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Synthesis and Physico-chemical Properties of Some Complexes of Tetradentate Macrocycles with Cd, Hg and Pb

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The reaction of 3,6-diaza-1,8-diaminooctane with α-diketones *viz.*, 2,3-butanedione, 2,3-pentanedione, 3,4-hexanedione or benzil in the presence of metal salts of Cd(II), Hg(II) and Pb(II) affords complexes of the type [MLX]X (M = Cd(II); X = NO_3, M = Pb; X = ClO_4) and [MLX_2] (M = Cd(II), Hg(II); X = Cl). Elemental analyses, molar conductivity, molecular weight determination and spectra (IR and ^1H NMR) have been used to characterize the structure of the isolated solid complexes. These studies suggest the coordination number five for Cd(II) and Pb(II) and six for Cd(II) and Hg(II).

INTRODUCTION

A wide variety of azamacrocyclic complexes has been formed by condesation reactions in the presence of metal ions. Macrocyclic complexes of transition metals containing α-diimines have been prepared by condensation of 2,3-butanedione and NN′-bis(3-aminopropyl) ethylenediamine[1, 2]. In our previous communication we have reported tetraazamacrocyclic complexes of Cd(II), Hg(II) and Pb(II)[3–5], which reflects the controlling influence of metal ion in a particular synthesis. In this paper we report the synthesis and characterization of Cd(II), Hg(II) and Pb(II) complexes of the macrocycle 2,3-dimethyl-1,4,7,10-tetraazacyclododeca-1,3-diene and their derivatives.

EXPERIMENTAL

Analytical and physical techniques are reported in earlier papers[3, 4].

Synthesis

To the n-butanolic solution of $Cd(NO_3)_2 \cdot 4H_2O$ (4.0 mmol in 20 mL), a solution of 2,3-butanedione (4.0 mmol in 10 mL n-butanol) was added. 3,6-Diaza-1,8-diaminooctane (4.0 mmol in 20 mL n-butanol) was added dropwise with constant stirring. A solid appeared during the addition of the diamine and the stirring was continued for 7 h. The resulting solid was filtered washed with cold methanol and dried *in vacuo*.

Similarly the complexes of other derivatives have been prepared by the same procedure.

RESULTS AND DISCUSSION

The analytical data of all the complexes correspond to the formulae [MLX]X where M = Cd; X = NO_3^- (compounds 1–4), M = Pb; X = ClO_4^- (compounds 13–16) and [MLX_2] where M = Cd, Hg; X = Cl^- (compounds 5–12) (L = macrocycles derived from 3,6-diaza-1,8-diaminooctane and α-diketone, *viz.*, 2,3-butanedione, 2,3-pentanedione, 3,4-hexanedione or benzil). All the complexes are coloured solids decomposing on heating to about 248°C, soluble in dimethylsulphoxide and insoluble in all organic solvents. Molecular weights of all the complexes are consistent with the proposed formulae weights indicating their monomeric nature. The molar conductances of Cd(II) and Hg(II) complexes measured in dimethylsulphoxide show that the complexes are non-electrolytes except those of Cd(II) and Pb(II) which are 2:1 electrolyte[6], but IR spectral data suggest that one nitrate or perchlorate is coordinated and that the other is ionic. The coordinated anion is dissociated in solution giving a 2:1 electrolytic behaviour[7, 8].

In general, the spectra of these complexes are identical with those of Co(III) and Ni(II) derivatives[1, 2] and strongly suggest of the cyclic nature of the ligand. A strong band at 1640–1570 cm^{-1} may be assigned to ν(C=N) vibrations. A characteristic sharp band at 1180 cm^{-1} is due to the ligand framework[1]. The additional bands attributable to the functional groups in the macrocyclic complexes such as absorption due to the benzene ring and out of plane bending of phenyl groups are observed[5] at 1570–1460 cm^{-1} and 740–710 cm^{-1}. The N—H stretching modes of the secondary amine groups are generally seen as sharp single band at 3230–3210 cm^{-1}, except in the case of nitrato complexes, where the band is somewhat broader and shifted to lower region (3150–3130 cm^{-1}) possibly as a consequence of hydrogen bonding to the axial nitrato group. In nitrato complexes of Cd(II), the spectra show some new bands at 1270–1260 cm^{-1}, 1025–1010 cm^{-1} and 880–860 cm^{-1} which may be assigned to a monodentate nitrate group[7] and 1385, 830 and 740 cm^{-1} due to ionic nitrate. In the spectra of chloro complexes of Cd(II) and Hg(II) bands in the region 290–260 cm^{-1} and 300–270 cm^{-1} are assigned to ν(Cd—Cl) or ν(Hg—Cl) respectively. Bands in the region 250–230 cm^{-1} are due to ν(Cd—O) of nitrate group. The appearance of bands in the region 460–360 cm^{-1} implies M ← N (azomethine) vibrational modes and confirms the involvement of azomethine nitrogen. Perchlorato complexes of Pb(II) show vibrations at *ca.* 1125, 1095, 1065 for unidentate and 610 cm^{-1} ionic perchlorate.

