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Research Article

**Structural Studies on Cu [II] Complexes of Some Schiff
Bases by Spectroscopic and Single Crystal X – Ray
Diffraction Techniques**

Dasharatham D

¹Department of Chemistry, Kakatiya University, Warangal, Andhra Pradesh, India.
India.

ABSTRACT

Cu[II] complexes of Schiff bases derived from the condensation of 2-aminonicotinaldehyde with 1,2-ethanediamine, 1,3-propanediamine, 1,2-propanediamine and 1,2-phenylenediamine have been synthesized and characterized by spectroscopic and single crystal X-ray diffraction data. The ligands show neutral, quadridentate behaviour towards Cu[II] forming a square planar structure with the ion.

Keywords: Quadridentate Schiff base Cu[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 co-ordination compounds. Azomethine is a potential donor group and it forms a 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 chelating agents 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. Partaking this, the present paper deals with the synthesis of Cu[II] complexes of N,N'-bis(2-aminonicotinaldehyde) – 1,2-ethanediamine(H₂anaen), N,N'-bis(2-aminonicotinaldehyde) – 1,3-propanediamine(H₂anpn) and N,N'-bis(2-aminonicotinaldehyde) – 1,2-phenylenediamine (H₂anaphen) (Fig. 1) and their characterization by spectroscopic and single crystal X-ray diffraction data.

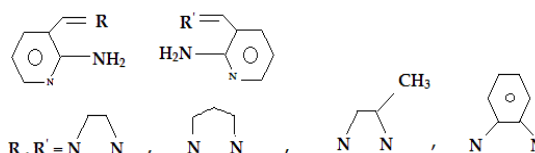


Fig. 1:

EXPERIMENTAL

All the chemicals used were of AR or BDH grade. The ligands H₂ anaen, 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 Cu[II] complexes were prepared by refluxing CuCl₂ · 2H₂O and the corresponding ligand in 1:1 mole ratio in ethanol for about 2 hrs. The brown or green compounds formed were filtered, washed with ethanol and ether and dried in vacuum.

The C, H, N analyses of the ligands and the Cu[II] complexes were carried out at C.D.R.I., Lucknow.

The copper 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 Shimadzu-5000 spectrophotometer. The single crystal X-ray diffraction data were collected on a Rigaku AFC-6S diffractometer using the ω - 2 θ mode at a fixed scans rate with multiple scans for weak reflections.

Table 1: Analytical and Physical data of Cu[II] complexes

Complex	Decomp Temp(°C)	Molar Cond. Ohm ⁻¹ cm ² mol ⁻¹	Per cent ^q				
			Cu	C N	H	Cl	
[Cu(H ₂ anaen)]Cl ₂ .2H ₂ O	255	124	14.21 (14.28)	38.10 (38.32)	4.48 (4.59)	19.20 (19.15)	15.97 (16.16)
[Cu(H ₂ anatn)]Cl ₂ .2H ₂ O	225	132	--	39.46 (39.79)	4.92 (4.90)	18.47 (18.56)	--
[Cu(H ₂ anapn)]Cl ₂ .2H ₂ O	250	110	--	39.66 (39.79)	4.88 (4.90)	18.52 (18.56)	--
[Cu(H ₂ anaphen)]Cl ₂ .2H ₂ O	265	105	12.78 (13.05)	44.12 (44.41)	4.12 (4.14)	17.11 (17.26)	14.27 (14.56)

Values in parentheses are the calculated ones.

^q Analysis carried out for the elements shown.

Table 2 : Crystal data of [Cu(H₂anaen)]Cl₂.2H₂O

Empirical formula	C ₁₄ H ₂₀ N ₆ O ₂ Cl ₂ Cu
Formula weight	438.80
Crystal colour, Habit	Yellow, Needles
Crystal dimensions	0.60 x 0.80 x 0.90 mm
Crystal system	Triclinic
Lattice type	Primitive
No. of reflections used for Unit cell determination (2 θ range)	25 (20.1 – 28.9°)
Lattice parameters	a = 10.141 °Å α = 97.65 ° b = 13.241 °Å β = 95.88 ° c = 7.41 °Å γ = 108.30 °
Space group	P-1 (# 2)
Z value	2
Density _{cal}	1.634 g / cm ³
F ₀₀₀	450.00
M (M ₀ K α)	15.46 cm ⁻¹

RESULTS AND DISCUSSION

All the metal complexes are stable at room temperature and are non-hygroscopic. They decompose, upon heating, without melting. The ligands and the complexes are slightly soluble in ethanol, methanol and acetone and fairly soluble in DMF and DMSO. The molar conductance values of the complexes are in the range 105-132 $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating that they are 1:2 electrolytes. The analytical and physical data of the complexes are presented in Table 1.

The ligands exhibit intense infrared bands in the region 3180 – 3310 cm^{-1} due to ν N-H of NH_2 group³. A sharp band around 1630 cm^{-1} has been ascribed to ν C=N⁴. The frequencies of these two groups have been lower shifted in their complexes indicating that the NH_2 and the C=N groups are involved in coordination with the Cu[II] ion. Thus, it may be inferred that the ligands act as neutral, quadridentate ones coordinating through nitrogens of NH_2 and C=N groups.

