

Synthesis and Characterization of Pb(II) Complexes of Macrocycles Derived from 2,3-Butanedione or Benzil and 1,*n*-Diaminoalkanes

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2,2-Cyclocondensation of 2,3-butanedione or benzil with 1,*n*-diaminoalkanes viz. 1,2-diaminoethane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane, 1,12-diaminododecane in the presence of $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ resulted in the formation of a new class of tetraazamacrocyclic complexes. The use of Pb^{2+} as a template agent gave only the mononuclear macrocyclic complexes of the type $[\text{PbLClO}_4]\text{ClO}_4$ under all conditions investigated. These were characterized by elemental analyses, conductivity measurements and spectral studies.

INTRODUCTION

The work of Curtis *et al.*¹ produced the first of many new tetraazamacrocyclic ligands especially with the hexamethyltetraazacyclotetradecadienes. Tetramine Schiff base macrocycles have generally been synthesized, as their metal complexes, through the 2,2-cyclocondensation of heterocyclic dicarbonyls and 1,*n*-diaminoalkanes, have proved to be versatile ligands for both mono and binuclear metal complexes². Complexes of the macrocyclic ligand TIM were originally prepared by Baldwin and Rose *via* a template synthesis in which 1,3-diaminopropane hydrochloride and 2,3-butanedione were allowed to react together followed by addition of metal salts of Ni³, Co⁴⁻⁶ and Fe^{7,8}. 14 to 16 Membered saturated tetraazamacrocyclic complexes of Pb(II) have been reported in literature^{9,10}. Fenton *et al.*¹¹ have synthesized hexaazamacrocyclic complexes of Pb(II) derived from 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane. Mononuclear Ba(II) and Pb(II) complexes of tetramine Schiff base macrocycles derived from the condensation of heterocyclic dicarboxyl 2,6-diacetylpyridine or furan 2,5-dicarbaldehyde and 1,*n*-diamino-*n*'-hydroxyalkanes (1,3-diamino-2-hydroxypropane, 1,4-diamino-2-hydroxybutane and 1,5-diamino-3-hydroxy pentane) are reported¹². In our previous papers we have reported a large number of tetraazamacrocyclic complexes having very large rings around Zn^{13,14}, Cd¹⁵, Hg¹⁶ and Pb¹⁷. In this paper we report the use of Pb cation as a template agent in the synthesis of macrocyclic Schiff base complexes. Mononuclear macrocyclic complexes of Pb are of great interest, because Pb cation combined with the potentially stereochemically active lone pair of electrons might give rise to unusual geometries. The later prospect is exemplified in the synthesis of mononuclear Pb(II) complexes reported herein.

EXPERIMENTAL

$\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ was prepared by the same procedure as reported¹⁸. 2,3-Butanedione (Fluka), 1,2-diaminoethane (BDH), 1,3-diaminopropane (E. Merck), 1,4-diaminobutane (Fluka) and 1,6-diaminohexane (E. Merck) were purified by distillation. Benzil was recrystallised from methanol. 1,8-Diaminooctane (Fluka) and 1,12-diaminododecane (Fluka) were used as supplied.

Nitrogen was determined by Kjeldahl's method and Pb was estimated volumetrically using E.D.T.A. and xylenol orange as indicator. Conductance of 10^{-3} M solutions was measured in dimethyl sulphoxide by Systronics Conductivity Meter 304 having a cell constant 1.0. IR spectra were recorded as KBr pellets in the region $200\text{--}4000\text{ cm}^{-1}$ on a Perkin Elmer 577 Grating IR Spectrophotometer and ^1H NMR spectra were recorded in DMSO-d_6 on a Jeol FX 90Q FT NMR spectrometer at 90 MHz using TMS as internal reference.

