Electronic Supplementary Material (ESI) for Dalton Transactions

Binding Multidentate Ligands to Ni^{2+}: Kinetic Identification of Preferential Binding Sites

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SUPPLEMENTARY INFORMATION

Spectroscopic and Kinetic Data

Table S1. The IR and ^{1}H NMR spectral characteristics of $H_2L^n{}_X$.

compound	IR	^{1}H NMR				$^{13}C\{^{1}H\}$ NMR
	ν(C=N)	OH	CH=N	Aromatic-H	CH_2	
$H_2L^0{}_H$	1630	13.2 (s)	8.4 (s)	6.7 – 7.3 (m)	4.0 (s)	
$H_2L^0{}_{Cl}$	1630	n.o.	8.3 (s)	6.9 – 7.3 (m)	3.9 (s)	
$H_2L^0{}_{MeO}$[a]	1630	n.o.	7.8 (s)	6.6 – 6.9 (m)	3.8 (s)	
$H_2L^0{}_{Me}$[b]	1630	n.o.	8.3 (s)	6.8 – 7.3 (m)	4.0 (s)	167.0 (C-OH) 159.0 (C=N) 132.0, 131.2, 119.2, 127.3, 117.8, 60.0, 21.0
$H_2L^1{}_H$	1630	9.95 (br)	8.5 (s)	6.9 – 7.3 (m)	3.0 (br)	166.3 (C-OH) 160.9 (C=N) 132.5, 130.8, 119.2, 118.8, 118.2, 59.8, 49.7
$H_2L^2{}_H$	1625	10.7 (br)	8.3 (s)	6.7 – 7.3 (m)	3.5 – 3.8 (br)	166.9 (C-OH) 161.6 (C=N) 132.6, 131.7, 131.2, 130.6, 119.2, 58.8, 53.2, 52.0
$H_2L^3{}_H$	1630	10.6 (br)	8.3 (s)	6.7 – 7.3 (m)	2.8 – 3.5 (br)	167.0 (C-OH) 162.0 (C=N) 133.0, 132.0, 131.0, 130.0, 119.0, 59.0, 58.0, 54.0, 53.0

Footnotes

s = singlet, m = multiplet, n.o. = not observed

a δ = 3.7 (s) MeO

b δ = 2.3 (s) Me

Table S2. The IR and ^{1}H NMR spectral characteristics of [Ni(L^{n}_{H})]

compound	IR	^{1}H-NMR		
	ν(C=N)	CH=N	Aromatic-H	CH_2
[Ni(L^{0}_{H})]	1600	8.3 (s)	6.5 – 7.3 (m)	3.2 (br)
[Ni(L^{1}_{H})]	1600	8.4 (s)	6.6 – 7.7 (m)	3.2, 2.8 (br)
[Ni(L^{2}_{H})]	1600	8.6 (s)	6.8 – 7.6 (m)	3.0, 2.5 (br)
[Ni(L^{3}_{H})]	1600	8.5 (s)	6.8 – 7.7 (m)	n.o.

Footnotes
s = singlet, m = multiplet, n.o. = not observed

Table S3. Kinetic Data for the Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^a_X$ (X = H, Cl or Me) at 25.0 °C in Methanol

		rate constants		spectroscopic changes		
$H_2L^a_X$	$[H_2L^a_X]$ / mmol dm^{-3}	k_{obs}^1 / s^{-1}	k_{obs}^2 / s^{-1}	$-\Delta A_1$	$-\Delta A_2$	A_f
$H_2L^a_H$ [1]	1.0	0.042		0.108		0.698
	2.0	0.060		0.197		0.960
	3.0	0.076		0.241		1.320
	4.0	0.098		0.246		1.663
$H_2L^a_{Me}$ [2]	1.0	0.45	0.060	0.10	0.14	0.665
	2.0	0.53	0.060	0.18	0.16	1.237
	3.0	0.61	0.070	0.26	0.29	1.695
	4.0	0.70	0.060	0.28	0.28	1.830
$H_2L^a_{Cl}$ [2]	1.0	0.55	0.20	0.10	0.10	0.600
	2.0	1.10	0.25	0.16	0.16	1.036
	3.0	1.35	0.20	0.20	0.19	1.475
	4.0	1.93	0.22	0.24	0.24	1.880

Fits to absorbance-time curves: ΔA_1 = absorbance change for first phase; $-\Delta A_2$ = absorbance change for second phase; A_f = final absorbance.

1. single exponential $A_t = A_f + \Delta A_1.\exp(-k_{obs}^1.t)$
2. two exponentials $A_t = A_f + \Delta A_1.\exp(-k_{obs}^1.t) + \Delta A_2.\exp(-k_{obs}^2.t)$

Table S4. Kinetic Data for the Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with H_2L_X-Cl (X = H, Cl or Me) at 25.0 °C in Methanol

		rate constants		spectroscopic changes		
H_2L_X-Cl	$[H_2L_X\text{-Cl}]$ / mmol dm^{-3}	k_{obs}^1 / s^{-1}	k_{obs}^2 / s^{-1}	$-\Delta A_1$	$-\Delta A_2$	A_f
H_2L_H-Cl [1]	1.0	0.12		0.210		0.483
	2.0	0.12		0.294		0.653
	3.0	0.13		0.367		0.957
	4.0	0.13		0.444		1.377
H_2L_{Me}-Cl [1]	1.0	0.033		0.268		0.359
	2.0	0.052		0.369		0.765
	3.0	0.070		0.425		1.118
	4.0	0.090		0.439		1.558
H_2L_{Cl}-Cl [2]	1.0	0.26	0.03	0.070	0.13	0.265
	2.0	0.29	0.03	0.256	0.260	0.650
	3.0	0.32	0.04	0.400	0.490	1.13
	4.0	0.35	0.04	0.413	0.673	1.43

Fits to absorbance-time curves: ΔA_1 = absorbance change for first phase; $-\Delta A_2$ = absorbance change for second phase; A_f = final absorbance.

