Supplementary Material (ESI) for Dalton Transactions

Supporting Information

for

Dissociation kinetics of Mn^{2+} complexes with NOTA and DOTA

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Table S1. Observed pseudo first-order rate constants k_{obs} ($\cdot 10^5$ s^{-1}), for dissociation of $[Mn(nota)]^-$ complex as a function of Zn^{2+} concentration and pH.

$c(Zn^{2+})$ [mM]/pH	3.5	4.0	4.6	5.0	5.6
5	19.4	7.52	2.51	1.30	0.46
10	18.1	7.11	2.38	1.20	0.42
20	16.8	6.03	2.19	1.05	0.37
30	15.3	5.90	1.98	0.95	0.36
50	15.1	4.96	1.66	0.82	0.23

Table S2. Observed pseudo first-order rate constants k_{obs} ($\cdot 10^6$ s^{-1}), for dissociation of $[Mn(dota)]^{2-}$ complex as a function of Zn^{2+} concentration and pH.

$c(Zn^{2+})$ [mM]/pH	3.8	4.1	4.6	5.1	5.6
5	10.58	5.24	1.47	0.54	0.26
10	9.22	4.17	1.22	0.47	0.26
20	7.18	3.27	0.88	0.32	0.25
30	6.73	2.75	0.75	0.28	0.27
50	5.00	1.93	0.53	0.23	0.30

Table S3 Experimental values of overall protonation/stability constants ($\log\beta_{hlm}$) of NOTA and its Mn^{2+} complex (25 °C, I = 0.1 M $(NMe_4)Cl$, standard deviations in parenthesis as calculated by OPIUM); $\beta_{hlm} = [H_hL_lM_m] / [H]^h \times [L]^l \times [M]^m$.

Ion	Equilibrium	stoichiometry			NOTA
		h	*l*	*m*	
H^+	$\mathbf{L} + H^+ \leftrightarrow H\mathbf{L}^{2-}$	1	1	0	13.17(2)
	$\mathbf{L} + 2H^+ \leftrightarrow H_2\mathbf{L}^-$	2	1	0	18.91(1)
	$\mathbf{L} + 3H^+ \leftrightarrow H_3\mathbf{L}$	3	1	0	22.13(1)
	$\mathbf{L} + 4H^+ \leftrightarrow H_4\mathbf{L}^+$	4	1	0	24.09(1)
Mn^{2+}	$\mathbf{L} + Mn^{2+} \leftrightarrow [Mn(\mathbf{L})]^-$	0	1	1	16.30(1)
	$\mathbf{L} + Mn^{2+} + H^+ \leftrightarrow [Mn(H\mathbf{L})]$	1	1	1	19.17(1)

Figure S1 Species distribution diagram of the Mn^{2+}–NOTA system ($c_{Mn2+} = c_L$ = 1mM, I = 0.1 M $(NMe_4)Cl$).

