IJCPS Vol. 5, No,-6,Nov-Dec 2016 ISSN:2319-6602
www.ijcps.org International Journal of Chemical and Physical Sciences

Synthesis and Photoelectron Spectroscopic Studies of Homonuclear Bimetallic Macrocyclic Complexes [M_2L]

ABHISHEK KUMAR[1], SHISHIR MALVIYA[2] , RAJESH KUMAR KUSHWAHA[3], RAJENDRA KUMAR[4] AND SHEKHAR SRIVASTAVA[5]

Department of Chemistry, University of Allahabad, Allahabad-211002- India
Corresponding Author: abhishekrajpoot02@gmail.com,

Abstract

Here, we have synthesized macrocyclic ligand [L] by using 1,3-benzaldehyde and diethylenetriamine. After that we used this macrocyclic ligand for the preparation of Bimetallic Macrocyclic Complexes [M_2L] through chemical condensation method. The synthesized complexes were characterized by elemental analysis, IR, XPS data, NMR and U.V. Visible spectroscopy.

Keywords: Binuclear complexes, heavy metals, photoelectron spectroscopy, macrocyclic complexes.

Introduction

Macrocyclic ligands have full potential to adopt metal ions. Several examples of such type of ligands as a crown ethers, porphyrin and saturated or unsaturated macrocyclic polyamines are well known and their chemical properties and function as metal complexes have been systematically heightened by the facile and diversified chemical modification of their macrocyclic framework[1]. Therefore the design and study of macrocyclic complexes with desirable properties is still a notable achievement. The direct synthesis or template synthesis is the heart of macrocyclic chemistry (Curtis 1968) and have been widely used for synthesis of macrocyclic complexes where transition metal ions are widely used as templating metal agents[2]. There are very few complexes of mono-oxygenases although tyrosinase is believed[3-4], Karlin et al[5]. A number of synthetic models of tyrosinase, based on open-chain binucleating ligands, have been reported[4].A Schiff base binucleating ligand with amino and one imidazole nitrogen donor per Cu(I)[6]. A large number of macrocycles[7-8] and their complexes with transition metal ion have been synthesized and characterized. Over the past decades great attention has been devoted to the design and synthesis of Schiff bases with enhanced ability to selectively encapsulate the given metal ion[9-10].Transition metal complexes of macrocyclic ligands have been studied for many years[11]. Recently, interest has drawn by their catalytic properties, which led to industrial applications[12-13].Macrocyclic complexes are significant as they can be used as catalysts in many organic oxidation reactions[13] and they have been found to act as possible models for biochemically important proteins and enzymes[14-18].

Prompted by these facts in the present paper some homonuclear M(II)(Where M=Pb(II),Zn(II),Ni(II),Cu(II) and Co(II)) complexes synthesized with macrocyclic ligand and characterized on reduced macrocyclic molecule derived from 1,3 benzyldehyde and diethyltriamine have been discussed and characterized by using ^{1}H NMR, IR, ESF-MS elemental analysis and photoelectron spectroscopy.

We report here the synthesis of macrocyclicbinucleating Schiff base ligand MX_2 $DIEN_2$ containing two m-Xylyl bridging moieties and two tertentatebis-imine nitrogen site and the activation of dioxygen by the corresponding dinuclear M(II) complex leading to hydroxylation of one of the arene rings.

Here, we have synthesized macrocyclic ligand [L] by using 1,3benzaldehyde and diethylenetriamine. After that we used this macrocyclic ligand for the preparation of Bimetallic Macrocyclic Complexes [M_2L] through chemical condensation method. The synthesized complexes were characterized by elemental analysis, IR, XPS data, NMR and U.V. Visible spectroscopy. IR spectra in KBr were recorded on a Perkin-Elmer 457 IR spectrophotometer.Elemental analysis was carried out in a Coleman automatic carbon, hydrogen and nitrogen analyser. The X-ray photoelectron spectra i.e. XPS were recorded on a VG Scientific ESCA-3MK II electron spectrometer.

Experimental

All chemical reagents starting materials as well as solvents were of analytical grade and purchased commercially and used without further purification.

