Supplementary information

Interaction of Zn(II)-cyclen complex with aminomethylphosphonic acid: Original simultaneous potentiometric and ^{31}P NMR data treatment

I. Rostášová[a], M. Vilková[b], Z. Vargová[a], R. Gyepes[c,d], M. Litecká[a], V. Kubíček[c], J. Imrich[b], I. Lukeš[c]

[a] *Department of Inorganic Chemistry, Institute of Chemistry, P. J. Šafárik University, Moyzesova 11, 04154, Košice, Slovak Republic*
[b] *Department of Organic Chemistry, NMR Laboratory, Institute of Chemistry, P. J. Šafárik University, Moyzesova 11, 04154, Košice, Slovak Republic*
[c] *Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40, Prague 2, Czech Republic*
[d] *Department of Chemistry, Faculty of Education, J. Selye University, Bratislavská cesta 3322, 945 01 Komárno, Slovak Republic*

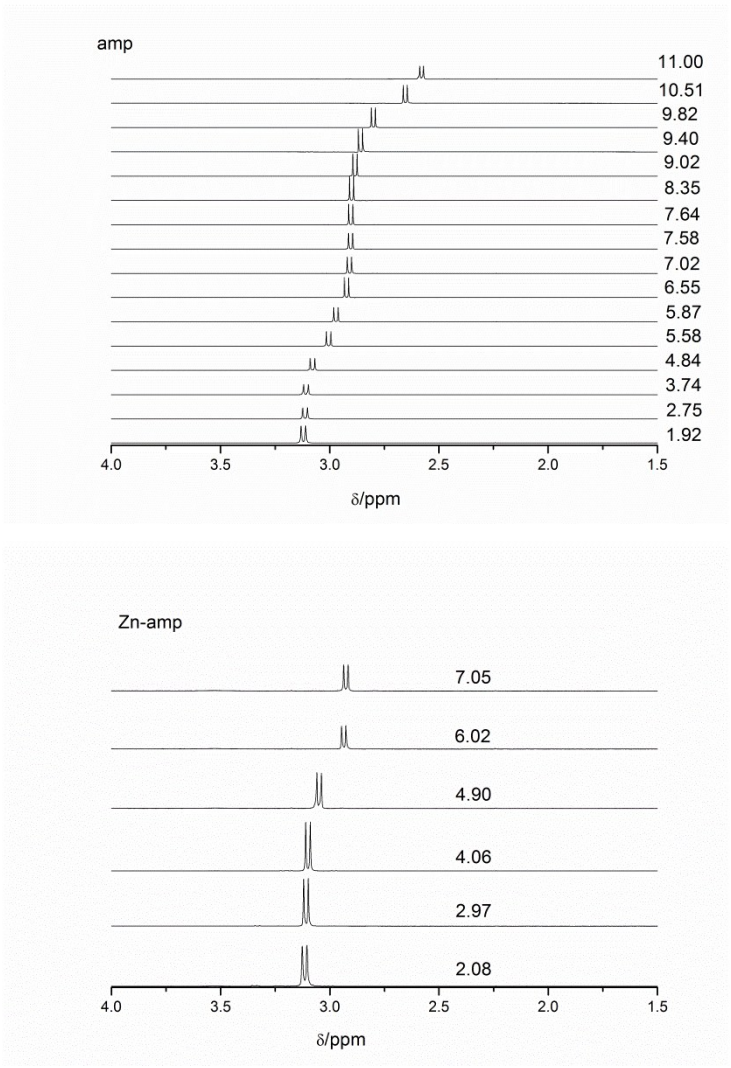


Figure S1. pH changes of ^{1}H NMR spectra of free H_2amp (top) and binary Zn(II)-amp system (bottom). $c_{amp} = c_{Zn} = 0.05$ M, 25 °C

