

Synthesis and Spectroscopic Characterization of Cobalt(II) and Nickel(II) Complexes with 5-Methyl-1-(2'-pyridyl)-pyrazole-3-carboxamide

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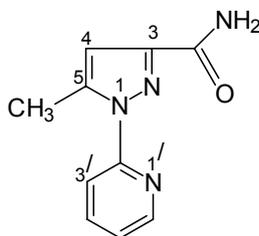
A host of novel Co(II) and Ni(II) complexes with the 5-Methyl-1-(2'-pyridyl)pyrazole-3-carboxamide ligand (MPyPzCA) have been synthesized and characterized through analytical and physico-chemical data. Magnetic and electronic spectral studies classify the reported *bis*-chelates as 6 coordinated distorted octahedral ones. A scrutiny of the IR spectra between the ligand and its complexes and in analogy with the crystal structure analysis indicates that one ligand exercises neutral tridentate (NNO) behaviour through pyrazolyl 2_N and pyridyl 1'_N and amidic oxygen whereas the second ligand binds the same central metal atom through pyrazolyl 2_N and pyridyl 1'_N, respectively in the *bis*-chelates. The coordinated H₂O molecule satisfies the sixth coordination site. The anions (X) in all the cases retain their ionic nature.

Key Words: Synthesis, Spectroscopy, Pyridyl-pyrazole carboxamide, *bis*-Chelate, Co(II), Ni(II).

INTRODUCTION

The importance of acid amides has been appreciated particularly in relevance to the chemistry of proteins which have in their structures a number of amide linkages. The biological activity of nicotinamide and its derivatives, is well-acclaimed; N,N-diethyl nicotinamide (coramine), for example, possesses a powerful stimulating action¹ on the central nervous systems and is found extensive use in medicine as a respiratory stimulant. A pyrazole-derivative containing an amide residue may, therefore, possesses potential biological activity. The present communication reports the synthesis and characterization of of Co(II) and Ni(II) complexes with 5-methyl-1-(2'-pyridyl)pyrazole-3-carboxamide (I).

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Structure of 5-Methyl-1-(2'-pyridyl)pyrazole-3-carboxamide (**I**)

EXPERIMENTAL

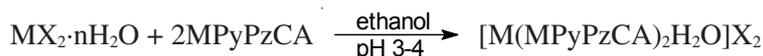
All the materials used were of GR/AR quality and were used without further purification. Spectrograde solvents were used for spectral and conductance measurements. The ligand, 5-methyl-1-(2'-pyridyl)pyrazole-3-carboxamide was prepared and characterized as reported method².

C, H and N of the ligand and its complexes with Co(II) and Ni(II) were analyzed at IACS, Calcutta, with a Perkin-Elmer CHN analyzer 2400. The cobalt content of the complexes was determined gravimetrically as anhydrous CoSO₄, except for the perchlorate species, where the metal was determined as the Co[Hg(SCN)₄] after decomposing the complex with conc. HNO₃ and H₂SO₄ mixture. The nickel content of the species was estimated gravimetrically as nickel dimethyl glyoximate, after decomposing the metal complex with an acid mixture. The halogen content of the complexes was determined as silver halide following the standard procedure. Magnetic susceptibilities were measured on a PAR 155 vibrating-sample magnetometer at IACS, Kolkata. The molar conductance values of the complexes in methanolic solution were obtained with a Systronics model 304 digital conductivity meter. The diffused reflectance spectra and the solution spectra of the complexes were recorded on U-3501 spectrophotometer. IR spectra were recorded on a Perkin-Elmer model 883 infrared spectrophotometer in the solid state (KBr pellets).

Synthesis of metal ion complexes of MPyPzCA: [M(MPyPzCA)₂H₂O]X₂ (M = Co(II)/Ni(II); X = Cl, Br, NO₃, SCN, BF₄, ClO₄): An ethanolic solution of MX₂.nH₂O (0.002 mol dissolved in 20 mL dry ethanol) was added to solution of the ligand, MPyPzCA (0.45 g, 0.002 mol dissolved in 20 mL dry ethanol) in the same solvent. The resultant solution (pH *ca.* 5) was concentrated on water bath temperature and cooled to room temperature (*ca.* 30 °C), when microcrystalline compounds separated out in each case. The compound was filtered off, washed with cold ethanol and dried over silica gel at room temperature *ca.* 30 °C)

