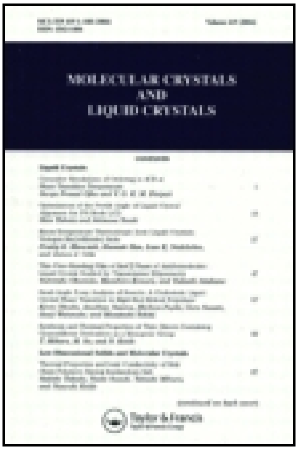

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Synthesis and Characterisation of Macrocyclic Liquid Crystalline Ligands and their Metal Complexes

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Synthesis and Characterisation of Macrocyclic Liquid Crystalline Ligands and their Metal Complexes

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Four macrocyclic liquid crystalline ligands derived from 1,8 dihydroxy ethyl 1,3,6,8,10,13 hexa aza cyclotetradecane(DHAT) and trans-4-n-alkoxy cinnamoyl chloride have been synthesised and their metal complexes using Cu(II),Ni(II),Pb(II),V(V) and U(VI) metal ions have been isolated. The ligands and their metal complexes were characterised by elemental analysis, FTIR,NMR,X-Ray and DSC studies. Polarising microscope was used to identify mesomorphic textures of the ligands and the complexes.

The transition temperature and mesophase textures of the ligands and complexes have been compared. The effect of presence of different metal ions on mesomorphic properties has been discussed.

INTRODUCTION

Metallomesogens have attracted much attention in recent years,due to combination of properties of both of organic liquid crystalline ligand and metal atom.[1] Coordination of liquid crystalline ligands to metal ions can give variety of molecular shapes and phase changes[1].

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Macrocyclic liquid crystalline compounds are very much welcome in the field of liquid crystals due to various phase changes exhibited by them and their metal complexes .Earlier we have reported [2] Pb(II) complexes of macrocyclic liquid crystalline ligands derived from DHAT and alkoxy benzoyl chloride.In this paper we are reporting liquid crystalline macrocyclic ligand derived from DHAT and trans -4-n-alkoxy cinnamoyl chlorides .The work is mainly based to study the change in mesomorphic properties of ligand and metal complexes by changing central linkage by taking different value of R=C6,C8, and C10.

EXPERIMENTAL:-

1 .Synthesis of macrocyclic liquid crystalline ligands

[a] 1,8 dihydroxy ethyl 1,3,6,8,10,13 hexa aza cyclotetradecane was synthesized as per our reported work [2]

[b] Preparation of trans -4-n-alkoxy (R=C6,C8,C10) cinnamoyl chloride:-trans -4-n-alkoxy benzaldehyde, trans -4-n- alkoxy cinnamic acid and trans-4-n-alkoxy cinnamoyl chloride were synthesized by the reported method.[3].

[c] Condensation of 1,8 dihydroxy ethyl 1,3,6,8,10,13 hexa aza cyclotetradecane [DHAT]with trans 4-n- alkoxy cinnamoyl chloride:-the DHAT [.002M] was dissolved in pyridine and to this [.004M] trans-4-n- alkoxy cinnamoyl chloride was mixed and refluxed for six hours

and was allowed to stand over night. Using 50% cold HCl to obtain the product, which was then recrystallised from ethanol, then acidified the condensed product.

2 Preparation of metal complexes:-The alcoholic solution of diester of DHAT was mixed with an alcoholic solution of metal salt in 1:1 proportion and refluxed on water bath for ten hours. The solid obtained was filtered,washed with ethanol and recrystallised from methanol.

The synthesized organic diesters [reaction c] macrocyclic ligands and their metal complexes were chracterised by elemental analysis,FTIR,X-ray,NMR and DSC studies. Polarising microscope was used to identify mesomorphic textures of the ligands and the complexes.