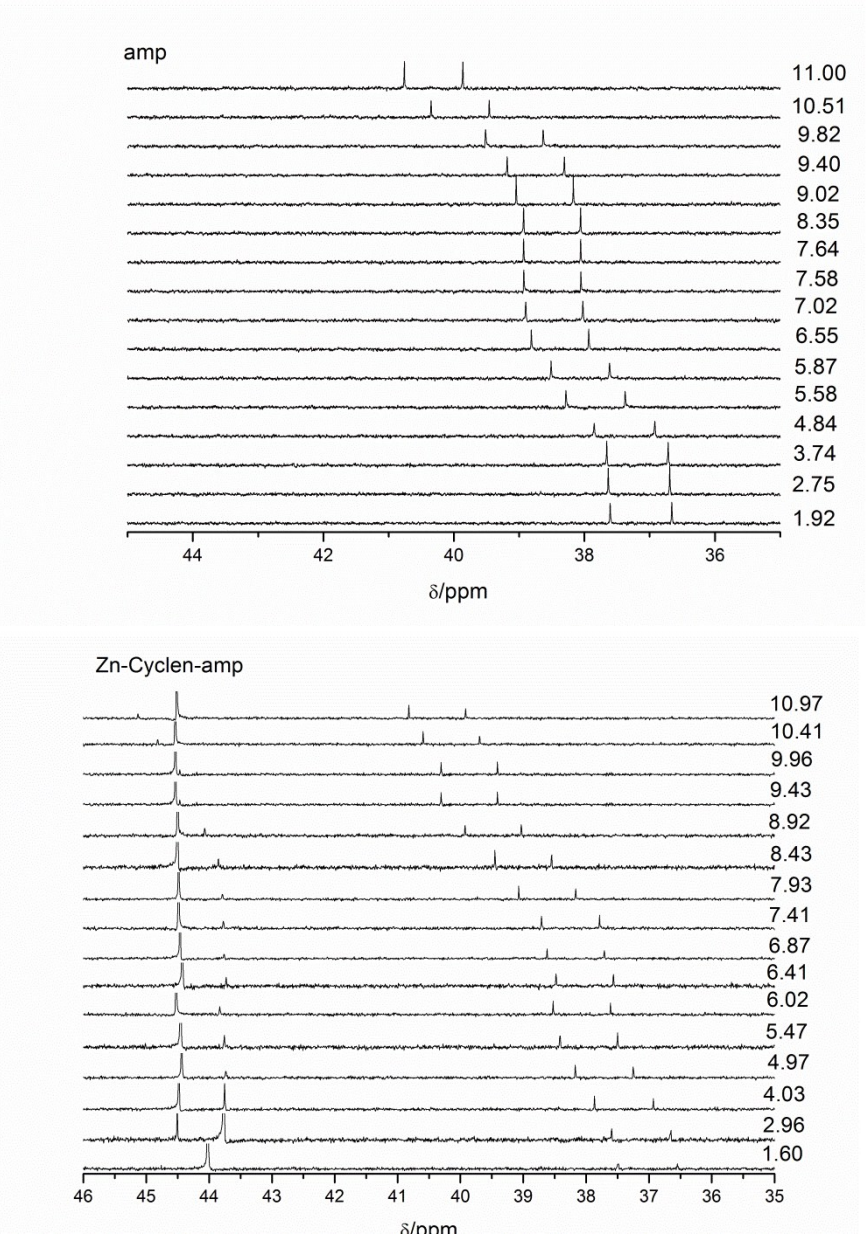


Figure S2. pH changes of ^{13}C NMR spectra of free H_2amp (top) and ternary Zn-cyclen-amp (bottom) system. $c_{amp} = c_{Zn} = c_{cyclen} = 0.05$ M, 25 °C.

