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Study of Imino Aceto Hydroxamicacid Magnetic and Spectral Behaviour

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ABSTRACT

The Schiff base of the e-amino aceto hydroxamic acid is higly prons to co-ordination when it is in the enol form. It is expected that one hyddroxy (OH) proton of the ligand molecule will be diprotonated forming mono-anionoc bidentate donor molecule. In this case (N-OH) proton of the hydroxamic acid moeity is lost producing uninegative ion. The resultant ligand acts as bidentate molecule which co-ordinat through imino nitrogen and one aldimino nitrogen atom of the ligand molecule. In complexes (OH) amide bands (C=O) and (N-O) of ligand molecule are affected appreciable. In the basis of infra-red spectra that aldimino (azo methine group nitrogen, C=N) nitrogen and deprotonated hydroxamic part (N-O) nitrogen atoms are the bonding sites of a(p-methoxy aceto phenone) imino aceto hydroxamic acid. In case of ammine complexes, the broad band at 3300 cis attributed to (N-H) band of co-ordinated ammonia molecules in the complexes. In pyridine and picoline containing complexes the position of (C=N) band could not be ascertained difinitaly due to bulky ligand molecule and amide as well as imids group (C=N) vibrations. The pyridine or picoline complexes, however display some extra bands in finger print and far infrared region. The pyridine ring breathing mode of vibration located at 990-1030 cm^3 in complexes has been taken to be characterstic vibration of co-ordinated pyridine and picolines. A new band obtained in the range of 430-450 cm^3 due to (M-N) vibrations further confirms the participation of aldimino and hydroxamino nitrogen atoms in the bond formations with the metal cations. It is proposed that one nitrogen atom (hydroxamino) of deprotonated hydroxamic acid part (N-O) and one nitrogen atom of the azo-methine group are the bonding sites of the ligand, (p-methoxy acetophenone) imino aceto hydroxamic acid. The electrical conductance of all the complexes show that these complexes are to be non-electrolyte in nature. Elemental analysis of the complexes indicate that all the complexes are monomeric in nature.

Keywords : Deprotonated, Uninegative, Ligand, Aldimino, Monomeric

1. Introduction

Hydroxamates are essentially growth factors, or vitamins, for some microbes. They function as iron-binding compounds (siderophores) that solubilise iron and transport it into the cell[1]. Iron is a key component of cytochromes and iron-sulphur proteins (involved in electron transport) and is thus important in cellular respiration. In an environment, absent from oxygen (anoxic); iron will be present in the ferrous +2 oxidation state (Fe^{2+}), which is water-soluble. Under oxic conditions; iron will be in the ferric +3 oxidation state (fe^{+3}), in insoluble mineral form. The powerful chelating properties of hydroxamic acid and its derivatives is exploited by

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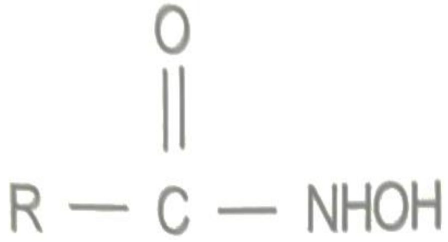
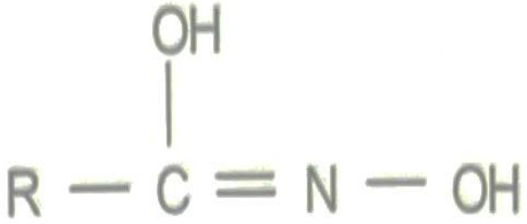
bacteria to obtain ferric iron. Once the iron hydroxamate complex has entered the cell, the iron is liberated and the hydroxamic acid can be excreted and reused for iron transport.

