Hetero-ligand Binuclear Chelates of Cu(II), Ni(II) & Zn(II) with Diethylenetriaminepentaacetic Acid as the Primary Ligand & Tiron as the Secondary Ligand

(Miss) SUJATA KHANNA, RAJIV KUMAR & G. K. CHATURVEDI
Department of Chemistry, Agra College, Agra

Received 7 September 1979; revised 13 February 1980; accepted 3 March 1980

Mixed ligand chelates of Cu(II), Ni(II) and Zn(II) with diethylenetriaminepentaacetic acid (DTPA) and tiron (disodium 1,2-dihydroxybenzene-3,5-disulphonate) have been studied potentiometrically. Formation of 2:1, M(II)-DTPA, and 2:1:2, M(II)-DTPA-Tiron \( [\text{where M}(\text{II}) = \text{Cu}(\text{II}), \text{Ni}(\text{II}) \text{ or Zn}(\text{II})] \) binuclear chelates is suggested on the basis of experimental data. The formation constants of the resulting polynuclear species have been evaluated at \( 25 \pm 1^\circ \left( \mu = 0.1 \text{ M KNO}_3 \right) \).

Materials and Methods

Stock solutions of metal nitrates (AR, BDH) were prepared in doubly distilled water, and the metal contents of the solutions were estimated by the usual methods. Solution of tetrapotassium salt of DTPA (Fluka) was prepared by dissolving the weighed amount of free acid in calculated volume of 0.1 M potassium hydroxide. The solutions of tiron (GR, E. Merck) and potassium nitrate were prepared by direct weighing. The concentrations of all the solutions were checked potentiometrically.

The \( pH \) measurements were recorded with a Philips pHmeter (PR 9405 M) having a working accuracy of \( \pm 0.02 \) \( pH \) units, using standard glass (PV 9011) and calomel (PV 9021) electrodes. The instrument was standardised against 0.05 M potassium hydrogen phthalate for \( \text{pH} = 4 \) at \( 25 \pm 1^\circ \) (maintained thermostatically). The total volume (50 ml), ionic strength \( (\mu = 0.1 \text{ M KNO}_3) \) and concentration \( (5 \times 10^{-3} \text{ M in metal ion and ligand}) \) were kept constant at the beginning of electrometric titration. Each titration was performed in duplicate to establish the reproducibility of the measurements.

The acid dissociation constants of tiron \( (pK_1 = 7.66 \text{ and } pK_2 = 12.6) \) were taken from the literature. The \( pK \) value of \( K_4\text{DTPA} \) \( (10.10 \pm 0.10) \) was calculated by the method of Chaberek and Martell.

The formation constants of the 2:1:2 M(II)-DTPA-tiron complex, supposed to exist between \( m = 1 \text{ and } 5 \), were calculated assuming that four phenolic protons (two from each of the tiron molecules) are made labile resulting in the simultaneous addition of the two tiron molecules to the initially formed 2:1 M(II)-DTPA complex as expressed in the following reaction equilibria by Martell et al.

\[
M_2L+2A\rightleftharpoons M_2LA_2 \quad \text{K}_{2L}=[M_2LA_2][\{M_2L\}][A]^2
\]

The stability constants \( K_{2L} \) were calculated during the following expressions:

\[
K_{M_2L} \cdot X = \frac{T_{M_2L}}{\{M_2L\} \cdot \{A\} \cdot \{A\} \cdot \{H^+\} \cdot \{OH^-\}}
\]

Here, \( [A] \), the free ligand concentration is given by equation,

\[
[A]=\frac{2T_{M_2L}-T_{OH}-[H^++[OH^-]]/[2\{H^+\}^2/K_1K_2]+[H^+]/K_2}{(\{H^+\}/K_2)}
\]

and \( X=([H^+][K_1K_2]+[H^+]/K_2)+1 \)

(where \( T_{OH} \) is base used per mole of ligand)

The formation of 2:1:2 species was alternatively considered by the addition of the second tiron molecule to the initially formed 2:1:1 \( (M_2LA) \) species, probably formed between \( m = 1 \text{ and } 3 \). The addition of second tiron molecule to \( M_2LA \), however, occurs between \( m = 3 \text{ and } 5 \) in overlapping steps. The method of Thompson and Loraas was extended to study the following equilibria in order to calculate the formation constants of the mixed species.
(i) \[ M_2L + A \rightleftharpoons M_2LA; \quad K_{M2LA} = [M_2LA]/[M_2L][A] \quad \ldots (1) \]

(ii) \[ M_2LA + A \rightleftharpoons M_2LA_2; \quad K_{M2LA_2} = [M_2LA_2]/[M_2LA][A] \quad \ldots (2) \]

Since the acid dissociation constants of the ligand are:

\[ K_1 = [HA^-][H^+]/[H_2A] \] and

\[ K_2 = [H^+][A^{2-}]/[HA^-] \quad \ldots (2a) \]

\[ [HA^-] = [A^{2-}] [H^+]/K_2; \quad [H_2A] = [A^{2-}] [H^+]/K_1 \quad \ldots (2b) \]

Between \( m = 1 \) and 3, the following relationships can be employed,

\[ T_M = [M_2L] + [M_2LA] \quad \ldots (3) \]

\[ T_A = [H_2A] + [HA^-] + [A^{2-}] + [M_2LA] \quad \ldots (4) \]

