

Investigations on some Amino Complexes of Copper(II) Phthalimide. I

## Preparation and Preliminary Investigations

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### Abstract

Co-ordination complexes between copper(II) phthalimide and some aliphatic amines have been prepared. The molecular formulae on the basis of the percentages of constituent elements are  $\text{Cu}(\text{Phthalimide})_2 \cdot (\text{amine})_2$ . Conductivity measurements in nitrobenzene indicate the complexes to be nonelectrolytes and hence it is suggested that phthalimide ions are also co-ordinated. Molecular weight measurements in the same solvent confirm this.

### Introduction

A survey of the literature shows that a large number of copper complexes with ammonia and various amines have been studied. However, only a few solid complexes, have been prepared with aliphatic amines as ligands<sup>1) 2)</sup>. There are also a number of evidences to suggest that the nature of the anion is a contributing factor towards stability<sup>3)</sup> coordination number<sup>4)</sup> and colour<sup>5)</sup> of the complexes. Although an extensive series of investigations with inorganic salts of copper are reported, comparatively very little work of this type has been done with the organic salts<sup>6) 7)</sup>.

We have undertaken the study of a series of complexes prepared with copper phthalimide and a number of aliphatic amines, with a view to find out:

- i) the effect of phthalimide ion on the properties of the complexes,

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ii) the possible changes this ion could bring about in the coordination number of copper and

iii) whether phthalimide ion besides neutralizing the charge of the metal, is also coordinated to it either through its nitrogen or through the oxygen of the carbonyl group.

In the present paper the synthesis and some of the preliminary investigations as regards the molecular weight and conductivity measurements are reported. The complexes have been prepared with ammonia, methyl, ethyl, propyl, butyl, amyl, diethyl, dipropyl and dibutyl amines.

## Experimental

### I. Synthesis

The complexes have been prepared by using the following two general methods.

#### (i) Preparations involving the use of copper metal and phthalimide

About 1 gm of copper foil purified with nitric acid and washed several times with water, alcohol and ether was placed in a conical flask, along with 4 gms of phthalimide. 25 cc of 95% alcohol and then a little more than the calculated quantity of amine was added to it. The neck of the flask was connected to a balloon filled with oxygen and the mixture was shaken for 6 hours. The fluffy copper bronze complex was left overnight, filtered and recrystallized.

#### (ii) Method involving the use of copper(II)phthalimide

This procedure involved 2 steps.

##### (a) Preparation of copper (II) phthalimide

It was prepared by treating copper sulphate pentahydrate with potassium phthalimide in 1:4 ratio. The blue precipitate was washed several times with water, then dried over  $P_2O_5$  and analysed. (Found Cu = 17.8%, N = 7.85%, C = 46.80%, H = 3.80%,  $C_{16}H_8O_4N_2$ . Cu requires Cu = 17.8%, N = 8.05%, C = 47.2%, H = 4.20%).

##### (b) Preparation of complexes

500 mgm of this was suspended in 15 cc of acetone and was shaken with approximately 2.5 mole of amine for two hours. Resulting complex was filtered and recrystallized. The percentage composition of the individual complexes and the solvents used for recrystallization are given below:

#### Bi phthalimido, bi(ammino) copper(II)

Recrystallized from acetone containing a few drops of ammonia. (Found Cu = 16.00%, N = 14.39%, C = 50.31%, H = 3.71%,  $C_{16}H_{14}O_4N_4$ . Cu requires Cu = 16.5%, N = 14.32%, C = 50.02% and H = 3.50%).

#### Bi phthalimido, bi(methylamino) copper(II)

Recrystallized from acetone containing a little of methylamine. (Found Cu = 15.1%, N = 13.52%, C = 51.64%, H = 4.98%;  $C_{18}H_{18}O_4N_4$ . Cu requires Cu = 15.40%, N = 13.49%, C = 51.82%, H = 4.95%).

**Bi phthalimido, bi(ethylamino) copper(II)**

Recrystallized from nitrobenzene and washed repeatedly with alcohol to remove excess of solvent. (Found Cu = 14.21%, N = 12.39%, C = 53.51%, H = 4.53%;  $C_{20}H_{22}O_4N_4$ . Cu requires Cu = 14.9%, N = 12.62%, C = 53.93% and H = 4.92%).

**Bi phthalimido, bi(n-propylamino) copper(II)**

Recrystallized from chloroform containing a drop of amine. (Found Cu = 13.2%, N = 11.79%, C = 56.37%, H = 5.31%;  $C_{22}H_{26}O_4N_4$ . Cu requires Cu = 13.45%, N = 11.70%, C = 56.00% and H = 4.95%).