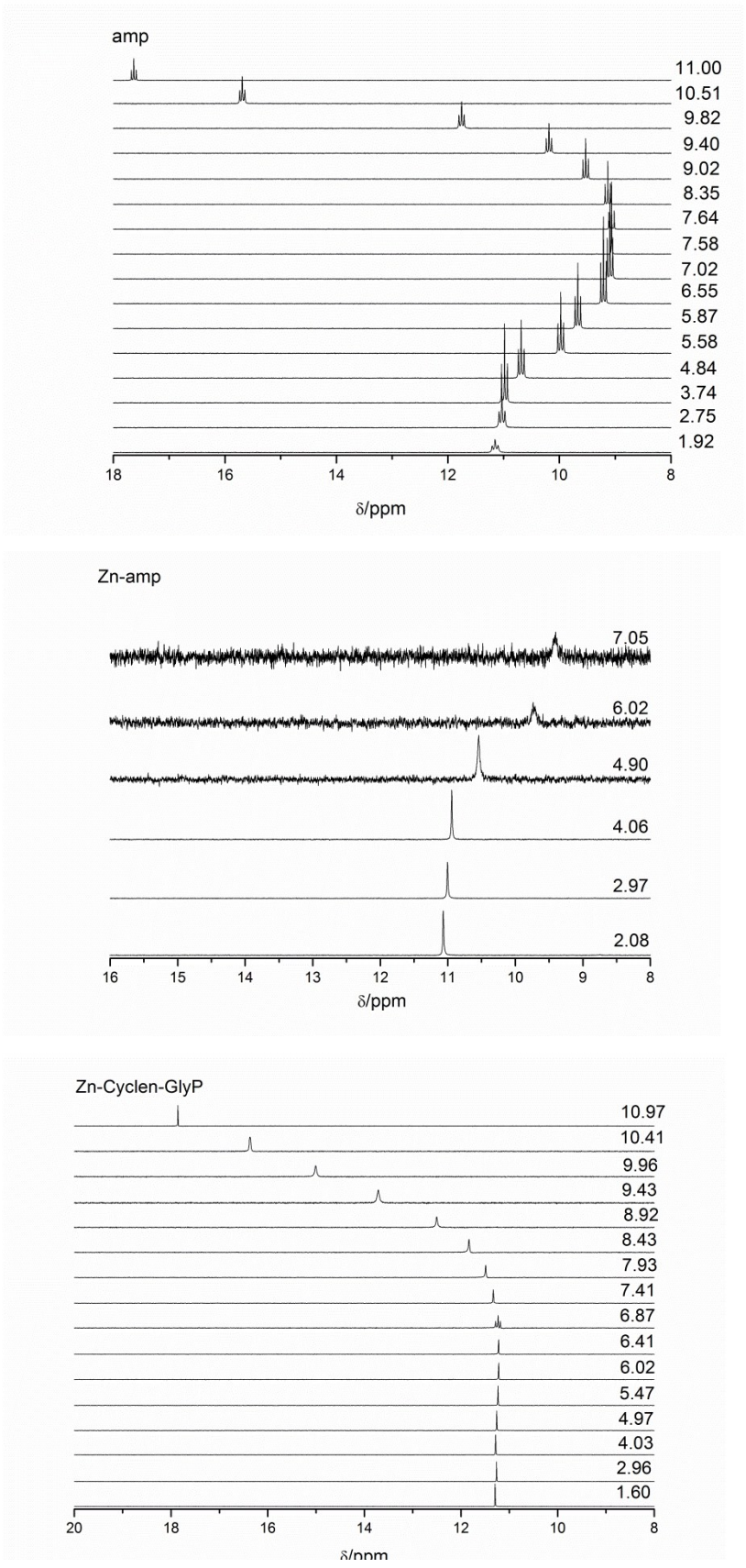


Figure S3. pH changes of ^{31}P NMR spectra of free H_2amp (top), binary Zn(II)-amp system (middle) and ternary Zn-cyclen-amp (bottom) system. $c_{amp} = c_{Zn} = c_{cyclen} = 0.05$ M, 25 °C.

Table S1. Protonation constants of H_2amp (I = 0.1 M, 25 °C).

$\log\beta_{HL}$	$\log\beta_{H2L}$	$\log\beta_{H3L}$	$\log K_1$	$\log K_2$	$\log K_3$
9.991(8)	15.34(1)	-	9.991	5.35	-
10.05 [1]	15.44 [1]	15.90 [1]	10.05 [1]	5.40 [1]	0.45[1]

Table S2. Overall stability constants logβ of Zn(II)-amp complexes (I = 0.1 M, 25 °C).

$[Zn(HL)]^+$	$[Zn(L)]$	$[Zn(L)(OH)]^-$	$[Zn(L)_2]^{2-}$
11.65(6)	5.62(1)	-3.43(3)	8.81(5)
11.72 [2]	5.00 [2]	-1.9 [2]	

Table S3. Protonation constants of cyclen (I = 0.1 M, 25 °C).

$\log\beta_{HL}$	$\log\beta_{H2L}$	$\log K_1$	$\log K_2$
11.206(9)	21.01(2)	11.206	9.80
10.67 [3]	20.25 [3]	10.67 [3]	9.58 [3]

Table S4. Overall stability constants logβ of Zn(II)-cyclen complexes (I = 0.1 M, 25 °C).

$[Zn(HL)]^{3+}$	$[Zn(L)]^{2+}$	$[Zn(L)(OH)]^+$	$[Zn(L)(OH)_2]$
19.3(2)	15.41(6)	7.4(1)	-4.6(1)
-	14.77 [3]	7.36 [3]	-

Table S5. Overall stability constants logβ determined for the ternary system Zn(II)-cyclen-amp systems (25 °C).

$[Zn(cyclen)(Hamp)]^+$	$[Zn(cyclen)(amp)]$	$[\{Zn(cyclen)\}_2(amp)]$	$[\{Zn(cyclen)\}_2(amp)(OH)]^-$
28.45(7)	18.7(1)	37.17(8)	27.8(1)

[1] A.E. Martell, R.M. Smith, R.J. Motekaitis, Critical Stability Constants Database, Texas A&M University, College Station, TX, USA, 1997

[2] M. Wozniak, G. Nowogrocki, Talanta, 26 (1979) 1135–1141.

[3] Z. Vargová, J. Kotek, J. Rudovský, J. Plutnar, R. Gyepes, P. Hermann, K. Györyová, I. Lukeš, Eur. J. Inorg. Chem. (2007) 3974–3987.

