Electronic Supplementary Information (ESI) for Dalton Transaction

Thermodynamic, kinetic and solid-state study of divalent metal complexes of 1,4,8,11-tetraazacyclotetradecane (cyclam) bearing two *trans* (1,8-) methylphosphonic acid pendant arms

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Thermodynamic stability of metal complexes

Figure S1 Ligand and selected metal-ligand (M:L=1:1) titration curves.

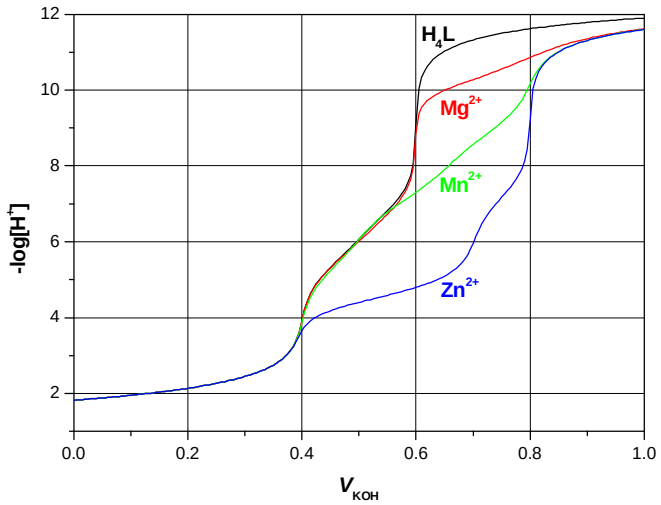
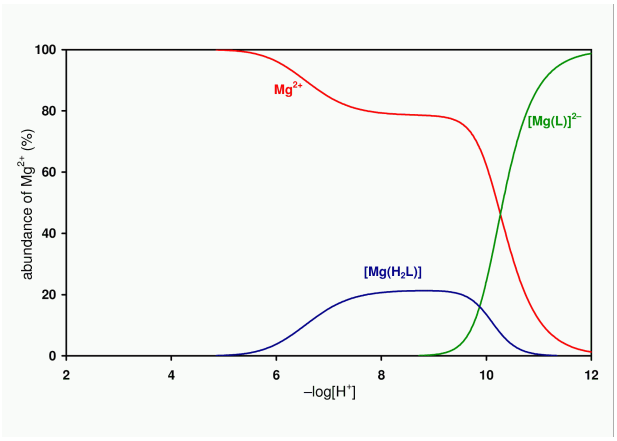
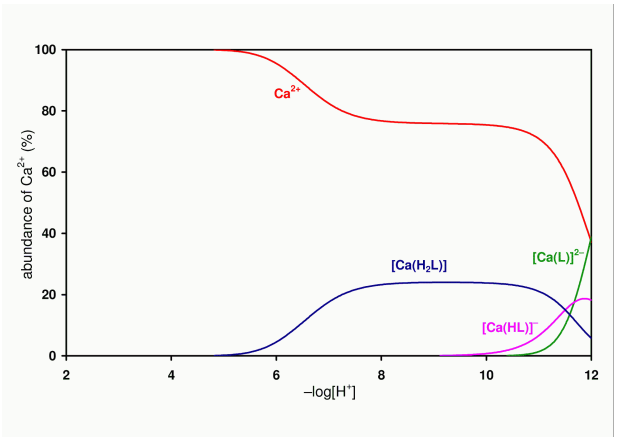


Figure S2 Distribution diagrams of M^{2+}–1,8-H_4te2p systems ($c_M = c_L = 0.004$ mol dm^{-3}); M = Mg (**A**), Ca (**B**) and Mn (**C**).

