Studies on Mixed Complex of Copper(II) with Orthophenylene-
diamine and Salicylic Acid

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A detailed study of the system Cu(II)-Salicylic acid-Orthophenylenediamine has been carried out by potentiometric and conductometric methods. These studies show the formation of a mixed complex

\[
\text{C}_2\text{H}_4\text{O}^-(\text{COO})\text{Cu}^2+\text{H}_2\text{N}^-(\text{NH})\text{C}_6\text{H}_4\text{N}^2+2\text{H}_2\text{O}
\]

which has been further confirmed by the preparative studies.

The orthophenylenediamine derivatives of various metals have been studied by a number of workers. The existence of copper-orthophenylenediamine complex has been reported during the kinetic studies of auto-

The formation constants of two Cu(II)-orthophenylenediamine complexes, Cu(II)L, Cu(II)L₂ in aqueous solution have been evaluated by potentiometrical and spectrophotometrical methods by the above authors. The properties of some five coordinated Cu(II)-mixed complexes of the type, [Cu(Che-
late)₃L₂(CIO₄)₂] containing 1,10 Phenanthroline or 2,2' bipyridine and a neutral ligand molecule (L = NH₃, Pyridine and imidazole on oxidation rate of amine in presence of Cu(II) catalyst.

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late)₃L₂(CIO₄)₂] containing 1,10 Phenanthroline or 2,2' bipyridine and a neutral ligand molecule (L = NH₃, H₂O and C₆H₅CN), have been studied and structures suggested by Harris and coworkers.

The tendency of Cu(II) of coordinating itself with more than one ligand simultaneously to form mixed complex referred to above, exhibiting an unusual five coordination number, is rather interest-

Experimental

Materials: Copper Nitrate [Cu(NO₃)₂·3H₂O] used was E. Merck G. R. product. It was dissolved in doubly distilled water and the solution standardised iodometri-
cally.

Salicylic acid (A. R. BDH) and orthophenylenediamine (E. Merck L. R.) were used. The amine was recrystallised twice from alcohol.

Stock solutions: 0.01 M solution of salicylic acid was prepared by dissolving appropriate amount of salicylic acid in doubly distilled water.

0.01 M solution of orthophenylenediamine hydrochloride was prepared by dissolving the calculated amount of amine in calculated volume of 0.1 N hydro-
chloric acid. The solution was kept well stoppered.

KOH pallets of (A. R. BDH) grade were dissolved; the solution was standardised and kept protected from atmosphere.

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4 C. M. HARRIS, T. N. LOCKER, and Coworkers, Nature [Lon-
don] 192, 424 [1961].

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The solution of the desired concentrations were prepared by subsequent dilution of the stock solution with doubly distilled water.

**Instruments:** pH studies were carried out with a Cambridge bench pH meter at room temperature (32 °C). The instrument was first standardised against 0.05 M solution of potassium hydrogen phthalate for pH 4.

Tesla Conductivity Bridge (model Tesla RLC Bridge) and Phillips dip type conductivity cell were employed for conductivity measurements.

**Potentiometric studies:** The following solutions were titrated against $4 \times 10^{-2}$ M KOH. The results have been shown in curves (1), (2), (3), (4), (5) and (6) in fig. 1. The ionic strength was maintained constant with the help of ($\mu = 0.1$) KNO$_3$ throughout these investigations.

**Discussion**

Curve (1) Fig. 1: A sudden inflection on adding one mole of alkali is due to the replacement of hydrogen of the carboxy group of salicylic acid and exhibits the formation of C$_6$H$_5$(OH)(COOK).

Curve (2) Fig. 1: It shows two inflections, the one at one mole and the other at 2 moles of KOH. These inflections represent the reaction of orthophenylendiamine hydrochloride with KOH liberating the free base.

\[
\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot 2 \text{HCl} + 2 \text{KOH} \rightarrow \text{C}_6\text{H}_4(\text{NH}_2)_2 + 2 \text{H}_2\text{O} + 2 \text{KCl} .
\]

This curve is similar to that obtained in the case of titration of a weak dibasic acid with a strong base. The inflection at one mole of KOH is not as sharp as that at two moles. This is probably due to the hydrolytic effect on the hydrochloride of orthophenylendiamine.