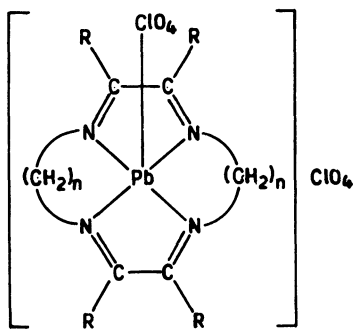
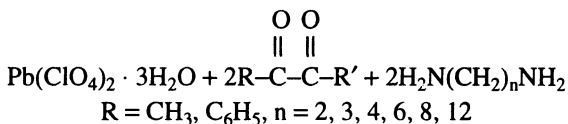
Synthesis

$\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (1 mmol) was dissolved in 20 mL hot methanol with stirring. 2,3-Butanedione (2 mmol) or benzil (2 mmol) in 10 mL methanol was added. To this yellow solution, 1,2-diaminoethane (2 mmol) was added dropwise with constant stirring. Precipitate occurred immediately. It was stirred for 6–12 h at 60°C . The resulting solid was filtered, washed with cold methanol and dried *in vacuo*.

Similarly complexes of higher diamines have been prepared.

RESULTS AND DISCUSSION

Tetraazamacrocyclic complexes of Pb(II) have been synthesized by the reaction of α -diketones and 1,*n*-diaminoalkanes according to the following scheme:



The analytical data (Table 1) show that in case of the metal ion only one molecule of ligand is coordinated. All the complexes are coloured solids and are soluble in dimethyl sulphoxide and insoluble in most of the organic solvents. The molar conductances in DMSO are in the usual range of 2 : 1 electrolytes¹⁹. But from IR spectra it is evident that one perchlorate is ionic and other is coordinated suggesting that coordinated perchlorate group is dissociated in solution giving 1 : 1

electrolytic behaviour. The formation of macrocyclic complexes has generally been related with the size of the metal ions and cavity of the macrocycles and it has been argued that stable complexes are formed only when the size of the metal ion matches with the size of macrocyclic cavity. Pb^{2+} being of larger size can conveniently fit in the larger ring macrocycles giving stable complexes. In case of smaller ring macrocycles (e.g., 12-membered) the size of the cavity is small in comparison to the size of metal ion and hence metal atom sits a top and not inside the macrocyclic cavity. Macrocycles with slightly larger cavities (14 to 16-membered) can accommodate the metal ion which is of proper size. In case of the macrocycles with very large rings (20 to 32 membered) there is a greater flexibility due to which they can provide cavity of appropriate size to fit the metal ion. This type of condensation results in the formation of the macrocyclic ligands which completely encircle the metal ion through its four azomethine nitrogen atoms. The metal ion on the other hand acts a template directing the steric course of reaction in the above manner and a completely closed ring structure results around the metal ion.

TABLE I
ANALYTICAL AND PHYSICAL DATA OF THE TETRAAZAMACROCYCLIC
COMPLEXES OF LEAD(II)

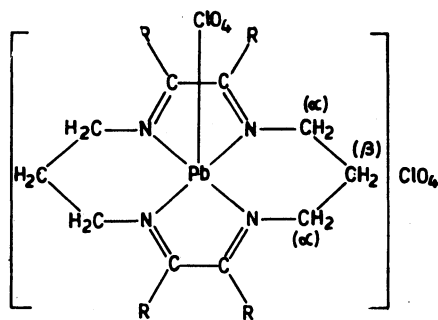
S. No.	Compounds/Colour and decomp. temp. (°C)	Yield (%)	Analyses (%) Found(Calcd.)		Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
			N	Pb	
1.	[(Me ₄ [12]tetraeneN ₄)PbClO ₄]ClO ₄ (Brown, 134)	42	8.54 (8.94)	32.65 (33.08)	82
2.	[(Me ₄ [14]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 145)	54	8.37 (8.56)	31.34 (31.66)	95
3.	[(Me ₄ [16]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 160)	51	7.93 (8.21)	30.15 (30.36)	98
4.	[(Me ₄ [20]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 190)	58	7.30 (7.58)	27.90 (28.05)	87
5.	[(Me ₄ [24]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 200)	60	6.81 (7.05)	25.81 (26.07)	*
6.	[(Me ₄ [32]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 180)	61	6.97 (6.31)	23.20 (23.36)	*
7.	[(Ph ₄ [12]tetraeneN ₄)PbClO ₄]ClO ₄ (Orange, 160)	32	6.19 (6.40)	23.21 (23.69)	75
8.	[(Ph ₄ [14]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 175)	45	6.04 (6.21)	22.75 (22.95)	83
9.	[(Ph ₄ [16]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 178)	42	5.76 (6.02)	22.10 (22.26)	85
10.	[(Ph ₄ [20]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 198)	55	5.40 (5.68)	20.76 (20.99)	83
11.	[(Ph ₄ [24]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 168)	29	5.16 (5.37)	19.73 (19.86)	*
12.	[(Ph ₄ [32]tetraeneN ₄)PbClO ₄]ClO ₄ (Yellow, 186)	38	4.48 (4.85)	17.68 (17.93)	*