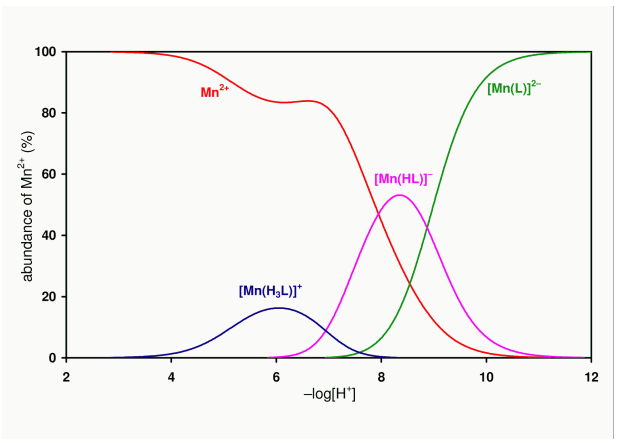
A



B



C



X-ray crystal structures

Figure S3 Crystal packing in the structure of *trans*-O,O-[Zn(H_2L)] complex. The view down to *x* axis. Hydrogen atoms attached to carbon atoms are omitted for clarity. Hydrogen bonds are dashed. C, N, O, P and Zn

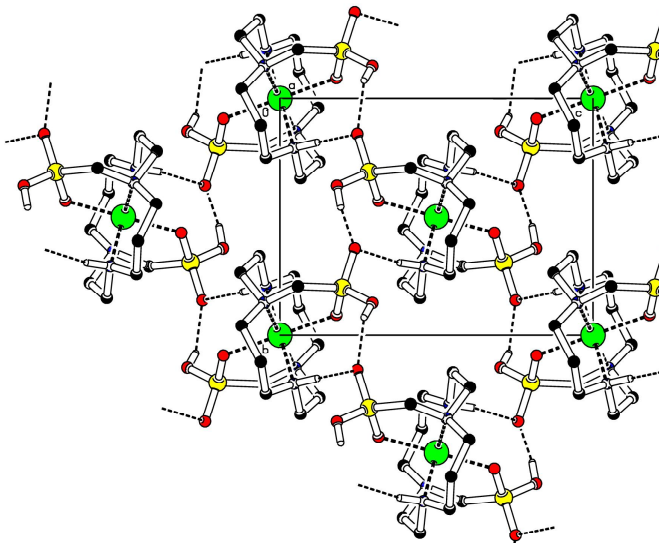


Figure S4 The crystal packing in the structure of [{$(H_2O)_5Mn$}$_2$(μ-H_2L)](H_2L)·21H_2O. The view down to *x*-axis. Uncoordinated water molecules and hydrogen atoms attached to carbon atoms are omitted for clarity.C, N, O, P and Mn

