



Synthesis, Spectral Characterization and Antibacterial Activity of Copper(II) Complexes of Functionalized Hydrazones

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Received: 18 January 2019;

Accepted: 12 February 2019;

Published online: 29 April 2019;

AJC-19370

Copper(II) complexes having the formula CuL_2 {where, L = 2-acetylthiophene acetylhydrazone (ATAH), 2-acetylthiophene benzoylhydrazone (ATBH)} have been investigated on the basis of elemental analysis, molar conductivity measurements, magnetic susceptibility, UV-visible, IR and ESR spectral data. Non-electrolytic nature of the complexes are revealed by molar conductance data. IR spectral data suggested that hydrazones act as tridentate ligands. The spin Hamiltonian, orbital reduction and bonding parameters of complexes are calculated using ESR spectra of complexes. The compounds are screened for their antibacterial activities against *Pseudomonas aureoginos* and *Bacillus cereus*. Acetylhydrazones show more antibacterial activity than the corresponding benzoyl hydrazones. Some of the Cu(II) complexes show more activity than hydrazone ligands.

Keywords: Copper(II) complexes, Trifunctional donor ligands, Octahedral geometry, Antibacterial activity.

INTRODUCTION

Copper proteins have attracted considerable attention owing to their biological functions such as electron transport, oxygen transport, copper storage and many oxidase activities [1]. Copper is biostatic metal and its surface have natural properties which can destroy a wide range of microorganisms [2].

Current interest in copper complexes springs from their immense use as pharmacological agents. Tridentate Schiff base ligands form stable complexes by bonding through potential donor atoms. However, copper complexes with tridentate ligands with thiophene moiety and having assorted donor (N,O,S) atoms are limited [3].

Metal complexes of hydrazones have wide applications in biological processes [4-15]. A good number of transition metal complexes with hydrazones have been reported [16]. Our survey of literature revealed that only few reports are available on the antibacterial activity of such complexes with hydrazones. Cu(II) and Zn(II) complexes with 2-benzoylpyridinemethylhydrazone are reported by Beraldo *et al.* [17]. Koo *et al.* [18] reported Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of 2-acetylpyridine benzoylhydrazone. Recently, we have studied

[19-22] lanthanide complexes of 2-benzoylpyridine benzoylhydrazone, 2-acetylpyridine acetylhydrazone, 2-benzoylpyridine acetylhydrazone and 2-formylpyridine benzoylhydrazone. Recently, DNA binding and cleavage activities on Cu(II) complexes with tetradentate ligands is also reported in the literature [23]. However, there is no report on antibacterial property of copper derivatives of hydrazones derived from 2-acetylthiophene. These ligands contain assorted donor (N, O and S) atoms and expected to form complexes with copper and to show interesting properties and activities.

Based on the lacuna identified and to renew our research interests [24-28], herein we reported the current findings on copper(II) complexes of 2-acetylthiophene acetylhydrazone (ATAH) and 2-acetylthiophene benzoylhydrazone (ATBH).

EXPERIMENTAL

The organic precursors (2-acetylthiophene, acetic hydrazide and benzhydrazide) were purchased from Sigma-Aldrich Chemicals Pvt. Ltd. India. The copper salt ($CuCl_2 \cdot 2H_2O$) was purchased from Merck Company. Only distilled solvents were used in the preparation of hydrazones and their metal derivatives.

Preparation of 2-acetylthiophene acetoxyhydrazone (ATAH): Acetic hydrazide (3.0 g, 0.03 mol) dissolved in 20 mL methanol was added to a hot methanolic solution (20 mL) of 2-acetylthiophene (5.03 mL, 0.03 mol) in a 100 mL round bottom flask. Few drops of glacial CH_3COOH was added to the reaction mixture. The contents were refluxed over water bath for 2 h and cooled to room temperature. By filtration, the compound was collected. It was washed 3-4 times with 2 mL portions of hot water and finally dried *in vacuo*. The product was recrystallized from methanol (**Scheme-I**). Yield: 80 % m.p.: 176-178 °C.

