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## Synthesis and Characterization of a Novel 32-Membered Unsymmetrical Dinucleating $[N_{12}]$ Macrocycle: Preparation of Bimetallic Complexes $M_2LX_2(ClO_4)_2$ (M = Zn, Cd, or Hg; X = Cl, NCS, or NO<sub>3</sub>)

## Zafar Ahmad Siddiqi\* and Mohammad Mansoob Khan

Department of Chemistry, Division of Inorganic Chemistry, Aligarh Muslim University, Aligarh, India

#### ABSTRACT

The condensation reaction of *N*-acetylaniline with 1,3-diaminopropane in 2:1 mole ratio under reflux condition generates an intermediate species having C=N bonds. The *in situ* reaction of the intermediate with HCHO and 1,3-diaminopropane in the presence of perchloric acid results in an off-white solid product. Analytical, FAB mass, IR, <sup>1</sup>H NMR and electronic spectral data of this solid are consistent with the formation of the dihydroperchlorate salt of an unsymmetrical 32-membered [N<sub>12</sub>] macrocycle [L · 2HClO<sub>4</sub>] via a capping mechanism of the intermediate

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<sup>\*</sup>Correspondence: Zafar Ahmad Siddiqi, Department of Chemistry, Division of Inorganic Chemistry, Aligarh Muslim University, Aligarh 202 002, India; E-mail: nabilah@sancharnet.in.

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species. Reactions of  $[L \cdot 2HClO_4]$  with Group 12 metal salts, MX<sub>2</sub>, and their precursors,  $[M(Ph_3P)_2Cl_2]$ , produce bimetallic complexes with the stoichiometries  $M_2LX_2(ClO_4)_2$  (M = Zn, Cd or Hg; X = Cl, NO<sub>3</sub>, or NCS) and  $M_2LCl_2(ClO_4)_2$ , respectively, with liberation of 2 mol equiv. of the ancillary ligand, Ph<sub>3</sub>P, from the precursors. Physico-chemical and spectroscopic data of the complexes confirm encapsulation of two metal ions in the macrocyclic cavity via coordination through nitrogen atoms of the unsymmetrical aza groups and the counter anions occupy apical positions in the octahedral geometry around the metal ions. The thermodynamic first ionic association constant and related parameters have been determined from conductometric studies using the Fuoss and Edelson method and are discussed.

*Key Words:* Unsymmetrical macrocycle; Electronic spectral data; Bimetallic complex; Macrocyclic ligand.

## INTRODUCTION

Macrocyclic ligands that can incorporate two or more metal ions giving discrete homo- or heterodinuclear complexes have been a subject of considerable interest during recent years. Some of these heterodinuclear complexes are interesting as they mimic the active sites<sup>[1]</sup> of metalloenzymes, such as cytochrome-c oxidase and bovine erythrocyte superoxide dismutase. Such systems are also helpful in investigating mutual influences<sup>[2]</sup> of the two metal centers on electronic, magnetic, and electrochemical properties. The polyazamacrocycle of the type (3k)-ane[Nk] has been shown to produce bimetallic complexes<sup>[3]</sup> when k > 6. However, for the macrocycle (24)-ane[N<sub>6</sub>], e.g., [1,5,9,13,17,21]hexaazacyclotetracosane, encapsulation of only one metal ion has been reported.<sup>[4]</sup> The metal-template condensation of a diamine with 2,6-diformyl-4-methylphenol was the first one-pot reaction to yield a dinuclear bimetallic macrocyclic complex.<sup>[5]</sup> Large-size macrocycles contain-ing different lateral chains are obtained<sup>[1]</sup> through stepwise cyclization using two dissimilar alkyldiamines by a template procedure. However, most of the earlier reports<sup>[6-9]</sup> describe isolation of symmetrical macrocycles because the preparations of such macrocycles, in general, involves simple synthetic routes. Symmetrical polyaza macrocycles are those, which provide identical binding sites to encapsulate metal ions in their cavities. Macrocycles that contain two or more different types of coordinating sites to bind metal ions have been classified<sup>[10-12]</sup> as unsymmetrical macrocycles. The large unsymmetrical macrocycles reported<sup>[10,13-15]</sup> in the literature are those, which, usually, involve heteroatomic binding centers like [N<sub>4</sub>O<sub>2</sub>], [N<sub>4</sub>OS], [N<sub>7</sub>O], [N<sub>4</sub>O<sub>10</sub>],

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and [N<sub>4</sub>O<sub>8</sub>S<sub>2</sub>] etc. A small unsymmetrical hexaaza [N<sub>6</sub>] macrocycle binding metal ions in two different environments of aza groups recently has been reported.<sup>[12]</sup> This  $[N_6]$  macrocycle is obtained through a multistep procedure using N-acetyl-1,3-diaminopropane as a reagent to generate an intermediate that undergoes cyclization with 1,3-diaminopropane in the presence of metal ions as templating agent. However, to our knowledge large unsymmetrical polyaza macrocycles  $[N_k]$  with k > 8 to encapsulate more than one metal ion are not reported. It was our interest to investigate condensation reactions of diamines with suitable reagents, which may lead to cyclization in the absence of metal ions as templating tool to produce metal ion-free unsymmetrical polyaza macrocycles. Herein, we are the first to report that N-acetylaniline undergoes condensation with 1,3-diaminopropane under refluxed conditions generating an intermediate species with C=N bonds, which is followed by a capping reaction with 1,3-diaminopropane and HCHO in the presence of HClO<sub>4</sub> yielding an off-white dihydroperchlorate salt of a 32-membered unsymmetrical [N<sub>12</sub>] macrocycle, 8,14, 24,30-tetramethyl-7,15,23,31-tetraphenyl[1,5,7,9,13,15,17,21,23,25,29,31] dodecaazacyclodotriaconta-8,14,24,30-tetraene dihydroperchlorate, i.e.,  $[L \cdot 2HClO_4]$ . Its reactivity towards MX<sub>2</sub> (X = Cl, NCS, or NO<sub>3</sub>) and a few derivative complexes  $[M(Ph_3P)_2Cl_2]$  (M = Zn, Cd, or Hg) has also been investigated.

