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Research Article

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Synthesis and Spectral Investigation of Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Novel N4 Ligands

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Abstract: Four new tetradentate amine-N donor ligands have been prepared by reducing Schiff bases derived from the condensation of 2-aminonicotinaldehyde with 1,2-diaminoethane (APMED)/ 1,2-diaminopropane (APMPD)/1,3-diaminopropane (APMP'D)/*trans*-cyclohexane-1,2-diamine (APMCD). The ligands react with transition metal [Co(II)/Ni(II)/Cu(II)/Zn(II)] salts to give microcrystalline solid complexes of 1 : 1 (M : L) composition. The ligands and the metal complexes have been characterized with analyses, molar conductance measurements, magnetic susceptibility measurements and spectroscopic investigations like mass, IR, electronic, NMR and ESR. All the complexes were found to have octahedral geometry holding 0-6 water molecules in the lattice with a general molecular formula $[MLCl_2].n\ H_2O$.

Keywords: Complexes of Co(II), Ni(II), Cu(II), Zn(II), N_4 donors, TGA, FT-IR, NMR, Mass, ESR, Electronic spectra

1. INTRODUCTION

The coordination compounds of transition metals are found to have added a great deal of chemistry and made it more interesting and applied oriented and applications span the areas such as biological, industrial, pharmaceutical, catalysis and material chemistry, *etc*., [1-7]. Among different types of ligands that influence the chemistry of transition metals and modify their spectral, catalytic and biological properties, the Schiff bases occupy a special place [7-13]. The Schiff bases, which contain imine (>C=N-) functional group afford potential sites for bio-chemically active compounds that are related to intermolecular hydrogen bonding and proton transfer equilibria [14]. Structurally, a Schiff base (also known as imine or azomethine) is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (>C=O) has been replaced by an imine or azomethine group (**Fig. 1**).

In recent times, transition metal complexes of Schiff base ligands have attracted considerable attention, not only due to their spectroscopic properties and applications [15] but also due to their remarkable antifungal, antibacterial and antitumor activities [16]. Among different carbonyl compounds,

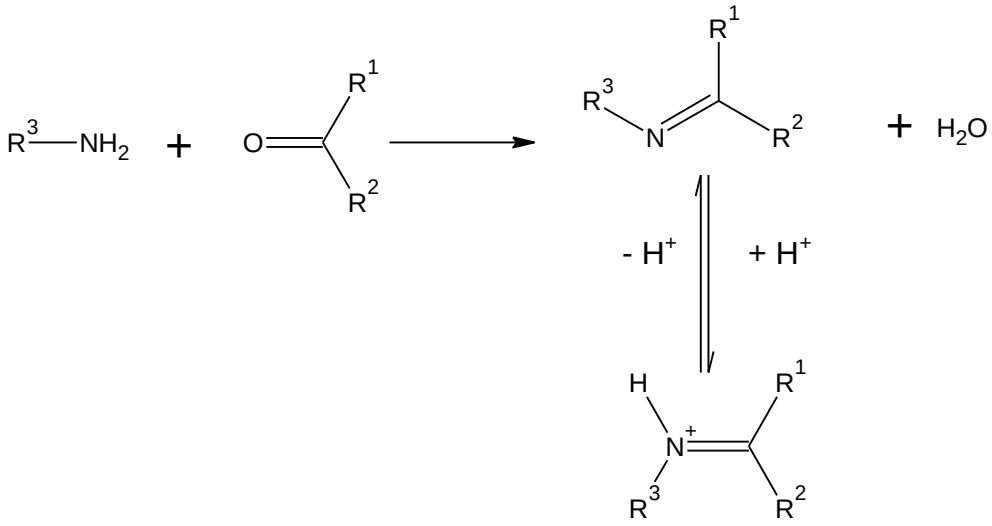
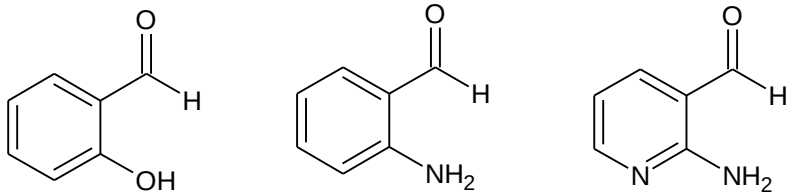