Preparation of 2-acetylthiophene benzoylhydrazone (ATBH): Benzhydrazide (3 g, 0.02 mol) dissolved in 20 mL methanol was added to a hot methanolic solution (20 mL) of 2-acetylthiophene (2.7 mL, 0.03 mol) in a 100 mL round bottom flask. Few drops glacial CH_3COOH was added to the reaction mixture. The contents were refluxed over water bath for 2 h and cooled to room temperature. By filtration, the compound formed was collected and washed 3-4 times with 2 mL portions of hot water and finally dried *in vacuo*. It was recrystallized from methanol (**Scheme-II**). Yield: 85 %; m.p. 198-200 °C.

Synthesis of copper complexes

Preparation of $\text{Cu}(\text{ATAH})_2$: The complex was prepared by mixing hot methanolic solution (20 mL) of 2-acetylthiophene acetoxyhydrazone (ATAH) (1 g, 0.55 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.63 g, 0.55 mmol) dissolved in methanol (20 mL) in 1:1 ratio in a clean 100 mL round bottom flask and the contents were refluxed on water bath for 3 h. The resulting solution was allowed to stand at room temperature and after slow evaporation, light green coloured complex which separated out was collected by filtration, washed with methanol followed by

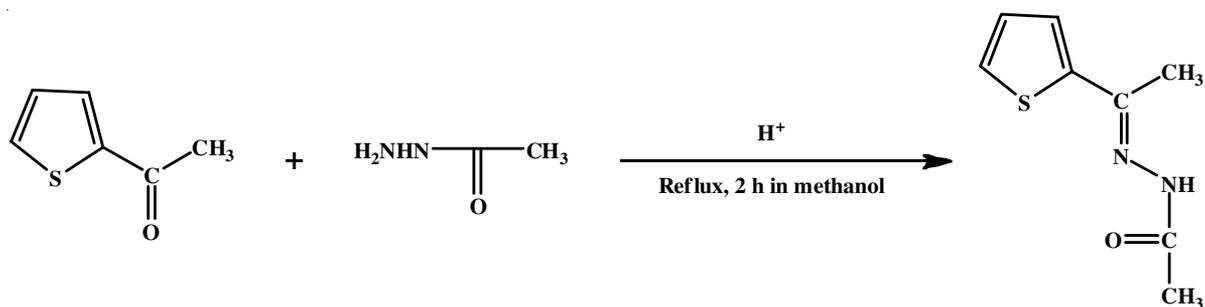
hexane and dried *in vacuo*. Yield, 72 %; decomposition point: > 290 °C.

Preparation of $\text{Cu}(\text{ATBH})_2$: It was prepared by mixing hot ethanolic solution (20 mL) of 2-acetylthiophene benzoylhydrazone (ATBH) (1 g, 0.410 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.53 g, 0.410 mmol) dissolved in ethanol (spirit) (20 mL) in 1:1 ratio in a clean 100 mL round bottom flask and the contents were refluxed on water bath for 3 h. The resulting solution was allowed to stand at room temperature and after slow evaporation, dark green coloured complex which was separated out by filtration, washed with methanol followed by hexane and dried *in vacuo*. Yield: 70 %; decomposition point: above 290 °C.

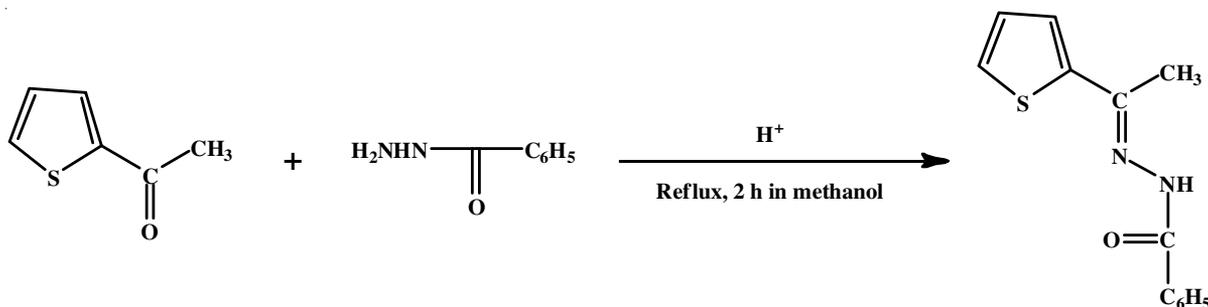
Preparation of sample solution for antimicrobial activity: With different concentrations of 200, 300 and 500 μg of each compound was prepared in DMF that had no influence on the microbial growth.