1. single exponential $A_t = A_f + \Delta A_1.\exp(-k_{obs}^1.t)$
2. two exponentials $A_t = A_f + \Delta A_1.\exp(-k_{obs}^1.t) + \Delta A_2.\exp(-k_{obs}^2.t)$

Table S5. Kinetic Data for the Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^0{}_X$ (X = H, MeO, Me or Cl) and H_2salphen at 25.0 °C in Methanol

ligand	[ligand] / mmol dm^{-3}	rate constants $k_{obs}{}^1$ / s^{-1}	spectroscopic changes $-\Delta A_1$	A_f
$H_2L^0{}_H{}^1$	1.0	0.29	0.320	0.755
	2.0	0.35	0.357	0.916
	3.0	0.40	0.435	1.269
	4.0	0.49	0.480	1.640
$H_2L^0{}_{MeO}{}^1$	1.0	0.019	0.020	0.096
	2.0	0.025	0.035	0.104
	3.0	0.029	0.049	0.218
	4.0	0.036	0.059	0.500
$H_2L^0{}_{MeO}{}^{1, a}$	2.0	0.025	0.015	0.036
	3.0	0.031	0.019	0.060
	4.0	0.035	0.022	0.073
$H_2L^0{}_{Me}{}^1$	0.5	0.019	0.020	0.076
	1.0	0.020	0.029	0.092
	1.5	0.021	0.048	0.152
	2.0	0.022	0.053	0.179
$H_2L^0{}_{Cl}{}^1$	1.0	0.025	0.040	0.094
	2.0	0.036	0.055	0.177
	3.0	0.050	0.080	0.270
	4.0	0.064	0.120	0.381
H_2salphen ^{1}	1.0	0.015	0.046	0.176
	2.0	0.018	0.111	0.199
	3.0	0.023	0.148	0.232

Fits to absorbance-time curves: ΔA_1 = absorbance change for first phase; A_f = final absorbance.
1. single exponential $A_t = A_f + \Delta A_1.\exp(-k_{obs}{}^1.t)$

Footnotes
a $[Ni^{2+}] = 0.2$ mmol dm^{-3}

Table S6. Kinetic Data for the Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^n_H$ (n = 1 - 3) at 25.0 °C in Methanol

		rate constants		spectroscopic changes		
$H_2L^n_H$	$[H_2L^n_H]$ / mmol dm^{-3}	k_{obs}^1 / s^{-1}	k_{obs}^2 / s^{-1}	$-\Delta A_1$	$-\Delta A_2$	A_f
$H_2L^1_H$ [1]	2.0	2.3	0.040	0.380	0.169	0.816
	4.0	4.1	0.040	0.448	0.156	1.031
	6.0	6.5	0.035	0.472	0.123	1.239
	10.0	11.8	0.035	0.438	0.099	1.577
	12.0	12.4	0.040	0.484	0.100	1.728
	15.0	16.5	0.040	0.429	0.100	1.975
$H_2L^2_H$ [1]	2.0	3.0	0.050	0.126	0.060	0.248
	4.0	6.0	0.050	0.116	0.078	0.534
	6.0	8.0	0.040	0.100	0.050	0.677
	10.0	11.8	0.050	0.128	0.074	0.773
	12.0	14.1	0.050	0.108	0.070	1.052
	15.0	18.0	0.050	0.110	0.074	1.368
$H_2L^3_H$ [1]	2.0	3.8	0.010	0.133	0.099	0.398
	4.0	6.7	0.010	0.206	0.050	0.561
	6.0	8.5	0.015	0.214	0.045	0.866
	10.0	13.8	0.010	0.207	0.048	1.238
	12.0	17.5	0.010	0.200	0.042	1.423
	15.0	21.8	0.010	0.200	0.040	1.488

Fits to absorbance-time curves: ΔA_1 = absorbance change for first phase; $-\Delta A_2$ = absorbance change for second phase; A_f = final absorbance.

1. two exponentials $A_t = A_f + \Delta A_1.\exp(-k_{obs}^1.t) + \Delta A_2.\exp(-k_{obs}^2.t)$

Table S7. Kinetic Data for the Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with L_{py} or L^{n}_{py} (n = 1 - 3) at 25.0 °C in Methanol

ligand	[ligand] / mmol dm^{-3}	rate constants k_{obs} / s^{-1}	spectroscopic changes $-\Delta A_1$	A_f
$L_{py}{}^{1}$	5.0	5.6	0.015	0.0460
	6.0	5.6	0.017	0.0500
	9.0	6.8	0.018	0.0518
	12.5	12.4	0.020	0.0559
	15.0	14.6	0.019	0.0600
	20.0	16.4	0.020	0.0647
	25.0	19.4	0.018	0.0724
$L^{0}{}_{py}{}^{1}$	5.0	12.0	0.0249	0.041
	10.0	26.3	0.0244	0.048
	15.0	46.3	0.0247	0.067
	20.0	63.6	0.0242	0.092
	25.0	76.9	0.0242	0.121
	30.0	100.7	0.0255	0.156
$L^{1}{}_{py}{}^{1}$	5.0	18.0	0.0263	0.066
	10.0	38.6	0.0262	0.104
	15.0	71.4	0.0260	0.143
	20.0	89.9	0.0268	0.184
	25.0	111.9	0.0272	0.215
	30.0	124.4	0.0273	0.253
$L^{2}{}_{py}{}^{1}$	5.0	20.4	0.0213	0.038
	10.0	43.7	0.0260	0.047
	15.0	70.8	0.0260	0.062
	20.0	99.7	0.0260	0.126
	25.0	121.4	0.0300	0.202
	30.0	140.7	0.0300	0.269
$L^{3}{}_{py}{}^{1}$	5.0	17.9	0.0215	0.059
	10.0	42.7	0.0219	0.091
	15.0	67.6	0.0229	0.120
	20.0	106.7	0.0230	0.157
	25.0	143.8	0.0240	0.225
	30.0	164.3	0.0244	0.225

Fits to absorbance-time curves: ΔA_1 = absorbance change for first phase; $-\Delta A_2$ = absorbance change for second phase; A_f = final absorbance.

