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Ambidentate behavior of pentadentate *N,N′*-bis(2-hydroxyphenyl)-pyridine-2,6-dicarboxamide towards transition metal(II) salts

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Abstract

Complexes of Co(II), Ni(II), Cu(II), Mn(II), Zn(II) and Cd(II) with *N,N′*-bis(2-hydroxyphenyl)pyridine-2,6-dicarboxamide have been synthesized and characterized by elemental analysis, conductivity measurements, spectral (electronic, i.r., n.m.r. and e.p.r.), electrochemical and thermal studies. I.r. studies show that the ligand behaves in an ambidentate way. It coordinates through the pyridine nitrogen, two amide oxygens and two phenolic oxygens in the Co(II), Ni(II), and Cu(II) complexes, whereas in the Mn(II), Zn(II) and Cd(II) complexes it coordinates through the pyridine nitrogen, two uncharged amide nitrogens and two-phenolic oxygens under similar experimental conditions.

Introduction

The amide linkage is an essential building unit in proteins, which has attracted much attention because of its high resistance to hydrolysis. This fact is of crucial importance in biological systems, since it allows for the construction of peptides from relatively simple amino acid precursors [1]. Pyridinecarboxamide, containing this linkage, acts as a multidentate ligand towards transition metal salts [2, 3] and has found use in asymmetric catalysis [4, 5], molecular receptors [6, 7], dendrimer synthesis [8] and platinum(II) complexes with anti-tumor properties [9]. Many derivatives of 2,6-pyridinedicarboxamides show anti-inflammatory, anti-pyretic and analgesic activity [10].

Iron(III) complexes of the title ligand have been reported and reveal that the ligand can behave as (i) a pentadentate ligand *via* pyridine nitrogen, doubly deprotonated amide nitrogen and doubly deprotonated phenolic oxygen with sodium hydride at 60 °C, and (ii) as a bidentate ligand through two phenolic oxygens *via* deprotonation with sodium hydroxide at room temperature [11].

Our interest in the transition metal complexes of ligands that contain amide moieties stems from their different modes of coordination towards different metal ions. In principle, transition metal ions can form complexes with amide *via* oxygen or nitrogen atoms. Depending upon the basicity differences between oxygen lone pairs and nitrogen lone pairs, complexes of uncharged amides with transition metals show almost exclusive coordination through the oxygen atom [12]. Nickel(II), copper(II) and zinc(II) complexes of urea-carrying pyridine ligands have been reported in which the ligand is coordinated to nickel(II) and copper(II) *via* the amide nitrogen without deprotonation, whereas in the zinc(II) complex the ligand is binding to the metal ion *via* the amide oxygen [12].

Many metal complexes of pyridine-2,6-dicarboxamides have crystallographically proved that deprotonated nitrogen rather than amide oxygen is involved in coordination [11–15]. Recently Borgne *et al.* [16] reported the X-ray crystal structure of the terbium complex with a pyridine-2,6- dicarboxamide ligand in which the amide oxygen is coordinated to the metal ion. Because of the interesting structural diversity in the coordinating behavior of the amide moiety towards transition metal ions, we aimed to synthesize and characterize transition metal complexes with *N,N′*-bis(2-hydroxyphenyl) pyridine-2,6-dicarboxamide with an uncharged amide functional group.

Experimental

2,6-Pyridinedicarboxylic acid (Spectrochem) and *o*-aminophenol (S.d.fine chem. Ltd.) were used without further purification. *Ortho*-anisidine (Sisco Chem.) and other solvents were distilled before use. The ligand, *N,N′*-bis(2-hydroxyphenyl)pyridine-2,6-dicarboxamide [BHPPDAH], was synthesized by two methods.

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Ligand synthesis

1st method

It involves two steps as outlined in Scheme 1.

