

Synthesis and spectral characterisation of Ni(II) complexes with amide group ligands containing 1,8-Naphthyridines

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ABSTRACT

Complexes of Nickel(II) with 2-amino-1,8-naphthyridine-3-carboxamide (ANC), 2-amino-N-phenyl-1,8-naphthyridine-3-carboxamide (APNC), 2-amino-N-(p-methyl phenyl)-1,8-naphthyridine-3-carboxamide (AMPNC), 2-amino-N-(p-bromo phenyl)-1,8-naphthyridine-3-carboxamide (ABPNC), 2-amino-N-(p-chloro phenyl)-1,8-naphthyridine-3-carboxamide (ACPNC), 2-amino-N-(p-methoxy phenyl)-1,8-naphthyridine-3-carboxamide (AMYPNC), 2-methyl-N-O-carboxyphenyl-1,8-naphthyridine-3-carboxamide (MCNC) and 2-phenyl-N-O-carboxyphenyl-1,8-naphthyridine-2-carboxamide (PCNC) have been synthesized. These complexes were characterized by elemental analysis, molar conductance, thermal studies, magnetic susceptibility, IR and electronic spectra. Based on the above studies, the ligands coordinated to the metal ion in a bidentate fashion through the amide nitrogen and oxygen. The remaining coordination centers are satisfied by acetates and H₂O molecules. Electronic spectra and magnetic susceptibility measurements reveal octahedral geometry around the metal ion. The complexes were found to be non-electrolytic in nature on the basis of low value of molar conductance.

Key words: Ni(II) complexes, amide group ligands, 1,8-Naphthyridines.

INTRODUCTION

An amide group offers two potential binding atoms, the oxygen and nitrogen, for complexation of metal ions. A number of complexes have been reported with amide group ligands which exhibit diverse coordinating behaviours with different metal ions¹⁻⁴. A large number of metal complexes of amide group ligands consisting of imidazole, purine pyrimidine, oligopeptides and 1,8-naphthyridines have been investigated. The metal ion interaction with amide group ligands play an important role in a large number of biological processes⁵⁻⁶.

EXPERIMENTAL

Material and methods

All the chemicals used were of A.R. grade, ANC, APNC, AMPNC, ABPNC, ACPNC, AMYPNC⁷. MCNC⁸ and PCNC⁹ were prepared by the literature method. The purity of these compounds was checked by TLC and melting point determination.

Synthesis of complexes

The complexes were prepared by mixing methanolic solution of Nickel acetate (0.001 m mol) was dissolved in methanol. To this solution (30ml) of ligand solution (0.002 m mol) was added with constant stirring over a period of 15 min then the reaction mixture was refluxed on a water bath for 4 hours or until solid separated out. The solids were suction filtered and purified by repeated washing with 1:1 diethyl ether, methanol and dried in vacuum over a fused CaCl₂ in a desiccator.

The percentage of Carbon, Hydrogen and Nitrogen present in organic compounds (ligands) and metal complexes were carried out at Central Drug Research Institute, Lucknow using Elementar Vario EL III Carlo Erba 1108. Nickel is estimated with EDTA using Murexide indicator in the complexometric titrations.

Physical measurements

The magnetic susceptibility measurements were made at room temperature were obtained

using CAHN 2000 Faraday balance (using $\text{Hg}[\text{Co}(\text{CNS})_2] \chi_g - 16.44 \times 10^{-6} \text{g cc}^{-1}$ as standard). Molar conductivities of the complexes in DMF were measured using a Digisun Digital Conductivity Meter, Model DI 909 with 0.1 M KCl solution was employed for conductivity measurements. The thermal data of the complexes were obtained using Mettler-Toledo, DSC and TGA 822e series at Central Instrumentation Center, Kakatiya University, Warangal. The electronic spectra of complexes in solutions of DMF were recorded in Shimadzu UV-Vis Spectrophotometer, Model 2401 PC and the IR spectra of ligands and metal complexes were recorded in KBr pellets or Nujol nulls on Perkin Elmer-BX system-The scanning time was 6 minutes in the range of 4000-400 cm^{-1} .

Preparation of the complexes

All the Ni (II) complexes have been formed by reacting methanolic solution of Nickel acetate in 30ml ligands was dissolved in 50ml of solution in molar ratio 1:2. The reaction mixture with stirring over a period of 15min. Then the reaction refluxed for 4-5 hour. During this period the solid complex started separating. The solvent was then removed under reduced pressure to half of the volume, and cooled at room temperature. The solid complex was filtered under solution dried over fused CaCl_2 in desiccator.