First of all, hydroxamic acid was reported due to the re-action of hydroxylamine on dietyl oxalate by H. Lossen[3] in 1869. The production of violet colouration with Fe(III) and green colouration with Cu(II) are the characteristic reactions of hydroxamic acids. Hydroxamic acids are generally prepared by the reaction of hydroxylamine on organic esters or its derivatives in presence of sodium ethoxide. Hydroxamic acid has the following tautomeric structures such as



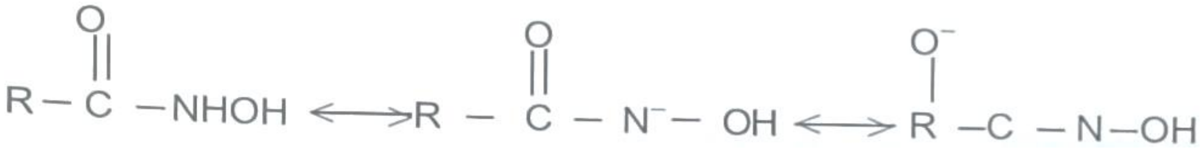
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NHOH$$



$$R-\overset{\overset{\displaystyle OH}{|}}{C}=N-OH$$

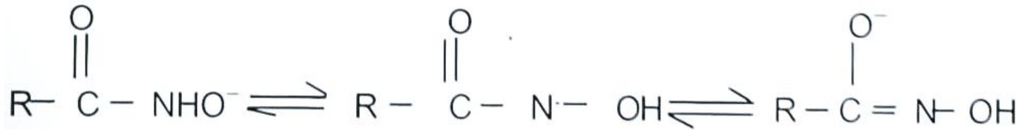
Structure represents hydroxamic acid in solid state as supported by X-ray analysis of crystalline aceto hydroxamic acid semi hydrate and N-hydroxyl urea[4] spectral analysis also support that structure (II) is predominant.

Exner and Kakac[5] argue from spectroscopic evidence that the proton bound to the nitrogen atom is the acidic proton and ionisation gives rise to the anions shown below:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NHOH \longleftrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-N^{-}-OH \longleftrightarrow R-\overset{\overset{\displaystyle O^{-}}{|}}{C}-N-OH$$

Other workers[6] report that two anions are formed in essentially equal concentrations in the case of benzo hydroxamic acid. The equilibrium is shown below:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NHO^{-} \rightleftharpoons R-\overset{\overset{\displaystyle O}{\|}}{C}-N^{\cdot}-OH \rightleftharpoons R-\overset{\overset{\displaystyle O^{-}}{|}}{C}=N-OH$$

<u>EXPERIMENT</u>

1. Preparation of Cu(II) complexes with a(p-methoxy aceto phenone) imino aceto hydroxamic acid

0.24 grams (0.001 mole) of the ligand, a(p-methoxy acetophe none) imino aceto hydroxamic acid was dissolved in a minimum volume of ethyl alcohol. It was then treated with an ethanolic solution of 0.25 gram (0.001 mole) of Cu(II) chloride hexahydrade. The resulting solution was heated under reflux on water bath for 2 hours when a deep green crystalline solid was obtained which was separated by filteration and washed with small quantity of alcohol followed by ether and dried over KOH pillets placed in desiccator. It was further analysed and found to contain. 1. Preparation of Co(II) complexes with a(p-methoxy aceto phenone) imino aceto hydroxamic acid

Table – 1

Components	Found %	Calculated %
Copper	11.40	11.72
Carbon	48.42	48.1875
Hydrogen	5.56	5.54
Nitrogen	10.40	10.34

Which corresponds to the molecular formula **[$Cu(C_{11}H_{13}N_2O_3)_2(H_2O)_2$]**

2. Preparation of Cu (II) complexes with a(p-methoxy aceto phenone) imino aceto hydroxamic acid

0.24 grams (0.001 mole) of the ligand, a(p-methoxy acetophe-none) imino aceto hydroxamic acid was dissolved in a minimum volume of ethyl alcohol. It was then treated with an ethanolic solution of 0.24 gram (0.001 mole) of Cu(II) chloride hexahydrade. 2 to 4 drops of quinoline was added to the resulting solution with regular shaking. The resulting solution was heated under reflux on water bath for 2 hours when a green crystalline solid was obtained which was separated by filteration and washed with small quantity of alcohol followed by ether and dried over KOH pillets placed in desiccator. It was further analysed and found to contain.