1. single exponential $A_t = A_f + \Delta A_1.\exp(-k_{obs}^{1}.t)$

Table S8. Kinetic Data for the Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^0{}_H$ in the presence of NEt_3 and $NHEt_3^+$ at 25.0 °C in Methanol

				rate constants		spectroscopic changes		
	$[H_2L^0{}_H]$ / mmol dm^{-3}	$[NEt_3]$ / mmol dm^{-3}	$[NHEt_3^+]$ / mmol dm^{-3}	$k_{obs}{}^1$ / s^{-1}	$k_{obs}{}^2$ / s^{-1}	$-\Delta A_1$	$-\Delta A_2$	A_f
$H_2L^0{}_H$	2.5	20.0	0.0	120	21.5	0.170	0.091	0.706[1]
	2.5	20.0	1.0	72	21.0	0.133	0.138	0.717[1]
	2.5	20.0	2.5	48	20.7	0.071	0.199	0.730[1]
	2.5	20.0	5.0	24		0.268		0.718[2]
	2.5	20.0	10.0	9.9		0.280		0.727[2]
	2.5	20.0	20.0	6.1		0.279		0.731[2]
	2.5	20.0	30.0	4.8		0.280		0.723[2]
	2.5	10.0	0.0	118	21.0	0.088	0.143	0.708[1]
	2.5	10.0	1.0	59	19.5	0.077	0.192	0.772[1]
	2.5	10.0	2.5	21.2		0.231		0.752[2]
	2.5	10.0	5.0	9.2		0.233		0.756[2]
	2.5	10.0	10.0	6.4		0.234		0.747[2]
	2.5	10.0	20.0	4.9		0.227		0.743[2]
	2.5	10.0	30.0	3.2		0.213		0.735[2]
	1.0	10.0	20.0	1.6		0.248		0.750[2]
	2.5	10.0	20.0	3.8		0.250		0.893[2]
	3.5	10.0	20.0	5.1		0.260		1.282[2]
	4.0	10.0	20.0	6.5		0.260		1.650[2]

Fits to absorbance-time curves: ΔA_1 = absorbance change for first phase; $-\Delta A_2$ = absorbance change for second phase; A_f = final absorbance.

1. two exponentials $A_t = A_f + \Delta A_1.\exp(-k_{obs}{}^1.t) + \Delta A_2.\exp(-k_{obs}{}^2.t)$
2. single exponential $A_t = A_f + \Delta A_1.\exp(-k_{obs}{}^1.t)$

Kinetic Analyses: Figures S1 – S5 and Table S9[1]

Figures S1 – S5 show examples of absorbance-time curves and the kinetic analyses.

Figure S1 Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with H_2L_H-Cl (1.0 mmol dm^{-3})
Figure S2 Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^0_H$ (2.5 mmol dm^{-3})
Figure S3 Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with L^3_{py} (5.0 mmol dm^{-3})

Figures S1 – S3 show the high quality fits using exponentials, even when the reactions are studied under conditions far from pseudo first-order.

Figure S4a Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with H_2L_{Cl}-Cl (4.0 mmol dm^{-3}) showing biphasic behaviour and the excellent fit to two exponentials.

Figure S4b Analysis of the data shown in Figure S4a by second order plot[2], showing the biphasic behaviour is also observed in this analysis and the rate constants derived from the second order analysis are in good agreement with those derived using exponential curve fits.

Figure S4c Same second order analysis as shown in Figure S4b but showing how the straight line fit for the the slow phase extends over long times.

Figure S5a Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^a_{Me}$ (1.0 mmol dm^{-3}) showing biphasic behaviour and the excellent fit to two exponentials.

Figure S5b Analysis of the data shown in Figure S5a by second order plot[2], showing the biphasic behaviour is difficult to discern in this case because under the conditions used in this experiment the slopes of the fast and slow phases for this plot are very similar.

Figure S5c Reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^a_{Me}$ (3.0 mmol dm^{-3}) showing biphasic behaviour and the excellent fit to two exponentials.

Figure S5d Analysis of the data shown in Figure S5c by second order plot[2], showing the biphasic behaviour is also observed in this analysis and the rate constants derived from the second order analysis are in good agreement with those derived using exponential curve fits.

Table S9 Table showing the calculated 'reacting concentrations' ($[Ni^{2+}]_r$) in the equilibrium reactions of Ni^{2+} with H_2L_X-Cl, $H_2L^a_X$, $H_2L^0_X$ and H_2salphen ($[Ni^{2+}]_0$ = 0.5 mmol dm^{-3}, $[ligand]_0$ = 1.0 mmol dm^{-3}).

Footnotes

1. The values of the rate constants presented in the text and Tables 5 and 6 are derived from exponential fits to the absorbance-time curves.

[continued….

2. Second order analysis for the reactions of Ni^{2+} with ligand (L) when the concentrations of the two reactants are similar (not pseudo first-order conditions), are plots of $\log_e\{[L]_t/[Ni^{2+}]_t\}$ versus time when $[L]_0 > [Ni^{2+}]_0$ (subscript t = at time t, and 0 = at time t = 0).

Using Beer's Law (where A_f = final absorbance, A_i = initial absorbance and A_t = absorbance at time t) it can be shown that:

$$\text{plot of } \log_e\left\{\frac{[L]_t}{[Ni^{2+}]_t}\right\} \text{ versus time } =$$

$$\text{plot of } \log_e\left\{\frac{(A_f - A_i)[L]_0 - (A_t - A_i)[Ni^{2+}]_0}{(A_f - A_t)[Ni^{2+}]_0}\right\} \text{ versus time}$$

Figure S1. Stopped-flow absorbance-time curve for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with H_2L_H-Cl (1.0 mmol dm^{-3}) showing good fit to a single exponential curve. Experimental data is shown in black and the superimposed single exponential curve fit is shown in grey. The equation of the curve fit used is $A_t = 0.483 - 0.21e^{-0.12t}$ (see Table S4).