**Bi phthalimido, bi(iso-propylamino) copper(II)**

Recrystallized from chloroform. (Found Cu = 12.85%, N = 11.79%, C = 55.65%, H = 5.19%;  $C_{22}H_{26}O_4N_4$ . Cu requires Cu = 13.45%, N = 11.70%, C = 56.00%, H = 4.95%).

**Bi phthalimido, bi(n-butylamino) copper(II)**

Recrystallized from chloroform. (Found Cu = 11.55%, N = 10.85%, C = 63.63%, H = 7.19%;  $C_{24}H_{30}O_4N_4$ . Cu requires Cu = 11.95%, N = 11.02%, C = 63.01%, H = 7.25%).

**Bi phthalimido, bi(diethylamino) copper(II)**

Recrystallized from acetone. (Found Cu = 11.65%, N = 11.15%, C = 64.21%, H = 5.79%;  $C_{24}H_{30}O_4N_4$ . Cu requires Cu = 11.95%, N = 11.02%, C = 64.70% and H = 6.2%).

**Bi phthalimido, bi(di-n-propylamino) copper(II)**

Recrystallized from acetone containing a drop of amine. (Found Cu = 11.6%, N = 9.38%, C = 62.37%, H = 3.24%;  $C_{25}H_{35}O_4N_4$ . Cu requires Cu = 11.19%, N = 9.81%, C = 62.75%, H = 4.00%).

**Bi phthalimido, bi(di-iso-propylamino) copper(II)**

Recrystallized from acetone. (Found Cu = 11.75%, N = 9.72%, C = 62.50%, H = 3.30%;  $C_{25}H_{35}O_4N_4$ . Cu requires Cu = 11.19%, N = 9.61%, C = 62.75%, H = 4.00%).

**Bi phthalimido, bi(di-n-butylamino) copper(II)**

Recrystallized from acetone containing a drop of amine. (Found Cu = 10.50%, N = 9.50%, C = 57.97%, H = 3.51%;  $C_{32}H_{46}O_4N_4$ . Cu requires Cu = 10.35%, N = 9.05%, C = 56.80% and H = 3.15%).

**Bi phthalimido, bi(n-amyl-amino) copper(II)**

Recrystallized from chloroform. (Found Cu = 11.75%, N = 10.79%, C = 58.9%, H = 6.12%;  $C_{25}H_{34}O_4N_4$ . Cu requires Cu = 12.50%, N = 11.02%, C = 58.02%, H = 6.70%).

**II. Determination of Percentage of total Bases**

A known weight of copper phthalimide (0.1 gm) was refluxed with 10 cc of N/10 sulphuric acid for half an hour and then the unreacted acid was titrated with N/10 sodium

carbonate. The same weight of complex was also treated like wise. The percentage was calculated on the basis that two molecules of amine combine with 1 molecule of the acid.

### III. Molecular weight Measurements

The molecular weights were determined by the method of freezing point depression, using nitrobenzene as the solvent. As the complexes dissolve only to a very limited extent a BECKMANN Thermometer with a scale of 1 °C. and with a least count of 0.002 °C. was used. The thermometer was extremely sensitive to supercooling and hence a modified freezing point apparatus was constructed. A glass vessel containing the freezing point tube was placed in a copper cylinder filled with water maintained at 0.5 °C and constantly stirred with a mechanical stirrer. This cylinder was surrounded by another well lagged copper cylinder containing ice.

### IV. Conductivity Measurements

Measurements were done in nitrobenzene at a concentration of  $10^{-3}$  M. The cell used had a cell constant of 0.0245.

### V. Purification of Solvents

Alcohol used for synthesis was obtained by distilling rectified spirit twice. Acetone was of A. R. Grade. Nitrobenzene was purified first by steam distillation and then by distillation at reduced pressure after keeping it over calcium chloride for a week.

## Results

The percentages of constituent elements have been given along with the synthesis of complexes. The results of the determination of percentage of total bases, molecular weights and conductivity are tabulated below.

## Discussion

On the basis of the percentage of metal, carbon, hydrogen, nitrogen and total bases, the molecular formulae turn out to be  $\text{Cu}(\text{Phthalimide})_2 \cdot (\text{amine})_2$  showing that only two molecules of amine are added per molecule of copper phthalimide and that no water molecules are included. The complexes are all copper bronze in colour probably due to their anhydrous nature. These dissolve only in chloroform, nitrobenzene and formamide and the solution has the typical ink blue colour characteristic of cupric amine complexes.