Table – 2

Elements	Found %	Calculated %
Copper	8.10	8.31
Carbon	62.36	62.86
Hydrogen	5.20	5.23
Nitrogen	11.10	11.00

Which corresponds to the molecular formula **[$Cu(C_{11}H_{13}N_2O_3)_2(C_9H_7N)_2$]**

3. Preparation of Cu(II) complexes with (p-methoxy aceto phenone) imino aceto hydroxamic acid

0.24 grams (0.001 mole) of the ligand, o(p-methoxy acetophe hone) imino aceto hydroxamic acid was dissolved in a minimum volume of ethyl alcohol. It was then treated with an ethanolic solution of 0.24 gram (0.001 mole) of Cu(II) chloride hexahydrade. 2 to 4 drops of pyridine was added to the resulting solution with regular shaking. The resulting solution was heated under reflux on water bath for 2 hours when a ight green crystalline solid was obtained which was separated by filteration and washed with small quantity of alcohol followed by ether and dried over KOH pillets placed in desiccator. It was further analysed and found to contain

Table – 3

Elements	Found %	Calculated %
Copper	9.30	9.57
Carbon	57.48	57.87
Hydrogen	5.45	5.42
Nitrogen	12.70	12.66

Which corresponds to the molecular formula **[$Cu(CH_{11}H_{13}N_2O_3)_2(C_5H_5N)_2$]**

4. Preparation of Cu(II) complexes with a(p-methoxy aceto phenone) imino aceto hydroxamic acid

0.24 grams (0.001 mole) of the ligand, (p-methoxy acetophe-none) imino aceto hydroxamic acid was dissolved in a minimum volume of ethyl alcohol. It was then treated with an ethanolic solution of 0.24 gram (0.001 mole) of Cu(II) chloride hexahydrade. 2 to 4 drops of a-picoline was added to the resulting solution with regular shaking. The resulting solution was heated under reflux on water bath for 2 hours when a light green crystalline solid was obtained which was separated by filteration and washed with small quantity of alcohol followed by ether and dried over KOH pillets placed in desiccator. It was further analysed and found to contain.

Table – 4

Elements	Found %	Calculated %
Copper	8.92	9.18
Carbon	58.60	59.00
Hydrogen	5.82	5.78
Nitrogen	12.18	12.14

Which corresponds to the molecular formula $[Cu(C_{11}H_{13}N_2O_3)_2(C_5H_4NCH_3)_2]$

RESULT AND DISCUSSION

On the basis of the consideration of magnetic properties, Cu (II) complexes, fall into two broad classes:

(i) Those having essentially temperature independent magnetic moments in the range 1.75-2.20 B.M.; and

(ii) Those having temperature dependent, magnetic moment values below the spin only value.

In such complexes the pair of copper(II) ions are held together by hydroxy or carboxylate anions. There are examples in which the two Cu (II) ions are coupled together and the dimer becomes diamagnetic[7]. Ray and Sen[8] have studied several Cu (II) com-plexes and have categorised several Cu(II) complexes them into two sub-groups:

(a) Complexes having magnetic moments between 1.73 and 1.84 B.M.; and

(b) Those having magnetic moment values between 1.94 and 2.2 B.M.

They assigned the former to square planar with dsp^2 hybridisation and the latter tetrahedral or octahedral with sp^3d^2 bonding.

