

Exchange reactions of copper complexes with amines

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Abstract. Square planar mixed ligand complexes of the type $[CuLL']$ where L = 5-chlorosalicylaldehyde and L' = acetoacetanilide, have been synthesized on treatment with ammonia. Amine exchange of the above Schiff base complexes has been carried out on treatment with different amines. The reaction with ethanol amine is quite interesting compared to other amines. It reacts with 5-chlorosalicylaldehyde to form a Schiff base, while the β -diketone part is removed in the complex formation. All the complexes were characterized by elemental analysis, spectral studies, magnetic measurement, TLC, and conductance.

Keywords. Mixed ligand copper complexes; amine exchange; Schiff bases.

1. Introduction

The present work was undertaken in order to explore the synthesis, structure and reactions of the corresponding mixed ligand complexes of copper(II). Mixed ligand complexes of the type $[CuLL']$, where L = 5-chlorosalicylaldehyde is a primary ligand and L' = acetoacetanilide the secondary ligand, are prepared. The mixed ligand complex on treatment with ammonia gives a mixed imine Schiff base (SB) complex. Amine exchange (transamination) reactions were also carried out by treatment of the mixed imine Schiff base complex with methyl amine [M], *n*-butylamine [NB], aniline [A], *m*-toluidine [MT], *p*-toluidine [PT], *p*-anisidine [PA], *p*-phenilidine [PP], α -naphthylamine [N] and ethanol amine [E].

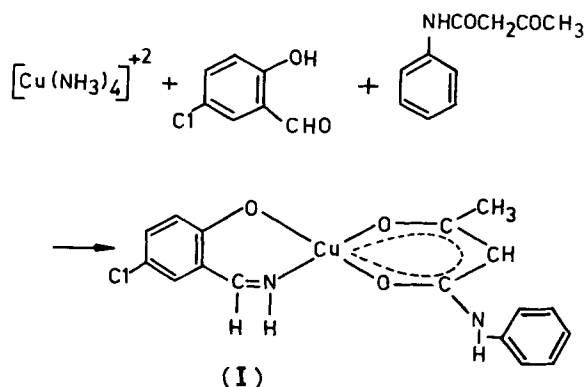
2. Experimental

All the chemicals used were of AnalaR or chemically pure grade.

2.1 Preparation of parent complexes (type I) $[Cu-SB_1-AAA]$

To an aqueous solution (1 M) of copper acetate in excess ammonia, alcoholic solution of respective 5-chlorosalicylaldehyde (1 M) and acetoacetanilide [AAA] (1 M) were added. The mixture was stirred well, and the solid that separated out was filtered and washed successively with water and 50% alcohol. The product was recrystallised from chloroform.

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2.2 Preparation of complexes using methyl and other amines (type II)

An ethanolic solution (0.005 M) of a copper(II) complex of the type (I) was warmed for half an hour on a water-bath. Using methyl amine [M] (30 ml) as solvent the contents were refluxed for two hours. The product was obtained by pouring water into the reaction mixture, filtering, washing with water and 50% ethanol, and finally recrystallizing from chloroform.

The amine exchange reactions of *n*-butyl amine, aniline, *m*-toluidine, *p*-toluidine, *p*-anisidine, *p*-phenilidine, and α -naphthylamine were carried out as described above.

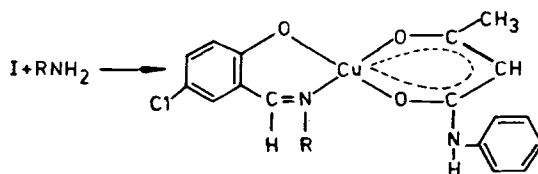


Chart 2.

where R = CH₃, C₄H₁₀, C₆H₅, *m*-C₇H₇, *p*-C₇H₇, *p*-C₇H₇O, *p*-C₈H₉O, and α -C₈H₇.

2.3 Preparation of complexes using ethanol amine (type III)

Copper(II) mixed ligand complexes containing salicylaldimine and β -diketone (type I) were treated with an ethanolic solution of ethanolamine (0.05 M, 20 ml) on a waterbath for 2–3 hours. The solid product precipitated on addition of water to the reaction mixture was filtered, washed with water and finally with 50% ethanol. The complex was recrystallized from chloroform. Analysis of the products showed that the β -diketone part was replaced by a water molecule and the basic bidentate Schiff base is converted to a tridentate.

