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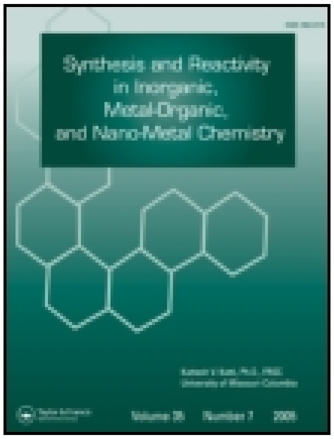

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF BIVALENT LEAD MACROCYCLIC COMPLEXES

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SYNTHESIS AND SPECTROSCOPIC CHARACTERIZATION OF BIVALENT LEAD MACROCYCLIC COMPLEXES

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ABSTRACT

Lead(II) macrocyclic complexes of some 12- and 13-membered tetraazamacrocycles have been synthesized by the template process using bis(benzil)ethylenediamine as precursor. The change in ring size has been achieved solely by varying the number of methylene carbon that link adjacent benzil nitrogen atoms. Bis(benzil)ethylenediamine (L) reacts with $PbCl_2$ or $Pb(OAc)_2$ and primary diamines, *i.e.*, 1,2-diaminoethane (1,2-en) or 1,3-diaminopropane (1,3-pn) in a 1:1:1 molar ratio in methanol to give several solid complexes of the general composition $[Pb(L)X_2]$ ($L =$ macrocyclic ligand, $X =$ Cl or OAc). The precursor and the metal complexes of the macrocycles have been characterized by elemental analyses,

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molecular weight determinations, molar conductances, IR, ^{1}H NMR, ^{13}C NMR, electronic and mass spectral studies. On the basis of the IR and NMR spectral data the involvement of amido nitrogen in coordination to the central metal ion has been confirmed. An octahedral geometry around the metal ion is suggested for the complexes. Based on molecular weights and conductivity measurements, their monomeric and non-electrolytic nature has been confirmed.

INTRODUCTION

The coordination chemistry of lead(II) with macrocyclic ligands has been investigated in the past decade, although not extensively. The coordination chemistry of macrocyclic ligands is a fascinating area which has attracted the attention of many inorganic chemists. Macrocyclic ligands form stable complexes with lanthanides and they serve as a springboard to explore the coordination chemistry of these metal ions[1]. Tetraazamacrocycles and their metal complexes have been studied extensively in connection with their resemblance to naturally occuring porphyrins. Saturated macrocycles with various numbers of ring members have been synthesized regularly. These compounds have produced interesting information concerning both the stabilities and structures of their metal complexes[2].

The novel approach to macrocyclic synthesis, therefore, overcomes the usual limitations of the more traditional template routes where the metal tends to be ''locked'' into the macrocycle with demetallation often resulting in decomposition[3]. The influence of variation of the structural feature on metal complexation, namely the length of the alkyl bridge linking the benzil nitrogen atoms, was investigated[4]. Increasing the length of this bridge is expected to increase the ''lopsidedness'' of the N_4-donor set. In this way, it was intended not only to increase the available macrocyclic cavity size, but also to introduce increasing ''lopsidedness'' into the larger members of this series. The use of metal ions as templates in such reactions has led to the synthesis of many metal complexes of macrocyclic ligands[5]. These ligands display a number of features of chemical interest. They are relatively rigid in nature and thus impose a specific coordination geometry on the metal ion[6]. The catalytic activity of vitamin B_{12} is in part due to the presence of an unsymmetrical and flexible equatorial ligand system[7]. An iron(III) macrocyclic complex as a model system for catalase has been reported[8]. This report shows that iron(III) macrocyclic system can function as substitute for catalase. A large number of enzymes requiring two or more metal ions for activity have been discovered and many of these appear to owe their catalytic activity to finely balanced metal-metal interactions[9].

In this paper, we report the synthesis and characterization of new lead(II) complexes of twelve- and thirteen-membered tetraazamacrocycles from the reaction of bis(benzil)ethylenediamine with aliphatic diamines, which show the marked effect of any build-up of ligand strain on the coordination geometry of the central metal.

