

**INTERNATIONAL JOURNAL OF ADVANCES IN PHARMACY,
BIOLOGY AND CHEMISTRY**

Research Article

Synthesis and Characterization of some Schiff bases and their Co (II) complexes

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ABSTRACT

Schiff bases derived from the condensation of 2 – aminonicotinaldehyde with 1,2-ethanediamine, 1,3-propanediamine, 1,2-propanediamine and 1,2-phenylenediamine and their Co(II) complexes have been synthesized and characterized by spectroscopic and single crystal X-ray diffraction data. The ligands behave towards the Co(II) as neutral, quadridentate ones forming a square planar structure with ion.

Keywords: Quadridentate Schiff base Co(II) complexes, synthesis, characterization.

INTRODUCTION

Schiff bases, characterized by the presence of azomethine group, =C=N-, have been among the most widely studied ligands in understanding the structure and reactivity of metal complexes. Azomethine is a potential donor group forming a large number of metal complexes whose stability is aided by the presence, in appropriate position, of a second such group containing donor atoms like N, O, S to form chelates. Research on multidentate ligands has been stimulated by a number of factors such as their interesting and, very often, unique stereochemical properties and their wide-spread occurrence in nature. This has led to the synthesis and study of a wide variety of new chelating agents and their metal complexes. Against this background, the present paper deals with the synthesis of Co(II) complexes of N,N'-bis(2-aminonicotinalidene) – 1,2- ethanediamine (H₂anaen), N,N'-bis(2-aminonicotinalidene) – 1,3-propanediamine (H₂anpn), N,N'-bis(2-aminonicotinalidene) – 1,2-propanediamine (H₂anpn) and N,N'-bis(2-aminonicotinalidene) -1,2-phenylenediamine (H₂anaphen) (Fig.1) and their structural characterization by physico-chemical data.

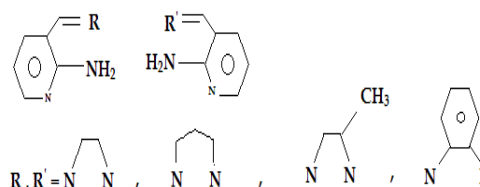


Fig. 1:

EXPERIMENTAL

All the chemicals used were of AR or BDH grade. The ligands H₂anaen, H₂anpn, H₂anpn and H₂anaphen were prepared by reacting 2-aminonicotinaldehyde with 1,2 – ethanediamine, 1,3 – propanediamine, 1,2-propanediamine and 1,2-phenylenediamine respectively in 2:1 mole ratio in presence of a few drops of Con. HCl at 90°C. The Schiff base formed was filtered, washed with water and ethanol and recrystallized in ethanol-DMF mixture to give yellow crystalline compound.

The Co(II) complexes were prepared by refluxing CoCl₂.2H₂O and the corresponding ligand in 1:1 mole ratio in ethanol for about 2hrs. The reddish brown crystalline compounds formed were filtered, washed with ethanol and ether and dried in vacuum.

The C, H, N analyses of the ligands and the Co(II) complexes were carried out at C.D.R.I., Lucknow. The cobalt and the chloride contents in the representative complex, after decomposition, were

determined by standard procedures¹. A DI-909 model Digisun digital conductivity meter with a cell calibrated with 0.1 M KCl solution was used for conductance measurements of the complexes in DMF at 10^{-3} M concentration. Magnetic susceptibility of the complexes in solid state at room temperature was measured by vibrating sample magnetometer. The infrared spectra of the ligands and the complexes in the range $4000 - 600$ cm^{-1} were recorded in KBr matrix or in Nujol mulls on Perkin – Elmer – 283 spectrophotometer. The electronic spectra of the complexes in DMF were recorded on Schimadzu – 5000 spectrophotometer. The single crystal X-ray diffraction data on H_2anatn were collected on a Rigaku AFC – 6S diffractometer with graphite monochromated $\text{Mo-K}\alpha$ radiation.

RESULTS AND DISCUSSION

(a) Crystal structure of H_2anatn

As yellow needle crystal of H_2anatn (Molecular formula : $\text{C}_{15}\text{H}_{18}\text{N}_6$) having approximate dimensions of $0.80 \times 0.90 \times 0.70$ mm was mounted on a glass fiber. The crystal data of the compound obtained are in Table 1 and its molecular structure is shown in Fig. 2. The structure was solved by direct methods² and expanded using Fourier techniques³.

The bond lengths between selected atoms C(1) - N(1) 1.350 Å, C(1) - C(2) 1.445 Å, C(2) - C(3) 1.374 Å, C(3) - C(4) 1.379 Å, C(4) - C(5) 1.389 Å, C(5) - N(6) 1.312 Å, C(1) - N(6) 1.344 Å, C(2) - C(6) 1.459 Å, C(6) - N(2) 1.260 Å, N(2) - C(7) 1.457 Å, C(7) - C(8) 1.538 Å do not differ significantly from the values reported for similar derivatives. The pyridine rings of the molecule are planar. The torsion angles N(1) - C(1) - C(2) - C(6) - 2.9° , N(2) - C(6) - C(2) - C(1) - 0.9° , N(2) - C(6) - C(2) - C(3) - 177.3° , N(3) - C(10) - C(11) - C(15) 173.4° , N(3) - C(10) - C(11) - C(12) 7.0° , N(4) - C(12) - C(11) - C(10) 0.0° indicate that the molecular fragments made of 2-aminonicotinaldimimines are almost planar. The planar geometry of these fragments are possibly stabilized by the formation of intramolecular hydrogen bonding

N(1) - H --- N(2) with a distance of 2.085 Å at an angle of 126° and N(4) - H --- N(3) with a distance of 2.058 Å at an angle of 127° .