Preparation of Ligand

The ligand was prepared by direct synthesis as Schiff base dimerization condensation of reaction between 1,3benzaldehyde and triamine with 1:1 molar ratio. A solution of MeCN(150 mL) was added dropwise to solution of diethylenetriamine (1 mmol) with continuous stirring in MeCN solution for 2 hr. A white precipitate is formed after 16 hr and was recrsytallized from CH_2Cl_2/MeCN. Elemental analysis for complexes for $C_{24}H_{30}N_6$ on C, N, H based.

The ^{I}H NMR and ^{13}C NMR spectra suggested the presence of macrocyclic complex MX_2DIEN_2 (2). The macrocyclic ligand was reduced with $NaBH_4$ in absolute ethanol. After the completion of reaction the solvent was removed under reduced pressure and product was extracted with CH_2Cl_2 from aqueous solution. A colorless oil obtained upon removal of CH_2Cl_2 solvent under reduced pressure. About 4 ml of 50% HBr was added to the oily product. The white precipitate was recrsytallized from mixture of H_2O and MeOH (20 ml and 125 ml) colorless crystal of (4) formed after 50 hr.

Preparation of [M_2.L].X_2 Complexes with Macrocyclic ligand(L)

Where M=Pb(II), Zn(II), Ni(II), Cu(II) and Co(II), (X= NO^-_3,$^-$ ClO^-_3):

The metalsalts of$MCl_2$was refluxed with the macrocyclic ligand MX_2DIEN_2 (I) in 2:1 molar ratio (in CH_2Cl_2). The colorless ligand solution formed colored complexes and these M(II)macrocyclic complexes (II) were stable at room temperature. When these complexes exposed to dioxygen at room temperature color gradually turned dark. The metal complexes were recrsytallized with ethanol. The MeCN solution of green solid obtained upon evaporation of CH_2Cl_2 respectively IR band about 3500cm^{-1} a near U.V. band at 365 nm and an ^{I}H NMR peak CD_3CN at δ 12.6 (reference Me_4Si) assigned to an OH bond to M(II). These spectral data characterized of phenoxo and hydroxo – bridged binuclear M(II) complexes.

Experimental Data of complex [Pb_2L]X_2:

IR band about 3500cm^{-1} a near U.V. band at 365 nm and an ^{I}H NMR peak CD_3CN at 12.6 (reference Me_4Si) assigned to an OH bond to M(II). Elemental analysis of [$C_{24}H_{28}N_6O_{10}Pb_2$]4+found as C= 27.4(cal 27.3), N= 8.04(8.0),O= 15.2(15.3), Pb= 39.4(39.6) % and Molar conductivity was found as 22 ohm^{-1}cm^{2}mole^{-1}.

Experimental Data of complex [Zn_2L]X_2:

IR band about 3500cm^{-1} a near U.V. band at 365 nm and an ^{I}H NMR peak CD_3CN at 12.6 (reference Me_4Si) assigned to an OH bond to M(II). Elemental analysis of [$C_{24}H_{28}N_6O_{10}Zn_2$]4+ found as C= 37.6(cal 37.8), N= 11.0(11.3),O= 20.8(21.0), Zn= 17.4(17.6) % and Molar conductivity found as 20 ohm^{-1}cm^{2}mole^{-1}.

Experimental Data of complex [$Ni_2L]X_2$:

IR band about 3500cm^{-1} a near U.V. band at 365 nm and an ^{I}H NMR peak CD_3CN at δ 12.6 (reference Me_4Si) assigned to an OH bond to M(II). Elemental analysis of $[C_{24}H_{28}N_6O_{10}Ni_2]4+$ found as C= 35.4(cal 38.5), N= 11.0(11.2),O= 21.6(21.4), Ni= 15.4(15.6) % and Molar conductivity found as 28 ohm^{-1}cm^{2}mole^{-1}.

