

# *Chapter - 7*

**Synthesis of hexaaza schiff base macrocyclic complexes and their physico-chemical properties.**

## **7.1 SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF 14-16 MEMBERED HEXAAZAMACROCYCLIC COMPLEXES OF TRANSITION METAL IONS DERIVED FROM 2,6-DIAMINOPYRIDINE AND DIONES**

### **7.1.1 INTRODUCTION**

In the past decade a great attention has been devoted to the design and synthesis of schiff bases with enhanced ability to selectively encapsulate given metal ions.<sup>1-4</sup> Macrocyclic complexes containing nitrogen donor atoms formed by the template condensation between carbonyl groups with amine in the presence of a metal ion have been reported.<sup>5-7</sup> The relationship of electronic properties and reactivities of these synthetic macrocyclic complexes to those of naturally occurring macrocycles, such as porphyrins<sup>8</sup> and corrins continues to promote great interest in their design and preparation. Studies of macrocyclic complexes have shown that some are involved in important biological process<sup>9</sup>, such as photosynthesis and dioxygen transport<sup>10</sup>, in addition to their catalytic properties<sup>11</sup> which may lead to important industrial applications. Their enhanced kinetic and thermodynamic stabilities led to a widespread study of the features which also influence their potential applications as metal extractants<sup>12</sup>, as radiotherapeutic<sup>13</sup>, as medical imaging agents<sup>14</sup>, as MRI contrast agents<sup>15</sup> and can also be used as effective sequestering agents for toxic metals.<sup>16</sup> Cyclic tetraamines have received considerable attention owing to their coordination properties towards various

metal cations.<sup>17</sup> The increasing need of finely tuned macrocycles requires the development of new synthetic tools for the preparation of such ligands. The metal template synthesis is found to be an effective method to synthesize macrocyclic complexes. It direct the steric course of the condensation reaction resulting in ring closure.<sup>18,19</sup> Here we report the synthesis and characterization of hexaazamacrocyclic complexes  $[ML^1X_2]$   $[ML^2X_2]$  for  $M = Mn (II), Co (II), Ni (II), Cu (II)$  and  $Zn (II)$ ;  $X = Cl$  or  $NO_3$  obtained from the template condensation reaction of 2,6-diaminopyridine with 2,3- butanedione and 2,4-pentanedione.

### 7.1.2 MATERIALS AND METHODS

2,6-Diaminopyridine, 2,3-butanedione and 2,4-pentanedione (**all Aldrich**) were used as received. Metal salts,  $MnX_2 \cdot 4H_2O$ ,  $CoX_2 \cdot 6H_2O$ ,  $NiX_2 \cdot 6H_2O$ ,  $CuX_2 \cdot 2H_2O$  ( $X = Cl$  or  $NO_3$  ).  $ZnCl_2$  and  $Zn (NO_3)_2 \cdot 6H_2O$  (**all BDH**) were commercially available pure samples.

**Synthesis of dichloro/nitrato (2:14,7:9-dipyridyl-4,5,11,12- tetramethyl-1,3,6,8,10,13- hexaazacyclotetradecane-3,5,10,12-tetraene)metal(II),  $[ML^1X_2]$   $[M = Mn (II), Co (II), Ni (II), Cu (II)$  and  $Zn (II)$ ;  $X = Cl$  or  $NO_3$  ]**

2,6-diaminopyridine (**20 mmol, 0.218 g**) dissolved in methanol (**20 mL**) was added to the methanolic solution of the corresponding metal salts (**10 mmol**). This reaction mixture was stirred for about 24hours and then methanolic solution (**20 mL**) of 2,3- butanedione (**20 mmol, 0.178 mL**) was added in a stirred reaction mixture. Then the resultant mixture was refluxed on a water bath for about 12-15

hours which led to the formation of polycrystalline solid product. It was filtered and washed several times with methanol and dried in vacuo.