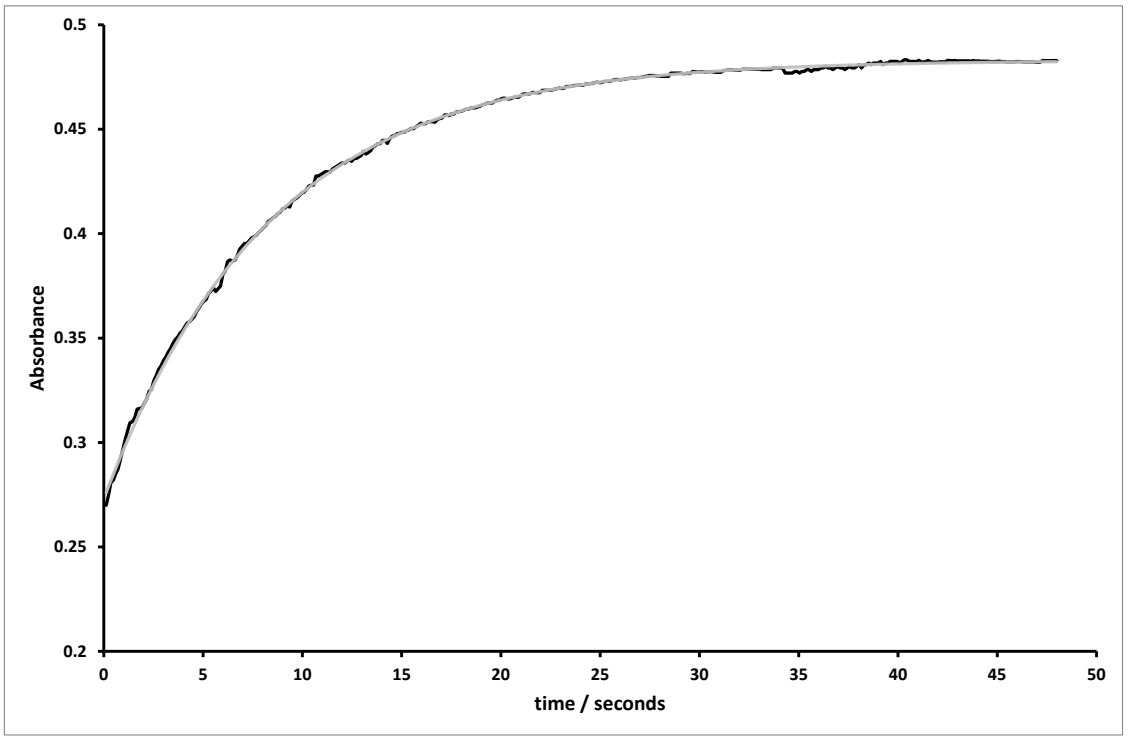

Figure S2. Stopped-flow absorbance-time curve for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^0_H$ (2.5 mmol dm^{-3}) in presence of $NHEt_3^+$ (5.0 mmol dm^{-3}) and NEt_3 (10 mmol dm^{-3}) showing good fit to a single exponential curve. Experimental data is shown in black and the superimposed single exponential curve fit is shown in grey. The equation of the curve fit used is $A_t = 0.756 - 0.233e^{-9.2t}$ (see Table S8).

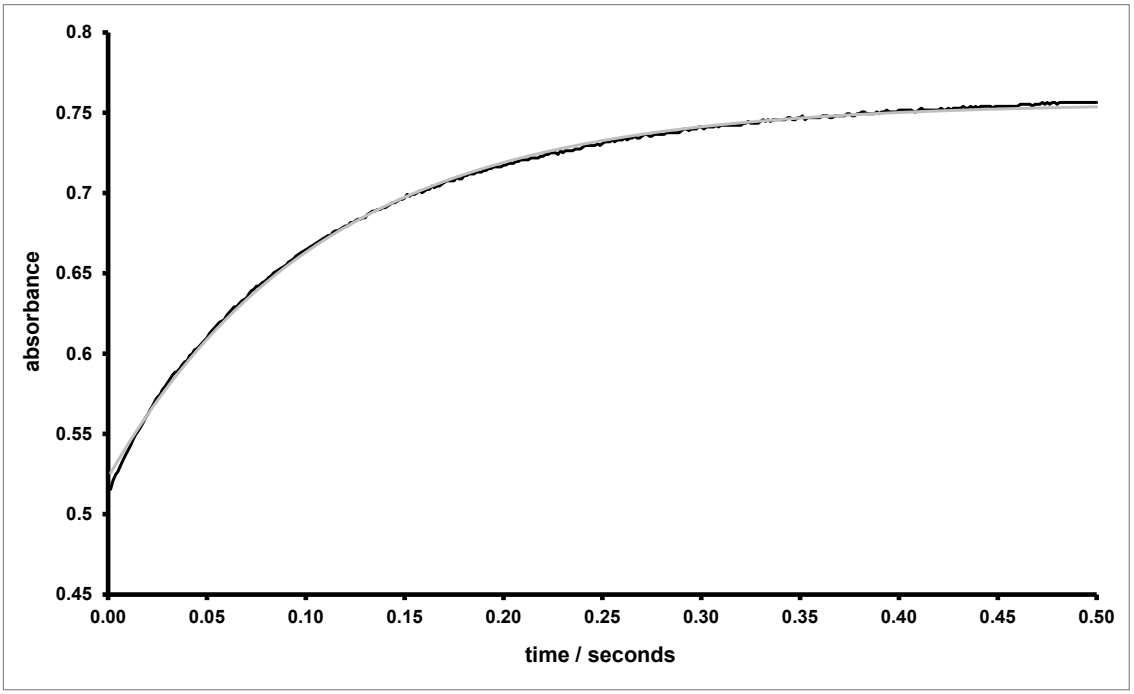

Figure S3. Stopped-flow absorbance-time curve for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with L^3_{py} (5.0 mmol dm^{-3}) showing good fit to a single exponential curve. Experimental data is shown in black and the superimposed single exponential curve fit is shown in grey. The equation of the curve fit used is $A_t = 0.059 - 0.215e^{-17.9t}$ (see Table S7).

