**Ternary complexes of iron(III) with 1,2-bis(2-hydroxybenzamido)ethane, thiocyanate and sulphur(IV): A kinetic study.**

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The kinetics of anation of (diaqua)(1,2-bis(2-hydroxybenzamido)iron(III) by NCS\(^-\) and S\(^{IV}\) (HSO\(_3\)\(^-\) and SO\(_2\)\(^{2-}\)) are reported at 25°C, \(I = 0.5\) mol dm\(^{-3}\) in 20% (v/v) MeOH + H\(_2\)O medium. The formation of the monothiocyanato complex, Fe(L)OH\(_2\)(NCS), is reversible. The monosulphito complex, Fe(L)(OH\(_2\))(SO\(_3\)\(^-\)), is formed via the reaction of the diaqua complex with HSO\(_3\)\(^-\) and SO\(_2\)\(^{2-}\); dissociation of the sulftito complex to the reactants has not been observed. Ion-pairing of the diaqua complex with SO\(_2\)\(^{2-}\) (but not with HSO\(_3\)\(^-\)) has been identified kinetically and resulted in the reduced reactivity of SO\(_2\)\(^{2-}\) in comparison to HSO\(_3\)\(^-\). The results are consistent with the dissociative mode of activation for the aqua ligand substitution of Fe(L)(OH\(_2\))\(^{2+}\). It has been found that there is no significant labilising action of the coordinated phenoxy and amide functions of the primary ligand (L\(^2\)) on the aqua ligand replacement reaction at iron(III) center.

The formation of binary complex of iron(III) with 1,2-bis(2-hydroxybenzamido)ethane (herein after mentioned as H\(_2\)L) has been reported by us earlier\(^1\). The FeL\(^{2+}\) catalysed hydrolysis of 4-nitrophenyl acetate\(^2\), however, did not indicate the formation of a ternary complex between the two, while S\(^{IV}\) reduction of this iron(III) complex was shown to proceed via ternary complex Fe\(^{III}\)(L)(SO\(_3\)\(^-\)) for which amide deprotonation at pH-9 was evident\(^3\). These studies prompted us to examine the kinetics of the ternary complex formation between Fe\(^{III}\)(L) and other secondary ligands. We report herein the said reaction with NCS\(^-\) and SO\(_2\)\(^{2-}\)/HSO\(_3\)\(^-\) which has not been reported earlier. It will be of interest to elucidate the labilising action of the coordinated amide and phenoxy moieties of the ligand (L) on the water replacement reaction at iron(III) center. Relevant data on Fe\(^{III}\)(OH\(_2\))\(_6\) + NCS\(^-\)/S\(^{IV}\) (ref. 4&5) and trans-(salen)Fe\(^{III}\)(OH\(_2\))\(_2\) -S\(^{IV}\) (ref.6) (salen = N,N'-ethylenebis-salicylidiniminate) are available for comparison.

**Materials and Methods**

The ligand, H\(_2\)L, and Fe(ClO\(_4\))\(_3\) solution were received from our earlier work\(^2\). Sodium metabisulphite, Na\(_2\)S\(_2\)O\(_5\), was the source of S\(^{IV}\), which on dissolution in water rapidly hydrolysed to an equilibrium mixture of SO\(_3\)/HSO\(_3\)/SO\(_2\)\(^{2-}\). Fresh solution of S\(^{IV}\) was always prepared by weight just before the experiment. NaNCS was extra pure quality. The stock NaNCS solution was estimated for NCS\(^-\) argentometrically by Volhards method\(^7\). All other chemicals were of Analar grade. Solutions were prepared in freshly twice distilled water received from an all glass distillation apparatus, the second distillation being made from alkaline KMnO\(_4\). Ionic strength was adjusted to 0.5 mol dm\(^{-3}\) with NaClO\(_4\). All rate measurements were made in 20% MeOH + H\(_2\)O (v/v) to avoid difficulties due to solubility of the ligand/complex.

The pH measurements were made with an Elico digital pH meter model LI 120 using a combined glass-Ag/AgCl, Cl\(^-\) (3 mol dm\(^{-3}\) NaCl) electrode CL 51. Solvent correction of pH was made\(^8\). The UV-visible spectra were recorded on a Perkin-Elmer Lambda 20 spectrophotometer using 1 cm matched quartz cells. A Hi-Tech (U K) stopped flow spectrophotometer model SF 51 was used to collect the rate constants. All measurements were made at 25.0 ± 0.1°C. All calculations were done on a 586 P C by a least squares program.

