Electronic Supplementary Information

Cyclam derivatives containing three acetate pendant arms: synthesis, acid-base, metal complexation and structural studies

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Table S1 Hydrogen bond dimensions found in solid state for the compounds **1**–**5**

	H···A /Å[a]	D···A / Å[a]	D–H···A /[o]
(Hte3am)I.MeOH **1**			
N(11)–H(11A)···N(1)	2.25(2)	2.890(2)	133(2)
N(11)–H(11B)···N(4)	2.55(2)	3.222(2)	133(2)
N(23)–H(23A)···N(8)	2.49(2)	2.829(2)	103(2)
N(17)H(17A)···O(101) [*x*-1/2, -*y*+5/2, *z*-1/2]	2.03(2)	2.883(2)	167(2)
N(11)–H(11A)···O(161)	2.26(2)	2.962(2)	141(2)
N(17)–H(17B)···O(161) [-*x*, -*y*+3, -*z*]	2.08(2)	2.951(2)	177(2)
N(11)–H(11B)···O(191)	2.08(2)	2.874(2)	148(2)
N(23)–H(23A)···O(191)	2.11(2)	2.931(2)	152(2)
N(20)–H(20B)···I [-*x*+1, -*y*+1, -*z*]	2.84(2)	3.696(2)	169(2)
N(23)–H(23B)···I	2.97(2)	3.792(1)	160(2)
O(101)–H(10F)···I	2.71(3)	3.537(1)	173(2)
$(H_2te2lac)ClI\cdot 0.25H_2O$ **2**			
N(14)–H(14)···Cl [*x*-1/2, -*y*+1/2, *z*]	2.13	3.035(7)	170
N(24)–H(24)···O(100) [-*x*-1/2, *y*-1/2, -*z*]	2.15	2.815(9)	129
N(24)–H(24)···Cl [*x*-1/2, -*y*+1/2, *z*]	2.58	3.292(7)	136
$(H_4te2a2p^{OEt2})(I_3)_2\cdot 0.5I_2$ **3**			
N(4)–H(4)···O(161) [-*x*+2, -*y*+2, -*z*+1][b]	1.88	2.77(1)	169
N(24)–H(24)···O(361) [-*x*+1, -*y*+1, -*z*+2][c]	1.92	2.81(1)	165
$(H_7te3a1p)(ClO_4)_2.4.25H_2O$ **4**[d]			
N(4)–H(4)···O(182)	2.19	2.720(4)	115
N(8)–H(8)···O(202)	2.39	2.718(5)	101
N(11)–H(11)···O(222)	2.32	2.720(5)	106
N(4)–H(4)···O(163) [*x*-1/2, -*y*+1, *z*]	1.87	2.703(4)	148
N(11)–H(11)···O(201) [*x*+1/2, -*y*, *z*]	2.27	3.080(5)	145
N(11)–H(11)···O(182) [-x-1/2, *y*, *z*-1/2]	2.45	3.039(4)	121
N(8)–H(8)···O(700) [-*x*+1/2, *y*, *z*-1/2]	1.93	2.820(5)	159
$[Cu_2(Hte3a)(H_2O)_3Cl]Cl_{0.5}(ClO_4)_{0.5}\cdot 2H_2O$ **5**[d]			
O(1)–H(B)···O(181) [*x*+1/2, -*y*+1/2, *z*+1/2]	1.86(5)	2.677(7)	170(6)
O(2)–H(C)···O(182) [*x*+1/2, -*y*+1/2, *z*+1/2]	1.90(4)	2.726(8)	178(7)
O(2)–H(D)···Cl(1)[-*x*+1, -*y*, -*z*+2]	2.46(6)	3.246(4)	159(6)
O(2)–H(F)···O(202) [-*x*+1/2, *y*-1/2, -*z*+3/2]	1.93(6)	2.720(8)	159(6)

[a] A, D denote the proton acceptor and donor, respectively; [b] and [c] correspond to the hydrogen dimensions found for the first and second molecule of **2**, respectively; [d] the hydrogen bonds involving disordered water molecules are not quoted.