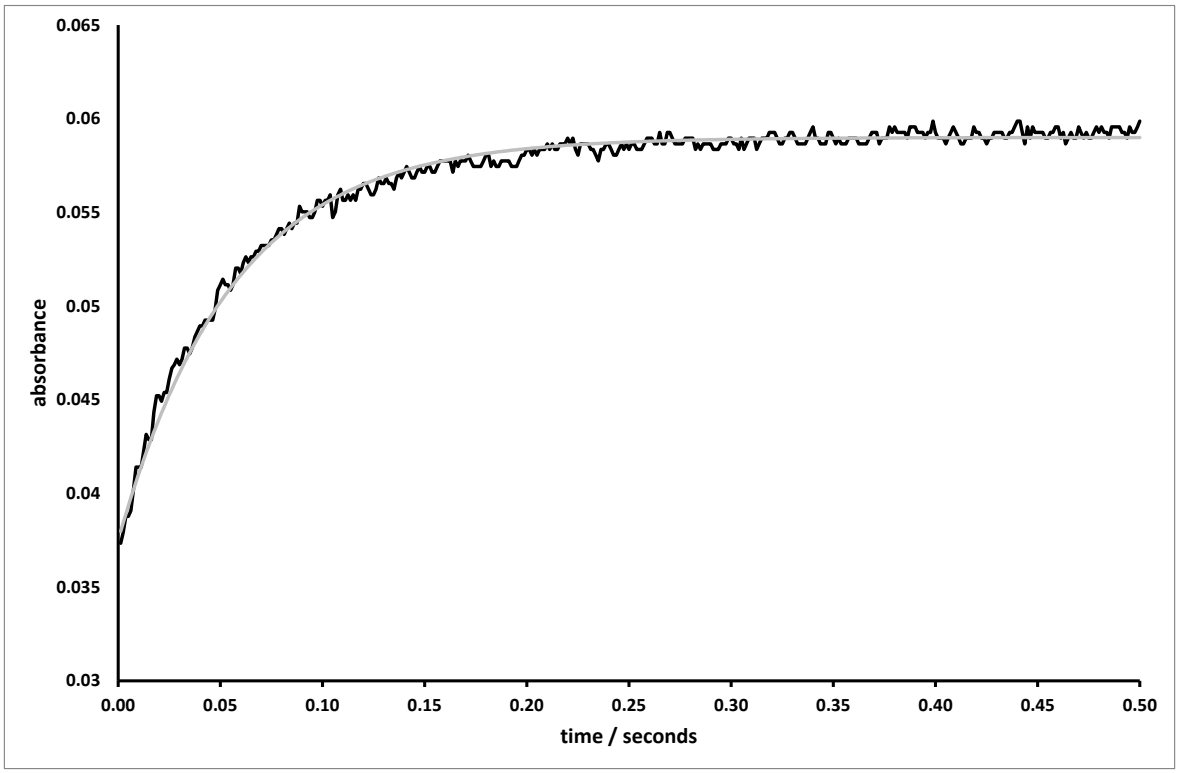

Figure S4a. Stopped-flow absorbance-time curve for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with H_2L_{Cl}-Cl (4.0 mmol dm^{-3}) showing good fit to a two exponential curves. Experimental data is shown in black and the superimposed two exponential curve fit is shown in grey. The equation of the curve fit used is $A_t = 1.43 - 0.413e^{-0.35t} - 0.673e^{-0.04t}$ (see Table S4).

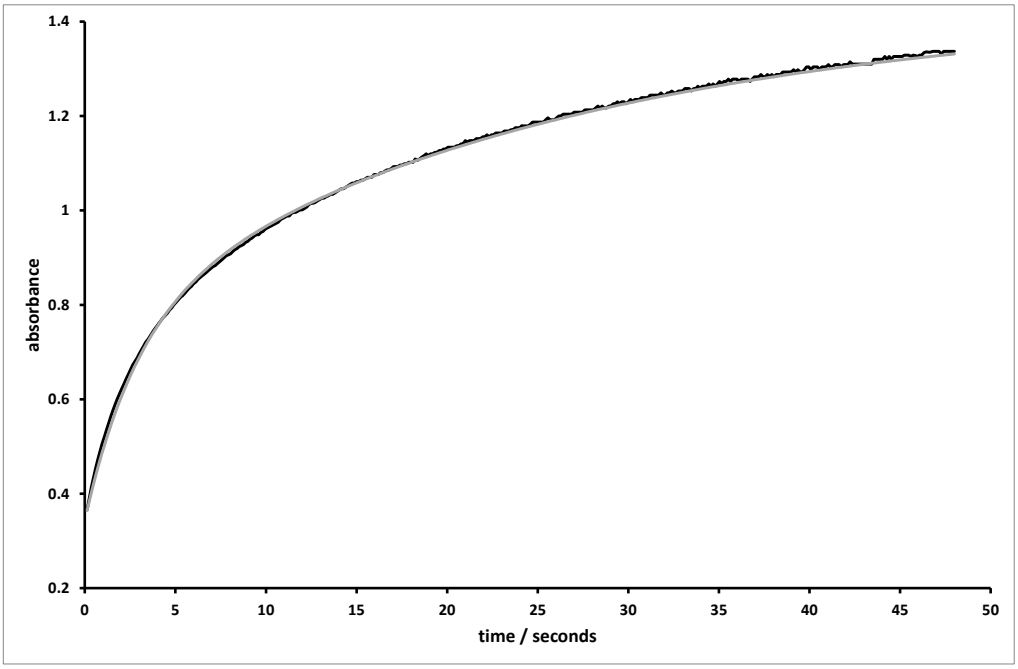

Figure S4b. Second order kinetic analysis for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with H_2L_{Cl}-Cl (4.0 mmol dm^{-3}). Experimental data is shown in black and the tangential lines are drawn for the two phases (red line = slow phase, $\log_e\{[H_2L_{Cl}\text{-}Cl]_t/[Ni^{2+}]_t = 2.45 + 0.04t$; green line = fast phase, $[H_2L_{Cl}\text{-}Cl]_t/[Ni^{2+}]_t = 2.08 + 0.13t$). Rate constant for slow phase (independent of $[H_2L_{Cl}\text{-}Cl]$), k_b = 0.04 s^{-1}; rate constant for fast phase (dependent on $[H_2L_{Cl}\text{-}Cl]$), k_a = slope/($[H_2L_{Cl}\text{-}Cl]_0 - [Ni^{2+}]_0$) = 0.13/3.5 x 10^{-3} = 37.1 dm^3 mol^{-1} s^{-1}. The values of both k_a and k_b from this analysis are in good agreement with the values determined using exponential curve fits (see Table 5). Note that the deviations from linearity (red line) occur for up to 10 s. This corresponds to about 57% of the total absorbance change (see Fig S4a).