#### **EXPERIMENTAL**

#### Reagents

All the chemicals viz. aniline (E. Merck, India), 1,3-diaminopropane (E. Merck, Germany), ethyl acetate (BDH, India), formaldehyde (37–41% aqueous, E. Merck, India), HClO<sub>4</sub> (70% aqueous, BDH, India), triphenylphosphine (SISCO, India), and metal salts viz. ZnCl<sub>2</sub> (E. Merck, India), CdCl<sub>2</sub> (E. Merck, India), Hg(NO<sub>3</sub>)<sub>2</sub> (E. Merck, India), Hg(SCN)<sub>2</sub> (LOBA chemicals, India), HgCl<sub>2</sub> (E. Merck, India), were commercially pure samples used as received, while the solvents were purified by reported methods.<sup>[16]</sup> The precursors [M(Ph<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub>] (M = Zn, Cd, or Hg) were prepared and purified by reported methods.<sup>[17]</sup> *N*-Acetylaniline was obtained as a syrupy liquid in 60% yield according to the procedure reported elsewhere<sup>[18]</sup> for acylation of diamines. The analytical and spectroscopic data of the oily mass are as follows: Calcd. for C<sub>8</sub>H<sub>9</sub>NO (FW 135): C, 71.11; H, 6.66; N, 10.37. Found: C, 71.00; H, 6.50; N, 10.30%. IR: 1700 s, 3320 b cm<sup>-1</sup>; UV-visible:  $\lambda_{max}$  320 nm (characteristic<sup>[19,20]</sup> of -CO-NH- group) are consistent with *N*-acetyl-aniline.

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## Preparation of the Macrocyclic Ligand, 8,14,24,30-Tetramethyl-7,15,23,31-tetraphenyl-[1,5,7,9,13,15,17,21,23,25,29,31]dodecaazacyclodotriaconta-8,14,24,30-tetraene Dihydroperchlorate [L · 2HClO<sub>4</sub>]

1,3-Diaminopropane (5.1 mL, 0.06 mol) and  $HClO_4$  (6.3 mL, 0.06 mol) in 150 mL ethanol was placed in a three-necked round-bottomed flask fitted with a condenser to which N-acetylaniline (18.36 g, 0.12 mol) was added dropwise with continuous stirring for  $\sim 1 \, \text{hr}$  and then it was refluxed for  $\sim$ 12 hr. The reaction has been monitored by recording UV-visible spectra of the reaction mixture at intervals. The intensity of the 320 nm band of Nacetylaniline started diminishing with the concomitant appearance of a new band at  $\sim$ 385 nm characteristic of the presence of a C=N bond<sup>[21]</sup> suggesting the progress of the condensation process. Refluxing was stopped to bring the temperature down to room temperature. Formaldehyde (15 mL,  $\sim 0.2 \text{ mol}$ ) and 1,3-diaminopropane (5.1 mL, 0.06 mol) dissolved separately in 50 mL ethanol were added, simultaneously, through two dropping funnels to the above reaction mixture with stirring. Stirring was continued for about 2 days at room temperature giving an off-white precipitate which was filtered, washed with methanol, and dried in vacuo, m.p. 178-180°C; yield, 18 g (70%).

### **Preparation of Complexes**

Preparation of  $M_2LCl_2(ClO_4)_2$  [M = Zn (1), (2); M = Cd (4), (5)]

The ligand (0.64 g, 0.63 mmol) dissolved in 20 mL THF was added drop-wise to the solution of ZnCl<sub>2</sub> (0.17 g, 1.26 mmol) or CdCl<sub>2</sub> (0.22 g, 1.26 mmol) dissolved in 30 mL methanol with stirring, which was continued for about 48 hr at room temperature. The precipitate formed was filtered and washed with methanol followed by 10 mL portions of THF till washings were colorless and then dried *in vacuo*; (1) m.p. 270–272 °C (dec.); yield, 0.18 g (~36%); (4) m.p. 200–203 °C; yield, 0.21 g (~35%).

The mother liquor was concentrated to 1/3 of its original volume under reduced pressure and kept in a refrigerator for a fortnight which afforded a second crop; (2) m.p. 258-260 °C; yield,  $0.16 \text{ g} (\sim 32\%)$ ; (5) m.p. 268-270 °C (dec.); yield,  $0.28 \text{ g} (\sim 36\%)$ . Total yield: (1) + (2):  $0.34 \text{ g} (\sim 34\%)$ ; (4) + (5):  $0.49 \text{ g} (\sim 36\%)$ .



Preparation of  $Hg_2LX_2(ClO_4)_2$  [X = NO<sub>3</sub> (8) or NCS (9)]

Hg(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (0.43 g, 1.262 mmol) or Hg(SCN)<sub>2</sub> (0.468 g, 1.479 mmol) dissolved in 10 mL methanol was added drop-wise to the ligand (0.64 g, 0.631 mmol) solution in 30 mL THF with stirring, which was continued for about 48 hr at room temperature. The precipitate formed was filtered and washed with methanol followed by THF till washings were colorless and then dried *in vacuo*; (8) m.p. 228–230 °C (dec.); yield, 0.28 g (~58%); (9) m.p. 318–320 °C (dec.); yield, 0.21 g (~43%). The mother liquor in both cases, however, did not produce second crops.