Experimental Data of complex [$Cu_2L]X_2$:

IR band about 3500cm^{-1} a near U.V. band at 365 nm and an ^{I}H NMR peak CD_3CN at 12.6 (reference Me_4Si) assigned to an OH bond to M(II). Elemental analysis of $[C_{24}H_{28}N_6O_{10}Cu_2]4+$ found as C= 38.2(38.0), N= 11.0(11.0),O= 21.2(21.0), Cu= 16.7(17.8) % and Molar conductivity found as 24 ohm^{-1}cm^{2}mole^{-1}.

Experimental Data of complex [$Co_2L]X_2$:

IR band about 3500cm^{-1} a near U.V. band at 365 nm and an ^{I}H NMR peak CD_3CN at 12.6 (reference Me_4Si) assigned to an OH bond to M(II). Elemental analysisof $[C_{24}H_{28}N_6O_{10}Co_2]4^+$ found as C= 38.2(38.3), N= 11.2(11.2),O= 21.4(21.5), Co= 15.6(15.7) % and Molar conductivity found as 30 ohm^{-1}cm^{2}mole^{-1}.

Table 1: Analytical data of $[M_2.L].X_2$Where M=Pb(II), Zn(II), Ni(II), Cu(II) a nd Co(II), X= NO^-_3,ClO^-_3

Sr. No.	Compound	% (Calculated) Found					Molar conductance ohm^{-1}cm^{2}mole^{-1}
		M	C	H	N	O	
1.	$[Pb_2.L].X_2$	39.6 (39.4)	27.6 (27.3)	2.7 (2.8)	8.0 (7.8)	5.7 (5.6)	22
2.	$[Zn_2.L].X_2$	17.6 (17.4)	37.8 (37.7)	3.7 (3.7)	11.0 (11.0)	21.0 (21.0)	20
3.	$[Ni_2.L].X_2$	15.6 (15.5)	38.5 (38.5)	3.7 (3.6)	11.2 (12.2)	21.3 (21.2)	28
4.	$[Cu_2.L].X_2$	16.7 (16.6)	38.0 (38.0)	3.7 (3.6)	11.0 (11.0)	21.0 (21.0)	24
5.	$[Co_2.L].X_2$	15.7 (15.6)	38.3 (38.2)	3.7 (3.6)	11.2 (11.2)	21.3 (21.2)	30

Table 2: M $3p_{1/2,\,3/2}$ binding energies (eV) in $[M_2.L]Cl_2$ Where M=Pb(II), Zn(II), Ni(II), Cu(II) and Co(II), X= NO^-_3, ClO^-_3

Sr. No.	Compound	$Pb3p_{1/2,3,2}$	
		Pb $3p_{1/2}$	Pb $3p_{3/2}$
1.	$[Pb_2.L].X_2$	559.6	531.6
2.	$[Zn_2.L].X_2$	1044.8	1021.8
3.	$[Ni_2.L].X_2$	872.8	855.8
4.	$[Cu_2.L].X_2$	951.6	931.6
5.	$[Co_2.L].X_2$	794.8	780.8

