

Full Length Research Paper

Synthesis and characterization of three new benzylidene acetohydrazide copper (II) complexes

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The synthesis and characterization of three complexes with copper (II) are described. The reaction between $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with bis[(E)-N'-(3-nitrobenzylidene) acetohydrazide], (NBAH) and bis[(E)-N'(4-methylbenzylidene) acetohydrazide], (MBAH) and bis[(E)-N'-(2,4-dichlorobenzylidene)acetohydrazide], (DBAH) produced three new ionic complexes. One of them is bis[(E)-N'-(3-nitrobenzylidene) acetohydrazide] copper(II) nitrate, $[\text{Cu}(\text{NBAH})_2]^{2+}$, second is bis[(E)-N'(4-methylbenzylidene) acetohydrazide]copper(II) nitrate, $[\text{Cu}(\text{MBAH})_2]^{2+}$ and third is bis[(E)-N'-(2,4-dichlorobenzylidene)acetohydrazide] copper(II) nitrate, $[\text{Cu}(\text{DBAH})_2]^{2+}$. The copper complexes have been characterized on the basis of elemental analysis and spectral data. The electronic and vibrational spectra of $[\text{Cu}(\text{NBAH})_2]^{2+}$, $[\text{Cu}(\text{MBAH})_2]^{2+}$ and $[\text{Cu}(\text{DBAH})_2]^{2+}$ have been measured and studied.

Key words: Synthesis, characterization, bis[(E)-N'-(3-nitrobenzylidene) acetohydrazide] copper(II) nitrate, bis[(E)-N'(4-methylbenzylidene) acetohydrazide]copper(II) nitrate, bis[(E)-dichlorobenzylidene)acetohydrazide] copper(II) nitrate.

INTRODUCTION

In principle, the central transition metal atoms of different soft and hard Lewis acidity usually need to be satisfied in the most suitable fashion. Copper containing ligands are known to form stable complexes with class b metal ions, such as gold (I) (Eikens et al., 1994; Ahmad et al., 2002; Anvarhusein et al., 2006) because copper is considered to be a soft Lewis base (Arnold et al., 1986; Levason et al., 1977). The coordination chemistry of copper(II) differs from most other transition metals due to its large size and d^9 configuration. Copper is an important element present in several cell types with essential functions in the human

body, participating in various biochemical and biological cycles. Complexes of copper with nitrogen ligand are of considerable interest due to broad spectrum of biological activities (Cobine et al., 2006; Gatteschi et al., 1991; Alexander et al., 1997). In this paper, the synthesis and characterization of copper(II) complexes of Schiff base ligands, NBAH, MBAH and DBAH are reported and characterized by UV-Vis and IR spectra. NBAH, MBAH and DBAH compounds are capable to form complexes with transition metal ions in the form Schiff bases. The spectroscopic data of the complexes indicate that the copper(II) ions are coordinated by the oxygen and nitrogen atoms (C=N) of the ligands. Formula of synthesized complexes is $[\text{CuL}_2]^{2+}$.

We have managed to prepare three new complexes of copper(II) that have not been synthesized and reported so far.

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Abbreviations: NBAH, bis[(E)-N'-(3-nitrobenzylidene) acetohydrazide]; MBAH, bis[(E)-N'(4methylbenzylidene) acetohydrazide]; DBAH, bis[(E)N'(2,4dichlorobenzylidene)acetohydrazide]; UV-Vis, ultraviolet visible spectroscopy; IR, infrared; DMSO, dimethyl sulfoxide; Dmf, dimethylformamide.