Figure 1: General Scheme for formation of Schiff bases

Salicylaldehyde (**1**) and 2-aminobenzaldehyde (**2**) are extensively used for the preparation of Schiff base ligands by condensing with different amines [17-19], and their complexes with different transition metal ions, while only a few attempts [20,21] were made to prepare and investigate similar ligands with 2-aminonicotinaldehyde (**3**) and their complexes. Further, a great deal of literature is available on metal complexes of Schiff bases and their biological and catalytic applications, but a very limited attention is paid towards the chemistry of the complexes of transition metals with reduced Schiff bases [22,23]. It is of considerable interest to investigate the complexes of new Schiff bases on one hand and comparing their coordinating behavior with amines obtained by reducing the imine group of Schiff bases. There is a great difference in electron donating abilities between >C=N- group and -C-N< group, as the >C=N group is less basic (pK_a of the protonated form is ~7.0) than -C-N< group (pKa of the protonated amine is ~10.6). The lone pair of electrons on amine nitrogen are involved in coordinate bond formation more easily than the lone pair of electrons of an imine group. Hence, the amine complexes are expected to be more stable than the imine complexes. But one should exercise a bit of care before drawing a conclusion when the imine group is a part of chelate ring involving the metal ion and an aromatic ring. In chelates of such imines there is a possibility of greater electron delocalization involving the metal *d*-orbitals and aromatic ring π-cloud, which offers somewhat greater stability to the chelate rings formed. In view of this interesting aspect and as part of our interest in developing new N, O donor ligands and their complexes [24-29] the present investigations are taken up.



1 **2** **3**

In view of the striking similarity between **1, 2** and **3**, and less quantum of literature on Schiff bases derived from **3** and more so their reduced analogues, we have prepared four new N4 ligands by condensing 2-aminonicotinaldehyde with different diamines and then reducing them. The study also involves the

synthesis of the metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) of the four new ligands: N,N'-*bis*-[(2-aminopyridin-3-yl)methyl]-ethane-1,2-diamine (**APMED**); N,N'-*bis*-(2-amino-pyridin-3-ylmethyl)-propane-1,2-diamine **(APMPD)**; N,N'-*bis*-(2-amino-pyridin-3-ylmethyl)-propane-1,3-diamine **(APMP'D)**; and N,N'-*bis*-[2-aminopyridin-3-yl-methyl]-*trans*-cyclohexane-1,2-diamine **(APMCD)**.

2. EXPERIMENTAL

All chemicals used were of AR grade, and purchased from Sigma-Aldrich. Metal chlorides were procured from E-Merk and were used as received. The solvents were dried and distilled before use.

The analytical and spectral data were measured using the following instruments: Elemental analysis (Perkin-Elmer CHN analyzer-2400, IICT, Hyderabad, and Technische Universität, Berlin); TGA and DSC thermograms (Mettler-Toledo TGA 822e series instrument); Magnetic susceptibility (EG&G PARC VSM 155 Vibrating Sample Magnetometer, RSIC, IICT Madras, Chennai); Molar conductance (Digisun Digital Conductivity Meter DI-909); IR spectra – KBr pellets (Perkin-Elmer BX1 series); UV-Vis spectra (Shimadzu UV-2401 PC); ^{1}H- and ^{13}C- NMR spectra (Jeol 300/75 MHz FT NMR spectrometer, RSIC, IIT Madras, Chennai, and Bruker 300 MHz FT NMR spectrometer, IICT, Hyderabad); Mass spectra (CEC-21-110B and Finnigan MAT-1210 massspectrometers, IICT, Hyderabad); and ESR spectra (Varian E112 X- & Q-band spectrometer, RSIC, IIT Madras, Chennai).

The metal content and the chloride ion in the complexes are determined using the procedures described elsewhere [30]. The ligands **APMED**, **APMPD**, **APMP'D** and **APMCD** were prepared by reducing the Schiff bases obtained by the reactions between 2-aminonicotinaldehyde, **3,** and different diamines (**4**, **5**, **6** or **7**) as shown in **Fig 2**. The preparation and purification of the ligands and their metal complexes are described below:

