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Synthesis, Characterization and Antibacterial Studies of Mixed Ligand Complexes of Cobalt(II) and Nickel(II) with Pyrrolidinobenzylurea and Nitrate ion

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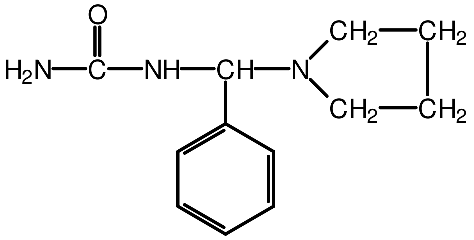
Mixed ligand complexes of cobalt(II) and nickel(II) with a Mannich base derived from benzaldehyde, pyrrolidine and urea, *i.e.*, pyrrolidinobenzylurea and nitrate ion have been synthesized and characterized. The analytical data include elemental analysis, determination of molar mass, conductivity, spectral and X-ray power diffraction studies. The antibacterial activity of the ligand and the metal complexes have also been studied.

Key Words: Synthesis, Characterization, Antibacterial activity, Co(II), Ni(II), Pyrrolidinobenzylurea, Mixed ligand complexes.

INTRODUCTION

Studies of metal complexes with benzaldehyde based Mannich bases, N,N'-*bis*(morpholinobenzyl)urea[1], piperidinobenzylurea[2,3] and N-(morpholinobenzyl)benzamide[4] have been reported. Another work, the complexing characteristics of pyrrolidinobenzyl-benzamide are reported by Raman *et al.*[5,6]. In continuation of these studies, the synthesis of N-(pyrrodinobenzyl)-urea (PBU, **I**) and its complexation characteristics with cobalt(II) and nickel(II) nitrates and the antibacterial activity of the ligand and the complexes are described in this work.



Structure of N-(pyrrolidinobenzyl)urea (PBU) (**I**)

EXPERIMENTAL

All the chemicals used were of AnalaR or G.R (Merck) grade. Organic solvents were purified by standard methods.

Synthesis of N-(pyrrodinobenzyl)urea (PBU): To urea dissolved in minimum amount of water, pyrrolidine was added followed by benzaldehyde (1:1:1 mole ratio) maintaining a temperature of 10 ºC and stirred. The resulting solid was washed with water, filtered and recrystallized from methanol, m.p. 159-161 ºC.

Synthesis of metal complexes: The nitrato complex of cobalt was prepared by mixing the ligand and metal salt in the ratio 2:1 in 50 mL ethanol and refluxing for 8 h. The resulting solution was concentrated to half its volume and filtered the solid complex formed, washed with methanol and benzene to remove excess metal salt and ligands. It was finally washed with ether to get finely powdered complexes. It was dried over silica gel in desiccators. Nickel(II) complex was prepared by similar procedure.

The metal content of the complexes was determined gravimetrically[7]. The nitrate contents of the complexes were determined as nitron-nitrate by using nitron reagent[7]. The molar conductances of the complexes in acetonitrile, methanol and DMF (*ca.* 10^{-3} M) solutions were measured at room temperature using an Elico conductivity bridge type CM82T with a dip type conductivity cell having platinum electrodes (cell constant 0.94 cm^{-1}). Magnetic susceptibilities were measured at room temperature by the Gouy method. The molar masses of the ligand and the complexes were determined by Rast method by using biphenyl as the solvent[8]. The infrared spectra of the ligand and the complexes were recorded in the range 4000-400 cm^{-1} employing the KBr disc technique. The X-ray powder patterns were recorded by using Philips diffractometer (Model PW 1710) for Co(II) and Ni(II) complexes.

Antibacterial study: The ligand, pyrrolidinobenzylurea (PBU) and the metal complexes were tested for their antimicrobial activity[9] against the gram positive bacteria *viz.*, *Staphyllococcus aureus* and three gram negative bacteria *viz.*, *Klebsiella pneumoniae, Proteus Vulgaris* and *Escherichia coli* by disc diffusion method. By this method, the zone of inhibition values of the complex and the ligand against the growth of microorganisms in two proportions (10 and 15 mg) are noted.

About 5.7 g of Muller Hinton agar (MH agar) was weighed out and was taken in a conical flask containing 150 mL distilled water. The conical flask was tightly plugged with cotton and kept for 120 ºC/15lbs. Washed the petriplates properly and kept in an oven at a temperature of 260 ºC, sterilized for 1 h and left the petriplates for cooling. After cooling the petriplates were kept in a laminar air chamber and then poured the medium (MH agar) into it and kept for 10 min. After that, innoculation by swabing using sterilized swabs. Then the weighed (10 and 15 mg) complex and the ligand were keenly put into the petriplates and a disc was placed on the top of it and then kept in the incubator for 24 h.

