

Synthesis and spectral studies of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) complexes of a new macroacyclic ligand *N,N'*-bis(2-benzothiazolyl)-2,6-pyridinedicarboxamide

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Abstract: A new macroacyclic amide ligand *N,N'*-bis(2-benzothiazolyl)-2,6-pyridinedicarboxamide (BPD), formed by the condensation of 2,6-pyridinedicarbonyldichloride with 2-aminobenzothiazole, and its Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) complexes were synthesized. Their structures were elucidated on the basis of elemental analyses, conductance measurements, magnetic moments, spectral (IR, NMR, UV-Visible, EPR and FAB) and thermal studies. The complexes exhibit an octahedral geometry around the metal center. Conductance data of the complexes suggested them to be 1:1 electrolytes. The pentadentate behavior of the ligand was proposed on the basis of spectral studies. The X-band EPR spectra of the Cu(II) and Mn(II) complexes in the polycrystalline state at room (300 K) and liquid nitrogen temperature (77 K) were recorded and their salient features are reported.

Keywords: *N,N'*-bis(2-benzothiazolyl)-2,6-pyridinedicarboxamide, 2,6-pyridinedicarboxylic acid, 2-aminobenzothiazole, spectral study, thermal behavior.

INTRODUCTION

The amide bond [–C(O)NH–] has long attracted much attention since it is an essential building unit in proteins. The high stability of the amide linkage toward hydrolysis is of crucial importance to biological systems, since it allows the construction of peptides from relatively simple amino acid precursors.¹

The coordination chemistry of amide ligands is an important part of a number of chemical problems. The review of Sigel and Martin² clearly shows that research interest is centered on the structure and stability of metal ion complexes of amide, oligopeptides and related ligands. Of special interest are the deprotonation process and the species thereby formed. The amide group offers two potential binding atoms, the oxygen and nitrogen, for complexation of metal ions. A number of com-

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plexes have been reported with amide group ligands, which exhibit diverse coordinating behavior with different metal ions.^{3–5}

In recent years, pyridine carboxamides, a burgeoning class of multidentate ligands containing the amide linkage, have received much importance because these ligands have found use in asymmetric catalysis,^{6,7} molecular receptors,^{8,9} dendrimer synthesis,¹⁰ and platinum(II) complexes with antitumour properties.¹¹ Compounds similar to the title compound (BPD) containing two 2,6-diaminopyridine units are being used as receptors for organic molecules. 2,6-Diaminopyridine linked *via* and isophthanyloxy group is used as functional receptors for organic molecules, such as barbiturates, which are used as sedatives and anticonvulsants.^{8,9} The incorporation of 2,6-diamidopyridino H-bonding sites into the internal regions of a polyamido dendrimer facilitates the selective encapsulation of “guest” molecules, such as barbituric acid and 3'-azido-2',3'-dideoxythymidine (AZT), into the interior of the dendrimer. Moreover, modification of the dendritic exterior is being explored to produce dendrimers for chromatography additives, antibody conjugates, gene therapy, and electrically conducting materials.¹⁰ Many derivatives of pyridine carboxamides show anti-inflammatory, antipyretic and analgesic activities.¹²

Our interest in metal complexes of ligands that contain amide moieties stems from their occurrence in metalloproteins and metal complexes of glycopeptide antibiotics, such as bleomycin (BLM).^{13–16} In this pursuit, the ligand *N,N'*-bis(2-benzothiazolyl)-2,6-pyridinedicarboxamide was designed and synthesised. The ligating behavior of this ligand is highly diverse. It can act as a compartmental ligand, a pentadentate macrocyclic ligand coordinating through N_2O_2 or S_2NO_2 sites. In addition, it can be used as a precursor for template synthesis, and also as a receptor for organic molecules.