Reactions of  $L \cdot 2HClO_4$  with the Precursors  $[M(Ph_3P)_2Cl_2]$  (M = Zn, Cd, or Hg); Preparation of  $Zn_2LCl_2(ClO_4)_2$  (**3**); Cd<sub>2</sub>LCl<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (**6**), (**7**), and Hg<sub>2</sub>LCl<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> (**10**)

 $[M(Ph_3P)_2Cl_2]$  (M = Zn 0.977 g, Cd 1.046 g, Hg 1.177 g, 1.479 mmol) dissolved/suspended in 20 mL CH<sub>2</sub>Cl<sub>2</sub> was reacted with the ligand (0.75 g, 0.739 mmol) in 25 mL THF at room temperature with stirring, which was continued for  $\sim$ 48 hr. The solid products formed were filtered, washed with THF and  $CH_2Cl_2$  and then dried in vacuo; (3) m.p. 258–260 °C; yield, 0.39 g  $(\sim 56\%)$ ; (6) m.p. 200–202 °C; yield, 0.32 g  $(\sim 37\%)$ ; (10) m.p. 218– 220 °C; yield, 0.38 g (~54%). The filtrate and washings were combined and concentrated to 1/4 of the total volume, kept in a refrigerator for 5 days to give colorless crystals. The crystals (m.p. 79 °C) have been identified as free Ph<sub>3</sub>P by microanalytical, <sup>1</sup>H and <sup>31</sup>P NMR spectroscopic data. The amount of free Ph<sub>3</sub>P collected corresponded approximately to 2 mol equiv. of the precursors used in the reaction, suggesting a total release of  $Ph_3P$ from the precursor during the course of this reaction. The mother liquor was again concentrated under vacuum, which produced a second crop (7) for the reaction of the Cd(II)-precursor only, (7) m.p. 278-280 °C (dec.); yield,  $0.29 \text{ g} (\sim 31\%).$ 

*Warning*: The compounds contain perchlorate groups, care should be taken as these are liable to explode at the decomposing temperature on a sudden strong heating.

#### **Physical Measurements**

IR spectra were recorded as KBr discs on a Perkin Elmer model spectrum GX, <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded in DMSO- $d_6$  on a Bruker DRX-300 spectrometer using SiMe<sub>4</sub> as internal reference or 85% H<sub>3</sub>PO<sub>4</sub> as external reference, respectively. The FAB mass spectra were recorded on a Jeol

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102/DA-6000 mass spectrometer using argon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded in a *m*-nitrobenzyl alcohol (NBA) matrix. The matrix peaks appeared at m/z = 136, 137, 154, 289, and 307. Microanalyses were obtained from the Micro-Analytical Laboratory of the Central Drug Research Institute, Lucknow, India. Conductivity measurements were carried out at a frequency of 1 kHz on a Systronics conductivity bridge using distilled DMSO as solvent. The cell content was thermostated at  $25 \pm 0.5$  °C and the cell constant of the conductivity cell  $(1.00 \text{ cm}^{-1})$  was determined by using 0.01 mol L<sup>-1</sup> of KCl as standard solution. The concentration range of the complex solution studied was  $10^{-3}-10^{-4} \text{ mol L}^{-1}$ .

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## **RESULTS AND DISCUSSION**

The reaction of N-acetylaniline with 1,3-diaminopropane in 2:1 mole ratio in the presence of HClO<sub>4</sub> in ethanol under reflux condition has been monitored by recording the UV-visible spectrum of the reaction mixture at intervals. The reagent N-acetylaniline shows a band at 320 nm characteristic<sup>[20]</sup> of the  $n \rightarrow \pi^*$  transition of the -CO-NH- function. However, the reaction mixture exhibited an additional new band at  $\sim$  385 nm, which gradually intensified with a concomitant decrease in the intensity of the band at  $\sim$  320 nm as the reaction progressed. The new band at  $\sim$ 385 nm is assignable to the  $\pi \rightarrow \pi^*$  excitation<sup>[21]</sup> of electrons from low-lying HOMO (i.e.,  $\pi$  orbital) to LUMO (i.e.,  $\pi^*$  orbital) of the C=N bonds. The C=N bond is formed due to the condensation process between 1,3-diaminopropane and the reagent N-acetylaniline, similar to that reported<sup>[12]</sup> for the reaction of a diamine with N-acetyl-1,3-diaminopropane, giving an intermediate species in the reaction mixture. The capping reaction (in situ) of this intermediate with HCHO and 1,3-diaminopropane has resulted in the formation of an off-white amorphous solid. The mechanism of the reaction is presented by the scheme shown in Fig. 1. The first step (1st step) of the scheme shows formation of the intermediate species while the 2nd step indicates the capping mechanism involving a cyclization process resulting in the macrocyclic moiety. The presence of mineral acids like HCl or HClO<sub>4</sub> is known<sup>[22]</sup> to facilitate the cyclization process in non-template procedures. Its presence, usually, minimizes the extent of various unwanted side reactions, which may reduce the yield of the desired macrocycles. Moreover, in non-template procedures the presence of mineral acids also helps in the isolation of stable salts of the macrocycles. Here, too, the presence of  $HClO_4$  has afforded a good yield of the final product in the form of a solid dihydroperchlorate salt of the macrocycle, i.e.,  $[L \cdot 2HClO_4]$ . The analytical data of the final product (Table 1)





Figure 1. Scheme showing the mechanism for the formation of  $L \cdot 2HClO_4$ .

are consistent with the molecular formula  $C_{48}H_{70}Cl_2N_{12}O_8$ . Its FAB mass spectrum recorded in NBA matrix failed to show the molecular ion peak, which may be due to its low thermal stability. It readily eliminates a  $Ph_2^+$ ion, evidenced by the appearance of a high-abundance peak (100%) at m/z = 153 (Table 2) and a peak at m/z = 658 (10% abundance) consistent with the L-2Ph molecular ion peak. In addition, the spectrum contained peaks (Table 2) assignable to various fragments arising from the thermal cleavage of the macrocycle and, therefore, supports its molecular formula (Fig. 1). The IR spectrum exhibited various important bands (Table 3) characteristic of