I step. Synthesis of BMPPDA (Scheme 1)

2,6-Pyridinedicarboxylic acid (1) (1.67 g, 10 mmol) was boiled under reflux in $SOCl_2$ (2) (15 cm^3) for 4 h. Excess of $SOCl_2$ was removed under reduced pressure to leave (3), which was cooled in an ice bath. To this, dry toluene (20 cm^3) was added. *o*-Anisidine (4) (2.5 cm^3, 20 mmol) was added to the cooled contents of the flask and was boiled under reflux until no more HCl was evolved. A white crystalline product, BMPPDA which was isolated on cooling to room temperature, was filtered, washed with petroleum ether, followed by 5% $NaHCO_3$. Recrystallization from the mixture of EtOH and $CHCl_3$ (1:1, v/v) gave white needles, dried in air. m.p. 198–200 °C, yield = 90%, I.r. spectrum in KBr, $\nu(cm^{-1})$; 3371 (NH) 1685 (C=O), 1602 (m), 1537 (s), 1488(m), 1461 (m), 1290 (m), 1247 (m), 1070 (m), 758 (s), 672 (m); ^1H-n.m.r. spectrum in dmso-d_6, δ(p.p.m); 10.38 (s, 2H, NH), 8.39 (d, Ar-2H, J = 7.0 Hz), 8.32, (m, Ar-1H), 8.15 (d, Ar-2H, J = 7.6 Hz), 7.20(m, Ar-4H), 7.04 (t, Ar-2H, J = 7.0 Hz), 3,89 (s, OCH_3-6H). Mass spectrum M^+ (molecular ion peak); 377.

II step: Synthesis of BHPPDAH (Scheme 1)

Demethylation of the $-OCH_3$ group in BMPPDA was carried out according to the reported method [17]. A mixture of BMPPDA (3.77 g, 10 mmol) and anhydrous $AlCl_3$ (3.96 g, 30 mmol) was placed in dry xylene (50 cm^3) and heated at 90–95 °C, for 2 h. under anhydrous conditions, then cooled to room temperature. The reaction mixture was poured onto crushed ice (~200 g), treated with concentrated HCl (40 cm^3) and the whole mixture was extracted with Et_2O. The organic layer was again extracted thrice with 10% NaOH. The aqueous layer was then cooled in ice. Acidification with concentrated HCl yield a white solid, which was filtered, washed with H_2O and dried in air. Recrystallization from aqueous EtOH (50%) yielded a yellowish solid BHPPDAH. Mass spectrum M^+ (molecular ion peak); 349. m.p. 220–222 °C, yield, 95%.

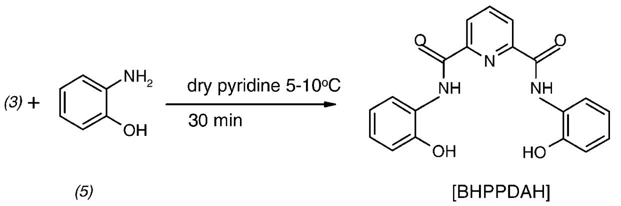
2nd method (Scheme 2)

2,6-Dicarbonyldichloride (3) (*Scheme 1*) was prepared as described in the first method, and was cooled at 5–10 °C. Dry pyridine (50 cm^3) was added to this followed by 2-aminophenol (5) (2.18 g, 20 mmol). The reaction mixture was stirred for 30-min at 5–10 °C, then poured into ice cold H_2O (200 cm^3). The isolated precipitate of BHPPDAH was washed with 5% $NaHCO_3$, followed by cold water, dried and recrystallized from aqueous EtOH (50%, v/v). The purity of the product was checked by t.l.c with a (70:30) mixture of benzene and ethyl acetate, which gave a single spot. The elemental analysis (C, H and N), i.r., ^1H-n.m.r, and mass spectral data tallied with the product obtained by the first method and also with the reported one. m.p. 220–222 °C, yield, 95%.

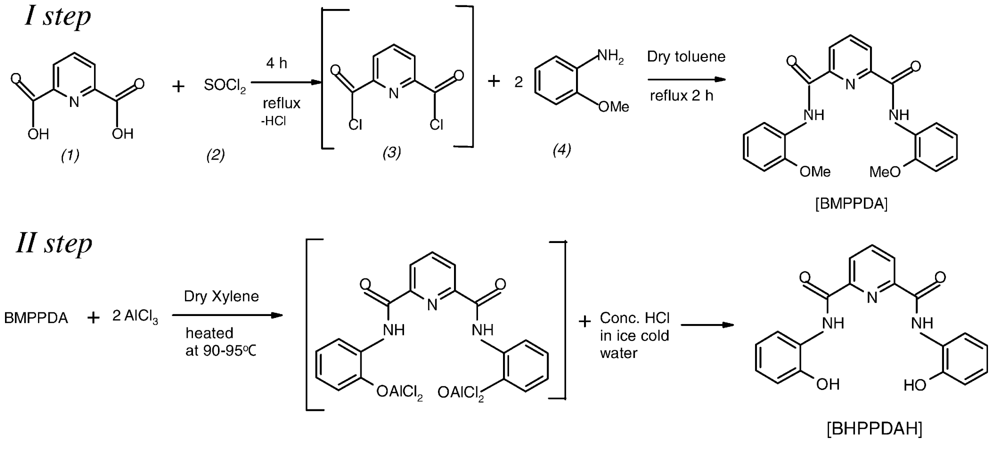
The second method is more convenient compared to the first method, which involves multisteps, is time consuming, and laborious.