2.1 Preparation of Schiff's bases

0.02 moles (2.44 g) of 2-aminonicotinaldehyde and 0.01 mole of a diamine (viz. 1,2-diaminoethane, **4** (0.5 g); 1,2-diaminopropane, **5** (0.74 g)**;** 1,3-diaminopropane, **6** (0.74 g) or *trans*-cyclohexane-1,2-diamine), **7** (1.14 g); were placed in a 250 mL R. B. flask and heated carefully at 100 °C on an oil bath for about 30 minutes. The contents of the flask were then cooled and the TLC revealed the disappearance of the starting materials and formation of the product, the respective Schiff base. The products were purified by column chromatography (60-120 mesh silica gel) using methanol : dichloromethane in the ratio of 1 : 9. The yield was about 70–85%. The Schiff bases of 2-aminonicotinaldehyde with ethylene diamine, 1,2-diaminopropane and 1,3-diaminopropane were reported earlier [31]. The Schiff base of 2-aminonicotinaldehyde with *trans*-cyclohexane-1,2-diamine, **7**, was characterized by analysis and spectral data. - Yield 82%; m.p. 150 ^{o}C. Anal. Calcd. for $C_{18}H_{22}N_6$; C 67.06, H 6.88, N 26.07; Found C 66.92, H 6.76, N 26.11. FT-IR: 2926 cm^{-1} (Methyne str), 1634 cm^{-1} υ(C=N). The signals observed in ^{1}H NMR spectra are 8.34 ppm (s, -C*H*=N), pyridine ring H's 7.99 ppm (d, 2H), 7.35 ppm (d, 2H), 6.91 ppm (dd, 2H), 6.54 ppm (br, 4H, -NH2), 3.25 (m, 2H), 1.48 to 1.93 ppm (m, 8H). The mass spectrum (Electro spray, positive ionization) of the compound exhibited the molecular ion peak at m/z 323 amu corresponding to M+1^{+}.

2.2 Reduction of Schiff's bases

The Schiff's bases were reduced with $NaBH_4$ in methanol [23,32]. A typical reaction is: in a 250 mL round bottom flask 1 mmol of the Schiff's base was dissolved in 20 ml methanol under nitrogen

Table 1. Analytical and spectral data of the ligands

Compound	Elemental Analysis (%)	Mass, m/z $(M+1)^+$	^{1}H NMR, ppm	^{13}C NMR, ppm	UV, nm
APMED	C 61.74 (61.12) H 7.40 (7.24) N 30.86 (30.81)	273	7.98, 7.24, 6.58$_{dd}$ (Py H's, 6H) 5.49$_{br}$ (N*H*$_2$, 4H) 3.73$_s$ (NC*H*$_2$, 4H) 2.73$_s$ (CC*H*$_2$, 4H) 1.72$_{br}$ (>N*H*, 2H)	158.47-113.53 (Py C's) 52.12 (*C*H$_2$-N) 48.60 (H$_2$*C*-*C*H$_2$)	295, 234
APMPD	C 62.91 (62.81) H 7.74 (7.85) N 29.35 (29.41)	287	7.99 – 6.57 (Py ring, 6 H) 5.43 (Py-NH2, 4H) 3.70m (Py-CH2-, 4H) 2.77m (-NH-CH2-, 2H) 2.56m (NH-CH<, 1H) 1.11d (-CH-CH3- 1.60br (>NH-,2H)	158.52 – 113.57 (Py- C) 54.5,52.39 (Py-CH2) 49.67 (-CH2-) 52.33 (-CH-) 18.69 (-CH3-)	295, 235
APMP'D	C 62.91 (62.76) H 7.74 (7.86) N 29.35 (29.41)	287	7.98 – 6.55 (Py ring Hs, 6 H) 5.49, (Py-NH2, 4H) 3.72 (Py-CH2-, 4H) 2.64 (-NH-CH2-, 4H) 1.67quintet (-CH2-CH2-CH2-, 2H) 1.64-1.62br (>NH-, 2H)	158.65 – 113.49 (Pyridine ring carbons) 52.41 (Py-CH2-) 47.22, 30.30 (propylene C's)	296, 235
APMCD	C 66.23 (66.29) H 8.03 (8.11) N 25.74 (25.81)	327	7.56 – 6.58 (Py-H's, 6 H) 5.5 (Py-NH2 4H) 3.88 – 3.58 (-CH2-, 4H) 2.24 – 0.88 (C$_6$H$_{10}$ & >NH- 12H)	158.74 – 112.74 (Py-C's) 60.56 (CH2-) 47.71, 30.9, 24.84 (C6H10)	294, 234

atmosphere and 4 mmol of $NaBH_4$ was then added slowly while controlling the temperature of the flask. The reaction mixture was stirred for 2 more hours. Then it was concentrated, and poured into ice cold water and extracted the product twice into 20 ml portions of dichloromethane. The products were purified chromatographically over 60-120 mesh silica gel and eluting with methanol : dichloromethane mixture. The yields are in the range of 75 - 90%. The melting points, analytical and spectral data of the compounds are presented in **Table 1**.