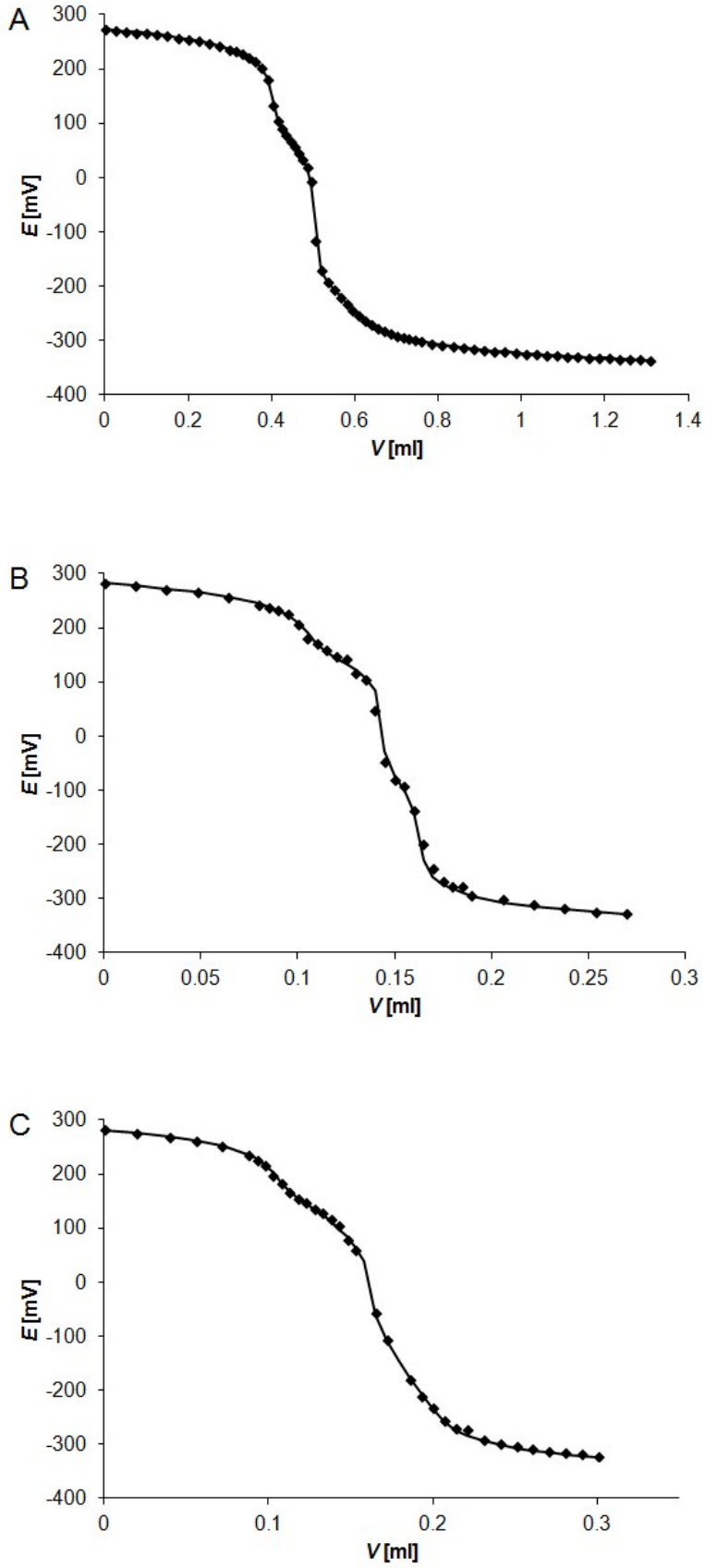


Figure S4. Titration curves of amp (A), Zn(II)-cyclen system (B) and ternary Zn(II)-cyclen-amp system (C). $c_{amp} = c_{Zn} = c_{cyclen} = 4$ mM, 25 °C, $I = 0.1$ M. The lines represent the best fits.

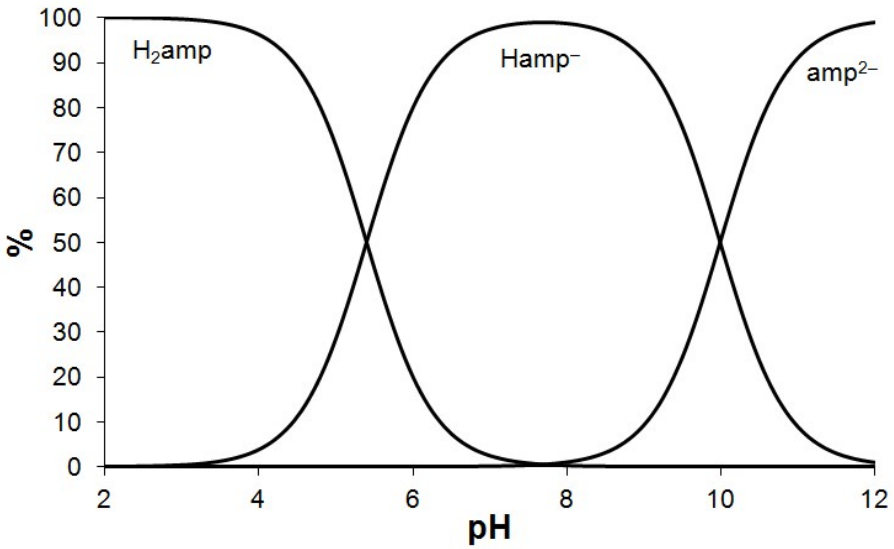


Figure S5. Distribution diagram of H_2amp (c_L = 4 mM, I = 0.1 M, 25 °C).

