SYNTHESIS AND STUDY OF SOME TRANSITION METAL COMPLEXES OF SCHIFF BASE LIGAND

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ABSTRACT

Schiff base ligand HMBPEA was prepared by the condensation of 2-hydroxy-5-methylbenzophenone with 2-phenylethylamine. A series of metal complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) was synthesized with new Schiff base ligand by reaction with metal acetates in suitable solvent medium. The Schiff base ligand was characterized by elemental analysis, FT-IR and ^{1}H NMR spectra and the metal complexes have been characterized by elemental analysis, FT-IR, magnetic measurements and electronic spectra and thermal analysis techniques. The metal complexes were found to have different geometries octahedral, tetrahedral and square planar.

Keywords: Schiff base ligand, Infrared, Diffuse reflectance, Magnetic studies, TGA

1. Introduction

Schiff bases are the compounds containing azomethine (-CH=N-) group [1] usually formed by the condensation of carbonyl compounds with primary amines. In the synthesis of various bioactive products the Schiff bases are very important materials [2]. Schiff bases show various significant photochromic and catalytic properties [3]. Schiff bases are reported to have various antibacterial, antifungal, herbicidal and clinical activities [4, 5]. Schiff bases form a very important class of organic compounds [6] popularly used as a ligand for the synthesis of coordination compounds of transition, inner transition and main group elements. Schiff base metal complexes also showed some degree of antibacterial, antifungal, antitumor and anti-inflammatory activity [7]. Many Schiff base metal complexes have been reported to show catalytic activities in various redox reactions of biological and environmental importance [8].

Transition metals generally form stable complexes with Schiff base ligands. In last few decades transition metal complexes of Schiff base ligands containing donor atoms (like N, O etc.) have been synthesized and extensively investigated for their various synthetic, biological and medicinal applications [9]. The benzophenone derivatives have various biological and physicochemical properties, therefore various benzophenone based Schiff base ligands and their transition metal complexes have been synthesized, characterized and extensively studied for their biological and medicinal applications [10]. Some Schiff base metal complexes have been found to show antitumor activity. Such complexes were synthesized and evaluated for their DNA binding abilities [11, 12]. Nowadays, the Schiff base coordination chemistry research has been expanded enormously in the field of biomedicinal applications, supramolecular chemistry, bioinorganic chemistry, separation processes, catalysis and material sciences. The formation of compounds of unusual structure and properties has been well recognized [13].

In this extent, a new Schiff base was synthesized from 2-hydroxy-5-methylbenzophenone with 2-phenylethyamine and its transition metal complexes were prepared and characterized by various physicochemical and spectroscopic techniques to suggest the stereochemistry.

2. Experimental

All the chemicals used for synthesis were of AR grade. The solvents required were used after distillation if necessary. The metal acetates of

Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were used for the synthesis of complexes. All glassware used was made of Borosilicate glass. The Schiff base was synthesized in two steps. In first step benzophenone was synthesized and in second step it was condensed with amine to yield Schiff base ligand. The newly prepared Schiff base ligand was used for the synthesis of complexes.

2.1. Synthesis of 2-hydroxy-5-methylbenzophenone

The following synthetic route has been adopted for the synthesis of 2-hydroxy-5-methylbenzopnenone:

Step-I: Preparation of 4-methylphenylbenzoate

A mixture of p-cresol (5.4 g) and benzoyl chloride (7.03 g) in 50 ml 10% NaOH solution was shaken for 15 minutes in a conical flask capped with rubber cork. The crude 4-methylphenylbenzoate separated out as a white solid. The completion of reaction was indicated by disappearance of pungent smell of Benzoyl chloride [14]. The product was filtered, washed several times with distilled water, dried and recrystallised with alcohol (yield = 9 g).