2.3 Preparation of complexes

1 mmole of the ligand (0.272 g of **APMED**/0.286 g of **APMPD**/0.286 g of **APMP'D**/ 0.326 g of **APMCD**) was dissolved in 10 ml of methanol and to this a solution of 1 mmol of corresponding metal chloride hexahydrate ($MCl_2.6H_2O$: 0.2379 g Co salt/0.2377 g Ni salt/ 0.1705 g Cu salt/0.2444 g Zn salt) was added. The contents of the flask were refluxed for 3 hours. The solid complex separated was filtered, collected on a fine frit and washed with ice cold methanol and then with acetone and ether, and dried under vacuum. The yield, decomposition temperature and analytical data of the complexes are presented in Table 2.

3. RESULTS AND DISCUSSION

3.1 Characterization of ligands

The analytical and spectral data of the ligands, **APMED**, **APMPD**, **APMP'D** and **APMCD** are presented in Table 1. The CHN analytical data are in conformity with the proposed formulae of the ligands. The mass spectra of the compounds exhibit the molecular ion peak corresponding to the ion $M+1^+$. The absence of absorption around 1650 cm^{-1} υ(C=N) in the IR spectra of the compounds confirmed that the >C=N group is reduced to secondary amine group >CH-NH-. In addition to the $–CH_2–$ stretching and bending modes, all the four compounds exhibit absorptions due to 1^o and 2^o amine groups in the IR spectra between 3300 and 3000 cm^{-1}. The ^1H NMR spectra (δ, ppm) of the compounds show the signals corresponding to pyridine ring protons, amine protons, methylene and methyne protons. The ^{13}C NMR spectra show the signals (Table 1) corresponding to the different carbon atoms in the compounds. Based on the results obtained, the formation of the ligands is proposed as shown in **Fig 2**.

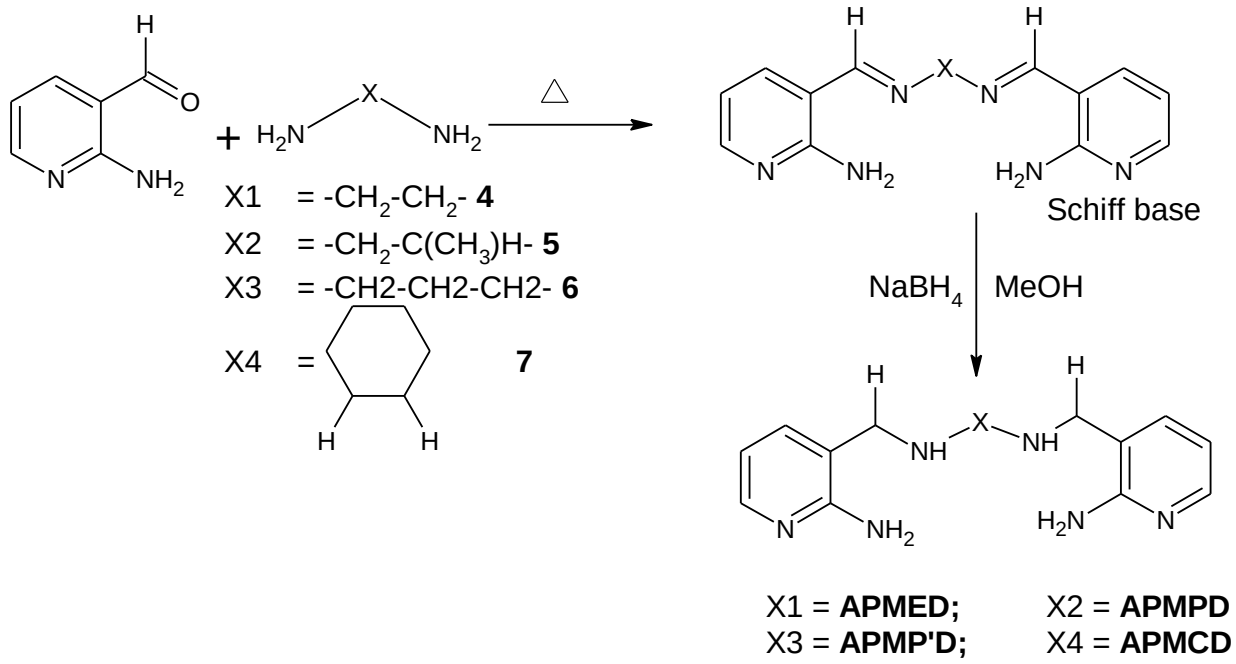


Figure 2. Scheme showing the reactions for the preparation of Ligands

3.2 Characterization of complexes

The complexes reported are stable, non-hygroscopic and freely soluble in DMSO and DMF; moderately soluble in methanol and ethanol and insoluble in acetone, diethylether and benzene. The analytical data of the complexes presented in Table 2 indicate that the metal ions are coordinated to one ligand molecule and two chloride ions. The low molar conductivities of the complexes in DMF (9–14 ohm^{-1} cm^2 mol^{-1}) indicate that they are non-electrolytic in nature [33].