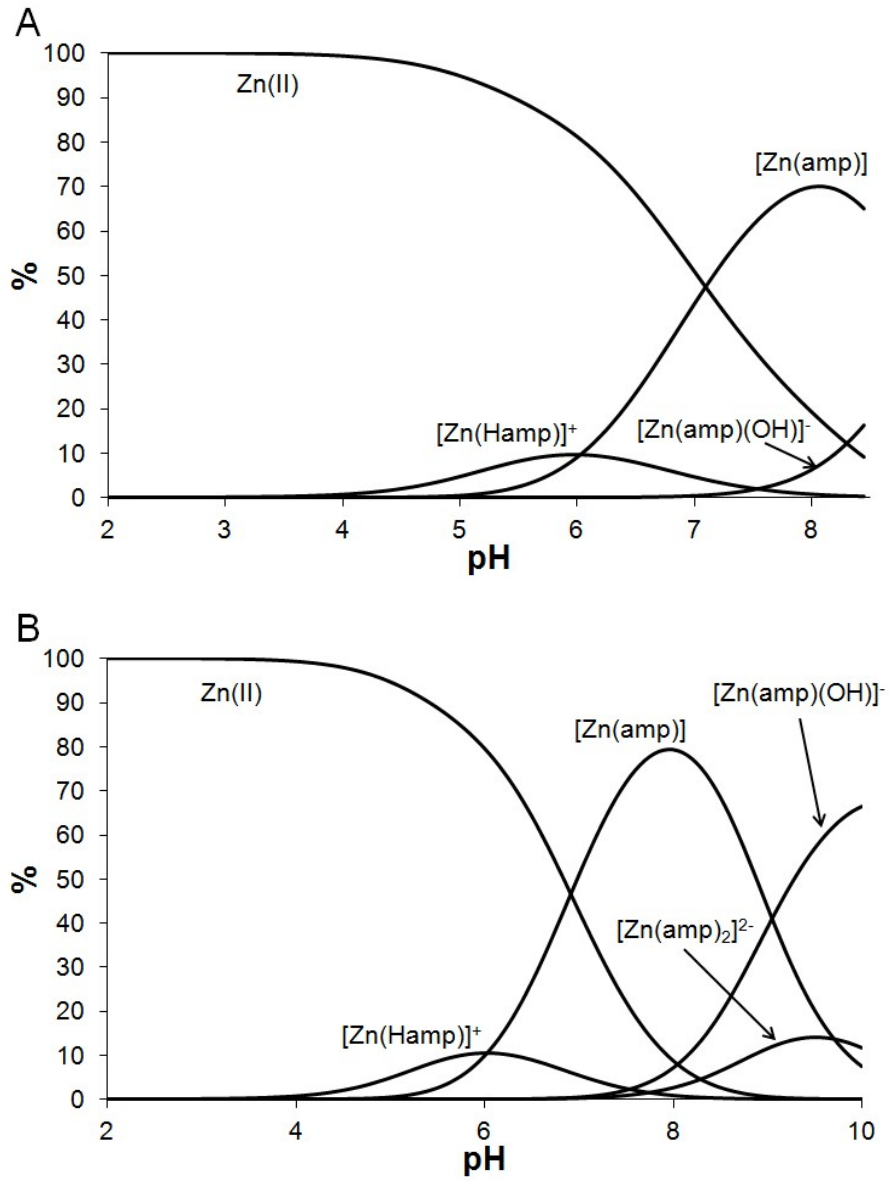


Figure S6. Distribution of Zn(II) in the Zn(II)-amp system (A: $c_L = c_M = 4$ mM; B : $c_L = 4$ mM $c_M = 2$ mM; $I = 0.1$ M, 25 °C).

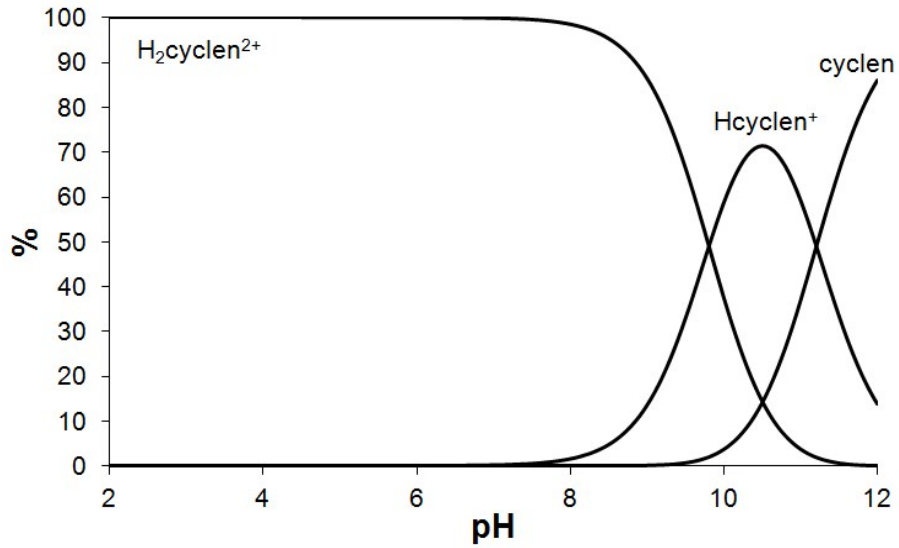


Figure S7. Distribution diagram of cyclen (c_L = 4 mM, I = 0.1 M, 25 °C).