RESULTS AND DISCUSSION

The analytical data, molar masses and magnetic moments of the complexes are presented in Table-1. Both the complexes are coloured and non-hygroscopic in nature. These complexes are soluble in acetonitrile, methanol and DMF.

TABLE-1
ANALYTICAL DATA, MOLAR MASS AND MAGNETIC MOMENT DATA OF THE MIXED LIGAND COMPLEXES OF Co(II) AND Ni(II)

Complex	Colour	Molar mass	Metal (%)	Nitrate (%)	μ_{eff} (BM)
$[Co(PBU)_2(NO_3)_2]$	Brown	727.92 (729.04)	8.2 (8.15)	17.92 (17.01)	5.10
$[Ni(PBU)_2(NO_3)_2]$	Green	726.08 (728.78)	7.92 (8.11)	17.21 (16.99)	3.18

Calculated values are given in parenthesis.

The molar conductance values of the complexes are given in Table-2. The values were compared with the data available for standard substances to see whether the anions are coordinated or not[10,11]. It is observed that both the complexes behave like non-electrolytes in all the solvents used indicating that the nitrate ions are coordinated to respective metal ions. The comparatively higher values of conductance for the complexes in methanol are probably due to partial displacement of the coordinated anions by polar methanol molecules[12].

TABLE-2
MOLAR CONDUCTANCE DATA OF THE COMPLEXES OF PBU WITH Co(II) AND Ni(II) NITRATES

Complex	Molar conductance (ohm^{-1} cm^2 mol^{-1})		
	Acetonitrile	DMF	Methanol
$[Co(PBU)_2(NO_3)_2]$	16	4	20
$[Ni(PBU)_2(NO_3)_2]$	15	3	22

Octahedral Co(II) can exist in two possible spin states: (i) low-spin with a magnetic moment of 1.18 BM and (ii) high spin with a magnetic moment of 4.2-5.2 BM. The observed magnetic moment (5.10 BM) of the Co(II) complex indicates high spin nature of the complex. In the Ni(II) complex with octahedral or slightly tetragonally distorted geometry two unpaired electrons are present. The ground state makes no orbital contribution to the magnetic moment. So these moments are expected to be not greatly different from the spin-only moment value of 2.83 BM. In tetrahedral geometries also two unpaired electrons are present. However, in this case there will be considerable orbital contribution to the magnetic moment through the degeneracy of the incompletely filled t_2 orbitals. Due to this, the magnetic moment values in these cases are 3.4 to 4.0 BM. Since the nickel(II) complex has a magnetic moment of 3.18 BM, it can be assigned an octahedral geometry around nickel(II) ion. The reported μ_{eff} values of the Ni(II) and Co(II) complexes are slightly higher than the spin only value of the respective metals, indicating the spin-free octahedral environment around the metal ions[13].

The electronic spectrum of the cobalt(II) complex in DMF showed the absorption maximum around 550 nm which is characteristic of the cobalt(II) in octahedral environment. This may be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition in octahedral cobalt(II). The electronic spectrum of the nickel(II) complex showed absorption bands around 420, 620 and 860 nm which are in good agreement with the expected bands for octahedral nickel(II).

In the infrared spectrum of N-(pyrrolidinobenzyl)urea, the ν(NH) modes appear at 3458 (asymmetric) and 3356 cm^{-1} (symmetric). The carbonyl and C–N–C stretching frequencies PBU appear at 1660 and 1160 cm^{-1}, respectively. The ν(NH) modes appearing at 3460 and 3368 cm^{-1} in the spectrum of the ligand remain unaltered in the spectra of the complexes showing the non-participation of nitrogen of NH_2 in coordination. The infrared spectrum of the ligand shows a band at 1660 cm^{-1} which is due to the carbonyl stretching frequency[10]. The spectra of the complexes shows negative shift to 1640-1620 cm^{-1} showing the coordination through the carbonyl group. The band at 1160 cm^{-1} in the ligand[14], which is due to the C–N–C stretching frequency shifts to 1150-1130 cm^{-1}. This shows the coordination through the tertiary nitrogen of pyrrolidine ring. There are no additional bands in the region 800 and 3500 cm^{-1} showing the absence of coordinated water. The additional bands in the region 440-430 and 580-560 cm^{-1} are assigned to ν(M–O) and ν(M–N), respectively. The additional bands at 1458, 1338 and 1020 cm^{-1}, which are not present in the spectrum of PBU are attributed to ν_4, ν_1 and ν_2 modes of coordinated[15-17] nitrate ions. As the difference between ν_4 and ν_1 is *ca.* 120 cm^{-1}, it is suggested that the nitrate ions are coordinated unidentately to the metal ions[18]. The neutral nature of the complex indicates the presence of two nitrate ions in the coordinate sphere. The molar conductance value is also in support of this.