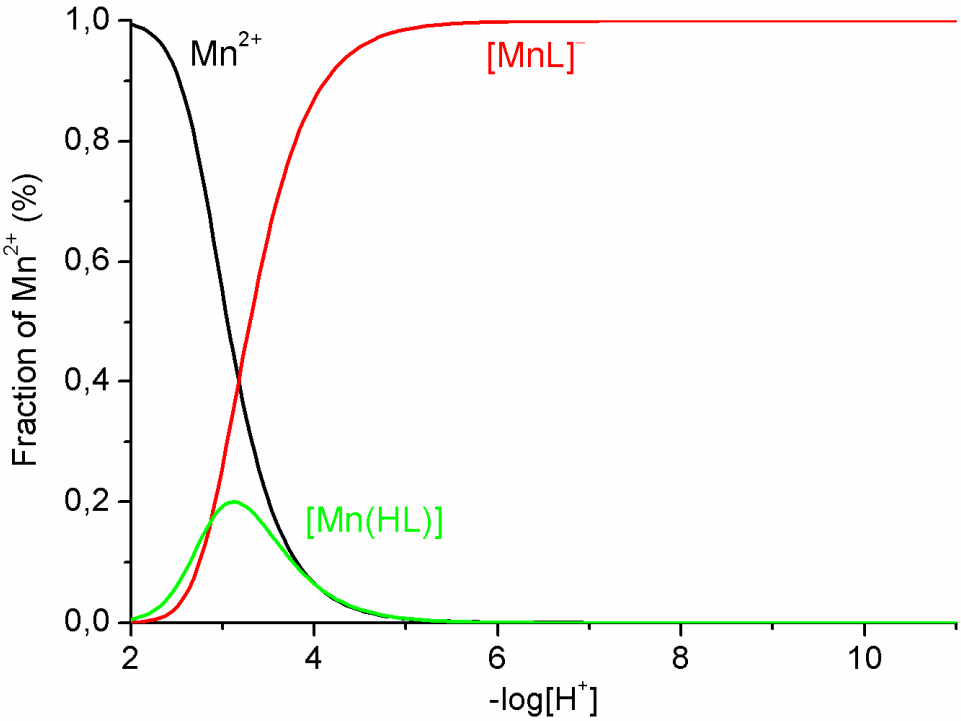

Figure S2 Species distribution diagram of the Mn^{2+}–DOTA system ($c_{Mn2+} = c_L$ = 1mM, I = 0.1 M $(NMe_4)Cl$).

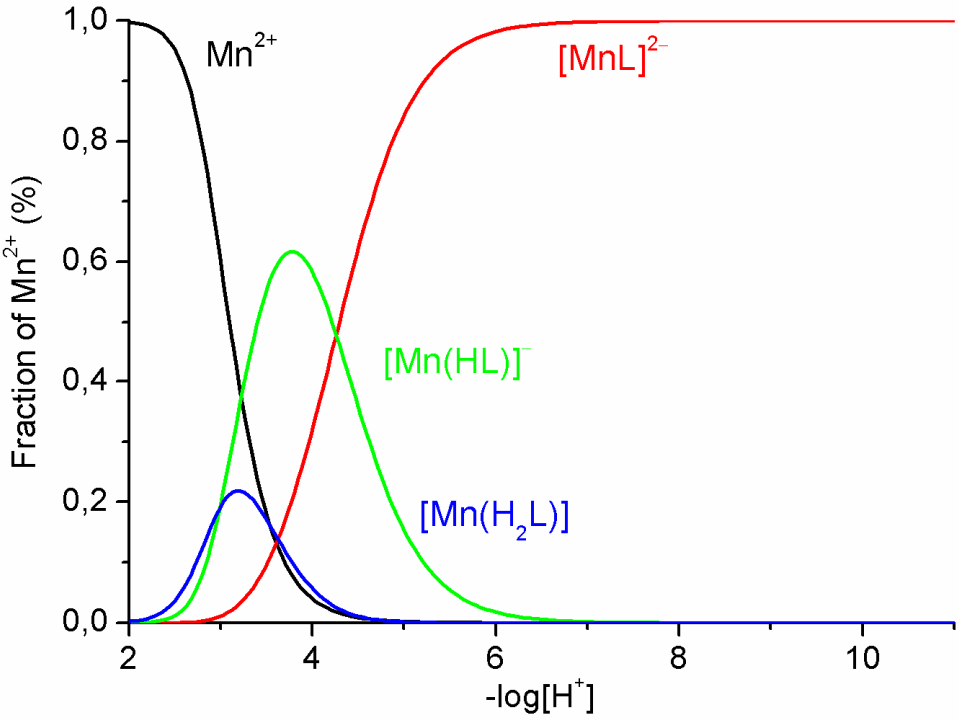

Figure S3 ^{1}H NMR titration curves of NOTA (■ signal of pendant arms CH_2; ● signal of macrocycle CH_2) with fitted curve (full line) as obtained by OPIUM.