MATERIALS AND METHODS

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck, p.a.) were used. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on

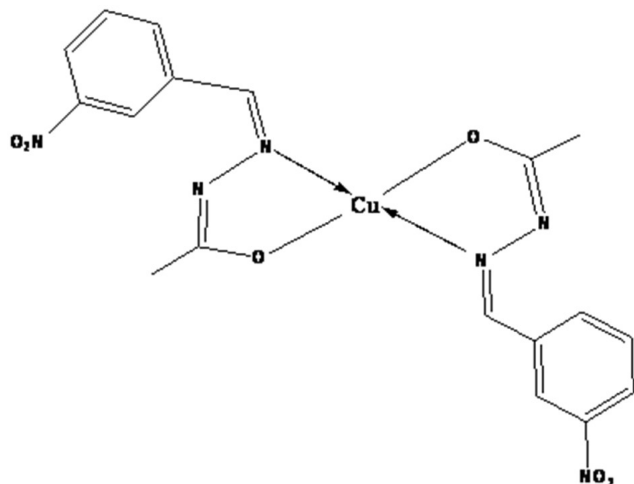


Figure 1. Structure of the copper complex of NBAH.

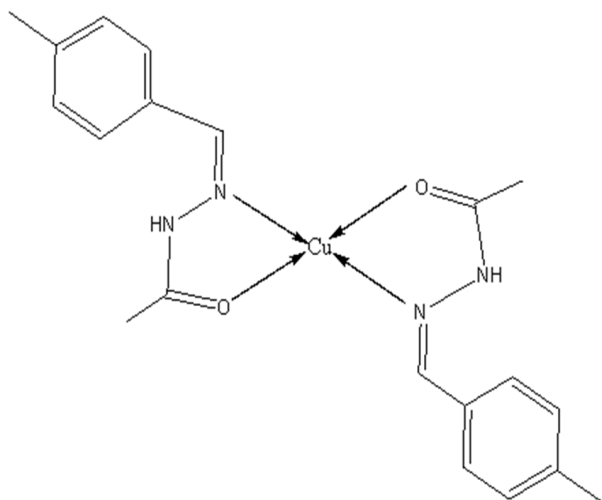


Figure 2. Structure of the copper complex of MBAH.

a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. The percent compositions of elements were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Synthesis of bis[(E)-N'-(3-nitrobenzylidene)acetohydrazide]copper(II) nitrate, $[\text{Cu}(\text{NBAH})_2]^{2+}$

$[\text{Cu}(\text{NBAH})_2]^{2+}$ was prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.20 g, 5 mmol) in ethanol and adding this blue solution to a white solution of NBAH ligand 2.25 g, 10 mmol in ethanol. The mixture was refluxed for 24 h and subsequently was allowed to stirring at room temperature for 30 min and then a dark green precipitate was formed after evaporation of solvent. Precipitate was washed with ether and dried at room temperature. M.p is 97.6-99.1°C. Anal. calc. for $\text{C}_{18}\text{H}_{16}\text{N}_6\text{O}_{12}\text{Cu}$: C, 36.027; H, 2.66; N, 18.68. Found: C, 36.019; H, 2.59; N, 18.60%.

Synthesis of bis[(E)-N'-(4-methylbenzylidene)acetohydrazide]copper(II) nitrate, $[\text{Cu}(\text{MBAH})_2]^{2+}$

Bis[(E)-N'-(4-methylbenzylidene)acetohydrazide]copper(II) nitrate, $[\text{Cu}(\text{MBAH})_2]^{2+}$ was prepared as follows: To a yellow solution of MBAH ligand (1.77 g, 10 mmol) in THF the $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.20 g, 5 mmol) was added under stirring at room temperature until a green precipitate was formed. After 3 h stirring, the mixture was filtered, washed with ether, and dried at room temperature. M.p is 174.3-176.6°C. Anal. calc. for $\text{C}_{20}\text{H}_{24}\text{N}_6\text{O}_8\text{Cu}$: C, 44.48; H, 4.44; N, 15.56. Found: C, 44.40; H, 4.41; N, 15.49%.

