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Synthesis, Characterization and Antibacterial Activity of Cu(II), Co(II), Ni(II) and Zn(II) Complexes Using Mannich Base Ligand

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This paper describes the synthesis and characterization of Mannich base, N-(1-pyrrolidino- benzyl)nicotinamide (PBN) and its complexes with Cu(II), Co(II), Ni(II) and Zn(II) ions. The structural features of the complexes have been confirmed by microanalytical analysis, IR, UV-visible, NMR, EPR, Mass, magnetic susceptibility and CV technique. The electronic absorption spectra and magnetic susceptibility measurement values of the complexes indicate octahedral geometry for copper, square-planar geometry for nickel and tetrahedral geometry for cobalt and zinc complexes. The non-electrolytic nature of the complexes is characterized from their low molar conductance values. The cyclic voltammogram of copper complex in acetonitrile solution shows a quasi-reversible one-electron transfer. The EPR spectra of the copper complex in DMSO at 300 K and 77 K were recorded and its salient features are reported. The antimicrobial activity of the complexes has been extensively studied on microorganisms such as *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas aeruginosa* by well-diffusion technique using DMF as solvent. The values of zone of inhibition were found out at 37 °C for a period of 24 h. It has been found that all the complexes have higher activity than the Mannich base ligand and the standard.

Keywords: Synthesis, Transition metal(II) complexes, Mannich base, N-(1-Pyrrolidinobenzyl)nicotinamide.

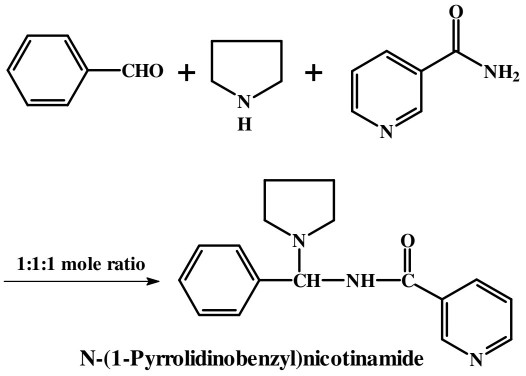
INTRODUCTION

It is well known from the literature that amides form an interesting class of ligands possessing –NH_2 and >C=O groups which can act as donor sites. The amide derivatives have been investigated extensively by coordination chemists [1-5]. Substituted amides and its derivatives are well known to possess biological properties such as fungicidal, herbicidal and insecticidal activities [3,4]. Such organic compounds when coordinated with metal salts could exhibit enhanced microbiological activities when administered in the form of metal complexes [6-8]. However, the direct use of transition metal salts as antimicrobial agents cannot be recommended, as they are very toxic to both the microbes and the host animals. It is quite likely that the presence of aminobenzyl substituent on nicotinamide moiety could effectively alter the extent of antimicrobial activities of the nicotinamide compound. Further, several types of amino benzyl compounds possessing varied biological and pharmacological activities have also been reported in literature [3,8]. In continuation of our earlier work [9-12], herein we report the synthesis of N-(1-pyrrolidinobenzyl)nicotinamide and its complexation characteristics with Cu(II), Co(II), Ni(II) and Zn(II) salts. The ligand behaved as a bidendate manner coordinates to the metal ions through the carbonyl oxygen and nitrogen atom of pyrrolidine moiety.