RESULTS AND DISCUSSION

The analytical data shows that the macrocyclic metal complexes were found to be of ML type see figure 1, where L= diester [R=C6, C8, C10] of DHAT and M= Cu(II),Ni(II),Pb(II),V(V) and U(VI). The X-ray diffraction studies showed good number of peaks for both ligands and metal complexes proving crystalline nature of both. Using X-ray diffraction data the unit cell parameters were calculated by trial and error method[4].All the main peaks have been indexed and their SinO values compared with the calculated ones. The observed values fit well in tetragonal system for ligands and their metal complexes.The number of units per cell [n values] were found to be 3 for both ligands and metal complexes proving the metal being incorporated inside the cyclic structure.

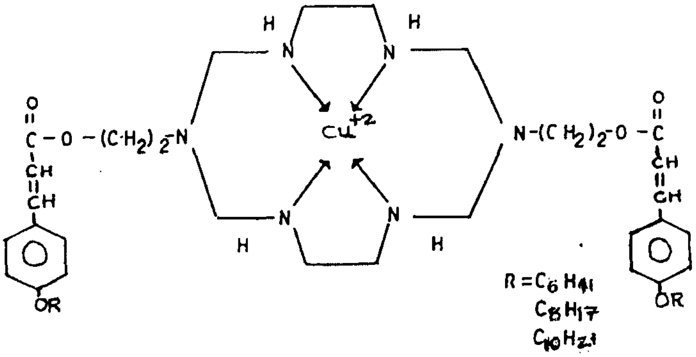
The FTIR data of free ligand showed bands corresponding to the functional groups present in the compound. The broad band observed at 2950 cm^{-1} corresponds to N-H stretching vibration of secondary amine[5]. This is further supported by a band 1610cm^{-1} as N-H bending vibration of secondary amine[5].These bands are shifted to lower frequency on coordination.A band observed at 1730 cm^{-1} corresponds to stretching vibration of esters[6].The band due to ester group remains undisturbed in the metal complexes indicating noninvolvement of ester group in the coordination.The nonligand bands observed in the metal complexes 620 Cm^{-1} to 650 $^{-1}$ correspond to V M-N [6]. NMR results are awaited.

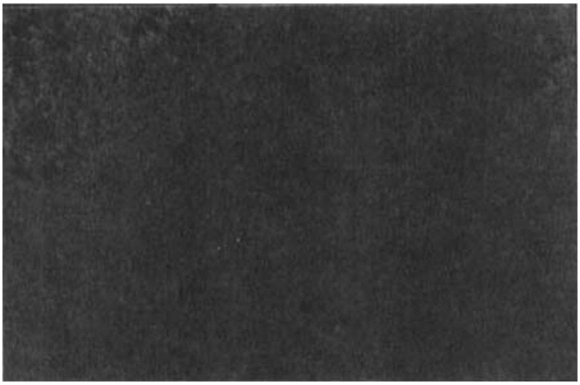
The DSC study was carried out using differential scanning calorimeter Mettler 20 MS. The macrocyclic ligand showed broad peak around 140-176 °C on cooling ,indicating a possible merging of phase change and crystallisation, This was also confirmed by using Leitz Laborlux 12 POL polarising microscope fitted with a heating stage. The Smectic phase changes were observed at 174 °C,162 °C and 148 °C for R= C6,C8and C10 respectively. This indicates that as the value of R is increased i.e.more the number of methylene groups are introduced into the terminal alkoxy group, molecule becomes more flexible and hence the transition temperature is gradually going down. The coloured photos show their liquid crystalline properties.

In DSC study of metal complexes ,only one sharp peak was observed on cooling in the range of 169 to 189 °C, which may correspond to isotropic state of complexes. Polarising microscope study also showed their non mesogenic character.

The lack of mesomorphism in metal complexes may be attributed to the loss of flexibilty of macrocyclic ligand as the metal ion gets into cyclic moiety. The complexes are more thermally stable than ligand due to the presence of metal ion, which gives more symmetry to the molecular geometry.

General Structure :





See Color Plate XXVIII at the back of this issue.

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