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# Synthesis, FTIR and Electronic Spectra Studies of Metal (II) Complexes of Acethydrazide Derivative

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**Abstract**

Acethydrazide was modified by addition of benzaldehyde refluxing in ethanol to obtain a new product: N'-Benzylideneacethydrazide. The new product obtained was complexed with Iron (II) and Copper (II) salt. The result of the FT-IR analysis of acethydrazide, N'-Benzylideneacethydrazide and its complexes were compared to ascertain the possible points and mode of coordination to the metal (II) centre. The shift in the absorption band of the N'-Benzylideneacethydrazide (N'-BA) from 3337 cm-1 (N-H) to 3462 cm-1 and 3406 cm-1 (N-H) in the spectra of the Fe(II) and Cu(II) complexes respectively, indicates the coordination of the N'-Benzylideneacethydrazide to the metal ion via O and N atoms of the carbonyl and amide functional groups. The products were further characterized by UV/Visible spectroscopic technique and other physical measurements like melting point and solubility test.

**Keywords:** Acethydrazide; Ligand; Metal-complex; N'-Benzylideneacethydrazide; Infrared spectroscopy; Ultraviolet visible spectroscopy

## Introduction

Acethydrazide belongs to the hydrazine/hydrazone group which plays an important role for the anti-microbial activity. Recently, Acethydrazide has gained great importance due to the anti-tuberculosis activity it possesses [1]. A disease caused by parasites represents a major world health problem with very limited therapeutic options.

Most of the available treatments are limited in their efficacies as a result of being decades old and are suffering from limited efficacy and/or undesirable side effects. The efficacy of therapeutic agent is known to be enhanced upon coordination to metal ion [2]. Metal ions are electron deficient whereas most biological molecule drugs are electron rich. The attraction between these opposite charges leads to a general tendency for metal ions to bind and interact with biological molecules [3].

To the best of our knowledge, this represents the first Synthesis, FTIR, and electronic spectra studies of metal(II) complexes of Acethydrazide and Pyrazine-2-carboxylic acid derivatives.

## Materials and Methods

### Materials

All reagents and chemicals were of analytical grade obtained from commercial sources and were not further purified. Acethydrazide (98%) and ethanol (98%) were obtained Sigma Aldrich (UK), benzaldehyde (96%) was obtained from Fisher scientific, UK. Hydrated metal salts: ($CuSO_4.5H_2O$), ($FeSO_4.7H_2O$) used for complexation were obtained from British Drug House (BDH) Poole, England. UV-Visible spectra were recorded on a Jenway 7305 UV-Vis spectrophotometer and FTIR spectra were recorded on a Shimadzu scientific model 8400S IR Prestige 21 spectrophotometer with KBr pellets.

### Synthesis of N'-Benzylideneacethydrazide (N'-BA)

Three (3) mmol (0.222 g) of acethydrazide was dissolved in 10 ml of ethanol; 5 ml of benzaldehyde was added and refluxed for 4 hours with stirring. The resulting solution was a wine colour and was cooled at room temperature and allowed to stand for 5 days without disruption. The resulting solution was then concentrated for 10 minutes using a hot plate and then allowed to cool at room temperature. Colourless rod-like crystals were formed on cooling at room temperature.

### Synthesis of $[FeSO_4(N'\text{-}BA)].7H_2O$

One (1) mmol (0.278 g) of Iron (II) sulphateheptahydrate was dissolved in 10 ml solvent system (Ethanol 1:1 deionised water) and the 0.6 mmol (0.099 g) of N'-Benzylideneacethydrazide (N'-BA) was added slowly while stirring. On heating it dissolved completely giving a yellow colouration and on cooling it settles and a precipitate formed. It was filtered and dried in a dessicator, well-shaped green/brown crystals was obtained.

Equation of Reaction: $FeSO_4.7H_2O + N'\text{-}BA \rightarrow [FeSO_4(N'\text{-}BA)].7H_2O$

### Synthesis of $[CuSO_4(N'\text{-}BA)].5H_2O$

One (1) mmol (0.249 g) of Copper (II) sulphatepentahydrate was dissolved in 10 ml solvent system (Ethanol 1:1 deionised water) and the 0.6 mmol (0.099 g) of N'- benzylideneacethydrazide (N'-BA) was added slowly while stirring. On heating it dissolved completely giving a deep green colouration and on cooling it settles and a deep blue precipitate formed. It was filtered and dried in a dessicator. A pale blue crystal well shaped was obtained.