Synthesis of [M(BHPPDA)H_2O] complexes

BHPPDAH (0.349 g, 1 mmol) was boiled under reflux with NaOH (0.080 g, 2 mmol) in 75% aq. EtOH (10 cm^3) for 30 min. The metal(II) chloride (1 mmol) dissolved in EtOH was added and the mixture was refluxed further for 2 h. EtOH was then removed under reduced pressure to leave a precipitate, which was filtered, washed with H_2O and dried in air.



Scheme 2.



Scheme 1.

Analysis and physical measurements

The metal content of the complexes was determined by EDTA titration after decomposition with a mixture of HCl and $HClO_4$. Elemental analyses (C, H and N) were performed using a Thermoquest CHN analyzer. Magnetic susceptibility measurements were made at room temperature on a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant and diamagnetic corrections were made by direct weighing of the ligand for diamagnetic pull. Electronic spectra were recorded on a Cary-Bio-50 Varian spectrometer in DMSO solution (10^{-3} M). I.r. spectra were recorded in the 4000–400 cm^{-1} region (KBr discs) on a Nicolet 170SX-FT-IR spectrometer. ^{1}H-n.m.r. spectra were obtained in DMSO-d_6 using TMS as the internal reference on a BRUKER AMX 400 n.m.r. spectrometer. Conductance measurements were performed in DMSO (10^{-3} M) using an ELICO-CM-82 conductivity bridge with cell type CC-01 and cell constant 0.53. Thermal studies were carried out in the 25–1000 °C range using a TGA 7 Analyser, Perkin-Elmer, US with heating rate of 10 °C min^{-1}. in a N_2 atmosphere. The e.p.r. spectra of a polycrystalline sample were recorded at room temperature and also at liquid N_2 temperature on a Varian E-4-X-band spectrometer using TCNE as a 'g' marker. The mass spectrum was recorded on a Thermofinnigan automated 1020 GCMS. Electro chemical measurements were performed at room temperature in DMF under O_2 free conditions using an Optoprecision potentiostat. A three-electrode assembly comprising a glassy carbon-working electrode, a Pt auxiliary electrode and a saturated Calomel reference electrode (SCE) were used. The supporting electrolyte was 0.1 M TBAP (Bu_4NClO_4) and the sample concentration was 0.002 M. Ferrocene was used as a standard showing the Fe(III)/Fe(II) couple at 0.38 V (*versus* SCE) under similar experimental conditions in MeCN containing 0.1 M TBAP.

Results and discussion

All the complexes have 1:1 (M:L) stoichiometry. They are soluble to a limited extent in EtOH , MeOH, DMF and DMSO, but insoluble in H_2O, $CHCl_3$ and C_6H_6. Analytical data are presented in Table 1. The molar conductivities in DMSO [10^{-3} M] suggest the non-electrolytic nature of the complexes.

Magnetic and electronic spectral studies

Magnetic and electronic spectral data are summarized in Table 1. The manganese(II) complex has a magnetic moment of 5.92 BM as expected for high-spin octahedral geometry. The magnetic moment, 4.90 BM, for the cobalt(II) complex suggests a high-spin octahedral arrangement [18, 19]. The nickel(II) complex with a magnetic moment of 2.80 BM reveals the spin free octahedral configuration. The copper(II) complex shows a magnetic moment of 1.90 BM indicating a distorted octahedral geometry [19]. Zinc(II) and cadmium(II) complexes are diamagnetic, as expected for a d^{10} configuration.

