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Synthesis, characterization and antibacterial activity of hydrazone derivative of α -Benzilmonoxime ligand and its Iron (III), chromium (III) and ruthenium (III) metal complexes

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Abstract

The synthesis of a title ligand Hydrazone Derivative of α -Benzilmonoxime (HBMOH) (1) and its Iron(III) (2), Chromium(III) (3) and Ruthenium(III) (4) are described. The ligand was prepared in Ethanol from the reaction of α -Benzilmonoxime with Hydrazine Hydrate. The reaction of Hydrazone Derivative of α -Benzilmonoxime (HBMOH) in 1M sodium hydroxide with anhydrous ferric chloride, chromium chloride and ruthenium chloride yielded $[\text{Fe}(\text{BMOH})_3]$ as reddish orange, $[\text{Cr}(\text{BMOH})_3]$ as a light green and $[\text{Ru}(\text{BMOH})_3]$ as red precipitate respectively. The ligand HBMOH and its metal complexes $[\text{Fe}(\text{BMOH})_3]$, $[\text{Cr}(\text{BMOH})_3]$ and $[\text{Ru}(\text{BMOH})_3]$ were characterized by elemental analysis, PMR, FT(IR), electronic spectra and magnetic moments. The analysis of FT(IR) suggests that title ligand Hydrazone Derivative of α -Benzilmonoxime (HBMOH) bonded with Fe(III), Cr(III), and Ru(III) metal ions through the nitrogen atom only. The electronic spectral data and magnetic moments suggest Fe(III), Cr(III), and Ru(III) complexes are octahedral geometry. The antibacterial and antifungal screen of the synthesized compounds was performed in vitro by the agar cup borer method.

Keywords: Fe (III), Cr (III), and Ru (III), octahedral complexes, antibacterial activity, benzilmonoxime

1. Introduction

The field of the Schiff base complexes is fast developing because of the wide variety of possible structures for the ligands, depending on the aldehyde and amines used. Many Schiff bases and their complexes have been widely studied because of their industrial and biological applications [1-2]. Some Schiff bases were tested for fungicidal activity, which is related to their chemical structure³. Schiff bases are important class of ligands and have got wide applications in various fields [4-5]. The benzil monohydrazone ligand and its Fe (II), Pd (II), Zn (II), Cd (II), Hg (II) also reported [6-7]. In this present paper we have synthesized Hydrazone Derivative of Benzilmonoxime (HBMOH) ligand and its Fe (III), Cr (III), and Ru (III) metal complexes and the structure was elucidated using different physical and analytical tools and also antibacterial activity.

2. 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. 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 AV 300 NMR spectrometer using TMS as internal standard.

2.1 Preparation of ligand

α -Benzilmonoxime was prepared using Benzil and Hydroxyl amine hydrochloride⁸. The ligand was prepared by the reaction between 10g (4.4mmol) of α -Benzilmonoxime and 2.25g (4.5mmol) of hydrazine hydrate (80% aqueous) was drop wise added 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.

2.1.1 Orange-Red Fe (BMOH)₃

A reaction between 0.717g (3mmol) of HBMOH in 1M Sodium Hydroxide solution with an aqueous solution of 0.126g (1mmol) ferric chloride with constant stirring, then red colored precipitated was appeared. The precipitated was digested in a boiling water bath for 30 minutes and then filtered through Buckner funnel. The product was washed with hot water and recrystallized from chloroform, dried at 110 °C.

2.1.2 Light Green Cr (BMOH)₃

A solution of CrCl₃.6H₂O (269mg, 1mmol) in 10mL Ethanol was added to a solution of HBMOH ligand (717mg, 3mmol) in 15mL 1M NaOH solution. The mixture was heated under reflux for 5 hours. The solution was then placed in ice-water container to give light green precipitated, which was filtered off, washed with hot water and ethanol, dried. The product purified by recrystallization from chloroform.

2.1.3 Red Ru (BMOH)₃

An acidic solution of RuCl₃ (208mg, 1mmol) was added to a solution of HBMOH ligand (717mg, 3mmol) in 15mL of 1M NaOH solution. The mixture was heated under reflux for 7 hours. The solution was then placed in ice-water container to give red precipitated, which was filtered off, washed with hot water and ethanol, dried. The product purified by recrystallization from chloroform.

