

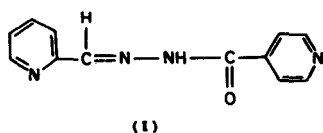
Synthesis & Characterization of Iron(II), Cobalt(II), Nickel(II), Copper(II) & Zinc(II) Complexes of Pyridine-2-carboxaldehyde Isonicotinoyl Hydrazone

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Pyridine-2-carboxaldehyde isonicotinoyl hydrazone (2-PINH) forms complexes of the types $M(2-PINH)_2$ [$M(II) = Fe, Co, Ni, Cu$ and Zn ; $X = Cl, Br$], $Co(2-PINH)(NCS)_2$, $Ni(2-PINH)_2(NCS)_2$ and $M(2-PIN)_2$ [$M(II) = Co, Ni, Cu$ and Zn]. Magnetic and electronic spectral studies suggest tetrahedral geometry for $Co(II)$ halide and thiocyanate complexes, trigonal-bipyramidal geometry for $Ni(2-PINH)Br_2$, high-spin octahedral geometry for $Fe(2-PINH)Cl_2$, $Co(2-PIN)_2$, $Ni(2-PIN)_2$, and $Ni(II)$ chloride and thiocyanate complexes. ESR spectral studies show that $Cu(2-PINH)Cl_2$ is dimeric whereas $Cu(2-PIN)_2$ is monomeric in nature. Infrared spectral studies suggest neutral bidentate or tridentate behaviour of the ligand in the complexes of the $M(2-PINH)_2$ ($X = Cl, Br, NCS$) type or $Ni(2-PINH)_2(NCS)_2$ and uninegative tridentate behaviour in the complexes with deprotonated ligand, PIN.

In continuation of our previous studies¹ on pyridine-4-carboxaldehyde isonicotinoyl hydrazone (4-PINH) complexes of some first row transition metal ions, we now report the synthesis and structural studies of pyridine-2-carboxaldehyde isonicotinoyl hydrazone (2-PINH, I) complexes of $Fe(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$.



All the chemicals used were of AR grade or reagents of equivalent purity. Isonicotinoyl hydrazine (INH) was obtained from M/s Sigma Chem. Co., U.S.A. Pyridine-2-carboxaldehyde was prepared by the literature method². Pyridine-2-carboxaldehyde isonicotinoyl hydrazone was obtained by the condensation of INH with pyridine-2-carboxaldehyde, as reported in literature, m.p. 172° (lit.³ 174.5°).

Metal(II) halide and thiocyanate complexes, $M(2-PINH)_2$ [$M(II) = Fe, Co, Ni, Cu$ and Zn ; $X = Cl, Br$], $Co(2-PINH)(NCS)_2$ and $Ni(2-PINH)_2(NCS)_2$, were prepared by mixing together an ethanolic solution of the respective metal(II) salt and the ligand in appropriate molar ratio. The complexes with the deprotonated ligand, $M(2-PIN)_2$ [$M(II) = Co, Ni, Cu$ and Zn], were prepared by mixing an aq. ethanolic or

aq. methanolic solution of the metal(II) acetate and the ligand in a 1:2 molar ratio followed by the addition of requisite amount of sodium acetate. Zinc-doped copper(II) chloride complex was prepared just like the respective pure copper(II) complex employing 5:95 molar ratio of $Cu(II)$ and $Zn(II)$ chlorides. All the complexes, which precipitated immediately or on stirring the reaction mixture for sometime, were digested on a water-bath for ~ 30 min, cooled, suction filtered, washed with hot ethanol and dried *in vacuo*.

The complexes were analysed for their metal, halogen/thiocyanate, nitrogen and hydrazine contents employing standard literature procedures⁴. The metal analyses were done after destroying the organic matter at first with aqua-regia and then with conc. H_2SO_4 . Nitrogen was estimated by microanalysis.

The methods and apparatus employed for studying molar conductance, magnetic susceptibility, electronic and infrared spectra and the procedures for calculating the ligand-field parameters were the same as described elsewhere⁵. The pertinent experimental data are given in Tables 1 and 2.