*Insoluble

C, H Analyses were not possible because of their explosive character.

The IR spectra of these macrocyclic complexes show various vibrations of azomethine and α -diketone moiety. By comparing the spectra with those of amines a strong band in the region $1530\text{--}1640\text{ cm}^{-1}$ attributed to coordinated $\nu(\text{C}=\text{N})$ confirming the condensation of α -diketones with diamines and their appearance in the lower region indicates the coordination of azomethine group. This coordination is further supported by the presence of a sharp bond at *ca.* 450 cm^{-1} , which may be assigned to $\nu(\text{Pb}\leftarrow\text{N})$ ²⁰. The absence of bands at 1700 or $3200\text{--}3300\text{ cm}^{-1}$ due to unreacted $>\text{C}=\text{O}$ or —NH_2 groups respectively indicate that all amino groups of diamines have condensed with 2,3-butanedione or benzil. This contention is supported by the presence of bands *ca.* 2940 cm^{-1} , 1360 cm^{-1} , 1280 cm^{-1} and 700 cm^{-1} characteristic of the 2,3-butanedione moiety and may be assigned to ν_{CH_3} , $\nu_{\text{C—CH}_3}$, ν_{SymCH_3} and ring deformation modes respectively²⁰. The additional bands attributed to functional groups in the macrocyclic complexes such as absorption due to benzene ring and out-of-plane bending of phenyl groups are observed in the region $1470\text{--}1560\text{ cm}^{-1}$ and $710\text{--}750\text{ cm}^{-1}$ respectively and remained unshifted as expected²¹. Absorption bands in the region $1115\text{--}1120$, $1085\text{--}1095$ and $1055\text{--}1060\text{ cm}^{-1}$ are attributed to coordinated perchlorate. These $\nu_3(\text{ClO}_4)$ bands show some splitting in each case suggesting that perchlorate anions are involved in interactions which result in distortion from tetrahedral symmetry. The $\nu_4(\text{ClO}_4)$ vibrations observed in the region $605\text{--}630\text{ cm}^{-1}$ are not split showing ionic nature of other perchlorate group²².

¹H NMR spectra of soluble complexes are recorded in DMSO-*d*₆ and the (δ , ppm) values for different protons are given in Table 2. In the macrocyclic complex $[\text{Me}_4[14]\text{tetraeneN}_4\text{PbClO}_4]\text{ClO}_4(\text{II})$, each of the two hydrogen atoms on the α -carbon atom is flipping between an equatorial and an axial position so that they may undergo environmental averaging as do the β -hydrogen atoms giving rise to much similar spectrum to that which could have been observed if there was no flipping.



II R = CH₃; III R = C₆H₅

The complex has two six membered puckered rings resulting in the formation of same environment on both sides. The α -CH₂ protons exhibit a triplet at $\delta 3.06$

ppm which is at lower region corresponding to the free amine confirming the coordination of metal atom to the macrocyclic cavity. The β -CH₂ protons give rise to a quintet at δ 1.54 ppm due to coupling with the α -CH₂ protons. In free 1,3-diaminopropane, α -CH₂ protons at δ 2.79 ppm and β -CH₂ protons at δ 1.60 ppm (quintet)²³. In KIM(IV), the α -CH₂ protons appear as triplet at δ 3.63 ppm and the β -CH₂ protons as a quintet at δ 2.11 ppm²⁴.