2.2 Antibacterial Activity

Sterile and calibrated apparatus were used as and required. The antibacterial activity was investigated against bacteria (*B. Subtilis*, *S. Aureus*, *S. Typhi*, *E. Coli*, *K. Pneumoniae*, *P. Aeruginosa*) by agar cup borer method⁹ using *Streptomycin* as a standard for bacterial culture. The solution of the title ligand and its Fe (III), Cr (III), Ru (III) metal complexes were prepared in DMF and tested. The minimum inhibitory concentration (MIC) study was carried out at different concentration such as 50, 100, 200, 500 and 1000 ppm. A tube containing sterile melted soft agar (2% in distilled water 6.0mL) was maintained at 50 °C and inoculated with 0.2mL suspension of the test culture, mixed thoroughly and poured in the test petri dish containing sterile nutrient agar medium and allowed to solidify for 5 minutes. The cup borer was sterilized by dipping into absolute ethanol and flaming it and then allowed to cool down. With the help of sterile cup-borer, cups in the agar were marked and injected with 0.1mL of respective test sample solution in DMF, 0.1mL standard drug *Streptomycin* (1000 ppm) solution in distilled water respectively. Then the test sample was allowed to diffuse for one hour in refrigerator at 4-5 °C. The plates were incubated in upright position at 37 °C for 24 hours and on the next day the zone of inhibition surrounding each cup was observed.

The data for antibacterial activity in terms of zone of inhibition of title ligand and its Fe (III), Cr (III), Ru (III) metal complexes are shown in table-5.

3. Results and Discussions

The reaction of Hydrazonyl Derivative of α -Benzilmonoxime (HBMOH) with FeCl₃, CrCl₃.6H₂O and RuCl₃ in ethanol gave [Fe (BMOH)₃] (2) as orange-red, [Cr (BMOH)₃](3) as light green and [Ru (BMOH)₃] (4) as red complexes, respectively (Scheme-3).

The ligand HBMOH and its Fe (III), Cr (III) and Ru (III) complexes were characterized on the basis of elemental analysis, and pmr, FT (IR), electronic spectra and magnetic moments. The molar conductance off complexes 2, 3, 4 were 11.3, 9.6 and 1.5 Ω^{-1} cm²mol⁻¹ respectively, indicating that the Fe (III), Cr (III) and Ru (III) complexes are non-electrolyte in nature^[7].

3.1 FT (IR) spectra

A significant feature of the IR spectrum of α -benzilmonoximehydrazone is the absence of band between 1720-1680cm⁻¹ due to the ν C = O vibration reported^[10] 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 3390cm⁻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. Rest of the bands observed in HBMOH is 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 complexes^[10]. This observation is supported by insolubility in dilute alkali solution. All metal complexes of HBMOH exhibit medium intensity bands in the region 3398-3418cm⁻¹ that can be attributed at N-H vibrations. This suggests the non-involvement of -NH₂ group in bonding these complexes^[11]. The band at 1647cm⁻¹ due to ν (C=NO) of the oximino group in ligand was shifted to higher frequencies at in the region 1661-1662 cm⁻¹ in its complexes suggests that the coordination of oximino group with the metal ion^[12]. Also the band at 1493cm⁻¹ which was assigned the azomethine (C=NN) group of ligand was shifted to higher energy at 1550cm⁻¹, in the metal complexes, indicating the participation of the azomethine group in the coordination^[13]. In the metal complexes with the ligand in which an oxime group coordination through its nitrogen atom, the formation of N \rightarrow O linkages an essential feature. The facts are further supported by the appearance of new bands in the regions 518, 500 and 482, 519,513 and 498522, 505 and497cm⁻¹ in the Fe (III), Cr (III) and Ru (II) complexes which were assigned to the N-M stretching vibration respectively^[14].

3.2 PMR Spectra

The pmr spectrum of HBMOH in (d₆) DMSO solvent (Table 3), reveals a broad singlet at 12.42 δ , suggesting the highly acidic nature of this proton. A multiplet observed around 7.33 to 7.60 δ due to two phenyl rings in the ligand structure. The singlet observed at 7.8-7.9 δ is suggested to be due to azomethine proton or -NH₂ group in the ligand.