RESULTS AND DISCUSSION

The physico chemical and analytical data of Ni (II) complexes with the ligands ANC, APNC, AMPNC, ABPNC, ACPNC, AMYPNC, MCNC and PCNC are given in Table 1. The experimentally obtained percentage of elements C, H, N and Ni(II) are very close to the values calculated for the formula⁹ $[\text{Ni}(\text{ANC})_2(\text{OAc})_2]$, $[\text{Ni}(\text{APNC})_2(\text{OAc})_2]$, $[\text{Ni}(\text{AMPNC})_2(\text{OAc})_2]$, $[\text{Ni}(\text{ABPNC})_2(\text{OAc})_2]$, $[\text{Ni}(\text{ACPNC})_2(\text{OAc})_2]$, $[\text{Ni}(\text{AMYPNC})_2(\text{OAc})_2]$, $[\text{Ni}(\text{MCNC})_2(\text{H}_2\text{O})_2]$ and $[\text{Ni}(\text{PCNC})_2(\text{H}_2\text{O})_2]$. The conductance of all Ni(II) complexes were determined by preparing solution (10^{-3} M) in DMF. All the complexes exhibited very low conductance, indicating them to be non-ionic¹⁰. This confirms that the ligands lose the proton (MCNC and PCNC) and then coordinate to the metal ion. The +2 charge of Ni is balanced by the ligands anions and thus neutral molecular complexes are formed.

The thermograms are obtained by heating the samples in nitrogen atmosphere at the rate of 20°C per minute. The data of all the complexes were critically examined to ascertain the decomposition process and the presence of different species, like ligand, acetate and water molecules.

Thermogram of $[\text{Ni}(\text{ANC})_2(\text{OAc})_2]$ complex is thermally stable up to 270° and then undergoes decomposition in one step this decomposition occurs between 270° and 680°C with a weight loss of 86.02 (cal. 86.49%) corresponding to the loss of two acetate ions and two ligands molecules. The weight of the residue left suggests the formation of $\text{NiO}^{11,12}$ and agrees with weight 13.98% and calculated 13.51%. Thermogram of $[\text{Ni}(\text{PCNC})_2(\text{H}_2\text{O})_2]$ complex is thermally stable up to 172°C and then undergoes decomposition in two steps. The information about the extract nature of the complex and the existence of water molecule inside the coordination sphere can be obtained from thermal studies. The loss of water on heating is evidenced by an endothermic peak in DTA analysis.

I.R. Spectra

The characteristic infrared (IR) absorptions of Ni(II) complexes are presented in Table 2. The selected ligands exhibit $\nu(\text{C}=\text{O})$ vibrations at 1671 (ANC), 1673 (APNC), 1670 (AMPNC), 1672 (ABPNC), 1674 (ACPNC), 1670 (AMYPNC), 1685 (MCNC) and 1680 cm^{-1} (PCNC). The $\nu(\text{NH}_2)$ frequency in ligands 1-6 appears at 3447 (ANC), 3448 (APNC), 3449 (AMPNC), 3445 (ABPNC), 3448 (ACPNC) and 3485 cm^{-1} (AMYPNC). The amide $\nu(\text{NH})$ frequency shows up in ligands 2-8 around 3240, 3250, 3215, 3270, 3368, 3300 and 3250 cm^{-1} respectively. The $\nu(\text{OH})$ of carboxylic group absorbs in the range of 2500-2700 cm^{-1} in MCNC and PCNC. They indicate that the coordinating atoms are amide oxygen and amine nitrogen in the case of 1-6 ligands. The ligands 7 and 8 bond through carboxylate oxygen (on deprotonation) and amide nitrogen¹³.