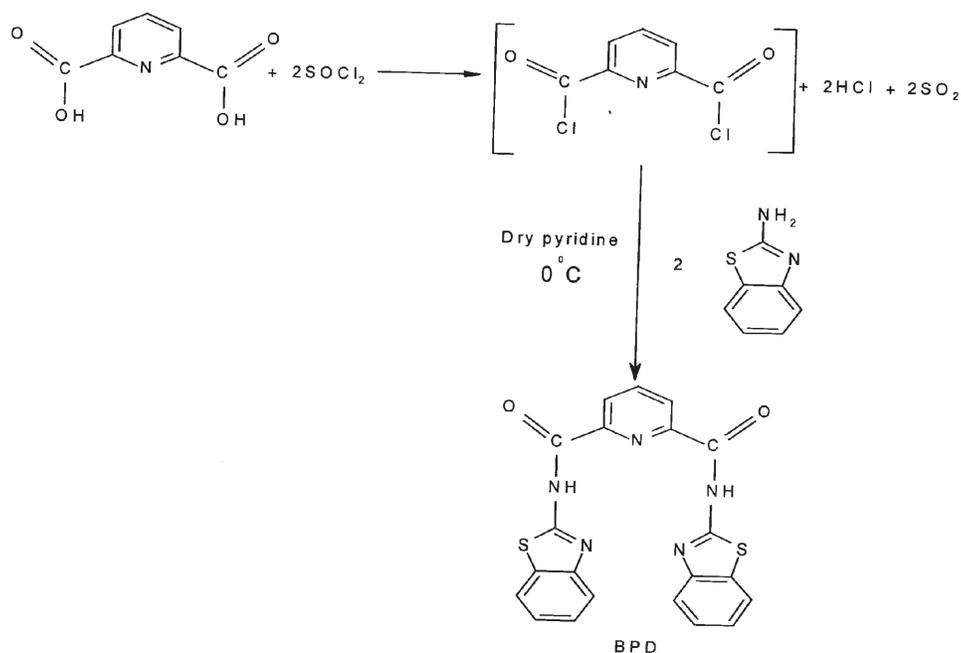
In this paper, the isolation of Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) complexes with *N,N'*-bis(2-benzothiazolyl)-2,6-pyridinedicarboxamide is reported. The complexes were analysed using elemental analyses, conductance measurement, magnetic moments, spectral (IR, NMR, UV-Visible, EPR and FAB) and thermal studies.

EXPERIMENTAL

Material and instrumentation

All the solvents used were of analytical grade and were used without further purification. The starting materials, 2,6-pyridinedicarboxylic acid, thionyl chloride and 2-aminobenzothiazole, were obtained from Spectrochem Ind. Ltd, s.d. Fine-chem Ltd. and Sisco-chem, respectively. The metal content of the complexes was determined by EDTA titration after decomposition with a mixture of HCl and $HClO_4$. The carbon, hydrogen and nitrogen contents of the ligand and the complexes were determined using a Heraeus C H N rapid analyzer. IR Spectra in the 4000–400 cm^{-1} range were measured on a Thermo Nicolet 320 FTIR spectrometer using KBr discs. 1H -NMR spectra were recorded in $DMSO-d_6$ as the solvent at 400 MHz on a BRUKER AMX 400 spectrometer using tetramethylsilane (TMS) as an internal reference. UV-VIS spectra of the complexes were recorded on a Varian CARY 50 Bio UV-VIS spectrometer. The EI mass spectrum of the ligand was recorded on a M.I Ver. 14 on UIC 002002. FAB Mass spectra of the complexes were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and the spectra were recorded at room temperature. The magnetic susceptibility

measurements were carried out on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant and diamagnetic corrections were made by direct weighing of the ligand for diamagnetic pull. The conductance measurements were recorded in DMSO (10^{-3} M) using an Elico conductivity bridge type CM-82, provided with a dip type conductivity cell fitted with platinum electrodes. EPR spectra were recorded on a Varian E-4 X-band spectrometer using TCNE as 'g' ($g = 2.0027$) marker at room temperature and at liquid nitrogen temperature. The thermal studies of the complexes were carried out in the temperature range 25 to 1000 °C on Perkin Elmer (Pyris Diamond) instrument at a heating rate of 10 °C per min.



Scheme 1. Synthetic route of ligand (BPD).

Synthesis of the ligand BPD

2,6-Pyridinedicarboxylic acid (1.67 g, 10 mmol) and thionyl chloride (20 – 25 ml) were refluxed under anhydrous conditions for 4 – 6 h until a clear solution was obtained. The excess thionyl chloride was removed under reduced pressure and the remaining mixture was cooled to 0°C and dry pyridine (30 – 35 ml) was added followed by 2-aminobenzothiazole (3.0 g, 20 mmol) with occasional stirring, until the evolution of HCl had ceased. The solid obtained was poured into ice cold water (200 ml), filtered off and washed with 5 % sodium bicarbonate solution, then with hot water and ethanol. The resulting compound was recrystallized from dioxane. The purity of the compound was controlled by TLC on pre-coated silica gel, which gave a single spot. (yield 90 %; m.p. 289°C , m/z 431). The synthetic route of BPD is given in Scheme 1.