The electronic spectrum of BHPPDAH showed a broad band near 289 nm which was assigned to a n–π^* transition associated with the carbonyl chromophore. In the electronic spectrum of the cobalt(II) complex, two spin allowed transitions at 560 and 460 nm were observed, assignable to $^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ indicating octahedral stereochemistry for the cobalt(II) ion [20]. A broad band at 510 nm in the nickel(II) complex was due to the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition, indicating octahedral geometry for the nickel(II) complex [21, 22]. A broad band at 610 nm appearing as an envelope in the copper(II) complex, assigned to the $^2Eg \rightarrow {}^2T_{2g}$ transition reveals the octahedral geometry [21]. The manganese(II), zinc(II) and cadmium(II) complexes did not show any d-d transitions.

I.r. spectra

I.r. spectral data for BHPPDAH and its complexes are listed in Table 2. The BHPPDAH exhibits a band of medium intensity at 3344 cm^{-1} and was assigned to ν(NH) [11]. A broad band in the 3180–3000 cm^{-1} region was attributed to ν(OH) [11]. Three bands appearing at 1668, 1544 and 1285 cm^{-1} were due to the amide I [ν(C=O)], amide II and amide III respectively [23]. A band of medium intensity at 1357 cm^{-1} was assigned to the phenolic C—O stretch. Only two ring C—C and C—N stretching bands of the pyridine moiety were

Table 1. Analytical data, electronic spectral data and magnetic moments of BHPPDAH and its complexes

Compound	Empirical formula	Found (calc)%				Conductance ΛM (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (BM)	λ_{max} (nm)
		C	H	N	M			
BHPPDAH	$C_{19}H_{13}N_3O_4$	65.3 (65.3)	4.3 (4.3)	12.0 (12.0)	–	–		289
[Mn(BHPPDA) H_2O]	[Mn $C_{19}H_{13}N_3O_4H_2O$]	54.2 (54.3)	3.55 (3.6)	10.0 (10.0)	13.05 (13.1)	0.43	5.92	–
[Co(BHPPDA) H_2O]	[Co $C_{19}H_{13}N_3O_4H_2O$]	53.63 (53.65)	3.5 (3.5)	9.8 (9.9)	13.85 (13.9)	0.45	4.90	560, 460
[Ni(BHPPDA) H_2O]	[Ni $C_{19}H_{13}N_3O_4H_2O$]	53.8 (53.8)	3.5 (3.5)	9.9 (9.9)	13.8 (13.85)	0.51	2.80	510
[Cu(BHPPDA) H_2O]	[Cu $C_{19}H_{13}N_3O_4H_2O$]	53.2 (53.2)	3.5 (3.5)	9.8 (9.8)	14.8 (14.8)	0.43	1.90	610
[Zn(BHPPDA) H_2O]	[Zn $C_{19}H_{13}N_3O_4H_2O$]	52.95 (53.0)	3.5 (3.5)	9.7 (9.8)	15.1 (15.2)	0.47	Dia	–
[Cd(BHPPDA) H_2O]	[Cd $C_{19}H_{13}N_3O_4H_2O$]	47.7 (47.75)	3.1 (3.1)	8.8 (8.8)	23.5 (23.5)	0.44	Dia	–

Table 2. I.r. spectral data of BHPPDAH and its complexes (cm^{-1})

Compound	ν(NH)	ν(OH)	ν(C=O) [Amide I]	Amide II	Amide III	ν(C—O) phenolic	Pyridine ring stretching		Pyridine ring C—H deformation	ν(OH) H_2O
BHPPDAH	3344m	3180b	1668s	1544s	1285w	1357m	1596m	1459s	749s	
[Mn(BHPPDA) H_2O]	3348w	–	1673s	1530m	1273w	1370w	1598m	1446m, 1473m	743m	3541m
[Co(BHPPDA) H_2O]	3327b	–	1606m	1567m	1288m	1373m	(n.o)	1452m, 1489m	759m	3551m
[Ni(BHPPDA) H_2O]	3388w	–	1609m	1567m	1293w	1375m	(n.o)	1452m, 1470m	738m	3480m
[Cu(BHPPDA) H_2O]	(n.o)	–	1612m	1571s	1285w	1376w	(n.o)	1449m, 1474m	752m	3520m
[Zn(BHPPDA) H2O]	3350b	–	1666s	1533s	1277m	1370w	1585s	1456m, 1469m	743m	3527m
[Cd(BHPPDA) H_2O]	3346b	–	1672m	1539m	1282s	1373m	1587m	1453m, 1473m	740m	3540m

m = medium, b = broad, s = strong, w = weak, n.o = not observed distinctly, might have merged with the amide I band

Table 3. ^{1}H-n.m.r spectral data of BHPPDAH and its zinc(II) complex (δ p.p.m.)