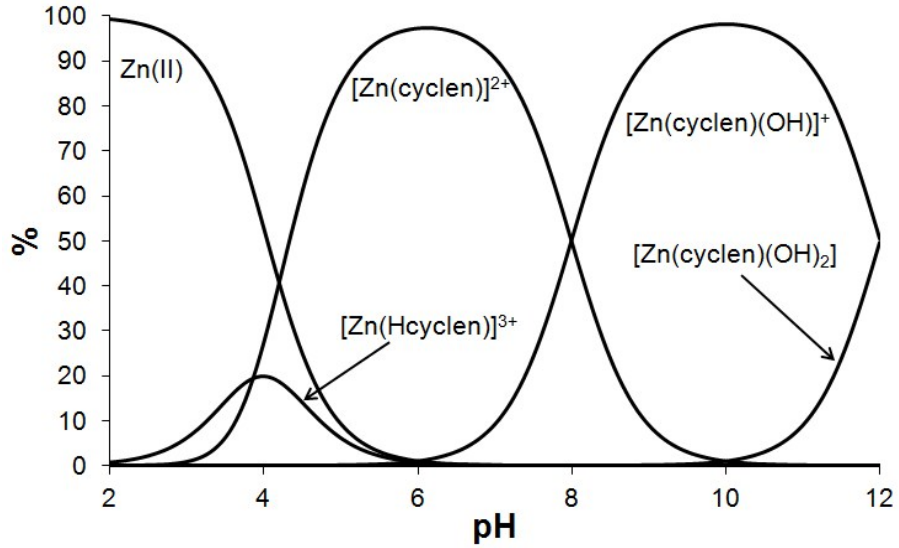
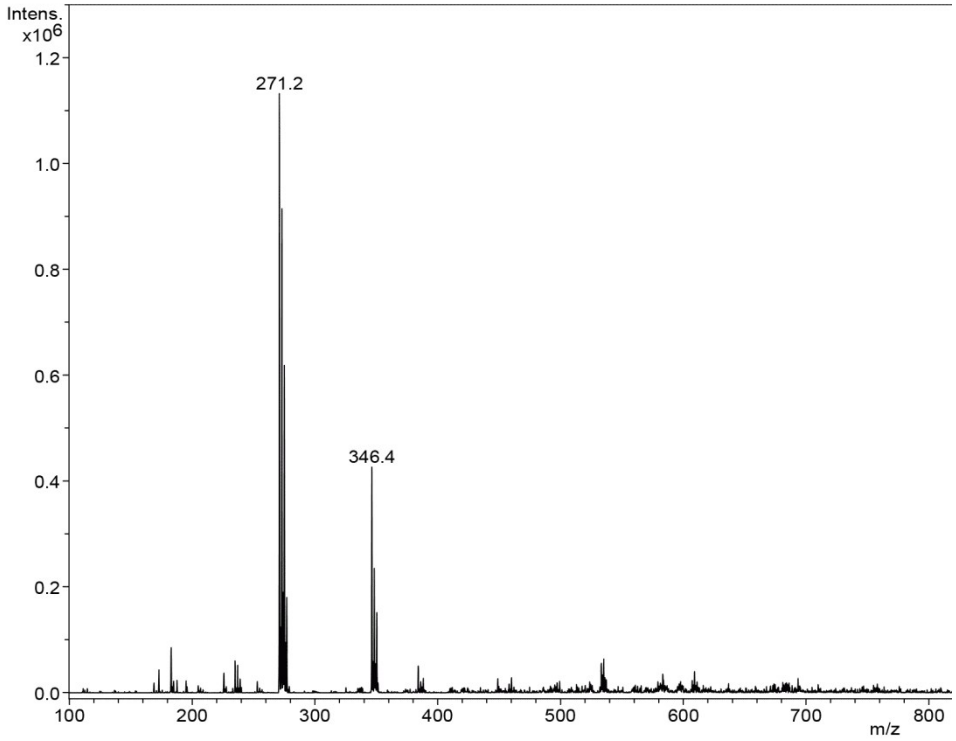


