Supplemental Information

Derivation of equation 3:

In a first order reversible reaction where reactant A goes to product P, the approach to equilibrium can be described in the rate of disappearance of the reactant. The system can be described as follows:

$$-\frac{\mathrm{dA}}{\mathrm{dt}} = \mathbf{k_1}[\mathbf{A}] - \mathbf{k_{-1}}[\mathbf{P}] \tag{2}$$

$$[A]_{o} + [P]_{o} = [A]_{t} + [P]_{t} = [A]_{e} + [P]_{e}$$
(3)

$$\frac{\left[\mathbf{P}\right]_{\mathbf{e}}}{\left[\mathbf{A}\right]_{\mathbf{e}}} = \mathbf{K} = \frac{\mathbf{k}_{1}}{\mathbf{k}_{-1}} \tag{4}$$

Combining equations 2, 3, and 4 give eq.5, manipulation of the variables gives eq.6, and simple integration leads to eq.7.

$$-\frac{\mathrm{dA}}{\mathrm{dt}} = ([\mathrm{A}]_{\mathrm{t}} + [\mathrm{A}]_{\mathrm{e}})(\mathrm{k}_{1} + \mathrm{k}_{-1})$$
(5)

$$\frac{\mathrm{dA}}{([\mathbf{A}]_{\mathbf{t}} + [\mathbf{A}]_{\mathbf{e}})} = -(\mathbf{k}_{1} + \mathbf{k}_{-1})\mathrm{dt}$$
(6)

$$\ln\left(\frac{[\mathbf{A}]_{\mathbf{t}} - [\mathbf{A}]_{\mathbf{e}}}{[\mathbf{A}]_{\mathbf{o}} - [\mathbf{A}]_{\mathbf{e}}}\right) = -(\mathbf{k}_{1} + \mathbf{k}_{-1})\mathbf{t}$$
(7)

It is seen here that a plot of $\ln([A]_t - [A]_e)$ with time will be linear, the negative of the slope of which is the observed rate constant of the reaction (k_{obs}) and is the sum of the forward and reverse rate constants. This same treatment can be applied to a second order reversible approach to equilibrium reaction where reactants A and B go to product P, given the pseudo-first order condition of $[B]_o >> [A]_o$. The system can be described as follows:

$$\mathbf{A} + \mathbf{B} \rightleftharpoons_{\mathbf{k}_1}^{\mathbf{k}_1} \mathbf{P}$$
(8)

$$-\frac{\mathrm{d}\mathbf{A}}{\mathrm{d}\mathbf{t}} = \mathbf{k}_{1}[\mathbf{A}][\mathbf{B}] - \mathbf{k}_{-1}[\mathbf{P}]$$
(9)

$$[A]_{o} + [B]_{o} + [P]_{o} = [A]_{t} + [B]_{t} + [P]_{t} = [A]_{e} + [B]_{e} + [P]_{e}$$
(10)

$$\frac{[\mathbf{P}]_{\mathbf{e}}}{[\mathbf{A}]_{\mathbf{e}}[\mathbf{B}]_{\mathbf{e}}} = \mathbf{K} = \frac{\mathbf{k}_{1}}{\mathbf{k}_{-1}} \tag{11}$$

$$[\mathbf{B}]_{\mathbf{o}} \approx [\mathbf{B}]_{\mathbf{t}} \approx [\mathbf{B}]_{\mathbf{e}} \tag{12}$$

Combination of equations 9, 10, and 11 and application of the pseudo-first order condition described in eq. 12 give eq. 13, manipulation of the variables and integration gives eq. 14.

$$-\frac{\mathbf{dA}}{\mathbf{dt}} = ([\mathbf{A}]_{\mathbf{t}} + [\mathbf{A}]_{\mathbf{e}})(\mathbf{k_1}[\mathbf{B}]_{\mathbf{o}} + \mathbf{k_{-1}})$$
(13)

$$\ln\left(\frac{[\mathbf{A}]_{\mathbf{t}} - [\mathbf{A}]_{\mathbf{e}}}{[\mathbf{A}]_{\mathbf{o}} - [\mathbf{A}]_{\mathbf{e}}}\right) = -(\mathbf{k}_{\mathbf{1}}[\mathbf{B}]_{\mathbf{o}} + \mathbf{k}_{-\mathbf{1}})\mathbf{t}$$
(14)

Again it is seen here that a plot of $\ln([A]_t - [A]_e)$ with time will be linear, the negative slope of which is the observed rate constant of the pseudo-first order reaction:

$$\mathbf{k}_{obs} = \mathbf{k}_1 [\mathbf{B}]_0 + \mathbf{k}_{-1} \tag{15}$$

This result shows that a plot of k_{obs} against [B]_o will give a straight line, the slope of which is the second order rate constant of the forward reaction and the intercept is the first order rate constant of the reverse reaction.