ESR spectra of $Cu(2-PINH)Cl_2$ doped in the diamagnetic host lattice of $Zn(2-PINH)Cl_2$ and that of $Cu(2-PIN)_2$ in chloroform solution were recorded at room temperature (RT) and liquid nitrogen temperature (LNT) on a Varian E-12 spectrometer using TCNE ($g = 2.00277$) as a standard.

The analytical data (Table 1) show that 2-PINH yields complexes of the types $M(2-PINH)_2$ and $M(PIN)_2$. The former type of complexes are formed at pH 3-4 while the latter type of complexes result at pH 6-7. $Ni(II)$ thiocyanate forms a 1:2 compound also, $Ni(2-PINH)_2(NCS)_2$. All the complexes have high melting or decomposition temperatures (about $300^\circ C$) except a few, which melt with decomposition in the range $200-292^\circ C$. All the complexes of type $M(2-PINH)_2$ are generally soluble in water, ethanol or methanol except $Cu(2-PINH)Cl_2$ while the complexes of type $M(2-PIN)_2$ are soluble only in coordinating solvents like DMF and DMSO. Molar conductance values of the soluble complexes in methanol ($34-65 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) show that they are non-electrolytes but some ionic dissociation takes place in methanol⁶.

The corrected magnetic moments of $Co(II)$ complexes fall in the range expected for tetrahedral geometry except for the $Co(2-PIN)_2$ complex, the magnetic moment for which indicates its octahedral geometry. The magnetic moments of $Ni(II)$ complexes indicate their high-spin five- or six-coordinated

Table 1—Characterization Data of Pyridine-2-carboxaldehyde Isonicotinoyl Hydrazone Complexes

Compound	Colour	m.p. (°C)	Found (Calc.), %				μ_{eff} (B.M.)
			Metal	Halogen/ thiocyanate	N	Hydrazine	
Fe(2-PINH)Cl ₂	Bottle green	188	15.50(15.70)	20.05(20.13)	15.85(15.90)	—	4.44
Co(2-PINH)Cl ₂	Dark green	225	16.35(16.56)	19.56(19.95)	15.25(15.73)	8.65(8.99)	4.47
Ni(2-PINH)Cl ₂	Parrot green	>300	15.86(16.50)	19.24(19.94)	15.55(15.76)	8.85(9.00)	2.93
Cu(2-PINH)Cl ₂	Green	200	17.25(17.65)	18.96(19.66)	15.25(15.54)	—	2.05
Zn(2-PINH)Cl ₂	Yellow	>300	17.75(18.04)	19.46(19.56)	15.25(15.45)	8.80(8.83)	diamagnetic
Co(2-PINH)Br ₂	Dark green	>300	13.02(13.25)	35.75(35.93)	12.05(12.59)	7.11(7.19)	4.52
Ni(2-PINH)Br ₂	Chocolate	255	13.02(13.04)	35.32(35.95)	12.50(12.59)	7.12(7.19)	3.15
Co(2-PINH)(NCS) ₂	Green	260	14.17(14.70)	28.66(28.94)	20.45(20.95)	7.85(7.98)	4.37
Ni(2-PINH)(NCS) ₂	Dark yellow	292	9.30(9.36)	18.25(18.50)	22.25(22.34)	10.15(10.21)	2.95
Co(2-PIN) ₂	Brick red	>300	11.25(11.59)	—	21.95(22.01)	12.55(12.58)	4.85
Ni(2-PIN) ₂	Yellowish brown	>300	11.50(11.53)	—	22.00(22.02)	12.56(12.58)	2.98
Cu(2-PIN) ₂	Light green	256	11.95(12.38)	—	21.58(21.81)	—	2.00
Zn(2-PIN) ₂	Pale yellow	>300	12.56(12.68)	—	21.58(21.73)	12.35(12.42)	diamagnetic

Table 2—Electronic Spectral Data and Ligand-field Parameters of Pyridine-2-carboxaldehyde Isonicotinoyl Hydrazone Complexes