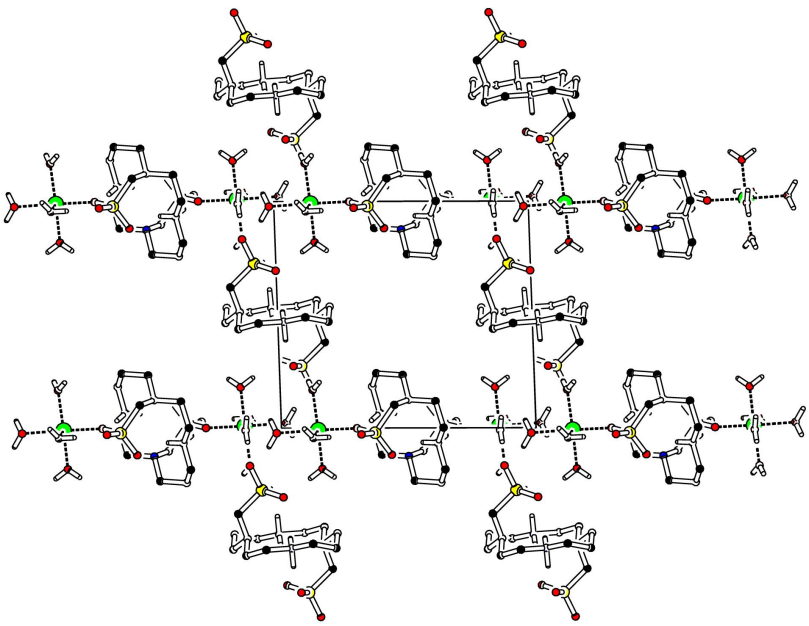
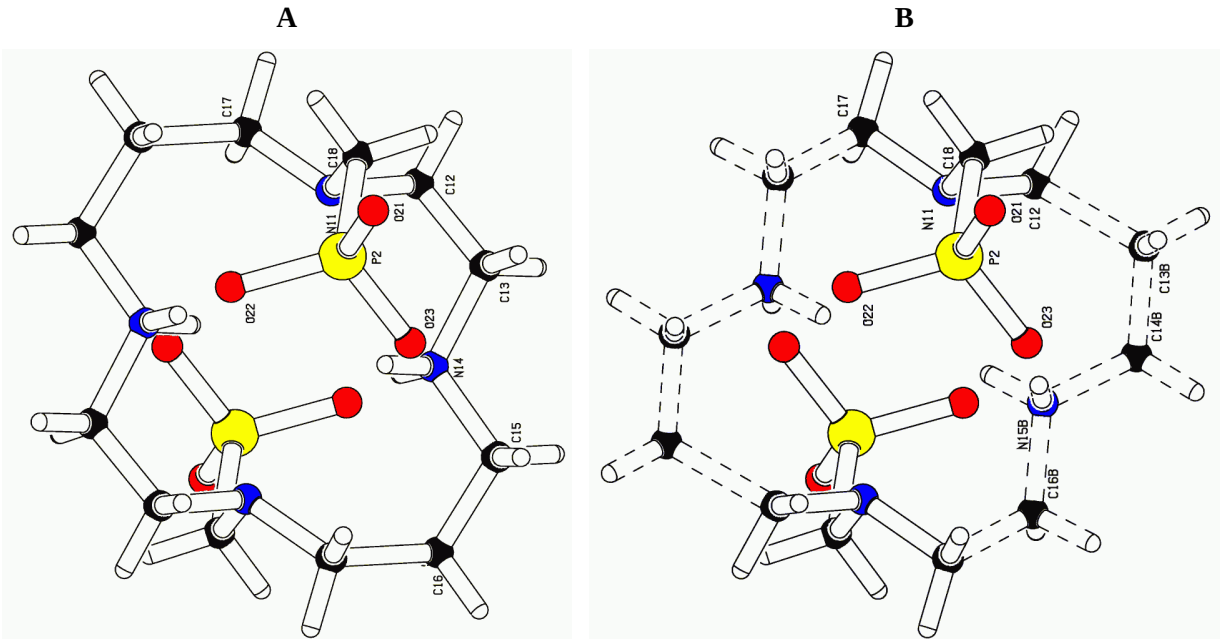


Figure S5 Disorder of the H_2L^{2-} anion found in the structure of $[\{(H_2O)_5Mn\}_2(\mu\text{-}H_2L)](H_2L)\cdot 21H_2O$. (**A**) The most abundant arrangement; (**B**) The less abundant arrangement. H, C, N, O, P



Formation kinetics

Figure S6 Speciation diagram of 1,8-H_4te2p (reproduced from ref.[1])

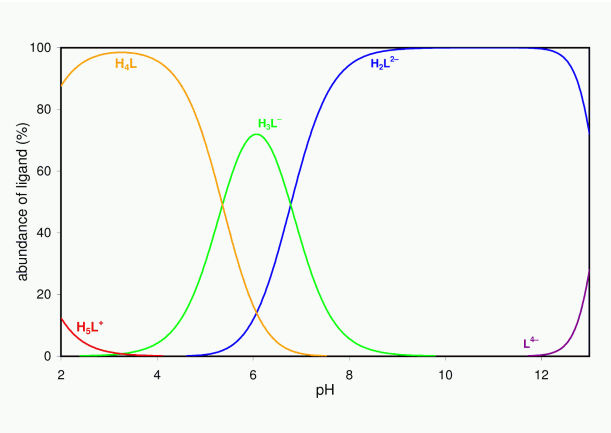


Figure S7 Example of dependence of experimental $^{f}k_{obs}$ constant on $[Zn^{2+}]$. Other experimental conditions are given in the text