Compound	H3 and H5	H4	H8 and H8′	H9 and H9′	H10 and H10′	H11 and H11′	OH	NH
BHPPDAH	8.40 (d, J = 7.2 Hz)	8.33 (m)	8.04 (d, J = 7.7 Hz)	7.07 (t, J = 7.5 Hz)	6.90 (t, J = 7.7 Hz)	6.98 (d, J = 7.5 Hz)	10.06 (s, 2H)	10.43 (s, 2H)
[Zn(BHPPDA)H_2O][a]	8.71	8.34	8.09	6.73	6.29	6.53	–	10.76

[a] Due to the poor solubility of the complex in dmso-d_6, the splitting pattern of the signals is obscured.

observed at 1596 and 1459 cm^{-1}. A strong band at 749 cm^{-1} was attributed to the pyridine ring CH-deformation mode [23].

In the spectra of cobalt(II), nickel(II) and copper(II) complexes, the amide I band shifts to lower frequencies by 56–62 cm^{-1}, while the amide II band increases in frequency by 23–27 cm^{-1} and amide III band shows a marginal shift to the higher frequency by 3–8 cm^{-1}. These changes in the amide group vibrations, due to the decrease in double bond character of the C=O group and subsequent increase in the C—N double bond character, indicates coordination of the amide oxygen to the metal ion [24].

The 1596 cm^{-1} band in the spectra of cobalt(II), nickel(II) and copper(II) complexes was indistinct. The broadness of the carbonyl frequency in the 1606–1612 cm^{-1} region is probably due to merging of the 1596 cm^{-1} pyridine ring breathing band. The band at 1459 cm^{-1} is split into two components in all the complexes and indicates clearly the coordination of pyridine nitrogen to the metal [24]. The increase in the ν(C—O) of the phenolic frequency in all the complexes by 13–19 cm^{-1} indicates coordination of the phenolic oxygen.

In the i.r. spectra of manganese(II), zinc(II) and cadmium(II) complexes the amide I band does not show any considerable shift, indicating the non-involvement of oxygen in coordination [26]. The amide II and amide III bands show a negative shift of 5–14 cm^{-1} suggesting the coordination of amide nitrogen. The 1596 cm^{-1} band was shifted to a lower wave number in the spectra of zinc(II) and cadmium(II) complexes by 9–11 cm^{-1} and it is shifted marginally (1598 cm^{-1}) in the manganese(II) complex. The band at 1459 cm^{-1} is split into two components, as in the case for cobalt(II), nickel(II) and copper(II) complexes, and indicates clearly the coordination of pyridine nitrogen to the metal [24]. The changes in the CH deformation mode in all of the complexes indicate the coordination of pyridine nitrogen.

The presence of a sharp band at *ca.* 3400–3550 cm^{-1} in all of the complexes was due to ν(OH) of coordinated water [25] followed by a non-ligand band at 723–790 cm^{-1} due to the rocking mode of coordinated water [26], which was further confirmed by thermal studies.

^{1}*H-n.m.r. spectral studies*

The ^{1}H-n.m.r. spectral data of BHPPDAH and its zinc(II) complex are given in Table 3. The ^{1}H-n.m.r spectrum of BHPPDAH showed only one set of signals indicating that the two pendant arms are magnetically equivalent in solution. Two broad singlets at 10.43 and 10.06 p.p.m. were assigned to four protons of NH and OH, respectively, in which each signal corresponds to two protons (D_2O exchange). Three doublets at 8.40 (H3 and H5), 8.05 (H8 and H8′) and 6.98 p.p.m. (H11 and H11′) (Figure 1) account for two protons each. A multiplet at 8.33 p.p.m. is attributed to the H4 proton. Triplets appearing at 7.07 (H9 and H9′) and 6.9 p.p.m. (H10 and H10′) account for two protons each. These

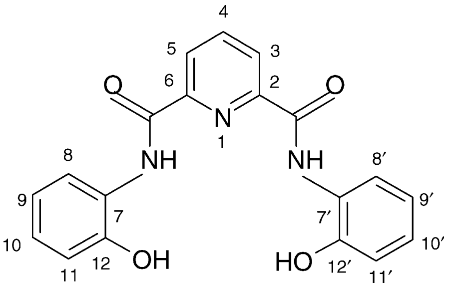


Fig. 1. Proton assignments in BHPPDAH.