Equation of Reaction: $CuSO_4.5H_2O + N'\text{-}BA \rightarrow [CuSO_4(N'\text{-}BA)].5H_2O$

## Results and Discussion

Some physical and spectroscopic data of the ligand and its metal complexes are presented in Table 1. The complexes showed a melting point value and N'- Benzylideneacethydrazide (N'-BA) showed a low

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melting point when compared together. The two complexes synthesized were crystalline in nature. Solubility of N'-Benzylideneacethydrazide (N'-BA) and the complexes are presented in Table 2.

## Infrared spectra of N'- Benzylideneacethydrazide (N'-BA) and metal complexes

A comparative study of the IR Spectra data of N'-Benzylideneacethydrazide (N'-BA) and Fe(II)/Cu(II) complexes measured from 400 to 4000 $cm^{-1}$. The important Infrared group frequencies of (N'-BA) and Fe(II)/Cu(II) complexes are given in Table 3. The spectra of the ligands and complexes exhibit strong absorption bands in the range of 3229-3462 $cm^{-1}$ assigned to **υ**(N-H) vibrations [4]. The band at (3337 $cm^{-1}$, 3229 $cm^{-1}$) in the spectrum of (N'-BA) is attributed to **υ**(NH) of the amide group but when compared to Fe(II)/Cu(II) complexes, there was a shift in the frequency of Fe(II)/Cu(II) complexes :(3462 $cm^{-1}$, 3385 $cm^{-1}$) and 3406 $cm^{-1}$ respectively to a higher frequency in the region of the **υ**(NH). For the spectrum of N'- Benzylideneacethydrazide, a weak and sharp band occurs at 1609 $cm^{-1}$ which is assigned to C=N stretching different from the 1655 $cm^{-1}$ and 1547 $cm^{-1}$ bands of Fe(II)/Cu(II) complex respectively. The characteristic absorption bands in the region 1680-1630 $cm^{-1}$ is assigned to the carbonyl group of an amide [5]. The sharp absorption band of C=O stretching observed at 1655 $cm^{-1}$ of N'-Benzylideneacethydrazide shifted to a lower frequency in the Fe(II) (1622 $cm^{-1}$), (1622 $cm^{-1}$) complex. The C-H stretch observed at 3044 $cm^{-1}$ of N'-Benzylideneacethydrazide shows a slight shift in lower frequency of the Fe(II) complex having 3258 $cm^{-1}$ with exception to Cu(II) complex. The bands at 507 $cm^{-1}$ and 517 $cm^{-1}$ of the Fe(II)/Cu(II) complexes are attributed to the Fe-N, Cu-N respectively also the bands at 615 $cm^{-1}$ and (660 $cm^{-1}$, 604 $cm^{-1}$) of the Fe(II)/Cu(II) complexes are attributed to the Fe-O, Cu-O respectively.

In the UV/Visible region of the $[FeSO_4(N'\text{-}BA)].7H_2O$ complex (Figure 1), two peaks were observed at 320 nm and 420 nm which are due to charge transition from ligands to metal and d-d transition respectively. The $[CuSO_4(N'\text{-}BA)].5H_2O$ complex (Figure 2) showed one sharp and broad peaks at 310 nm and 750 nm which are also due to charge transition from ligands to metal and d-d transition respectively (Table 4).

## Conclusion

The proposed molecular structure of the compound N'-Benzylideneacethydrazide (N'-BA) was achieved through refluxing method and there was a functional group transformation. From the interpretation of the UV/Visible spectroscopy and FT-IR spectrum of N'-Benzylideneacethydrazide and Fe(II)/Cu(II) complexes, the analysis indicates the co-ordination of the oxygen of the carbonyl group to the metal ion, co-ordination of the amide nitrogen to the metal ion, also the co-ordination of the oxygen of the sulphate ion.

| Compound | Physical state | Melting point | Colour | % Yield |
|---|---|---|---|---|
| **N'-BA** | Crystalline | 94.1°C | Colourless | 72 |
| **$[FeSO_4(N'\text{-}BA)].7H_2O$** | Crystalline | 106°C | Green/Brown | 57 |
| **$[CuSO_4(N'\text{-}BA)].5H_2O$** | Crystalline | 163°C | Pale Blue | 60 |

**Table 1:** Physical properties of N'-BA and Fe(II)/Cu(II) complexes.

| Compound | Deionized Water | | Ethanol | | Methanol | | Acetone | |
|---|---|---|---|---|---|---|---|---|
| | Cold | RT | Cold | RT | Cold | RT | Cold | RT |
| **N'-BA**<br>**$[FeSO_4(N'\text{-}BA)].7H_2O$** | SS<br>S | SS<br>S | S<br>SS | S<br>SS | S<br>INS | S<br>S | S<br>SS | S<br>SS |
| **$[CuSO_4(N'\text{-}BA)].5H_2O$** | SS | S | SS | SS | SS | SS | INS | INS |