Synthesis of the complexes

A solution of 5 mmol of MCl_2 [where $\text{M} = \text{Cu}(\text{II}), \text{Ni}(\text{II}), \text{Co}(\text{II}), \text{Mn}(\text{II}), \text{Zn}(\text{II})$ or $\text{Cd}(\text{II})$] in ethanol (10 ml) was added to the ligand (2.15 g, 5 mmol) suspended in nitrobenzene (10 ml), and the mixture was refluxed for 12 h. The obtained precipitate was filtered off, washed with water and ethanol and dried in air. All the isolated complexes were insoluble in most organic solvents, but soluble in DMF and DMSO. The complexes decompose without melting, when heated above 300°C .

TABLE I. Physical characterization, analytical and molar conductance data of the compounds

Compound	Color	Found (Calculated)/%				$\Lambda_M/S\text{ cm}^2\text{ mol}^{-1}$	MW	m.p./ $^{\circ}\text{C}$
		M	C	H	N			
BPD	Black	–	58.45 (58.54)	3.03 (3.02)	16.23 (16.21)	–	431.49	289
[Cu(BPD)Cl]Cl · 4H ₂ O	Blackish green	9.96 (9.92)	39.53 (39.51)	3.31 (3.33)	10.97 (10.95)	11.11 (11.10)	638.00	>300
[Co(BPD)Cl]Cl · 4H ₂ O	Dark brown	9.30 (9.32)	39.82 (39.81)	3.34 (3.35)	11.05 (11.07)	11.19 (11.21)	633.39	>300
[Ni(BPD)Cl]Cl · 6H ₂ O	Chocolate brown	8.77 (8.75)	37.69 (37.65)	3.76 (3.77)	10.46 (10.4)	10.59 (10.57)	669.11	>300
[Mn(BPD)Cl]Cl · 2H ₂ O	Light brown	9.25 (9.27)	42.50 (42.51)	2.88 (2.89)	11.80 (11.81)	11.94 (11.92)	593.37	>300
[Zn(BPD)Cl]Cl · 6H ₂ O	Brownish yellow	9.67 (9.65)	37.31 (37.33)	3.72 (3.71)	10.36 (10.37)	10.49 (10.48)	675.88	>300
[Cd(BPD)Cl]Cl · 6H ₂ O	Medium brown	15.54 (15.53)	34.89 (34.87)	3.48 (3.47)	9.68 (9.66)	9.80 (9.81)	722.90	>300

TABLE II. Magnetic moments and solution (DMSO) electronic spectral data of the Cu(II), Co(II), Ni(II), Mn(II), Zn(II) and Cd(II) complexes

Compounds	$\mu_{\text{eff}} (\mu_B)$	Intra ligand/Charge transfer (ν_{max} in cm^{-1}) bands	d-d Bands (ν_{max} in cm^{-1})	Dq/cm^{-1}	B'/cm^{-1}	β/cm^{-1}	$(\nu_2/\nu_1)/\text{cm}^{-1}$	$LFSE$ K cal mol^{-1}
[Cu(BPD)Cl]Cl · 4H ₂ O	1.71	3674; 32154	13869	—	—	—	—	—
[Co(BPD)Cl]Cl · 4H ₂ O	4.20	36363*; 29239–27397	8539; 16000; 19200	853	854	0.87	1.87	29.24
[Ni(BPD)Cl]Cl · 6H ₂ O	2.90	37453; 29850; 27027	11000; 17000; 26000	1100	666	0.641	1.54	37.71
[Mn(BPD)Cl]Cl · 2H ₂ O	5.60	37174; 31746	—	—	—	—	—	—
[Zn(BPD)Cl]Cl · 6H ₂ O	Diamagnetic	37878; 27777	—	—	—	—	—	—
[Cd(BPD)Cl]Cl · 6H ₂ O	Diamagnetic	36900; 28571–26666	—	—	—	—	—	—