EXPERIMENTAL

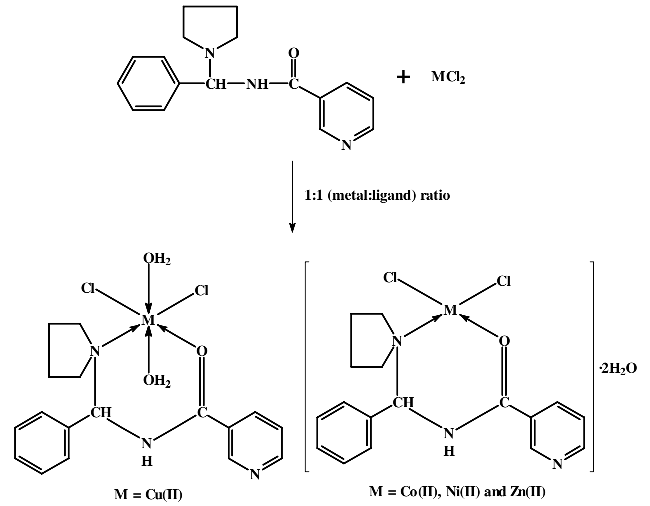
Preparation of N-(1-pyrrolidinobenzyl)nicotinamide: For the preparation of N-(1-pyrrolidinobenzyl)nicotinamide ligand, nicotinamide (12.1 g, 0.1 mol), pyrrolidine (10 mL, 0.1 mol) and benzaldehyde (10 mL, 0.1 mol) were taken in 1:1:1 mole ratio in ice-cold condition. Nicotinamide was mixed with pyrrolidine and stirred to get a clear solution. Benzaldehyde was then added drop-wise and stirred in ice-bath. The resulting reaction mixture was kept at room temperature for 4 days. The solid product formed was filtered, washed with distilled water to remove the unreacted nicotinamide and pyrrolidine followed by CCl_4 to remove any unreacted benzaldehyde (**Scheme-I**). N-(1-Pyrrolidinobenzyl)nicotinamide was then dried and recrystallized in ethanol. Yield: 62 %; m.p.: 164 °C.

Synthesis of metal complexes using N-(1-pyrrolidinobenzyl)nicotinamide: The ligand N-(1-pyrrolidinobenzyl)-nicotinamide being insoluble in water, all the complexes were prepared in non-aqueous medium. In a typical procedure, N-(1-pyrrolidinobenzyl)nicotinamide was dissolved in chloro-



Scheme-I: Formation of Mannich base

form and mixed with an ethanolic solution of the metal salt, MCl_2 [where M = Ni(II), Cu(II), Co(II) and Zn(II)] in 1:1 (metal:ligand) mole ratio. The reaction mixture was warmed on a water-bath for 1 h. The resulting solid complex formed was separated by filtration, washed with distilled water and dried *in vacuo* (**Scheme-II**).



Scheme-II: Formation of metal complexes

RESULTS AND DISCUSSION

All the coloured metal complexes are stable at room temperature. However, on heating they decomposed. The thermogravimetric analysis of metal complexes is found to be thermally stable up to 280 °C. The final product of thermal decomposition was found to be the metal oxide. Molar conductance values of the complexes reveal their non-electrolytic nature [13]. The magnetic susceptibility measurement values show tetrahedral for cobalt and zinc, square-planar for nickel and octahedral geometry for copper complexes.

Infrared spectra: The ligand N-(1-pyrrolidinobenzyl)-nicotinamide shows its characteristic bands at 3300, 1640 and 1100 cm^{-1} which have been assigned to ν(NH), amide ν(C=O) and ν(C-N-C) of pyrrolidine group, respectively [14]. In the IR spectra of all the complexes, the ν(NH) band remained at the same position as in the free ligand, indicating that the secondary nitrogen is not involved in the coordination to the metal ion. In all the complexes, the amide ν(C=O) and ν(C-N-C) of pyrrolidine bands displayed substantial negative shifts with fairly low intensity indicating coordination through the oxygen of amide moiety and nitrogen of pyrrolidine entity present in the ligand. The Cu(II) complex showed a hump at 3450-3000 cm^{-1} followed by sharp peaks at 850-820 and 650-620 cm^{-1} attributed to stretching and rocking modes, respectively of coordinated water molecules [15-18]. According to elemental analysis, the Co(II), Ni(II) and Zn(II) complexes also contain water molecule. However, a band around 880 cm^{-1}, characteristic for coordinated water, is not observed in the IR spectrum of those complexes. It may thus be assumed that the water molecules are lattice held. Some new bonds were found around 530-540, 440-450 cm^{-1} of M-O, M-N bonds, respectively [19,20] which further confirm that the ligands are bidentate in nature. In all the complexes, an additional medium band found at 325 cm^{-1} is assigned to M-Cl stretching vibration [21,22].

Electronic absorption spectra: The electronic absorption spectra of the ligand and its copper(II), cobalt(II) and nickel(II) complexes recorded in DMSO solution are shown in Fig. 1. The green Cu(II) complex showed a broad band at 14060 cm^{-1} which is assigned to $^2E_g \rightarrow {}^2T_{2g}$ transition indicating octahedral geometry [23] for the complex. The Co(II) complex exhibits a band with absorption maximum at 16680 cm^{-1} which is assigned to $^4A_2 \rightarrow {}^4T_1$ transition which supports tetrahedral geometry [24] for the complex. The Ni(II) complex showed a characteristic band at 14580 cm^{-1} which is assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition confirming a square-planar geometry [25] for the complex. The above facts are also evidenced by the magnetic susceptibility data.