Table S2 Protonation constants (log β_{HL}) [a] of the studied ligands determined by potentiometry; T = 298.2 K; I = 0.10 mol dm^{-3} in NMe_4NO_3

Species HL	H_5te3a1p	H_3te3a	H_4teta [b]	H_8tetp [b]
11	11.78(1) [c]	11.91(2)	10.59	-
12	21.66(1)	21.14(2)	20.68	25.28
13	28.00(1)	24.87(3)	24.80	34.13
14	31.85(1)	27.81(3)	28.09	41.81
15	34.48(2)	29.80(7)	29.9	48.04
16	36.62(2)	-	-	53.37
17	-	-	-	55.65

[a] Values in brackets are standard deviations in the last significant figure.
[b] From refs. 1 and 2. [c] Determined by ^{31}P NMR spectroscopy.

Table S2 Stability constants (log β_{MHL}) [a] of complexes of the studied ligands with some divalent metal ions determined by potentiometry. T = 298.2 K; I = 0.10 mol dm^{-3} in NMe_4NO_3

Ion	Species MHL	**H_5te3a1p**	**H_3te3a**	**H_4teta**	**H_8tetp**
Ca^{2+}	101	6.69(1)	5.08(2)	8.4[b]	-
	111	15.42(2)	-	15.6[b]	19.33
	1-11	-3.55(1)	-6.59(2)	-	-
	1-21	-15.29(2)	-	-	-
Mn^{2+}	101	11.64(2)	12.56(2)	11.3[b]	10.8[d]
	111	19.26(2)	18.59(4)	-	-
	121	25.67(3)	24.40(4)	-	-
	131	31.12(3)	27.83(7)	-	-
	1-11	2.40(3)	2.37(2)	-	-
	1-21	-8.44(5)	-	-	-
Co^{2+}	101	16.42(2)	19.53(2)	16.6[b]	15.3[d]
	111	23.74(1)	23.14(2)	20.8[b]	-
	121	27.53(1)	-	23.64[b]	-
	1-11	5.34(2)	7.48(4)	-	-
Ni^{2+}	101	20.04(3)	20.19(2)	19.91[b]	15.6[d]
	111	27.26(2)	23.81(2)	24.11[b]	-
	121	31.08(2)	-	27.31[b]	-
	1-11	10.52(3)	9.34(3)	-	-
Cu^{2+}	101	21.58(3)	21.84(3)	21.07(2)[e]	25.99(8)[e]
	111	28.43(1)	25.08(3)	24.51(2)[e]	34.08(7)[e]
	121	31.79(1)	-	26.98(3)[e]	41.01(7)[e]
	131	-	-	-	46.90(7)[e]
	141	-	-	-	51.93(4)[e]
	1-11	10.30(3)	9.93(4)	-	-
Zn^{2+}	101	18.16(3)	19.63(1)	17.48(4)[f]	18.31(4)[f]
	111	25.31(1)	23.09(1)	21.64(4)	27.44(4)
	121	28.84(2)	-	25.01(4)	34.63(4)
	131	-	-	-	41.29(3)
	141	-	-	-	46.79(3)
	1-11	6.95(4)	7.56(3)	6.68(6)	7.22(5)
Cd^{2+}	101	17.90(2)	18.14(1)	18.0[b]	16.7[d]
	111	25.22(1)	21.71(1)	22.04[b]	-
	121	28.81(1)	24.28(7)	24.44[c]	-
	1-11	8.34(3)	7.37(2)	-	-
	1-21	-2.82(3)	-	-	-
Pb^{2+}	101	13.58(4)	13.53(1)	14.3[b]	15.5[d]
	111	21.66(3)	19.25(2)	19.05[b]	-
	121	26.93(2)	24.42(1)	23.3 [b]	-
	131	30.81(7)	27.81(3)	-	-
	1-11	3.72(4)	2.83(1)	-	-
	1-21	-8.43(9)	-	-	-

[a] Values in brackets are standard deviations in the last significant figure. [b] From ref. 3. [c] From ref. 4; the value in ref. 3 is incorrect. [d] From ref. 5. [e] Previously cited in ref. 1. [f] Previously cited in ref. 6.