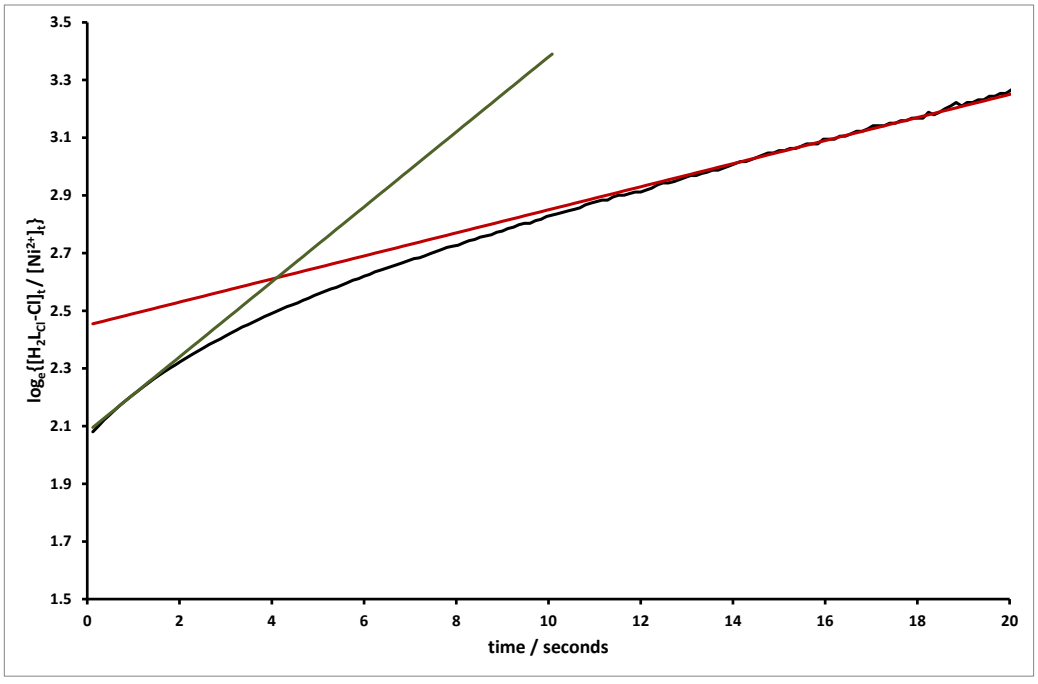

Figure S4c. Second order kinetic analysis for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with H_2L_{Cl}-Cl (4.0 mmol dm^{-3}). Same data as in Figure S4b but showing goodness of fit of the line $\log_e\{[H_2L_{Cl}\text{-}Cl]_t/[Ni^{2+}]_t = 2.45 + 0.04t$ for the slow phase over extended times. Experimental data is shown in black and the straight line fit is shown in red (see Table 5).

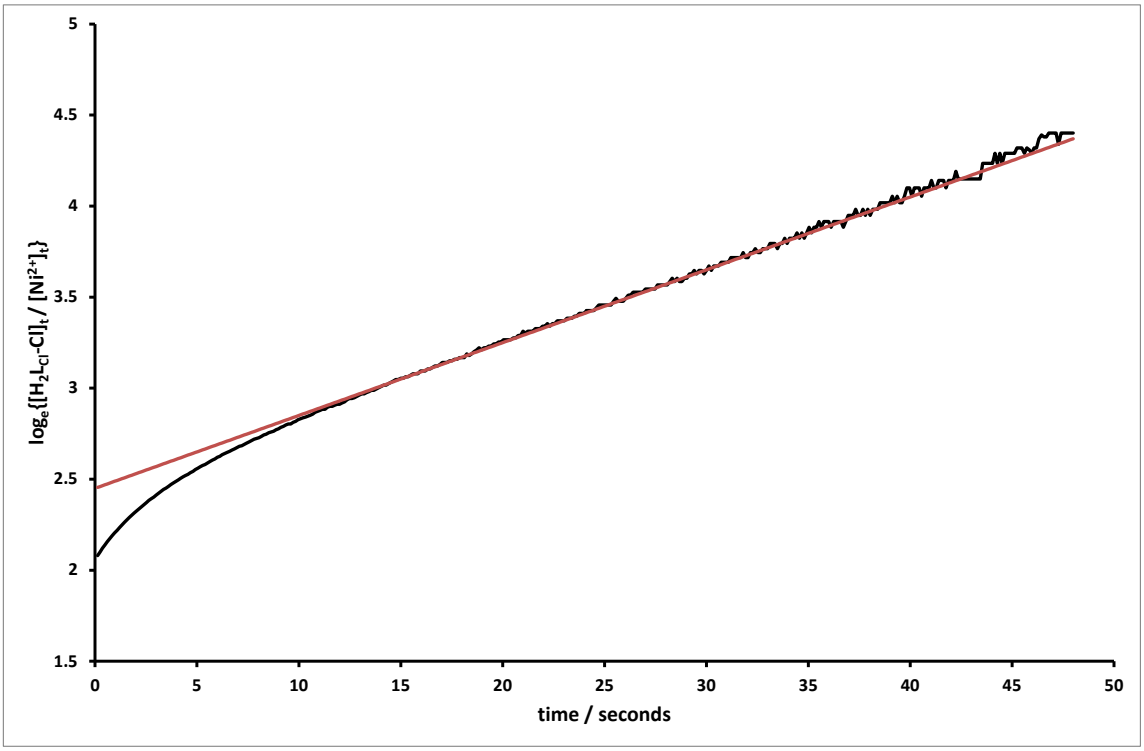

Figure S5a. Stopped-flow absorbance-time curve for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^a_{Me}$ (1.0 mmol dm^{-3}) showing good fit to a two exponential curves. Experimental data is shown in black and the superimposed two exponential curve fit is shown in grey. The equation of the curve fit used is $A_t = 0.665 - 0.10e^{-0.45t} - 0.14e^{-0.06t}$ (see Table S3).