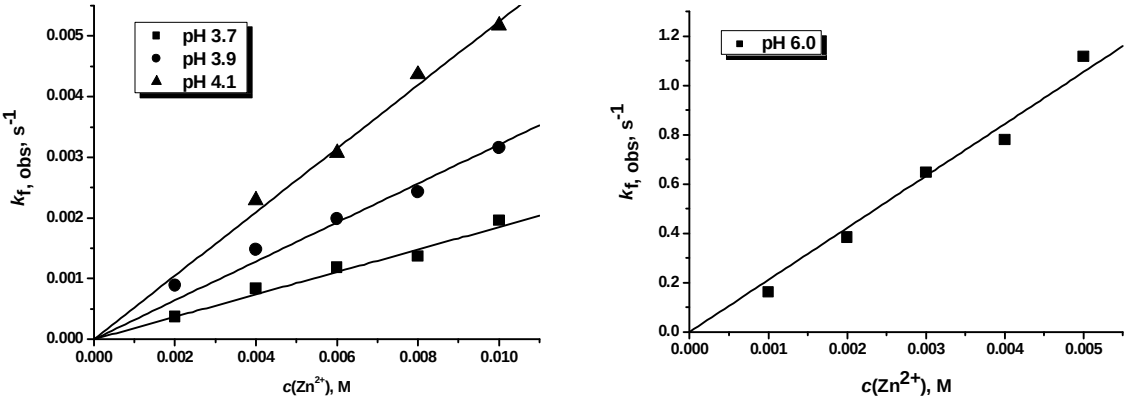


Figure S8 Examples of logarithmic analysis of kinetic experimental data for complexation of Zn^{2+} by 1,8-H_4te2p.

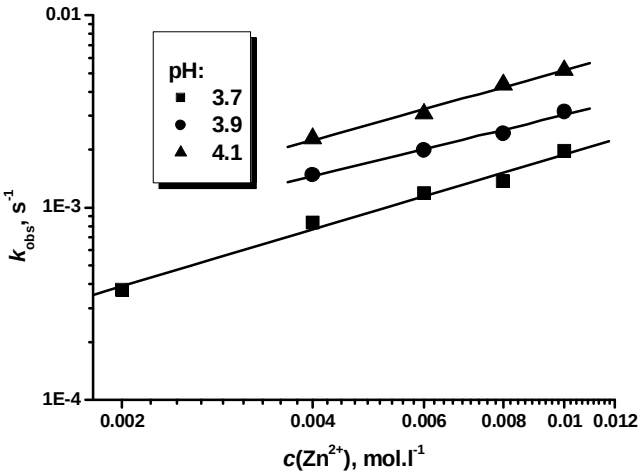


Table S1 Example of evaluation of the formation kinetics data for the Zn^{2+}–1,8-H_4te2p system by logarithmic analysis.

pH	Logarithmic analysis *n*
3.7	0.98 ± 0.06
3.9	0.80 ± 0.06
4.1	0.91 ± 0.07
6.0	1.18 ± 0.06

Figure S9 Examples of dependence of experimental $^{f}k_{obs}$ constant on [Cd^{2+}].