Table S3 Peak assignment of the ^{31}P NMR spectra of zinc(II) and cadmium(II) complexes of H_5te3a1p at different pH values in water solution

Metal	pH	Ligand resonance (ppm)	Complex resonance(s) (ppm)
Zn^{2+}	2.94	13.06	-
	6.47	13.85	14.20, 15.08
	7.97	6.90	12.63, 13.43
	8.78	6.58	12.36, 13.15
	10.50	7.08	12.33, 13.11
Cd^{2+}	2.50	11.92	16.75
	5.73	14.17	16.48
	8.60	6.64	14.39

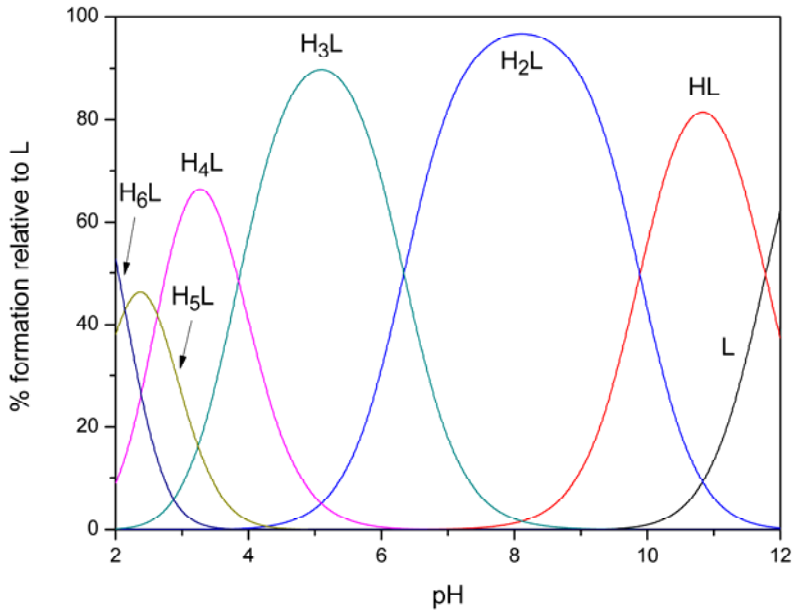

Fig. S1 Species distribution diagram for H_5te3a1p at 1×10^{-3} mol dm^{-3}.

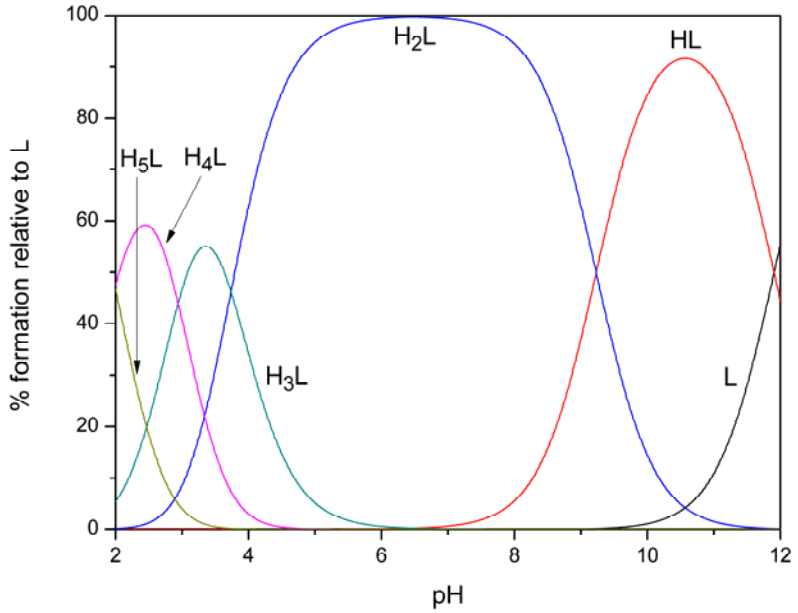

Fig. S2 Species distribution diagram for H_3te3a at 1×10^{-3} mol dm^{-3}.