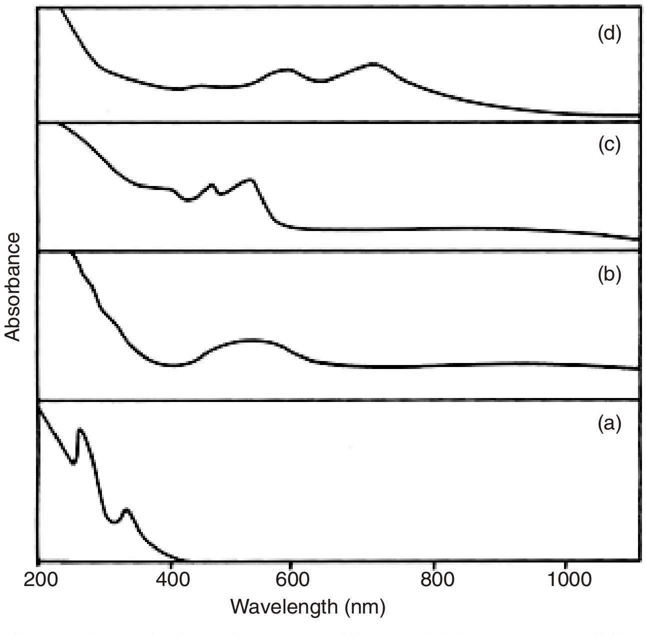


Fig. 1. Electronic absorption spectra of the Mannich base N-(1-pyrrolidinobenzyl)nicotinamide (a), Cu-PBN (b), Co-PBN (c) and Ni-PBN (d) complexes

Magnetic susceptibility measurements: The magnetic moment value for Cu(II) complex (1.9 B.M.) indicates the octahedral arrangement of the ligand around the central metal ion. The four coordinated Co(II) complex shows μ_{eff} value of 4.1 B.M. which supports the tetrahedral geometry for the complex. The observed zero magnetic moment value confirms the square-planar environment for the Ni(II) complex, in conformity with the fact that all known square-planar complexes of Ni(II) are diamagnetic. The Zn(II) complex is also found to be diamagnetic as expected for d^{10} configuration and on the basis of analytical and spectral data four coordinated tetrahedral geometry is proposed for the Zn(II) complex.

EPR spectra: The EPR spectrum of copper complex provides informations which are important in studying the metal ion environment. The X-band EPR spectra of the Cu(II) complex, recorded in DMSO at 77 and 300 K are shown in Figs. 2 and 3.

