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SPECTRAL STUDIES IN CHELATES OF NZILONOXIMEHYDRAZONE WITH Cu^{2+} METAL IONS

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^{*}Konkan Gyanpeeth Karjat College of ASC, Raigad, Maharashtra, India-410201**Abstract**

Absorption spectrum had been recorded to characterize and study the nature of geometry of complexes synthesized. It has been found that ligand had coordinated to metal ion through nitrogen atom only. The highly stable complexes is found to be non-electrolytic and assumed to adopt high spin octahedral arrangement.

1. Introduction:

Compounds containing isonitroso ketones in their structure have hydroxyl imino group as a functional group^{1,2}. Isonitroso ketones also known as pentad system have nitrogen and oxygen atoms for coordination with the metal ions^{3,4}. Owing to this isonitroketones forms stable complexes with transition metal ions. In addition to this metal complexes are used in extractive and analytical chemistry, biological studies and semi-conducting properties⁵⁻⁹. Ligation properties of isonitroso ketones^{10,11} finds its application also in corrosion inhibitors and anti-tuberculosis¹²⁻¹⁴. In the continuity of the studies in ligation properties of isonitroso ketones¹⁵, we studied further the physical properties of complexes from divalent copper metal and isonitroso ketones as ligand. The studies are based on spectral data.

2. Result and discussion:**2.1. Electronic Absorption Spectra:**

Table: 1: Electronic spectral data and ligand field parameters for the Cu(II) and Cu(II)Py₂ complexes of HBMOH in kK

Transition type	EAS ^a /DRS ^b	Solvent	Intra ligand charge transfer $\pi \rightarrow \pi^*$	Ligand field transition
HBMOH(1)	-	CH ₃ OH	47.62, 42.20	
-	-	0.1N NaOH	39.52, 32.26	
Cu(BMOH) ₂ (2)	EAS ^a	CHCl ₃	38.76	
² E _g → ² T _{2g} (15.83)	DRS ^b	-	37.76	
² E _g → ² T _{2g} (16.00)	EAS ^a	CHCl ₃	39.70	
Cu(BMOH) ₂ Py ₂ (3)	DRS ^b	-	38.55	
² E _g → ² T _{2g} (16.00)				
² E _g → ² T _{2g} (16.11)				

^aElectronic Absorption Spectra, ^bDiffuse Reflectance Spectra

The electronic spectrum of HBMOH in methanol for the UV region reveals two high intensity bands at 42.20kK and 47.62kK respectively (Table: 1). These bands may be due to $\pi \rightarrow \pi^*$ transitions possible from the azomethine and oximino environments in the molecules. The UV spectrum of HBMOH in dilute alkali (0.1N NaOH) solution shows that, the band at 42.20kK methanolic solution spectrum has suffered along with a bathochromic shift to 32.25kK. It means that this band could have its origin in the oximino linkage in the molecules as such; the band at 39.52kK in the dilute alkali solution spectrum could be assigned to the azomethine linkage. This band is suffered as bathochromic shift compared to methanolic solution.

The green $\text{Cu}(\text{BMOH})_2$ in chloroform solution of the visible spectrum exhibit a broad band at 14.83kK (Table-1) which may be assigned to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition. The diffuse reflectance spectrum of this complex shows a broad band at 16.00kK. From the position and the nature of this band, it is suggested that it probably consists of more than one band is attributed tentatively to the $d-d$ transitions in a distorted octahedral field. The green $\text{Cu}(\text{BMOH})_2\text{Py}_2$ in chloroform solution of the visible spectrum exhibit a similar nature of the $\text{Cu}(\text{II})$ complex in chloroform.

2.2. EPR Spectra:

The electronic paramagnetic resonance (EPR) experiments on the $\text{Cu}(\text{II})$ complex of HBMOH in polycrystalline form and $\text{Cu}(\text{II})\text{Py}_2$ complex of HBMOH in chloroform solution at liquid nitrogen temperature (LNT) were attempted to obtain analytical information on the type of bonding in these complexes.

The room temperature spectrum of the green $\text{Cu}(\text{BMOH})_2$ was poorly resolved with the LNT spectrum showing only slightly improved resolution. The poor resolution of the spectrum could be due to low crystallinity of the complex¹⁶. The green colored $\text{Cu}(\text{BMOH})_2\text{Py}_2$ complex, however, showed a four line hyperfine structure at the g_{II} position in the spectrum at LNT.

The nature of the EPR spectra of these complexes suggests distorted octahedral structure as only two g values, which follow the trend $g_{\text{II}} > g_{\perp} > 2.0023$, could be obtained. The EPR spectra of these complexes are shown significant bonding parameters computed therefrom are incorporated in Table 4.

The 'g' tensors were evaluated on the basis of Kneubuhl's analysis¹⁷ along with Piesach and Blumberg's method¹⁸. The values for A_{II} and A_{\perp} were obtained on the basis of Fujiwara's¹⁹ work.