<i>Table</i> compc	<i>I</i> . Analytical data, molar unds.	conductivities $(\Lambda_m)$ , and b	and positio	ns (A <sub>nm</sub> ) w	ith their ass	signment	in the l	JV-visible spectr	a of the
			Analysis	(%) found	l (calcd.)				
No.	Compounds	Emperical formula (mol. wt.)	С	Н	N	$\Lambda_{\rm m}{}^{\rm a}$	$\lambda_{ m nm}$	Assignments	$\varepsilon^{\mathrm{p}}$
	$[L \cdot 2HCIO_4]$	$C_{48}H_{70}Cl_2N_{12}O_8$	56.42	6.01	16.40	7.0	384	$\mu \rightarrow \mu^*$	1,507
		(1024)	(56.80)	(06.9)	(16.56)				
<b>1</b> )	$[Zn_2LCl_2(ClO_4)_2]$	$C_{48}H_{68}$ Cl <sub>4</sub> N <sub>12</sub> O <sub>8</sub> Zn <sub>2</sub>	47.34	5.50	13.71				
		(1212.76)	(47.49)	(5.60)	(13.85)				
5	$[Zn_2LCl_2(ClO_4)_2]$	$C_{48}H_{68} Cl_4N_{12}O_8Zn_2$	47.04	5.60	13.79	21	368	ש^ ש*	4,126
		(1212.76)	(47.49)	(5.60)	(13.85)		448	CT	2,463
<b>3</b> )	$[Zn_2LCl_2(ClO_4)_2]^c$	$C_{48}H_{68}Cl_4N_{12}O_8Zn_2$	47.01	5.30	13.76	30	365	ש ליש ש	4,054
		(1212.76)	(47.49)	(5.60)	(13.85)		390	CT	1,829
<b>4</b>	$[Cd_2LCl_2(ClO_4)_2]$	$C_{48}H_{68}$ Cd <sub>2</sub> Cl <sub>4</sub> N <sub>12</sub> O <sub>2</sub>	44.00	5.00	12.80	5	365	+ א א	4,201
		(1306.18)	(44.07)	(5.20)	(12.85)		403	CT	1,976
<b>(</b> 2)	$[Cd_2LCl_2(ClO_4)] \cdot ClO_4$	$C_{48}H_{68}$ Cd <sub>2</sub> Cl <sub>4</sub> N <sub>12</sub> O <sub>8</sub>	44.01	5.15	12.78	49	367	א+ +* א	4,454
		(1306.18)	(44.07)	(5.20)	(12.85)		415	CT	2,160

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9	$[Cd_{2}LCl_{2}(ClO_{4})_{2}]^{c}$	$C_{48}H_{68}$ Cd <sub>2</sub> Cl <sub>4</sub> N <sub>12</sub> O <sub>8</sub>	44.02	5.17	12.01	27	365	*ד אך	4,742	in
		(1306.18)	(44.07)	(5.20)	(12.85)		391	CT	1,838	ieta
6	$[Cd_2LCl_2(ClO_4)]^{c}$ ClO <sub>4</sub>	$C_{48}H_{68}$ Cd <sub>2</sub> Cl <sub>4</sub> N <sub>12</sub> O <sub>8</sub>	44.00	5.12	12.78	49	380	¥= ↑ ו	1,795	alli
		(1306.18)	(44.07)	(5.20)	(12.85)		390	CT	1,159	c N
8	$[Hg_2L(CIO_4)_2]\cdot 2(NO_3)$	$C_{48}H_{68}Cl_2Hg_2N_{14}O_{14}$	37.02	4.20	12.02	121	366	ז= ^ ⊨	4,015	1ac
		(1536.18)	(37.49)	(4.42)	(12.75)		454	CT	2,479	ero
6	$[Hg_2L(NCS)_2] \cdot 2(CIO_4)$	$C_{50}H_{68}Cl_2Hg_2N_{14}O_8S_2$	39.20	4.40	12.62	109	367	¥= ↑ ו	4,098	cyc
		(1528.18)	(39.26)	(4.45)	(12.82)		481	CT	2,645	lic
(10)	$[Hg_2LCl_2(ClO_4)_2]^c$	$C_{48}H_{68}Cl_4Hg_2N_{12}O_8$	37.91	4.42	11.03	15	381	ז= ^ ⊨	1,037	Co
		(1483.18)	(38.00)	(4.58)	(11.32)					mp
Note:	Calculated values in parentl	neses.								lexes

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 ${}^{a}cm^{2}ohm^{-1}mol^{-1}$ .  ${}^{b}Lmol^{-1}cm^{-1}$ .  ${}^{c}Products$  obtained from reactions with the precursors M(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>.

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*Table 2.* Abundance (%) of fragments with their assignments observed in FAB mass spectrum of  $L \cdot 2HClO_4$ .

m/z	Abundance %	Assignments	m/z	Abundance %	Assignments
658	10	$[L-2C_{6}H_{5}]$	449	16	$[L'-C_6H_5+B_{z1}]$
391	30	1/2[L-2Me] = [L']	603	10	$[L'-C_6H_5+B_{z2}]$
314	6	$[L' - C_6 H_5]$	512	30	$[L' - CH_3 + B_{z1}]$
239	25	$[L' - 2C_6H_5]$	391	30	$[L'-2C_6H_5+B_{z2}]$
371	16	[L'-CH <sub>3</sub> -4H]	153, 154	100	$[(C_6H_5)_2]^+$

*Note:*  $B_{z_1}$  (m/z = 136, 137) and  $B_{z_2}$  (m/z = 154) are fragments of matrix *m*-nitrobenzyl alcohol.