RESULTS AND DISCUSSION

The reaction of metal salts ($\text{MX}_2 \cdot n\text{H}_2\text{O}$; $\text{M} = \text{Co(II)}$ and Ni(II) ; $\text{X} = \text{Cl}$, Br , NO_3 , BF_4 , ClO_4) with two equivalents of the ligand in ethanol affords the solid compounds with varying colours in excellent yield at room temperature (*ca.* 30 °C). The reaction route is stated as follows:



Cobalt(II) complexes confirm to the general composition $[\text{Co}(\text{MPyPzCA})_2\text{H}_2\text{O}]\text{X}_2$ as ascertained from analytical data (Table-1). The room temperature (30 °C) magnetic moment values fall within the range 4.63-5.08 BM (Table-1) are grossly consistent with 6-coordinate high spin cobalt(II) complexes^{3,4}. The significant lowering of magnetic moment value (4.63 BM) for the nitrate-species indicates that the species has orbitally singlet ground state with distorted octahedral geometry⁵ and in addition to that there could be admixture of diamagnetic Co(III) species with Co(II) species. The molar conductance (Λ_M) values (Table-1) recorded in dry methanol ($\Lambda_M = 140$ -180 mho $\text{cm}^2 \text{mol}^{-1}$) are indicative of 1:2 electrolytic nature⁶.

The diffuse reflectance spectra of the Co(II) species indicate an overall octahedral environment in the complexes. The principal absorption bands in the spectral data are located in the region 9700-9900 and 19,190-20,665 cm^{-1} which may be assigned as $\nu_1[{}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})]$ and $\nu_3[{}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})]$ transitions^{7,8}, respectively in an idealized O_h symmetry. Using the two known relationships⁹, it has been possible to deduce the ligand field parameters ($\text{Dq} = 1020$ -965; $\text{B} = 698$ -870 cm^{-1} and $\beta = 0.71$ -0.83) from the assigned positions of ν_1 and ν_3 bands; these are quite consistent with those reported earlier¹⁰ for octahedral cobalt(II) species. In some cases, shoulders or weak bands appearing in the region 12,000-15,600 cm^{-1} in the electronic spectra of the examined Co(II) species could be due to spin-forbidden transition¹¹, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^2\text{T}_{2g}(\text{G})$. In all the cases appearance of bands in the region (26,900-29,940 cm^{-1}) are due to LMCT transitions. The electronic spectral data taken in methanolic solutions indicate that no significant change in geometry occurs on dissolutions of the complexes in the methanol. The low values of molar extinction coefficients ($\epsilon \geq 48 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) found for the spectral bands give additional support to an octahedral geometry of said species.

Nickel(II) complexes confirm to the general composition $[\text{Ni}(\text{MPyPzCA})_2\text{H}_2\text{O}]\text{X}_2$ as ascertained from analytical data (Table-1). The effective magnetic moment values (μ_{eff}) (Table-1) of the species fall in the range 2.98-3.20 BM at room temperature (30 °C) expected for six coordinate nickel(II) complexes¹². The methanolic solutions of these Ni^{2+} species furnish molar conductances ($\Lambda_M = 140$ -180 mho $\text{cm}^2 \text{mol}^{-1}$) are indicative of 1:2 electrolytic nature⁶.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF Co(II) AND Ni(II) COMPLEXES