Test microorganisms and growth media: *Bacillus cereus* (MTCC 1305) and *Pseudomonas aureoginosa* (MTCC 2453) were targeted in the present study and procured from Department of Microbiology, Osmania University College, Hyderabad, India. The bacteria were grown on Mueller-Hinton agar plates at 37 °C. The bacterial stock cultures were incubated for 24 h at 37 °C on nutrient agar. Antibacterial activities of ligands and complexes were determined by zone inhibition method. Standard procedures were used in the preparation of paper discs.

Antibacterial activity: The agar medium was sterilized at 121 °C for 30 min. By pouring about 10 mL of the medium into petri-dishes (diameter = 10 cm) under aseptic condition the agar plates were prepared. The plates left undisturbed for 2 h to solidify the medium. About 1 mL aliquot of inoculums (containing suspension) of bacteria was poured on to the plates



Scheme-I: Synthesis of 2-acetylthiophene acetoxyhydrazone (ATAH)



Scheme-II: Synthesis of 2-acetylthiophene benzoyl hydrozone (ATBH)

TABLE-1
ANALYTICAL DATA OF COPPER(II) COMPLEXES

Complex	Colour	Yield (%)	m.w.	m.p.* (°C)	Elemental analysis (%): Found (Calcd.)				Molar conductivity (Ω cm ² mol ⁻¹)
					C	H	N	M	
Cu(ATAH) ₂	Light green	72	423.6	290	45.10 (45.32)	4.28 (4.25)	13.60 (13.22)	14.70 (15.00)	4.9
Cu(ATBH) ₂	Dark green	70	547.5	280	57.25 (56.98)	4.40 (4.38)	10.15 (10.22)	11.50 (11.60)	4.1

*Decomposition temperatures

separately containing solidified agar media. The prepared sterile filter paper discs were dipped into the compound solutions and shaken well and these test plates incubated for a period of 2 days in BOD at 37 °C for the development of inhibitory zones. An average of two independent readings for each organism for different compound solutions was documented. The inhibition zones were measured after 24 h at 37 °C. The diameter of the inhibition zone was measured and recorded using plastic ruler.

RESULTS AND DISCUSSION

The complexes are sparingly soluble in H₂O and less soluble in CH₃OH and C₂H₅OH, but readily soluble in CH₃CN, (CH₃)₂SO and (CH₃)₂NC(O)H. Molecular formulae of the Cu(II) complexes are proposed based on analytical data. The complexes are non-electrolytes (Table-1). The magnetic moment values of the complexes are relative to their respective spin-only values.

IR spectral data of acetylthiophene acetylhydrazone (ATAH) and 2-acetylthiophene benzoylhydrazone (ATBH) and their copper(II) complexes and their assignments are given in Table-2. Data and assignments suggested that the heterocyclic sulphur atom, azomethine nitrogen atom and oxygen atom are involved in chelation.