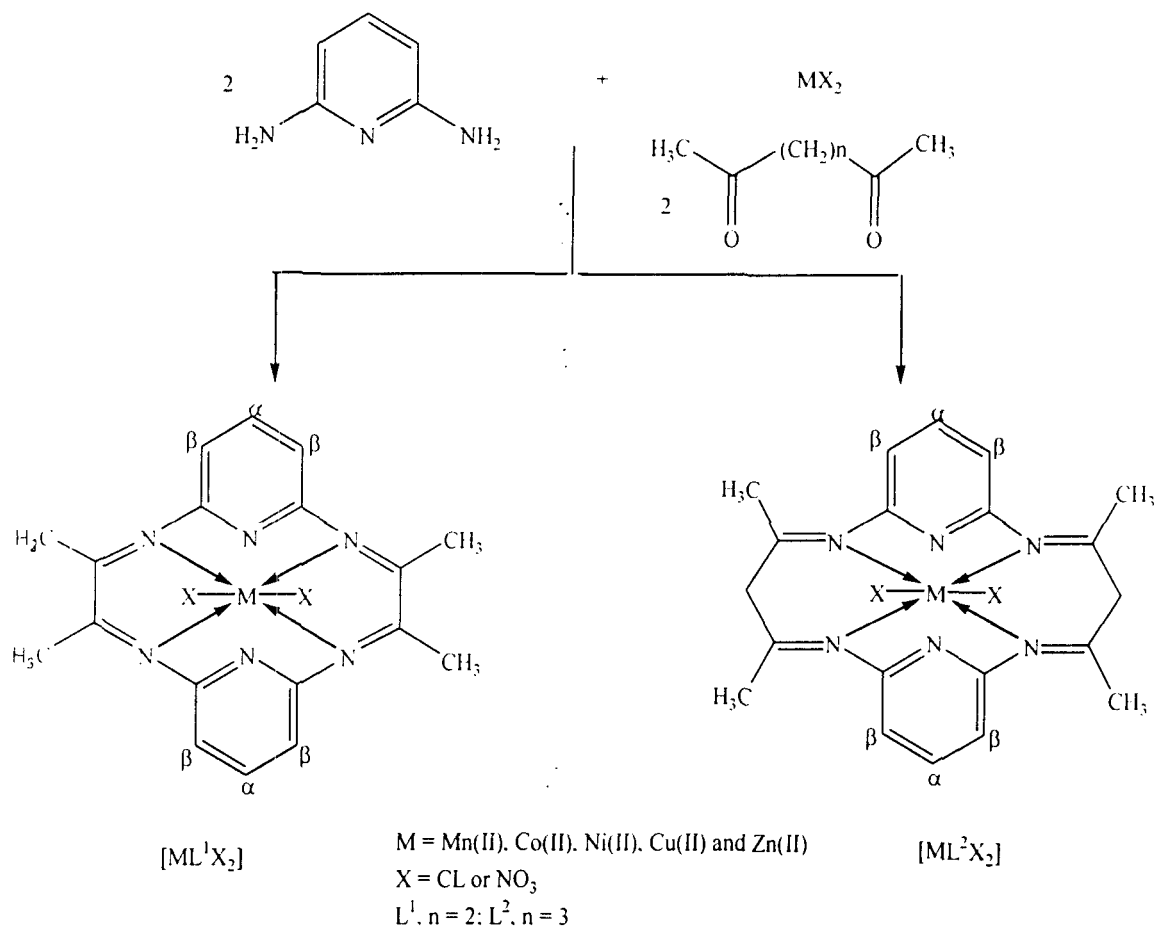
**Synthesis of dichloro/nitrato(2:16,8:10-dipyridyl-4,6,12,14-tetramethyl-1,3,7,9,11,15-hexaazacyclohexadecane-3,6,11,14-tetraene)metal(II),  $[ML^2X_2]$  [ $M = Mn(II), Co(II), Ni(II), Cu(II)$  and  $Zn(II)$ ;  $X = Cl$  or  $NO_3$ ]**

These complexes were prepared by the method described above but using 2,4-pentanedione (20 mmol, 0.207 mL) instead of 2,3-butanedione.

