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NOVEL COMPLEXES OF CU(II) AND CU(II)PY₂ WITH LIGAND DERIVED FROM BENZILMONOXIMEHYDRAZONE

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Abstract

The synthesis and characterization of Cu(II) and Cu(II)Py₂ complexes of benzilmonoxime hydrazone (HBMOH) are reported. Cu(II) and Cu(II)Py₂ which are distorted octahedral geometry as supported by its electronic and diffuse reflectance spectra. The complexes have been characterized on the basis of magnetic and spectral studies.

1. Introduction:

Isoitrosoketones are expected to behave as versatile potential ambidentated ligands as they have three donor atoms out of which only two can coordinate at a time to the same metal ion. They form stable chelates with transition metal ions showing a variety of structural features¹⁻³. It is therefore, interesting to synthesize the transition metal complexes of various isonitroketones and investigate their structures. In the present work, the synthesis and structural characterization of Cu(II) and Cu(II)Py₂ with benzilmonoximehydrazone are reported.

2. Result and discussion:

Table-1: Analytical and physical data for HBMOH and its for Cu(II), and Cu(II)Py₂ complexes.

Compound (M.P. in °C)	Color	Yield (%)	Percentage of Expected (Found)				Conductance	Magnetic moments (BM)
			C	H	N	M		
HBMOH	Colorless	72.03	70.29 (70.0)	5.44 (5.21)	17.57 (17.92)	-	-	-
Cu(BMOH) ₂ (203°C)	Green	76.26	62.77 (61.08)	4.44 (4.06)	15.56 (15.11)	11.78 (11.32)	5.98	2.26
Cu(BMOH) ₂ Py ₂ (201°C)	Green	82.38	65.82 (65.06)	4.30 (4.09)	13.76 (12.63)	9.11 (8.39)	9.22	2.10

The reaction of HBMOH (**1**) with CuCl₂·2H₂O gave [Cu(BMOH)₂] (**2**) as green and reaction of [Cu(BMOH)₂] with hot pyridine gave [Ni(BMOH)₂Py₂] (**3**) as green complexes respectively. The ligand HBMOH were characterized on the basis of elemental analysis, FT(IR), PMR, electronic spectral data. The molar conductance of [Cu(BMOH)₂] and [Cu(BMOH)₂Py₂] complexes were 5.98 and 9.22 for the concentration of 10⁻³ M respectively (Table-1), indicating that the complex to be non-electrolyte⁴.

2.1. FTIR spectra:

A significant feature of the FT(IR) spectrum of α -benzilmonoximehydrazone is the absence of band between 1720-1680 cm⁻¹ due to the ν C = O vibration reported⁵ at 1715cm⁻¹ in HBMO indicating a successful replacement of the carbonyl oxygen by the hydrazonyl group during Schiff base formation. The spectrum of HBMOH shows peak at 3390 cm⁻¹, which are described to symmetrical vibration of the '- NH₂' group present in the ligand. This band are absent of HBMO, indicating the

replacement of carbonyl group to imine group. Rests of the band observed in HBMOH are almost at the same frequencies in comparisons with bands of HBMO (Table: 2).

A strong and broad band is observed at 3287cm^{-1} for the free ligand due to N-OH which is absent in metal complexes, suggests the deprotonation of the hydroxyl group of the oxime in the process of formation of the complexes⁶. This observation is supported by insolubility in dilute alkali solution. All metal complexes of HBMOH exhibit medium intensity bands in the region $3387\text{-}3391\text{cm}^{-1}$ that can be attributed at N-H vibrations. This suggests the non involvement of -NH_2 group in bonding these complexes.

The band at 1647cm^{-1} due to $\nu(\text{C}=\text{NN})$ of the azomethine group in ligand was shifted to higher frequencies at in the region $1675\text{-}1677\text{ cm}^{-1}$ in its complexes suggests that the coordination of oximino group with the metal ion⁷. Also the band at 1493cm^{-1} which was assigned the oximino ($\text{C}=\text{NO}$) group of ligand was shifted to higher energy at in the region $1558\text{-}1560\text{cm}^{-1}$, in the metal complexes, indicating the participation of the azomethine group in the coordination. In the metal complexes with the ligand in which an oxime group coordination through its nitrogen atom, the formation of $\text{N} \rightarrow \text{O}$ linkages an essential feature. The facts are further supported by the appearance of new bands in the regions $582, 533, 511, 503\text{ cm}^{-1}$ in the Ni(II), Ni(II)Py₂ complexes which were assigned to the Ni-M stretching vibration respectively⁸. In pyridine adduct of Ni(BMOH)₂ complex additional band observed at 1479cm^{-1} may ascribed due to $\text{C}_5\text{H}_4\text{N-Cu}$ vibration. FT(IR) spectral data suggest both complexes coordinate with metal ion through nitrogen atom only.

Table-2: Important IR bands (cm^{-1}) and their assignments for HBMOH and Cu(II), Cu(II)Py₂ complexes