Table.4 shows that the lowest g value (g_{\perp} in the present case) is less than 2.1 which indicate distorted octahedral stereochemistry as also appreciable covalency in these complexes. Absence of any resolution at the g_{\perp} positions may imply that g_x and g_y are same or nearly the same. That g_{\perp} is not lower than 2.03 also indicates that the unpaired electron in the $\text{Cu}(\text{II})$ ion is in the dx^2-y^2 orbital. The unpaired electron is suggested to be in dz^2 orbital in $\text{Cu}(\text{II})$ complexes showing $g_{\perp} < 2.03$.

Hathaway et al²⁰ have shown that a factor G which is $g_{\text{II}} - 2 / g_{\perp} - 2$ can give important information on whether the observed g_{II} and g_{\perp} values reflect the local $\text{Cu}(\text{II})$ environment. Their reasoning was that since Kneubuhl's method ignores hyperfine coupling constants, the absolute g -values may be in error and further, that the factors which influence the relation between the g values of the local $\text{Cu}(\text{II})$ environment and the g values of the bulk crystal, are determined by the interaction between the separate $\text{Cu}(\text{II})$ ions in magnetically non-dilute systems.

These authors also proposed that, if exchange coupling interaction is greater than thermal energy, partial spin-pairing may occur. However, when the observed magnetic moments greater than the spin only moments, exchange coupling interaction if at all occurring, must have energy lower than the thermal energy. Then, such interactions influence the line shapes and do not reduce the magnetic moments below the spin only values. If the exchange interaction is between crystallographically equivalent ions than the absorption lines appear rather sharp and the observed g values reflect local g values. If the interaction is between crystallographically non-equivalent ions then marked broadening may occur and an isotropic spectrum would result. However, if the interaction is between non - crystallographically equivalent ions then the observed g_{\perp} could be

greater than the local g_{\perp} while the g_{\parallel} values could be smaller than the local g_{\parallel} values. This would be reflected in the values of G being ≤ 4 . Therefore, value of $G >$ would per se indicate absence of exchange coupling. In the cupric complexes of HBMOH then, the high G values found may be taken to imply negligible exchange interactions.

The A_{\parallel} and A_{\perp} values obtained from the EPR spectra of these complexes are in the range for covalent Cu(II) complexes²¹. The A_{\parallel} values could be used to obtain a factor α^2 from the equation given by Kivelson and Neiman²².

Table- 2: EPR spectral data for the metal complexes of HBMOH

Compound (x 10 ⁻⁴ cm)	g_{\parallel}	g_{\perp}	g_{ave}	A_{\parallel}	A_{\perp}	A_{ave} (x 10 ⁻⁴ cm)	G (x 10 ⁻⁴ cm)	α^2 (x 10 ⁻⁴ cm)
Cu(BMOH) ₂ (LNT) 0.7020	2.192	2.041	2.091	20	05	12	4.68	
Cu(BMOH) ₂ Py ₂ (LNT) 0.6920	2.188	2.037	2.088	80	08	57	5.08	

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In the cupric complexes of HBMOH then the high G values found may be taken to imply negligible exchange interactions.

The A_{\parallel} and A_{\perp} values obtained from the EPR spectra of these complexes are in the range for covalent Cu(II) complexes¹⁸. The A_{\parallel} values could be used to obtain a factor α^2 from the equation given by Kivelson and Neiman²³.

$$\alpha^2 = - [A/P] + (g_{\parallel} - 2) + (g_{\perp} - 2) \frac{3}{7} + 0.04$$

$$[P = 0.036 \text{ cm for Cu(II) ion}]^{20}.$$

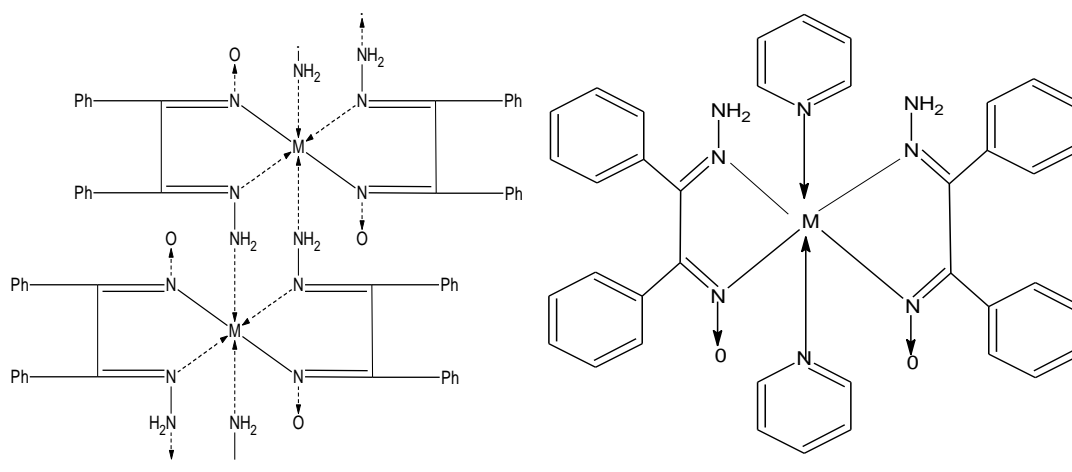
α^2 indicates covalent σ bonding in Cu(II) complexes. Thus ideally, $\alpha^2 = 1$ suggest completely ionic bond while $\alpha^2 < 0.5$ suggests completely covalent bond. However, since the overlap integral is often quite large, such a relation between completely ionic or covalent bond is not very accurate. Nevertheless, it may be said that smaller the α^2 value, greater is the covalent nature of the metal ligand bond. The α^2 values of 0.7020 for the Cu(BMOH)₂ complex and 0.6920 for the Cu(BMOH)₂Py₂ complex therefore indicate appreciable covalent character for them.

