Reactions

1. Reaction of uranium pentaethoxide with acetic acid (molar ratio 1:1)

Uranium pentaethoxide (1.075 g.) and acetic acid (0.1393 g.) were refluxed together in dry benzene (60 g.). After about four hours, the ethanol benzene azeotrope was fractionated at 68°C–80°C and the compound was dried at 40°C/0.4 mm. A brown powder (1.0 g.) sparingly soluble in benzene was obtained.

Found: Ethanol in the azeotrope 0.100 g. (one mole requires, 0.107 g.). U 50.13. Acetate, 13.0.
Calc. for U(OEt)₄(OOCCH₃)₂: U 49.9; Acetate 13.36.

Experimental details being the same as described above, the rest of the fractions of uranium pentaethoxide with acetic propionic, butyric, benzoic, and lactic acids are given in the tables I, II and III.

2. Reaction between Uranium Tetraethoxy monobenzoate and Tertiary butanol in excess

Uranium tetraethoxy monobenzoate (1.251 g.) was taken in benzene (55 g.). To this tertiary butanol (0.1393 g.) were refluxed together in dry benzene (1.0 g.) sparingly soluble in benzene was obtained.

Found: Ethanol in the azeotrope 0.42 g. (four moles require, 0.43 g.); U 37.05; Benzoate, 18.6.
Calc. for U(OBu)₄(OOCCH₃)₂: U 36.6; Benzoate, 18.6.

For brevity rest of the reactions are summarised in Table II.

The authors are indebted to Prof. R. C. MEHROTRA, Head, Chemistry Department, Rajasthan University, Jaipur, for valuable suggestions. Thanks are also due to Prof. R. C. KAPPOR, Head, Chemistry Department, Jodhpur University, Jodhpur, for providing laboratory facilities. One of the authors (S.D.) is greatful to the C.S.I.R., New Delhi (India) for research fellowship.

Potentiometric Studies on Stepwise Mixed Ligand Complex Formation

Cu(II), Ni(II), Zn(II) or Cd(II)-Iminodiacetic acid-Diamines

G. SHARMA and J. P. TANDON

Chemical Laboratories, University of Rajasthan, Jaipur (India)


Stepwise mixed ligand complex formation is observed in the systems containing metal ion, iminodiacetic acid (IMDA) as primary ligand and one of the diamines, such as ethylenediamine (en), 1,2-propanediamine (1,2-pn) and 1,3-propanediamine (1,3-pn) as secondary ligands. Potentiometric titrations indicate the formation of ternary complexes having a 1:1:1 molar ratio of metal ion to iminodiacetic acid to the secondary ligand. Initially, metal-IMDA (1:1) complex is formed in the lower buffer region prior to the formation of the ternary complex and the addition of the secondary ligand takes place only after the combination with the primary ligand is complete. Formation constants (log $K_{MAD}$) of the ternary complexes have been calculated and the probable reaction mechanism is suggested. The order of stability in terms of metal ion has been found to be Cu(II) > Ni(II) > Zn(II) > Cd(II) and in terms of secondary ligand as 1,2-pn > en > 1,3-pn.

Martell and coworkers ¹ reported that copper(II) forms with iminodiacetic acid a 1:1 complex with one water molecule to satisfy the fourth coordination number of the metal. Later on Bennett ² showed that the coordination number of Cu(II) can be extended to five by replacing the water molecule with a bidentate ligand, such as ethylenediamine and reported the formation of a ternary complex containing Cu(II), iminodiacetic acid and ethylenediamine in the ratio of 1:1:1. They also calculated the formation constant of the mixed ligand complex employing spectrophotometric data for the reaction:

$$\text{Cu} \cdot \text{IMDA} + \text{en} \rightleftharpoons \text{Cu} \cdot \text{IMDA} \cdot \text{en}.$$

It was, therefore, considered of interest to carry out potentiometric studies of the systems containing some bivalent metals, such as Cu(II), Ni(II), Zn(II)

¹ S. Chaberek, Jr., and A. E. Martell, J. Amer. chem. Soc. 74, 5652 [1952].
² W. E. Bennett, ibid. 79, 1290 [1957].
or Cd(II), iminodiacetic acid and some diamines, such as ethylenediamine, 1,2-propanediamine or 1,3-propanediamine as secondary ligands and to make a comparative study of the stabilities of the resulting 1:1:1 ternary complexes. In earlier communications from these laboratories, similar studies on Cu(II)-Iminodiacetic acid-Hydroxy acids and Cu(II), Ni(II) or Zn(II)-Nitrilotriacetic acid-Hydroxy acids have been reported.