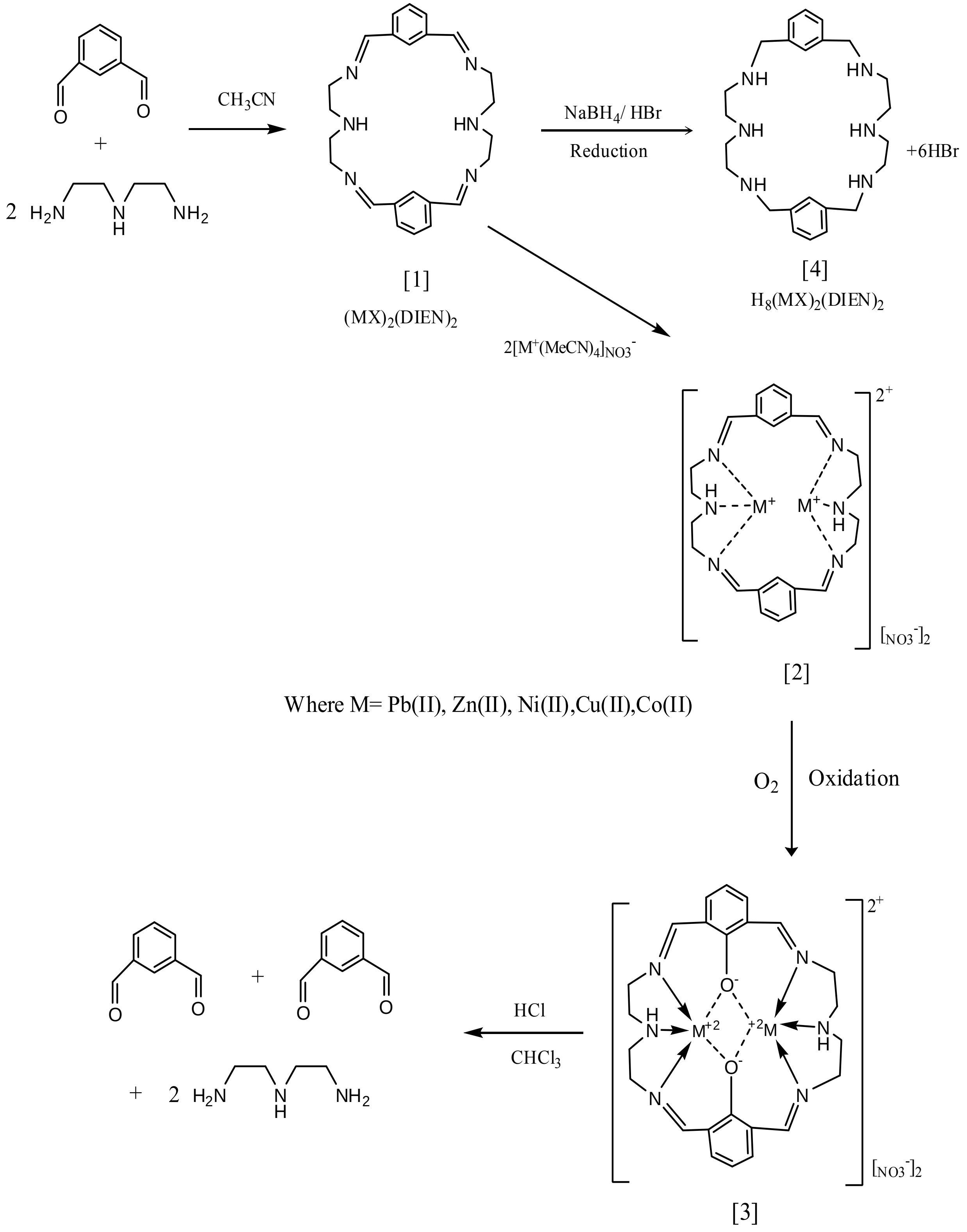

Fig. 1 Proposed scheme for the preparation of compounds $[M_2.L]X_2$

Table 3: N 1s binding energies (eV) in $[M_2.L]Cl_2$ Where M=Pb(II),Zn(II),Ni(II),Cu(II) and Co(II), X= NO^-_3,ClO^-_3

Sr.No.	Compounds	N1s	
		Uncoordinated	Coordinated
1.	$[Pb_2.L].X_2$	399.6(4)	403.4(6)
2.	$[Zn_2.L].X_2$	399.6(3)	403.4(7)
3.	$[Ni_2.L].X_2$	399.6(3)	403.4(7)
4.	$[Cu_2.L].X_2$	399.6(3)	403.4(7)
5.	$[Co_2.L].X_2$	399.6(3)	403.4(7)

