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Accessory Publication

Conjoint analysis of kinetic and equilibrium data for mechanistic elucidation in polynuclear complexation reactions, exemplified by metal(II) helicate complex formation

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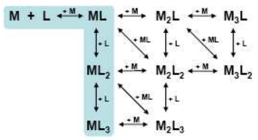
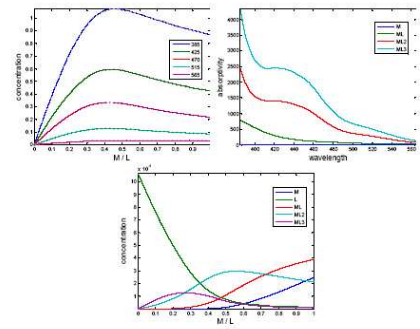
4) 		$M + L \leftrightarrow ML$ 5.004 ± 0.016 $ML + L \leftrightarrow ML_2$ 9.549 ± 0.015 $ML_2 + L \leftrightarrow ML_3$ 13.003 ± 0.019	
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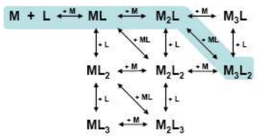
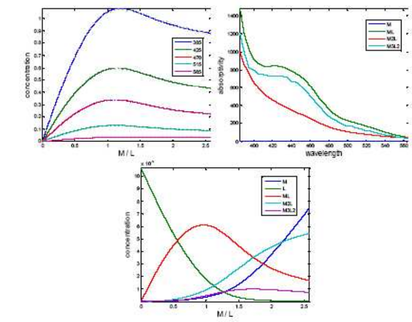
5) 		$M + L \leftrightarrow ML$ 4.979 ± 0.008 $M + L \leftrightarrow M_2L$ 8.616 ± 0.010 $M_2L + ML \leftrightarrow M_3L_2$ 16.506 ± 0.038	
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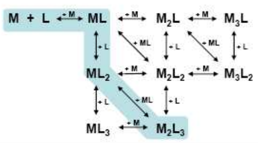
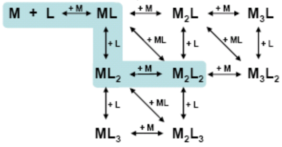
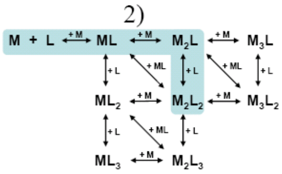
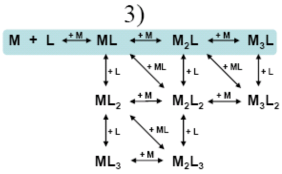
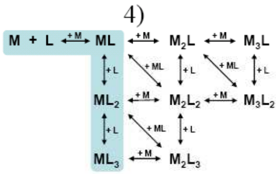
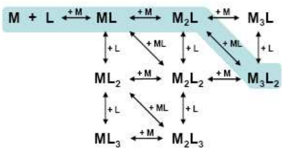
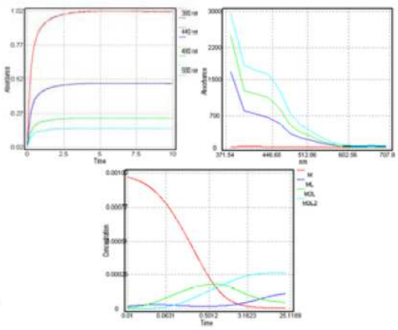
6) 		no convergence	

Supplementary Table 1: Analysis results for nickel(II) spectrophotometric titration – all models (see Scheme 1); their overall stability constants (log β) and quality of fit defined by the sum of squares; fits at selected wavelengths, concentration profiles and absorption spectra.