**Kinetics**

The complex was generated in situ \([\text{Fe}^{III}\text{L}]/\text{I} = 0.5\) mol dm\(^{-3}\), \(pH = 4.0\) for NCS\(^-\) and 4.0×10\(^{-4}\), \(pH = 4.2-6.58\) for S\(^{IV}\) complexation). The complex and the secondary ligand solutions (both adjusted to \(I = 0.5\) mol dm\(^{-3}\), 20% MeOH + H\(_2\)O thermally equilibrated separately in the drive syringes of the flow module of the stopped flow spectrophotometer were rapidly mixed in its mixing chamber and the progress of the complexation reaction was monitored at a suitable wavelength \(\lambda, \text{nm} = 450\) or 495 for
NCS"; 480 for SIV). The absorbance increased with time for NCS" while it decreased with time for SIV
complexation. The absorbance (A)- time (t/s) curves fitted well to the relationship $A_t - A_o = A_0 - A_l \exp(-
k_{obs}t)$. The $k_{obs}$ values reported are average of at least seven runs for each composition.

Results and Discussion

FeIII-H2L-NCS system

Figure 1 depicts the formation of ternary complex of NCS", FeIII and the primary ligand (H2L). All rate
measurements were made under conditions under which the in situ generated iron(III) complex of
the primary ligand was driven to completion (see Eqs 1, 2) and the acid dissociation of Fe(HL)2+ is virtually
complete ($pK_1 = 2.9$) (ref. 9).

$$\text{Fe(OH}_2)_6^{3+} + \text{H}_2\text{L} \rightarrow \text{(OH}_2)_2\text{Fe(L)}^+ + 2\text{H}^+ \quad (1)$$

$$\text{Fe(OH}_2)_6\text{L}^+ + \text{NCS} \rightarrow \frac{k_i}{k_{-1}}(\text{SCN})\text{Fe(OH}_2)_4\text{L} \quad (2)$$

Accordingly,

$$k_{obs} = k_1[NCS]^+ + k_{-1} \quad (3)$$

The $k_{obs}$ data at varying [NCS"] (see Table 1) were fitted to Eq. (3) and we obtained $k_1 = 35.7 \pm 1.3 \text{ dm}^{-3} \text{ mol}^{-1} \text{s}^{-1}$ and $k_{-1} = 1.37 \pm 0.16 \text{ s}^{-1}$ (25°C, $I = 0.5 \text{ mol dm}^{-3}$). The value of $k_1$ may be compared with the same for the anation of Fe(OH2)63+ by NCS" to form Fe(OH2)6(NCS)2+ $k_1(\text{dm}^{-3} \text{ mol}^{-1} \text{s}^{-1}, 25^\circ \text{C}) = 127$ (ref. 4a), 73 (ref. 4b), 399 (ref. 5) at $I = 0.4$, 1.5 and 0.1 mol dm$^{-3}$ respectively) taking account of the charge and ionic strength dependence. Also the

**Table 1—Rate constants of anation of Fe(OH2)$_2^+$ by NCS"**

<table>
<thead>
<tr>
<th>[NCS&quot;] (mol dm$^{-3}$)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
<th>$k_{cal}$ (s$^{-1}$)</th>
<th>[NCS&quot;] (mol dm$^{-3}$)</th>
<th>$k_{obs}$ (s$^{-1}$)</th>
<th>$k_{cal}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>2.20</td>
<td>1.71</td>
<td>0.100</td>
<td>4.62</td>
<td>4.89</td>
</tr>
<tr>
<td>0.025</td>
<td>2.72</td>
<td>2.24</td>
<td>0.140</td>
<td>6.10</td>
<td>6.36</td>
</tr>
<tr>
<td>0.028</td>
<td>2.60</td>
<td>2.35</td>
<td>0.150</td>
<td>6.49</td>
<td>6.66</td>
</tr>
<tr>
<td>0.038</td>
<td>3.04</td>
<td>2.70</td>
<td>0.190</td>
<td>8.51</td>
<td>8.07</td>
</tr>
<tr>
<td>0.045</td>
<td>2.90</td>
<td>2.95</td>
<td>0.200</td>
<td>8.61</td>
<td>8.43</td>
</tr>
<tr>
<td>0.050</td>
<td>2.87</td>
<td>3.12</td>
<td>0.250</td>
<td>10.5</td>
<td>10.2</td>
</tr>
<tr>
<td>0.095</td>
<td>4.30</td>
<td>4.71</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$I = 5$, $[\text{FeL(OH)}_2]^+ = 2.0 \times 10^{-4}$ mol dm$^{-3}$, $pH = 4.0 \pm 0.05$, $25.0 \pm 0.1^\circ \text{C}; \Sigma (k_{cal} - k_{obs})^2 = 1.33$