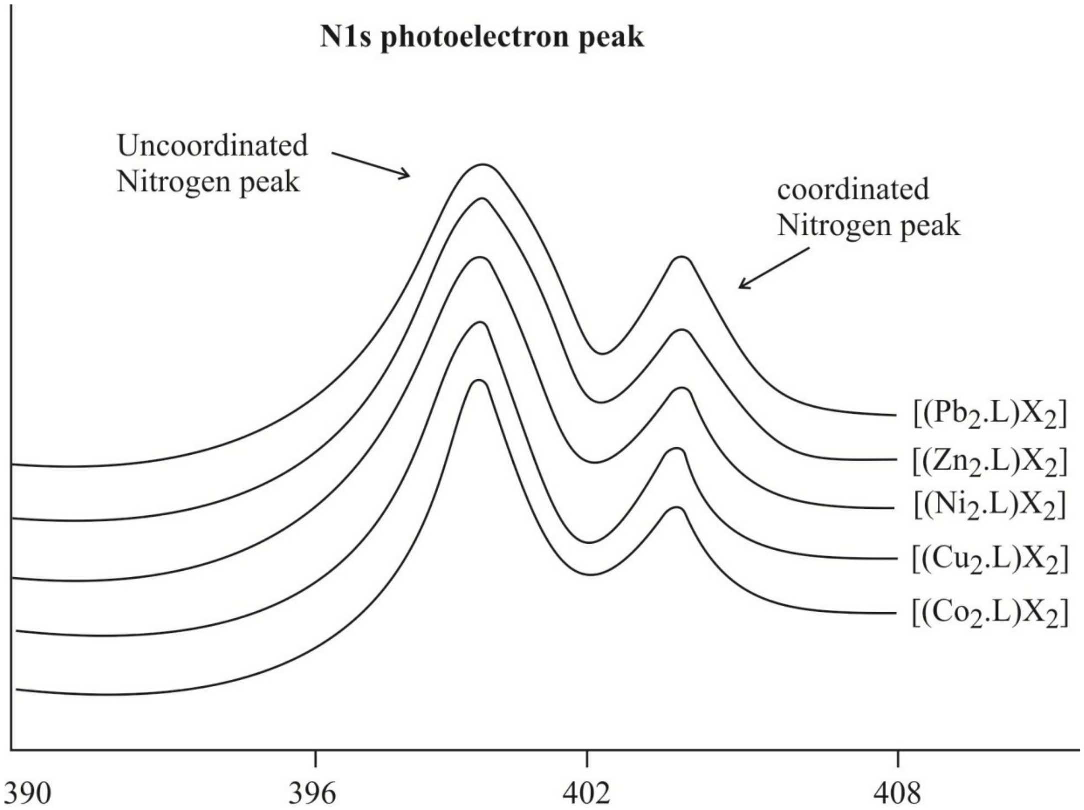

Fig. 2 N1s photoelectron peak BE(eV) in $[M_2.L]X_2$ compounds, where M= Pb(II), Zn(II), Ni(II), Cu(II) and Co(II).

Result and Discussion:

The binding energies (eV) of M $3p_{1/2,\ 3/2}$ in $[M_2.L].X_2$ Where M=Pb(II), Zn(II), Ni(II), Cu(II) and Co(II), X= NO^-_3, ClO^-_3 and N1s photoelectron peaks are listed in table 1-2 (Fig 2-3). It was observed that the binding energies of M $3p_{1/2,3/2}$ in starting material Ligand(L) was lower than their prepared molecular adducts i.e. $[M_2.L]X_2$. These observation suggested that electron density on the M(II) metal ion has increased due to coordination of ligands with M(II) metal ion[19]. (Fig 1-3). More ever, N1s photoelectron peaks with intensity ratio 6:6 in [M$_2$.L].X$_2$ Where M= Pb(II), Zn(II), Ni(II), Cu(II) and Co(II), X= NO$^-_3$, ClO$^-_{3.}$ at 399.6 (eV) in [M$_2$.L]X$_2$ suggested all six nitrogen are coordinated and at 403.4 (eV) in ligand suggested all six nitrogen are nitrogen are uncoordinated[19]. (Fig. 1) (Table 1,2).