 $\nu$ (N–H),  $\nu$ (C=N), and  $\nu$ (C–N) stretching vibrations along with those arising from  $\nu$ (C==C),  $\nu$ (C-C), and  $\nu$ (C-H) fundamental vibrations.<sup>[19]</sup> The absence of a strong broad band at  $\sim 1700 \text{ cm}^{-1}$  due to the -CO-NH- group of N-acetylanaline and appearance of a new band at 1610 cm<sup>-1</sup> characteristic of the  $\nu$ (C=N) stretching vibration<sup>[12]</sup> are in accordance with the capping (2nd step of Fig. 1) reaction. The IR spectrum contained additional bands (Table 3) characteristic of the fundamental frequencies<sup>[23]</sup> of the  $ClO_4$  ion. The observed splitting of the  $v_2$  stretching vibration (Table 3) of the ClO<sub>4</sub> group in the region  $1000-1200 \text{ cm}^{-1}$  is consistent with the lowering of its symmetry relative to the perfect  $T_d$  symmetry of the free anion. It is well known<sup>[23]</sup> that the perfect  $T_d$  symmetry of the ClO<sub>4</sub> anion is lowered to  $C_{3\nu}$ or  $C_{2\nu}$  as a result of its involvement in a weak to medium strength attachment or bonding to a cation. This indicates that the ClO<sub>4</sub> counter ion is complexed or encapsulated in the cavity of the macrocyclic cation  $[L \cdot 2H]^{2+}$ . The protonated form of a few polyaza macrocycles, e.g., [1,4,7,10,13,16]hexaazacyclooctadecane [1,5,9,13,17,21]hexaazacyclooctatetracosane and [1,5,9,13,17,21,25,29]octaaza-cyclodotriacontane are reported<sup>[4]</sup> to form stable complexes with various anions, such as Cl, NO<sub>3</sub>, succinate, and metal complex anions. The magnitude of the molar conductance  $(\Lambda_m)$  measured in DMSO (Table 1) in an ionizing high-dielectric constant solvent ( $\varepsilon \sim 46$ ), indicates its non-electrolytic<sup>[24]</sup> nature and suggests that the salt  $[L \cdot 2HClO_4]$  does not dissociate or ionize to produce ClO<sub>4</sub> ion even in solution. This is due to a strong attachment of the counter ion with the macrocyclic cation. The <sup>1</sup>H NMR spectrum of  $L \cdot 2HClO_4$  recorded in DMSO- $d_6$  (Table 4) exhibited signals assignable<sup>[12]</sup> to the protons from  $C_6H_5$  ( $\delta$  6.5),  $CH_3C=N$  ( $\delta$  7.0),  $-CH_2-N=C$  ( $\delta$  5.9), N-CH<sub>2</sub>-N ( $\delta$  4.0), NH ( $\delta$  4.9), and -CH<sub>2</sub>- ( $\delta$  2.5). The electronic spectrum (Table 1) exhibited a band at 384 nm ( $\varepsilon = 1.507 \times 10^3 \,\mathrm{L \, mol^{-1} \, cm^{-1}}$ ) arising



						$CIO_4$		
Compounds	$\nu(N-H)$	ν(C=N)	ν(C–N) Aromatic	ν(C–N) Aliphatic	٧ <sub>1</sub>	$\nu_2$	$\nu_3$	u(M-N)
L · 2HClO4	3,240 s	1,615 vs	1,316 s	1,252 s	1,118 m	1,095 m	624 m	I
(1)	3,200 s	1,620 vs	1,352 s	1,258 w	1,100 m	1,072 m 1,072 m	620 w	417 w, 432 w
(2)	3,298 s	1,608 vs	1,350 s	1,236 m	1,174 s	1,000 III 1,090 s	624 w	416 w, 448 m
(3)	3,208 s	1,610 vs	1,323 s	1,260 br	1,175 s	1,072 s 1,098 s 1.067 s	626 w	412 w, 428 w
(4)	3,201 s	1,613 vs	1,313 s	1,250 m	1,176 m	1,00/ S 1,110 m 1,001 m	624 w	412 w, 449 m
(5)	3,292 s	1,600 vs	1,356 s	1,260 w	1,175 w	1,004 III 1,025 w 1.015 w	642 w	422 w, 436 w
(9)	3,298 s	1,620 vs	1,342 s	1,258 m	1,122 w	1,021 m	632 w	415 w, 428 w
(L)	3,201 s	1,612 vs	1,315 s	1,248 m	1,113 w	1,000 ш 1,089 ш 1.078 ш	691 w	411 w, 437 w
( <b>8</b> ) <sup>a</sup>	3,294 s,br	1,607 s	1,328 br	1,258 br	1,176 s	1,070 m 1,095 m 1.007 m	623 m	412 m, 443 w
(9) <sup>b</sup> (10)	3,209 s 3,201 s	1,622 vs 1,608 vs	1,356 s 1,351 s	1,245 m 1,254 m	1,170 m 1,180 m	1,00/ III 1,070 s, br 1,098 s	616 w 629 m	418 m, 447 m 417 m, 439 m
						1,079 m		
<i>Note</i> : vs, very sha <sup>a</sup> Additional freque <sup>b</sup> Additional freque	rp; s, sharp; m, ncies observed ncies observed	medium; w, v for $\nu(NO_3)$ 13 for $\nu(NCS)$ 21	veak; br, broad 883 vs. and 760 100 m and 790	. × ::				





Compound	N=C- CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	C=N- CH <sub>2</sub> -	N-CH <sub>2</sub> - NH <sub>2</sub>	C-CH <sub>2</sub> - C	NH
$L \cdot 2HClO_4$	7.0 s	6.5 m	5.9 br	4.0 s	2.5 s	4.9 br
	(12H)	(20H)	(16H)	(8H)	(8H)	(4H)
(2), (3)	6.8 s	6.6 m	3.6 br	4.0 s	2.5 s	4.2 br
(5), (6)	7.0 s	6.5 m	5.8 br	4.0 s	2.5 s	4.8 br
(8)	7.2 s	6.5 m	4.0 br	4.0 s	2.5 s	5.2 br
(9)	7.0 s	6.6 m	4.4 br	3.7 s	2.5 s	5.3 br
(10)	7.0 s	6.5 m	3.6 br	4.0 s	2.5 s	5.0 w,br

Table 4. Resonance peaks (ppm) observed in <sup>1</sup>H NMR of the ligand and complexes.

Note: w, weak; br, broad; m, multiplet; s, singlet.