Calculation of equilibrium constants

The chemical equilibria for the complexation of the lanthanides or the lanthanide tris-lactate species with EDTA and DTPA are as follows

$$H_2 EDTA^{2-} + Ln^{3+} \rightleftharpoons Ln(EDTA)^- + 2 H^+$$
(1)

$$H_3 DTPA^{2-} + Ln^{3+} \rightleftharpoons Ln(DTPA)^{2-} + 3 H^+$$
(2)

$$H_2EDTA^{2-} + Ln(Lac)_3 \rightleftharpoons Ln(EDTA)^- + 2HLac + Lac^-$$
(3)

$$H_3 DTPA^{2-} + Ln(Lac)_3 \rightleftharpoons Ln(DTPA)^{2-} + 3HLac$$
(4)

The respective equilibrium constants for these systems are

$$\mathbf{K}_{\mathbf{LnEDTA}} = \frac{\left[\left[\mathbf{Ln}(\mathbf{EDTA})\right]^{-}\right] * \left[\left[\mathbf{H}\right]^{+}\right]^{2}}{\left[\left[\mathbf{Ln}\right]^{3+}\right] * \left[\left[\mathbf{H}\right]_{3}\mathbf{DTPA^{2-}}\right]}$$
(5)

$$\mathbf{K}_{\mathbf{LnDTPA}} = \frac{\left[\left[\mathbf{Ln}(\mathbf{DTPA})\right]^{2-}\right] * \left[\left[\mathbf{H}\right]^{+}\right]^{3}}{\left[\left[\mathbf{Ln}\right]^{3+}\right] * \left[\left[\mathbf{H}\right]_{3}\mathbf{DTPA}^{2-}\right]}$$
(6)

$$\mathbf{K}_{\mathrm{LnL3EDTA}} = \frac{\left[\left[\mathrm{Ln}(\mathrm{EDTA})\right]^{-}\right] * \left[\mathrm{HLac}\right]^{2} * \left[\left[\mathrm{Lac}\right]^{-}\right]}{\left[\left[\mathrm{Ln}(\mathrm{Lac})\right]_{3}\right] * \left[\left[\mathrm{H}\right]_{2} \mathrm{EDTA}^{2-}\right]}$$
(7)

$$\mathbf{K}_{\mathrm{LnL3DTPA}} = \frac{\left[\left[\mathrm{Ln}(\mathrm{DTPA})\right]^{-}\right] * \left[\mathrm{HLac}\right]^{3}}{\left[\left[\mathrm{Ln}(\mathrm{Lac})\right]_{3}\right] * \left[\mathrm{[H]}_{3}\mathrm{DTPA}^{2-}\right]}$$
(8)

Using the DTPA case as an example it can be seen that these equilibrium constants can be calculated using the known stability constants for the following reactions

$$\mathbf{DTPA^{5-} + Ln^{3+}} \rightleftharpoons \mathbf{Ln}(\mathbf{DTPA})^{2-} \qquad (\hat{a}_{\mathrm{LnDTPA}}) \tag{9}$$

$$\mathbf{DTPA^{5-} + 3H^{+} \rightleftharpoons H_{3}\mathbf{DTPA^{2-}} \qquad (\hat{a}_{H3DTPA}) \qquad (10)$$

$$Ln^{3+} + 3Lac^{-} \neq Ln(Lac)_{3} \qquad (\beta_{LnLac3}) \qquad (11)$$

$$\mathbf{H}^{+} + \mathbf{Lac}^{-} \rightleftharpoons \mathbf{HLac} \qquad (\mathbf{K}_{\mathrm{HLac}}) \qquad (12)$$

Rearranging and combining these equilibria allows for reproduction of equations 17 and 19 and therefore equations 21 and 23 can we written as

$$K_{LnDTPA} = \frac{\beta_{LnDTPA}}{\beta_{H3DTPA}}$$
(13)

$$K_{LnL3DTPA} = \frac{\beta_{LnDTPA} * K_{HLac}^{3}}{\beta_{LnLac3} * \beta_{H3DTPA}}$$
(14)

Using the stability constants (from the NIST Stability Constant database) in Table S.1 the equilibrium constants in equations 20-23 (in the text) can be calculated.

Ln	$log(\beta_{LnEDTA})$	$log(\beta_{LnDTPA})$	$log(\beta_{LnLac3})$
La	15.36	19.49	5.64
Ce	15.93	20.43	5.96
Pr	16.3	21.1	6.1
Nd	16.51	21.62	6.38
Sm	17.06	22.35	6.35
Eu	17.25	22.39	6.44
Gd	17.35	22.39	6.24
Tb	17.87	22.72	6.36
Dy	18.3	22.83	6.67
Но	18.56	22.79	6.81
Er	18.89	22.75	7.2
Tm	19.32	22.73	7.43
Yb	19.49	22.64	7.58
Lu	19.74	22.46	7.78

$log(\beta_{H2EDTA})$	$log(\beta_{H3DTPA})$	$log(K_{HLac})$
15.65	22.58	3.67

Table S.1 Literature stability constants used in equilibrium constant calculations. All values are for an ionic strength of 0.1 M and at 25 °C except β_{LnLac3} which are at 20 °C. $log(\beta_{H2EDTA})$ and $log(\beta_{H3DTPA})$ are summations of the stepwise protonation constants found in the literature.