The complexes appear to be quite stable as they do not decompose even if kept exposed to sulphuric acid for several weeks. But if warmed with acid or alkali, they decompose and blue copper phthalimide is formed. The apparent stability decreases as molecular weight of amine increases.

The complexes dissolve in nitrobenzene to give very dilute solution (concentration  $10^{-3}$  M) and the measurement of molar conductance of these

Table 1

No.	Formulae	Observed percentage of total bases		Calculated percentage	Molecular weight measurements			Molar conductance of 10 <sup>-3</sup> M solution
		Vol. of acid used for 0.1 gm	Difference		Observed percentage	Wt. of solute per 25 gms of solvent	$\Delta t$ (Depression)	
1.	Cu(Phth) <sub>2</sub>	4.3 cc	—	—	In soluble in nitrobenzene	—	—	—
2.	[Cu(Phth) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>o</sup>	9.7 cc	5.4 cc	9.00%	In soluble in nitrobenzene	—	—	—
3.	[Cu(Phth) <sub>2</sub> (CH <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	9.2 cc	4.9 cc	14.60%	0.025 gm	0.01 °C	415	0.45 mhos
4.	[Cu(Phth) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	10.8 cc	7.0 cc	25.01%	0.015 gm	0.012 °C	425	0.50 mhos
5.	[Cu(Phth) <sub>2</sub> (n-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	8.7 cc	4.4 cc	23.90%	0.05 gm	0.038 °C	440	0.52 mhos
6.	[Cu(Phth) <sub>2</sub> (iso-C <sub>3</sub> H <sub>7</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	8.4 cc	4.1 cc	24.00%	0.06 gm	0.024 °C	435	0.80 mhos
7.	[Cu(Phth) <sub>2</sub> (n-C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	8.6 cc	4.3 cc	28.60%	0.03 gm	0.018 °C	515	0.65 mhos
8.	[Cu(Phth) <sub>2</sub> (n-C <sub>5</sub> H <sub>11</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	9.7 cc	5.4 cc	32.80%	0.03 gm	0.01 °C	527	0.55 mhos
9.	[Cu(Phth) <sub>2</sub> (C <sub>4</sub> H <sub>10</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	10.0 cc	5.7 cc	43.85%	0.16 gm	0.025 °C	520	0.625 mhos
10.	[Cu(Phth) <sub>2</sub> (n-C <sub>6</sub> H <sub>14</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	9.8 cc	5.5 cc	56.50%	0.007 gm	0.012 °C	547	0.612 mhos
11.	[Cu(Phth) <sub>2</sub> (iso-C <sub>6</sub> H <sub>14</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	9.9 cc	5.7 cc	57.85%	0.006 gm	0.011 °C	540	0.642 mhos
12.	[Cu(Phth) <sub>2</sub> (C <sub>8</sub> H <sub>18</sub> NH <sub>2</sub> ) <sub>2</sub> ] <sup>o</sup>	9.9 cc	5.6 cc	70.82%	In soluble in nitrobenzene	—	—	—

Phth in the above table represents Phthalimide.

solutions gives a value varying from 0.5—0.8 mhos. This value being less than 1 indicates, that these complexes behave as nonelectrolytes<sup>8)</sup>. When a voltage is applied to two platinum electrodes dipping in this nitrobenzene solution in a U tube, no migration of the blue colour towards the negative electrode was noticed, showing, thereby that the complexes do not ionize.

The freezing point determinations in nitrobenzene give the normal absolute value of molecular weight. These results suggest that phthalimide ion is inside the coordination sphere, along with the two amine ligands. The formulae of the complexes must therefore be written as  $[\text{Cu}(\text{Phth})_2(\text{am})_2]^\circ$  and not as  $[\text{Cu}(\text{am})_2]^{+2}\text{Phth}_2$ .

If, however, the coloured solution of these in nitrobenzene or formamide is passed through a column containing a cationic resin either I. R. 120 (H) or I. R. (C) 50, the solution coming down is colourless. The introduction of the hydrogen ions of resin in solution is analogous to treating the complex with an acid. Therefore complex decomposes due to its unstable nature. It is the  $\text{Cu}^{+2}$  ion which is being absorbed and not  $[\text{Cu}(\text{am})_2]^{+2}$  ion.

The structure of the complexes is under investigation. The I. R. magnetic susceptibility and absorption spectrophotometrical investigations are nearing completion and it is hoped that these results will help in establishing the structure of the complexes and the site of the attachment of the phthalimide ion to copper.

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