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Synthesis, Characterization and Antimicrobial Study of Cu(II) and Ni(II) Complexes of Schiff base Ligand Derived from 2-hydroxy-5-methylbenzophenone and 2,3-butanedionedihydrazone

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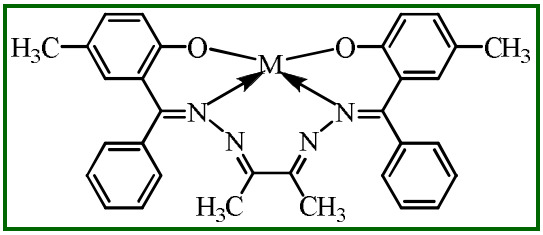
ABSTRACT

New Schiff base ligand was synthesized by the condensation of 2-hydroxy-5-methylbenzophonone and2, 3-butanedionedihydrazone. The Cu(II) and Ni(II)complexes of Schiff base were prepared. The ligand and complexes have been characterized by elemental analysis, FT-IR, ^{1}H NMR, diffuse reflectance spectroscopy, magnetic moment measurements and TGA. Study suggests 1:1 (metal:ligand) stoichiometry in the complexes. FT-IR spectra agreed with coordination of ligand to the metal ions through azomethine nitrogen and deprotonated oxygen atoms. On the basis of diffuse reflectance spectra, magnetic moment values and TGA both the synthesized complexes have been assigned square planer geometry. The antimicrobial study of the Schiff base and its Cu(II) and Ni(II) complexes was carried out, shows that the Schiff base and complexes show good to moderate active against some common bacterial strains and fungi.

Graphical Abstract:



M = Cu(II), Ni(II)

Keywords: Schiff base, Benzohenone, Buntanedionedihydrazone, TGA, Antimicrobial activities.

INTRODUCTION

In past few decades tremendous study have been carried out on the compounds containing azomethine group (>C=N-).The compounds are commonly known as Schiff bases [1]. Schiff bases are good chelating agents coordinate with different metal ions and form stable complexes having stereochemical significance [2, 3]. Schiff base metal complexes are exhibit wide range of biological activities such as anti-bacterial, antifungal, anti-inflammatory, antipyretic, anti-tumour, antiviral

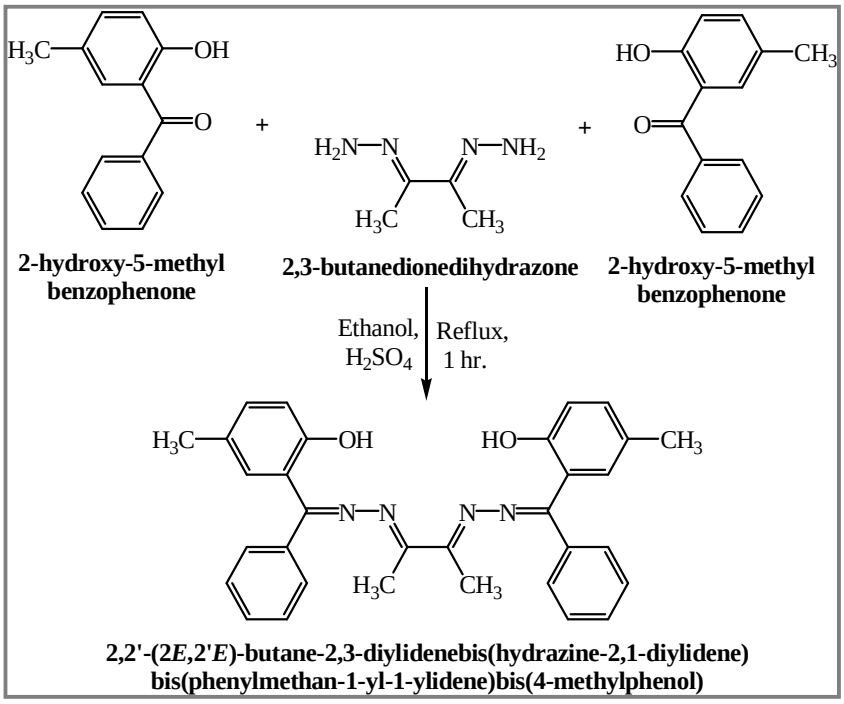
properties and have extensive industrial applications [4-6]. Some Schiff base complexes exhibit excellent catalytic properties and are widely used in catalytic reactions [7]. Considerable attention has been given by researchers to the metal complexes of Schiff bases containing nitrogen and oxygen donor atoms because of their interesting geometries and applications [8-11].

According to report herein, synthesis and study of some new metal complexes of Cu(II) and Ni(II) with N, O-donor Schiff base derived from 2-hydroxy-5-methylbenzophonone with 2, 3-butanedione dihydrazone. The Schiff base and its metal complexes characterized by different physicochemical and spectral techniques and tested for antimicrobial activities.