The X-ray powder patterns were recorded for both the complexes. The diffraction patterns were indexed by using the method developed by Hesse[19] and Lipson[20]. Both the complexes were found to be orthorhobic. The cell parameters have been calculated by the equation

$$\sin^2\theta\ (hkl) = Ah^2 + Bk^2 + Cl^2, \text{ where } A = \frac{\lambda^2}{4a^2}, B = \frac{\lambda^2}{4b^2} \text{ and } C = \frac{\lambda^2}{4c^2}$$

The lattice constants for [Co(PBU)$_2$(NO$_3$)$_2$] are A = 0.002850, B = 0.00581 and C = 0.015351 with edge lengths a = 14.441 Å, b = 10.192 Å and c = 6.231 Å. The cell volume is 917.09523(Å)^3 and density is 0.8012. This gives n = 1.0078. Thus, the number of molecules per unit cell is one. For the complex, [Ni(PBU)$_2$(NO$_3$)$_2$], the lattice constants are A = 0.0035, B = 0.00515 and C = 0.0191. Hence a = 13.102 Å, b = 10.8123 Å and c = 5.5671 Å. The cell volume of the complex is 788.6507 (Å)^3 and its density is 0.8574. This gives n = 0.92784. Thus, the number of molecules per unit cell is one.

The antibacterial activity shown by the ligand and the complexes are given in Table-3.

TABLE-3
ANTIBACTERIAL ACTIVITY AGAINST THE LIGAND AND THEIR COMPLEXES

Compound	Diameter of zone of inhibition (mm)							
	S. aureus		*K. pneumoniae*		*P. vulgaris*		*E. coli*	
Quantity of compound (mg)	10	15	10	15	10	15	10	15
PBU	20	26	18	22	8	14	8	14
Co(II) complex	24	30	22	28	10	18	12	18
Ni(II) complex	22	28	20	28	10	16	10	16

Organisms studied are *E. coli*, *Proteus vulgaris*, *Staphyllococcus aureus* and *Klebsiella pneumoniae*. The results of present investigation on the antibacterial activity reveal that the complexes exhibit much higher activity than the ligand towards the organisms studied. The results indicate that the ligand and both the Co(II) and Ni(II) complexes show enhanced antibacterial activity towards *Staphylococcus aureus* and *Klebsiella pneumoniae*. In the case of *Protus vulgaris* and *Escherichia coli*, the diameter of zone of inhibition of PBU and Ni(II) complex in both proportions are same. The activity of Co(II) complex is found to be greater than that of Ni(II) complex. The present study explains only the zone of inhibition obtained from only two proportions of chemicals.

Conclusion

From the above studies it is concluded that the complexes [Co(PBU)$_2$(NO$_3$)$_2$] and [Ni(PBU)$_2$(NO$_3$)$_2$] have octahedral geometry having coordination number six. The structures of the complexes may be represented as in Fig. 1.

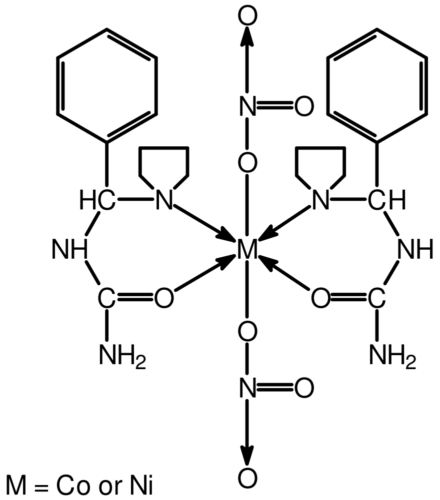


Fig. 1 Proposed structure of Co(II) and Ni(II)

The ligand and the complexes have antibacterial activity against *S. aureus, K. pneumoniae, P. vulgaris* and *E. coli*. The complexes are more active than the ligand. The increase in antimicrobial activity is due to faster diffusion of metal complexes through the cell membrane or due to the combined activity of the metal and the ligand. Cobalt complex is having higher activity compared to that of nickel complex. The antibacterial activity of the ligand and the complexes against *S. aureus* and *K. pneumoniae* is higher than that against *P. vulgaris* and *E. coli*.

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