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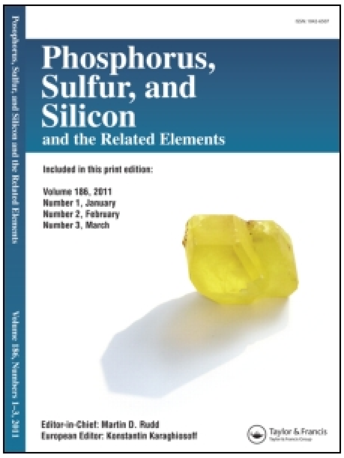

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Synthesis and Characterisation of Pb [II] Complexes of Liquid Crystalline Macrocyclic Ligands

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Three macrocyclic complexes of Pb^{2+} have been synthesised using liquid crystalline macrocyclic ligands derived from diesters of 1,8 dihydroxy ethyl 1, 3, 6, 8, 10, 13 hexa aza cyclotetradecane. The diesters are prepared by using butoxy benzoic acid, heptyloxy benzoic acid or octyloxy benzoic acid. The isolated ligands and their Pb^{2+} complexes are characterised by elemental analysis, TGA, FTIR, X-ray and DSC Studies.

The complexes are found to show four co-ordinated geometry with Pb^{2+} inside the cyclic structure. From polarising microscope and DSC studies, it is revealed that the Pb^{2+} complexes are non-mesogenic, though the ligands are mesogenic. The transition temperature of ligands is in the range of 125°C to 130°C. The complexes show isotropy in the range of 175°C to 185°C.

Keywords: Macrocyclic; Liquid Crystalline; Ligands

INTRODUCTION

Liquid crystalline materials containing metal ions [metallo mesogens] have attracted much attention in recent years, because, combination of the properities of organic liquid crystals [ligands] and of metal ions can produce new materials, exhibiting unique assembly structures, optical, magnetic and electrical properties[1]. Metal complexes show a remarkable variety of co-ordination geometry, so that co-ordination of liquid crystalline ligands to metal ions can give variety of molecular shapes.

Interest in the macrocyclic compound and their cation complexes has increased in recent years. The reactions with cation particularly metal ion involves a planar co-ordination sphere or three dimensional cage structures[2].

Recently some work on 1,8 dihydroxy ethyl 1, 3, 6, 8, 10, 13 hexa aza cyclotetradecane and gold was presented at 31st International Conference on Co-ordination Chemistry [5L40], but its liquid crystalline diesters were not studied and also Pb^{2+} complexes with liquid crystalline ligands remained unexplored. Hence we have thought of working on Pb^{2+} complexes using liquid crystalline diesters of 1,8 dihydroxy ethyl 1,3,6,8,10,13, hexa aza cyclotetradecane.

In the present investigation, we describe the synthesis and characterisation of Pb^{2+} complexes of liquid crystalline ligands derived from 1,8 dihydroxy ethyl 1,3,6,8,10,13 hexa aza cyclotetradecane and p-n-alkoxy benzoyl chlorides. The diesters are prepared by using butoxy benzoic acid, heptyloxy benzoic acid or octyloxy benzoic acid.

EXPERIMENTAL

1. Synthesis of macrocyclic liquid crystalline ligands

[a] Preparation of 1,8 dihydroxy ethyl 1,3,6,8,10,13 hexa aza cyclotetradecane : To 50 ml of methanolic solution of ethylene diamine [6-8 ml.], 20 ml. of 36%

formaldehyde was added dropwise followed by further dropwise addition of ethanolamine [8.6 ml.]. The mixure was refluxed for 24 hours on water bath with constant stirring. After refluxing the solution was heated on sand bath for few minutes to remove excess of methanol. Orange-yellow viscous liquid of 1,8 dihydroxy ethyl 1,3,6,8,10,13 hexa aza cyclotetradecane [DHAT] was obtained.

[b] Preparation of p-n-alkoxy benzoyl chlorides : p-alkoxy benzoyl chlorides were prepared by reacting p-n-butoxy benzoic acid, p-n-heptyloxy benzoic acid or p-n-octyloxy benzoic acid with excess of thionly chloride and refluxing it on water bath until the evolution of HCI gas had ceased. The excess of thionyl chloride was then distilled off under reduced pressure and the p-n-alkoxy benzoyl chloride left behind as a residue was used in next reaction without purification.

[c] Condensation of 1,8 dihydroxy ethyl 1,3,6,8,10,13 hexa aza cyclotetradecane [DHAT] with p-alkoxy benzoyl chlorides [Diester of DHAT] : The DHAT [0.002 M] synthesised in [a] was dissolved in Pyridine and to this [0.004M] of p-alkoxy benzoyl chloride was mixed and refluxed for hours and was allowed to stand overnight. This condensed product was then acidified by using 50% cold aqueous HCL to obtain the product, which was then recrystallised from ethanol.