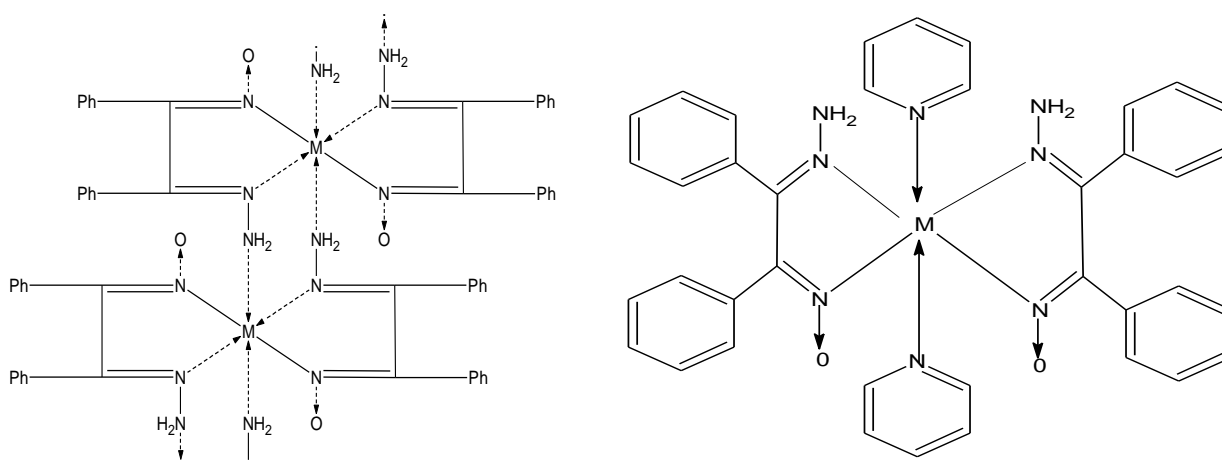
Vibration modes	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\text{C}=\text{NN}$	$\text{C}=\text{NO}$	$\text{C}_5\text{H}_4\text{N-Cu}$	N - N	N-O
M-N							
HBMOH (1)	3287	3387	1647	1493	-	1072	926
-							
Ni(BMOH) ₂ (2)	-	3409	1677	1560	-	1098	1026
582,533							
Ni(BMOH) ₂ Py ₂ (3)	-	3396	1675	1558	1479	1069	1000
511,503							

2.2: Magnetic moment:

The green colored Cu(II) and green colored Cu(II)Py₂ complexes show room temperature magnetic moments of 2.26 and 2.10BM (Table-1) respectively in the solid state, suggest distorted octahedral geometries of these complexes, which are only slightly higher than spin only value of 1.73 BM expected for d^4 system with one unpaired electron and are in the range normally found for Cu(II) complexes⁹. The magnetic susceptibility measurements of Cu(II) complexes indicate that they are magnetically dilute and nearly square planar. The values are slightly higher than the spin only value possibly due to same mixing in of the orbital angular momentum from the excited state via spin-orbit coupling.

3. Conclusion:

HBMOH ligand is insoluble in water but soluble in dilute alkali, common organic solvents. Its metal complexes are insoluble in dilute alkali, indicates that deprotonation of oxime group during complex formation. Ni(II) and Ni(II)Py₂ complexes have high decomposition points which suggest high thermal stability for metal complexes Ni(II) and Ni(II)Py₂ complexes are non electrolytic. The spectral and magnetic data suggests that Ni(II), Ni(II)Py₂ complexes are high spin octahedral environment. FT(IR) spectral data suggests that complexes coordinate with metal ion through nitrogen atom only.



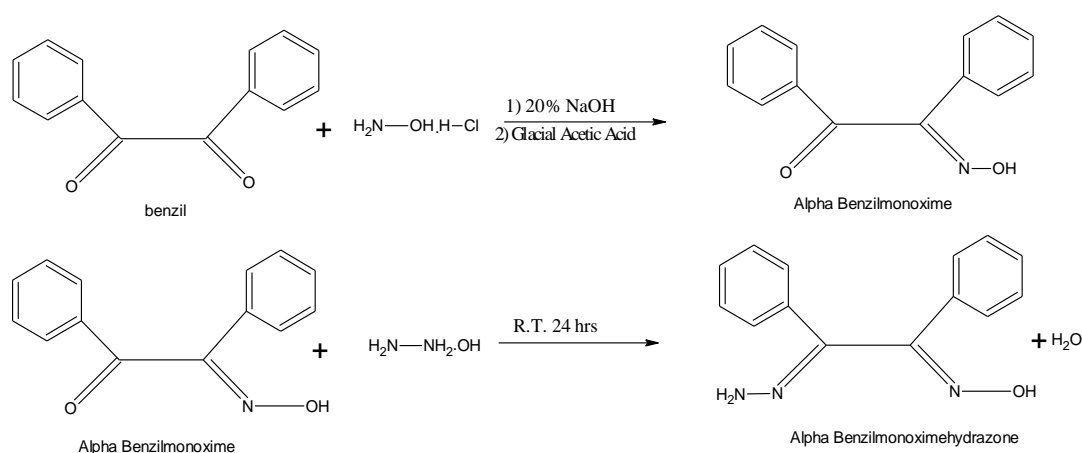
Scheme II: Cu(II) and Cu(II)Py₂ complexes of α -Benzilmonoximehydrazone

4. Experimental section:

All chemical used were of analytical reagent grade. Distilled water obtained from a glass distillation unit. Conductivity measurements were made on EQ - 660 laboratory conductivity meter using Nitrobenzene as solvent. 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 ligand:

α -benzilmonoxime was prepared using benzil and hydroxyl amine hydrochloride¹⁰. The ligand was prepared by the reaction between 10g 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, ¹H NMR (d₆ 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.



Scheme I: Two step preparation of α -Benzilmonoximehydrazone

4.2. Preparation of metal complexes:

A reaction between 1.0g (4 mmol) of ligand in 25cm³ of ethanol was added to a solution of (0.50g, 2 mmol) NiCl₂.6H₂O, 0.5N NaOH was added to obtain a colorless precipitate which was digested in a waterbath for 20-25 minutes and then filtered through Buchner funnel. The precipitate was washed with hot water and recrystallized from methanol, dried at 110°C and M.P. was found to be

200°C. This complex on dissolution in the minimum quantity of hot pyridine and gradual evaporation of the solution gave the adduct Ni(BMOH)₂Py₂.

5. References:

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