The electronic spectra of the complexes show a broad band in the range 14600-15110 cm^{-1} corresponding to ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transition, characteristic of tetragonal or square planar geometry⁵.

Based on these results the composition of the complexes can be presented as $[\text{CuL}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ where $\text{L} = \text{H}_2 \text{ anaen}, \text{H}_2 \text{ atan}, \text{H}_2 \text{ anapn}$ or $\text{H}_2 \text{ nanphen}$. However, in order to find out the actual behaviour of the ligands and the geometry of the resulting complexes, single crystal X-ray diffraction studies were carried out on $[\text{Cu}(\text{H}_2 \text{ anaen})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. X-ray crystal structure of $[\text{Cu}(\text{H}_2 \text{ anaen})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ complex.

An yellow needle crystal of $[\text{Cu}(\text{H}_2 \text{ anaen})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (molecular formula

$:\text{C}_{14}\text{H}_{20}\text{N}_6\text{O}_2\text{Cl}_2 \text{ Cu}$) complex having approximate dimensions of 0.60x0.80x0.90 mm was mounted on a glass fiber. The crystal data of the complex obtained are incorporated in Table 2 and the molecular structure is shown in Fig. 2. The structure was solved by direct⁶ and expanded using Fourier techniques⁷.

The structure consists of complex mononuclear cations, chloride ions and water molecules. Each copper ion coordinated by four nitrogen atoms N_1 , N_2 , N_3 and N_4 , displays a square planar geometry. Least – squares planes fit shows very slight distortions from idealized square planar geometry. N_1 and N_3 atoms are situated above the mean plane (deviation of 0.022 and 0.023 \AA respectively), while N_2 and N_4 atoms are situated below the mean plane (deviation of 0.025 and 0.027 \AA respectively) while copper ion is in the mean plane. The molecule thus bends slightly along the lines $\text{N}_1 \dots \text{N}_2$ and $\text{N}_3 \dots \text{N}_4$ resulting in a tetrahedral twist structure. The angles $\text{N}_1\text{-Cu-}\text{N}_3$ 174.6 $^\circ$, $\text{N}_2\text{-Cu-}\text{N}_4$ 174.0 $^\circ$ and dihedral angle between planes $\text{N}_1\text{-Cu-}\text{N}_2$ and $\text{N}_3\text{-Cu-}\text{N}_4$ only 2.02 $^\circ$ indicate that there is only slight distortion from perfect square planar structure, but the distortion is comparable to that of the well known square planar complexes such as $\text{N,N}'\text{-[bis(2-hydroxyl-1-naphthylmethylene) propane -1,3-diaminato] nickel(II)}$ with theta of 2.0 $^\circ$.

Thus, the structure supports the fact that $\text{H}_2 \text{ anaen}$ acts as a quadridentate ligand forming with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ a slightly distorted square planar complex of 1:2 electrolyte type. The same conclusions may be applicable for the Cu[II] complexes $\text{H}_2 \text{ atan}, \text{H}_2 \text{ anapn}$ and $\text{H}_2 \text{ nanphen}$.

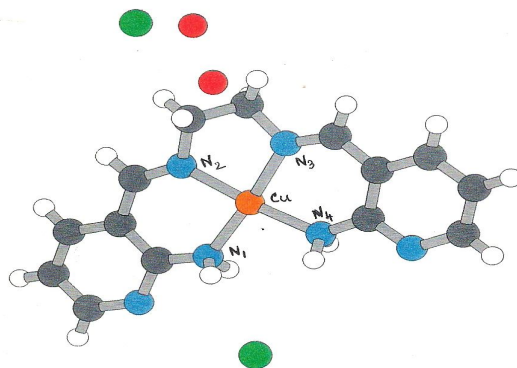


Fig. 2: Molecular Structure of $[\text{Cu}(\text{H}_2 \text{ anaen})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ together with water molecule and chloride ions outside the coordination sphere. Hydrogen atoms on Oxygen of water molecule are not shown. (central Reddish Brown – Copper ; blue – Nitrogen ; red – Oxygen ; Gray – Carbon ; White – Hydrogen)

REFERENCES

1. Vogel, A.I., AText book of quantitative inorganic analysis, Longman, 3rd ed., 1961, 358, 266.
2. Geary WJ. Coord Chem Rev. 1971;7: 81.
3. Drago RS. Physical methods in inorganic Chemistry, Affiliated East-West Press Pvt. Ltd. 1968;219.
4. Syamal A, Kumar D and Ahmed. Indian J Chem. 1982;21A: 634.
5. Lever ABP. Inorganic electronic spectroscopy. Elsevier, 2nd Ed., 1984, 557.
6. Sheldrick GM. In Crystallographic computing 3 (eds. Sheldrick, G.M., Kruger,C. and Goddard, R.), Oxford University Press, 1985;175.
7. Beurskens PT, Admiraal G, Beurskens G, Bosman WP, De Gelder R, Israel R and Smits JMM. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.