Experimental

A stock solution of metal nitrates (AnalaR BDH) was prepared and standardized against a solution of disodium salt of ethylenediamine-tetraacetic acid using murexide (Cu²⁺ and Ni²⁺), eriochrome black T (Zn²⁺) and pyrocatechol violet (Cd²⁺) as an indicator. The hydrochlorides of the diamines were first prepared and then recrystallized several times. Their solutions as such as ethylenediamine, 1,2-propanediamine or 1,3-propanediamine were titrated with standard solutions of potassium hydroxide solution (0.1 M) and then recrystallized. The stoichiometry of the reaction mixtures was maintained approximately constant using 0.1 M potassium nitrate and low concentrations (5 x 10⁻³ M) of the ligand and metal ion.

All the pH titrations were carried out at room temperature (30 ± 1 °C) with a Cambridge pH Meter, standardized against a 0.05 M solution of potassium hydrogen phthalate.

Calculations

The acid dissociation constants of the secondary ligands, en and 1,2-pn were determined by the method of CHABEREK and MARTELL using separate neutralization steps. Overlapping dissociation constants of 1,3-pn were determined employing NOYES method (Table I). The formation constants (log K_{MAB}) of ternary complexes were calculated by the method of THOMPSON and LORAAS.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>pK₁</th>
<th>pK₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylenediamine</td>
<td>7.05 ± 0.02</td>
<td>9.75 ± 0.02</td>
</tr>
<tr>
<td>1,2-propanediamine</td>
<td>6.91 ± 0.03</td>
<td>9.78 ± 0.02</td>
</tr>
<tr>
<td>1,3-propanediamine</td>
<td>8.74 ± 0.02</td>
<td>10.24 ± 0.04</td>
</tr>
</tbody>
</table>

Table I. Ionization constants of secondary ligands, t=30 ± 1 °C, µ=0.1 (KNO₃).

Results and Discussion

When the solution of iminodiacetic acid is titrated, it gives a sharp inflection at a = 1 (a = moles of base added per mole of metal ion) in the low pH region and a poor inflection at a = 2 in the higher pH region indicating two separate neutralization steps due to the large difference in the dissociation constants of IMDA. However, titration curves for the secondary ligands indicate a small difference in their pK values and only one well defined inflection is observed at a = 1. In the case of 1,3-propanediamine, a poor inflection at a = 1 is due to its overlapping dissociation constants.

Solutions containing Cu(II), Ni(II) or Zn(II) and IMDA in equimolar proportions give one inflection at a = 2 indicating the formation of a 1:1 complex in the lower buffer region. In all the systems precipitation starts after a = 2 with one more inflection at a = 3. The colour of the supernatant liquid and nature of the precipitate clearly indicate the formation of 1:2 M(II)-IMDA complex and precipitation of half of the metal as metal hydroxide, which in the case of Cu(II) turns black on standing. On the other hand in the case of Cd(II)-IMDA system three inflections are observed. Inflection at a = 1 is due to the neutralization of the free proton of the carboxylic group of IMDA and another inflection at a = 2 indicates the complexation of the ligand to Cd(II). Beyond this precipitation occurs and one more mole of alkali is consumed resulting in the formation of 1:2 Cd(II)-IMDA complex and metal hydroxide with an inflection at a = 3.

Systems containing equimolar proportions of Cu(II), Ni(II), Zn(II) or Cd(II) with ethylenediamine and 1,2-propanediamine give two inflections at a = 2 and a = 3 except in the case of Zn(II)-en, which gives only one inflection at a = 3. Inflection at a = 2 is due to the 1:1 metal-diamine complex formation. After this precipitation starts and an inflection at a = 3 is obtained, indicating the probable disproportionation of 1:1 complex into 1:2 metal-diamine complex and precipitation of half of the metal as metal hydroxide. The change in colour from light blue to light violet in the case of Cu(II) and Ni(II) during the addition of 2 to 3 moles of base supports the above statement. In the case of

Zn(II)-en and Cu(II), Ni(II) or Cd(II)-1,3-pn systems precipitation starts after adding 1.8, 1.6, 1.3 and 0.5 moles of alkali respectively, which shows that the disproportionation of the 1:1 complex takes place before it is completely formed and only one break at \( a = 3 \) is observed. In Zn(II)-1,3-pn system precipitation starts from the beginning of the titration and an inflection is observed at \( a \sim 3 \).