* Calculated value

RESULTS AND DISCUSSION

The elemental analyses show 1:1 (metal:ligand) stoichiometry for all the complexes. The analytical data together with some physical properties of the complexes are summarized in Table I and II. They correspond well with the general formula $MLCl_2 \cdot nH_2O$ (where $n = 2, 4, 6$ etc; $M = Cu(II), Ni(II), Co(II), Mn(II), Zn(II)$ and $Cd(II)$, $L = C_{21}N_{13}N_5O_2S_2$). All the complexes are insoluble in common organic solvents, but soluble in DMF and DMSO. The molar conductance values of all the complexes indicate their 1:1 electrolytic nature.¹⁷ The proposed structure of the complexes is given in Fig. 1.

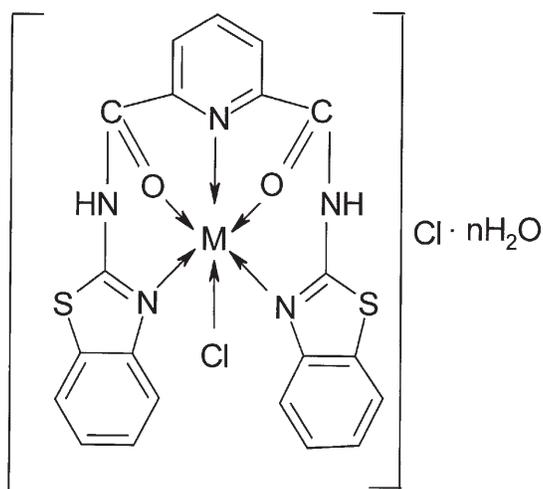


Fig. 1. The proposed structure of the complexes, where $M = Cu(II), Ni(II), Co(II), Mn(II), Zn(II)$ and $Cd(II)$ and $n = 2, 4, 6$ etc.

IR Spectra

In order to study the binding mode of the ligand to metal in the complexes, the IR spectrum of the free ligand was compared with those of the corresponding metal complexes. Selected vibrational bands of the ligand and its metal complexes and their assignments are listed in Table III. The infrared spectrum of the ligand shows a band at 3252 cm^{-1} which is assigned to $\nu(NH)$ vibration. In the spectra of all the metal complexes, the band characteristic of $\nu(NH)$ is almost unperturbed, indicating that it is not-involved in the coordination.¹⁸

The bands appearing at $1696, 1468$ and 1270 cm^{-1} may be assigned to amide-I [$\nu(CO)$], amide-II [$\nu(CN) + \delta(NH)$] and amide-III [$\delta(NH)$] vibrations, respectively. In the complexes these bands show shifts to lower frequencies ($\sim 60\text{--}80\text{ cm}^{-1}$). These changes indicate that the uncharged amide oxygen takes part in the coordination.¹⁹

The vibrations generally affected on coordination of the pyridine nitrogen to metal ions are the four pyridine ring stretching vibrations and one pyridine ring-breathing band. The four $\nu(C=C), \nu(C=N)$ bands in the ligand spectrum at 1610 (I – band), 1542 (II – band), 1456 (III – band), 1443 (IV – band) cm^{-1} were

TABLE III. Infrared spectral bands (cm^{-1}) and their assignments in the ligand and metal complexes

Compound/Complex	$\nu(\text{H}_2\text{O})$	$\nu(\text{NH})$	Amide (I)	Benzothiazole $\nu(\text{C}=\text{N})$	Pyridine ring stretching		Amide II	Amide III	Pyridine ring breathing		
BPD	–	3252m	1696s	1604s	1610m	1542m	1456m	1443m	1468	1270m	998w
$[\text{Cu}(\text{BPD})\text{Cl}]\text{Cl} \cdot 4\text{H}_2\text{O}$	3444b	3252m	1644s	1601s	1616m	1536m	1441m	1353m	1457s	1226m	1019w
$[\text{Co}(\text{BPD})\text{Cl}]\text{Cl} \cdot 4\text{H}_2\text{O}$	3434b	3252m	1644s	1602s	1614m	1532m	1389m	1357m	1457s	1270m	1028w
$[\text{Ni}(\text{BPD})\text{Cl}]\text{Cl} \cdot 6\text{H}_2\text{O}$	3412b	3252m	1634s	1537s	1615m	1530m	1395m	1361m	1428s	1270m	1016w
$[\text{Mn}(\text{BPD})\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}$	3399b	3252m	1638s	1598s	1616m	1532m	1390m	1354m	1457s	1269m	1024w
$[\text{Zn}(\text{BPD})\text{Cl}]\text{Cl} \cdot 6\text{H}_2\text{O}$	3434b	3252m	1644m	1592m	1615m	1533m	1423m	1391m	1448s	1271m	1017w
$[\text{Cd}(\text{BPD})\text{Cl}]\text{Cl} \cdot 6\text{H}_2\text{O}$	3552b	3252m	1640m	1588m	1627m	1532m	1389m	1357m	1455s	1267m	1025w