EXPERIMENTAL

Materials and Methods

Melting points were determined in capillary tubes and are uncorrected. All solvents used were of high purity and were distilled in the laboratory before use. Moisture was excluded from the glass apparatus using $CaCl_2$ drying tubes. $PbCl_2$, $Pb(OOCCH_3)_2$ (BDH) and the primary diamines, *i.e.*, 1,2-diaminoethane and 1,3-diaminopropane were used as obtained from E. Merck.

Conductivity measurements were made with a Systronic model 305 conductivity bridge in dry dimethylformamide. Molecular weights were determined by the Rast camphor method. IR spectra of the solid samples were recorded as KBr discs on a Nicolet Megna FTIR 550 spectrophotometer in the range 4000–200 cm^{-1}. ^1H NMR spectra were recorded on a Jeol FX 90Q spectrometer in DMSO-d_6 using TMS as the internal standard. Chemical shifts are reported in ppm units. ^{13}C NMR spectra were recorded in methanol using TMS as the internal reference. Electronic spectra were recorded on a Hitachi U-2000 spectrophotometer. Nitrogen and chlorine were determined by Kjeldahl's or Volhard's method, respectively. Carbon and hydrogen analyses were performed at the Central Drug Research Institute, Lucknow, India. Lead was determined gravimetrically as lead sulphate.

Synthesis of Bis(benzil)ethylenediamine

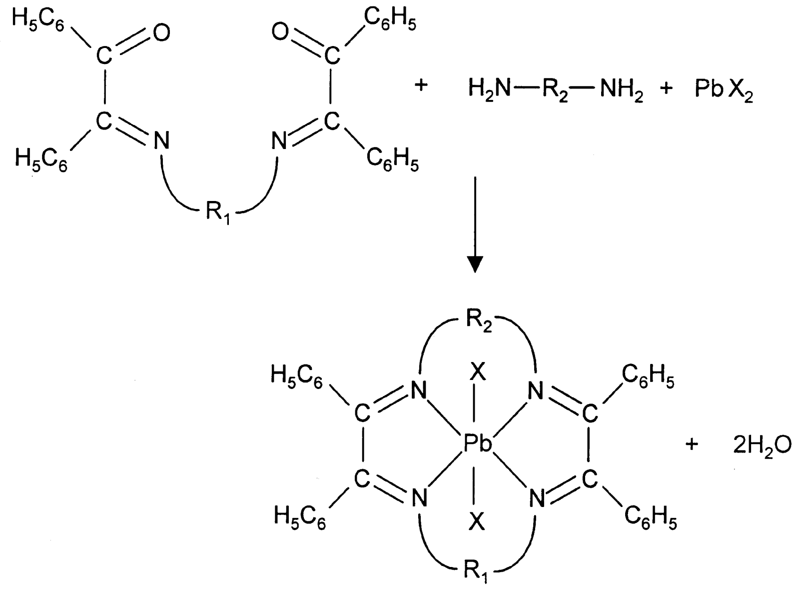
In a 100 mL short-necked round bottom flask, an ethanolic solution of benzil (5 g, 24 mmol) was added to a solution of 1,2-diaminoethane (0.80 mL, 12 mmol) in 15 mL of ethanol and the reaction mixture was refluxed for 8 h. After reducing the solvent to 1/2 of its original volume on a ratio head, the solution was cooled and the reddish yellow crystalline compound thus obtained was recrystallized from ethanol, m.p., 86–89 °C; yield, 3.7341 g (70%).

Synthesis of the Complexes

The reaction was carried out in 1:1:1 molar ratio by combining bis-(benzil)ethylenediamine (0.7818 g, 1.75 mmol or 0.7557 g, 1.70 mmol), 1,2-diaminoethane (0.1057 g, 1.75 mmol or 0.1022 g, 1.70 mmol) and $PbCl_2$ or $Pb(OAc)_2$ (0.4891 g, 1.75 mmol or 0.6449 g, 1.70 mmol) in methanol (25 mL). The mixture was heated under reflux for 5–6 h. The solution was cooled and transferred to an evaporating dish and set aside overnight at room temperature. The solid product that separated out was collected, washed with hot water, then with cold methanol and dried under *vacuo*. The complexes were recrystallized from a 1:1 solution of methanol and benzene; yields, 52–64%.