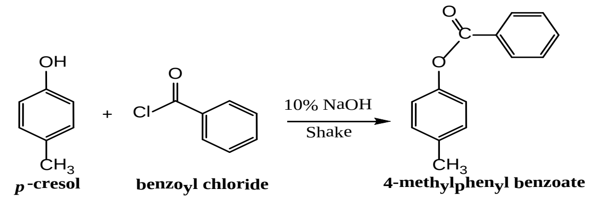


Fig. 1 – Preparation of 4-methoxybenzoate

Step-II: Fries rearrangement of 4-methylphenylbenzoate

4-methylphenylbenzoate (3.2 g) was heated to 80°C (till it melts). Now anhydrous aluminium chloride (5 g) was added in small portions with constant stirring and slowly increased the temperature so that the mixture melts. The reaction mixture was heated at 180-185°C for 2-3 hours. The flask was then cooled to room temperature. The reaction mixture was decomposes with 50% HCl. The crude product was recrystallised in ethanol. The product 2-hydroxy-5-methylbenzophenone obtained as yellow powder.

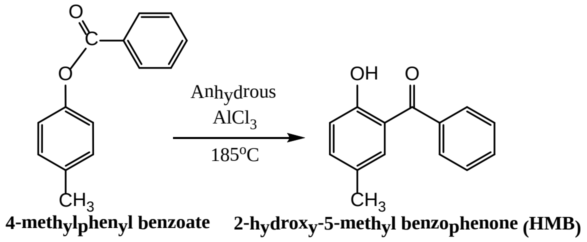


Fig. 2 –Preparation of 2-hydroxy-5-methylbenzophenone

2.2. Synthesis of Schiff base ligand (HMBPEA)

2-hydroxy-5-methylbenzopnenone (HMB) (8.5 gm) dissolved in 100 ml ethanol and 2-phenylethylamine (PEA) (4.3 ml) was added drop wise with constant stirring. The reaction mixture was refluxed for 1 hour on water bath at 80°C. Yellow precipitate of HMBPEA Schiff base was separated out. The flask was cooled to room temperature and crude product was filtered under the suction and washed several times with ethanol and dried. The yield of crude product was about 45% and melting point 280-285°C.

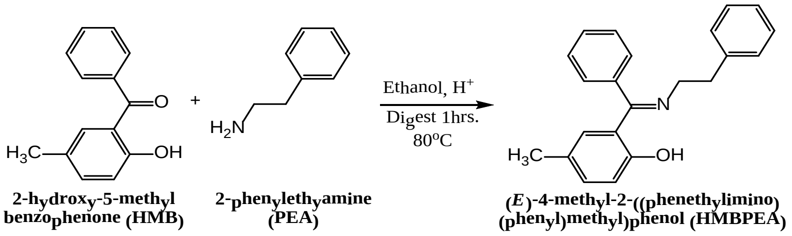


Fig. 3 – Preparation of Schiff base ligand (HMBPEA)

The newly synthesized Schiff base ligand HMBPEA was characterized by elemental analysis, IR and 1H NMR spectral studies. The analytical data suggested empirical formula $C_{22}H_{21}NO$ for the ligand HMBPEA found to contain 83.80% C; 6.66% H and 4.76% N.

The FT-IR spectra [15] show the following peaks 3664 cm^{-1} (phenolic–O-H stretching), 1608 cm^{-1} (C=N stretching), 1325 cm^{-1} (C-O phenolic stretching).

The ^1H NMR spectrum of ligand HMBPEA has been recorded in $CDCl_3$ which indicated that different non-equivalent proton resonates at different values of applied field. The δ-values are δ 7.220 – 7.441 (5H, m, Ar-H); δ 7.212 (1H, s, Ar-H); δ 6.919 – 7.191 (5H, m, Ar-H); δ 6.876 – 6.904 (1H, d, Ar-H); δ 6.484 – 6.490 (1H, d, Ar-H); δ 5.542 (1H, s, (broad) -OH); δ 3.547 – 3.595 (2H, t, $-CH_2-$); δ 2.891 – 2.990 (2H, t, $-CH_2-$); δ 2.080 (3H, s, $Ar-CH_3$).