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Fig. 1—Spectral evidence for the interaction of Fe(L)(OH2)$_2^+$ with
NCS", pH = 4.0, 25°C; A - [Fe(L)(OH2)$_2^+$] = 3.3x10$^{-4}$ mol dm$^{-3}$; B - [Fe(L)(OH2)$_2^+$]3.3x10$^{-4}$ mol dm$^{-3}$] + [NCS"] (0.05 mol dm$^{-3}$).
collected in Table 2. There is a small decrease in \( k_{\text{obs}} \) with increase in pH at a given \([SIV]_T\). \( k_{\text{obs}} \) however, tends to increase with \([SIV]_T\) at a given pH. \( S^IV \) exists as an equilibrium mixture of \( \text{HSO}_3^- \) and \( \text{SO}_3^{2-} \) in the experimental range of pH = 4.2-7.69 \( pK(\text{HSO}_3^-) = 6.51 \) at 25°C, \( I = 0.5 \text{ mol dm}^{-3}, 20\% \text{ MeOH + water} \) (this work), \( pK_1 = 1.8, pK_2 = 6.6 \) at 25°C, \( I = 0.5 \text{ mol dm}^{-3}, \text{aqueous medium}^{10} \). It is apparent that \( \text{SO}_3^{2-} \) does not react significantly faster than \( \text{HSO}_3^- \) for substituting an aqua ligand of \( \text{Fe}^{III}(L)(\text{OH})_2 \). Also it appears that the iron(III) species of higher reactivity are not generated with the increase in pH of the reaction mixture. Based on these facts and neglecting the contribution from the dissociation of the product sulphito complex the following mechanism in Scheme 1 is proposed

\[
\begin{align*}
\text{Fe}(L)(\text{OH})_2^+ + \text{HSO}_3^- & \xrightarrow{k_1} \text{Fe}(L)(\text{OH})_2(\text{SO}_3^-) + H^+
\end{align*}

\[
\begin{align*}
\text{Fe}(L)(\text{OH})_2^+ + \text{SO}_3^{2-} & \xrightarrow{k_2} \text{Fe}(L)(\text{OH})_2(\text{SO}_3^-) + \text{Q}
\end{align*}

(Scheme 1)

for which,

\[
k_{\text{obs}} = \left( \frac{k_1[H^+]}{K_{d} + k_2'} \right) [SIV]_T/(1 + [H^+]K_{d} + Q[SIV]_T) \]

... (4)

where \( k_2' = k_2Q \). Data were fitted to Eq. (4) and we obtained \( k_1 = (1.33 \pm 0.07) \times 10^2 \), \( k_2 = 65.4 \pm 29.1 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} \) and \( Q = 15.0 \pm 11.0 \text{ dm}^3 \text{ mol}^{-1} \). The value of \( Q \) was then held fixed and the data were refitted to Eq (4). This did not alter the calculated values of \( k_1 \) and \( k_2' \).

The best-fit values of these parameters also reproduce \( k_{\text{obs}} \) satisfactorily (see \( k_{\text{cal}} \) in Table 2). The ion-association constant for \((2-, +1)\) ion-pair calculated by Fuoss theory\(^{11} \) on the basis of hard sphere model using 5\( \AA \) as the distance of closest approach of ions and for aqueous medium is 5.4 \text{ dm}^3 \text{ mol}^{-1} \) at \( I = 0 \) (25°C); ionic strength correction (assuming that the activity coefficients are invariant to the ion and the ion-pair for the same charge type) to \( I = 0.5 \text{ mol dm}^{-3} \) yields 1.3 \text{ dm}^3 \text{ mol}^{-1} \). The value of \( Q \) is acceptable considering the possibility of enhanced thermodynamic stability of the sulfite ion-pair due to the flexible 8 membered hydrogen bonded structure (II) involving the amide N-H and the \( \text{SO}_3^{2-} \) ion.