RESULTS AND DISCUSSION

The template condensation of bis(benzil)ethylenediamine and 1,2-diaminoethane or 1,3-diaminopropane in the presence of $PbCl_2$ or $Pb(OOCCH_3)_2$ produced a new series of 12- and 13-membered tetraazamacrocyclic metal complexes of the types $Pb(L^1)X_2$ and $Pb(L^2)X_2$ as shown in Eq. (1).



(1)

L^1: $R_1 = C_2H_4$; $R_2 = C_2H_4$,
L^2: $R_1 = C_2H_4$; $R_2 = 1,3\text{-}C_3H_6$ and $X = Cl$ or OAc

The resulting metal derivatives are coloured solids which are stable at room temperature and are non-hygroscopic. The monomeric nature of these complexes is confirmed by molecular weight determinations. All the complexes are slightly soluble in methanol or ethanol but soluble in DMF and DMSO. The molar conductance of 10^{-3} M solutions for all the complexes in anhydrous DMF is in the range 15–20 $\text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ indicating their non-ionic nature. The analytical results of the isolated solid complexes, their colours and melting points are given in Table I.

The mode of bonding in these macrocyclic complexes is proposed on the basis of infrared, electronic, ^{1}H NMR, ^{13}C NMR and mass spectral evidence.

IR Spectra

The infrared spectra of the ligand $C_{30}H_{24}N_2O_2$ and the metal complexes show the absence of uncondensed functional groups (NH_2 and C=O), stretching modes of starting material and the appearance of bands characteristic of the imine group[10]. The bands characteristic of the benzil moiety appeared in all the complexes at 1477–1498 cm^{-1} ($\nu_{\text{asym}}C_6H_5$) and 1373–1392 cm^{-1} ($\nu_{\text{asym}}C_6H_5$). The major changes observed in the IR spectra of the macrocyclic complexes are the absence of stretching and deformation vibrations of NH_2 groups, indicating their deprotonation and the appearance of strong bands due to coordinated ν(C=N) vibrations[11] in the range 1626–1605 cm^{-1}. Strong and sharp bands for C-H stretching and bending vibrations appear at *ca.* 2810 and 1404 cm^{-1}, respectively[10]. In the IR spectra ν_{sym}(OCO) appears at 1370 cm^{-1} and ν_{asym}(OCO) together with the imine ν(C=N) as an intense broad absorption band in the region 1605–1626 cm^{-1}. Such widely spaced acetate bands are consistent with the monodentate coordination proposed in the metal complexes $Pb(L^1)(OAc)_2$ and $Pb(L^2)(OAc)_2$. The presence of new bands in the spectra of the metal complexes in the far-IR region at 430–475 cm^{-1} due to the ν(Pb-N) vibration supports the coordination of the imine nitrogen to the metal ion[12].

Electronic Spectra

The electronic spectra of bis(benzil)ethylenediamine and its derivatives have been recorded on a Hitachi U-2000 spectrophotometer. The absorption maximum at 400 nm ($\varepsilon = 148\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}$) in the case of bis(benzil)-ethylenediamine may be assigned to the n-π* transition of the azomethine

Table I. Physical Characteristics and Analytical Data of the Precursor and the Metal Complexes of the Macrocycles

					Analysis %					
Metal Salt (g)	(L) (g)	Diamines (g)	Compound, Empirical Formula and Yield (%)	Colour and M.p. (°C)	C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	Pb Found (Calcd.)	Cl Found (Calcd.)	Mol. Wt. Found (Calcd.)
–	$C_{30}H_{24}N_2O_2$	–	70	Reddish Yellow 86–89	80.76 (81.15)	5.32 (5.44)	5.92 (6.30)	–	–	412 (444)
$PbCl_2$ (0.4891)	$C_{30}H_{24}N_2O_2$ (0.7818)	1,2-en (0.1057)	$[Pb(L^1)Cl_2]$ $C_{32}H_{28}N_4Cl_2Pb$ 58	Light Brown 124	51.04 (51.45)	3.67 (3.78)	7.08 (7.50)	27.31 (27.74)	9.05 (9.49)	775 (747)
$PbCl_2$ (0.4413)	$C_{30}H_{24}N_2O_2$ (0.7054)	1,3-pn (0.1176)	$[Pb(L^2)Cl_2]$ $C_{33}H_{30}N_4Cl_2Pb$ 64	yellow 112	51.70 (52.08)	3.88 (3.97)	6.97 (7.36)	26.75 (27.23)	8.33 (8.82)	740 (761)
$Pb(OAc)_2$ (0.6449)	$C_{30}H_{24}N_2O_2$ (0.7557)	1,2-en (0.1022)	$[Pb(L^1)(OAc)_2]$ $C_{36}H_{34}N_4O_4Pb$ 61	Peach 122	54.03 (54.46)	4.20 (4.32)	6.62 (7.06)	25.69 (26.10)	–	763 (794)
$Pb(OAc)_2$ (0.6320)	$C_{30}H_{24}N_2O_2$ (0.7406)	1,3-pn (0.1235)	$[Pb(L^2)(OAc)_2]$ $C_{37}H_{36}N_4O_4Pb$ 52	Cream 115	54.61 (55.00)	4.39 (4.49)	6.53 (6.93)	25.19 (25.64)	–	827 (808)