Putting the value of \([HA^-]\) and \([H_2A]\) from Eqs. (2a) and (2b) in Eq. (4),

\[ [M_2LA] = T_A - \{[A^{2-}]/X, \quad \ldots (5) \]

Substituting the value of \([M_2LA]\) from Eq. (5) in Eq. (3),

\[ [M_2L] = T_M - \{T_A - (A)X \}

or \[ [M_2L] = T_A + (A)X \quad \ldots (6) \]

From the electroneutrality principle,

\[ aT_A + [H^+] - [OH^-] = [HA^-] + 2[A^{2-}] + 2[M_2LA] \quad \ldots (7) \]

Putting the value of \([M_2LA]\) from Eq. (4) in Eq. (7),

\[ aT_A + [H^+] - [OH^-] = 2T_A - 2[H_2A] - [HA^-] \quad \ldots (8) \]

Here \( a \) is the moles of base added per mole of ligand molecule A. On introducing ionisation constants from Eqs. 2a and 2b in Eq. (8), the free ligand concentration \([A^{2-}]\) is obtained,

\[ [A^{2-}] = \{2T_A - aT_A - [H^+] + [OH^-])/2[H^+] + 2[H^+]/K_1K_2 \quad \ldots (9) \]

From Eqs. (1), (5), (6) and (9), \( K_{M2LA} \) may be determined as,

\[ K_{M2LA} = \{T_A - \{[A^{2-}]X, \quad \ldots (10) \]

where \( T_M, T_A \) stand for total concentrations of ligand A and metal ion respectively.

The formation constants between \( m = 1 \) and 3 and \( m = 3 \) and 5 may be calculated using the above expressions.

**Results and Discussion**

Curve a in Fig. 1, representing the pH titration of two moles of tiron exhibits a single inflection at \( m = 2 \), which may be attributed to the neutralisation of two phenolic protons, one from each of the two tiron molecules. The absence of any inflection at \( m = 4 \) indicates that the remaining phenolic protons of both the tiron molecules remain non-labile during the titration.

Curve b Fig. 1 representing the titration of the system \( 2 : 1 \) M(II)-K₄DTPA exhibits an appreciable lowering in pH and a sharp inflection at \( m = 1 \), which may be attributed to the formation of \( 2 : 1 \) M(II)-DTPA complex, during which process the remaining carboxy proton of K₄DTPA is made labile. An additional inflection at \( m = 3, \) pH > 8 (except in the system Ni(II)-DTPA) may be ascribed to the disproportionation of \( 2 : 1 \) M(II)-DTPA complex,

\[ 0 < m < 1 \quad 1 < m < 3 \quad 2M + DTPA \rightleftharpoons M_2DTPA \rightleftharpoons M-DTPA + M(OH)_2 \]

Curve c representing the system \( 2 : 1 \) M(II)-K₄DTPA-tiron, superimposes on the curve b up to \( m = 1 \) indicating the initial formation of \( 2 : 1 \) M(II)-DTPA complex to which the molecules of secondary ligand (tiron) are probably added resulting in the formation of the mixed ligand complex \( 2 : 1 : 2 \) M(II)-DTPA-tiron. The sharp inflection at \( m = 1 \) and \( m = 5 \) may be attributed respectively to the formation of the intermediate species and its interaction with the secondary ligand.

The addition of the secondary ligand molecules to the intermediate \( 2 : 1 \) M(II)-DTPA species may
TABLE 1 — FORMATION CONSTANTS OF MIXED LIGAND CHELATES
AT 25 ± 1°

<table>
<thead>
<tr>
<th>Equilibrium quotient</th>
<th>Cu(II)</th>
<th>Ni(II)</th>
<th>Zn(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{M_2L}$</td>
<td>20.80 ± 0.40</td>
<td>16.75 ± 0.43</td>
<td>17.55 ± 0.40</td>
</tr>
<tr>
<td>$K_{M_2LA}$</td>
<td>11.24 ± 0.10</td>
<td>9.57 ± 0.15</td>
<td>9.85 ± 0.13</td>
</tr>
<tr>
<td>$K_{M_2LA}^2$</td>
<td>9.36 ± 0.10</td>
<td>6.86 ± 0.14</td>
<td>7.38 ± 0.15</td>
</tr>
</tbody>
</table>

The mechanism of the formation of $M_2LA_2$ may thus be suggested as:

$$M_2L + 2A \rightleftharpoons M_2LA + A \rightleftharpoons M_2LA_2$$

(L = DTPA, A = Tiron)

which may be supported by the values obtained by the addition of $\log K_{M_2L}$ and $\log K_{M_2LA}$ as shown in (Table 1). These values almost tally with the values of $\log K_{M_2L}$.

The absence of heterogeneous phase during the titration and non-superimposable nature of the theoretical composite curve², T (drawn by addition of horizontal distances of the curves representing the system 2 : 1 M(II)-K₄DTPA and the secondary ligand) in the region of ternary complex formation give additional support to the formation of heteroligand bicentric 2 : 1 : 2 M(II)-DTPA-Tiron complex.

Acknowledgement
The authors express their gratitude to Prof. J. P. Tandon, Head of the Chemistry Department, Rajasthan University, Jaipur and Prof. A. K. Dey and Dr. Madhup Chandra, Chemistry Department, Allahabad University for their valuable suggestions during the present course of investigation. Thanks are also due to Dr. S. M. L. Gupta, Head of the Chemistry Department, Agra College, Agra for providing necessary laboratory facilities.

References