Curve (3) Fig. 1: The potentiometric titration of copper nitrate with KOH is similar to that obtained by Britton with an inflection at about 1.5 moles of alkali.

Curve (4) Fig. 1: represents the potentiometric titration of Cu(NO$_3$)$_2$ in presence of an equimolar concentration of salicylic acid with KOH and shows an inflection at about 2 moles, thus indicates the formation of (1:1) complex of Cu(II) with salicylic acid.

\[
\text{C}_6\text{H}_4(\text{OH}) \quad + \quad \text{Cu(II)} + 2 \text{OH}^- \rightarrow \quad \text{C}_6\text{H}_4 \text{Cu}^+ \text{OH}_2
\]

The donation of a lone pair of electrons from the hydroxy oxygen atom renders the hydroxy hydrogen atom more labile and acidic; therefore, the lowering in the pH takes place indicating the liberation of hydrogen ion and chelate formation. It is clear from the comparison of curves (3) and (4) that the latter curve begins at much lower pH 3.22. After ad-

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ding more than 2.5 moles of alkali, the dispropor-
tionation of (1:1) copper salicylic acid complex 
into (1:2) complex takes place with the precipita-
tion of bluish white \( \text{Cu(OH)}_2 \), finally changing to 
black. Similarly curve (5) fig. 1 exhibits a sharp 
inflection at 2 moles of alkali and probably repre-
sents the formation of 1:1 ionic complex of cop-

\[
\begin{align*}
\text{NH}_2\cdot\text{HCl} - \text{NH}_2\cdot\text{HCl} + \text{Cu(II)} + 2 \text{OH}^- & \rightarrow \\
\left[\begin{array}{c}
\text{NH}_2 \text{+} \text{Cu} \text{+} \text{OH}_2
\end{array}\right]^2+ + 2 \text{Cl}^-.
\end{align*}
\]

The comparision of curves (2) and (5), clearly 
shows a marked difference. In the latter curve the 
inflection at 2 moles of alkali, is quite sharp and 
there is no inflection at one mole of alkali, whereas 
the former curve shows an ill-defined inflection at 
one mole of alkali and a sharp rise in pH on adding 
2 moles of alkali. The sharp inflection in the curve 
(5) exhibits the liberation of free amine from its 
hydrochloride just prior to complexation.

Curve (6) Fig. 1 represents the formation of mixed 
complex of Cu(II) with salicylic acid and amine. As 
the curve (6) showing the potentiometric titration 
of Cu(II)-salicylic acid-orthophenylenediamine in 
equimolar ratio with KOH, runs below curves (4) 
and (5), representing the lowering tendency in pH, 
it can safely be correlated to the probable formation 
of a mixed complex of copper (II) with salicylic acid 
and orthophenylenediamine; the formation of which 
can be represented as follows:

\[
\begin{align*}
\text{OH} - \text{COOH} + \text{Cu(II)} + 2 \text{HCl}\cdot\text{H}_2\text{N}^- & \rightarrow \left[\begin{array}{c}
\text{CO} \text{+} \text{Cu} \text{+} \text{H}_2\text{N}^-
\end{array}\right] + 4 \text{OH}^-.
\end{align*}
\]

The inflection after adding more than 4 moles of 
alkali probably represents further reaction of the 
complex with alkali.

**Conductometric Studies**

Curves (1), (2), (3), Fig. 2 represent the con-
donometric titrations of 25 ml of 0.002 M ortho-

\[
\begin{align*}
\text{H}_2\text{O} + 2 \text{Cl}^-.
\end{align*}
\]


Composition of the Complex

Job's Method of continued variations\(^8\) was ap-
plied to establish the composition of the mixed com-
plex of Cu(II) with salicylic acid and orthophe-
nylenediamine, \( \text{Cu(II)} : \text{Sal. acid} : \text{Amine, 1:1:1} \). For this purpose, 0.005 M of copper (II)-Salicylic 
acid (1:1) complex solution was obtained by mixing

\[\text{Cu(II)} : \text{Salicylic acid} : \text{Ortho-phenylenediamine hydrochloride}; \text{25 ml of 0.002 M Cu(II) salicylic acid (1:1) complex; and a mixture of 25 ml of 0.002 M of Cu(II) salicylic acid (1:1) complex with 25 ml of 0.002 M ortho-phenylenediamine hydrochloride respectively with 0.1 M KOH solution. In curve (1) Fig. 2 the breaks at 1 and 2 moles of KOH represent the formation of free ortho-phenylenediamine from its hydrochloride. The replacement of two moles of HCl from the salt by 
KOH takes place in two stages. Curve (2) Fig. 2 shows a break at two moles of KOH and probably represents the formation of (1:1) complex of Cu(II) 
with salicylic acid, which takes place by the replacement 
of two protons, one from carboxy and the other from the hydroxy group of salicylic acid.

