vibration in the range 3450 - 3420 cm$^{-1}$ in the IR spectra of coordination polymers supports the presence of water molecule in the coordination polymer. It is worth to be mentioned that $\nu(\text{O - H})$ vibration is absent in the free ligand.

**Powder X-Ray Diffraction**

Non–coincidence of the powder X-ray diffraction peak positions of the heterobimetallic coordination polymers with those of the corresponding monometallic polymers and equimolar mixture of monometallic coordination polymers indicates that heterobimetallic polymers are distinctly new species rather than the mixtures of respective monometallic polymers in an appropriate mole ratio. In addition to above, appearance of some new peaks in some heterobimetallic coordination polymers at different positions as compared to that of monometallic polymers further corroborates the formation of heterobimetallic coordination polymers as a distinctly different new species. DICVOL 06 method of indexing of PXRD lines of the coordination polymers 2, 3, 4, 6 and 7 shows triclinic structure for these polymers.
Transmission Electron Microscopy

TEM images and electron diffraction pattern of monometallic coordination polymers 2, 3 and representative heterobimetallic coordination polymer 4 and 7 shows their nanocrystalline nature. TEM image of nanocrystalline heterobimetallic polymer 4 is more regular and exhibit well defined shape as compared to those of their monometallic coordination polymers. Thus, TEM images confirm distinct identity of heterobimetallic coordination polymer and tunability of their morphology and size.

Thermal Analysis

Thermal analyses (TGA, DTG, DTA) shows that coordination polymers 2, 3, 4, 8, 12, 13 exhibit three step, 14, 17 exhibit two step and 7 shows four step decomposition pattern. The final residue after thermal degradation under air corresponds to respective metal oxide. Decomposition pattern of monometallic and heterobimetallic coordination polymers are different and their DTA and DTG peaks positions as well as intensities are different.

ESR Spectral Studies

Solid state ESR spectrum of polymer 2 room temperature (RT) as well as liquid nitrogen temperature (LNT) exhibits g values corresponding to square planar geometry. Full width half height (FWH) value for the polymer 4 is greater than that of polymer 2. ESR spectrum of the polymer 7 exhibits an axial spectrum with partially resolved parallel hyperfine lines as well as nitrogen super hyperfine splitting indicating diminution of spin–spin exchange interaction due to dilution of magnetic center Cu(II) by diamagnetic Zn(II) ions. Presence of nitrogen super hyper fine lines in the spectrum of 7 indicates that the unpaired electron of Cu(II) is delocalized over nitrogen atoms of the ligand. Absence of signal in ESR spectrum of 12 has been interpreted to arise due to redox reaction between Cu(II) and Ni(II) ions resulting into the formation of ESR inactive Cu(I) and Ni(III) ions. ESR spectrum of 9, also indicate redox reaction between hetero metal ions bridged by \( \pi \) – conjugated \( H_2 \)db i.e. occurrence of electronic communications between two adjacent metal centers. ESR spectrum of polymers 13, 14 and 17 at LNT indicates octahedral geometry around Fe(III) ions and square planar geometry around Cu(II) ions.
**Mössbauer Studies**

Mössbauer spectrum of the coordination polymers 13, 14 and 16 recorded at room temperature (300K) and 77 K indicates presence of Fe(III) centers as major contribution and traces of Fe(II) (< 10 %) ions in coordination polymers. Two different isomer shift values of Fe(III) ions indicating occurrence of two different Fe(III) centers in these polymers. The existence of different Fe(III) centers possibly arise due to presence of different adjacent metal centers (Fe$^{3+}$/Fe$^{3+}$ or Fe$^{3+}$/Fe$^{2+}$ and/or Cu$^{2+}$) in the coordination polymers. Isomer shift and quadrupole splitting values indicates the existence of high spin octahedral environment around Fe(III) ion in polymeric system.

**Magnetic Susceptibility Studies**

The magnetization (M) versus magnetic field (H) curve of the polymers 2, 8, 9, 10, 11, 13, 14 and 17 were recorded on vibrating sample magnetometer. The presence of narrow hysteresis loop in the M – H curve of polymers indicates that they are soft magnetic materials. Variable temperature magnetic susceptibility of coordination polymers 8, 9, 10, 11, 12, 13, 14 and 16 were recorded on SQUID magnetometer in the temperature range 298K to 2K. The increase of $\mu_{\text{eff}}$ value of polymers 8, 9, 10, 11, 12, 13 and 16 with decrease of the temperature indicate ferromagnetic interaction between metal centers. Decrease of $\mu_{\text{eff}}$ value on further lowering the temperature occurs due to antiferromagnetic interaction and/ or zero field splitting.

**Solid State Electrical Conductivity**

Variable temperature solid state electrical conductivity of ligand 1 and coordination polymers 2 – 7, 9 and 13 – 17 increases with increasing temperature indicating their semiconductor behaviour. Heterobimetallic polymers 10, 11, 14 and 17 show higher conductivity than those of monometallic polymers 2, 8 and 13. Increase of conductivity in heterobimetallic polymers as compared to that of their monometallic polymer arises due to greater delocalization of unpaired electron of Cu(II) ion onto the ligand atoms and existence of fractional oxidation state in other polymers. Polymers 8, 10 – 12 exhibits semiconducting and metallic behaviour.