nickel (II) models	k_+	k_-
1) 	No convergence	
2) 	No convergence	
3) 	no convergence	
4) 	no convergence	
5) 	$M + L \leftrightarrow ML$ $1.80\times 10^{3} \pm 0.05$ $ML + M \leftrightarrow M_2L$ $1.15 \times 10^{4} \pm 0.01$ $M_2L + ML \leftrightarrow M_3L_2$ $1.64 \times 10^{4} \pm 0.02$	$9.61 \times 10^{-5} \pm 0.07$ 2.98 ± 0.10 $4.75 \times 10^{-6} \pm 0.04$ 
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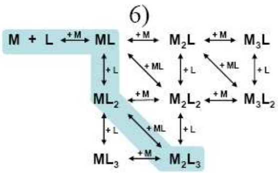
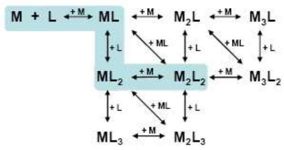
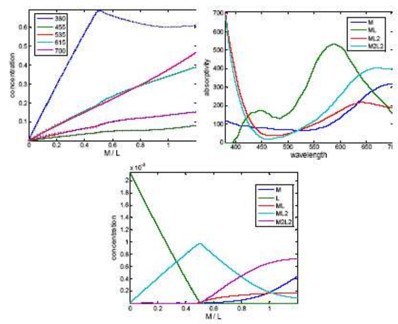
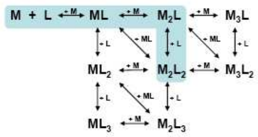
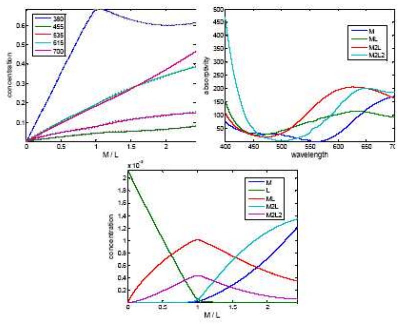
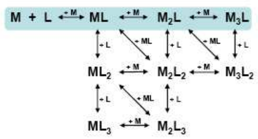
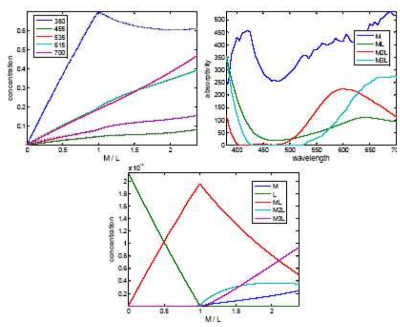
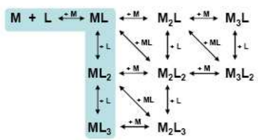
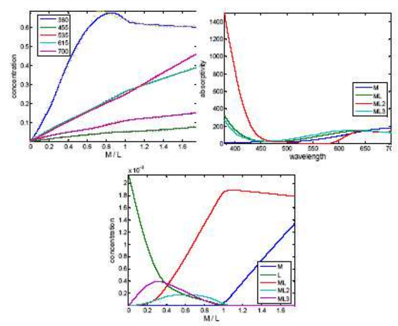
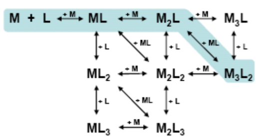
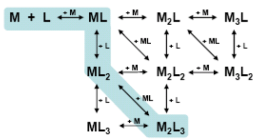
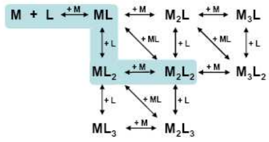
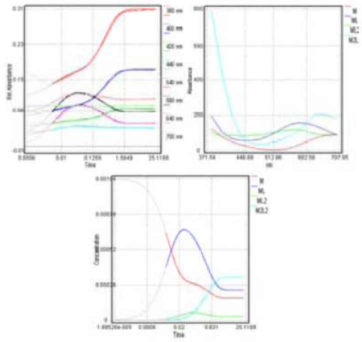
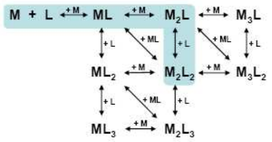
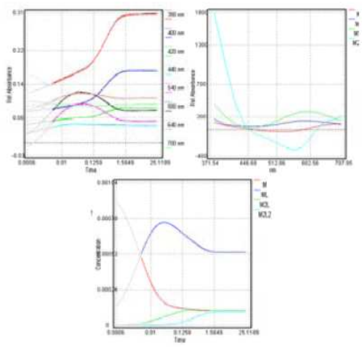
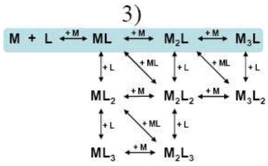
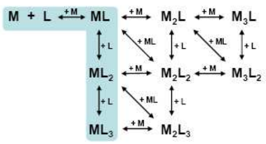
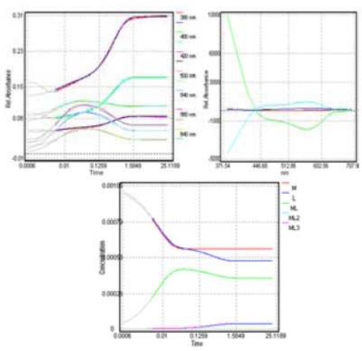
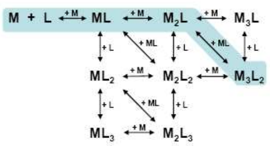
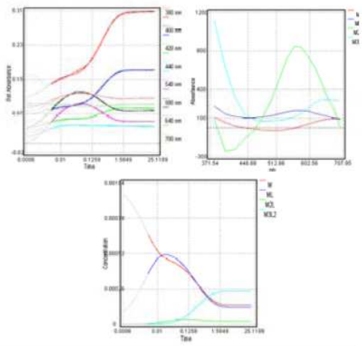
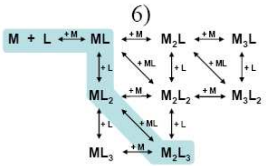
6) 	no convergence	

Supplementary Table 2: Analysis results for nickel(II) stopped-flow data – all models (see Scheme 1); forward (k_+) and reverse (k_-) rate constants and quality of fit defined by the sum of squares; fits at selected wavelengths, concentration profiles and absorption spectra.