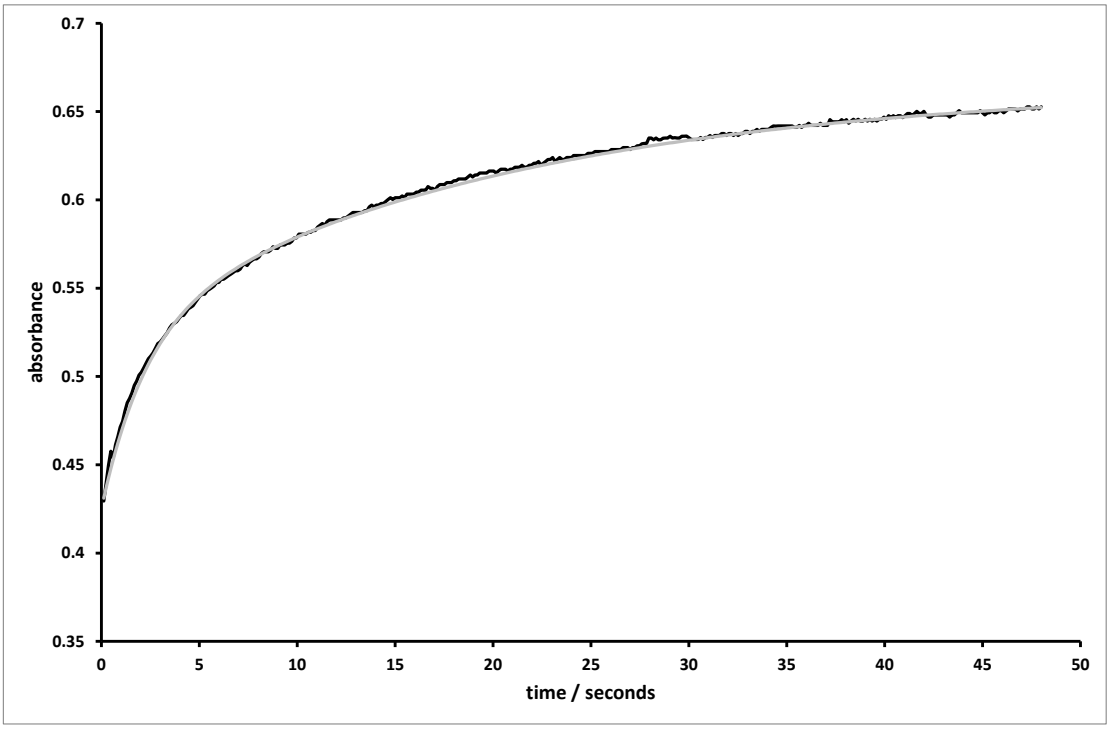

Figure S5b. Second order kinetic analysis for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^a_{Me}$ (1.0 mmol dm^{-3}). Experimental data is shown in black and the straight line drawn is, $\log_e\{[H_2L^a_{Me}]_t/[Ni^{2+}]_t = 0.85 + 0.045t$. Note the small deviation from the straight line at the beginning, because under the conditions used in this experiment the slopes of the fast and slow phases for this plot are very similar (calculated slope for fast phase = 0.044 s^{-1}; slope for slow phase = 0.060 s^{-1}).

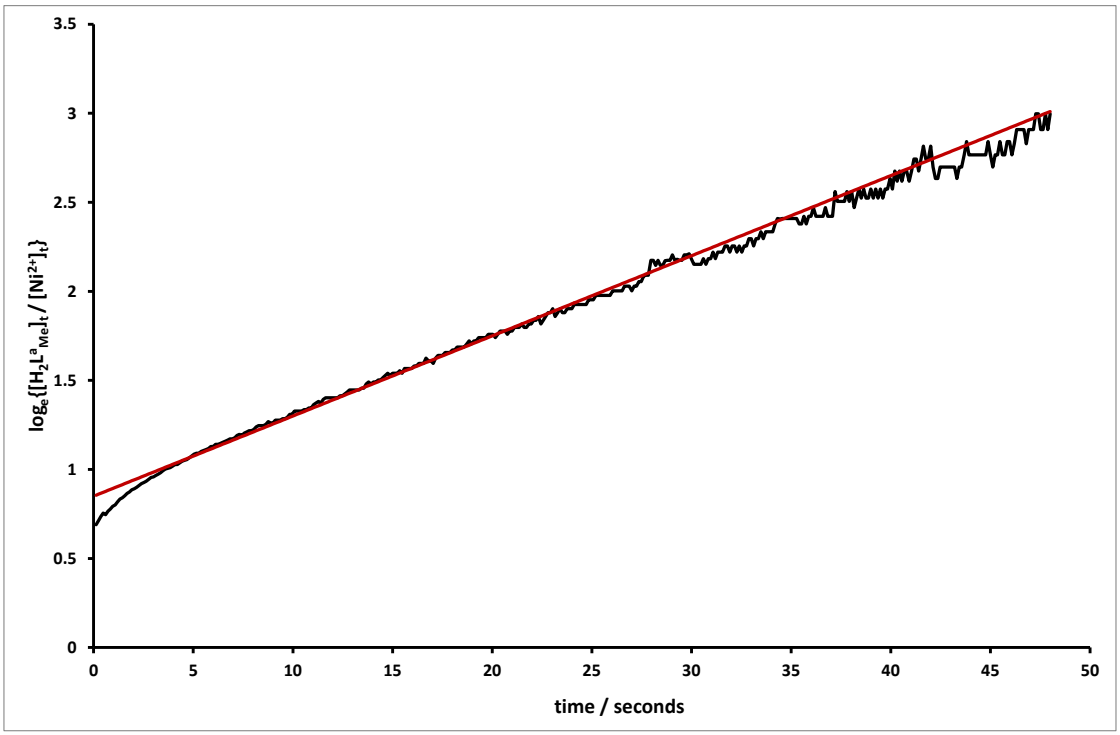

Figure S5c. Stopped-flow absorbance-time curve for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^a_{Me}$ (3.0 mmol dm^{-3}) showing good fit to a two exponential curves. Experimental data is shown in black and the superimposed two exponential curve fit is shown in grey. The equation of the curve fit used is $A_t = 1.695 - 0.27e^{-0.61t} - 0.30e^{-0.07t}$ (see Table S3).