3.2.1 Mass spectra

The mass spectra of all complexes exhibit high mass peak corresponding to $[MLCl_2]+1^+$ [34]. The m/z value of this peak is of the fragment after losing the lattice held water molecules. All the species containing metal ion were confirmed by good agreements between the observed and calculated isotopic distributions [35]. The other fragments observed in the mass spectra of the complexes are same as those found in the mass spectra of corresponding ligands.

3.2.2 Thermal analysis

The thermograms of Co(II), Ni(II), Cu(II) and Zn(II) complexes show initial weight loss in the temperature range of 50° –130 °C corresponding to different number of water molecules {6 – [Co(II), Ni(II)]; 2 – [Cu(II)] or 1/0 – [Zn(II)]} that are held in the lattice [36]. The number of water molecules in the lattice of each complex is given in Table 2. On further heating, the complexes exhibit mass loss curve from 200° to 950°C, after which the thermogram becomes parallel to the temperature axis. The percentage of the residue left was found to be that of the respective metal oxide; Co_3O_4, NiO, CuO, ZnO [37,38].

3.2.3 IR Spectra

The characteristic absorptions of the ligands are that of ν(N-H) of primary and secondary amine groups and pyridine ring modes in addition to υ(C-H) and δ(C-H) modes. In the IR spectra of the complexes, the stretching frequencies of the amine groups are found to have shifted by 20–40 cm^{-1} towards low frequency side indicating the coordination of the primary and secondary amine nitrogen atoms to the metal ions [27,28]. All the complexes except [Zn(**APMP'D**)Cl_2] and [Zn(**APMCD**)Cl_2] exhibit broad absorption between 3600 and 3000 cm^{-1} confirming the presence of water molecules. The non-coordination of water molecules to the metal ions is confirmed by the absence of an absorption corresponding to υ(M-O) around 400 cm^{-1} in the far-IR spectra [39]. In the far-IR region all the complexes exhibit two absorptions one around 340-370 cm^{-1} assignable to υ(M–N) [40] and the other absorption around 270–290 cm^{-1} is due to υ(M-Cl) [41]. The IR spectral data reveal that the metal ions are coordinated to the quadridentate ligand through four nitrogen atoms and to two chloride ions. The water molecules are outside the coordination sphere.

3.2.4 Magnetic moment

The magnetic moment values of the Co(II) complexes are in the range of 4.56–4.98 B. M. The high spin values of Co(II) complexes confirm that the complexes have octahedral geometry [42]. The magnetic moment values of the Ni(II) complexes are found to be between 2.98 and 3.12 B. M. indicating that there are two unpaired electrons and the geometry of the complexes is octahedral [43]. The magnetic moment values of Cu(II) complexes are in the range of 1.89-1.94 B. M., corresponding to one unpaired electron. These values are slightly higher than the spin-only value of 1.73 B. M. This indicates the absence of metal-metal interactions and monomeric nature [43]. The values at the higher side indicate that there is