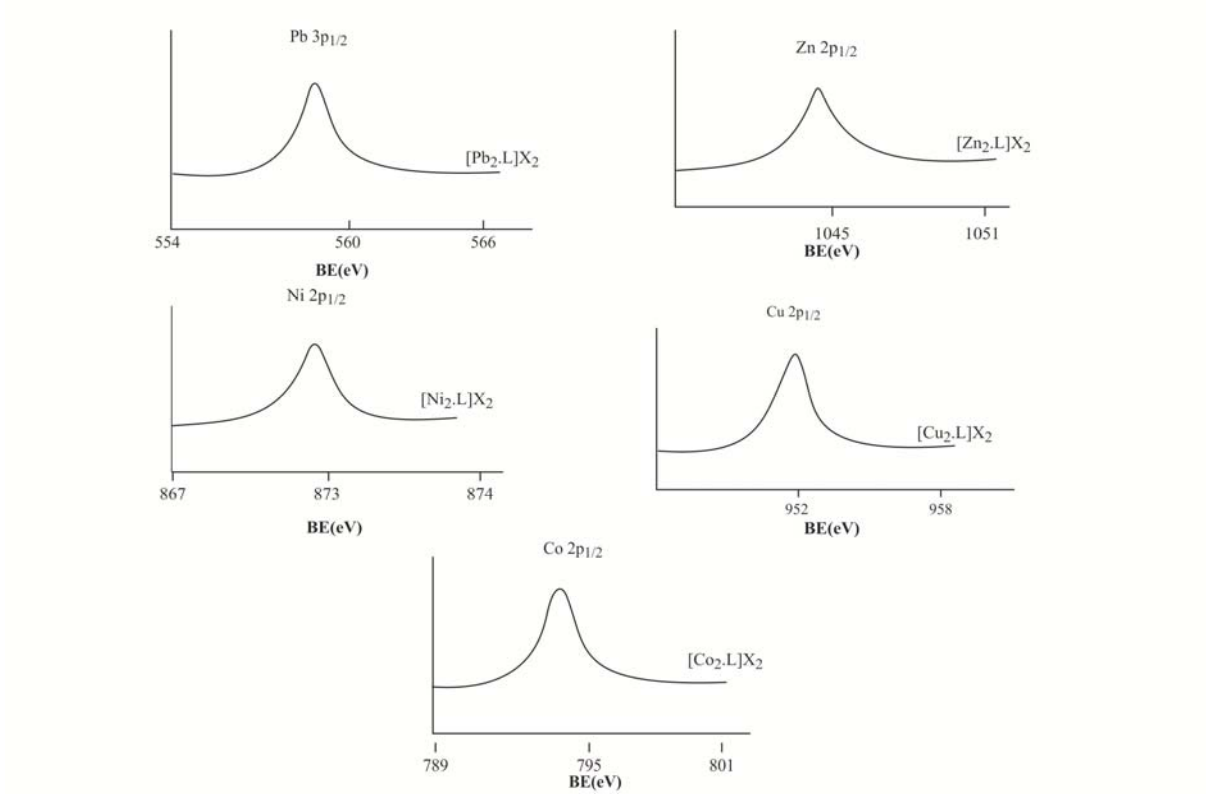

Fig. 3 M 3p1/2 binding energies(eV) in [M$_2$.L]X$_2$ compounds where M= Pb(II), Zn(II), Ni(II), Cu(II) and Co(II).

The elemental analysis data of compound (4) point out the presence of Schiff base type macrocyclic ligand.1H NMR data peak at δ=3.3 to 3.4 multiple of CH2 of DIEN), δ=4.32(singlet H for CH2 m-xylyl), δ=7.40 (singlet for aromatic H) and 7.60 (singlet aromatic H) in ratio of 8:4:3:1 respectively.

^{13}C NMRin CDCl$_3$ (reference Me4Si) product peaks at δ 41.95 and 43.86 (CH2 DIEN), 50.96 (CH2 of m-xylyl), 130.50, 131.80 and 132.06 (4 non equivalent aromatic corbon). Yield 2.20 gms 2.30 m mol 66%, overall yield 48%. A satisfactory elemental analysis C=70.20(calculated 70.20) H= 9.32(9.33),N=20.4(20.4) based on C$_{24}$H$_{38}$N$_6$ 6HBr i.e. H$_8$MX$_2$DIEN$_2$.6HBr was obtained.

Conclusion

The complexes 1-4 we synthesized are of good yield. We also show the effect of anions on coordination with metal. On the basis of elemental analysis, IR and XPS data the structural geometry of above complexes 1-4 are determined as octahedral geometry.

Acknowledgement

The author AK is thankful to Department of Chemistry University of Allahabad and University Grants Commission for providing financial assistance.

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