### 7.1.3 RESULTS AND DISCUSSION

The template reaction of 2,6-diaminopyridine and 2,3-butanedione or 2,4-pentanedione with respective metal salt in a 2:2:1 molar ratio resulted in the isolation of a new class of hexaazamacrocyclic complexes with stoichiometry  $[ML^1X_2]$  and  $[ML^2X_2]$ . The elemental analysis results (**Table 16**) are consistent with the 1:1 metal to ligand stoichiometry (**Scheme 15**). The observed molar conductances indicate<sup>20</sup> that the compounds are non-electrolytes in DMSO. They are obtained in a 30-49% yield and are stable in air and insoluble in most of the organic solvents except DMSO and DMF (**Table 16**).

The appearance of a new weak absorption band in the i.r spectra (**Table 17**) of all complexes (1570-1620  $cm^{-1}$  region) may be assigned to the imine  $\nu(C=N)$  stretching vibration whose position is consistent<sup>21</sup> with that of a coordinated C=N group and which indicates the formation of the azomethine group during the condensation. This result provides evidence for the formation of the macrocyclic



Scheme 15

**Table 16. Formula weight (calcd.), colour, melting point (°C), yield %, elemental analyses and molar conductance value of the compounds.**

Compound	F.W. (Calcd.)	Colour	M.P. (°C)	Yield (%)	Found calcd (%)					Molar Conductivity (cm <sup>2</sup> Ω <sup>-1</sup> mol <sup>-1</sup> )
					M	Cl	C	H	N	
[MnL <sup>1</sup> Cl <sub>2</sub> ]	444.22	Yellowish green	195	48	12.8 (12.3)	15.2 (15.9)	48.9 (48.6)	4.5 (4.0)	18.4 (18.9)	19
[MnL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	497.32	Yellowish green	185	38	11.5 (11.0)	-	43.7 (43.4)	3.2 (3.6)	22.1 (22.5)	16
[MnL <sup>2</sup> Cl <sub>2</sub> ]	472.27	Pale grey	250	40	11.8 (11.6)	15.5 (15.0)	50.4 (50.8)	4.1 (4.6)	17.2 (17.7)	20
[MnL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	525.38	Pale grey	260	45	10.8 (10.4)	-	45.1 (45.7)	4.4 (4.2)	21.7 (21.3)	25
[CoL <sup>1</sup> Cl <sub>2</sub> ]	448.22	Dark green	200	44	13.5 (13.1)	15.2 (15.8)	48.5 (48.2)	4.5 (4.0)	18.3 (18.7)	18
[CoL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	501.32	Dark green	250	42	11.2 (11.7)	-	43.6 (43.1)	3.9 (3.6)	22.6 (22.3)	16
[CoL <sup>2</sup> Cl <sub>2</sub> ]	476.27	Bright green	283	35	12.7 (12.3)	14.4 (14.8)	50.6 (50.4)	4.3 (4.6)	17.9 (17.6)	22
[CoL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	529.37	Bright green	270	30	11.6 (11.1)	-	45.6 (45.3)	4.5 (4.1)	21.5 (21.1)	20
[NiL <sup>1</sup> Cl <sub>2</sub> ]	447.99	Yellowish green	235	37	13.4 (13.1)	15.3 (15.8)	48.5 (48.2)	4.5 (4.0)	18.4 (18.7)	25
[NiL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	501.10	Yellowish green	255	42	11.4 (11.7)	-	43.5 (43.1)	3.2 (3.6)	22.0 (22.3)	18
[NiL <sup>2</sup> Cl <sub>2</sub> ]	476.05	Parrot green	170	39	12.6 (12.3)	14.4 (14.8)	50.0 (50.4)	4.5 (4.6)	17.1 (17.6)	14
[NiL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	529.15	Parrot green	220	43	11.5 (11.0)	-	45.7 (45.3)	4.4 (4.1)	21.5 (21.1)	23