The absence of orbital contribution in former category has been explained by the authors on the assumption of greater quenching affect of the crystal field in the orbital moment. distributed

The Pauling's valence bond theory[9] assumed that the tetrahedral complexes of Cu(II), owing to their symmetry have a greater crystal contribution to the magnetic moment than the square ones. In terms of crystal field theory the energies of the d-orbitals in a square and tetrahedral Cu(II) complex can be represented by the scheme:

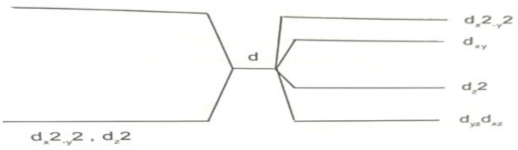


Fig. – 1. Spliting of d-orbitals of Cu(II) ion

Tetrahedral Square Planer

In the case of d^9 system]Cu (ii) ion] the Orgel diagram in T_d or O_h field is shown below

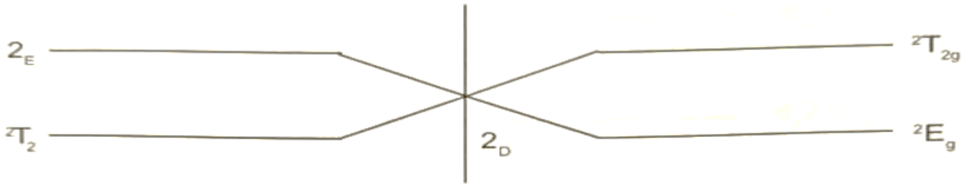


Fig. – 2. Spliting of the ground term of Cu (II) ion

Tetrahedral Octahedral

The orbital contribution to the magnetic moment is greater in the case of tetra-hedral Cu (II) complexes than Cu (II) octahedral complexes. Since the ground state is orbitally Imply degenerate[10]. The nine 3d electrons of cupric ion are distributed among the five d orbitals in such a way that the energy of the system is minimum. The stabilisation energy due to crystal field, than for a tetrahedral structure. It follows then that a tetracoordinated Cu (II) complex can take on terahedral configuration only when there exists among the ligands steric repulsions, that are large enough to compensate, for the diminution in crystal field stabilisation energy. Such a configuration will naturally be less difficult to obtain if the ligand field is weak. Furthermore, a perfectly tetrahedral copper complex is orbitally triply degenerate. So that by John-teller theorem it is unstable and must distort. These consideration account for the rarity of the tetrahedral complexes.

A planar complex is not degenerate. It should have μ_{eff} values approximately equal to spin only value e.g. 1.73 B.M. A slight excess value above the spin only value can be visualised from splitting of d-orbitals in planar field. For d^9 system, the energy order of d-electrons as shown below:

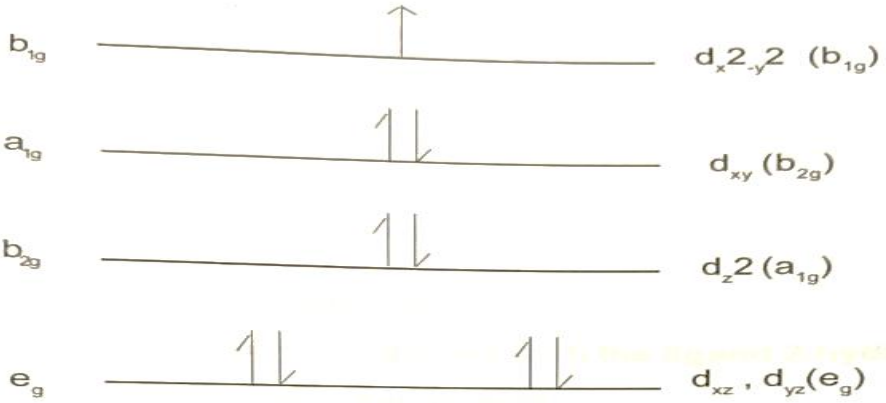


Fig. – 3. Arrangement of Electrons in split d-orbital for Cu (II) complexes

The unpaired electron of the d configuration is in the b_{1g} orbital giving a $^2B_{1g}$ ground term (non degenerate). In such circumstances the μ_{eff} is expected to be 15% above the spin only value in accordance with expression

$$\mu_{eff} = \mu_s \left(1-\frac{\alpha\lambda}{\Delta}\right)$$

where α= constant, the value of which for A_1=0, A_2=4, E=2 and for T >>> 4 and λ=spin orbit coupling constant.

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