Complex (colour)	Yield (%)	Elemental analysis: Found/Calcd. (%)						Λ_M (**)	μ_{eff} at 30°C (BM)
		C	H	N	M	Anion			
[Co(MPyPzCA) ₂ H ₂ O]Cl ₂ (Bright pink)	90	43.7 (43.4)	3.8 (3.9)	20.0 (20.1)	10.4 (10.6)	13.0 (12.8)	140	4.96	
[Co(MPyPzCA) ₂ H ₂ O]Br ₂ (Pink)	90	37.7 (37.5)	3.3 (3.4)	17.4 (17.4)	9.2 (9.1)	25.1 (24.9)	160	4.88	
[Co(MPyPzCA) ₂ H ₂ O] (NO ₃) ₂ (Light pink)	85	40.1 (39.6)	3.6 (3.5)	23.0 (23.1)*	9.8 (9.7)	—	150	4.63	
[Co(MPyPzCA) ₂ H ₂ O](BF ₄) ₂ (Light pink)	80	36.9 (36.6)	3.3 (3.2)	17.0 (17.1)	9.2 (9.0)	—	180	5.08	
[Co(MPyPzCA) ₂ H ₂ O] (ClO ₄) ₂ (Light pink)	85	35.6 (35.3)	3.1 (3.2)	16.2 (16.4)	8.6 (8.6)	—	180	4.82	
[Ni(MPyPzCA) ₂ H ₂ O]Cl ₂ (Light Blue)	90	43.8 (43.5)	3.7 (3.9)	20.0 (20.3)	10.6 (10.6)	12.9 (12.8)	140	3.20	
[Ni(MPyPzCA) ₂ H ₂ O]Br ₂ (Green)	85	37.0 (37.2)	3.4 (3.4)	17.0 (17.4)	9.0 (9.1)	24.6 (24.8)	160	3.18	
[Ni(MPyPzCA) ₂ H ₂ O](NO ₃) ₂ (Light pink)	80	40.0 (39.6)	3.5 (3.6)	23.0 (23.1)*	9.7 (9.7)	—	140	3.24	
[Ni(MPyPzCA) ₂ H ₂ O] (BF ₄) ₂ (Light pink)	85	36.4 (36.6)	3.1 (3.3)	17.0 (17.1)	8.7 (8.9)	—	160	3.07	
[Ni(MPyPzCA) ₂ H ₂ O] (ClO ₄) ₂ (Light Grey)	80	35.0 (35.3)	3.0 (3.2)	16.1 (16.4)	8.5 (8.6)	—	180	2.98	

*Including nitrogen present in the anions; **Molar conductance in MeOH (mho cm² mol⁻¹)

The diffuse reflectance spectra of the mono-chelate of Ni(II) consist of three main bands appearing in the region 9,560-10,585; 15,150-18,260 and 22,720-25,975 cm^{-1} which can be safely assigned to the transitions ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1), ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3), respectively in an O_h symmetry. The weak bands or shoulder appearing at 13,000 cm^{-1} are probably due to the spin-forbidden transition¹³. An additional band appearing around 32,000 cm^{-1} could be due to LMCT transitions. The ligand field parameters ($\text{Dq} = 956\text{-}1058 \text{ cm}^{-1}$; $\text{B} = 737\text{-}869 \text{ cm}^{-1}$, $\beta = 0.68\text{-}0.80$ and $\nu_2/\nu_1 = 1.55\text{-}1.89$) substantiate an overall octahedral geometry for the reported Ni(II) species^{12,14}. All the present mono-chelates of Ni(II) on dissolution in methanol afford green solutions and suggest that there is no gross departure from the stereochemical environment. The low values of molar extinction co-efficients ($\epsilon \geq 52 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) gives additional support to the octahedral geometry¹⁵.

A scrutiny of the infrared spectral data of all the metal complexes reveals that a negative shift of $\nu(\text{C}=\text{O})$ ($\Delta\nu = 5\text{-}20 \text{ cm}^{-1}$) as compared to the free ligand, which result is quite consistent with the participation¹⁶ of the amide oxygen in complexation. Comparatively a smaller negative shift in $\nu(\text{C}=\text{O})$ vibration than that usually observed in the reported^{17,18} amide-metal complexes could be due to the mixing of $\nu(\text{C}=\text{O})$ vibrations of the amide moiety in complexed and uncomplexed ligand molecules in the same metal *bis*-chelates¹. The $\nu(\text{C}=\text{N})$ (pyrazole) in all the species suffers a positive shift ($\Delta\nu = 5\text{-}15 \text{ cm}^{-1}$), $\nu(\text{N}-\text{N})$ (pyrazole) attains positive shift ($\Delta\nu = 20\text{-}35 \text{ cm}^{-1}$) and $\nu(\text{C}=\text{N})$ (pyridine) also gains positive shift ($\Delta\nu = 15\text{-}25 \text{ cm}^{-1}$) in the IR spectra of the metal ion complexes. These observations clearly indicate that the tertiary N atoms *i.e.*, pyrazolyl 2_{N} and pyridyl $1'_{\text{N}}$ are the points of attachment^{19,20} to the central metal ions, respectively. The presence of water molecule as coordinated is supported by the appearance of bands in the region 3500-3200 cm^{-1} (due to O-H stretching mode) and 820-800 cm^{-1} due to $\nu(\text{M}-\text{O})$, respectively²¹. Far IR data down to 200 cm^{-1} for the metal ion complexes show non-ligand bands which can be safely assigned to $\nu(\text{M}-\text{O})$ (amidic) (450-380 cm^{-1})^{19,20}, $\nu(\text{M}-\text{N})$ (310-280 cm^{-1} ; pyrazolyl 2_{N})²², $\nu(\text{M}-\text{N})$ (265-250 cm^{-1} ; pyridyl $1'_{\text{N}}$)^{23,24}, respectively.