Complex	λ_{max} (cm ⁻¹)	D_q (cm ⁻¹)	B (cm ⁻¹)	β	β^0 (%)	LFSE (KJ mol ⁻¹)
Fe(2-PINH)Cl ₂	10530	1053	—	—	—	50.39
Co(2-PINH)Cl ₂	7519, 16950, 18180	436	758	0.78	22	62.60
Co(2-PINH)Br ₂	8197, 16670	485	692	0.71	29	63.58
Co(2-PINH)(NCS) ₂	8197, 20000	463	938	0.36	64	66.50
Co(2-PIN) ₂	10000, 13510, 18180	797	433	0.44	56	76.32
Ni(2-PINH)Cl ₂	9804, 16670, 21740	632	903	0.85	15	90.74
Ni(2-PINH)Br ₂	8350, 11430, 21050	—	—	—	—	—
Ni(2-PINH) ₂ (NCS) ₂	9091, 14810	909	827	0.78	22	130.50
Ni(2-PIN) ₂	10260, 16000, 23530	962	641	0.60	40	138.00
Cu(2-PINH)Cl ₂	14810	1481	—	—	—	106.33
Cu(2-PIN) ₂	15150, 21740	1515	—	—	—	108.77

geometry. The subnormal magnetic moment of Fe(2-PINH)Cl₂ may be due to metal-metal interactions. The magnetic moments of Cu(II) complexes are normal and correspond to the presence of one unpaired electron without giving specific information about the stereochemistry.

The electronic spectral data of the complexes are given in Table 2. Fe(2-PINH)Cl₂ yields one broad band at 10530 cm⁻¹, which may be assigned to ⁵T_{2g} → ⁵E_g(D) transition in an octahedral geometry around Fe(II)⁷.

The spectra of Co(2-PINH)X₂ (X = Cl, Br, NCS) display two bands in the regions 7520-8200 and 16670-20000 cm⁻¹. These are assigned respectively as the ⁴A₂ → ⁴T₁(F)(ν₂) and ⁴A₂ → ⁴T₁(P)(ν₃) transitions of tetrahedral cobalt(II). The spectrum of Cu(2-PIN)₂, however, shows three bands at 10000, 13510 and 18180 cm⁻¹, which is consistent with high-spin six-coordinated cobalt(II); the bands may be assigned to the transitions ⁴T_{1g}(F) → ⁴T_{2g}(F)(ν₁), ⁴T_{1g}(F) → ⁴A_{2g}(F)(ν₂) and ⁴T_{1g}(F) → ⁴T_{1g}(P)(ν₃), respectively⁸.

The spectra of Ni(2-PINH)Cl₂, Ni(2-PINH)₂(NCS)₂ and Ni(2-PIN)₂ show three bands in the regions 9090-

10260, 14820-18180 and 21740-23530 cm⁻¹. These bands may be assigned as ³A_{2g}(F) → ³T_{2g}(F)(ν₁), ³A_{2g}(F) → ³T_{1g}(F)(ν₂) and ³A_{2g}(F) → ³T_{1g}(P)(ν₃) transitions, respectively, of six-coordinated nickel(II)⁹. The spectrum of Ni(2-PINH)Br₂, however, shows three bands at 8330, 11430 and 21050 cm⁻¹. The absence of a band in the 14000-16000 cm⁻¹ region and occurrence of the third band at a lower energy as compared to the ν₃ band of octahedral Ni(II) complexes is suggestive of a five-coordinated Ni(II)¹⁰. The band of medium intensity at 8330 cm⁻¹ may, therefore, be assigned ³E'(F) → ³E''(F) and the characteristic intense band at 11430 cm⁻¹ corresponds to the transition ³E'(F) → ³A''(F). A more intense band at 21050 cm⁻¹ is due to the transition derived from the ³P term of the nickel ion.

Cu(2-PINH)Cl₂ and Cu(2-PIN)₂ display a broad band at 14810 and 15150 cm⁻¹, respectively as has been found for distorted octahedral Cu(II) complexes¹¹. A high energy band occurring in this complex at 21740 cm⁻¹ may be assigned to a charge-transfer or intra-ligand transition.