MATERIALS AND METHODS

The chemicals and reagents used for synthesis were 'AR' grade further purified by standard procedures, if required. Schiff base was prepared in three steps.

Synthesis of Ligand: Ligand was synthesized by condensation of 2-hydroxy-5-methylbenzopnenone with 2, 3-butanedionedihydrazone in 2:1 molar ratio. The reaction was catalyzed by sulphuric acid. The crude product was recrystallized with DMF and dried under vacuum. The melting point of the product was 250-260°C.



Scheme. Synthesis of ligand.

Synthesis of metal complexes: The complexes of Cu(II) and Ni(II) have been prepared by refluxing solution of Schiff base and metal acetates in 1:1 ratio in DMF for 5-6 hours. The products obtained were filtered, washed with DMF and dried. The complexes were soluble in DMSO.

RESULTS AND DISCUSSION

The ligand was characterized by elemental, ^{1}H NMR and FT-IR spectra and the complexes by elemental, FT-IR, magnetic studies, diffuse reflectance spectra and TGA. All synthesized compounds were tested for their antimicrobial activities against some common bacteria and fungi.

Elemental Analysis: The analytical data of ligand and its metal complexes is given in table 1. The data suggests formation of complex of 1:1 [M:L] ratio.

Table 1. Elemental analysis of ligand and its complexes

Schiff Base/ Complex	Colour	M.P. (°C)	M.W.	Elemental Analysis % Found (Calculated)			
				M %	%C	%H	%N
Schiff base (HMBBD)	Pale Yellow	250-260	502.61	--	76.32 (76.47)	6.16 (6.02)	11.07 (11.15)
Cu-HMBBD	Dark Green	- -	- -	11.06 (10.92)	66.13 (66.02)	5.28 (5.19)	9.57 (9.62)
Ni-HMBBD	Pale Green	- -	- -	10.32 (10.17)	66.67 (66.58)	5.36 (5.24)	9.75 (9.70)

^{1}H NMR Spectra of HMBBD (300 MHz, $CdCl_3$, δ in ppm): The ^{1}H NMR spectra of ligand HMBBD has been recorded at CDRI, Lucknow. The spectrum shows different non-equivalent proton resonating at different applied field strengths [12-14]. The δ-values are: δ 7.261 – 7.324 (10H, m, Ar-H); δ 7.039 – 7.065 (2H, dd, Ar-H); δ 6.666 – 6.788 (2H, dd, Ar-H); δ 5.629 (2H, s, (broad)-OH); δ 3.210 (6H, s, $-CH_3$); δ 2.108 (6H, s, Ar-CH_3) [15, 16].

FT-IR Spectra (KBr, cm^{-1}): FT-IR spectrum of ligand HMBBD have been compared with its Cu(II) and Ni(II) complexes [17]. The spectrum of ligand shows broad band at 3534 cm^{-1} ν(O-H), i.e. intramolecular hydrogen bonded O-H group. The band was absent in the spectra of complexes showing coordination through deprotonated phenolic oxygen atom [18, 19]. A strong sharp band at 1617 cm^{-1} in the spectrum of ligand, assigned to ν(C=N) stretching, shifted to lower frequencies in complexes, indicating coordination of azomethine nitrogen with metal ion [20, 21]. The data is depicted in table 2.

Table 2. FT-IR spectra of HMBBD and its complexes

Ligand/ Complex	IR Spectra (cm^{-1})					
	O–H	C=N	C–O	M–O	M–N	(H_2O)
HMBBD	3534	1632	1321	- -	- -	--
Cu-HMBBD	- -	1583	1356	618	478	3369
Ni-HMBBD	- -	1609	1346	597	463	3394

Medium frequency band at 1321 cm^{-1} ν(C-O) of phenolic stretching in free ligand was shifted to higher frequency by 25-35 cm^{-1} in the complexes further supports involvement of phenolic oxygen in coordination [22]. New bands appeared in the spectra of complexes at 597-618 cm^{-1} and 463-478 cm^{-1} have been tentatively assigned to υ(M-O) and υ(M-N) stretching, respectively that confirms coordination of ligand through phenolic oxygen and azomethine nitrogen [23, 24]. New bands appear in IR spectra of Cu-complex at 3369 cm^{-1} and in Ni-complex at 3394 cm^{-1} indicates υ(H_2O) stretching of hydrated complexes [25].

Magnetic Studies and Diffuse Reflectance Spectra: The value of magnetic moments and assignments of diffuse reflectance spectra of complexes of HMBBD are given in table 3. The spectra of Cu(II) complexes shows three bands at 624, 553 and 415 nm assigned to $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2E_g$ and symmetry forbidden ligand to metal charge transfer transitions, respectively. The spectral band position suggests square planner geometry to the complex [26]. The magnetic moment value 1.75 B.M. further supports square planner geometry [27, 28].