The proton magnetic resonance spectra of all the complexes are consistent with the spectra of [Co(2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene)Br_2]Br [1]. Peak position and assignments are given in Table 1. In the ^1H NMR spectrum of ligand L^1 methyl protons are observed as a singlet at δ1.46 ppm, while in the complex [CdL^1NO_3]NO_3 these protons are observed at δ1.28 ppm. The ligand L^2 exhibit methyl protons at δ2.35 ppm as a singlet and methyl and methylene protons of ethyl groups show a triplet at δ1.06 ppm and quartet at δ2.74 ppm. In the complex [CdL^2NO_3]NO_3, methyl protons at δ2.10 ppm (singlet) and methyl and methylene protons of ethyl group are observed at δ1.08 ppm (triplet) and δ2.34 ppm (quartet). In the ligand L^3, methyl and methylene protons of ethyl group are observed at δ1.10 ppm and δ2.74 ppm. In the complex $[CdL^3NO_3]NO_3$, methyl and methylene protons are observed at δ0.98 ppm (triplet) and δ2.38 ppm (quartet). In the free ligand L^4, phenyl protons give a complex pattern at δ7.20–7.60 ppm while in the complex $[CdL^4NO_3]NO_3$ these protons give a complex pattern at δ7.75–8.16 ppm. The shift in the positions of these signals and the slight overlapping of phenyl protons are due to the coordination from the adjacent nitrogen atom.

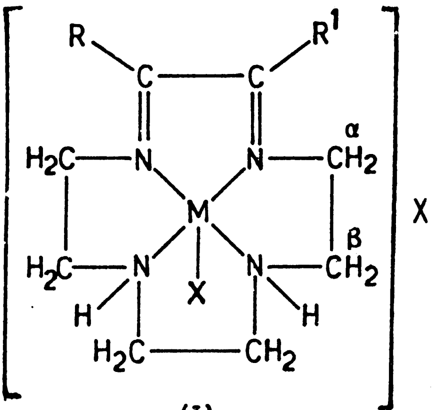
TABLE-1

^{1}H NMR DATA (δ, ppm) OF THE COMPLEXES

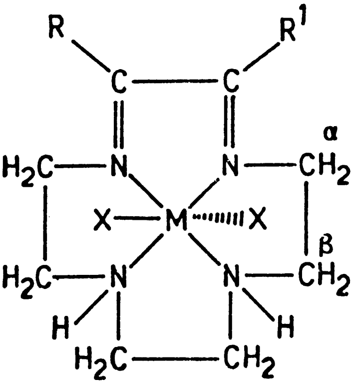
S. No.	Compounds	—CH_3	Ethyl protons		α—CH_2	β—CH_2	—C_6H_5
			—CH_3	—CH_2—			
1.	$[CdL^1NO_3]NO_3$	1.28 s	—	—	3.13 t	1.71 b	—
2.	$[CdL^2NO_3]NO_3$	1.92 s	1.02 t	2.46 q	3.10 t	1.68 m	—
3.	$[CdL^3NO_3]NO_3$	—	0.98 t	2.38 q	2.94 t	1.56 m	—
4.	$[CdL^4NO_3]NO_3$	—	—	—	2.98 b	1.68 m	7.75–8.16 m
5.	$[CdL^1Cl_2]$	0.89 s	—	—	2.81 t	1.36 b	—
6.	$[CdL^2Cl_2]$	1.98 s	0.98 t	2.42 q	2.94 t	1.46 b	—
7.	$[CdL^3Cl_2]$	—	1.05 t	2.48 q	2.78 b	1.54 b	—
8.	$[CdL^4Cl_2]$	—	—	—	2.88 t	1.64 b	7.79–8.35 m
9.	$[HgL^1Cl_2]$	1.12 s	—	—	2.81 t	1.65 b	—
10.	$[HgL^2Cl_2]$	2.14 s	1.02 t	2.36 q	2.99 b	1.38 b	—
11.	$[HgL^3Cl_2]$	—	1.04 t	2.48 q	2.89 b	1.46 b	—
12.	$[HgL^4Cl_2]$	—	—	—	2.48 t	1.68 b	7.48–7.98 m
13.	$[PbL^1ClO_4]ClO_4$	1.02 s	—	—	2.84 t	1.50 b	—
14.	$[PbL^2ClO_4]ClO_4$	1.92 s	1.05 t	2.52 q	2.93 t	1.60 b	—
15.	$[PbL^3ClO_4]ClO_4$	—	1.02 t	2.54 q	2.81 t	1.56 b	—
16.	$[PbL^4ClO_4]ClO_4$	—	—	—	3.06 t	1.58 b	7.28–7.68 m

s = singlet, t = triplet, q = quartet, b = broad, m = complex pattern

Thus it is concluded that ligands L^1, L^2, L^3 and L^4 encircle the metal ion through their two azomethines, two secondary amino groups and anions which occupy axial positions suggesting five or six coordinated structures (I and II).



(I)



(II)

M = Cd, X = NO_3, M = Pb, X = ClO_4, M = Cd, Hg; X = Cl

	L^1	L^2	L^3	L^4
R	CH_3	CH_3	C_2H_5	C_6H_5
R^1	CH_3	C_2H_5	C_2H_5	C_6H_5

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