2. Preparation of Pb^{2+} complexes

The alcoholic solution of diester of DHAT as prepared in [c] was mixed with an alcoholic solution of lead acetate in 1:1 proportion and refluxed on water bath for six hours. The solid obtained was filtered, washed with ethanol and recrystallised from methanol.

The synthesised organic diesters [reaction c] macrocyclic ligands and their Pb^{2+} complexes were characterised by elemental analysis, FTIR, X-ray, TGA and DSC studies. They were also studied for their luminescene property using 250 nm as exciation wavelength.

RESULTS AND DISCUSSION

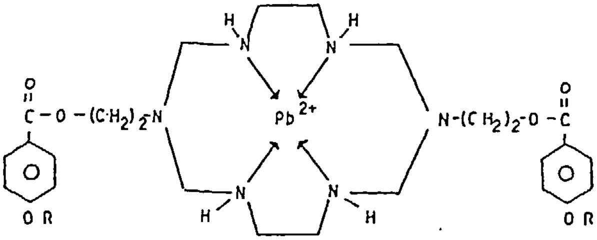
The analytical data see Table 1, shows that the macrocyclic Pb^{2+} complexes were found to be ML type see Figure 1, where L=diesters of DHAT and $M=Pb^{2+}$. The X-ray diffraction studies showed good number of peaks, proving crystalline nature of the lead complexes. Using X-ray diffaction data the unit cell parameters have been calculated by trial and error method[3]. All main peaks have been indexed and their $\sin^2\theta$ values compared with the calculated ones.

The observed values fit well in tetragonal system for ligands and their complexes and also the calculated values of the density are in good agreement with the observed ones. The number of units per cell [n-values] are found to be 4 for both ligands and metal complexes which show that Pb^{2+} is inside the cyclic structure[4].

Sr. No.	Ligands		Elemental Analysis Observed (Theoritical)				Transition or Isotropic Temp °C
			C%	H%	N%	M%	
1	$C_{34}H_{46}N_4O_4(L_1)$		62.75 (63.50)	8.01 (8.41)	12.83 (13.08)	-	128-130
2	$C_{37}H_{54}N_4O_4(L_2)$		63.21 (64.90)	8.63 (8.77)	11.98 (12.28)	-	125-127
3	$C_{38}H_{52}N_4O_4(L_3)$		64.95 (65.32)	8.71 (8.88)	12.01 (12.03)	-	128
	Complexes						
4	$[Pb\ C_{34}H_{46}N_4O_4]$	$(CH_3COO^-)_2$	46.80 (47.15)	5.80 (6.20)	8.52 (8.68)	21.30 (21.42)	185
5	$[Pb\ C_{37}H_{54}N_4O_4]$	$(CH_3COO^-)_2$	50.87 (51.12)	6.43 (6.53)	8.12 (8.32)	20.82 (20.53)	175
6	$[Pb\ C_{38}H_{52}N_4O_4]$	$(CH_3COO^-)_2$	50.85 (51.60)	6.05 (6.64)	7.98 (8.20)	20.19 (20.25)	178

Table 1

Analytical and Physical data of Ligands and Complexes



$R = C_4H_9$
C_7H_{15}
C_8H_{17}

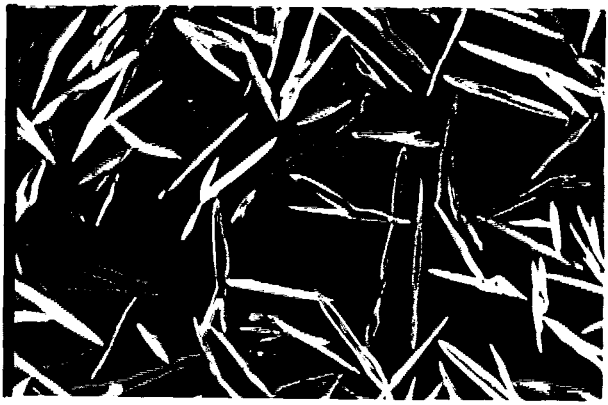
Figure 1

Metal Complex

The IR spectra were recorded in KBr pellets on a Perkin Elmer 577 spectrophotometer. The IR spectra of the free ligands showed a broad band ~ 2950 cmP^{-1} due to N-H stretching vibration of secondary amine[5]. This is further supported by a band ~ 1610 cm^{-1} as N-H bending vibrations of secondary amine[5]. These bands are shifted to lower frequency on co-ordination and showed a band ~ 1730 cm^{-1} corresponding to stretching vibration of benzoate esters[6]. The bands due to ester group remain same, which indicates the non-involvement, of the ester group in co-ordination with metal ion[8].

The IR spectra of Pb^{2+} complexes show non-ligand bands ~ 640 cm^{-1} which may correspond to ν_{M-N}[7].