copper(II) models		log β values	
1) 		$M + L \leftrightarrow ML$	
		7.66 ± 0.75	
		$ML + L \leftrightarrow ML_2$	
		15.43 ± 0.51	
		$ML_2 + M \leftrightarrow M_2L_2$	
		19.73 ± 0.51	
	ssq	0.0537	
2) 		$M + L \leftrightarrow ML$	
		6.121 ± 0.03	
		$ML + M \leftrightarrow M_2L$	
		9.628 ± 0.04	
		$M_2L + L \leftrightarrow M_2L_2$	
		14.872 ± 0.07	
	ssq	0.0500	
3) 		$M + L \leftrightarrow ML$	
		8.09 ± 0.15	
		$ML + M \leftrightarrow M_2L$	
		11.54 ± 0.15	
		$M_2L + M \leftrightarrow M_3L$	
		15.57 ± 0.16	
	ssq	0.0574	
4) 		$M + L \leftrightarrow ML$	
		6.58 ± 0.06	
		$ML + L \leftrightarrow ML_2$	
		9.70 ± 0.06	
		$ML_2 + L \leftrightarrow ML_3$	
		13.56 ± 0.07	
	ssq	0.0824	
5) 		no convergence	
6) 		no convergence	

Supplementary Table 3: Analysis results for copper(II) spectrophotometric titration – all models (see Scheme 1); their overall stability constants (log β) and quality of fit defined by the sum of squares; fits at selected wavelengths, concentration profiles and absorption spectra.

copper(II) models	k_+	k_-	
1) 	$M + L \leftrightarrow ML$		
	$7.99 \times 10^4 \pm 0.01$	7.78 ± 0.03	
	$ML + L \leftrightarrow ML_2$		
	$9.67 \times 10^3 \pm 0.02$	9.14 ± 0.06	
	$ML_2 + M \leftrightarrow M_2L_2$		
	$5.23 \times 10^4 \pm 0.09$	0.58 ± 0.01	
ssq	0.1960		
2) 	$M + L \leftrightarrow ML$		
	$1.05 \times 10^5 \pm 0.02$	3.54 ± 0.05	
	$ML + M \leftrightarrow M_2L$		
	$1.28 \times 10^4 \pm 0.09$	4.04 ± 0.07	
	$M_2L + L \leftrightarrow M_2L_2$		
	$7.22 \times 10^3 \pm 0.14$	3.02 ± 0.01	
ssq	0.1771		
3) 	no convergence		
4) 	$M + L \leftrightarrow ML$		
	$2.98 \times 10^4 \pm 0.09$	0.13 ± 0.05	
	$ML + L \leftrightarrow ML_2$		
	$1.22 \times 10^5 \pm 0.12$	4.98 ± 0.04	
	$ML_2 + L \leftrightarrow ML_3$		
	$3.03 \times 10^4 \pm 0.19$	0.05 ± 0.01	
ssq	0.3552		
5) 	$M + L \leftrightarrow ML$		
	$2.46 \times 10^4 \pm 0.04$	181.33 ± 0.05	
	$ML + M \leftrightarrow M_2L$		
	$2.75 \times 10^5 \pm 0.02$	17.58 ± 0.10	
	$M_2L + ML \leftrightarrow M_3L_2$		
	$4.67 \times 10^4 \pm 0.12$	0.69 ± 0.09	
ssq	0.1251		
6) 	no convergence		

Supplementary Table 4: Analysis results for copper(II) stopped-flow data – all models (see Scheme 1); forward (k_+) and reverse (k_-) rate constants and quality of fit defined by the sum of squares; fits at selected wavelengths, concentration profiles and absorption spectra.

	$[L]_0$ in cuvette	[M] in burette	final M:L ratio in cuvette
Cu^{2+}	2.13×10^{-3} M	3.35×10^{-2} M	1.0
	1.07×10^{-3} M	3.35×10^{-2} M	1.2
	6.09×10^{-4} M	9.80×10^{-3} M	1.6
Ni^{2+}	1.07×10^{-3} M	9.95×10^{-3} M	1.0
	7.11×10^{-3} M	9.95×10^{-3} M	2.3
	3.55×10^{-4} M	9.95×10^{-3} M	2.4
	1.78×10^{-4} M	9.95×10^{-3} M	4.6

Supplementary Table 5: Experimental details for spectrophotometric titrations. For each metal ion all titrations were fitted globally, resulting in one set of stability constants and absorption spectra

M:L ratio	$[Ni^{2+}]$	$[Cu^{2+}]$	[L]
1:1	9.96×10^{-4} M	1.04×10^{-3} M	
1:2	5.02×10^{-4} M	4.98×10^{-4} M	1.05×10^{-3} M
1:3	3.22×10^{-4} M	3.33×10^{-4} M	

Supplementary Table 6: Typical initial concentrations for stopped-flow measurements. For each metal ion all measurements were fitted globally, resulting in one set of rate constants and absorption spectra