The diffuse reflectance spectrum of Ni(II) complexes show three bands at 892, 546 and 412 nm assigned to spin allowed $^1A_{1g}\rightarrow{}^1E_g$; $^1A_{1g}\rightarrow{}^1A_{2g}$ and $^1A_{1g}\rightarrow{}^1B_{1g}$ transitions, respectively suggesting square planar geometry [29]. The magnetic moment measurement shows diamagnetic nature of the complex that further confirms square planar geometry of the complex [30].

Table 3. Magnetic moments and Assignments of diffuse reflectance spectra of HMBBD and its complexes

Schiff Base Complex	μ_{eff} B.M.	Absorption band (nm)	Absorption band (cm^{-1})	Assignments
Cu-HMBBD	1.75	624	16025	$^2B_{1g}\rightarrow{}^2A_{1g}$
		553	18083	$^2B_{1g}\rightarrow{}^2E_g$
		415	24096	C. T.
Ni-HMBBD	--	892	11210	$^1A_{1g}\rightarrow{}^1E_g$
		546	18315	$^1A_{1g}\rightarrow{}^1A_{2g}$
		412	24271	$^1A_{1g}\rightarrow{}^1B_{1g}$

Thermogravimetric Analysis: TGA curves of both complexes are stable up to 90°C. Initial weight loss obtained between90-125°C corresponding to loss of one lattice water molecules in Cu(II) and Ni(II) complexes[31, 32]. No further weight loss obtained further up to 260°C indicating absence of coordinated water molecules [33, 34].

Both metal complexes show rapid weight loss between 260-390°C due to degradation of free part of coordinated ligand [35] followed by gradual weight loss up to 570°C corresponds to complete decomposition of ligand. Above 600°C the TGA curve is almost horizontal indicating the formation of corresponding metal oxides [36]. The TGA data of HMBBD and its metal complexes is given in table 4.

Table 4. TGA data of HMBBD and Its Metal Complexes

Compounds	Molecular Weigh	Degradation Temperature (°C)	% loss	Assignment
HMBBD	502.61	>275	--	Parts of Ligand
		95-125	3.23	1 H_2O
[Cu(HMBBD)].H_2O	--	260-390	--	Parts of Ligand
		>570	--	Metal oxide
		90-120	3.28	1 H_2O
[Ni(HMBBD)].H_2O	--	260-390	--	Parts of Ligand
		>275	--	Metal oxide

APPLICATION

Antimicrobial activity: The ligand HMBBD and its Cu(II) and Ni(II) complexes were screened for antibacterial activity against *E. coli, P.aeruginosa, P. vulgaris, S.aureus,* and *K.pneumoniae,* in Mullar-Hilton agar medium and antifungal activity against *A.niger*and *C. albicans* in potato dextrose agar medium [37]. The results are given in table 5.

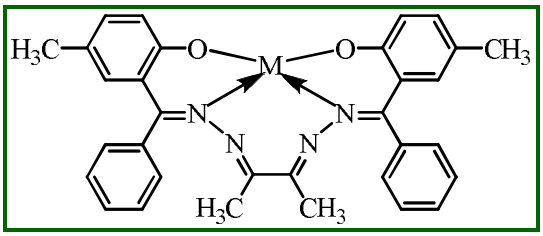
The ligand HMBBD shows moderate to good activity against all the bacterial and fungal strains under study. The Cu(II) complex exhibit strong activity against *S. aurius, K. pneumoniae* and *A. niger*, while moderate to weak inhibitory effect against rest of the pathogens. Ni(II) complexes shows moderate to weak activity against all bacterial strains, while strong activity against fungi. Ni(II) complex show strong to moderate activity against most of the bacterial and fungal culture.

Table 5. Antimicrobial Activities of Ligand HMBBD and its Metal Complexes

Compound	Antibacterial					Antifungal	
	E. coli	*P. aeruginosa*	*P. vulgaris*	*S. aureus*	*K. pneumonia*	*A. niger*	*C. albicans*
HMBBD	16	15	17	16	11	15	22
Cu- HMBBD	12	23	14	16	12	20	13
Ni-HMBBD	18	19	24	20	14	21	19
Amikacin	28	25	27	24	26	--	--
Fluconazole	--	--	--	--	--	25	26

CONCLUSION

Schiff base ligand HMBBD and its Cu(II) and Ni(II) complexes were synthesized and studied by elemental, spectral, magnetic moment measurements and thermal analysis. Results of the study suggest that HMBBD is tetradentate ligand coordinating through azomethine nitrogen and phenolic oxygen atoms. The metal complexes with Cu(II) and Ni(II) ions are forming in 1:1 (M:L) ratio. On the basis of studies, four-coordinated square planar geometry assigned for Cu(II) and Ni(II) complexes. Antimicrobial study of the ligand and its metal complexes shows moderate to good activity against most of microorganisms under study. The suggested geometry of complexes is:



M = Cu(II), Ni(II)

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