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# Complexation Studies of Copper (II) with Some S-phenyl mercaptoacetic Acids

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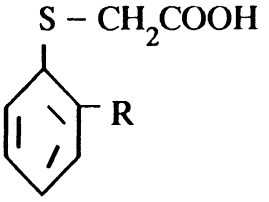
The proton-ligand stability constants of s-phenylmercaptoacetic acid,*ortho*-fluoro-s-phenylmercaptoacetic acid and *ortho*-methoxy-s-phenylmercaptoacetic acid and stepwise formation constants of copper(II) with these ligands have been determined in 50% (v/v) dioxane-water medium using Calvin-Bjerrum pH titration technique as modified by Irving and Rossotti. The stability constants of the complexes follow the order; parent acid > —$OCH_3$ > —F. The variations in the magnitude of the stability constants are accounted by considering the participation of sulphur also in coordination.

## INTRODUCTION

Phenoxyalkanoic acid (PAA) and substituted phenoxyalkanoic acids have interesting complexing modes apart from the usual coordination through hydroxyl oxygen (monodentate ligand)[1, 2] and through hydroxyl and carbonyl oxygen (bidentate ligand).[3] Prout *et al.*[4] have reported a different bidentate behaviour of phenoxyacetic acid in $[Cu(PAA)_2(H_2O)_2]$ in which the ligand is coordinated to copper through ether oxygen and hydroxyl oxygen. Moreover, participation of carbonyl and ether oxygen also in coordination in $[CuL_2(H_2O)_2]$ where L is *para*-chlorophenoxyacetato or *para*-methoxyphenoxyacetato[5] has been reported in literature. Little attention has been paid to the complexing mode of the analogous thio-acids *i.e.*, s-phenylmercaptoacetic acid. It has been reported previously that thioether-S enters into coordination in $[Cu(H_2O)_2L_2]$[6] where L is isopropyl thioacetate. Though few studies have been made regarding the stabilities of phenoxyalkanoic acid complexes[7, 8] no work has been done on the stabilities of analogous s-phenylmercaptoacetic acid complexes.

The substituents in the benzene ring, especially *ortho*-substituents are expected to have a marked effect on the stabilities of the s-phenylmercaptoacetic acid complexes, if sulphur is involved in coordination. Therefore the present investigation was undertaken to find whether sulphur is involved in coordination or not in *ortho*-substituted s-phenylmercaptoacetic acid complexes. This paper deals with the potentiometric determination of stability constants of s-phenylmercaptoacetic acid (I) *ortho*-fluoro-s-phenylmercaptoacetic acid (II) and *ortho*-methoxy-s- phenylmercaptoacetic acid (III) with copper (II) in 50% dioxane-water medium. The effect of *ortho* substituents on the proton-ligand stability constants and metal-ligand stability constants has also been studied in detail.



(I) R = H; (II) R = F; (III) R = —$OCH_3$.

## EXPERIMENTAL

Stock solution of copper(II) was prepared from AR grade copper sulphate and standardised by known procedure.[9] Ligands I. II, and III were prepared following the method of Gabriel[10] and recrystallised from alcohol. The melting points are 63° (I), 88° (II) and 116°C (III). The stock solution of the ligand was prepared in dioxane. A digital pH/mv meter (DPH 14, accuracy ± 01 pH) with glass and calomel electrode assembly was employed for pH measurements.

The experimental procedure involves potentiometric titrations in 50% (v/v) dioxane-water medium of carbonate free-solutions of

(1) perchloric acid ($2{\cdot}0 \times 10^{-3}$ M)
(2) perchloric acid ($2{\cdot}0 \times 10^{-3}$ M) + ligand ($1{\cdot}0 \times 10^{-2}$ M)
(3) perchloric acid ($2{\cdot}0 \times 10^{-3}$ M) + ligand ($1{\cdot}0 \times 10^{-2}$ M) + metal ion solution ($2{\cdot}0 \times 10^{-3}$ M)

against standard carbonate free NaOH (0.2 M). The total volume was kept as 50 mL in each case. The temperature of the solution was maintained at 35 ± .01°C and the ionic strength of the solution was maintained constant (0.1 M) by the addition of 1 M sodium perchlorate. The titrations were carried out in an inert atmosphere by bubbling oxygen-free nitrogen gas through an assembly containing the electrodes in order to keep away $CO_2$.