s-Strong, m-medium, b-broad, 2-weak

assigned to pyridine ring stretching vibrations. The upward shift ($10 - 20 \text{ cm}^{-1}$) of the I-band and downward shift ($20 - 40 \text{ cm}^{-1}$) of the remaining three bands in the spectra of the complexes supports the coordination of pyridine nitrogen to the metal ion. The ring-breathing band, observed at 998 cm^{-1} in the free ligand, disappeared in the spectra of the complexes and is replaced by a band at $1020 - 1030 \text{ cm}^{-1}$. This shift is also indicative of coordination of the pyridine nitrogen to the metal ion.²⁰⁻²² A medium strength band at 1604 cm^{-1} corresponds to $\nu(\text{C}=\text{N})$ of the benzothiazole moiety. On complexation it undergoes a negative shift of $5 - 20 \text{ cm}^{-1}$, indicating coordination of the benzothiazole nitrogen to the metal ion.²³⁻³⁴ The infrared spectra of all the complexes exhibit a broad band at $\sim 3450 - 3500 \text{ cm}^{-1}$, which supports the presence of lattice held water molecules,³⁵ which was further confirmed by thermal studies.

¹H-NMR Spectra

The ¹H-NMR spectra of the ligand and its Zn(II) and Cd(II) complexes were recorded in DMSO-d₆ solution and the data along with the assignments are included in Table IV. The numbering system of ligand is shown in Fig. 2. Only one set of signals were observed for the ligand and its Zn(II) and Cd(II) complexes, indicating that the two arms of the ligand in its free state as well as in its complexed form are magnetically equivalent in solution on the corresponding NMR time scale.

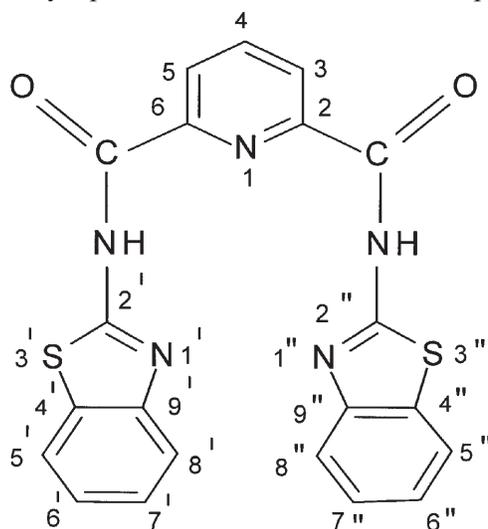


Fig. 2. Numbering system of *N,N'*-bis(2-benzothiazolyl)-2,6-pyridinedicarboxamide.

The spectrum of the ligand exhibits a singlet at 13.60 ppm due to the NH (N1H and N2H) proton, which disappears on D₂O exchange. A doublet at 8.53 and a triplet at 8.25 ppm correspond to the two (H3 and H5) and one (H4) protons of the pyridine moiety, respectively. The two doublets and two triplets appearing at 7.92 (H8' and H8''), 7.87 (H5' and H5''), 7.49 (H7' and H7'') and 7.36 ppm (H6' and H6'') are attributed to the eight aromatic protons of the benzothiazole moiety.³⁶