Synthesis of bis[(E)-N'-(2,4-dichlorobenzylidene)acetohydrazide]copper(II) nitrate, $[\text{Cu}(\text{DBAH})_2]^{2+}$

$[\text{Cu}(\text{DBAH})_2]^{2+}$ was prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.20 g, 5 mmol) in methanol and adding this blue solution to a white solution of DBAH ligand (2.30 g, 10 mmol) in methanol. The mixture was refluxed for 3 h and subsequently was allowed to stirring at room temperature for 30 min and then a dark blue precipitate was formed after evaporation of solvent. Precipitate washed with ether and dried at room temperature. M.p is 132-135.2°C. Anal. calc. for $\text{C}_{18}\text{H}_{14}\text{Cl}_4\text{N}_6\text{O}_8\text{Cu}$: C, 33.36; H, 2.16; N, 12.97. Found: C, 33.29; H, 2.13; N, 12.90%.

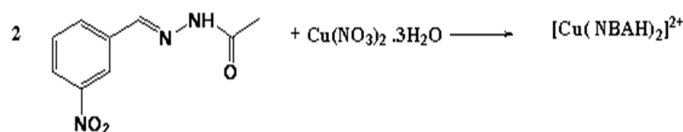
RESULTS AND DISCUSSION

Schiff bases are potentially capable of forming stable complexes with metal ions (Johnson et al., 1996). Copper(II) salt react with Schiff base ligands in 2:1(L/M) molar ratio in solvent to afford complexes. The ligands and their complexes are stable at room temperature. In this paper, a direct, simple and one-step method has been used to synthesize these compounds. The advantages of the method are; that there is no side product, the reaction is quite fast, there are mild conditions, and the accompanied color change that provides visual means for ascertaining the progress of the reaction.

All of the infra red (IR) spectra information supports the suggestion of coordination of the nitrogen and oxygen atoms to the metal ion. Therefore, the general structures for the metal complexes are proposed as shown in Figure 1 for $[\text{Cu}(\text{NBAH})_2]^{2+}$, in Figure 2 for $[\text{Cu}(\text{MBAH})_2]^{2+}$ and in Figure 3 for $[\text{Cu}(\text{DBAH})_2]^{2+}$.

bis[(E)-N'-(3-nitrobenzylidene)acetohydrazide]copper(II) nitrate, $[\text{Cu}(\text{NBAH})_2]^{2+}$

$[\text{Cu}(\text{NBAH})_2]^{2+}$ was prepared by the reaction of (NBAH) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in ethanol solvent as follows:



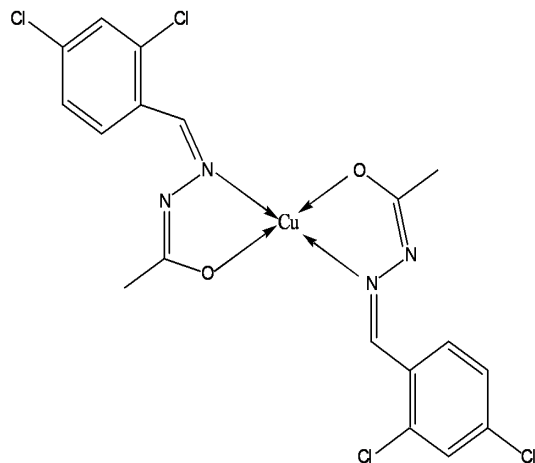


Figure 3. Structure of the copper complex of DBAH.

Table 1. The frequencies (cm^{-1}) of $[\text{Cu}(\text{NBAH})_2]^{2+}$.

Vibration	ν (cm^{-1})	Intensity
ν (C-H)	2867	m
ν (C=C)	1698	m
ν (C=N)	1612	s
ν (N-N)	1155	s
ν (NO_3)	1349,818	s,m
ν (NO_2)	1349,1530	s,s
ν (C-O)	1085	m
ν (Cu-N)	478	w
ν (Cu-O)	529	m

Table 2. Electronic spectrum of $[\text{Cu}(\text{NBAH})_2]^{2+}$

λ_1 (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	λ_2 (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)
220(126)	263(65)

1349, 818, 1530, 1085, 478, 529, 1155, 1612 cm^{-1} (Table 1). Electronic spectrum of $[\text{Cu}(\text{NBAH})_2]^{2+}$ shows two transitions (Table 2).