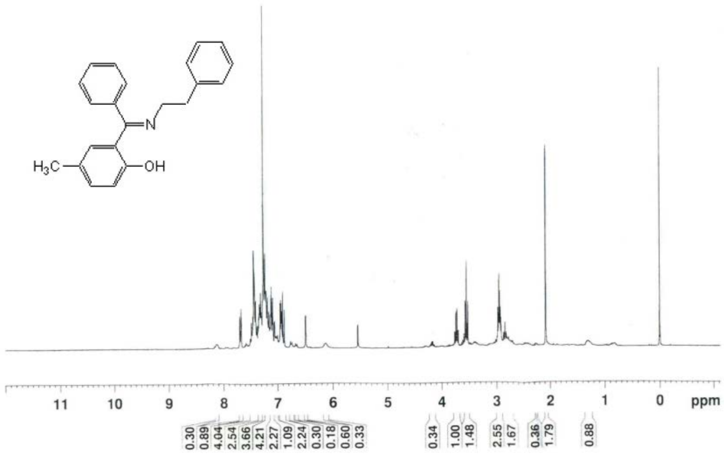


Fig. 4 – ^{1}H NMR Spectra of ligand HMBPEA

The elemental analysis and spectroscopic data is fully agreement with the formulated structure of the Schiff base ligand HMBPEA.

2.3. Synthesis of transition metal complexes of HMBPEA

The transition metal complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared by dissolving equimolar quantities of metal acetates and Schiff base ligands in minimum quantity (30-50 ml) of suitable solvents like hot methanol, ethanol and/or DMF separately. Both the solutions were filtered and mixed in hot condition. Then the reaction mixture was refluxed on a sand bath using water condenser for a suitable time. The colored products obtained with different metal salts were filtered and washed number of time with methanol and finally with petroleum ether to remove unreacted salts. The products were then dried in vacuum desiccators over calcium chloride. The complexes ware found insoluble in most of the organic solvents, while the complexes are soluble in DMSO.

The newly synthesized complexes were characterized by elemental analysis, FT-IR, magnetic susceptibility measurements and diffuse reflectance spectroscopic techniques.

The elemental analysis is used to fix the stoichiometric composition of the ligand and metal ion in complexes. The metal content of complex was estimated by chemical oxide method while carbon, hydrogen and nitrogen analyzed on a Perkin Elmer-2400 CHN elemental analyzer available at SAIF, C.D.R.I., Lucknow. The FT-IR spectra of metal complexes were recorded at Shri Shivaji College of Arts, Commerce and Science, Akola, Maharashtra on KBr pellets on SHIMADZU FTIR-Affinity-1 instrument in the range 400-4000 cm^{-1}.

Gouy's balance method was used to determine magnetic susceptibility of Schiff base metal complexes at room temperature. The diffuse reflectance spectra of Schiff base metal complexes was recorded in the range 200-1200 nm on a Varian Cary-2390 Spectrophotometer using MgO as calibrant at SAIF-STIC, Cochin University, Cochin, Kerala.

Thermal analysis of complexes was performed in the temperature range 25–800 °C in dynamic nitrogen atmosphere at SAIF, Cochin (Kerala).

3. Results and Discussion

3.1. Elemental Analysis

The stoichiometric composition of Schiff base ligand and its metal complexes has been confirmed by elemental analysis and physicochemical data [16]. The analytical data suggested that the metal and Schiff base ligand present in all complexes in the ratio of 1 : 2 (M : L). All complexes except the complex of Cd(II) contain coordinated or lattice water molecules (H_2O). The elemental analysis the metal complexes can be used to determine their composition. Analytical and Physicochemical data are listed in Table 1.

Table 1 – Analytical and Physicochemical data of complexes

Empirical Formula of the Complex	Colour	Molecular Weight	Elemental Analysis % found (Calculated)			
			M	C	H	N
HMBPEA	Pale Yellow	315.4	--	83.80 (83.78)	6.66 (6.71)	4.76 (4.44)
$[Mn(HMBPEA)_2(H_2O)_2]$	Light Brown	719.7	7.72 (7.63)	73.33 (73.42)	6.24 (6.16)	3.81 (3.89)
$[Co(HMBPEA)_2(H_2O)_2]. H_2O$	Light Pink	741.7	7.89 (7.94)	71.29 (71.24)	6.21 (6.25)	3.72 (3.78)
$[Ni(HMBPEA)_2(H_2O)_2]. 2 H_2O$	Light Green	759.5	7.76 (7.73)	69.68 (69.58)	6.43 (6.37)	7.68 (7.73)
$[Cu(HMBPEA)_2]. H_2O$	Olive Green	710.3	8.87 (8.95)	74.46 (74.39)	5.88 (5.96)	3.98 (3.94)
$[Zn(HMBPEA)_2(H_2O)_2]. H_2O$	Light Gray	748.2	8.79 (8.74)	70.57 (70.63)	6.26 (6.20)	3.65 (3.74)
$[Cd(HMBPEA)_2]$	Light Yellow	741.2	15.11 (15.17)	71.27 (71.30)	5.38 (5.44)	3.69 (3.78)