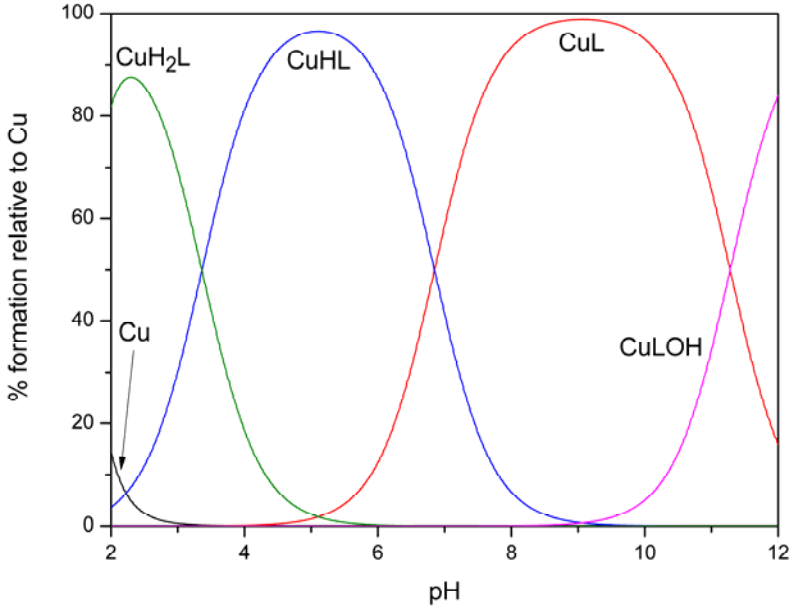

Fig. S3 Species distribution diagram for Cu^{2+}-H_5te3a1p at $C_M = C_L = 1\times10^{-3}$ mol dm^{-3}.

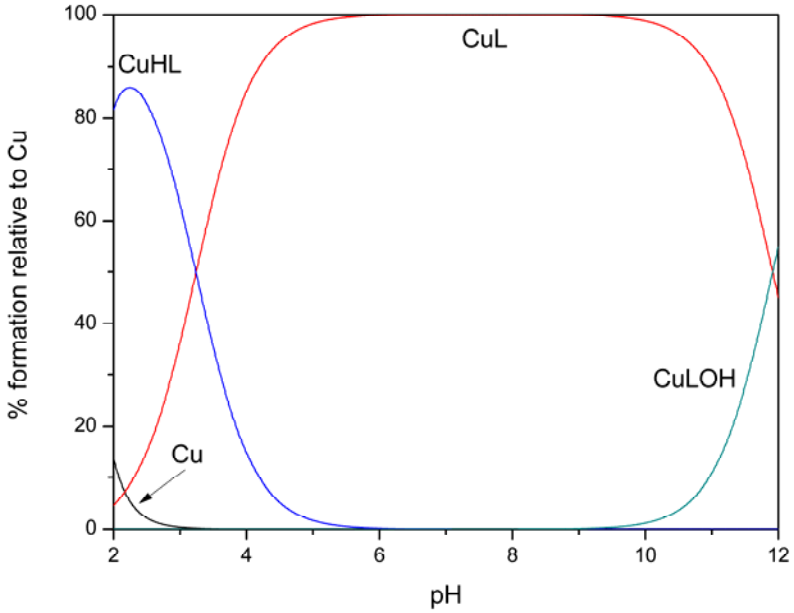

Fig. S4 Species distribution diagram for Cu^{2+}-H_3te3a at $C_M = C_L = 1\times10^{-3}$ mol dm^{-3}.

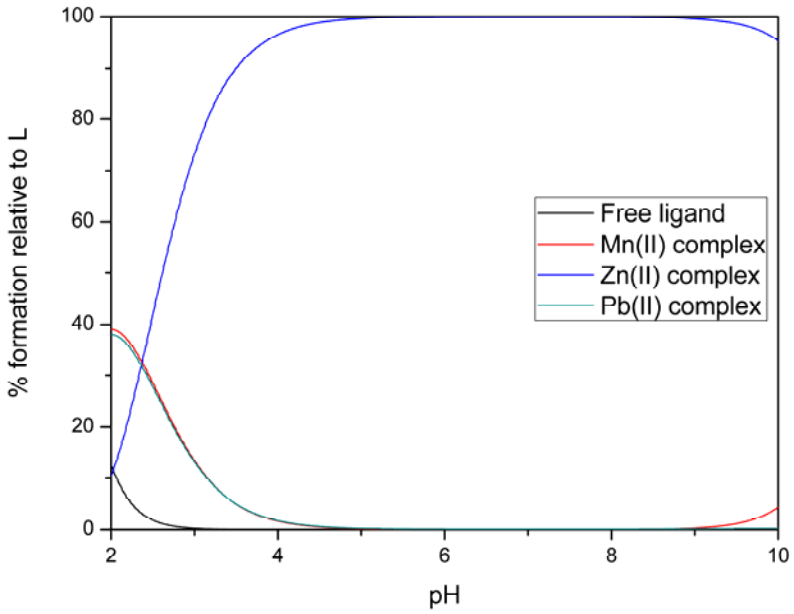

Fig. S5 Species distribution diagram for an equimolar mixture of Mn^{2+}, Zn^{2+}, Pb^{2+} and H_3te3a at 1×10^{-1} mol dm^{-3}. The amount of free ligand and metal complexes is expressed as the sum of all of their protonated species in percentage relative to the initial amount of H_3te3a.

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