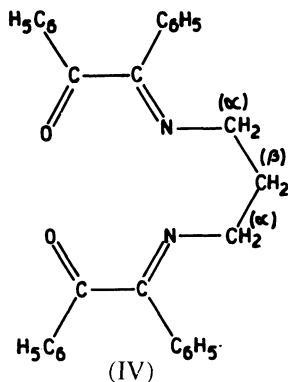


TABLE 2
SPECTROSCOPIC DATA (IR AND ¹H NMR OF THE COMPLEXES OF LEAD(II)

S. No.	Complex	IR spectra (cm ⁻¹) ν _{C=N}	N.M.R.-spectra (δ, ppm)			
			-CH ₃	α-CH ₂	β-CH ₂	-C ₆ H ₅
1.	[(Me ₄ [12]tetraeneN ₄)PbClO ₄]ClO ₄	1580	1.06 t	3.24 b	—	—
2.	[(Me ₄ [14]tetraeneN ₄)PbClO ₄]ClO ₄	1590	0.98 t	3.06 t	1.54 q	—
3.	[(Me ₄ [16]tetraeneN ₄)PbClO ₄]ClO ₄	1590	1.34 t	3.02 t	1.83 b	—
4.	[(Me ₄ [20]tetraeneN ₄)PbClO ₄]ClO ₄	1600	1.29 t	2.88 t	1.73 b	—
5.	[(Me ₄ [24]tetraeneN ₄)PbClO ₄]ClO ₄	1600	0.98 t	2.85 t	1.82 m	—
6.	[(Me ₄ [32]tetraeneN ₄)PbClO ₄]ClO ₄	1600	Insoluble	—	—	—
7.	[(Ph ₄ [12]tetraeneN ₄)PbClO ₄]ClO ₄	1590	—	3.50t	—	6.96–7.40m
8.	[(Ph ₄ [14]tetraeneN ₄)PbClO ₄]ClO ₄	1630	—	3.29t	1.96q	7.55–8.13m
9.	[(Ph ₄ [16]tetraeneN ₄)PbClO ₄]ClO ₄	1630	—	3.12t	1.60m	7.46–7.85m
10.	[(Ph ₄ [20]tetraeneN ₄)PbClO ₄]ClO ₄	1625	—	2.88t	1.46m	8.08–8.15m
11.	[(Ph ₄ [24]tetraeneN ₄)PbClO ₄]ClO ₄	1630	—	2.66t	1.42m	7.55–8.30m
12.	[(Ph ₄ [32]tetraeneN ₄)PbClO ₄]ClO ₄	1625	Insoluble	—	—	—

t = triplet, q = quantet, m = multiplet, b = broad

^a J = ca. 2 Hz ^b J = ca. 6 Hz

This downfield shift is due to the deshielding by the π electrons of the $\nu_{C=N}$ bond. In the complex [Ph₄[14]tetraeneN₄PbClO₄]ClO₄(III), triplet at δ 3.29 ppm have been observed due to the α -CH₂ protons. The β -CH₂ protons exhibit a quintet at δ 1.96 ppm. Upfield shifting of the α -CH₂ and β -CH₂ protons in II and III than in IV supports the coordination of the C=N group to the metal atom. The free macrocyclic TIM or Ph-TIM would have exhibited these resonances at almost the

similar positions as in the KIM. A triplet at δ 0.98 ppm is assigned to the methyl protons of (II) due to homoallylic type coupling ($J = 2$ Hz) with the α -CH₂ protons of the amine residue²⁵. In other lead complexes α -CH₂ protons exhibit a triplet in the region δ 2.66–3.50 ppm and β -CH₂ protons appear as a multiplet in the region at 1.42–1.83 ppm. The methyl protons in lead complexes derived from 2,3-butanedione appear as a triplet in the region δ 1.02–1.34 ppm and the complexes derived from benzil exhibit multiplet in the region δ 6.96–8.30 ppm due to the aromatic protons.

Thus on the basis of above studies lead atom is bonded to the four azomethine nitrogen and one perchlorate group confirming pentacoordination.

Financial assistance from CSIR is gratefully acknowledged.

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(Received: 18 September 1993; Accepted: 29 January 1994)

AJC-773