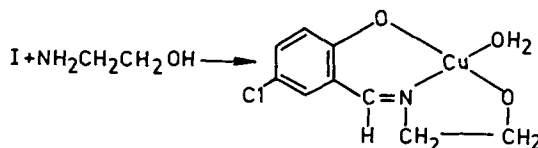


Chart 3.

2.4 Elemental analyses

Carbon, hydrogen and nitrogen were estimated by C-H and N Coleman analysers. Halogen was estimated by the well-known Carius method.

2.5 Metal contents in the complexes

The metal content of each of the complexes was estimated by volumetric analysis. Weighed quantities of metal chelates of copper(II) were decomposed with a mixture of perchloric acid, nitric acid, sulphuric acid and hydrochloric acid, all AR grade. After carefully evaporating to dryness, the residue in powder form was extracted with distilled water and diluted to a finite volume. The metal ion in solution was estimated by titration against standard EDTA solution using an appropriate indicator.

2.6 Physical measurements

The effective magnetic moments were calculated from the equation

$$\mu_{\text{eff}} = 2.83[(\chi_A - N_\alpha)T]^{1/2},$$

where χ_A is the molar magnetic susceptibility corrected using Pascal's constants and N_α is the temperature independent paramagnetism per gram-ion of copper (II). N_α was assumed to be 60×10^{-6} cgs (Muto and Tukki 1972).

TLC analysis of all the complexes was carried out on silica gel (Sichem) using a mixture of chloroform and ether (6 : 4) as solvent. The solvent was selected after several trials. Solutions of the copper (II) complexes were prepared. The solution indicated two spots in TLC whereas the mixed ligand complex is pure and a single compound rather than the mixture of *bis* complexes of the two ligands.

Conductivity measurements were carried out in chloroform using a Toshniwal conductivity bridge, model CLO/O1A.

ESR measurements of the powdered samples were carried out at room temperature on a Varian E-4 EPR spectrometer operating at 9.5 GHz with 100 kHz field modulation.

Reflectance spectra in the visible region were recorded on a Beckman-Du-Spectrophotometer at room temperature fitted with a standard Beckman reflectance attachment; MgO (BDH) was used as diluent.

The infrared spectra of the complexes were taken as KBr pellet on a Perkin-Elmer 983 IR spectrophotometer. Percentage transmission was recorded against wave number.

3. Results and discussion

The aldehyde part undergoes Schiff base formation. The β -keto-anilides, however, remain unaffected. No Schiff base formation takes place in the β -ketoanilide part of the molecules. The amine exchange reaction proceeds by a nucleophilic attack of the exchanging amine on the electron deficient carbon of the polarised imine (Olszowski and Martin 1965). Amine exchange was carried out using excess amine and employing amine as the reaction solvent.

In the amine exchange reaction with ethanolamine the β -ketoanilide part (acetoacetanilide part) is completely removed and the aldimine part reacts with ethanolamine to form a tridentate ligand, in which the $-\text{OH}$ group of ethanolamine provides the third coordination site, the final compound (III) attained is tetracoordinated through coordination of water molecules (Bhattacharya and Uma 1979).

The elemental analyses of Cu(II) complexes are in agreement with the suggested structures (table 1). All the Schiff base complexes obtained are soluble in chloroform. They are found to be non-conducting, indicating their non-electrolytic nature.

All the Cu(II) complexes are paramagnetic showing the presence of one unpaired electron. The room temperature magnetic moments in the present amine exchange complexes lie in the range 1.8–2.0 B.M. (table 2) are within the range expected for square planar Cu(II) complexes (Hathaway and Thomlinson 1970).

The diffuse reflectance spectra of copper(II) mixed ligand complex and its amine exchange are shown in figure 1 and summarized in table 2. Copper(II) mixed ligand complex, derived from $\text{SB}_1\text{-AAA}$ exhibits two bands at 16,395 and 25,640 cm^{-1} and is consistent with square planar stereochemistry (Aly and Asmal 1981). The first band is assigned to $d-d$ transition while the band at 25,640 cm^{-1} can be attributed to charge transfer or interligand transition (Dave *et al* 1974). All the amine exchange complexes showed these two bands in the region 15000–17000 cm^{-1} and 24000–26000 cm^{-1} respectively.