The crystal structure of H_2anatn also shows that it is folded about C(9) atom and the pyridine rings are making an angle of 64° . There are intramolecular hydrogen bonding interactions between hydrogen atom on amine nitrogen and nitrogen atom of pyridine ring N(1)-H --- N(6) 2.38 Å at an angle of 126° . This intramolecular hydrogen bonding causes in the formation of wave like ribbons.

The conformation of the molecule is lattice imposed. In fact, the structure is quite flexible and can fold in such a way that it can form square

planar metal complexes coordinating through N(1), N(2), N(3) and N(4).

(b) Characterization of Co(II) complexes

The Co(II) complexes of the ligands are slightly soluble in methanol, ethanol and acetone but are freely soluble in water, DMF and DMSO. The molar conductance values for the complexes in DMF solution are in the range 110 - 138 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating that they are 1:2 electrolytes. The analytical and physical data of the complexes are presented in Table 2.

The ligands exhibit intense infrared bands around 3200 cm^{-1} due to $\nu\text{C} = \text{N}^6$. The frequencies of these two groups have been lower shifted in their complexes indicating that the NH_2 and $\text{C} = \text{N}$ groups are involved in coordination with the Co(II) ion. Thus, it may be inferred that the ligands act as neutral, quadridentate ones coordinating through nitrogens of NH_2 and $\text{C} = \text{N}$ groups. In addition, there are non-ligand bands in the complexes in the region $505 - 520 \text{ cm}^{-1}$ which may be assigned to $\nu\text{C}_0 - \text{N}$ mode⁷.

The magnetic susceptibility measurements show that the magnetic moment values of the Co(II) complexes are in the range 2.20 - 2.31 BM which tally with those reported for many four coordinated low spin Co(II) complexes⁸.

Electronic spectra of the complexes show that they absorb strongly in the uv region giving two intense charge transfer bands around 23250 and 18600 cm^{-1} . In addition, they show a low intensity band around 10750 cm^{-1} due to d-d transition. This kind of electronic spectrum is characteristic of low spin square planar Co(II) complexes⁹.

Based on the foregoing results and discussion, a square planar structure has been proposed for the present Co(II) complexes in which the ligands act as neutral, quadridentates coordinating through the nitrogen atoms.

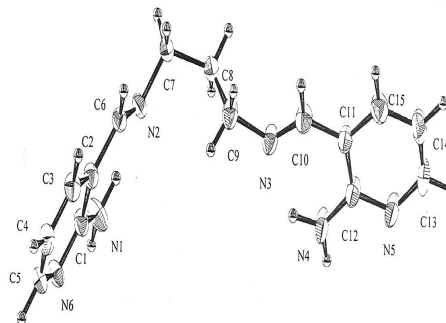


Fig. 2: Molecular structure of H_2anatin

Table 1: Crystal data of H₂ anatr

Empirical formula	C ₁₅ H ₁₈ N ₆
Formula weight	282.35
Crystal colour, Habit	Yellow, Needles
Crystal dimensions	0.80 x 0.90 x 0.70 mm
Crystal system	Triclinic
Lattice type	Primitive
No. of reflections used for Unit cell determination (2θ range)	25 (32.6 – 39.3°)
Lattice parameters	a = 9.761 °Å, α = 103.86 ° b = 12.247 °Å, β = 108.01 ° c = 7.039 °Å, γ = 72.29 ° V = 752.4 °Å ³
Space group	P-1 (# 2)
Z value	2
Density _{cal}	1.246 g / cm ³
F ₀₀₀	300.00
μ (M ₀ K _α)	0.80 cm ⁻¹

Table 2: Analytical and Physical data of Co [II] complexes

Complex	Decomp Temp(°C)	Molar Temp(°C)	Cond Ohm ⁻¹ cm ² mol ⁻¹	Per cent ^a				
				Co	C	H	N	Cl
[Co(H ₂ anaen)]Cl ₂ .2H ₂ O	300	138	13.26	38.02 (13.57)	4.69 (38.73)	19.36 (4.64)	16.12 (19.36)	(16.33)
[Co(H ₂ anatr)]Cl ₂ .2H ₂ O	285	116	--	40.14	4.88 (40.20)	18.72 (4.95)	--	(18.75)
[Co(H ₂ anapn)]Cl ₂ .2H ₂ O	270	122	--	40.06	4.78 (40.20)	18.80 (4.95)	--	(18.75)
[Co(H ₂ anaphen)]Cl ₂ .2H ₂ O	300	110	--	43.95	4.22 (44.83)	17.24 (4.18)	--	(17.43)

Values in parentheses are the calculated ones.

^a Analysis carried out for the elements shown.

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