## RESULTS AND DISCUSSION

From the titration curves, the average number of protons associated with the ligand $\bar{n}_A$, average number of ligands associated with the metal $\bar{n}$, and free ligand exponent ρL were calculated by employing the relationships derived by Irving and Rossotti[11]. From $\bar{n}_A$–pH relationship the protonation constant of the ligand *i.e.*, log $K^H$ were calculated[12] by Bjerrum's half-integral method and graphical method and the average of these values is taken as the best values of log $K^H$. The formation curves for the metal-ligand complex system were constructed by plotting $\bar{n}$–ρL relationship. These plots indicate that the value of $\bar{n}$ obtained is of the order of two for all the systems. Bjerrum's half-integral method, graphical method and least square treatment were used to calculate log $K_1$ and log $K_2$.[12] Averages of all these values are taken as the best values. The values of proton-ligand stablility constants and metal-ligand stability constants thus obtained in this manner are presented in Table 1.

TABLE-1
PROTON-LIGAND AND METAL-LIGAND STABILITY CONSTANTS OF SOME MERCAPTOACETIC ACID COMPLEXES OF COPPER(II)

| Ligands | Proton-ligand formation constants | Methods | | Average |
|---|---|---|---|---|
| | | Bjerrum's half-integral | Graphical | |
| s-phenylmercapto-acetic acid (I) | $\log K^H$ | 4.76 | 4.73 | 4.75 |
| *Ortho*-fluoro s-phenyl mercaptoacetic acid (II) | | 4.78 | 4.77 | 4.78 |
| *Ortho*-methoxy-s-phenylmercapto-acetic acid (III) | | 4.86 | 4.79 | 4.83 |

| System | Metal-ligand formation constants | Methods | | | Average |
|---|---|---|---|---|---|
| | | Bjerrum's half-integral | Graphical | Least square | |
| Cu(II)-s-phenyl-mercaptoacetic acid | $\log K_1$<br>$\log K_2$<br>$\log \beta_2$ | 2.55<br>1.80<br>4.35 | 2.51<br>1.83<br>4.34 | 2.40<br>1.82<br>4.22 | 4.30 |
| Cu(II)-*ortho*-fluoro-s-phenylmercapto-acetic acid | $\log K_1$<br>$\log K_2$<br>$\log \beta_2$ | 2.55<br>1.64<br>4.19 | 2.54<br>1.70<br>4.24 | 2.18<br>2.00<br>4.18 | 4.20 |
| Cu(II)-*ortho*-methoxy-s-phenylmercapto-acetic acid | $\log K_1$<br>$\log K_2$<br>$\log \beta_2$ | 2.50<br>1.66<br>4.16 | 2.45<br>1.63<br>4.08 | 2.26<br>1.85<br>4.11 | 4.12 |

The order of proton-ligand stability constants is found to be $—OCH_3 > —F >$ parent acid. The ability of sulphur atom to accept electrons from the methoxy group (electron releasing group) by entering into d-orbital resonance is responsible for the higher value of the protonation constant of the *ortho*-methoxy compound (III). Fluorine can exert both electron withdrawing inductive effect (–I) and electron- releasing mesomeric effect (+M). The combined effect is responsible for the lower value of the protonation constant of *ortho*-fluoro compound 2 relative to *ortho*-methoxy compound (III). The predominance of the mesomeric effect over the inductive effect in the *ortho*-fluoro compound (II) is responsible for its high value of $\log K^H$ compared to the parent compound (I).

Metal-ligand stability constants however follow the order

parent acid $> —OCH_3 > —F$

In these systems one should expect a correlation between the proton-ligand stability constants and the metal-ligand stability constants if sulphur is not involved in coordination. But the results reveal that the metal-ligand stability constants are slightly lower for *ortho*-substituted s-phenylmercaptoacetic acid complexes compared to the s-phenylmercaptoacetic acid complex. This necessitates that sulphur also should take part in coordination. As result a five-membered ring is formed during complexation (Fig. 1).

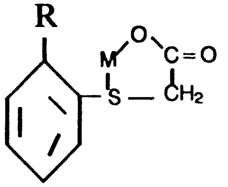


Fig. 1

The presence of bulky *ortho*-substituents in benzene ring decreases the stability of the five-membered ring due to steric effect. In the *ortho*-methoxy complex +M effect of methoxy group stabilises the complex whereas steric effect destabilises the complex. However, in *ortho*-fluoro complex in addition to the above two effects destabilisation occurs due to –I effect of fluorine substituent also. This is responsible for the lower value of the metal-ligand stability constant of the *ortho*-fluoro complex compared to *ortho*-methoxy complex.

The probable structures of the 1 : 1 and 1 :2 complexes are

$$[Cu(O_2C\ CH_2SC_6H_4R)(H_2O)_4]$$

and

$$[Cu(O_2C\ CH_2SC_6H_4R)_2(H_2O)_2]$$

where R is —H, —$OCH_3$ or —F.

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