In the mixed ligand systems (1:1:1); Cu(II)-IMDA-en, Cu(II)-IMDA-1,2-pn, Cu(II)-IMDA-1,3-pn, Ni(II)-IMDA-en, Ni(II)-IMDA-1,2-pn, Ni(II)-IMDA-1,3-pn (Figs. 1 and 2, curves 1–3), Zn(II)-IMDA-en and Zn(II)-IMDA-1,2-pn (Fig. 3, curves 1 and 2) two inflections at \( a = 2 \) and \( a = 4 \) are obtained. In the lower buffer region all these curves superimpose over the corresponding M(II)-IMDA curve and this indicates that initially M(II)-IMDA (1:1) complex is formed in the above systems. Deviation from the M(II)-IMDA curve starts after \( a = 2 \) and further inflection at \( a = 4 \) is due to the neutralization of the two protons attached to the diamines, which are given out during the mixed chelate formation. The lower pH in comparison to the corresponding theoretical composite curve\(^7\) (drawn by adding horizontal distance of the secondary ligand curve to the horizontal distance of the M(II)-IMDA curve at the same pH) (Figs. 1–3, curves 4–6) between \( a = 2 \)–4 clearly indicates the formation of a new specie, which can only be a ternary complex. Inflection at four moles of alkali shows the completion of 1:1:1 mixed ligand complex formation.

In systems involving Cd(II)-IMDA-en and Cd(II)-IMDA-1,2-pn (Fig. 4, curves 1 and 2) the first inflection is observed at \( a = 1 \) and the second at \( a = 4 \). In these cases also the experimental curve superimposes over the Cd(II)-IMDA curve upto \( a = 1.5 \) and the theoretical composite curve upto \( a = 2 \), which indicates that the ternary complex formation starts before the formation of the 1:1 Cd(II)-IMDA complex is complete. Similar observations have been made for the corresponding Zn(II) systems and the lower pH between \( a = 2 \)–4 in comparison to the theoretical composite curve shows the ternary complex formation.

Another evidence which confirms the formation of mixed ligand complexes is the change in colour of

---

\(^7\) G. H. Carey and A. E. Martell, J. Amer. chem. Soc. 89, 2859 (1967).
the solutions during the pH titrations. Initially, the colour of the Cu(II)-IMDA-diamine systems is light greenish blue, which changes to light blue during the addition of 0–2 moles of alkali and finally turns intense blue when 2–4 moles of the base are added. In the case of nickel systems the colour changes from light green to light blue.

Non-appearance of the precipitate in the 1:1:1 mixture during and after the completion of titration in the case of Cu(II) and Ni(II) also supports the mixed complex formation. The sequence of the reactions involved in these systems with ethylenediamine as an example of the secondary ligand may be summarized as follows:

\[
\begin{align*}
\text{Cu}^{2+} + \text{HHN} &\rightarrow \text{Cu}^0 + 2 \text{OH}^- \\
\text{Cu}^0 + \text{CH}_2\text{COO}^- &\rightarrow \text{Cu}^0 + \text{CH}_2\text{COO}^- \\
\text{NH} &\rightarrow \text{CH}_2\text{COO}^- + \text{Cu}^0 + \text{H}_2\text{N}^- \\
\text{NH} &\rightarrow \text{CH}_2\text{COO}^- + \text{Cu}^0 + \text{H}_2\text{N}^- \\
\text{NH} &\rightarrow \text{CH}_2\text{COO}^- + \text{Cu}^0 + \text{H}_2\text{N}^- \\
\end{align*}
\]

However, in Zn(II)-IMDA-1,3-pn and Cd(II)-IMDA-1,3-pn systems, the pH titration curves do not give any evidence for the mixed complex formation which is supported by the following facts:

1. Just after adding 2 moles of alkali precipitation starts.
2. No appreciable lowering of pH in comparison to the theoretical composite curve is observed in the range where ternary complex formation takes place in other systems.

<table>
<thead>
<tr>
<th>System</th>
<th>log $K_{MAB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)-IMDA-en</td>
<td>7.93 ± 0.03</td>
</tr>
<tr>
<td>Cu(II)-IMDA-1,2-pn</td>
<td>8.36 ± 0.04</td>
</tr>
<tr>
<td>Cu(II)-IMDA-1,3-pn</td>
<td>7.10 ± 0.02</td>
</tr>
<tr>
<td>Ni(II)-IMDA-en</td>
<td>6.32 ± 0.03</td>
</tr>
<tr>
<td>Ni(II)-IMDA-1,2-pn</td>
<td>6.45 ± 0.04</td>
</tr>
<tr>
<td>Ni(II)-IMDA-1,3-pn</td>
<td>5.29 ± 0.02</td>
</tr>
<tr>
<td>Zn(II)-IMDA-en</td>
<td>4.96 ± 0.08</td>
</tr>
<tr>
<td>Zn(II)-IMDA-1,2-pn</td>
<td>5.14 ± 0.06</td>
</tr>
<tr>
<td>Zn(II)-IMDA-1,3-pn</td>
<td>—</td>
</tr>
<tr>
<td>Cd(II)-IMDA-en</td>
<td>4.59 ± 0.10</td>
</tr>
<tr>
<td>Cd(II)-IMDA-1,2-pn</td>
<td>4.76 ± 0.09</td>
</tr>
<tr>
<td>Cd(II)-IMDA-1,3-pn</td>
<td>—</td>
</tr>
</tbody>
</table>