TABLE IV. ¹H-NMR spectral data of BPD and its Zn(II) and Cd(II) complexes

Protons	DPB	Chemical shifts in δ /ppm	
		Zn(II) complex	Cd(II) complex
N1H and N2H	13.50 (<i>s</i> , 2H)	13.50 (<i>s</i> , 2H)	13.50 (<i>s</i> , 2H)
H3 and H5	8.53 (<i>d</i> , 2H; J = 10.4 Hz)	8.54 (<i>d</i> , 2H; J = 7.60 Hz)	8.54 (<i>d</i> , 2H; J = 7.60 Hz)
H4	8.25 (<i>t</i> , 1H; J = 8.0 Hz)	8.41 (<i>t</i> , 1H; J = 8.00 Hz)	8.42 (<i>t</i> , 1H; J = 8.24 Hz)
H8' and H8''	7.92 (<i>d</i> , 2H; J = 11.2 Hz)	8.10 (<i>d</i> , 2H; J = 7.60 Hz)	8.10 (<i>d</i> , 2H; J = 8.0 Hz)
H5' and H5''	7.82 (<i>d</i> , 2H; J = 10.4 Hz)	7.92 (<i>d</i> , 2H; J = 7.60 Hz)	7.93 (<i>d</i> , 2H; J = 7.60 Hz)
H7' and H7''	7.49 (<i>t</i> , 2H; J = 8.80 Hz)	7.54 (<i>t</i> , 2H; J = 7.20 Hz)	7.54 (<i>t</i> , 2H; J = 7.60 Hz)
H6' and H6''	7.36 (<i>t</i> , 2H; J = 8.0 Hz)	7.40 (<i>t</i> , 2H; J = 7.20 Hz)	7.41 (<i>t</i> , 2H; J = 7.60 Hz)

In the spectra of the Zn(II) and Cd(II) complexes, the signal due to the NH proton appeared at the same position as in the ligand (13.60 ppm), indicating that the amide nitrogen is not included in the coordination. The signals due to the H3, H5 and H4 protons exhibit a downfield shift (0.01 – 0.17 ppm) in the Zn(II) and Cd(II) complexes, suggesting the involvement of the pyridine nitrogen in the coordination to the metal ion. In the Zn(II) and Cd(II) complexes, the signals due to the H8', H8'', H5', H5'', H7', H7'', H6' and H6'' protons shift to downfield region by 0.05 – 0.18 ppm, indicating the coordination of the benzothiazole nitrogen to the metal ion.³⁷

Magnetic and electronic spectral studies

The Cu(II) complex shows a normal magnetic moment of 1.71 μ_B observed for a d^9 system with an unpaired electron.³⁸ The Ni(II) complex with a magnetic moment of 2.90 μ_B reveals a spin free octahedral configuration.³⁸ The magnetic moment of 4.20 μ_B for the Co(II) complex suggests a highspin octahedral arrangement.³⁸ The Mn(II) complex has a magnetic moment of 5.60 μ_B , as expected for high spin octahedral geometry.³⁹ The Zn(II) and Cd(II) complexes are diamagnetic as expected for a d^{10} configuration.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The electronic spectral measurements were used to assign the stereochemistries of the metal ions in the complexes based on the positions and number of d-d transition peaks. The electronic absorption spectra of the ligand and its complexes were recorded at room temperature using DMSO as the solvent. The UV–VIS spectrum of the ligand shows only one broad band at 35587 cm^{-1} , which is assigned to the $n \rightarrow \pi^*$ transition of the C=O chromophore. On complexation, this band is shifted to lower wavelengths, suggesting coordination of the uncharged amide oxygen to the metal ion.

The electronic spectrum of the Cu(II) complex exhibited only one broad d-d transition at 13869 cm^{-1} assigned to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition, which is in conformity with the octahedral configuration around the copper ion. Though three transi-

tions are expected in this case, they are very close in energy and often appear in the form of one broad band envelope.⁴⁰ The spectrum also exhibits a band at 32154 cm^{-1} , which is assigned to a charge transfer band. The Co(II) complex displays a charge transfer band at 29239 cm^{-1} and a shoulder at 27397 cm^{-1} tailing into the visible region. The occurrence of two d-d bands at 16000 and 19200 cm^{-1} are attributed to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g} (\nu_2)$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P}) (\nu_3)$ transitions, respectively, in an octahedral geometry around the Co(II) ion.⁴¹ The electronic spectrum of Ni(II) complex exhibits three bands in the region 26000, 17000 and 11000 cm^{-1} which are assigned to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P}) (\nu_3)$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F}) (\nu_2)$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F}) (\nu_1)$ transitions, respectively, indicating an octahedral geometry around the Ni(II) ion.⁴² The spectrum of Ni(II) complex also exhibits a charge transfer band at 29850 cm^{-1} . The octahedral geometry of Co(II) and Ni(II) complexes is further supported by the value of the ν_2/ν_1 ratio, which are 1.87 and 1.54 cm^{-1} , respectively.⁴³ Various ligand field parameters (Table II), such as the Racah inter-electronic repulsion parameter (B'), ligand field splitting energy ($10Dq$), covalency factor (β) and ligand field stabilization energy ($LFSE$) have been calculated for Co(II) and Ni(II) complexes.⁴⁴