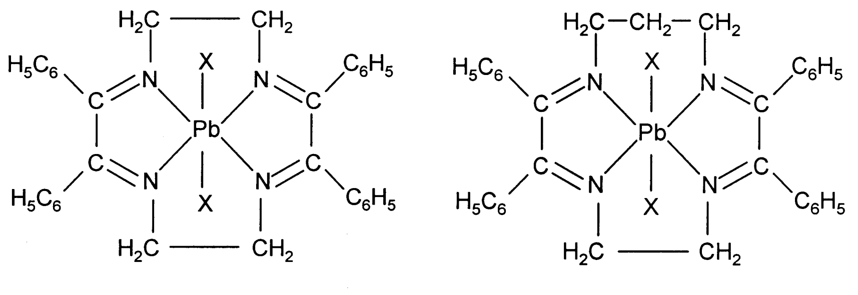
Table II. ^{1}H NMR Spectral Data (δ, ppm) of the Precursor and the Metal Complexes of the Macrocycles

Compound	$-NCH_2$ (bs)	$-NCH_2$ (t)	$OOCCH_3$	Aromatic Protons 2	3	4
$C_{30}H_{24}N_2O_2$ (L)	3.12	–	–	8.00 (d)	7.36 (dd)	7.65 (d)
$[Pb(L^1)Cl_2]$	3.52	–	–	8.11 (d)	7.32 (dd)	7.58 (d)
$[Pb(L^2)Cl_2]$	–	3.46	–	8.02 (d)	7.28 (dd)	7.49 (d)
$[Pb(L^1)(OAc)_2]$	3.61	–	1.32	8.24 (d)	7.31 (dd)	7.86 (d)
$[Pb(L^2)(OAc)_2]$	–	3.57	1.18	8.35 (d)	7.38 (dd)	7.60 (d)

group. The shift of this band (*ca.* 15 nm) in the spectra of the complexes indicated the coordination of the nitrogen to the metal atom[13,14]. In addition to this band, the spectra of the metal complexes exhibit bands around 275 nm ($\varepsilon = 703\,dm^3\,mol^{-1}\,cm^{-1}$) and 326 nm ($\varepsilon = 1366\,dm^3\,mol^{-1}\,cm^{-1}$) due to π-π^* electronic transitions. However, the position of these bands remains almost unchanged on complexation.

^{1}H NMR Spectra

The bonding pattern in the resulting complexes has been further substantiated by the proton magnetic resonance spectra of the precursor and the metal complexes of the macrocycles (Table II). The ^{1}H NMR spectra of the complexes do not show any signal corresponding to primary amino protons. This suggested that the proposed macrocyclic skeleton has been formed. A singlet observed at δ 3.52–3.61 ppm in the complexes $[Pb(L^1)Cl_2]$ and $[Pb(L^1)(OAc)_2]$ and a triplet observed at δ 3.46–3.57 ppm in $[Pb(L^2)Cl_2]$ and $[Pb(L^2)(OAc)_2]$ complexes may be assigned to methylene protons adjacent to the nitrogen atoms, respectively. The shift of the signals towards lower field is an indication of the coordination of the macrocycles. In case of unsymmetrical chelates, a multiplet in the region δ 2.19–2.24 ppm is assigned as the middle methylene protons of the 1,3-diaminopropane moiety. The multiplet of aromatic protons was observed at δ 7.28–8.35 ppm in the spectra of the precursor and the metal complexes of the macrocycles. The ^{1}H NMR spectra of the complexes with acetate groups in DMSO-d_6 show a proton resonance in the region δ 1.18–1.32 ppm and the ^{13}C NMR spectra in DMSO show an acetate-methyl resonance at 20.3–21.7 ppm. A carboxylate resonance at 169.2–170.6 ppm is consistent with the structure of the complexes $[Pb(L^1)(OAc)_2]$ and $[Pb(L^2)(OAc)_2]$ shown in Figure 1.