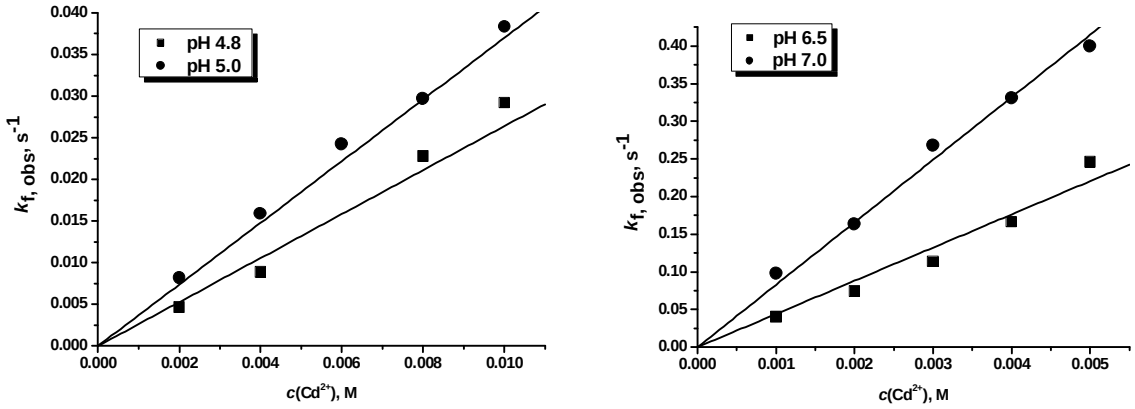


Figure S10 Examples of logarithmic analysis of kinetic experimental data for complexation of Cd^{2+} by 1,8-H_4te2p.

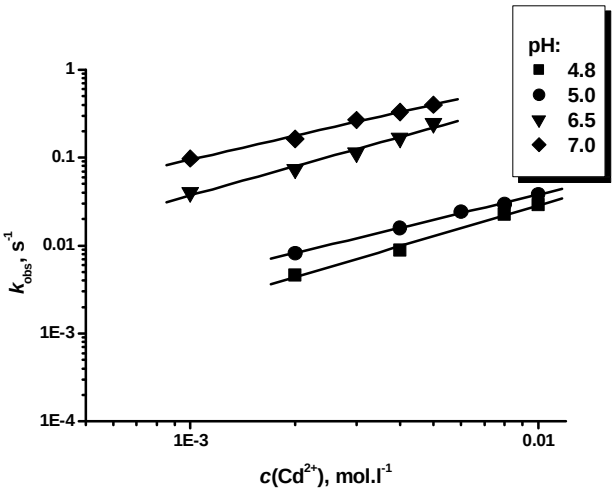


Table S2 Example of evaluation of the formation kinetics data for the Cd^{2+}–1,8-H_4te2p system by logarithmic analysis

pH	Logarithmic analysis *n*
4.8	1.17 ± 0.07
5.0	0.94 ± 0.05
6.5	1.10 ± 0.08
7.0	0.90 ± 0.04

Table S3 Summary of the second-order rate constants ($^{f}k_2$) for complexation in the Zn^{2+}–1,8-H_4te2p and Cd^{2+}–1,8-H_4te2p systems. The standard deviation of the rate constants corresponds with the last digit.

Zn^{2+}		Cd^{2+}	
pH	$^{f}k_2$, M^{-1} s^{-1}	pH	$^{f}k_2$, M^{-1} s^{-1}
3.7	0.185(6)	4.6	$1.5_6(2_7)$
3.9	$0.32_1(1_2)$	4.8	$2.64(2_2)$
4.1	$0.52_4(1_9)$	5.0	$3.7_0(1_3)$
4.5	$0.88_3(8_0)$	5.2	$4.1_0(1_0)$
4.7	$1.42_3(7_9)$	5.4	7.9(9)
5.2	5.8(9)	5.6	13.2(5)
6.0	211(7)	5.9	14.5(2)
6.3	1851(119)	6.1	25(1)
6.5	1650(97)	6.3	41(1)
6.7	3487(170)	6.5	44(2)
6.8	3165(167)	6.8	112(6)
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Figure S11 Partial speciation in Cu^{2+}–OH^-, Zn^{2+}–OH^- and Cd^{2+}–OH^- systems (c_M = 0.002 mol dm^{-3}, I = 0.1 M; constructed with data from refs.[2,3]). The metal hydroxides are given as not precipitating species.