In case of the Co(II) complex, the Racah inter-electronic repulsion parameter (B') is given by the following equation:

$$B' = 1/510 \{7 (\nu_3 - 2\nu_2) + 3 [81 \nu_3^2 - 16 \nu_2 (\nu_2 - \nu_3)]^{1/2}\}$$

In case of the nickel(II) complex, B' is given by the following equation:

$$B' = \nu_2 + \nu_3 - 3\nu_1/15$$

The ligand field splitting energy ($10Dq$) is calculated as follows:

For the Co(II) complex,

$$10Dq = 1/3 (\nu_2 - \nu_3) + 15B'$$

For the Ni(II) complex,

$$10Dq = \nu_1$$

The covalency factor (β) is obtained in the following manner:

$$\beta = B'/B \text{ (where } B \text{ is the free ion value)}$$

The ligand field stabilization energy ($LFSE$) is expressed by the equation:

$$LFSE = 12Dq$$

The B' values for the complexes are lower than that of the free ion, which is an indication of orbital overlap and delocalisation of the d-orbitals. The obtained β values are less than unity, suggesting the metal–ligand bonds have a considerable amount of covalent character. The β value for the Ni(II) complex is less than that for the Co(II) complex, indicating the greater covalent nature of the former.

The Mn(II), Zn(II) and Cd(II) complexes do not show any d-d transitions but display charge transfer bands at 31746, 27777 and 28571 – 26666 cm^{-1} ,⁴⁵ respectively.

EPR Spectra

The EPR spectra of polycrystalline samples of the Cu(II) and Mn(II) complexes were recorded at room temperature (300 K) and at liquid nitrogen temperature (77 K). The room temperature EPR spectrum of the Cu(II) complex is shown in Fig. 3. The g_{\parallel} and g_{\perp} values were calculated. The spectra exhibit no hyperfine splitting, which may be due to the fact that the paramagnetic center is not diluted. In a dx^2-y^2 ground state, the EPR spectrum should give $g_{\perp} > g_{\parallel} > 2.02$, whilst a dz^2 ground state usually gives a spectrum with $g_{\perp} > g_{\parallel} \approx 2.02$.⁴⁶ In the present Cu(II) complex, the g_{\parallel} and g_{\perp} value are 2.23 and 2.07, respectively, which suggest that the unpaired electron resides in the dx^2-z^2 ground state. In axial symmetry, the g value is related by the expression $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$, which measures the exchange interaction between the copper centers in a polycrystalline solid state. The calculated G value for the present complex is 2.93, which suggests the existence of considerable exchange interaction in the solid complex. It should be noted that for an ionic environment $g_{\parallel} > 2.3$, while for a covalent environment $g_{\parallel} < 2.3$. The copper complex shows $g_{\parallel} < 2.3$ indicating its considerable covalent character.⁴⁶⁻⁴⁹

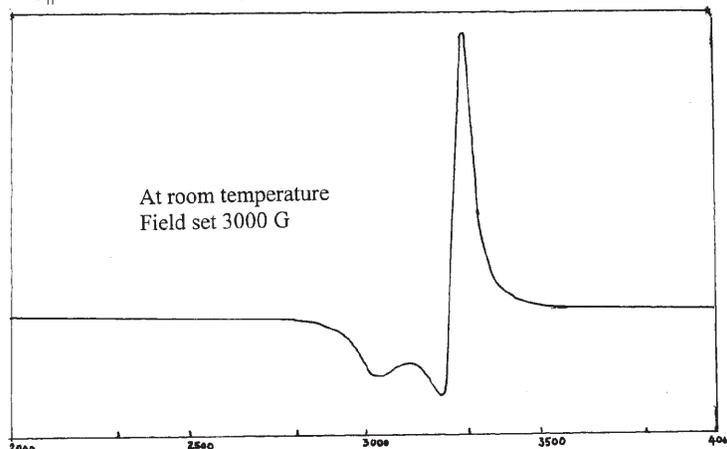


Fig. 3. EPR Spectrum of the Cu(II) complex at 300 K in the polycrystalline state.