Table II. Formation constants of mixed ligand complexes, $t=30±1^\circ\text{C}$, $\mu=0.1$ (KNO$_3$).
Formation constants of mixed ligand chelates:
A comparison of the formation constants (log $K_{MAB}$) given in Table II indicates that the order of stability of the ternary complexes in terms of the metal ion is $Cu(II) > Ni(II) > Zn(II) > Cd(II)$ and in terms of secondary ligand as $1,2$-pn $> en > 1,3$-pn. The greater stability of ethylenediamine and 1,2-propanediamine complexes can be explained on the basis of ring size. In these cases five-membered rings are formed, whereas in 1,3-propanediamine due to the increased chain length six-membered ring formation takes place.

The authors are grateful to Dr. R. C. Mehrotra, Professor and Head of the Chemistry Department, University of Rajasthan, Jaipur, for providing facilities in the Department and wish to thank the CSIR, New Delhi, for the award of a Junior Research Fellowship to one of them (G. Sharma).

Potentiometric Studies on Mixed Ligand Complexes
Copper(II)-oxalic Acid-diamine
G. K. CHATURVEDI and J. P. TANDON

Chemical Laboratories, Agra College, Agra (India)


The potentiometric studies of the systems, copper(II)-oxalic acid and one of the diamines, o-phenylenediamine (phenen), ethylenediamine (en) and 1,2-diaminopropane (pn) have been carried out. These studies show the formation of mixed ligand complexes in which all the three species are present in the ratio of 1:1:1.

In earlier publications $^1$, $^2$, physico-chemical studies on the systems, copper(II)-o-phenylenediaminesalicylic or sulphosalicylic acids have been reported. A survey of the literature on the mixed (ternary) complexes revealed that spectrophotometric studies $^3$ on copper(II)-oxalic acid-en, potentiometric studies $^4$ on copper(II)-sulphosalicylic-1,2-diaminopropane and polarographic studies $^5$ on copper(II)-oxalic acid-en have already been carried out. However, potentiometric studies on the system, copper(II)-oxalic acid-diamines have not so far been described. It was, therefore, considered worthwhile to undertake detailed studies of these systems and in the present communication the results of the potentiometric studies have been presented. The diamines used are o-phenylenediamine (phenen), ethylenediamine (en) and 1,2-diaminopropane (pn).

Experimental

Materials: Copper nitrate $Cu(NO_3)_2 \cdot 3 H_2O$ used was E. Merck G.R. product. It was dissolved in doubly distilled water and standardised as described in an earlier communication $^1$. 0.025 $M$ copper nitrate was obtained by subsequent dilution of the stock solution. Oxalic acid (AnalR BDH) was directly weighed and its stock solution (0.025 $M$) was prepared. o-Phenylenediamine dihydrochloride solution (0.025 $M$) was prepared as described previously. Ethylenediamine and 1,2-diaminopropane (pn) were dissolved in doubly distilled water and the solutions standardised by titrating against 0.1 $M$ hydrochloric acid potentiometrically. 0.025 $M$ solutions of their hydrochlorides were prepared by adding twice the equivalent of hydrochloric acid to the calculated volumes of the respective amine solutions. The hydrochloride solutions were kept well stoppered.

Instrument: Cambridge pH Meter (Bench type) reading up to 0.02 was used. The pH measurements were recorded at the room temperature ($37 \pm 1 ^\circ C$).

Potentiometric studies: The volume of the solutions to be titrated was always kept constant (50 ml) by mixing with a requisite volume of double distilled water and the ionic strength was maintained constant ($\mu = 0.1$) with the help of $KNO_3$ throughout the investigations. For this purpose 5 ml of 1 $M$ $KNO_3$ was added to each of the following solutions titrated against 0.1 $M$ KOH solution.

3 W. E. BENNETT, J. Amer. chem. Soc. 79, 1290 [1957].