[CuL <sup>1</sup> Cl <sub>2</sub> ]	452.83	Light green	214	42	14.5 (14.0)	15.2 (15.6)	47.3 (47.7)	4.5 (4.0)	18.3 (18.5)	24
[CuL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	505.93	Light green	185	35	12.0 (12.5)	-	42.9 (42.7)	3.0 (3.5)	22.4 (22.1)	16
[CuL <sup>2</sup> Cl <sub>2</sub> ]	480.88	Dark green	250	38	13.5 (13.2)	14.9 (14.7)	49.4 (49.9)	4.8 (4.6)	17.8 (17.4)	21
[CuL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	533.98	Dark green	190	47	11.4 (11.9)	-	44.5 (44.9)	4.4 (4.1)	20.5 (20.9)	22
[ZnL <sup>1</sup> Cl <sub>2</sub> ]	454.66	Olive green	175	38	14.0 (14.3)	15.0 (15.5)	47.0 (47.5)	3.5 (3.9)	18.0 (18.4)	15
[ZnL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	507.77	Olive green	185	49	12.4 (12.8)	-	42.8 (42.5)	3.2 (3.5)	22.4 (22.0)	19
[ZnL <sup>2</sup> Cl <sub>2</sub> ]	482.72	Olive green	150	38	13.8 (13.5)	14.9 (14.6)	49.2 (49.7)	4.2 (4.5)	17.0 (17.4)	18
[ZnL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	535.82	Olive green	193	45	12.5 (12.2)	-	44.4 (44.8)	4.5 (4.1)	20.7 (20.9)	20

Table 17. I.R vibration frequency ( $\text{cm}^{-1}$ ) of the compounds.

Compounds	$\nu$ (C=N)	$\nu$ (C-H)	$\delta$ (C-H)	$\nu$ (M-N)	$\nu$ (M-O)	$\nu$ (M-Cl)	Pyridine ring		
							In-plane ring deformations	Out-of-plane ring deformations	In plane ring deformations
							(6a)	(16b)	(8a)
[MnL <sup>1</sup> Cl <sub>2</sub> ]	1590 w	2910 s	1440 s	515 m	-	310 m	602 s	410 m	1590 s
[MnL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1615 w	2900 s	1410 s	500 m	250 m	-	607 s	412 m	1580 s
[MnL <sup>2</sup> Cl <sub>2</sub> ]	1600 w	2880 s	1420 s	490 m	-	300 m	605 s	408 m	1580 s
[MnL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1580 w	2890 s	1450 s	480 m	248 m	-	608 s	405 m	1585 s
[CoL <sup>1</sup> Cl <sub>2</sub> ]	1620 w	2890 s	1430 s	485 m	-	340 m	610 s	409 m	1586 s
[CoL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1610 w	2910 s	1460 s	470 m	230 m	-	608 s	412 m	1592 s
[CoL <sup>2</sup> Cl <sub>2</sub> ]	1570 w	2890 s	1415 s	510 m	-	350 m	609 s	404 m	1595 s
[CoL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1595 w	2870 s	1445 s	500 m	245 m	-	605 s	407 m	1582 s
[NiL <sup>1</sup> Cl <sub>2</sub> ]	1590 w	2895 s	1435 s	520 m	-	282 m	606 s	407 m	1595 s
[NiL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1580 w	2925 s	1465 s	495 m	240 m	-	607 s	405 m	1580 s
[NiL <sup>2</sup> Cl <sub>2</sub> ]	1600 w	2905 s	1415 s	505 m	-	298 m	610 s	415 m	1600 s



[NiL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1615 w	2900 s	1405 s	515 m	250 m	-	603 s	410 m	1590 s
[CuL <sup>1</sup> Cl <sub>2</sub> ]	1585 w	2900 s	1440 s	500 m	-	310 m	608 s	413 m	1600 s
[CuL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1590 w	2910 s	1420 s	510 m	230 m	-	604 s	409 m	1590 s
[CuL <sup>2</sup> Cl <sub>2</sub> ]	1605 w	2890 s	1410 s	470 m	-	295 m	605 s	411 m	1593 s
[CuL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1620 w	2880 s	1420 s	490 m	220 m	-	603 s	415 m	1585 s
[ZnL <sup>1</sup> Cl <sub>2</sub> ]	1580 w	2890 s	1440 s	520 m	-	350 m	605 s	409 m	1584 s
[ZnL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1600 w	2900 s	1410 s	480 m	250 m	-	603 s	408 m	1600 s
[ZnL <sup>2</sup> Cl <sub>2</sub> ]	1615 w	2905 s	1450 s	500 m	-	330 m	610 s	412 m	1595 s
[ZnL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1590 w	2895 s	1460 s	510 m	240 m	-	608 s	415 m	1580 s

Table 18:  $^1\text{H}$  NMR Spectroscopic data of the compounds.