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from the excitation<sup>[21]</sup> of  $\pi$  electrons (HOMO) of the C=N bond to an antibonding  $\pi^*$  orbital (LUMO), i.e.,  $\pi \to \pi^*$  transition. The above physicochemical and spectroscopic data agree with the presence of unsymmetrical aza groups<sup>[12]</sup> in the molecular formula of the macrocyclic ligand 8,14,24,30tetramethyl-7,15,23,31-tetraphenyl[1,5,7,9,13,15,17,21,23,25,29,31]dodecaazacyclodotriaconta-8,14,24,30-tetraene dihydroperchlorate, i.e., L · 2HClO<sub>4</sub>, which is formed through a 2:2 cyclization as shown in the scheme of Fig. 1.

#### **Metal Encapsulated Derivatives**

The macrocyclic ligand exhibited considerable reactivity towards metal salts, MCl<sub>2</sub>, producing two crops [M = Zn (1), (2); M = Cd (4), (5)] in good yields. The decomposition temperatures of the two crops are different, however, their analytical data (Table 1) are very close and are consistent with the stoichiometry  $[M_2LCl_2(ClO_4)_2]$ . Reactions with HgX<sub>2</sub> produced a single crop with the stoichiometry  $[Hg_2LX_2(ClO_4)_2]$  [X = NO<sub>3</sub> (8); X = NCS (9)]. Reactions with the precursors  $[M(Ph_3P)_2Cl_2]$  (M = Zn, Cd, or Hg) are accompanied by the liberation of 2 mol equiv. of ancillary Ph<sub>3</sub>P as free ligand in the mother liquor (see Experimental). A complete displacement of Ph<sub>3</sub>P from the precursors in the complexation reaction affords products consistent with the stoichiometries  $[M_2LCl_2(ClO_4)_2]$  [M = Zn (3), M = Hg (10), and M = Cd (6), (7)]. The analytical (Table 1) and spectroscopic data (vide infra, Tables 3 and 4) for (3), (6), and (7) have been found identical to that of the corresponding products (2), (4), and (5) obtained from reactions using MCl<sub>2</sub>.



#### **Conductance and Spectroscopic Studies**

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The molar conductivities  $(\Lambda_m)$  of the complexes have been measured in DMSO except for (1) as it does not dissolve in any solvents. The magnitudes of  $\Lambda_{\rm m}$  (Table 1) indicate a non-electrolytic nature for (2), (3), (4), (6), and (10). However, a full-fledged 1:2 electrolytic nature for (8) and (9) was indicated in DMSO solution. The magnitudes of  $\Lambda_{\rm m}$  (49 cm<sup>-2</sup> ohm<sup>-1</sup> mol<sup>-1</sup>) for the complexes (5), (7) lie at the borderline of a 1 : 1 electrolyte<sup>[24]</sup> (50–75 cm<sup>-2</sup> ohm<sup>-1</sup> mol<sup>-1</sup>) supporting an appreciable degree of dissociation of the semi-coordinated counter ClO<sub>4</sub> ion in these complexes in solution giving an equilibrium as shown below by Eq. (1)

$$[Cd_2LCl_2(ClO_4)_2] \Longrightarrow [Cd_2LCl_2ClO_4]^+ + ClO_4^-$$
(1)

A similar behavior for metal complexes containing BF4 counter ions has also been reported.<sup>[25]</sup>

IR spectra (Table 3) of complexes contained characteristic frequencies of the macrocyclic ligand, as well as those of ClO<sub>4</sub>, NCS, or NO<sub>3</sub> as counter ion. A small shift in the positions of the  $\nu$ (N–H) and  $\nu$ (C=N) bond frequencies relative to the free ligand has been observed after complexation. The observed splitting of the fundamental  $\nu_2$  stretching vibration of the ClO<sub>4</sub> group in (1), (2), (3), (4), (5), (6), (7), (8), and (10) suggest that the counter ion is coordinated to the metal ions, resulting in a decrease in the symmetry of the free ClO<sub>4</sub> ion from perfect  $T_d$  to a  $C_{3v}$  or  $C_{2v}$  symmetry upon coordination in a monodentate (Fig. 2) or a bidentate (Fig. 3) manner.<sup>[23]</sup> The strong broad band at 1382 cm<sup>-1</sup> and a band of medium intensity at  $817 \,\mathrm{cm}^{-1}$  observed in (8) are characteristic of an uncoordinated<sup>[23]</sup> NO<sub>3</sub> counter ion. It has been reported that the free NO<sub>3</sub> ion has  $D_{3h}$ symmetry exhibiting a strong broad band at  $\sim$  1400 cm<sup>-1</sup> which, however, splits if the symmetry is reduced to  $C_{2\nu}$  or  $C_{3\nu}$  due to its involvement in coordination to metal ions. It, therefore, indicates that in complex (8), NO<sub>3</sub> is not involved in coordination compatible with its 1:2 electrolytic nature in solution.

The thiocyanate group is a well-known ambidentate ligand providing both N as well as S atoms as potential sites for coordination<sup>[26]</sup> depending on the soft or hard nature of the metal ions. In general, soft metal ions tend to bind through S centers while hard counter parts favor N coordination. There may be some exceptions depending on the nature of the main supporting ligands already bound or chelated to the metal ions. IR spectroscopic studies are useful in identifying the nature and mode of coordination of this ambidentate group. It has been concluded that the  $\nu(C \equiv N)$  stretching vibration, invariably, lies in the region  $2100-2150 \text{ cm}^{-1}$  whether it is N- or S-bonded. However, the position of the  $\nu$ (C-S) stretching vibration is a more reliable guide<sup>[26]</sup> to ascertain the coordination mode. Thiocyanate bridged bimetallic complexes, M-N-C-S-M, exhibit  $\nu(C \equiv N)$  at  $\sim 2090 \,\mathrm{cm}^{-1}$  and a  $\nu(C-S)$  band at



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*Figure 2.* Molecular structure of metal encapsulated macrocyclic complexes (a) M = Zn (1), (2), and (3); M = Cd (4) and (6); M = Hg (10). (b) M = Cd (5) and (7).