TABLE-2
IMPORTANT IR SPECTRAL BANDS*
(cm⁻¹) AND THEIR ASSIGNMENT

Cu(ATAH) ₂	Cu(ATBH) ₂	Assignment
–	–	v(N-H)
(3174)	(3327)	
–	–	v(C=O)
(1666)	(1651)	
1590	1502	v(C=N)
(1606)	(1508)	
476	472	v(Cu-O)
407	393	v(Cu-N)

*Ligands' bands are given in parenthesis

In FTIR spectrum of acetylthiophene acetylhydrazone (ATAH), the bands at 3174, 1666, 1606 cm⁻¹ are assigned to v(C=N), v(C=O) and v(NH) vibrations, respectively. The ¹H NMR spectra (recorded in CDCl₃ solvent) shows δ (2.35) (singlet 3H), δ (2.28) (singlet 3H), δ (7.00-7.30) (multiplet 3H), δ (9.50) (singlet 1H) are respectively assigned to -CH₃ (acetyl), -CH₃

(acetyl), thiophene and >NH protons. GC-MS spectrum of ATAH shows a peak at *m/z* 182 due to the formation of molecular ion.

The FTIR spectrum of 2-acetylthiophene benzoylhydrazone (ATBH) shows the peaks at 3327, 1651 and 1608 cm⁻¹, which are assigned to v(C=N), v(C=O) and v(NH) vibrations, respectively. The ¹H NMR spectrum of ATBH (recorded in CDCl₃ solvent) shows δ (2.34) (singlet 3H), δ (7.03- 8.00) multiplet 8H and δ (8.88) (singlet 1H) respectively assigned to -CH₃, and aromatic (thiophene + phenyl ring) protons and *NH protons. GC-MS spectrum of ATBH shows a peak at *m/z* 244 due to the formation of molecular ion.

UV-visible spectral data of complexes are given in Table-3. In the electronic spectra of Cu(ATAH)₂ and Cu(ATBH)₂, the bands at 27322 and 27030 cm⁻¹ are related to M–L charge transfer transitions. The spectra of Cu(ATAH)₂ and Cu(ATBH)₂ complexes showed symmetrical peaks at 12755 and 12936 cm⁻¹, respectively. These weak Laporte forbidden bands are assigned to ³E_g → ²T_{2g} electronic transition [1] in favour of octahedral geometry for the complexes.

TABLE-3
ELECTRONIC SPECTRAL DATA (cm⁻¹) OF
METAL COMPLEXES IN SOLUTION STATE*

Cu(ATAH) ₂	Cu(ATBH) ₂	Assignment	Structure
27322 (3100)	27030 (4500)	Charge transfer transition (M→L)	
12755 (280)	12936(460)	<i>d-d</i> transition (² T _{2g} → ² E _g)	Octahedral

*Spectral of complexes were recorded in DMF solvent.

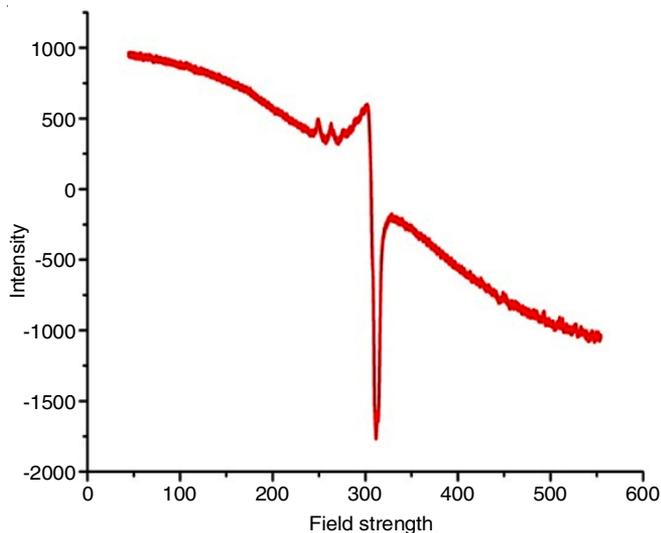
Molar absorptivity (L mol⁻¹ cm⁻¹) values are given in parenthesis.

Table-4 gives ESR spectral data of both Cu(II) complexes. Well resolved peaks are observed (Fig. 1) at low field and at high field region and these are related to g_{||} and g_⊥, respectively. Tetracyanoethylene (TCNE) free radical was used as the g marker for computing g values.