Bis[(E)N'(4methylbenzylidene)acetohydrazide]copper (II) nitrate, $[\text{Cu}(\text{MBAH})_2]^{2+}$

$[\text{Cu}(\text{MBAH})_2]^{2+}$ was prepared by the reaction of MBAH and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in THF solvent as follows:

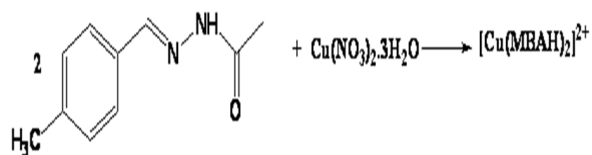


Table 3. The frequencies (cm^{-1}) of $[\text{Cu}(\text{MBAH})_2]^{2+}$.

Vibration	ν (cm^{-1})	Intensity
ν (C-H)	3064	m
ν (C-N)	1317	m
ν (C=N)	1559	s
ν (C=O)	1620	s
ν (N-N)	1176	m
ν (NO_3)	1370,832,717	s,m,w
ν (Cu-N)	421	m
ν (Cu-O)	508	m

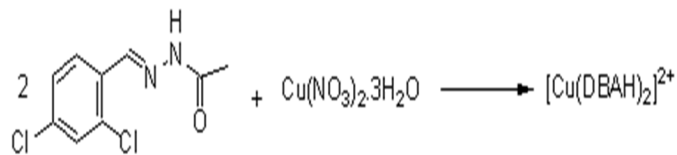
Table 4. Electronic spectrum of $[\text{Cu}(\text{MBAH})_2]^{2+}$.

λ_1 (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)
253 (539)

The complex is soluble in polar solvents, such as DMSO, DMF, and chloroform but not soluble in hexane and benzene. The IR spectrum of this compound shows ν : 508, 421, 1370, 832, 717, 1176, 1620, 1559 cm^{-1} (Table 3). There is one absorption band in this compound electronic spectrum (Table 4).

Bis[(E)-N'-(2,4-dichlorobenzylidene)acetohydrazide]copper(II)nitrate, $[\text{Cu}(\text{DBAH})_2]^{2+}$

$[\text{Cu}(\text{DBAH})_2]^{2+}$ was prepared by the reaction of (DBAH) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in methanol solvent as follows:



The complex is soluble in polar solvents, such as DMSO and chloroform but not soluble in hexane, benzene. The IR spectrum of this compound shows ν : 599, 463, 1139, 674, 1369, 861, 781, 1149 cm^{-1} (Table 5). There are two absorption bands in this compound electronic spectrum (Table 6).

Conclusion

In summary, the synthesis and characterization of complexes have been described. Three complexes of copper (II) were synthesized simply. $[\text{Cu}(\text{NBAH})_2]^{2+}$ was prepared by the reaction of NBAH and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in ethanol solvent. $[\text{Cu}(\text{MBAH})_2]^{2+}$ was

Table 5. The frequencies (cm^{-1}) of $[\text{Cu}(\text{DBAH})_2]^{2+}$.

Vibration	ν (cm^{-1})	Intensity
ν (C-H)	2863	m
ν (C=N)	1580	s
ν (N-N)	1149	s
$\nu(\text{NO}_3)$	1369,861,781	s,m,m
ν (C-Cl)	674	m
ν (C-O)	1139	s
ν (Cu-N)	463	w
ν (Cu-O)	599	m

Table 6. Electronic spectrum of $[\text{Cu}(\text{DBAH})_2]^{2+}$.

λ_1 (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	λ_2 (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)
205(1593)	257(591)

prepared by the reaction of MBAH and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in THF solvent and $[\text{Cu}(\text{DBAH})_2]^{2+}$ was prepared by the reaction of DBAH and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in a 2:1 ratio in methanol solvent. Electronic and vibrational spectra of these three new complexes were studied. These compounds were characterized by IR, UV/Visible techniques.

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