The EPR spectra of polycrystalline Mn(II) complex gives only one broad isotropic signal centered at 2.00 at 300 K (room temperature) and at 77 K (liquid nitrogen temperature), which is equal to the free electron g -value ($g = 2.0027$). The broadening of the spectrum might be due to spin relaxation.^{50,51}

FAB-Mass spectral analysis and thermal studies

In the present investigation, the FAB-mass spectrum of the $[\text{Cu}(\text{BPD})\text{Cl}]\text{Cl} \cdot 4\text{H}_2\text{O}$ complex was recorded and shows a molecular ion peak (M^+) at $m/z = 638$, indicative of the monomeric nature of the complex.

Thermal studies of the Zn(II) and Cd(II) complexes were performed in the temperature range 25 – 1000 °C, at a heating rate of 10 °C/min in a nitrogen atmosphere. The Zn(II) and Cd(II) complexes decompose in three stages. The first step 100 – 110 °C resulted in a mass loss of 15.99 % (Calcd. 15.98) and 14.95 % (Calcd. 14.97), respectively, corresponding to the loss of six lattice held water molecules. The temperature range rules out the possibility of coordinated water molecules. In the second step, two chloride molecules were lost in the 110 – 350 °C range from the Zn(II) complex and in the 110 – 348 °C range from the Cd(II) complex, with a mass loss of 10.49 % (Calcd. 10.89) and 9.88 % (Calcd. 9.97), respectively. In the third step, the ligand was lost in the 350 °C – 800 °C range from the Zn(II) complex and the 348 – 790 °C range from the Cd(II) complex, with a mass loss of 63.84 % (Calcd. 63.89) and 59.68 % (Calcd. 59.97), respectively. A plateau was obtained after heating above 800 °C, which corresponds to the formation of stable ZnO and CdO. The weight of ZnO and CdO amounted to 12 and 17 %, respectively, which agrees with the metal analysis. The presence of two lattice held water molecules in the Mn(II) and four in the Cu(II) and Co(II) complexes was confirmed by heating at a temperature of 100 – 110 °C in a muffle furnace.

CONCLUSION

Condensation of 2-aminobenzothiazole with 2,6-dicarbonyldichloride yielded a new amide ligand having potential binding sites towards metal ions. It acts as a neutral pentadentate ligand by coordinating through two uncharged amide oxygens, the pyridine nitrogen and two benzothiazole nitrogens, *i.e.*, in a NONON fashion. It forms octahedral cationic complexes with Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Cd(II) ions. FAB Spectral analysis reveals the existence of monomeric complexes and thermal studies support the presence of lattice held water molecules.

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ИЗВОД

СИНТЕЗА И СПЕКТРАЛНО ПРОУЧАВАЊЕ Cu(II), Ni(II), Co(II), Mn(II), Zn(II) И Cd(II) КОМПЛЕКСА СА НОВИМ МАКРОЦИКЛИЧНИМ ЛИГАНДОМ *N,N'*-БИС(2-БЕНЗЕНТИАЗОЛИЛ)-2,6-ПИРИДИНДИКАРБОКСАМИДОМ

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Нови макроциклични амидни лиганд *N,N'*-бис(2-бензотиазолил)-2,6-пиридиндикарбоксамид (BPD) направљен је кондензацијом 2,6-пиридиндикарбонилдихлорида са

2-аминобензотиазолом и његови Cu(II), Ni(II), Co(II), Mn(II), Zn(II) и Cd(II) комплекси су синтетисани. Њихове структуре су изведене на основу елементалне анализе, мерења проводљивости, магнетних момената, спектралних (IR, NMR, UV-VIS, EPR и FAB) и термичких студија. Комплекси имају октаедарску геометрију око металног центра. Подаци о проводљивости указују на електролите типа 1:1. Пентадентатно понашање лиганда је предложено на основу спектралних проучавања. X-Траке у EPR спектру Cu(II) и Mn(II) комплексима у поликристалном стању на собној температури (300 K) и температури течног азота (77 K) су снимљене и пикови су објављени.

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