Table 2. Physical and analytical data of metal complexes

Sl. No.	Compound, m/z and yield	DT,* °C	Elements, %, Found (Calculated)					μ_{eff} B. M.	$\Lambda_M^{\#}$
			C	H	N	Cl	M		
1	$Co(APMED)Cl_2]6H2O$, 510, 403, 46%	230	32.95 (32.68)	6.32 (6.41)	16.47 (16.40)	13.90 (13.27)	11.55 (11.02)	4.98	10.6
2	$[Ni(APMED)Cl_2]6H_2O$ 510, 403, 63%	245	32.97 (32.91)	6.32 (6.45)	16.48 (16.27)	13.90 (13.41)	13.90 (13.41)	3.03	9.7
3	$[Cu(APMED)Cl_2]2H_2O$ 442, 407, 44%	231	37.97 (37.41)	5.46 (5.05)	18.98 (18.45)	16.01 (16.42)	14.35 (14.12)	1.91	11.2
4	$[Zn(APMED)Cl_2]H_2O$ 426, 409, 48%	258	39.41 (39.49)	5.20 (5.01)	19.70 (19.05)	16.62 (16.41)	15.33 (15.02)	-	12.0
5	$[Co(APMPD)Cl_2].6H_2O$ 524, 417, 54%	230	34.36 (34.06)	6.54 (6.64)	16.03 (16.19)	13.52 (13.42)	11.24 (11.01)	4.89	13.4
6	$[Ni(APMPD)Cl_2].H_2O$ 433, 416, 45%	252	41.51 (41.59)	6.57 (6.42)	19.36 (19.91)	16.34 (16.54)	13.52 (13.96)	2.98	12.0
7	$[Cu(APMPD)Cl_2].2H_2O$ 456, 420, 58%	208	39.48 (39.48)	5.54 (5.45)	18.21 (18.40)	15.52 (15.46)	13.91 (13.48)	1.92	11.6
8	$[Zn(APMPD)Cl_2].H_2O$ 440, 422, 60%	258	40.88 (40.62)	5.49 (5.36)	19.07 (19.92)	16.09 (16.42)	14.84 (14.64)	-	10.8
9	$[Co(APMP'D)Cl_2]6H_2O$ 524, 417, 60%	210	34.36 (34.16)	6.54 (6.72)	16.03 (16.82)	13.52 (13.63)	11.24 (11.33)	4.94	11.6
10	$[Ni(APMP'D)Cl_2]6H_2O$ 524, 417, 54%	247	34.38 (34.21)	6.54 (6.66)	16.04 (16.71)	13.53 (13.46)	11.20 (11.10)	3.05	12.8
11	$[Cu(APMP'D)Cl_2]H_2O$ 438, 421, 49%	233	41.05 (41.42)	5.51 (5.46)	19.15 (19.27)	16.16 (16.09)	14.48 (14.22)	1.89	10.1
12	$[Zn(APMP'D)Cl_2]$ 422, 56%	247	40.88 (40.92)	5.49 (5.69)	19.07 (19.01)	16.09 (16.49)	14.84 (14.76)	-	10.9
13	$[Co(APMCD)Cl_2]6H_2O$ 564, 457, 49%	250	38.31 (38.41)	6.79 (6.43)	14.89 (14.80)	12.56 (12.71)	10.44 (10.48)	4.56	12.0
14	[Ni(APMCD)Cl2]6H2O 564, 457, 55%	237	38.32 (38.49)	6.79 (6.42)	14.90 (14.67)	12.5 (12.41)	10.40 (10.12)	3.12	11.9
15	[Cu(APMCD)Cl2]2H2O 496, 461, 42%	246	43.51 (43.64)	6.09 (6.12)	16.91 (16.84)	14.27 (14.41)	12.9 (12.80)	1.94	10.7
16	[Zn(APMCD)Cl2] 462/461, 40%	233	46.72 (46.19)	5.66 (5.46)	18.16 (18.23)	15.32 (15.42)	14.13 (14.01)	-	10.8

* Decomposition temperature, $^{\#}$ ohm^{-1} cm^2 mol^{-1}

considerable orbital contribution at room temperature [42,43]. All Zn(II) complexes reported here are found to be diamagnetic.

Table 3. Electronic spectral absorptions and ligand field parameters of the complexes

Sl. No.	Compound	Absorptions, cm^{-1}	ν_2/ν_1	ν_3/ν_1	Dq, cm^{-1}	β	B
1	$Co(APMED)Cl_2]6H_2O$	23153, 14970, 10152	1.47	2.28	1015	511	0.53
2	$[Ni(APMED)Cl_2]6H_2O$	24420, 16103, 10335	1.56	2.36	1033	634	0.64
3	$[Cu(APMED)Cl_2]2H_2O$	14224	-	-	-	-	-
4	$[Co(APMPD)Cl_2].6H_2O$	24271, 15003, 10810	1.39	2.24	1081	456	0.47
5	$[Ni(APMPD)Cl_2].H_2O$	24420, 16103, 10535	1.53	2.32	1053	594	0.56
6	$[Cu(APMPD)Cl_2].2H_2O$	14492	-	-	-	-	-
7	$[Co(APMP'D)Cl_2]6H_2O$	24191, 14450, 10548	1.37	2.08	1055	466	0.48
8	$[Ni(APMP'D)Cl_2]6H_2O$	24260, 16080, 10454	1.54	2.32	1045	598	0.57
9	$[Cu(APMP'D)Cl_2]H_2O$	15010	-	-	-	-	-
10	$[Co(APMCD)Cl_2]6H_2O$	24205, 14727, 10501	1.21	1.80	1219	495	0.51
11	[Ni(APMCD)Cl2]6H2O	24271, 16000, 10540	1.35	2.04	1184	576	0.55
12	[Cu(APMCD)Cl2]2H2O	14409	-	-	-	-	-

3.2.5 Electronic spectra

The electronic spectral absorptions of the complexes of Co(II), Ni(II) and Cu(II) along with the derived parameters are presented in Table 3. The three spectral absorptions of Co(II) complexes may be assigned to the transitions: $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$. The position of the bands in conjunction with the magnetic moment data confirms that the geometry of the complexes is octahedral [42]. The ligand field parameters like 10 Dq, B and β were obtained using the following relations:

$$10\ Dq = \nu_1;\ B = (\nu_3 + \nu_2 - 3\nu_1)/15 \text{ and } \beta = B_{complex} / B_{free\ ion}.$$

