

CHAPTER 6
SUMMARY

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A brief summary of the work reported chapter-wise (**Chapter 3-5**) highlighting the salient findings is presented herein -

In **Chapter 3**, synthesis, characterization and systematic investigation of the mesomorphic and photoluminescence properties of an N-alkylated bidentate [N,O]-donor rod-shaped salicylaldimine Schiff base ligand and its complexes with Group 12, d^{10} -metal ions has been described. The ligand is non-luminescent and non-mesomorphic. However, the zinc(II) and cadmium(II) complexes show highly ordered mesophases, an observation not quite ubiquitous for tetrahedral complexes. The complexes are also luminescent, emitting in the blue region of the spectrum. The mercury(II) complex though luminescent, decomposed prior to melting.

Chapter 4 and **5** deals with the synthesis, characterization, and exploration of mesomorphism and photophysical properties of new series of tetradentate ‘salen’ and ‘salphen’ type ligands and their metal complexes. The ‘salen’ type ligands with flexible asymmetric methyl substituted spacer are all non-mesomorphic. These ligands are non-luminescent too. On the contrary, the ‘salphen’ type ligands with asymmetric halogen (F, Cl, Br) substituted aromatic spacer are all mesomorphic. These ligands exclusively exhibit 2D-columnar phases of oblique, rectangular or hexagonal types which are occasionally stable at room temperature. The vicinal di-halogen (Cl,Cl) substituted salphen ligands are, however, non-mesomorphic. Moreover, both of the varieties are luminescent emitting in the blue-green region of visible spectrum. Coordination of Zn(II) ion to the ‘salen’ type ligands induces lamello-columnar mesomorphism and photoluminescence in the ligands, mesophases being stable till ambient temperature. While, Zn(II) complexes of the salphen variants display solely rectangular columnar phases with $p2gg$, $p2mm$ or $p2mg$ symmetry; mesophase of dichloro substituted complexes being stable down to room temperature, thus affording room temperature mesomorphism. The Zn(II)-salphen complexes emit green

light, in contrast to the Zn(II)-salen complexes which emit blue light in the condensed state and solution. Besides, the Zn(II) complexes of both the types form H-type aggregates in dilute solutions of different non-coordinating solvents, while monomers are dominant in coordinating solvents, suggesting the Lewis acidity of the metal ion in the newly synthesized complexes. Further, oxovanadium(IV), nickel(II) and copper(II) complexes of the salphen ligands were also explored to understand the role of metal-coordination and/or spacer group influence on the mesomorphic and photophysical properties. Amongst the oxovanadium(IV) complexes of the respective mono and di-halogenated salphen ligands, both mono-fluoro and chloro substituted ones are mesomorphic, displaying rectangular columnar phase($p2mm$), while complexes of mono bromo- and dichloro-substituted ligands are not, which decompose at temperatures greater than 270°C. Ni(II) complexes of mono and di-halogenated (-Cl,Cl) ligands are all mesomorphic and display oblique columnar phase($p1$) and/or rectangular columnar phase ($p2mm$), respectively. The mono-halogenated Ni(II) derivatives also display weak emission in the blue region of the visible spectrum. The dichloro substituted analogues are however, non-emissive. The Cu(II) complexes of all the ligand series are non-mesomorphic, and decompose prior to melting. Furthermore, solvatochromic studies involving selected VO(IV), Cu(II) and Ni(II) complexes of the dichloro-substituted ligands has also been carried out. The axial vacant coordination site at the square-pyramidal VO(IV) center facilitates solvatochromism in solvents of different coordinating ability. The Cu(II) and Ni(II) complexes lack such 'solvatochromism'. Based on the DFT study a slightly distorted square planar geometry is conjectured around the metal center in all the complexes.

Based on the work documented in this thesis, certain areas, amongst others, which have scope for future exploration, are:

1. Investigation of non-linear optical (NLO) response of the aggregate Zn(II) Schiff base complexes, and the switching of the quadratic hyperpolarizability upon de-aggregation in polar coordinating solvents.
2. Vapochromism and sensory activity of some selected compounds.
3. Reactivity of the coordinatively unsaturated metal complexes with neutral and anionic donors to access newer complexes.