The DSC study was carried out using differential scanning Calorimeter Mettler 20 MS. The organic ligands show broad peak around 126-129°C, on cooling, indicating a possible merging of phase change and crystallisation, the coloured photograph shows its liquid crystalline property. This is also confirmed by using a Leitz Laborlux 12 POL polarising microscope fitted with a heating stage. In case of metal complexes, only one sharp peak was observed on cooling ~ 180°C which may correspond to isotropic state of complexes. Polarising microscope study also showed their non mesogenic character.



See Color Plate II at the back of this issue.

The general lack of mesomorphism may be attributed to loss of flexibility of the macrocyclic ligand as Pb^{2+} ion gets into cyclic moiety[9].

TGA results reveal that the ligands and complexes follow a single step decomposition. This is also further supported by DSC traces in which lead complexes show only a single exothermic sharp peak. From TGA traces, it is observed that curves for lead complexes are steeper while for the ligand it is broader. The complexes are more stable than ligands due to the presence of Pb^{2+} ion which gives more symmetry to the molecular geometry.

Luminescene Study

All the ligands and complexes showed good fluorescene property. The study was carried out using 250 nm as an excitation wave length. The fluorescence spectrta of ligands showed two emission peaks at - 310 nm and 380 nm the observed two peaks in the emission spectra of complexes do not show any shift but there is an increase in the intensities, see figure 2.

In the ligands, the process of fluorescence consists of photon absorption by a molecule to go to an excited state, relaxation from higher vibration levels of the state to its lower vibrational levels[10]. Fluorescence arises from the singlet-singlet transition[11]. In case of Pb^{2+} complexes the higher intensity values are due to heavy metal effects and because the rate of inter system crossing appears to predominate[11].

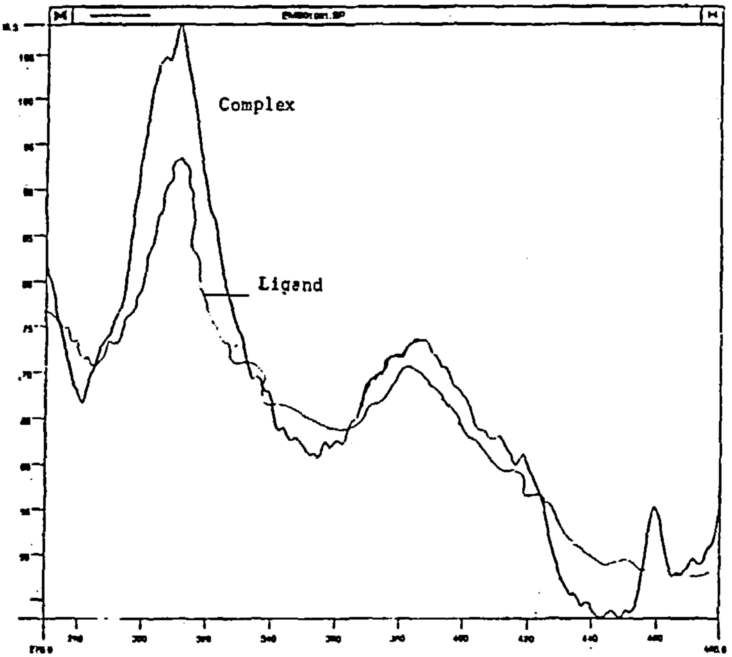


Figure 2

Flourescence Spectra of Macrocyclic Pb^{2+} complex &, Ligand

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References

[1] (a) D.W.Bruce *Inorganic materials* Eds. D.W.Bruce & D.O. Hore, Wiley, Chichester, UK, [1996] (b) J.L.Serano [Editor] *Metallomesogens* VCH Weinheim, [1996].

[2] Reed M Izatt & James J. Cristensen *Synthetic, Multidenatate Macrocyclic Compounds* Academic Press, New York 325, [1978].

[3] B.D. Cuility, *Elements of X-ray Diffraction* 2nd edition [Weisley Publishing Co. Inc] P324 [1977].

[4] Sami A. Zabin & C.R. Jejurkar, *Indian J. Chem.* vol 34A, 241, [1995].

[5] K. Nakamoto, *Infrared spectra of Inorganic and co-ordination compounds* Willey Inter-Science [New York] 198, 239, [1970].

[6] N.G. Gaylord & Maiti Sukumar, *J. Macromole. Chem* A6 [8], 1481 [1972].

[7] I.R. Ferraro, *Low frequency vibrations of Inorganic and co-ordination compounds* Plenum Press, New York, [1971].

[8] K.Nakamoto & A.E.Martell, *J.Chem. Phys.* 246, [1979].

[9] B.Donnio & D.W. Bruce, *J. Chem. Soc. Dalton Trans.*41, 809 [1979].

[10] D.M. Hercules *Fluorescence and Phosphorescene Analysis* Int. Sc. Publichers, New York, 113, [1965].

[11] J.P. Paris and W.W. Brandt., *J. Am. Chem. Soc.*81, 5000 [1959].