Compound	$\text{CH}_3\text{-C=N}$	$\text{C-CH}_2\text{-C}$	Pyridine ring proton $\text{H}\alpha$	$\text{H}\beta$
$[\text{ZnL}^1\text{Cl}_2]$	2.53 s	-	8.42(t)	7.72(d)
$[\text{ZnL}^1(\text{NO}_3)_2]$	2.50s	-	8.40(t)	7.74(d)
$[\text{ZnL}^2\text{Cl}_2]$	2.48s	2.02 s	8.34(t)	7.55(d)
$[\text{ZnL}^2(\text{NO}_3)_2]$	2.42s	2.05 s	8.38(t)	7.60(d)

Chemical Shift ( $\delta/\text{ppm}$ ) with multiplicities in parenthesis

s = singlet; d = doublet; t = triplet;

Table 19: Magnetic moment value, electronic Spectra data, their Assignments and EPR data of the compounds.

Compound	$\mu_{\text{eff}}$ (B.M.)	Band position ( $\text{cm}^{-1}$ )	Assignment	EPR data		
				$g_{\parallel}$	$g_{\perp}$	g
[MnL <sup>1</sup> Cl <sub>2</sub> ]	5.79	18,500	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>	-	-	-
		22,700	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub>			
[MnL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	5.85	18,650	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>	-	-	-
		22,500	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub>			
[MnL <sup>2</sup> Cl <sub>2</sub> ]	5.95	18,900	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>	-	-	-
		22,500	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub>			
[MnL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	5.82	18,740	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub>	-	-	-
		22,650	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub>			
[CoL <sup>1</sup> Cl <sub>2</sub> ]	4.68	14,900	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F)	-	-	-
		21,800	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)			
[CoL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	4.80	14,600	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F)	-	-	-
		21,900	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)			
[CoL <sup>2</sup> Cl <sub>2</sub> ]	4.70	14,800	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F)	-	-	-
		21,400	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)			
[CoL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	4.95	14,700	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F)	-	-	-
		21,500	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)			
[NiL <sup>1</sup> Cl <sub>2</sub> ]	2.95	11,400	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)	-	-	-
		17,300	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)			
[NiL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	2.93	11,200	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)	-	-	-
		17,600	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)			
[NiL <sup>2</sup> Cl <sub>2</sub> ]	3.25	11,300	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)	-	-	-
		17,500	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)			
[NiL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	3.10	11,500	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)	-	-	-
		17,400	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)			

[CuL <sup>1</sup> Cl <sub>2</sub> ]	1.95	16,100 21,600	<sup>3</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>	2.21	2.12	1.7
[CuL <sup>1</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1.88	16,340 20,500	<sup>3</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>	2.27	2.14	1.9
[CuL <sup>2</sup> Cl <sub>2</sub> ]	1.80	16,200 21,600	<sup>3</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>	2.25	2.10	2.5
[CuL <sup>2</sup> (NO <sub>3</sub> ) <sub>2</sub> ]	1.79	15,900 21,800	<sup>3</sup> B <sub>1g</sub> → <sup>2</sup> B <sub>2g</sub> <sup>2</sup> B <sub>1g</sub> → <sup>2</sup> E <sub>g</sub>	2.28	2.15	1.8

framework. The bands observed in the 2870-2925 and 1405-1465  $\text{cm}^{-1}$  ranges can be assigned to  $\nu(\text{C-H})$  and  $\delta(\text{C-H})$  respectively. The pyridine moiety exhibits three important ring vibrations<sup>22,23</sup>, i.e. 6a and 8a vibrations (in-plane ring deformations) appearing at 602-610 and 1580-1600  $\text{cm}^{-1}$  respectively<sup>22</sup>, while the 16b vibration (out of plane ring deformation) is observed at 404-415  $\text{cm}^{-1}$  regions. However a medium intensity band at 470-520  $\text{cm}^{-1}$  in all the complexes is due to the  $\nu(\text{M-N})$  vibrations.<sup>24</sup> The spectra of nitrate complexes gave additional bands around 1240, 1060 and 830  $\text{cm}^{-1}$ , which are consistent with the monodentate nature of this group. Bands appearing in the nitro and chloro complexes in the regions 220-250 and 282-350  $\text{cm}^{-1}$  are assignable to  $\nu(\text{M-O})$  and  $\nu(\text{M-Cl})$  respectively.<sup>25, 26</sup>