The mode of attachment of the anions (X) [$\text{X} = \text{Cl}, \text{Br}, \text{NO}_3, \text{BF}_4, \text{ClO}_4$] in the reported metal ion species can be qualitatively inferred from the IR spectroscopy. The spectra of the halo complexes do not show metal-halogen stretching frequencies around 300 cm^{-1} [differentiable from $\nu(\text{M}-\text{N})$ (ring)] indicating ionic nature.

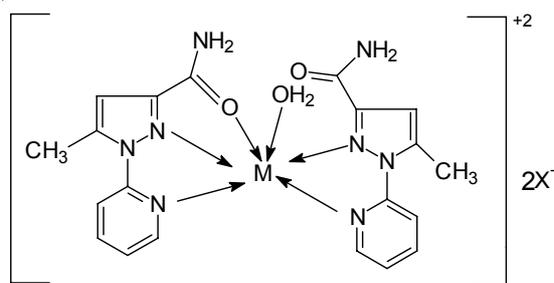
IR spectra of Co(II) and Ni(II) nitrate species exhibit one broad band in the region (1380-1275 cm^{-1}) and another band *ca.* 800 cm^{-1} ; these could be attributed to ν_3 and ν_2 modes of ionic nitrate in D_{3h} symmetry^{25,26}.

The IR spectra of the fluoroborato complexes of Co(II) and Ni(II) exhibit a broad band in the region 1110-1020 cm^{-1} which can be assigned to of ν_3 mode of ionic BF_4 in T_d symmetry^{27,28}.

Perchlorato complexes in the IR spectra of Ni(II) and Cu(II), show a broad band in the region $1150-1030\text{ cm}^{-1}$ and two moderate bands around 1000 and 620 cm^{-1} which can be assigned to the ν_3 , ν_1 and ν_4 modes of ionic perchlorate in T_d symmetry^{28,29}.

Conclusion

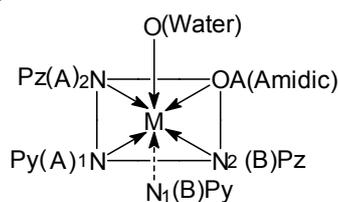
Thus, in the light of the discussion from elemental, spectral and in analogy with the X-ray crystallographic structure analysis² the stereochemistry of the ligand about the central metal atom is interesting and is described as the following structure II. In the same *bis*-chelate, one ligand (say ligand A) binds the metal atom through pyridyl-N (N1A), pyrazole-N (N2A) and amidic O (OA) whereas the second ligand (say ligand B) does this through pyridyl-N (N1B) and pyrazole-N (N2B) respectively. The sixth position is occupied by H_2O . Thus ligand A is neutral tridentate (NNO) and ligand B is neutral bidentate (NN) respectively in these species.



II

M = Co/Ni; X = Cl, Br, NO_3 , BF_4 , ClO_4

The chromophore in these species is $\text{MN}_4\text{O}(\text{amidic})\text{O}(\text{water})$ and is pictorially shown as follows:



ACKNOWLEDGEMENTS

The author (NA) is thankful to the UGC, India for financial help to the Minor Research Project [No.F. PSW-020/05-06 (ERO)] and Prof. S.K. Kar, Department of Chemistry, Calcutta University, Kolkata for various helps and discussions. The author also thanks the Principal and colleagues, Department of Chemistry, A.P.C. College, New Barrackpore, India for their constant encouragement.

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(Received: 22 November 2006;

Accepted: 14 September 2007)

AJC-5853