The g_{||} values for Cu(ATAH)₂ and Cu(ATBH)₂ complexes are respectively found to be 2.415 and 2.253. The g_⊥ values suggest ionic character for former complex and covalent character for latter complex [30]. The trend, g_{||} > g_⊥ > 2.0023 suggested that the unpaired electron predominantly in the d_{x²-y²} orbital [31,32] characteristic of octahedral geometry. The axial symmetry parameter G is defined as:

TABLE-4
HAMILTONIAN AND ORBITAL REDUCTION PARAMETERS OF COPPER(II) COMPLEXES

Complex	In DMF at RT				In DMF at LNT								
	g	g _⊥	g _{av}	G	g	g _⊥	g _{av}	G	λ	K	K _⊥	A ×10 ⁵	A _⊥ ×10 ⁵
Cu(ATAH) ₂	2.142	2.028	2.066	4.48	2.415	2.079	2.181	5.334	659	0.891	0.755	0.00238	0.00018
Cu(ATBH) ₂	2.149	2.006	2.054	3509	2.225	2.092	2.136	2.478	360	0.656	0.846	-	-

Fig. 1. ESR spectrum of Cu(ATAH)₂ complex at LNT

$$G = \frac{[g_{\parallel} - 2.0023]}{[g_{\perp} - 2.0023]}$$

The calculated G value for Cu(ATAH)₂ and Cu(ATBH)₂ complexes are respectively found to be 5.33 and 2.47. The G value is more than 4 for Cu(ATAH)₂ complex which indicates the absence of exchange coupling and mis-alignment of molecular axes. The G value is less than 4 for Cu(ATBH)₂ complex which indicates the absence of exchange coupling and mis-alignment of molecular axes.

The following equations are used in the calculation of orbital reduction parameters (K_{\parallel} , K_{\perp}):

$$g_{\parallel} = g_e - \frac{8K_{\parallel}^2\lambda}{\Delta E(d-d)}$$

$$g_{\perp} = g_e - \frac{2K_{\perp}^2\lambda}{\Delta E(d-d)}$$

Hathaway pointed that that for pure sigma bonding $K_{\parallel} = K_{\perp} = 0.77$ and for in-plane pi bonding $K_{\parallel} < K_{\perp}$, while for out-plane pi bonding $K_{\parallel} > K_{\perp}$.

For Cu(ATAH)₂ complex, K_{\parallel} and K_{\perp} are found to be 0.891 and 0.755, respectively. These values suggested the presence of out-plane π -bonding in the complex. For Cu(ATBH)₂ complex

K_{\parallel} and K_{\perp} are 0.656 and 0.846, respectively. These values suggested the presence of in-plane π -bonding in the complex.

The covalency factor (α^2) is evaluated by the following expression:

$$\alpha^2 = A_{\parallel}/p + (g_{\parallel} - 2.0023)/7(g_{\perp} - 2.0023) + 0.004$$

The α^2 value for the complex (0.3085) suggested the covalent nature of metal ligand bond.

The dipolar term P is estimated from the expression

$$P = (A_{\parallel} - A_{\perp})/(g_{\parallel} - 2) - 5/4(g_{\perp} - 2) - 6/7$$

Giordano and Bereman [33] suggested the identification of bond on groups from the values of dipolar term "P". The reduction of "P" value from the free ion value (0.036 cm⁻¹) may be attributed to the presence of covalent character of M-L bonding.

Antibacterial activity studies: The antibacterial activities of hydrazone ligands and their copper(II) complexes were investigated. The zone inhibition diameters (mm) are given in Table-5. The compound 2-acetylpyridine acetoxyhydrazone (APAH) shows more activity than 2-acetylpyridine benzoylhydrazone (APBH). Similarly, 2-acetylthiophene acetoxyhydrazone (ATAH) is more active than 2-acetylthiophene benzoylhydrazone (ATBH). This trend indicates that acetoxyhydrazones are more active than benzoylhydrazones against Gram-positive and Gram-negative bacteria. Moreover, APAH is more active than ATAH and APBH is more active than ATBH. This trend suggested that pyridine based hydrazones show more activity than thiophene based hydrazones against Gram-positive and Gram-negative bacteria.