3.2. FT-IR Spectra

The ligand contains different atoms or groups having ability to coordinate with metal ions known as coordination sites. The coordination sites of the Schiff base ligand involved in the bonding with metal ions had been determined by careful comparison of FT-IR spectra of complexes with that of the parent ligands [17]. The FT-IR spectra of Schiff bases ligand HMBPEA showed a strong band at 1628 cm^{-1}, which is characteristic of the azomethine group (C=N stretching). This band is slightly shifted to lower frequency in all complexes indicating the coordination of Schiff base ligand through azomethine nitrogen atom [18, 19]. The strong band at 3664 cm^{-1} is due to phenolic group (phenolic O-H stretching) of the free Schiff base ligand which was absent in the spectrum of the complexes indicates coordination of phenolic oxygen after deprotonation [20]. Another important strong band at 1325 cm^{-1} observed in the spectrum of the free ligand corresponds to phenolic (C-O stretching) group is shifted to lower frequency in all complexes. Disappearance of the strong (O-H) band and Shifting of (C-O) band to lower frequency in the complexes indicates that the ligand involved in coordination with metal ions through the deprotonated oxygen of phenolic group [21, 22].

In all complexes, the bands in the region of 529-584 cm-1 corresponds to (M-O) stretching while that of the 472-496 cm-1 corresponds to (M-N) stretching [23]. The bands in the region of 3367-3434 cm^{-1}, 1507-1531 cm^{-1} and 832-865 cm^{-1} indicate presence of lattice and coordinated water molecules in the complex. The FT-IR spectral data of transition metal complexes of Schiff base ligand HMBPEA has been given in Table 2.

Table 2 – FT-IR data of transition metal complexes of HMBPEA (cm^{-1})

Ligand/ Complex	υ(O–H) stretching	υ(C=N) stretching	υ(C–O) stretching	υ(M–O)	υ(M–N)	$\upsilon(H_2O)$
HMBPEA	3664	1628	1325	--	--	--
$[Mn(HMBPEA)_2(H_2O)_2]$	--	1602	1296	532	479	3418, 1531, 832
$[Co(HMBPEA)_2(H_2O)_2]. H_2O$	--	1582	1305	569	496	3395, 1513,

						865
[Ni(HMBPEA)$_2$(H$_2$O)$_2$].2 H$_2$O	--	1597	1285	548	485	3367, 1507, 806
[Cu(HMBPEA)$_2$]. H$_2$O	--	1593	1272	556	468	3435, 1559, 842
[Zn(HMBPEA)$_2$(H$_2$O)$_2$]. H$_2$O	--	1589	1319	529	481	3445, 1530, 845
[Cd(HMBPEA)$_2$]	--	1586	1316	584	472	--

3.3. Magnetic Moments and Electronic Spectra of Complexes

The magnetic susceptibilities of all complexes were recorded at room temperature using Gouy’s balance method. The magnetic moment values of Mn(II), Co(II), Ni(II) and Cu(II) complexes with HMBPEA corresponds to paramagnetic character, while the Zn(II) and Cd(II) complexes have diamagnetic character.

The magnetic moment values of Mn(II) complex with HMBPEA were found to be 5.94 BM. This value is in the range of spin free value for five unpaired electrons indicating that the complex is high spin [24]. The electronic spectrum of Mn(II) complex shows three absorption peaks at 17578 cm^{-1} expected for $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$, at 23035 cm^{-1} corresponding to $^6A_{1g} \rightarrow {}^4T_{2g}(^4G)$ and a broad band at 25053-25173 cm^{-1} may be due to $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}$, suggesting octahedral geometry [25].