The  $^1\text{H}$  NMR spectra (**Table 18**) of all the zinc (II) complexes show a sharp signal observed at 2.42-2.53 ppm corresponding to imine methyl ( $\text{CH}_3\text{-C=N-}$ ; 12H) protons.<sup>27</sup> The complexes of the type  $[\text{ZnL}^2\text{Cl}_2]$  and  $[\text{ZnL}^2(\text{NO}_3)_2]$  give a singlet in the region 2.02-2.05 ppm, which may be assigned<sup>28,29</sup> to methylene ( $\text{C-CH}_2\text{-C-}$ ; 4H) protons of 2,4-pentanedione moiety. A triplet at 8.34-8.42 ppm and a doublet at 7.55-7.72 ppm may reasonably be assigned<sup>30,31</sup> to pyridine moiety of 2,6-diaminopyridine molecule corresponding to  $\text{H}_\alpha$  and  $\text{H}_\beta$  of pyridine ring.

The EPR spectra of the polycrystalline copper (II) complexes were recorded at room temperature. The hyperfine splitting signals were absent in all cases instead they showed only a single broad signal. The absence of hyperfine signals may be due to the strong dipolar and exchange interaction between copper

(II) ion in the unit cell.<sup>32</sup> The  $g_{\parallel}$  and  $g_{\perp}$  have been calculated and observed in the 2.21-2.28 and 2.10-2.15  $\text{cm}^{-1}$  regions respectively, which are characteristic<sup>33</sup> of distorted octahedral geometry around copper (II) complexes. This suggests that the unpaired electron is present in the  $d_{x^2-y^2}$  orbital ( $g_{\parallel} > g_{\perp} > 2.02$ ). The  $g$  values are related<sup>34</sup> by the expression  $G = (g_{\parallel}-2)/(g_{\perp}-2)$ , which measure the exchange interaction between copper centres in the polycrystalline solid.<sup>34</sup> If  $G > 4$  exchange interaction is negligible and  $G < 4$  indicates considerable exchange interaction in the solid complexes. The calculated  $G$  value appeared in the range 1.7-2.5, which suggests the existence of a considerable exchange interaction in these solid complexes. All the complexes show  $g_{\parallel} < 2.3$ . It should be noted<sup>35</sup> that for an ionic environment  $g_{\parallel} > 2.3$ , while for a covalent environment  $g_{\parallel} < 2.3$ . The  $g_{\parallel}$  values indicate that these complexes exhibit considerable covalent character.

The spectra of all the complexes (**Table 19**) are consistent with the proposed structures. The electronic spectra (**Table 19**) of the manganese complexes exhibit two bands in the 18,500-18,900 and 22,500-22,700  $\text{cm}^{-1}$  regions, assignable<sup>36</sup> to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  and  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  transitions, respectively, corresponding to an octahedral geometry for the manganese ion. The cobalt complexes exhibit two bands in the 14,600-14,900  $\text{cm}^{-1}$  and 21,400-21,900  $\text{cm}^{-1}$  regions, characteristic<sup>36</sup> of the  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transitions, respectively, corresponding to an octahedral geometry for the cobalt ion. The nickel complexes showed two bands in the 11,200-11,500 and 17,300-17,600  $\text{cm}^{-1}$

regions, which may be assigned<sup>36</sup> as  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  transitions, respectively, arising from the octahedral geometry of  $Ni^{2+}$ . The copper complexes exhibit two bands in the 15,900-16,340 and 20,500-21,800  $cm^{-1}$  regions, respectively, which are characteristic<sup>36</sup> of a distorted octahedral geometry around the copper (II) ion. The magnetic moment data<sup>37</sup> (**Table 19**) is in further support of octahedral geometry of the complexes.

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