Table 1. Analytical data of $[\text{Cu-SB}_1\text{-AAA}]$ and its amine exchange complexes.

| Compound | Experimental (theoretical) % | | | | |
|---|------------------------------|------------------|----------------|-----------------|------------------|
| | Metal | Carbon | Hydrogen | Nitrogen | Halogen |
| Cu-SB ₁ -AAA | 16.47 (16.14) | 50.84 (51.47) | 3.39 (3.80) | 7.42 (7.106) | 9.39 (9.01) |
| Cu-SB ₁ M-AAA | 14.6 (15.57) | 52.57 (52.94) | 4.0 (4.16) | 6.54 (6.86) | 8.32 (8.70) |
| Cu-SB ₁ NB-AAA | 13.92 (14.76) | 55.79 (56.0) | 4.78 (5.1) | 6.08 (6.22) | 7.59 (7.88) |
| Cu-SB ₁ A-AAA | 14.21 (13.95) | 58.96 (58.72) | 3.72 (4.04) | 5.67 (5.95) | 7.29 (7.55) |
| Cu-SB ₁ MT-AAA | 13.38 (13.13) | 59.11 (59.61) | 4.1 (4.33) | 5.52 (5.78) | 7.15 (7.33) |
| Cu-SB ₁ PT-AAA | 14.24 (13.13) | 59.34 (59.51) | 4.16 (4.33) | 5.6 (5.78) | 7.46 (7.33) |
| Cu-SB ₁ PA-AAA | 12.08 (12.07) | 57.96 (57.6) | 4.44 (4.2) | 5.84 (5.6) | 6.83 (7.1) |
| Cu-SB ₁ PP-AAA | 12.13 (11.72) | 55.07 (55.45) | 4.1 (4.25) | 5.33 (5.17) | 6.33 (6.56) |
| Cu-SB ₁ N-AAA | 12.18 (12.82) | 61.03 (60.60) | 4.54 (4.24) | 5.38 (5.65) | 6.87 (7.17) |
| $[\text{Cu-SB}_1\text{E}]\cdot\text{H}_2\text{O}$ | 24.21 (22.78) | 39.24 (38.70) | 3.24 (3.58) | 5.19 (5.01) | 12.49 (12.78) |

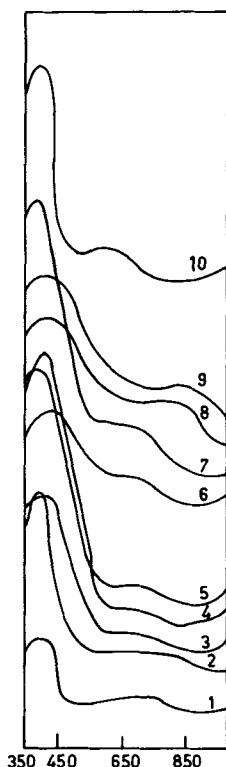


Figure 1. Reflectance spectra of copper(II) complexes.

1. Cu-SB₁-AAA;
2. Cu-SB₁M-AAA;
3. [Cu-SB₁E]·H₂O;
4. Cu-SB₁NB-AAA;
5. Cu-SB₁A-AAA;
6. Cu-SB₁MT-AAA;
7. Cu-SB₁PT-AAA;
8. Cu-SB₁PA-AAA;
9. Cu-SB₁PP-AAA;
10. Cu-SB₁N-AAA.

The ESR spectra of powder samples of Cu-SB₁-AAA and Cu-SB₁A-AAA have $g_{\perp} = 2.0027$ and $g_{\perp} = 2.025$, respectively. It may be concluded that square planar geometry is possible around copper(II) (Gajapathy *et al* 1983).

The IR spectra of mixed ligands complexes are complicated and difficult to interpret. However, only those peaks that could be assigned with reasonable certainty are listed. Mixed imine Schiff base complexes of Cu(II) show stretching frequency at 1605 cm^{-1} when R is H, which disappears after amine exchange reaction and a new band appears around 1630 cm^{-1} (table 3). The band at 1615 cm^{-1} is due to $\nu\text{ C=N}$ of the imine linkage. The band around 1570 cm^{-1} is due to $\nu\text{ C=O}$ of diketone. There is also a band around 3220 cm^{-1} corresponding to the free $\nu\text{ N-H}$ of diketone. This band indicates that there is no bonding through the nitrogen of the diketone.

The IR spectrum of complex [Cu-SB₁E]·H₂O exhibits a broad band around 3410 cm^{-1} corresponding to O-H stretch, confirming the presence of water. There is also a band around 800 cm^{-1} corresponding to the O-H out-of-plane deformation. This indicates the presence of coordinated water.