The electronic spectrum of Co(II) complex showed two bands at 15936 cm^{-1} and 19120 cm^{-1} due to the $^4T_{1g}$ (F) → $^4A_{2g}$ (F) and $^4T_{1g}$ (F) → $^4T_{1g}$ (P) transitions, respectively [26]. This indicates the octahedral configuration around Co(II) ions. Again the magnetic moment value of Co(II) complex was found to be 4.72 BM which further support the octahedral geometry of the complex [27].

The electronic spectrum of Ni(II) complex showed a broad absorption band at 15337 cm^{-1} which may be assigned to $^3A_{2g}$ (F) → $^3T_{1g}$ (F), while the absorption band at 28169 cm^{-1} is due to $^3A_{2g}$ (F) → $^3T_{1g}$ (P) transition. The third band at 10131 cm^{-1} is due to $^3A_{2g}$ (F) → $^3T_{2g}$ (F) transition. This indicates that the HMBPEA coordinated to Ni(II) ion in an octahedral geometry [28, 29]. The magnetic moment of the Ni(II) complex is 2.96 BM which agrees with the presence of octahedral geometry [30].

The electronic spectrum of Cu(II) complex showed absorption bands at 14025, 19120 and 37594 cm^{-1} which could be attributed to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2E_{1g}$ and charge transfer transitions respectively that characterized Cu(II) ion in a square-planar geometry. The square-planar geometry of Cu(II) ion in the complex is further confirmed by the measured magnetic moments values, 1.86 BM. The square-planar geometry is achieved by the coordination of two molecules of ligand [31, 32].

The Zn(II) and Cd(II) complexes are diamagnetic as there are no unpaired electrons in d orbital. The electronic spectrum of the Zn(II) complex is dominated by ligand bands at 36231 cm^{-1} which is assignable to $\pi \rightarrow \pi^*$ transition [33-35], while the Cd(II) complex show band at 30211 and 38910 cm^{-1} expected for $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition respectively [36]. The Zn(II) and Cd(II) complexes show charge transfer transitions at 26315 and 28248 cm^{-1} respectively which can be assigned to charge transfer from ligand to metal and vice versa. No d-d transition is expected for d^{10} Zn(II) and Cd(II) complexes [37]. Hence, the geometry of Zn(II) and Cd(II) cannot be predicted on the basis of electronic spectra alone. The magnetic moments, absorption bands and assignments of transition metal complexes of HMBPEA are given in Table 3

Table 3 – Magnetic moments, Absorption band and Assignments of transition metal complexes of HMBPEA

Complex	μ_{eff} (B.M.)	Absorption Band		Assignments	Expected Geometry
		(nm)	(cm^{-1})		
$[Mn(HMBPEA)_2(H_2O)_2]$	5.94	569 434 399	17578 23035 25053	$^6A_{1g} \rightarrow {}^4T_{1g}$ (^4G) $^6A_{1g} \rightarrow {}^4T_{2g}$ (^4G) $^6A_{1g} \rightarrow {}^4E_g$	Octahedral
$[Co(HMBPEA)_2(H_2O)_2].H_2O$	4.72	627 523 354	15936 19120 28248	$^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$ (F) $^4T_{1g}$ (F) $\rightarrow {}^4T_{1g}$ (P) C.T.	Octahedral
$[Ni(HMBPEA)_2(H_2O)_2].2H_2O$	2.96	987 652 355	10131 15337 28169	$^3A_{2g}$ (F) $\rightarrow {}^3T_{2g}$ (F) $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (F) $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (P)	Octahedral
$[Cu(HMBPEA)_2].H_2O$	1.86	713 523 266	14025 19120 37594	$^2B_{1g} \rightarrow {}^2A_{1g}$ $^2B_{1g} \rightarrow {}^2E_{1g}$ C.T.	Square Planar
$[Zn(HMBPEA)_2(H_2O)_2].H_2O$	--	380 276	26315 36231	C.T. $\pi \rightarrow \pi^*$	Octahedral
$[Cd(HMBPEA)_2]$	--	354 331 257	28248 30211 38910	C.T. $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Tetrahedral

3.4. Thermal Analysis of Schiff base metal complexes

The thermal behavior of the metal complexes showed that the hydrated complexes first lost molecules of water, followed by decomposition of the ligand molecules in the subsequent steps [38]. In general the decomposition curve of complexes show weight loss (< 150 °C) temperature range corresponds to the loss of lattice water molecules and that of the (>150°C) temperature range corresponds to coordinated water or ligand molecules [39 - 41].

