# Magnetic Susceptibilities of Copper(II) Complexes of Tetradentate Schiff Bases

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**Summary:** The copper(II) complexes of the tetradentate Schiff bases show normal paramagnetic behaviour at room temperature. The values for effective magnetic moments, $\mu_{eff}$, are in the range 1.34-2.41 B.M. which is normal for paramagnetic compounds having $d^9$ configuration. Electronic reflectance spectra show a very broad band around 18000 $cm^{-1}$ due to d-d transition.

## Introduction

Although a number of magnetic investigations have been reported for copper(II) complexes [1-3], little or no data is available regarding magnetic susceptibility investigations of copper(II) complexes of tetradentate Schiff bases (Fig. 1). The investigations have been carried out in order to determine whether the compounds exhibit normal paramagnetic behaviour or behave anomalously on coordination. The effect of different substituents in the complexing reagents on the magnetic behaviour is also reported.

## Results and Discussion

Copper has a single s-electron outside the filled 3d shell. Because of the relatively low sym-

metry (i.e. less than cubic) of the environments in which the copper(II) ion is characteristically found, detailed interpretations of magnetic properties are somewhat complicated.

The ground term $^2D$ 5/2 for copper(II) gives expected value for μeff in the range 1.8-2.2. If μ s.o. = n(n+2) is applied, the expected value for copper(II) is 1.85 B.M. [10]. The magnetic moments of simple copper(II) compounds (those lacking Cu-Cu interactions) are generally in the range 1.75-2.20 B.M. regardless of stereochemistry and independently of temperature except at extreme ( 4 °K).

The values of effective magnetic moments, μeff, recorded at room temperature are listed in the Table 1. The values of most the compounds are within the range (1.34-2.41 B.M.). The small decrease in the value for Bis(trifluoroacetylacetone) meso-stilbenediimine copper(II) (1.64 B.M.) and Bis(*n*-propanoylacetyl)-meso-stilbenediimine copper(II) (1.46 B.M.) may be attributed to Cu-Cu interactions because of distortion [10,5,13] from square planar configurations.

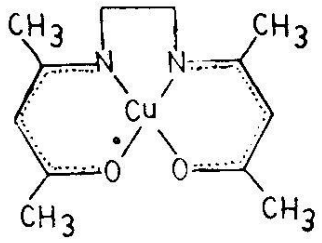


Fig. 1: Structural diagram of bis(acetylacetone)-ethylenediimine.

The value of μeff for bis(acetylacetone)ethyle nediimine copper(II) is 1.90 B.M. whereas the value for bis(triluoroacetone)ethylenediimine copper(II) is 1.70 which may be due to the presence of fluoro groups which are electron withdrawing. The value for bis(acetylacetone) dl-stilbenediimine copper(II) (2.05 B.M.) is slightly increased due to the substitution of phenyl group at bridge position. The decrease in the value of bis(acetylpivalymethane)dl-stilbenediimine copper(II) (1.60 B.M.) as compared to bis(acetylacetone)dl-stilbenediimine (2.05 B.M) is due to the substitution of tertiary butyl in place of methyl groups.

