TEMPLATE SYNTHESIS OF Zn(II), Cd(II) AND Pb(II) COMPLEXES WITH A 16-MEMBERED MACROCYCLIC LIGAND: DIBENZO(f,n)2,10-DIMETHYL-4,12-DIPHENYL-1,5,9,13-TETRAAZACYCLOHEXADECA[16]-1,4,9,12-TETRAENE

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ABSTRACT

Macrocyclic complexes of Zn(II), Cd(II) and Pb(II) possessing a general formulae $[MLX_2]$,(whereL=dibenzo(f,n)2,10-dimethyl-4,12-diphenyl-1,5,9,13-tetraazacyclohexadeca[16]-1,4,9,12- tetraene, M=Zn, Cd; X=NO_3, Cl, NCS, ClO_4, M=Pb; X=NCS, ClO_4.) have been synthesized by template method. The isolated complexes are characterized to be octahedral by elemental analyses, molecular weight, conductance data and spectral (IR and ^1H NMR) studies. The ligand coordinates through four azomethine nitrogen atoms bridged by ketonic moiety.

INTRODUCTION

Various metal cations have been used as template in the synthesis of complexes containing macrocyclic ligands with four nitrogen donor atoms[1-3]. Metallomacrocycles like metallocyanines and tetrabenzoporphyrins, besides their many possible applications as eg-dyes, pigments and catalysis have recently been investigated[4,5]. In this connection, much work in this field has resulted in substantial progress in the development of cyclization reactions usually involving metal ions, which has led to a variety of macrocyclic complexes[6-8]. Several tetraazamacrocyclic complexes have been synthesized by the reactions of α -or ß-diketones with aliphatic or aromatic diamines[9-12]. Thus, keeping in view the above aspects, a new series of the complexes of Zn(II), Cd(II) and Pb(II) with tetraazamacrocyclic ligand derived by 2:2 cyclocondensation of m-phenylenediamine with 1- phenyl-1,3-butanedione have been synthesized and characterized.

EXPERIMENTAL

Materials : All the metal salts used are of AR/GR grade. 1- Phenyl-1,3-butanedione and m-phenylenediamine were purified by recrystallization.

Measurements : Infrared spectra (KBr pellets) were recorded on a Perkin Elmer 577 spectrophotometer in the region 4000-200 cm^{-1} and ^1H NMR spectra on a Jeol Fx 90 Q spectrometer using TMS as internal reference. Molecular weights were determined on a Knauer Vapour pressure Osmometer in methanol solution. Conductance data (10^{-3}M solution) were evaluated on a Systronics digital conductivity meter 304.

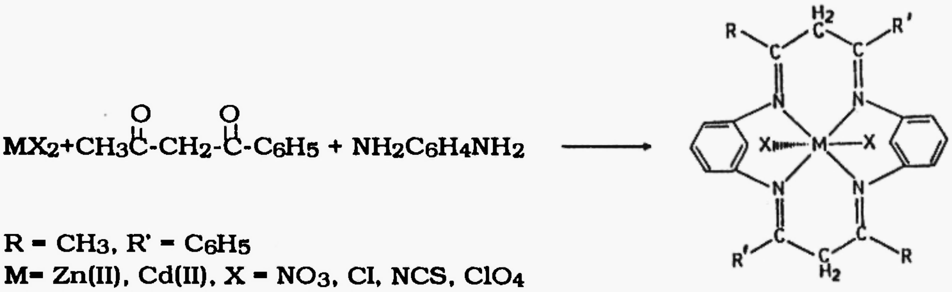
Analyses : Carbon and hydrogen were determined on a Coleman C,H Analyser 33. Nitrogen was determined by Kjeldahl's method. Chlorine was determined volumetrically by Vohlard's method. Metals were estimated by standard E.D.T.A. titrations using Xylenol orange as an indicator.

All the macrocyclic complexes have been synthesized by a similar route and hence, synthesis of only one representative compound is described below :

Synthesis : A solution of m-phenylenediamine (0.02 mol) in 25 ml methanol was mixed with 1-phenyl-1,3-butanedione (0.02 mol) in 20 ml methanol. To this mixture a methanolic solution of $Zn(NO_3)_2.6H_2O$ (0.01 mol) was added followed by the addition of 1 ml Conc. HCl with stirring. The reaction mixture was refluxed for 8 hrs when the colour of the solution intensified. The solvent was removed under reduced pressure and the solid product was washed with ether and dried in vacuo. These complexes have been recrystallized from methanol-ether (1:1) mixture.