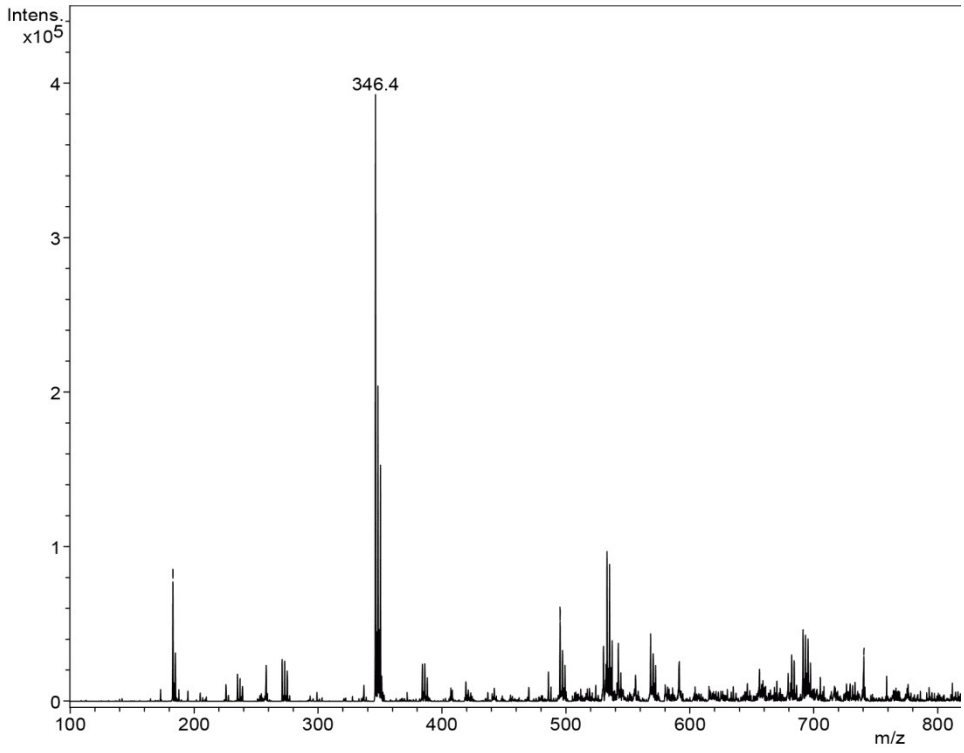
Figure S8. Distribution of Zn(II) in the Zn(II)-cyclen system (c_L = c_M = 4 mM, I = 0.1 M, 25 °C).

Figure S9: ESI-MS spectra of Zn(II)-cyclen-amp system at equimolar conditions (A), at 10-fold amp excess (B) and at 10-fold Zn(II)-cyclen excess (C).

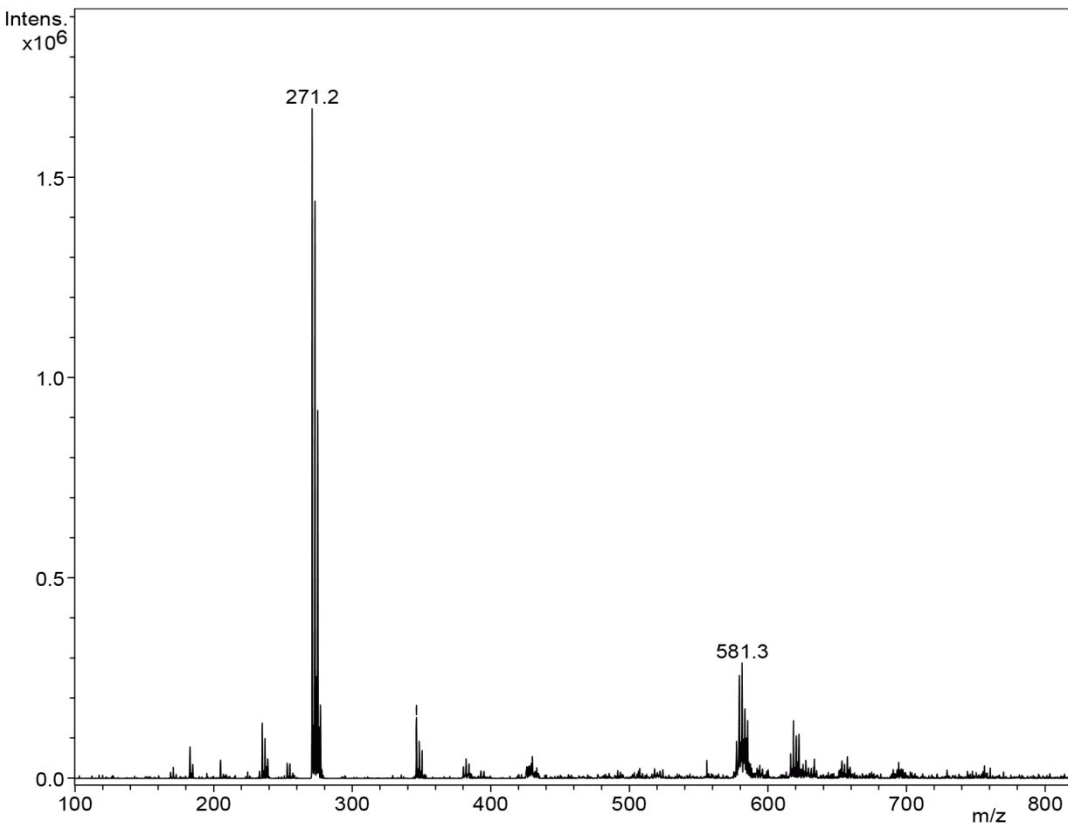
A



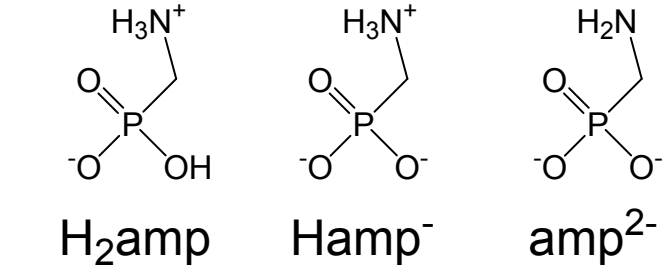
B



C


Intens.
x10^6
271.2
581.3
1.5
1.0
0.5
0.0
100
200
300
400
500
600
700
800
m/z

Scheme S1. Structures of amp and Zn(II)-cyclen species identified in the studied systems (L=cyclen).