3.3 Electronic Spectra

The electronic spectra of hydrazone derivative of benzilmonoxime (HBMOH) in methanol/0.1N sodium hydroxide and its iron (III), chromium (III) and ruthenium(III) complexes in chloroform exhibit absorption bands at 45249-42553 and 31447-30211cm⁻¹ with high molar extinction coefficient (table-4) that can be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intra ligand charge transfer, respectively¹⁵. The electronic spectra of the complexes were recorded in chloroform solution in the region 11110–50000cm⁻¹ and the spectral data are listed in Table 3.

According to the Tanabe-Sugano diagram for high spin d^5 configuration, the bands to the regions 18375cm⁻¹ and 22095 cm⁻¹ were assigned to the ${}^6A_{1g} \rightarrow {}^4T_{2g}(v_1)$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}(v_2)$ transitions respectively¹⁶. In the iron(III) complex $\frac{\nu_2}{\nu_1} = 1.202$ and the ration correspond to $\frac{\Delta_0}{B}$ being equal to 30.5 on the Tanabe-Sugano diagram. By using this value in the calculation of the Racah parameter, splitting energy, unobserved third transition, and nephelauxetic parameter for the iron(III) complex, the following results were obtained $B=706\text{cm}^{-1}$, $\Delta_0=21510\text{cm}^{-1}$, $\nu_3=30333\text{cm}^{-1}$ and $\beta=0.638$.

Two low intensity transitions ($\log \epsilon \leq 2$) were observed in the spectra of Cr (III) complex and most probably are due to spin allowed $d-d$ transitions. The octahedral complexes of Cr(III) have $(t_{2g})^3$ configuration. It was confirm by magnetic moment value 3.56B.M. for the Cr (III) complex. According to the Tanabe-Sugano diagram for $(t_{2g})^3$ configuration¹⁷, the bands at the regions 18512cm⁻¹ and 24122cm⁻¹ chromium(III) complex, were assigned to the ${}^4A_{2g} \rightarrow {}^4T_{2g}(v_1)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)(v_2)$ transitions, respectively¹⁶. In the Cr (III) complex $\frac{\nu_2}{\nu_1} = 1.32$ and the ration correspond to $\frac{\Delta_0}{B}$ being equal to 33 on the Tanabe-Sugano diagram. By using this value in the calculation of the Racah parameter, splitting energy, unobserved third transition, and nephelauxetic parameter for the chromium (III) complex, the following results were obtained $B=561\text{cm}^{-1}$, $\Delta_0=18399\text{cm}^{-1}$, $\nu_3=37000\text{cm}^{-1}$ and $\beta=0.62$. The ground state of ruthenium (III) is ${}^2T_{2g}$ and the first excited doublet levels in the order of increasing energy are ${}^2A_{2g}$ and ${}^2A_{1g}$, which arise from $t_{2g}^4e_g^1$ configuration¹⁹. All the ruthenium (III) complexes in the visible region display strong band shows at 16949cm⁻¹ followed by a weak shoulder around 24096cm⁻¹ and are assigned to be the LMCT transitions¹⁸. In a d^5 system, especially in ruthenium (III) which has relatively high oxidizing properties, the charge transfer bands of the type $L\pi_y \rightarrow T_{2g}$ are prominent in the low energy region, which obscures the weaker bands due to $d-d$ transitions. The band observed around 40000cm⁻¹, which is also present in the free ligands, is assigned to $\pi \rightarrow \pi^*$ transition from the benzene ring and the double bond of the azomethine group. The band at 28736cm⁻¹ is due to $n \rightarrow \pi^*$ transition of non-bonding electrons present on the nitrogen of the azomethine group in the ruthenium (III) complexes. The patterns of the electronic spectra of all complexes indicate the presence of an octahedral environment around the ruthenium ion.

3.4 Magnetic Moment

Orange-red Fe (III) complex shows a room temperature magnetic moment of 4.93BM (Table no.1), which is higher than the spin only magnetic moment of 4.89BM expected for

the four unpaired electrons in high spin Ferrous complexes^[21]. However, the 6A_1 term for the high spin octahedral complexes of Fe(III) is expected to contribute significantly to the room temperature magnetic moment and the observed moment for most high spin complexes of Fe (III) is expected to be greater than the spin only moment and are often observed in the range between 5.1-5.7BM. Tetrahedral complexes of Fe (III) are expected to reveal moment in the range between 5.00-5.20BM. Where, the orbital contribution to the observed moment is expected to be lower than for octahedral complexes. Further, for ligands containing 'N' and 'O donor atom, Fe (III) is known to coordinate to give octahedral complexes^[21]. In HBMOH 'N' as donor atom, therefore Fe (III) complex suggests a high spin octahedral geometry. The observation is amply supported by the electronic absorption spectral data from the complex.