 $\sim$ 790 cm<sup>-1</sup>. The appearance of medium-intensity bands at 2100 and 790 cm<sup>-1</sup> in (9) favors a thiocyanate-bridged structure. The spectrum exhibited an additional unsplit strong band at 1070 cm<sup>-1</sup> assignable to the  $\nu_2$  stretching frequency characteristic of the presence of uncoordinated<sup>[23]</sup> ClO<sub>4</sub> anions in the complex. This has been substantiated by the observed 1:2 electrolytic nature of (9) in solution (vide supra). The encapsulation of metal ions in the macrocyclic cavity is indicated from the observed  $\nu$ (M–N) stretching frequency in the 400–450 cm<sup>-1</sup> regions.<sup>[19]</sup> The observed splitting of the  $\nu$ (M–N) bond frequency is probably, due to coordination of unsymmetrical aza groups of the macrocyclic moiety.

The UV-visible spectra of (1)–(10) contained bands arising from the  $\pi \to \pi^*$  excitation characteristic of the C=N bond in the ligand moiety as well as ligand  $\to$  metal charge transfer (CT) transition.<sup>[27]</sup> The position of the  $\pi \to \pi^*$ 

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*Figure 3.* Molecular structure of metal encapsulated macrocyclic complex  $X = ClO_4$ ,  $Y = NO_3$  (8); X = NCS,  $Y = ClO_4$  (9).

transition in the complexes is shifted to shorter wavelength (blue-shift) or higher energy compared to that observed in the free uncomplexed ligand. This shift is due either to a destabilization of LUMO ( $\pi^*$  energy level) or a stabilization of HOMO ( $\pi$  energy level) after chelation from the aza group of the (C==N) function. The latter seems more plausible in view of the macrocyclic effect.

The <sup>1</sup>H NMR spectra of (2), (3), (5), (6), (8), (9), and (10) were nearly identical and exhibited resonance peaks arising from ligand protons (Table 4). A small change in the position of some of the resonance peaks observed in the complexes relative to the free macrocycle may be the consequence of metal ion encapsulation.

The physico-chemical and spectroscopic data presented here agree with the cyclization mechanism to produce the salt of the macrocyclic ligand 8,14,24,30-tetramethyl-7,15,23,31-tetraphenyl[1,5,7,9,13,15,17,21,23, 25,29,31]dodecaazacyclodotriaconta-8,14,24,30-tetraene dihydroperchlorate, i.e.,  $L \cdot 2HClO_4$ . The macrocycle possesses unsymmetrical aza groups, i.e., -C=N-as well as C–NH–C in the molecular unit and the ClO<sub>4</sub> counter anion is encapsulated in the cavities as shown in Fig. 1. The macrocycle encapsulates two metal ions resulting in bimetallic complexes where each metal ion attains hexa-coordination, the counter ions occupy, preferably, the apical positions of the octahedral structure as illustrated in Figs. 2(a and b) and 3.

## Evaluation of Thermodynamic First Ionic Association Constant ( $K_1$ ) and Free Energy Change ( $\Delta G$ )

The thermodynamic ionic association constant  $K_1$  as well as the corresponding free energy change ( $\Delta G$ ) of the complexes (5), (7), (8), and (9) in

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DMSO have also been determined by carrying out a detailed conductometric study at room temperature. Conductometric data have been analysed using the modified Onsagar limiting equation according to the Fuoss and Edelson method.<sup>[28,29]</sup> The Onsagar limiting equation at the low concentration range of the electrolyte is given by the relation:

$$\Lambda = \Lambda^{\circ} - S C_{\rm o}^{1/2} \tag{2}$$

Here,  $\Lambda$  is the equivalent conductance at each concentration  $C_0$ ,  $\Lambda^o$  are the limiting equivalent conductances and *S* represents slope of the plot of  $\Lambda$  vs.  $C_0^{1/2}$ . The consecutive association equilibria of the complexes in solution may be represented by Eqs. (3) and (4) as follows:

$$A^{2+} + X^{-} \Longrightarrow AX^{+}$$
(3)

and

$$AX^+ + X^- \Longrightarrow AX_2 \tag{4}$$

where  $A^{2+}$  indicates the complex cations and  $X^{-}$  is the counter anion. The corresponding ionic association constants,  $K_1$  and  $K_2$ , are given by the expressions:

$$K_1 = \frac{[AX^+]f_+}{[A^{2+}][X^-]f_{2+}f_-}$$
(5)

$$K_2 = \frac{[AX_2]f}{[AX^+][X^-]f_+f_-}$$
(6)

The quantities in brackets indicate molar concentrations of the corresponding species while  $f_{2+}$ ,  $f_+$ , f and  $f_-$  are the activity coefficients of  $A^{2+}$ ,  $AX^+$ ,  $AX_2$ , and  $X^-$ , respectively. According to the Fuoss and Edelson method, an adequate limiting description of the ionic complexes could be obtained assuming<sup>[29]</sup>  $K_2 \neq 0$  and  $K_1 \gg K_2$ . With this assumption, there is a negligible association to give an electrically neutral  $AX_2$  structure and a certain amount of pair-wise association of complex cations  $A^{2+}$  with the counter anions X to give singly charged  $AX^+$  ions. This method works very well to determine the first ionic association constant ( $K_1$ ) using Eq. (5), which expresses the ionic equilibrium for the formation of ionic species in solution. The Onsagar limiting law becomes:

$$\Lambda F = \Lambda^{\circ} - \frac{DK_1}{\Lambda^{\circ}} \tag{7}$$



where

$$D = C_{\rm o} f_{2+} \Lambda F \left( \Lambda F - \frac{\Lambda^{\circ}}{2} \right)$$
$$F = \frac{(1 - \delta C_{\rm o}^{1/2})^{-1} + (\Lambda^{\circ} - \lambda_{\rm o-})/2\Lambda}{1 + (\Lambda^{\circ} - \lambda_{\rm o-})2\Lambda^{\circ}}$$