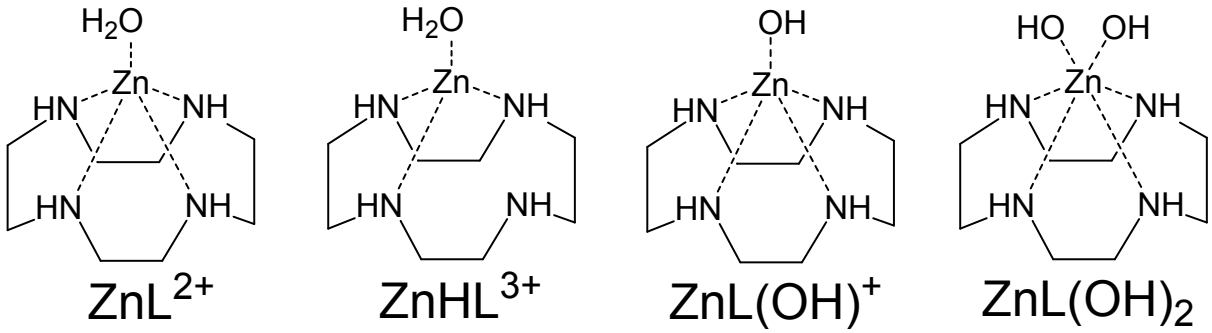


Table S6. Selected bond lengths in the solid-state structure of $[Zn(Hamp)_2]\cdot 4H_2O$

Bond distances			
Zn1-O1	1.915(2)	P1-O2	1.528(2)
$Zn1\text{-}O3_{polymeric}$	1.940(2)	P1-O3	1.511(2)
$Zn1\text{-}O4_{polymeric}$	1.954(2)	P2-O4	1.523(2)
Zn1-O5	1.934(2)	P2-O5	1.519(2)
P1-O1	1.518(2)	P2-O6	1.519(2)
Bond angles			
O1-Zn1-O5	117.45(9)	O2-P1-O3	114.7(1)
O1-Zn1-O3	112.28(9)	O4-P2-O5	113.4(1)
O1-Zn1-O4	104.86(7)	O4-P2-O6	108.1(1)
O5-Zn1-O3	108.06(9)	O5-P2-O6	113.7(1)
O5-Zn1-O4	102.61(9)	Zn1-O1-P1	126.9(1)
O3-Zn1-O4	111.14(9)	P1-O3-Zn1	125.8(1)
O1-P1-O2	111.0(1)	P2-O4-Zn1	123.7(1)
O1-P1-O3	111.9(1)	Zn1-O5-P2	131.3(1)

Table S7. Hydrogen bonds in the solid state structure of $[Zn(Hamp)_2]\cdot 4H_2O$.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1C	0.910	2.174	135.14	2.891	O7 [-x+1/2, y, z-1/2]
N1-H1C	0.910	2.558	116.55	3.074	O4
N1-H1D	0.910	1.944	160.51	2.818	O8
N1-H1E	0.910	1.991	157.07	2.852	O5 [-x+1, -y, z+1/2]
N2-H2NA	0.927	1.911	161.16	2.804	O10 [-x+1/2, y, z-1/2]
N2-H2NB	0.845	2.367	132.69	3.005	O2 [-x+1, -y, z-1/2]
N2-H2NB	0.845	2.412	131.13	3.035	O4 [-x+1, -y, z-1/2]
N2-H2NC	0.944	2.012	147.74	2.854	O5 [x-1/2, -y, z]
O7-H7A	0.782	1.953	170.35	2.727	O3 [x-1, y, z]
O7-H7B	0.847	2.144	161.25	2.959	O8
O8-H8A	0.838	1.938	170.66	2.768	O3 [x-1/2, -y+1, z]
O8-H8B	0.810	1.984	173.95	2.791	O9
O9-H9A	0.762	2.059	173.57	2.818	O7 [-x, -y+1, z-1/2]
O9-H9B	0.725	2.074	168.49	2.788	O3 [x-1, y, z]
O10-H10A	0.869	1.893	176.01	2.761	O5 [x-1/2, -y, z]
O10-H10B	0.830	2.006	165.91	2.818	O9

Figure S10. Coordination motif in the solid-state structure of $[Zn(Hamp)_2]\cdot 4H_2O$.