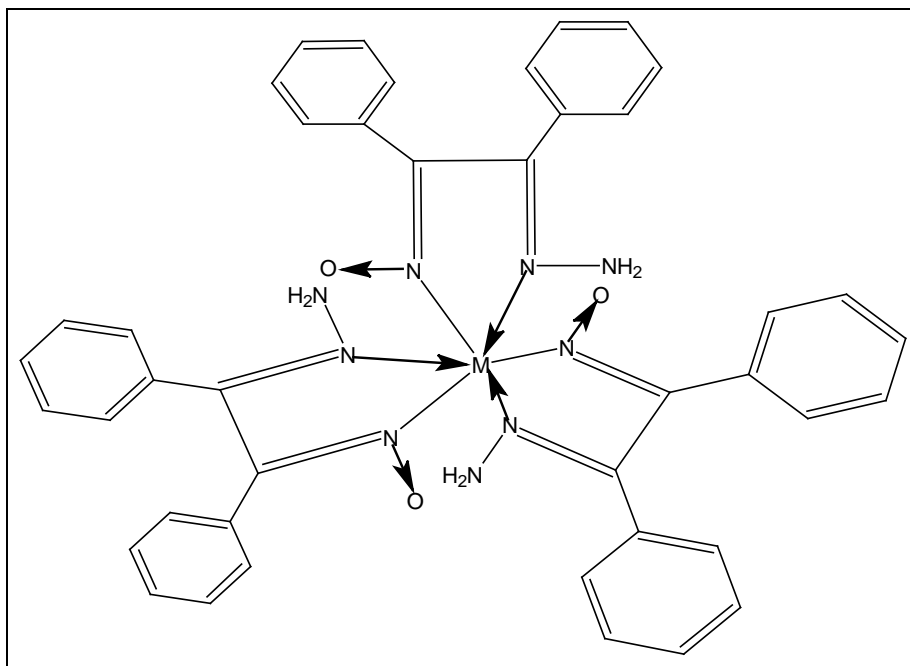
The chromium complex shows magnetic moments corresponding to three unpaired electrons, i.e. 3.83 B.M., expected for high spin octahedral chromium (III) complexes^[22]. The observed magnetic moment of chromium (III) complex is 3.89 B.M., indicate that high spin octahedral geometry for chromium (III) complex. The room temperature magnetic moment of ruthenium (III) Schiff base complex is 1.70 BM. It is lower than the predicted normal value, this low value may be indicative of the presence of low symmetry ligand field and the formation of molecular orbital may be extended overlap of the metal and ligand orbital^[23]. Progressive quenching of the angular orbital momentum by spin orbit coupling that remove the degeneracy of the triplet ground term causes lower magnetic moment²⁴. Thus the extensive spin orbit coupling can reduce the magnetic moment below that of the spin only value.

3.5 Antibacterial activity

The result *in vitro* study of antibacterial activity of title ligand and its Fe (III), Cr (III), Ru (III) metal complexes against bacterial species (*B. Subtilis*, *S. Aureus*, *S. Typhi*, *E. Coli*, *K. Pneumoniae*, *P. Aeruginosa*) are reported in table-5 and 6. The synthesized compounds have shown excellent antibacterial activities against all pathogens comparable to that of *streptomycin*. They inhibited the bacterial growth upto 98-100% at 1000 ppm. The minimum inhibitory concentration is 100ppm of all compounds against all pathogens^[25].

4. Conclusion

Hydrazone derivative of benzilmonoxime (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. These complexes have high decomposition points which suggest high thermal stability for metal complexes and they are non-electrolytic in nature. All the synthesized compounds show moderate to good activity against selected fungal and bacterial strain. The spectral and magnetic data suggests that Fe (III), Cr (III) and Ru (III) are high spin octahedral geometries. FT (IR) spectral data suggests that complexes coordinate with metal ion through nitrogen atom only. On the basis of magnetic and spectral data, structure of Fe (III), Cr (III) and Ru (III) tentatively assigned as;



Where; M = Fe (III), Cr (III) and Ru (III)

Table 1: Analytical and physical data of the ligand and its metal complexes.