Table 1

| No. | Complex | T/K | μeff | Diamagnetic correction/ c.g.s. units x10$^6$ |
|---|---|---|---|---|
| 1. | Bis(acetylacetone)-ethylenediimine copper(II) [$AA_2$enCu] | 300 | 1.90 | -130 |
| 2. | Bis(trifluoroacetyl-acetone)dl-stilbene-diimine copper(II) [dl-$F_3AA_2$SCu) | 300 | 1.34 | -335 |
| 3. | Bis(acetylacetone)dl-stilbenediimine copper(II) [dl-$AA_2$SCu] | 300 | 2.05 | -298 |
| 4. | Bis(trifluoroacetyl)-acetone)meso-stilbene-diimine copper(II) [$F_3AA_2$SCu) | 300 | 1.64 | -334 |
| 5. | Bis(trifluoroacetyl-acetone)propylenediimine copper (II) [$F_3AA_2$PnCu] | 300 | 2.10 | -251 |
| 6. | Bis(trifluoroacetyl-acetone)ethylenediimine copper(II) [$F_3AA_2$enCu] | 300 | 1.70 | -243 |
| 7. | Bis(acetylacetone)-propylenediimine copper (II) [$AA_2$PnCu] | 300 | 1.72 | -185 |
| 8. | Bis(salicylaldehyde)-dl-stilbenediimine copper(II) [dl-$SA_2$SCu] | 300 | 1.69 | -292 |
| 9. | Bis(acetylpivalyl-methane)dl-stilbene-diimine copper (II) [dl-$APn_2$SCu] | 300 | 1.68 | -359 |
| 10 | Bis(n-propanoyl-acetyl)meso-stilbene-diimine copper (II) [$PA_2$SCu] | 300 | 1.46 | -357 |
| 11 | Bis(trifluoroacetyl-mesityloxide)ethyl-methylethylenediimine copper(II) [$F_3AM_2$EMCu] | 300 | 1.61 | -328 |
| 12 | Bis(trifluoroacetyl-acetone)ethylmethyl-ethylenediimine copper(II) [$F_3$AAEMCu] | 300 | 2.41 | -275 |

*Electronic Spectra*

The diffuse reflectance spectra of the compounds are shown in Fig. 2. The energies of the bands are listed in Table 1. Most spectra show a

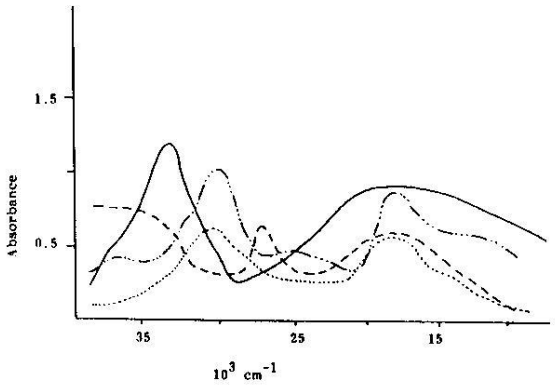


Fig. 2: Diffuse reflectance spectra of Copper (II) Complexes of _____bis(acetylacetone)ethylenediimine, ----------bis-(trifluoroacetylacetone) dl-stilbenediimine,.....bis(acetylacetone) dl-stilenediimine and ..... _____..... _____bis(n-propanoylacetone)meso-stilbenediimine.

very broad band at 18200 $cm^{-1}$ and a sharp band at 25000-26000 $cm^{-1}$. In addition to these bands, a shoulder in the region 14000-15000 $cm^{-1}$ is observed in the complexes dl-$F_3AA_2SCu$, meso-$F_3AA_2SCu$, $F_3AA_2enCu$, dl-$APM_2SCu$, $F_3AA_2EMCu$, meso-$PA_2SCu$, $F_3AM_2EMCu$, and $F_3AA_2EMCu$. The broad band found at 18200 $cm^{-1}$ has been assigned to d-d transition in $AA_2enCu$ and dl-$AA_2SCu$ to square planar complexes, which has been supported by X-ray crystallography [11]. The presence of Cu-Cu interactions can not be ruled out in the complexes containing shoulders in the region 13000-16000 $cm^{-1}$. These may be due to the distortion in the square planar geometry. Therefore, the values of μeff of these complexes are slightly lower. Kanatomi [12] *et al.* have reported these bands at 18.6 kK and shoulder at 16-16.7 kK in the complexes meso-$AA_2SCu$ and meso-$SA_2SCu$. Khuhawar and Vasandani [7] have also reported these bands at 18.3 and 19.2 kK in tetradentate Schiff bases complexes of copper (II).