Thermogravimetric analysis was performed for the Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of HMBPEA. The thermogram of complexes show slightly different decomposition pattern. The complexes of Co(II), Cu(II) and Zn(II) lose their weight in the temperature range of 95-120°C, 95-125°C and 105-125°C corresponding to two lattice water molecules while the weight loss in Ni(II) complex in the range of 90-110°C corresponding to one molecule of lattice water [42]. The Mn(II) and Cd(II) complexes does not show weight loss <150°C indicating absence of lattice water molecules.

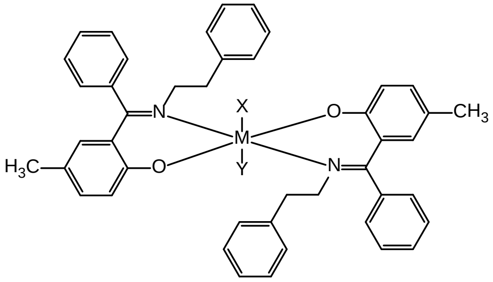
After dehydration of lattice water molecules, the complexes lose their weights in the range of 185-280°C due to coordinated water molecules [43]. The Cu(II) and Cd(II) complexes show no weight loss in this temperature range indicates absence of coordinated water molecules in these complexes [44, 45].The complexes of Mn(II), Co(II), Ni(II) and Zn(II) lose their weight in the temperature range ~180-210°C, 200-240°C, 235-280°C and 210-250°C corresponding to two coordinated water molecules. All complexes show weight loss >300°C which is consistent with the loss of Schiff base ligand molecules. The thermal analysis data of the metal complexes is shown in Table 4.

Table 4 – Thermal Analysis Data for metal complexes of HMBPEA

Complex	Degradation Temperature Range (°C)	Lost Fragment	Weight Loss % Observed (Calc.)
[Mn(HMBPEA)$_2$(H$_2$O)$_2$]	185 – 210 >300	2 H_2O Parts of Ligand	4.96 (5.00) --
[Co(HMBPEA)$_2$(H$_2$O)$_2$]. H$_2$O	95 – 120 200 – 240 >300	1 H_2O 2 H_2O Parts of Ligand	2.48 (2.43) 4.78 (4.85) --
[Ni(HMBPEA)$_2$(H$_2$O)$_2$]. 2 H$_2$O	90 – 110 235 – 280 >300	2 H_2O 2 H_2O	4.68 (4.74) 4.77 (4.74)
[Cu(HMBPEA)$_2$]. H$_2$O	95 – 125 >300	1 H_2O Parts of Ligand	2.59 (2.53) --
[Zn(HMBPEA)$_2$(H$_2$O)$_2$]. H$_2$O	105 – 125 210 – 250 >300	1 H_2O 2 H_2O Parts of Ligand	2.46 (2.41) 4. 78 (4.81) --
[Cd(HMBPEA)$_2$]	>300	Parts of Ligand	--

4. Conclusion

In present studies we reports synthesis of Schiff base ligand HMBPEA and its transition metal complexes. The analytical data and spectral study suggests that azomethine nitrogen and phenolic oxygen are involved in the coordination with metal ions. The spectral, magnetic and thermal studies proposed octahedral geometry for Mn(II), Co(II), Ni(II) and Zn(II) complexes; square-planar geometry for Cu(II) complex and tetrahedral for Cd(II) complex. The general structure of the complexes is shown in Figure 5.



M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)
X = Y = H_2O, for Mn(II), Co(II), Ni(II) and Zn(II)
X = Y = 0, for Cu(II) and Cd(II)

Fig. 5 – General Structure of Metal Complexes of HMBPEA

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