In the octahedral field Ni (II) has an orbitally non-degenerate ground state ${}^3\text{A}_2(t_{2g}^6 e_g^2)$ and no orbital contribution is expected. Hence, the magnetic moment values are very close to the spin-only value to 2.83 B.M. But, slightly higher values may often

Table 1: Analytical data and Physicochemical data of Ni (II) complexes

S. No.	Complex	Mol. wt.	C	Found (Calcd%)			Molar Conductance λ_m ohm ⁻¹ cm ² mol ⁻¹	M _{eff} B.M.
				H	N	M		
1.	[Ni(ANC) ₂ (OAc) ₂]	553.13	46.98 (47.76)	4.27 (4.01)	20.54 (20.24)	10.29 (10.61)	6.70	3.21 (3.29)
2.	[Ni(APNC) ₂ (OAc) ₂]	705.33	57.32 (57.89)	4.02 (4.29)	15.17 (15.87)	8.51 (8.32)	8.00	3.29 (3.20)
3.	[Ni(AMPNC) ₂ (OAc) ₂]	733.39	58.02 (58.95)	4.25 (4.68)	15.67 (15.27)	7.82 (8.00)	7.20	3.45 (3.25)
4.	[Ni(ABPNC) ₂ (OAc) ₂]	863.11	46.97 (47.31)	3.64 (3.27)	11.92 (12.97)	7.01 (6.79)	7.00	3.33 (3.21)
5.	[Ni(ACPNC) ₂ (OAc) ₂]	774.34	52.22 (52.73)	3.15 (3.65)	15.00 (14.46)	7.02 (7.57)	7.90	3.07 (3.27)
6.	[Ni(AMYPNC) ₂ (OAc) ₂]	765.39	56.92 (56.48)	4.28 (4.48)	14.55 (14.63)	7.46 (7.66)	6.90	3.14 (3.28)
7.	[Ni(MCNC) ₂ (H ₂ O) ₂]	707.31	57.02 (57.73)	3.42 (3.99)	11.29 (11.87)	8.56 (8.29)	6.80	3.17 (3.26)
8.	[Ni(PCNC) ₂ (H ₂ O) ₂]	831.45	63.01 (63.55)	3.25 (3.88)	10.52 (10.10)	7.24 (7.05)	6.90	3.15 (3.26)

Table 2: Infrared spectra data (cm⁻¹) of Ni (II) complexes

S.No.	Complexes	$\nu(\text{NH}_2)$	$\nu(\text{NH})$	$\nu(\text{C=O})$	$\nu(\text{C-N})$
1.	[Ni(ANC) ₂ (OAc) ₂]	3414 (3447)	-	1650 (1671)	1440
2.	[Ni(APNC) ₂ (OAc) ₂]	3402 (3448)	3254 (3240)	1649 (1673)	1448
3.	[Ni(AMPNC) ₂ (OAc) ₂]	3391 (3449)	3266 (3250)	1644 (1670)	1439
4.	[Ni(ABPNC) ₂ (OAc) ₂]	3422 (3445)	3234 (3215)	1654 (1672)	1448
5.	[Ni(ACPNC) ₂ (OAc) ₂]	3405 (3448)	3289 (3270)	1659 (1674)	1448
6.	[Ni(AMYPNC) ₂ (OAc) ₂]	3439 (3485)	3277 (3268)	1652 (1670)	1439
7.	[Ni(MCNC) ₂ (H ₂ O) ₂]	-	3269 (3300)	1652 (1685)	1440
8.	[Ni(PCNC) ₂ (H ₂ O) ₂]	-	3219 (3250)	1630 (1680)	1449

arise from some mixing of ground state with a multiple excited states. In the case of Ni(II) in tetrahedral environment, the 3T_1 ground term leads to temperature-dependent orbital contribution to the magnetic moment. Though both octahedral and tetrahedral Ni(II) complexes contain two unpaired electrons.

The magnetic moment values of transition metal complexes often given an important clue about the stereochemistry¹⁴. In the octahedral field Ni(II) has an orbitally non-degenerate ground state ${}^3A_2(t_{2g}^6e_g^2)$ and no orbital contribution is expected. Hence, the magnetic moment values are very close to the spin-only value of 2.83 B.M. But, slightly higher values may often arise from some mixing of ground state with a multiple excited states.

Contrary to this situation, in the case of Ni(II) in tetrahedral environment, the 3T_1 ground term leads to temperature-dependent orbital contribution to the magnetic moment. Though both octahedral and tetrahedral Ni(II) complexes contain two unpaired electrons, the tetrahedral complexes have magnetic moments in the range of 3.2-4.1 B.M. The square planar Ni(II) complexes are always diamagnetic with paired electrons and the magnetic moment values of Ni(II) complexes prepared in the present investigation are obtained as 3.21, 3.29, 3.45, 3.33, 3.07, 3.14, 3.17 and 3.15. These values coupled with dentacy and number of the ligands coordinated to the metal ion confirm that the Ni(II) ion in the complexes is in octahedral geometry.