Here, *F* is a function which corrects the conductance ratio  $(\Lambda/\Lambda^{\circ})$  for the effect of interionic forces on the mobility,  $\delta$  is the ratio of the slope (*S*) and limiting equivalent conductance  $(\Lambda^{\circ})$  of the complex cations and  $\lambda_{o^-}$  is the limiting equivalent conductance of counter anions X. The ionic activity coefficient  $(f_{2+})$  of  $\Lambda^{2+}$  has been determined<sup>[28]</sup> using the following Debye–Hückel equation:

$$-\log f_{2+} = 250.3 Z_{\rm B}^2 \sqrt{\frac{3C_0}{\varepsilon^{3/2}}}$$
(8)

where  $Z_B = 2$  (effective charge on the complex cation) and  $\varepsilon$ , dielectric constant of the solvent.

The experimental equivalent conductivity data for the complexes (5), (7), (8), and (9) measured in DMSO at 25 °C and the determined several relevant parameters, like limiting equivalent conductance ( $\Lambda^{\circ}$ ), the activity coefficient ( $f_{2+}$ ), and *D* are summarized in Table 5. These parameters and  $K_1$  (Table 6) have been evaluated using expressions given by Eqs. (2), (5), (7), and (8). The magnitude of the limiting equivalent ionic conductance ( $\lambda_{o+}$ ) of the complex cation (Table 6) has been determined according to Kohlrausch law<sup>[29]</sup> given by Eq. (9):

$$\Lambda^{\circ} = \lambda_{0+} + \lambda_{0-} \tag{9}$$

The free energy changes (Table 6) due to first ionic association reaction have been obtained using the thermodynamic relationship given by Eq. (10):

$$\Delta G = -RT \ln K_1 \tag{10}$$

It can be concluded from Table 6 that the ionic association constants ( $K_1$ ) for the complexes is in the order (7) > (9) > (5) > (8). The plot of  $\Lambda$  vs.  $C_o^{1/2}$  for the complexes also provides<sup>[30]</sup> information regarding the limiting concentration (i.e., concentration at which the curve deviates from linearity) where ion-pair formation in solution becomes more significant. The

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Compounds	Concentration	Λ	$\Lambda^\circ$	$f_{2+}$	F	D
(5)	$0.8657 \times 10^{-4}$	92.28	120	0.8900	1.2955	0.5435
	$1.7315 \times 10^{-4}$	75.00		0.8481	1.4496	0.7778
	$3.4631 \times 10^{-4}$	57.67		0.7921	1.8720	1.4468
	$5.1947 \times 10^{-4}$	53.83		0.7517	2.2476	2.9088
	$6.9263 \times 10^{-4}$	51.93		0.7192	2.7118	5.6909
	$0.8657 \times 10^{-3}$	49.60		0.6918	3.3509	10.7927
(7)	$0.8657 \times 10^{-4}$	85.00	102	0.8900	1.1712	0.8686
	$1.7315 \times 10^{-4}$	74.97		0.8481	1.3368	0.7254
	$3.4631 \times 10^{-4}$	60.55		0.7921	1.5672	1.1695
	$5.1947 \times 10^{-4}$	51.90		0.7517	1.3569	0.4919
	$6.9263 \times 10^{-4}$	49.02		0.7192	1.5201	0.8715
	$0.8657 \times 10^{-3}$	48.44		0.6918	1.7001	1.4959
(8)	$0.8853 \times 10^{-4}$	62.02	67.5	0.8888	1.0926	0.1814
	$1.7706 \times 10^{-4}$	62.02		0.8465	1.1376	0.3892
	$3.5412 \times 10^{-4}$	56.38		0.7900	1.2041	0.6487
	$5.3118 \times 10^{-4}$	54.50		0.7493	1.2624	0.9599
	$7.0825 \times 10^{-4}$	52.15		0.7166	1.3156	1.2142
	$0.8853 \times 10^{-4}$	50.00		0.6889	1.3738	2.4837
<b>(9</b> )	$0.8787 \times 10^{-4}$	95.91	105	0.8892	1.4697	0.9744
	$1.7574 \times 10^{-4}$	70.52		0.8470	1.8965	1.6180
	$3.5149 \times 10^{-4}$	56.42		0.7907	3.0684	5.8036
	$5.2723 \times 10^{-4}$	52.66		0.7502	5.9970	32.8869

*Table 5.* Magnitudes of several parameters calculated for the metal complexes from conductivity data.

magnitudes of this limiting concentration determined for the complexes (5), (7), (8), and (9) are  $5 \times 10^{-4}$ ,  $5 \times 10^{-4}$ ,  $7 \times 10^{-4}$ , and  $4 \times 10^{-4}$  equiv. L<sup>-1</sup>, respectively. The magnitude is in the order (8) > (5), (7) > (9) suggesting that there is the least tendency to give ion-pair in solution for (8), while it is highest for (9). The present conductivity data, therefore, indicate that ion-

*Table 6.* Magnitudes of ionic association constant  $(K_1)$ , free energy  $(\Delta G)$  and limiting equivalent conductance of the complex cations  $(\lambda_{o+})$  for the complexes.

Compounds	$K_1 (\mathrm{L} \mathrm{mol}^{-1})$	$-\Delta G (\mathrm{kJmol}^{-1})$	$\lambda_{o+}(ohm^{-1} cm^2 mol^{-1})$
(5)	1,164	17.4907	49.1
(7)	2,652	19.5300	31.1
(8)	162	12.6040	-4.3
(9)	1,200	17.5660	34.1



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pair association in DMSO solution for the complex  $[Hg_2L(ClO_4)_2](NO_3)_2$  (8) is very low when compared to that of  $[Hg_2L(NCS)_2](ClO_4)_2$  (9).

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