**Table 2**—Rate constants for the formation of \([\text{Fe}(L)(\text{OH})_2(\text{SO}_3^-)\]^{3-}

<table>
<thead>
<tr>
<th>([SIV]_T) (mol dm(^{-3}))</th>
<th>(pH)</th>
<th>(k_{\text{obs}}) (s(^{-1}))</th>
<th>(k_{\text{cal}}) (s(^{-1}))</th>
<th>([SIV]_T) (mol dm(^{-3}))</th>
<th>(pH)</th>
<th>(k_{\text{obs}}) (s(^{-1}))</th>
<th>(k_{\text{cal}}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.040</td>
<td>5.32</td>
<td>5.63</td>
<td>4.98</td>
<td>0.050</td>
<td>6.30</td>
<td>4.47</td>
<td>4.17</td>
</tr>
<tr>
<td>0.040</td>
<td>5.72</td>
<td>5.50</td>
<td>4.57</td>
<td>0.050</td>
<td>6.94</td>
<td>2.59</td>
<td>2.71</td>
</tr>
<tr>
<td>0.040</td>
<td>6.05</td>
<td>4.16</td>
<td>4.01</td>
<td>0.020</td>
<td>6.51</td>
<td>2.16</td>
<td>1.73</td>
</tr>
<tr>
<td>0.040</td>
<td>6.25</td>
<td>3.79</td>
<td>3.60</td>
<td>0.020</td>
<td>6.80</td>
<td>1.35</td>
<td>1.48</td>
</tr>
<tr>
<td>0.040</td>
<td>6.42</td>
<td>3.27</td>
<td>3.24</td>
<td>0.020</td>
<td>7.09</td>
<td>1.33</td>
<td>1.29</td>
</tr>
<tr>
<td>0.040</td>
<td>6.58</td>
<td>3.22</td>
<td>2.92</td>
<td>0.020</td>
<td>7.64</td>
<td>0.63</td>
<td>1.10</td>
</tr>
<tr>
<td>0.050</td>
<td>5.33</td>
<td>4.25</td>
<td>4.59</td>
<td>0.020</td>
<td>5.86</td>
<td>2.62</td>
<td>2.40</td>
</tr>
<tr>
<td>0.050</td>
<td>5.72</td>
<td>4.94</td>
<td>5.13</td>
<td>0.020</td>
<td>5.97</td>
<td>1.90</td>
<td>2.21</td>
</tr>
<tr>
<td>k_1 (dm(^3) mol(^{-1}) s(^{-1}))</td>
<td>(1.33 \pm 0.05) \times 10^2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>k_2 (dm(^3) mol(^{-1}) s(^{-1}))</td>
<td>65.5 \pm 11.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q (dm(^3) mol(^{-1}))</td>
<td>15.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

\(^a\) \(25.0 \pm 0.1°C, [\text{Fe}(L)(\text{OH})_2]_T = 4.0 \times 10^{-4}, I = 0.5 \text{ mol dm}^{-3}, 20\% (v/v) \text{ MeOH + H}_2\text{O}; \sum(k_{\text{cal}} - k_{\text{obs}})^2 = 3.63.\)

\(^b\) \( k_2 = k_2Q \)

\(^c\) \( Q \) held fixed to calculate errors of \( k_1 \) an \( k_2' \).
It is worth noting that ion-pairing with $\text{SO}_3^{2-}$ was not observed in the reaction of $\text{SIV}$ with $\text{Fe(salen)(OH}_2)_2^+$ (ref. 6) and $\text{Mn(salen)(OH}_2)_2^+$ (ref. 12) and anation by $\text{SO}_3^{2-}$ was faster than by $\text{HSO}_3^-$ in the latter case and for $\text{Fe(ida)(OH}_2)_3^+$ ($\text{ida}^{2-} = \text{iminodiacetate}$) ion-pairing with $\text{SO}_3^{2-}$ was also kinetically detected for the $\text{Fe(ida)(OH}_2)_3^+$ complex ($Q = 15 \text{ mol dm}^{-3}$, $I = 0.5 \text{ mol dm}^{-3}$, 10-15°C) (ref. 13). We are compelled to believe that this contrasting feature is due to the availability of suitably sited protons for hydrogen bonding. However, further experimentations on similar systems are in progress to clarify the picture.

It is also interesting to note that ion-pairing reduces the reactivity of $\text{SO}_3^{2-}$ in relation to $\text{HSO}_3^-$ (note $k_2' < k_1$). This can be reconciled with the dissociative mode of activation for aqua ligand substitution for $\text{Fe(L)(OH}_2)_2^+$. A further comparison of the rate constants shows that the aqua ligand substitution by $\text{HSO}_3^-$ for $\text{Fe(L)(OH}_2)_2^+$ is ~20 times faster than that for $\text{Fe(salen)(OH}_2)_2^+ (k_1 = 6.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 25°C, $I = 0.5 \text{ mol dm}^{-3}$) (ref. 6). Thus significant difference in reactivity is observed when the imine function (in salen) is replaced by the amide function (in L). However, the $\text{L}^{2-}$ does not seem to exert substantial labilising action considering the value of the anation rate constant of $\text{Fe(OH}_2)_6^{3+}$ by $\text{HSO}_3^-$ ($\text{Fe(OH}_2)_6^{3+} + \text{HSO}_3^- \rightarrow \text{Fe(OH}_2)_6(\text{SO}_3^-)^+$; $k = 270 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 25°C, $I = 1.0 \text{ mol dm}^{-3}$)

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**References**