S=Soluble; SS=Sparingly Soluble; INS=Insoluble; RT=Room temperature

**Table 2:** Solubility of ligand and metal complexes in different solvents.

| Ligands/Complex | Assignment ($cm^{-1}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | υ(N-H) | υ(=C-H) | υ(C=O) | υ(C=N) | υ(C-H) | υ(C-O) | υ(-N=N) | υ(M-N) | υ(M-O) |
| Acethydrazide | 3453 br, S<br>3266 br, S | 3038 br, S | 1663 br, S | ---------- | 2938<br>2853 | --------- | ---------- | ---------- | -------- |
| N'- Benzylideneacethydrazide (N'-BA) | 3337 br, w<br>3229 Sh, S | 3044 Sh, m | 1655 Sh, w | 1609 Sh, w | 2843 br, w<br>2726 br, w | ---------- | 1699 Sh, S | ---------- | --------- |
| $[FeSO_4(N'\text{-}BA)].7H_2O$ Complex | 3462 br, S<br>3385 br, S | 3258 br, S | 1622 Sh, w | 1655 Sh, w | ---------- | 1111 br, S | ---------- | 507 br, w | 615 Sh, S |
| $[CuSO_4(N'\text{-}BA)].5H_2O$ Complex | 3406 br, S | ---------- | 1622 br, w | 1547 br, w | ---------- | 1155 br, S | ---------- | 517 Sh, w | 660 br, m |

**Key:** br=broad, Sh=Sharp, S=Strong, m=medium, w=weak

**Table 3:** Selected FTIR absorption bands for Acethydrazide, N'-Benzylideneacethydrazide(N'-BA) and Fe(II)/Cu(II) complexes.

| Compound | **Absorbance** Maximum | **Wavelength** $\lambda_{max}$ (nm) | **Assignment** |
|---|---|---|---|
| $[FeSO_4(N'\text{-}BA)].7H_2O$ | 3·000<br>3·000 | 320<br>420 | C-T Band<br>d-d Transition |
| $[CuSO_4(N'\text{-}BA)].5H_2O$ | 3·000<br>0·222 | 310<br>750 | C-T Band<br>d-d Transition |

C-T=Charge transition

**Table 4:** Electronic spectra data on UV/Vis spectrophotometry.

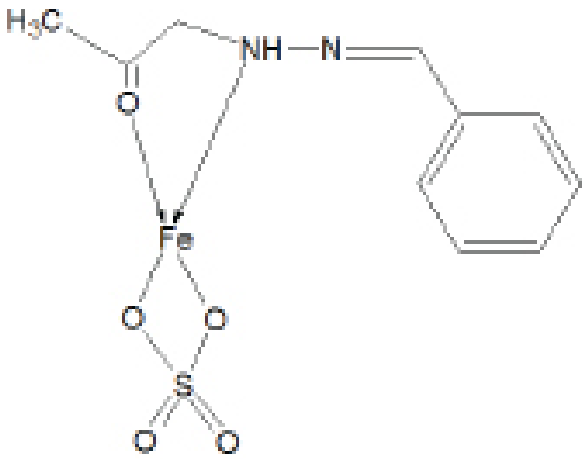


**Figure 1:** Proposed Structure of $[FeSO_4(N'\text{-}BA)].7H_2O$ complex.

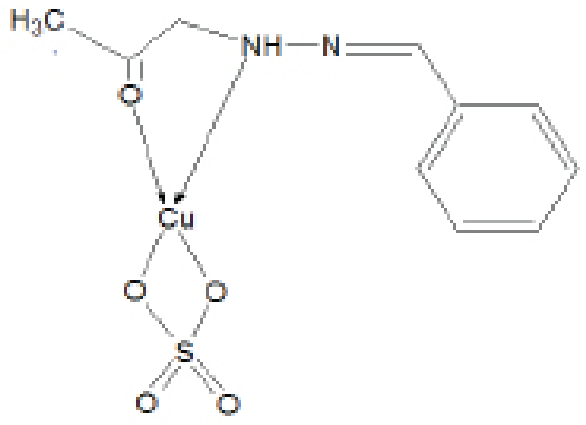


**Figure 2:** Proposed Structure of $[CuSO_4(N'\text{-}BA)].5H_2O$ complex.

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