The data given in Table-5 also suggested that the ligands showed more activity against *E. coli* and *Staphylococcus aureus* than the complexes. However, copper(II) complexes exhibited higher antibacterial activity than the free ligand, in the cases of *Bacillus* and *P. aureoginosa* in analogy with previous observations [34-36]. Overton's concept [37] and Tweedy's chelation theory [38] would explain the enhanced activity of complexes. According to former concept, the lipid membrane surrounding the cell support the passage of only lipid-soluble materials, which means that lipid solubility is an important element for controlling antimicrobial activity. The polarity of a metal ion is greatly reduced on chelation. Delocalization of π -electrons over the whole chelating ring enhances the penetration ability

TABLE-5
ANTIBACTERIAL ACTIVITY OF THIOPHENE BASED HYDRAZONES AND ITS COPPER(II) COMPLEXES

Compound	Zone of inhibition (mm)											
	Gram-negative						Gram-positive					
	<i>E. coli</i>			<i>P. aureoginosa</i>			<i>B. cereus</i>			<i>S. aureus</i>		
	200 μ g	300 μ g	500 μ g	200 μ g	300 μ g	500 μ g	200 μ g	300 μ g	500 μ g	200 μ g	300 μ g	500 μ g
APAH	4.2	5.6	6.6	7.0	8.0	8.5	5.0	6.0	6.5	7.0	8.0	9.0
Cu(APAH) ₂	2.5	2.7	3.0	2.5	2.5	3.3	4.0	5.0	7.0	4.0	5.0	5.5
APBH	2.0	4.0	6.0	6.0	7.0	7.5	5.0	5.5	6.0	4.0	6.0	8.0
Cu(APBH) ₂	1.5	1.7	2.4	4.5	6.6	8.4	6.0	6.5	7.0	2.5	4.0	6.0
ATAH	4.0	6.0	6.5	5.0	6.0	7.0	5.0	6.0	7.0	6.0	8.0	9.0
Cu(ATAH) ₂	2.2	2.5	3.4	6.2	7.3	8.4	4.0	4.2	5.0	4.0	5.0	5.5
ATBH	3.5	4.5	5.5	5.0	5.0	6.0	4.0	5.0	6.0	4.0	6.0	7.0
Cu(ATBH) ₂	2.4	2.8	3.6	8.3	8.5	9.2	5.0	5.5	6.0	3.0	5.0	7.0

APAH = 2-Acetyl pyridine acetoxyhydrazone; APBH = 2-Acetylpyridine benzoylhydrazone; ATAH = 2-Acetyl thiophene acetoxyhydrazone; ATBH = 2-Acetyl thiophene benzoylhydrazone

of the complexes into the lipid membranes. Metal ion is released when the complex enters the cell. The ligand free metal ion inhibits enzymes of the microorganisms [39].

Conclusion

In the present study two ligands *viz.* 2-acetylthiophene acetylhydrazone (ATAH) and 2-acetylthiophene benzoylhydrazone (ATBH) were synthesized and characterized based on spectral data. Copper(II) complexes of these functionalized hydrazones were investigated. Current studies revealed that the complexes have general formula ML_2 (where, L = ATAH and ATBH) and acted as monoanionic tridentate ligands. Copper complexes are six coordinated and have octahedral structure. Copper(II) complexes showed more activity than the corresponding hydrazone ligands.

ACKNOWLEDGEMENTS

One of the authors, KHR is thankful to UGC, New Delhi for the sanction of one-time grant (sanction Lr. No. F. 19-106/2013 (BSR) as financial support. The authors are also thankful to the authorities of SAIF Centers of IIT-Madras and IIT-Bombay, India for providing the spectral analysis. The authors thank UGC and DST, New Delhi, for providing the equipment facilities under UGC-SAP and DST-FIST programs, respectively.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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