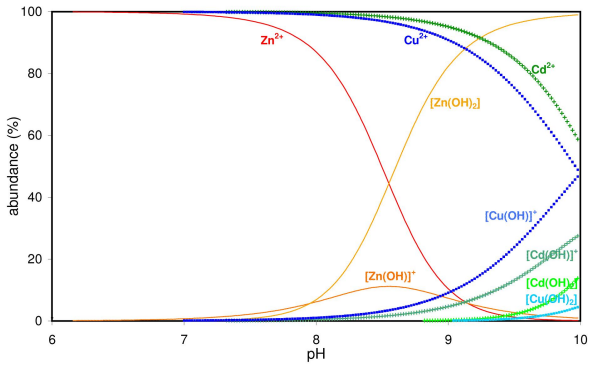
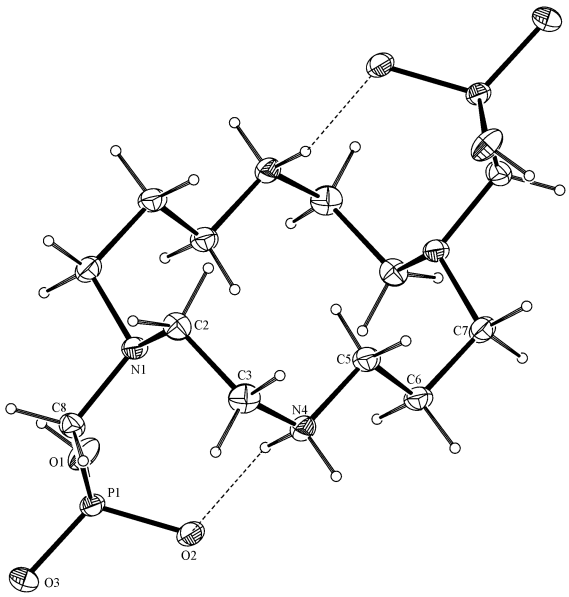


Figure S12 Molecular structure of 1,8-H_4te2p in the solid state.[1]



Dissociation kinetics

Table S4 Example of experimental kinetic data for dissociation of the $[Zn(L)]^{2-}$ complex with Cu^{2+} ion as a ligand scavenger. The standard deviation of the rate constants corresponds with the last digit.

pH	$^{d}k_{obs}\times10^{3}$, s^{-1}			average value $^{d}k_{obs}\times10^{3}$, s^{-1}
	$c(Cu^{2+})$, mol dm^{-3}			
	0.001	0.002	0.003	
3.71	5.0(5)	5.1(5)	4.9(5)	5.0(1)
4.50	1.56(7)	1.46(6)	1.59(6)	1.54(7)
4.71	1.11(5)	1.14(4)	1.13(4)	1.13(1)

Table S5 Summary of the pseudofirst-order rate constants ($^{d}k_{obs}$) for the dissociation of the $[Zn(L)]^{2-}$ and $[Cd(L)]^{2-}$ complexes. The standard deviation of the rate constants corresponds with the last digit.

pH	Zn^{2+}		Cd^{2+}	
	$^{d}k_{obs}\times10^{3}$, s^{-1}		pH	$^{d}k_{obs}\times10^{3}$, s^{-1}
	Cu^{2+}	PAR		
3.71	5.0(1)	5.5(5)	4.50	177(3)
3.91	4.3(5)	4.9(5)	4.73	41(3)
4.12	3.1(4)	4.3(2)	5.15	10.8(1)
4.32	2.1(2)	3.0(2)	5.50	2.49(3)
4.50	1.54(7)	2.2(1)	5.83	1.273(8)
4.71	1.13(1)	1.72(7)	6.11	0.664(9)
4.80	0.86(3)	---	---	---

References:

[1] J. Kotek, P. Vojtíšek, I. Císařová, P. Hermann, P. Jurečka, J. Rohovec and I. Lukeš, *Collect. Czech. Chem. Commun.*, 2000, **65**, 1289.

[2] (a) A. E. Martell and R. M. Smith, *Critical Stability Constants*. Plenum Press, New York, 1974–1989, Vols. 1-6; (b) *NIST Standard Reference Database 46 (Critically Selected Stability Constants of Metal Complexes*), Version 7.0, 2003.

[3] C. F. Baes, Jr. and R. E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, 1976.