It is interesting to note that although the calculated g tensors for these complexes suggest a distorted octahedral coordination for the Cu(II) ions, the ratio $g_{\parallel}/A_{\parallel}$ which is expected to be between 105 - 135 X 10⁻⁴ cms for square planar Cu(II) complexes is much higher. Although the immediately

discernible cause for the high g_{II}/A_{II} values is the low A_{II} values the reason for the low A_{II} is not clear. It may only be said that such low A_{II} values are reported for the laccase and ceruloplasmin complexes of $Cu(II)^{23}$.

2. Conclusion:

3. The UV and EPR studies revealed the oximino linkages in the ligation with bathochromic shift for distorted octahedral geometries. α^2 and low A_{II} values unveiled the significant covalent character in the complexes. Further stabilities of complexes had shown that it can very well store and values of physical properties were supportive to get this as a potential complex for further studies.



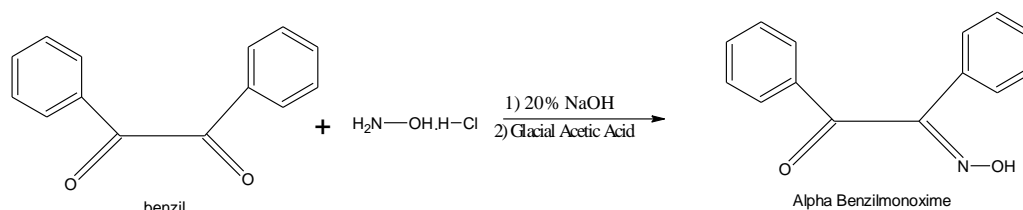
Scheme I: $Cu(II)$ and $Cu(II)Py_2$ complexes of α -Benzilmonoximehydrazone

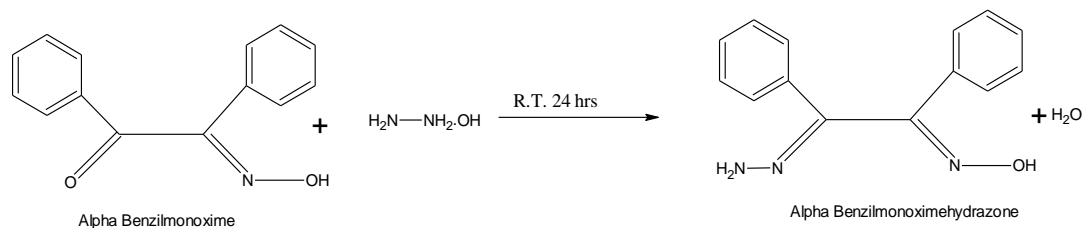
4. Experimental section:

UV- visible spectra of the ligand and its metal complexes were recorded on JASCO V - 650 spectrophotometer, methanol/ 0.1N NaOH was used as a solvents to record UV spectrum of the ligand, while Chloroform were used as solvent to record the spectra of the complexes in the UV- visible region. FT(IR) spectra in KBr discs were recorded on Perkin – Elmer spectrum 100 model. PMR spectra were recorded on Bruker AV300 NMR spectrometer using TMS as internal standard.

4.1. Preparation of ligand¹⁵:

α -benzilmonoxime was prepared using benzil and hydroxyl amine hydrochloride²⁴. The ligand was prepared by the reaction between 10g of α -Benzilmonoxime and 2.25g of hydrazine hydrate (80% aqueous) with stirring. The reaction mixture was allowed to stand at room temperature overnight. The white crystals obtained in presence of ice cold water were filtered through a Buchner funnel, washed thoroughly with cold water, and recrystallized from 60% ethanol to yield ~ 77% (8.13g) of the ligand. m.p. 172 °C, UV-vis(MeOH/0.1N NaOH) λ_{max} : 210, 237/ 253, 310nm; 1H NMR (d_6 DMSO δ ppm) 7.8-7.9(m, 2H), 7.3-7.6(m, 10H), 12.4(s, 1H); IR (KBr Cm^{-1}) 3390, 3287, 1647, 1493, 1072, 926, 692. Anal. Calc. for $C_{14}H_{13}N_3O$ (%) C 70.27, H 5.32, N 17.58, O 6.78; found C 70.40, H 5.00, N 17.98, O 6.82.





Scheme II: Two step preparation of α -Benzilmonoximehydrazone

4.2. Preparation of metal complexes¹⁵:

Equimolar mixture of ligand and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were made soluble mixture of ethanol and 0.5 N NaOH. Obtained colourless precipitate was digested in a water bath for 20-25 minutes. The precipitate was washed with hot water and recrystallized from methanol.

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