RESULTS AND DISCUSSION

The macrocyclic complexes of Zn(II), Cd(II) and Pb(II) have been synthesized by the reaction of m-phenylenediamine and 1-phenyl- 1,3-butanedione in methanol as shown below :



$$MX_2 + CH_3\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_5 + NH_2C_6H_4NH_2 \longrightarrow$$

$R = CH_3$, $R' = C_6H_5$
M= Zn(II), Cd(II), X = NO_3, Cl, NCS, ClO_4
M = Pb; X = NCS, ClO_4

The elemental analyses of the complexes show 1:1 metal to ligand stoichiometry. The complexes are soluble in common organic solvents. The complexes do not melt but decompose on heating. The molar conductance of these complexes in CH_3CN indicate their nonelectrolytic behaviour[13] accordingly these complexes can be formulated as $[MLX_2]$ (where L = macrocyclic ligand; M = Zn(II), Cd(II); X = NO_3, Cl, NCS, ClO_4, M = Pb; X=NCS, ClO_4). Molecular weights of the complexes are consistent with the proposed formulae showing the monomeric nature.

IR spectra of all compounds do not show any band in the region 1700 cm^{-1} or 3330-3400 cm^{-1}, that could be assigned to unreacted C=O or $-NH_2$ groups. The complexes show strong absorption vibrations at 1610-1625 cm^{-1} which normally appear at higher wave number (20-30 cm^{-1}) in free ligand[14]. The lowering of this band suggests the coordination of azomethine nitrogens to the metal atom[15]. This is further supported by the presence of weak band at 450-480 cm^{-1} which can be assigned to ν M$\leftarrow$N vibration[16].

The absorptions associated with anions in these complexes are identified at 1260, 1020 and 840 cm^{-1} for nitrato groups, 280-310 cm^{-1} for chloro groups, 2110, 815 and 490 cm^{-1} for N-bonded thiocyanato groups and 1120, 1085 and 610 cm^{-1} for perchlorato groups. The new bands 230-250 cm^{-1} are assignable to ν M-O of nitrato group and 270-290 cm^{-1} assignable to ν M-NCS in the complexes.

The ^1H NMR spectra of the complexes for different protons are given in Table 1. In the spectrum of the complex $[ZnLCl_2]$, singlets due to methyl and methylene protons appear at δ 2.14 ppm (6H) and δ 4.36 ppm (4H), while phenyl protons are merged with (C_6H_4) protons and give a complex pattern in the region δ 6.88- 7.46 ppm (18H). The disappearance of $-NH_2$ protons in these spectra suggest the macrocyclic ring formation via C=N linkage. The shift of the signals towards low field as compared to the free ligand is indicative of the coordination of macrocycles to the metal atom.

Table 1. ^1H NMR Spectral Data (δ ,ppm) of the Macrocyclic Complexes of Zn(II), Cd(II), and Pb(II).

S.No.	Compounds	$-CH_3$	$-CH_2-$	$-C_6H_5+m-C_6H_4-$
1.	$[ZnLCl_2]$	2.14s	4.36s	6.88-7.46cp
2.	$[ZnL(NO_3)_2]$	2.08s	4.44s	6.72-7.48cp
3.	$[ZnL(NCS)_2]$	2.08s	4.32s	6.92-7.78cp
4.	$[ZnL(ClO_4)_2]$	2.10s	4.36s	6.90-7.38cp
5.	$[CdLCl_2]$	2.10s	4.40s	6.88-7.50cp
6.	$[CdL(NO_3)_2]$	2.12s	4.42s	6.94-7.54cp
7.	$[CdL(NCS)_2]$	2.18s	4.36s	6.86-7.46cp
8.	$[CdL(ClO_4)_2]$	2.12s	4.34s	6.96-7.48cp
9.	$[PbL(NCS)_2]$	2.14s	4.44s	6.92-7.50cp
10.	$[PbL(ClO_4)_2]$	2.08s	4.40s	6.82-7.42cp

s = singlet, cp = complex pattern

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