The value of $B_{free\ ion}$ of Co(II) ion is 971 cm^{-1}. The calculated value of β for the Co(II) complexes is in the range of 0.47 – 0.53 indicating that M–L bond is appreciably covalent. Electronic spectra of Ni(II) complexes show three absorptions in the region 10300 – 24400 cm^{-1} and they may be attributed to the transitions to the excited states from the ground state $^3A_{2g}$ [44]:

$$^3A_{2g}\ (F) \rightarrow {}^3T_{2g}\ (F)\ (\nu_1);\ {}^3A_{2g}\ (F) \rightarrow {}^3T_{1g}\ (F)\ (\nu_2);\ {}^3A_{2g}\ (F) \rightarrow {}^3T_{1g}\ (P)\ (\nu_3)$$

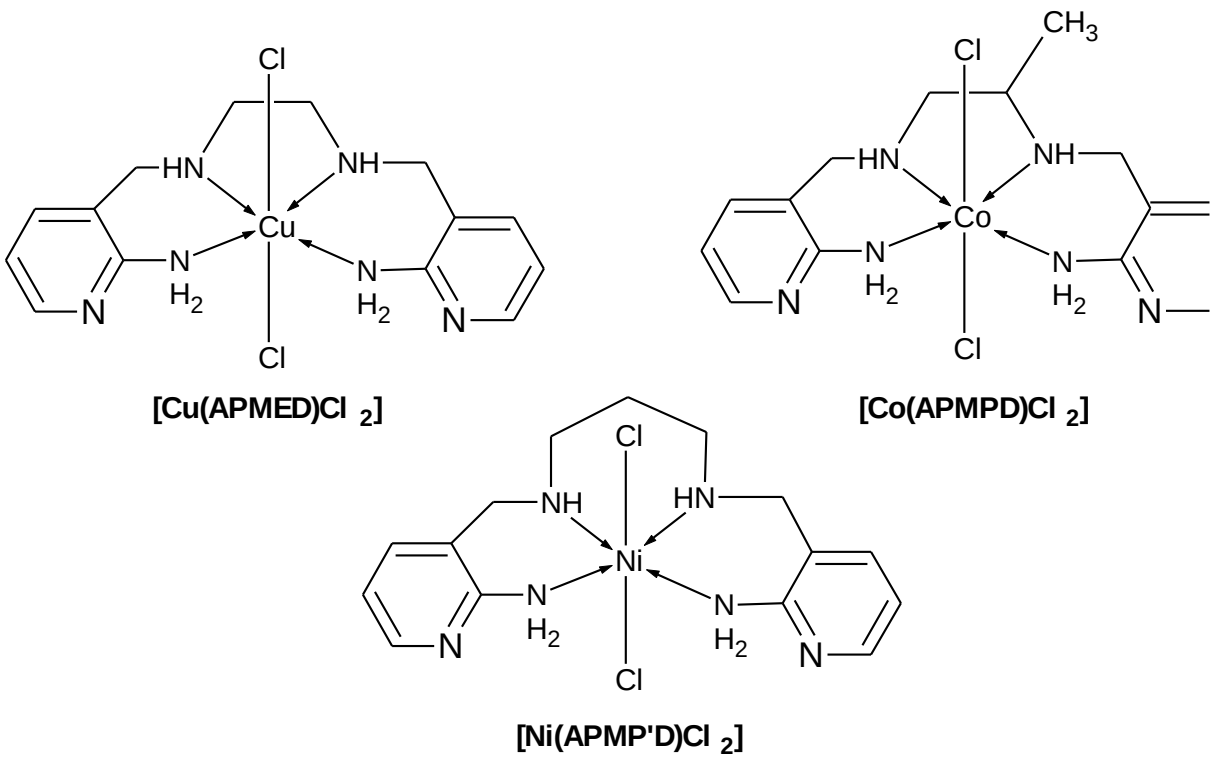


Figure 3. Tentative structures of the complexes

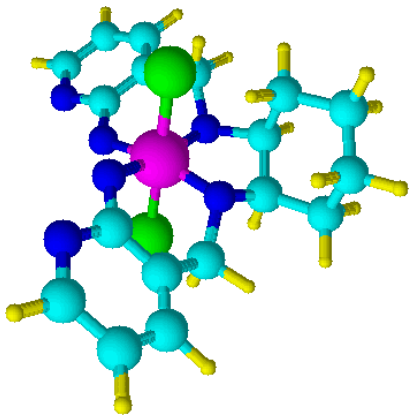


Figure 4. Optimized view of the complex [Ni(APMCD)Cl_2]

These transitions are characteristic of octahedral Ni(II) species [44]. The $B_{free\ ion}$ value of Ni(II) is 1056 cm^{-1}. The β values of the Ni(II) complexes are found to be between 0.55 and 0.58, and indicate the covalent nature of the Ni–L bond.

