The cases highlighted below, are for purposes of exemplification only, and are not intended to indicate that the intimate kinetic mechanism has been established. Indeed, the timing of deprotonation of the ligand ring protons is quite likely to vary form one ligand type to another, and the nature of the anion in solution, will affect metal ion speciation (at a given pH) as well as the propensity for the ligand to deprotonate.

Dissociation

consider a stepwise protonation scheme, i.e. acid-catalysed decomplexation, see reference 2a

\[
[H^+] + [ML]^3+ \xrightleftharpoons[k_3]{k_3} [MLH]^4+ + [H^+] \xrightarrow[k_2]{k_2} [MLH_2]^5+ \xrightarrow[k_1]{k_1} [M^3+] + [LH_2]^{2+}
\]

if the total complex concentration is \( [S_{tot}] = [ML]^3+ + [MLH]^4+ + [MLH_2]^5+ \)

\[
K_3 = \frac{k_3}{k_3} = \frac{[ML]^3+[H^+]}{[MLH]^4+}
K_2 = \frac{k_2}{k_2} = \frac{[MLH]^4+[H^+]}{[MLH_2]^5+}
\]

so:

\[
[S_{tot}] = [MLH_2]^5+ \left( \frac{K_2K_3 + K_3[H^+] + [H^+]^2}{[H^+]^2} \right)
\]

observed rate of dissociation \( v = k_{-1}[MLH_2]^5+ \) \( = \frac{k_{-1}[S_{tot}][H^+]^2}{K_2K_3 + K_2[H^+] + [H^+]^2} \)

if \( [MLH_2]^5+ \ll [ML]^3+ + [MLH]^4+ \)

then \( [S_{tot}] = K_2K_3 [MLH_2]^5+ + K_2[MLH_2]^5+ \)

rate \( = \frac{k_{-1}[S_{tot}][H^+]^2}{K_2([H^+] + K_3)} \)

and when \( [H^+] \gg K_3 \) (high acid), \( rate = k_{-1}[S_{tot}][H^+]/K_2 \)

Association kinetics

\[
[M]^3+ + [LH_2]^2+ \xrightleftharpoons[k_1]{k_1} [MLH_2]^5+ \xrightleftharpoons[k_2]{k_2} [MLH]^4+ + H^+ \xrightleftharpoons[k_3]{k_3} [ML]^3+ + 2H^+
\]

in water, assume water can act as a general base assisting the deprotonation of the ring and that a steady state approximation applies for the intermediate diprotonated species; i.e. \( k_2 \) and \( k_3 \) are assumed to be small, with \( k_1 >> k_2 \) and \( k_3 >> k_2 \):

\[
rate = k_1 [M^3+] [LH_2]^2+ \left( \frac{k_2}{k_1 + k_2} \right) \left( \frac{k_3}{k_2 + k_3} \right) = \frac{k_1k_2 [M^3+] [LH_2]^2+}{k_1}
\]