The magnetic moment values have also been obtained utilizing the spectral absorptions in electron spectra¹⁵ using the equation.

$$\mu_{\text{eff}(\text{cal})} = \mu_{\text{eff}(\text{s.o})} [1 - 4\lambda/10Dq]$$

The electronic spectral absorption of all the Ni(II) complexes recorded in methanol solution Ni(II) is the only common d^8 ion, and hence its spectroscopic and magnetic properties have been studied extensively¹⁶⁻¹⁷. Ni(II) usually exhibit three bands which are assigned as.

$$\begin{aligned} {}^3T_{2g}(\text{F}) \leftarrow {}^3A_{2g}(\text{F}) &= 10Dq \nu_1 \\ {}^3T_{1g}(\text{F}) \leftarrow {}^3A_{2g}(\text{F}) &\quad \nu_2 \\ {}^3T_{1g}(\text{F}) \leftarrow {}^3A_{2g}(\text{F}) &\quad \nu_3 \end{aligned}$$

With ν_1 giving the value of Δ or $10Dq$ directly. In some of eth Ni(II) Oh complexes, a weak spin-forbidden absorption (triplet \rightarrow singlet ${}^1E_g \leftarrow {}^3A_{2g}$) may be found due to the influence of spin-orbit coupling in mixing of a spin singlet (1E_g) with the spin triplet [${}^3T_{1g}(\text{F})$] term. The spectra of all Ni(II) complexes show three absorption with any shoulder around two absorption. The spectral data has been used to evaluate the parameters using the relationship^{18,19}. To calculate the energies of the ${}^3T_{1g}(\text{F})$ and ${}^3T_{1g}(\text{P})$ states, the P and Dq values are substituted in to equation 2 and the equation was solved for E . Two roots and obtained, E_x and E_y . Since the transition is ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ or ${}^3T_{1g}(\text{P})$, the absorption bands correspond to the differences.

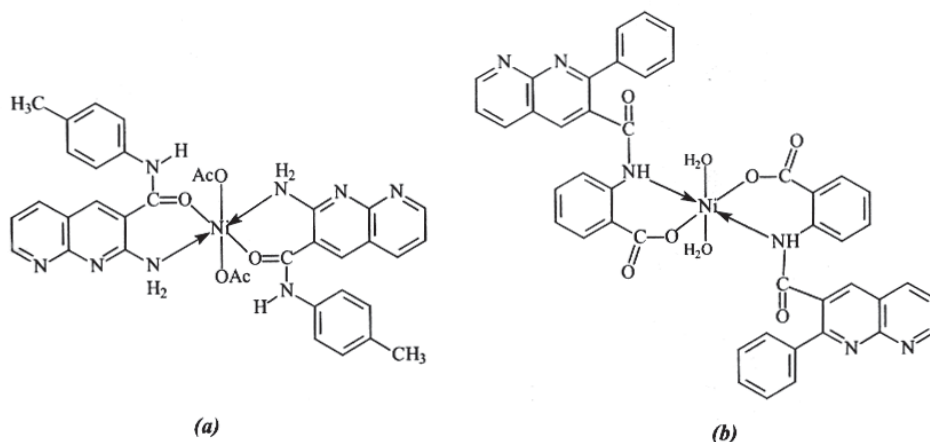


Fig. 1: Ni(II) complexes of (a) AMPNC and (b) PCNC

$$E[{}^3T_{1g}(F)] - [{}^3A_{2g}] \text{ and } E[{}^3T_{1g}(P)] - E[{}^3A_{2g}] \dots(6)$$

$${}^3T_{1g}(F) \leftarrow {}^3A_{2g} E_x - [-12Dq] \dots(7)$$

$${}^3T_{1g}(P) \leftarrow {}^3A_{2g} E_y - [-12Dq] \dots(8)$$

The ν_2 ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ transition value calculated from the above equations agree well. This supports the β and Dq reported for the complexes.

Comparison of the $10Dq$ and B values suggest that reasonably strong ligand exist in the complexes and the metal-ligand bonds have been appreciable covalent character.

Based on the experimental observations, the Ni(II) complexes are proposed to have octahedral geometry. The tentative structure of the Ni(II) complexes of 2-amino-N-(p-methyl phenyl)-1,8-naphthyridine-1,8-naphthyridine-3-carboxamide (AMPNC) **a** and 2-Phenyl-N-O-carboxyphenyl-1,8-naphthyridine-3-carboxamide (PCNC) **b** complexes are presented in Fig.1

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