In curve (3) Fig. 2 the well defined break at 
4 moles of KOH is probably owing to the formation of a (1:1:1) mixed complex\(^6\) of Cu(II) with salicylic acid and orthophenylenediamine. The break 
at 2 moles of KOH is not, however, very sharp. 
Only one break at 4 moles of KOH, is due to the 
simultaneous chelation of one mole each of salicylic 
acid and orthophenylenediamine with one of 
Cu(II).

On comparing the three curves (1), (2) and (3) 
in Fig. 2 it can be inferred that the slope of curve 
(3) is very much different from those of curves (1) 
and (2). If there had been no complexation among 
the Cu(II) salicylic acid (1:1) complex and ortho-phenylenediamine, the curve (3) would have shown 
breaks at 1, 2 and 4 moles of KOH. Further, the 
curve (3) would not have shown a steep rise and 
instead would have been displaced towards curves 
(1) and (2) and had run almost parallel to 
them. In that case the slope of the curve (3) 
would have been more or less similar to that of 
curve (1) or (2). From this also, it can be safely 
inferred that probably the formation of a mixed 
ligand complex as stated above, has taken place\(^7\).

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\(^7\) H. B. Jonassen, J. inorg. nuclear Chem. 24, 1595 [1962].

\(^8\) P. Job, Ann. Chim. x, 9, 113 [1928].
Fig. 2. Moles of KOH/Moles [Cu (II) Sal-acid] + Moles of Amine-HCl.

equimolar solutions of copper nitrate and salicylic acid; 0.005 M of orthophenylenediamine hydrochloride solution was prepared by adding calculated volume of standard HCl solution to calculated amount of the amine. The solutions of Cu(II): Sal. acid (1:1) complex and orthophenylenediamine hydrochloride were mixed in different ratios ranging from 1:9 to 9:1. The total volume after dilution was always kept constant at 25 ml. The specific conductances of the mixtures were measured at 32 °C. Similarly the conductances of solutions of Cu(II): Sal. acid complex and orthophenylenediamine hydrochloride, having increasing concentration from 1 to 9 moles, were also measured separately. The deviations from the additivity rule (difference in conductances, A cond.) were calculated from the experimental values and plotted (Fig. 3).

The maximum at 0.5, establishing (1:1) complex between Cu(II):Sal. acid (complex) and orthophenylenediamine hydrochloride was obtained.

Preparative Studies

The results obtained by the above physico-chemical studies, have been confirmed further by isolating and analysing the mixed complex.

Fig. 3. Ratio: Moles of Cu Salicylic-acid(1:1) Complex Moles of Cu Sal.(1:1) Complex+ Moles of C₆H₄(NH₂)₂·2 HCl.

Salicylic acid (2.76 g) and orthophenylenediamine (2.16 g) were dissolved together in minimum amount of alcohol. The alcoholic solution of the two ligands was added to an aqueous solution of copper nitrate [Cu(NO₃)₂·3 H₂O] (4.83 g). The solution was mixed vigourously and the pH of the mixture was adjusted to about 5.2 by adding strong KOH solution. A deep green solid separated out. It was kept overnight and then filtered under suction. It was washed thoroughly with distilled water and finally with rectified spirit, and then dried at room temperature. The compound was analysed for copper and nitrogen. The results of the analysis are given below:

Found: Cu, 18.38 %, 18.25; N, 8.21 %, 8.29.

Calc. for C₆H₄\(\text{O}^-\text{Cu}^+\text{H}_2\text{N}^-\text{H}_2\text{N}^-\text{C}_6\text{H}_4\cdot2\text{H}_2\text{O}\) .
Cu, 18.48; N, 8.14.

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