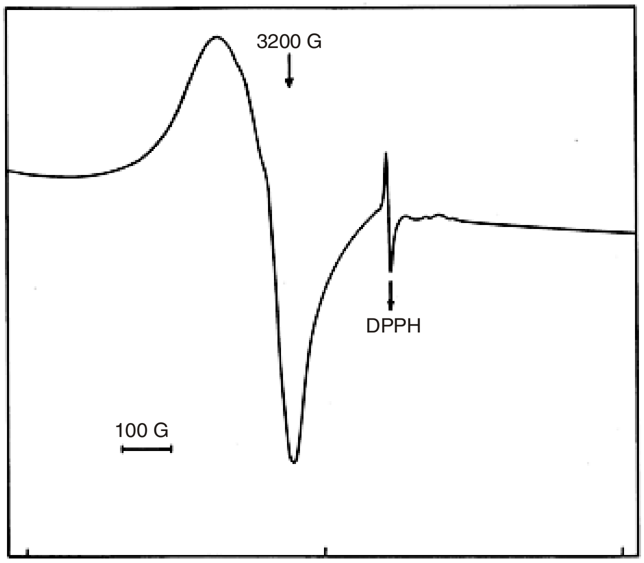


Fig. 2. EPR spectrum of Cu-PBN complex in DMSO at 300 K

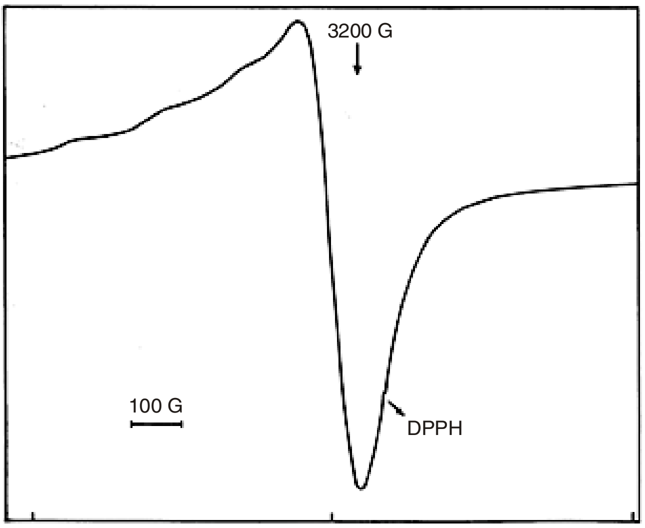


Fig. 3. EPR spectrum of Cu-PBN complex in DMSO at 77 K

The spectrum of the copper complex at room temperature shows one intense absorption band in the high field and is isotropic due to the tumbling motion of the molecules. However, this complex at liquid nitrogen temperature shows four well-resolved peaks with low intensities in the low field region and one intense peak in the high field region. The copper complex exhibits the $g_{\parallel}$ value of 2.266 and $g_{\perp}$ value of 2.083 which indicate that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital [26]. The observed $g_{\parallel}$ value is less than 2.3 for the complex indicating covalent nature. The λ value (-528 cm^{-1}) calculated using the relations, $g_{av} = 1/3\ [g_{\parallel} + 2g_{\perp}]$ and $g_{av} = 2(1-2\lambda/10Dq)$, is less than the free Cu(II) ion (-832 cm^{-1}) which also supports covalent character of M-L bond in the complex. The G value of 3.84 indicates negligible exchange interaction of Cu-Cu in the complex. The in-plane σ-bond strength represented by molecular orbital coefficients, α^2 (covalent in-plane σ-bonding) and β^2 (covalent in-plane π-bonding) were calculated using the following equations:

$$\alpha^2 = -\ (A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

$$\beta^2 = (g_{\parallel} - 2.0023)\ E/-8\lambda\alpha^2$$

If the value of $\alpha^2 = 0.5$, it indicates a complete covalent bonding, while the value of $\alpha^2 = 1.0$ suggests a complete ionic bonding. The observed value of $\alpha^2 = 0.88$ suggests that the unpaired electron spends 88 % of its time on metal and 12 % on the ligand atoms. Since the α^2 of the complex [27] is less than unity which indicates that the complex has some covalent character in the ligand environment.

Cyclic voltammetry: The cyclic voltammogram of the Cu(II) complex (0.01 M) in MeCN solution in 1.0 to -1.2 V potential range indicates quasi-reversible one-electron process [28]. A noteworthy feature has been observed in the cyclic voltammogram of Cu(II) complex which is shown in Fig. 4.

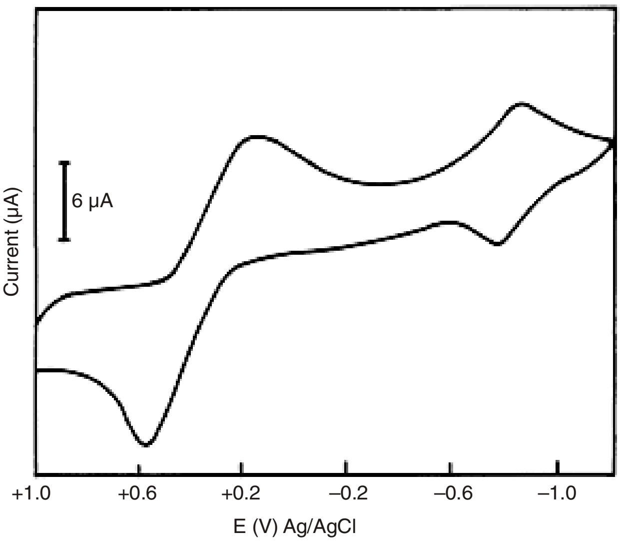


Fig. 4. Cyclic voltammogram of Cu-PBN complex in MeCN at 300 K (0.1 TMAP); scan rate 50 mV s^{-1}

During the forward scan, it shows two cathodic reduction peaks, one at +0.24 V and another at -0.84 V which are attributed to reduction of Cu(II) → Cu(I) and Cu(I) → Cu(0), respectively. During the reverse scan, it shows two anodic oxidation peaks, one at -0.76 V and another at +0.56 V which are attributed to oxidation of Cu(0) → Cu(I) and Cu(I) → Cu(II), respectively.