ESR spectrum of Cu(2-PINH)Cl₂ at 77 K shows a

high field transition around 2800 G ($\Delta M_s = 1$) with the parallel, perpendicular and average g values of 2.317, 2.038 and 2.131 respectively. A half-field transition around 1450 G ($\Delta M_s = 2$) is also observed with the parallel, perpendicular and average g values of 4.474, 3.980 and 4.145, respectively. The presence of half-field signal shows the dimeric nature of the Cu(II) complex¹².

The room temperature spectrum of Cu(2-PIN)₂ in chloroform solution consists of a well resolved signal giving $g_{\text{iso}} = 2.124$. A high field transition around 2880 G ($\Delta M_s = 1$) at 77 K gives the parallel, perpendicular and average g values of 2.252, 2.054 and 2.120, respectively. The 77 K spectra of these compounds show better resolution as compared with the room temperature spectra. The trend $g_{\parallel} > g_{\perp} > g_e$ (free ion value) shows that the unpaired electron is in the $d_{x^2-y^2}$ orbital of Cu(II).

The infrared spectrum of 2-PINH in nujol and KBr shows a band at 3280 cm⁻¹ which may be assigned to $\nu(\text{N}-\text{H})$; the band remains practically unchanged in the spectra of complexes of the type M(2-PINH)₂X₂ and Ni(2-PINH)₂(NCS)₂ but disappears in the complexes with deprotonated ligand i.e. M(2-PIN)₂, indicating that the imino nitrogen is not involved in bonding in the first two types of complexes while this group is involved in coordination in the third type of complexes after enolisation and deprotonation.

In the complexes of the types M(2-PINH)₂X₂ and Ni(2-PINH)₂(NCS)₂, the amide I band [$\nu(\text{C}=\text{O})$] shifts towards lower frequency values (20-40 cm⁻¹) as compared to its position in the ligand (1650 cm⁻¹), while the amide II [$\nu(\text{CO}) + \delta(\text{NH})$] and the amide III [$\delta(\text{NH}) + \nu(\text{CO})$] bands shift slightly to lower (15-20 cm⁻¹) and higher (15-20 cm⁻¹) frequencies respectively compared to their positions in the ligand at 1540 and 1275 cm⁻¹ indicating that the carbonyl oxygen is coordinated to metal atom¹³. The band at 1615 cm⁻¹ is assigned to $\nu(\text{C}=\text{N})$ of the azomethine group; it undergoes a downward shift (15-25 cm⁻¹), showing that the azomethine nitrogen is coordinated to the metal atom^{14,15}.

In the spectra of the M(2-PIN)₂ complexes, amide I band is found to be absent; however, a new band, which may be assigned to $\nu(\text{NCO})$, appears at ~ 1555 cm⁻¹ showing the enolisation of the keto group and its subsequent deprotonation during complex formation. A sharp band occurring at 1590-1600 cm⁻¹ may be attributed to the presence of the $>\text{C}=\text{N}-\text{N}=\text{C}<$ group suggesting that the amide oxygen is bonded in the enolic form upon deprotonation. The pyridine ring vibrations are observed at higher frequencies (~ 1005 ,

640 cm⁻¹) in the spectra of the complexes as compared with the ligand spectrum (985 and 615 cm⁻¹) in all the complexes except Fe(II), Co(II) and Ni(II) chloride, Co(II) bromide and Ni(II) and Co(II) thiocyanate complexes, indicating pyridine nitrogen as an additional bonding site¹⁶. The infrared spectral studies thus show neutral bidentate or tridentate behaviour of the ligand in the M(2-PINH)₂X₂ complexes and uninegative tridentate behaviour in the M(2-PIN)₂ complexes.

In the thiocyanate complex of Co(II) and Ni(II) the bands occurring at (2065-2080 cm⁻¹(ν_1), 470-480 cm⁻¹(ν_2) and 775-780 cm⁻¹(ν_3) due to $\nu(\text{C}\equiv\text{N})$, $\delta(\text{NCS})$ and $\nu(\text{C}=\text{S})$ modes of thiocyanate respectively indicate the presence of N-bonded thiocyanate group in these complexes¹⁷.

The $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ modes are observed in all the complexes in the regions¹⁸ 285-300 and 320-330 cm⁻¹ respectively.

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