The electronic spectra of Cu(II) complexes show a broad absorption in the range of 14200 – 15000 cm^{-1} that may be assigned to the transition $^2B_{1g} \rightarrow {}^2A_{2g}$ [45]. This broad absorption suggests distorted octahedral geometry as expected from the Jahn-Teller effect in hexa-coordinated d^9 metal ion.

3.2.6 ESR spectra

ESR spectra of Cu(II) complexes are recorded at liquid nitrogen temperature. The spectra and the derived parameters indicate the absence of Cu–Cu interactions [46]. From the spectra, the values of $g_{||}$ and $g_{\perp}$ have been evaluated and are found to be in the range of: 2.23–2.34 ($g_{||}$) and 2.048–2.078 ($g_{\perp}$). The observed trend of $g_{||} > g_{\perp}$ indicates that the unpaired electron is present in the $d_{x}2\text{-}_{y}2$ orbital and the ground state is $^{2}B_{1g}$. This suggests that there is considerable mixing of ground and excited state terms and this is also evident from the observed magnetic moment values which are slightly greater than the spin-only value for Cu(II) ion, i.e., 1.73 B. M. This also suggests that the Cu(II) complexes are mononuclear without any Cu(II)–Cu(II) interactions [47,48].

3.2.7 ^{1}H NMR Spectra

The ^{1}H NMR spectra of diamagnetic Zn(II) complexes recorded in d_6-DMSO exhibit pyridine ring protons and aliphatic group protons in the same range as observed in the spectra of the ligands (Table 1). The signals corresponding to –NH and $–NH_2$ group protons have shifted to low field side indicating that the nitrogen atoms are coordinated to the metal ion [29,47]. The ^{1}H NMR spectra of Zn(II) complexes of APMED and APMPD show one new absorption at 3.56 and 3.83 ppm respectively which may be assigned to the protons of the water molecules held in the lattice.

All attempts to grow crystals of the complexes suitable for single crystal X-ray diffraction studies gave only microcrystalline solids which could not be used for collecting diffraction data. However, the analytical, physicochemical and spectral data of the complexes give unequivocal evidence for the structure of the complexes as presented in **Fig. 3** and the optimized view of one of the octahedral complexes, $[Ni(APMCD)Cl_2]$ is shown in **Fig. 4**.

4. CONCLUSION

The $NaBH_4$ reduction of Schiff bases obtained by the condensation of 2-amino-nicotinaldehyde with four different diamines give new N4 ligands which are characterized by the spectral analysis. The reaction of the ligands with hydrated chloride salts of Co(II), Ni(II), Cu(II) and Zn(II) give the respective metal complexes in almost quantitative yield. From the analytical and spectral data the four ligands are found to coordinate to the metal ions through four nitrogen atoms. No evidence is found with regard to the coordination of pyridine nitrogen atom to the metal ions. Attempts to grow crystals suitable for single crystal diffraction studies to ascertain possible interaction between pyridine nitrogen atoms and the metal ions were not successful. In our recent investigations on molecular structures of Ni(II) and Cu(II) complexes of 2-(pyridin-2-yl)-1,8-naphthyridine, it is established that only one N-atom (N1) of the naphthyridine moiety is involved in coordination to the metal ions along with the pyridnyl-N (N9) atom [49]. In the present case also, as the 1º amine and 2º amine nitrogen atoms are involved in the chelation, the pyridinyl N atom, which is in similar position as that of N8 in 2-(pyridin-2-yl)-1,8-naphthyridine, is not expected to coordinate to the metal ions. The elemental analyses, molar conductance, thermogravimetric analyses, magnetic moment data and mass, IR, electronic, ESR and NMR spectral studies support the tentative structures for the complexes as shown in **Fig. 3**. Further studies in our laboratory have established potential application of these complexes as catalysts in C-H bond activation (to be published). In view of the flexibility offered by the C-N single bond in the reduced Schiff bases over the C=N double in Schiff bases, and its greater basicity it will be interesting to study and compare the stabilities of complexes of these two types of ligands and the work is in progress.

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The authors declare no conflict of interest

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