assignments have been achieved by comparing ^{1}H-n.m.r. spectral data of BHPPDAH with pyridine 2,6-dicarboxylic acid and 2-aminophenol [28]. In the case of the zinc(II) complex, the signal due to H3 and H5 proton was shifted downfield by 0.31 p.p.m. indicating the coordination of pyridine nitrogen [25]. The downfield shift of the NH signal by 0.33 p.p.m. reveals the coordination of amide nitrogen. The disappearance of the OH signal from the complex indicates the coordination of phenolic oxygen *via* deprotonation. The upfield shifts of phenyl protons (H9 and H9′, H10 and H10′, H11 and H11′) supports the coordination of phenolic oxygen, thereby shielding these protons.

E.p.r. spectral studies

From the observed *g* values of the copper(II) complex at RT and LNT $(g|| = 2.14, g^{\perp} = 2.03)$, it is evident that the unpaired electron lies predominantly in the $d_{x^2} - d_{y^2}$ orbital with the possibility of some d_{z^2} character being mixed with it because of low symmetry [29]. The $g||$ value $(g|| = 2.14 < 2.3)$ indicates the larger percentage of covalency [30]. The G value (G = 4.66), being more than 4, rules out the interaction between the copper centers. The relation $(g|| > g^{\perp} > 2.0)$ in the present case suggests an elongated octahedral geometry [31].

Electrochemistry

The electrochemical behavior of the copper(II) complex was studied over the potential range from −0.25 to −0.95 V in DMF containing 0.1 M TBAP. A single quasi-reversible reduction wave was observed in the negative region, characteristic of the copper(II)–copper(I) couple at $Ep_c = -0.688$ V, with the associated anodic peak at $Ep_a = -0.562$ V for copper(I)–copper(II) oxidation. The half-wave potential for a copper(II) → copper(I) couple is $E_{1/2} = -0.625$ V. The ligand does not show any electrochemical response over the working potential range. There is no electrochemical response in the anodic potential range, i.e., oxidation of copper(II) to copper(III).

Thermal studies

The nickel(II) and copper(II) complexes decompose in two stages. The first step, 150–220 °C, results in a mass loss of 4.28 (calc. 4.24) and 4.33% (calc. 4.20), respectively, corresponding to the loss of a coordinated water molecule. In the second step, the ligand is lost in the 220–460 °C range in the nickel(II) complex, and the 220–470 °C range in the copper(II) complex, with a mass loss of 81.50% (calc. 81.89) and 80.77% (calc. 80.97), respectively. A plateau is obtained after heating above 500 °C, which corresponds to the formation of stable NiO and CuO. The weight of NiO and CuO corresponds to 18 and 19% respectively, and tallies with the metal analysis. The temperature range rules out the possibility of lattice-held water molecules.

Conclusions

From spectroscopic characterization, it can be concluded that the ligand acts as an ambidentate ligand towards different metal ions under similar experimental conditions. In the case of cobalt(II), nickel(II) and copper(II) complexes, the ligand binds to the metal ion through the pyridine nitrogen, two amide oxygens and two deprotonated phenolic oxygens (Figure 2), whereas it coordinates to the metal ion through the pyridyl nitrogen, two uncharged amide oxygens and two deprotonated phenolic oxygens (Figure 3) in zinc(II), manganese(II) and cadmium(II) complexes. In both the cases it acts as a pentadentate ligand.

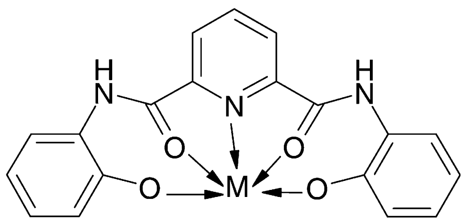


Fig. 2. Mode of coordination of BHPPDAH in cobalt(II), nickel(II) and copper(II) complexes.

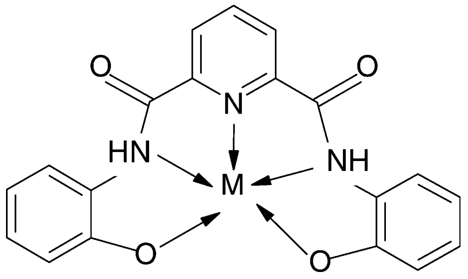


Fig. 3. Mode of coordination of BHPPDAH in manganese(II), zinc(II) and cadmium(II) complexes.

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