Complex with L^1 Complex with L^2

Figure 1. Suggested structures of the complexes.

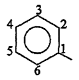
The ^{13}C NMR spectral data of the precursor and the metal complexes of the macrocycles (Table III) also support the formation of these complexes and the formulation of the macrocyclic ring structure. Similar synthetic work in case of metal complexes have also been reported by other workers[15–17].

Mass Spectra

The FAB mass spectrum of one of the lead complexes, $[Pb(L^1)(OAc)_2]$, was recorded on a Jeol SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 KV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectrum was recorded at room temperature (34°C). *m*-Nitrobenzyl alcohol (NBA) was used as matrix. In the mass spectrum, the molecular ion peak of the complex $[Pb(C_{32}H_{28}N_4)(OOCCH_3)_2]$ appeared at *m/z* 794 $[M]^+$, 796 $(M+2]^+$ and 798 $[M+4]^+$. Some other peaks appeared at *m/z* 469, 588, 616, 679, 716 and 766 corresponding to the $[C_{32}H_{28}N_4]^+$, $[Pb(C_{18}H_{18}N_2)(OOCCH_3)_2]^+$, $[Pb(C_{18}H_{18}N_4)(OOCCH_3)_2]^+$, $[Pb(C_{30}H_{24}N_2)(OOCCH_3)]^+$, $[Pb(C_{26}H_{23}N_4)\text{-}(OOCCH_3)_2]^+$ and $[Pb(C_{30}H_{26}N_4)\text{-}(OOCCH_3)_2]^+$species, respectively, which resulted from the loss of the $Pb(OOCCH_3)_2$, $C_{14}H_{10}N_2$, $C_{14}H_{10}$, $C_4H_7N_2O_2$, C_6H_5 and C_2H_4 fragments, respectively, from the parent compound. Two peaks at *m/z* 676 and 735 are due to the loss of two and one acetate ions, respectively. Lead occurs in several isotopic forms and out of these, four having the mass numbers 204, 206, 207 and 208 are important. The last isotope is, however, the most abundant one (52.3%). In the mass spectra, a particular ion consisting of lead shows the expected combination of peaks corresponding to the various isotopes of lead. The molecular ion peak of $[Pb(C_{32}H_{28}N_4)(OOCCH_3)_2]$

Table III. ^{13}C NMR Spectral Data (δ, ppm) of the Precursor and the Metal Complexes of the Macrocycles

	Chemical Shift Values						
Compound	$>C{=}O$	$>C{=}N$	$-CH_2-N<$	$-CH_2-$	$OOCCH_3$	OOC	Aromatic Carbons
$C_{30}H_{24}N_2O_2$ (L)	176.62	160.92	42.37	–	–	–	C_1, 128.61; C_2, 127.20; C_3, 126.77; C_4, 126.12
$[Pb(L^1)Cl_2]$	–	159.76	46.16	–	–	–	C_1, 131.65; C_2, 129.33; C_3, 128.44; C_4, 126.32
$[Pb(L^2)Cl_2]$	–	159.13	45.68	33.53	–	–	C_1, 127.88; C_2, 125.58; C_3, 126.03; C_4, 125.84
$[Pb(L^1)(OAc)_2]$	–	154.34	43.52	–	21.7	170.6	C_1, 128.32; C_2, 128.10; C_3, 127.45; C_4, 126.66
$[Pb(L^2)(OAc)_2]$	–	153.82	42.47	34.16	20.3	169.2	C_1, 129.31; C_2, 127.48; C_3, 127.08; C_4, 128.37



is obtained at m/z 794 (calcd. on the basis of ^{208}Pb) and peaks at 793, 792 and 790 are also observed having the expected abundances.

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