## Experimental

The copper chelates were prepared as reported earlier by refluxing together equimolar solutions of copper (II) acetate (0.01 mole) in methanol and the appropriate reagents (for 30 min.). Sufficient water was then added to cause precipitation and mixture filtered. The precipitate was recrystallized from ethanol [4-9].

Table 2:

| No. | Complexes | T/K | $\nu_{max}/cm^{-1}$ |
|---|---|---|---|
| 1. | Bis(acetylacetone)ethyl-enediimine copper(II) | RT | 18300 vbr 34400 s |
| 2. | Bis(trifluoroacetyl-acetone)dl-stilbene-diimine copper (II). | RT | 18100 vbr 27700 s |
| 3. | Bis(acetylacetone)dl-stilbenediimine copper (II) | RT | 18300 vbr 27700 s |
| 4. | Bis(trifluoroacetyl-acetone)meso-stilbene-diimine copper(II) | RT | 18200 vbr 28200 s 15200 sh |
| 5. | Bis(trifluoroacetyl-acetone)propylenediimine copper(II) | RT | 18300 vbr 25600 s |
| 6. | Bis(trifluoroacetyl-acetone)ethylenediimine copper(II) | RT | 18200 vbr 25500 s 14700 sh |
| 7. | Bis(acetylacetone)propyl-enediimine copper(II) | RT | 18300 vbr 25600 s |
| 8. | Bis(salicylaldehyde)dl-stilbenediimine copper (II) | RT | 18200 vbr 25300 s |
| 9. | Bis(acetylpivalylmethane) dl-stilbenediimine copper(II) | RT | 18100 vbr 32000 w 15800 sh |
| 10 | Bis(n-propanoylacetone)-meso-stilbenediimine copper(II) | RT | 18100 vbr 32000 sh 15800 sh |
| 11 | Bis(trifluoroacetyl-mesityloxide)ethyl-methylethylenediimine copper(II) | RT | 18200 vbr 30000 s 14700 sh |
| 12 | Bis(trifluoroacetyl-acetone)ethylmethyl-ethylenediimine copper(II) | RT | 18100 vbr 31000 s 13800 sh |

The Microanalyses of the compounds were carried out by Elemental Microanalysis Ltd. Devon, England.

The Magnetic susceptibility measurements were done on a magnetic susceptibility balance (Sherwood Scientific, Cambridge, England). The sample was ground to fine powder form. The calibration constant of the balance was determined by using Analar $CuSO_4.5H_2O$. The tube (supplied by the same company) was filled with sample with the length not less than 1.5 c.m.

Xg (gram susceptibility) was calculated by using the formula,

$$X_g = \frac{C_{Bal} \times 1 \times (R-Ro)}{10^9 \times m}$$

Where $C_{Bal}$ = Constant of Balance

l = length of the sample
R = Reading with magnet on
$R_o$ = Reading with magnet off
m = mass of the sample

From $X_g$, $X_m$ (molar susceptibility) was determined by multiplying Xg with the molecular weight of the compound. $X_A$ (corrected susceptibility) was obtained by substracting from the molar subceptibility the susceptibilities of the diamagnetic groups.

The reflectance spectra of the copper chelates within 870-190 nm were recorded on Schimadzu-365 UV-Vis-NIR spectrophotometer.

## Conclusion

The copper(II) complexes of tetradentate Schiff bases ligands have effective magnetic moments in the range of 1.34-3.4 B.M. The slight decrease in the effective magnetic moment values of most of the compounds may be ascribed to the interactions caused by the presence of trifluoromethyl, tertiary butyl or Cu-Cu interactions. The diffuse reflectance spectra of the compounds $AA_2$enCu dl-$AA_2$SCu, $F_3AA_2$pnCu, $AA_2$pnCu and dl-$SA_2$SCu indicate a single band within 18300-18200 $cm^{-1}$ which is characteristic of square planar complexes [14].

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