A further examination of the IR spectra, indicates that the copper is coordinated through C=N and the oxygen of water molecule. The C=N stretching frequency is observed at 1630 cm^{-1} (Nakamoto 1970). The disappearance of the $\nu\text{ N-H}$ band present at $3200\text{--}3300\text{ cm}^{-1}$ and $\nu\text{ C=O}$ at $1510\text{--}1590\text{ cm}^{-1}$ indicate removal of the β -diketone part. A medium band observed at 660 cm^{-1} is assigned to the Cu-O stretching vibration (Samantaray *et al* 1983).

Table 2. Spectral (electronic and ESR) and magnetic moment data of Cu-SB₁-AAA and its amine exchange complexes.

| Compound | Absorption maxima (cm ⁻¹) | Assignment | <i>g</i> _⊥ value | Magnetic moment (B. M.) |
|---|---------------------------------------|--|-----------------------------|-------------------------|
| Cu-SB ₁ -AAA | 16,395 25,640 | ² B _{1g} - ² A _{1g} Charge transfer | 2.00277 | 1.8 |
| Cu-SB ₁ M-AAA | 15,615 25,925 | Charge transfer | — | 1.83 |
| Cu-SB ₁ NB-AAA | 16,360 24,995 | Charge transfer | — | 1.89 |
| Cu-SB ₁ A-AAA | 16,190 24,990 | Charge transfer | 2.025 | 1.97 |
| Cu-SB ₁ MT-AAA | 16,715 24,965 | Charge transfer | — | 1.9 |
| Cu-SB ₁ PT-AAA | 16,530 24,770 | Charge transfer | — | 1.86 |
| Cu-SB ₁ PA-AAA | 16,480 25,645 | Charge transfer | — | 1.93 |
| Cu-SB ₁ PP-AAA | 15,145 24,990 | Charge transfer | — | 1.84 |
| Cu-SB ₁ N-AAA | 15,875 24,895 | Charge transfer | — | 2.0 |
| [Cu-SB ₁ E]·H ₂ O | 15,530 25,640 | Charge transfer | 2.019 | 1.78 |

Table 3. Infrared frequencies of Cu-SB₁-AAA and its amine exchange complexes (cm⁻¹).

| Compound | Group | | | | | |
|---|----------------|----------------|---------------|---------------|--------------|------------------|
| | N-H | C=N | C=O | m-O | M-N | H ₂ O |
| Cu-SB ₁ -AAA | 3220 <i>b</i> | 1615 <i>s</i> | 1570 <i>m</i> | 690 <i>s</i> | 515 <i>w</i> | — |
| Cu-SB ₁ M-AAA | 3280 <i>b</i> | 1635 <i>s</i> | 1550 <i>s</i> | 665 <i>ms</i> | 500 <i>w</i> | — |
| Cu-SB ₁ NB-AAA | 3285 <i>mb</i> | 1620 <i>s</i> | 1590 <i>s</i> | 670 <i>m</i> | 545 <i>m</i> | — |
| Cu-SB ₁ A-AAA | 3260 <i>w</i> | 1615 <i>s</i> | 1590 <i>m</i> | 680 <i>mw</i> | 545 <i>w</i> | — |
| Cu-SB ₁ MT-AAA | 3245 <i>w</i> | 1625 <i>ms</i> | 1580 <i>s</i> | 700 <i>s</i> | 535 <i>b</i> | — |
| Cu-SB ₁ PT-AAA | 3260 <i>b</i> | 1610 <i>m</i> | 1590 <i>m</i> | 680 <i>m</i> | 540 <i>m</i> | — |
| Cu-SB ₁ PA-AAA | 3230 <i>b</i> | 1620 <i>s</i> | 1515 <i>m</i> | 680 <i>m</i> | 545 <i>b</i> | — |
| Cu-SB ₁ PP-AAA | 3250 <i>mb</i> | 1630 <i>s</i> | 1555 <i>s</i> | 660 <i>m</i> | 530 <i>b</i> | — |
| Cu-SB ₁ N-AAA | 3290 <i>b</i> | 1625 <i>s</i> | 1575 <i>s</i> | 675 <i>m</i> | 520 <i>b</i> | — |
| [Cu-SB ₁ E]·H ₂ O | — | 1630 <i>s</i> | — | 660 <i>s</i> | 540 <i>w</i> | 3410 <i>b</i> |

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