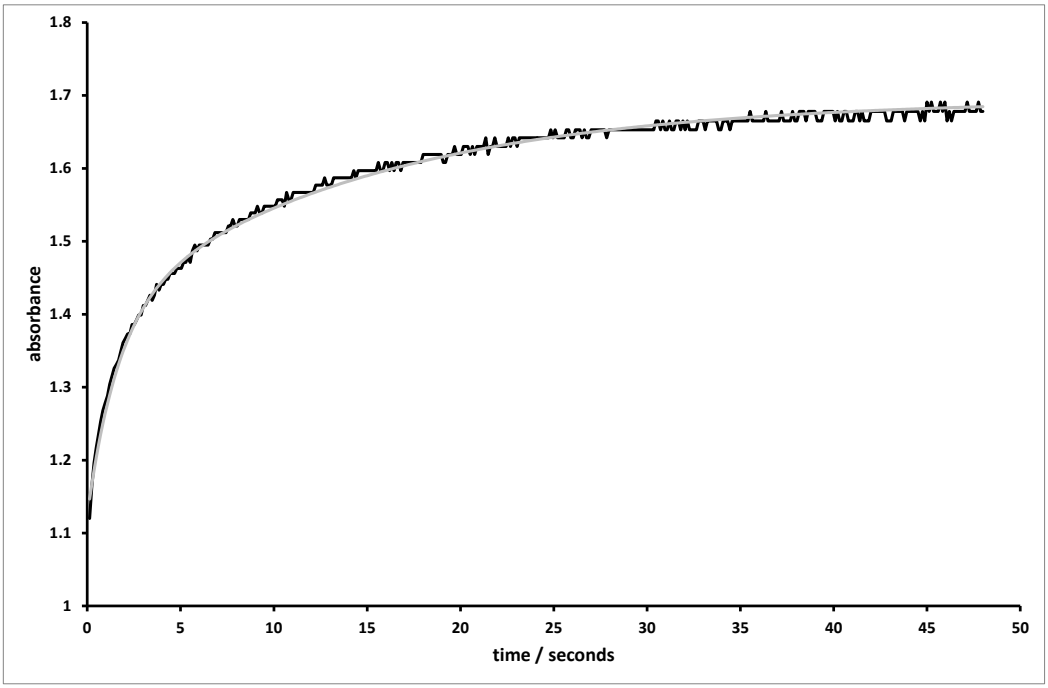

Figure S5d. Second order kinetic analysis for the reaction of Ni^{2+} (0.5 mmol dm^{-3}) with $H_2L^a_{Me}$ (3.0 mmol dm^{-3}). Experimental data is shown in black and the tangential lines are drawn for the two phases (red line = slow phase, $\log_e\{[H_2L^a_{Me}]_t/[Ni^{2+}]_t = 2.5 + 0.06t$; green line = fast phase, $[H_2L^a_{Me}]_t/[Ni^{2+}]_t = 1.85 + 0.21t$). Rate constant for slow phase (independent of $[H_2L^a_{Me}]$), k_b = 0.06 s^{-1}; rate constant for fast phase (dependent on $[H_2L^a_{Me}]$), k_a = slope/$([H_2L^a_{Me}]_0 - [Ni^{2+}]_0)$ = 0.21/2.5 x 10^{-3} = 84 dm^3 mol^{-1} s^{-1}. The values of both k_a and k_b from this analysis are in good agreement with the values determined using exponential curve fits (see Table 5). Note that the two phases are more evident in this plot than in Fig S5b, because under the conditions used in this experiment the slopes of the fast and slow phases for this plot are significantly different.

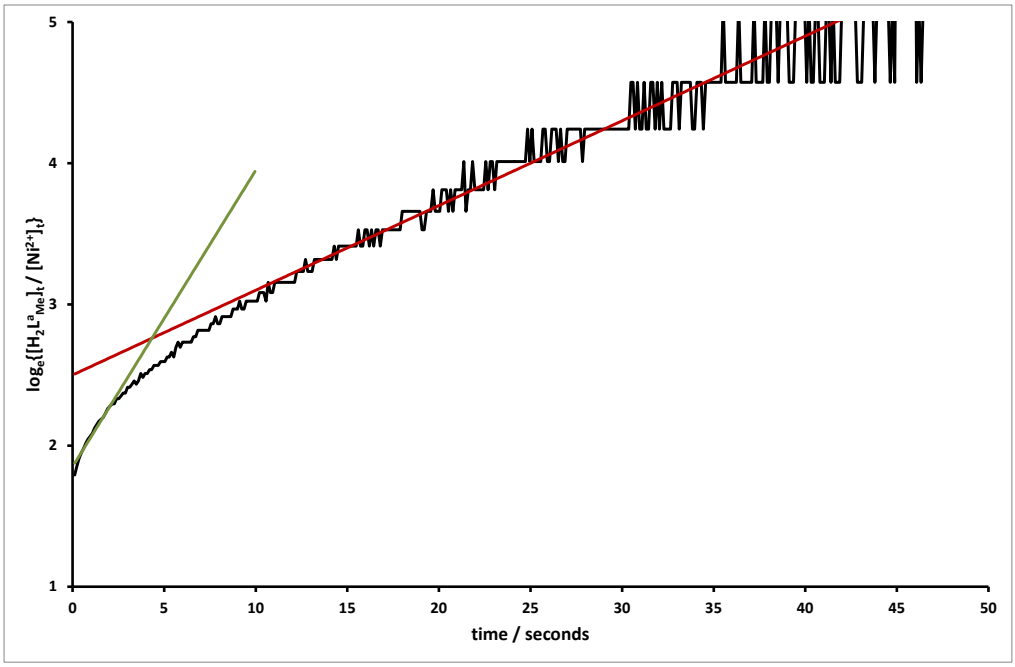

Table S9.

Comparison of the added concentrations ($[Ni^{2+}]_0 = 0.5$ mmol dm^{-3}) with the reacting concentrations ($[Ni^{2+}]_r$) for the equilibrium reactions of Ni^{2+} with H_2L_X-Cl, $H_2L^a{}_X$, $H_2L^0{}_X$ and H_2salphen ($[ligand]_0 = 1.0$ mmol dm^{-3}).

Ligand	K_a [1] / dm^3 mol^{-1}	$[Ni^{2+}]_r$ / mmol dm^{-3}	$[ligand]_0 / [Ni^{2+}]_r$
$H_2L^a{}_H$	863	0.20	5.0
$H_2L^a{}_{Me}$	250	0.092	10.9
$H_2L^a{}_{Cl}$	813	0.20	5.0
H_2L_H-Cl	46	0.025	40.0
H_2L_{Me}-Cl	1485	0.26	4.0
H_2L_{Cl}-Cl	147	0.060	16.7
$H_2L^0{}_H$	260	0.086	11.6
$H_2L^0{}_{MeO}$	393	0.128	7.8
$H_2L^0{}_{Me}$	110	0.047	21.3
$H_2L^0{}_{Cl}$	923	0.21	5.0
H_2salphen	400	0.13	7.7

footnotes

1. $K_a = k_a / k_{-a}$ (values shown in Table 5)