Compound (Color)	Yield % (M.P. °C)	Elemental Analysis [Found (Calculated)]					Magnetic Moments (B.M.)	Electrical Conductance $10^{-3}M$ (in Nitrobenzene) mhos
		% M	% C	% H	% N	% O		
HBMOH (Colorless)	72.03 (172)	-----	70.29 (70.27)	5.44 (5.32)	17.57 (17.58)	6.69 (6.75)	----	----
[Fe(BMOH) ₃] (Orange-Red)	75.06 (215)	7.09 (7.25)	65.00 (65.47)	4.60 (4.68)	15.70 (15.79)	5.99 (6.24)	4.93	11.3
[Cr(BMOH) ₃] (Light Green)	79.99 (211)	6.45 (6.79)	65.22 (65.80)	4.52 (4.70)	14.69 (14.43)	6.15 (6.27)	3.89	9.6
[Ru(BMOH) ₃] (Red)	80.21 (216)	12.09 (12.40)	61.92 (61.82)	4.21 (4.42)		5.81 (5.89)	1.70	1.5

Table 2: FT (IR) spectral data for HBMOH and its metal complexes

Compound	$\nu(\text{O-H})$	$\nu(\text{N-H})$	Ar. C-H	$>\text{C=NO}$	$>\text{C=NN}$	N - O	N-N	M-N
HBMOH	3287	3387	3058	1647	1493	926	1072	----
[Fe(BMOH) ₃]	-	3418	3071	1661	1550	1006	1091	518, 500, 482
[Cr(BMOH) ₃]	-	3392	3096	1662	1550	1010	1092	519, 513, 498
[Ru(BMOH) ₃]	-	3400	3077	1661	1550	1015	1092	522, 505, 497

Table 3: Electronic spectral data for HBMOH and its metal complexes

No.	Compound	Solvent	Band position (cm^{-1})	Intensity (ϵ)	Assignment
1	HBMOH	Methanol	47620	12252	Oximino $p \rightarrow p^*$ transition
			42200	11181	Azomethine $p \rightarrow p^*$ transition
		0.1N NaOH	39520	12116	Oximinop $\rightarrow p^*$ transition
			32260	11288	Azomethine $p \rightarrow p^*$ transition
2	[Fe(BMOH) ₃]	Chloroform	18375	271	${}^6A_{1g} \rightarrow {}^4T_{2g}$ transition
			22095	5444	${}^6A_{1g} \rightarrow {}^4T_{1g}$
2	[Cr(BMOH) ₃]	Chloroform	18512	399	$A_{2g} \rightarrow {}^4T_{2g}$
			24122	1269	${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F)
3	[Ru(BMOH) ₃]	Chloroform	16949	3958	Charge transfer $M \rightarrow L$ transition
			24096	3465	Charge transfer $M \rightarrow L$ transition
			28736	8633	Charge transfer $M \rightarrow L$ transition

Table 4: PMR spectral data of the HBMOH

Compound	Signal	Assignment
HBMOH	δ 12.42	1H, O - H
	δ 7.80	2H, - NH ₂ group
	δ 7.33-7.60	10H, Phenyl group

Table 5: Zone of inhibition of ligand and its complexes against selected bacterial strains.

Zone of inhibition (in 10 mm)						
Compound	<i>B.subtilis</i>	<i>S. Aureus</i>	<i>S. Typhi</i>	<i>E. Coli</i>	<i>K. Pneumoniae</i>	<i>P. Aeruginosa</i>
HBMOH	5	7	6	-	-	-
[Fe(BMOH) ₃]	10	9	6	4	7	9
[Cr(BMOH) ₃]	10	8	6	9	8	9
[Ru(BMOH) ₃]	9	8	7	9	9	9

Table 6:- Minimum inhibitory concentration (MIC) of Ligand and their metal complexes against selected bacterial

Minimum inhibitory concentration (µg/ml)						
Compound	<i>B.subtilis</i>	<i>S. Aureus</i>	<i>S. Typhi</i>	<i>E. Coli</i>	<i>K. Pneumoniae</i>	<i>P. Aeruginosa</i>
HBMOH	100	100	100	-	-	-
[Fe(BMOH) ₃]	200	200	200	100	100	100
[Cr(BMOH) ₃]	100	100	100	100	100	200
[Ru(BMOH) ₃]	100	100	100	200	200	100

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