Antimicrobial activity: The ligand N-(1-pyrrolidinobenzyl)nicotinamide and its copper(II), cobalt(II), nickel(II) and zinc(II) complexes were tested for antibacterial activity. Mueller-Hinton agar was used for testing the susceptibility of microorganisms to antibacterial agents by well diffusion method [29,30], using DMF as solvent, at a concentration of 0.01 M against the Gram-positive bacteria like *S. aureus*, *B. subtilis* and Gram-negative bacteria such as *E. coli*, *P. auroginosa*. Ampicillin was used as the standard for comparing the results. The zone of inhibition values were determined at the end of an incubation period of 24 h at 35 °C. It has been observed from the results that the metal complexes have a higher activity than that of the free ligand and the standard.

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REFERENCES

1. A.D. Ahmed and S.N. Bose, *J. Inorg. Nucl. Chem.*, **31**, 2883 (1969).
2. A.N.M. Kasim, D. Venkappayya and G.V. Prabhu, *J. Indian Chem. Soc.*, **76**, 67 (1999).
3. P.S. Desai and K.R. Desai, *J. Indian Chem. Soc.*, **70**, 177 (1993).
4. A. Sabastiyan and D. Venkappayya, *J. Indian Chem. Soc.*, **67**, 584 (1990).
5. A. Rajasekaran and S. Murugesan, *Asian J. Chem.*, **16**, 791 (2004).
6. D.R. Williams, *Chem. Rev.*, **72**, 203 (1972).
7. I. Sougandi, R. Mahalakshmi, R. Kannappan, T.M. Rajendiran, R. Venkatesan and P. Sambasiva Rao, *Transition Met. Chem.*, **27**, 512 (2002).
8. G.D. Tiwari and M.N. Mishra, *Curr. Sci.*, **49**, 8 (1980).
9. N. Raman and S. Ravichandran, *Int. J. Chem. Sci.*, **2**, 191 (2004).
10. N. Raman and S. Ravichandran, *Asian J. Chem*., **14**, 1551 (2002).
11. M. Petchiammal, S. Ravichandran and L. Singh, *Int. J. Chem. Tech. Res.*, **6**, 3680 (2014).
12. N. Raman and S. Ravichandran, *Synth. React. Inorg. Met.Org. Nano-Metal Chem.*, **35**, 439 (2005).
13. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
14. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York, edn 3 (1978).
15. M.N. Patel and R.P. Patel, *J. Indian Chem. Soc.*, **52**, 1046 (1975).
16. V. Kumar and R. Dhakarey, *J. Indian Coun. Chem.*, **20**, 46 (2003).
17. G.F. De Sá, E. Giesbrecht and L.C. Thompson, *J. Inorg. Nucl. Chem.*, **37**, 109 (1975).
18. K. Nakamoto, Spectroscopy and Structure of Metal Chelate Compounds, John Wiley, New York (1988).
19. K.K. Narang and A. Aggarwal, *Inorg. Chim. Acta*, **9**, 137 (1974).
20. D.M. Adams, Metal-ligand and Related Vibrations, St. Martin's Press, New York (1968).
21. J.R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum, New York (1971).
22. A.B.D. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, (1968).
23. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 338 (1959).
24. H.B. Gray and C.J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).
25. R.M. Silverstein, G.C. Bassler and T.C. Morril, Spectroscopic Identification of Organic Compounds, Wiley, New York, edn 4, p. 112 (1981).
26. B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1961).
27. Z. Shirin and R.M. Mukherjee, *Polyhedron*, **11**, 2625 (1992).
28. A. Syamala and A.R. Chakravarty, *Polyhedron*, **12**, 1545 (1993).
29. N. Raman, A. Kulandaisamy, C. Thangaraja, P. Manisankar, S. Viswanathan and C. Vedhi, *Transition Met. Chem.*, **29**, 129 (2004).
30. C.H. Collin and P.M. Lyne, Microbiological Methods, Butterworth, London, edn 3 (1970).