Interaction of phytate with cyclic polyamines

Supplementary material

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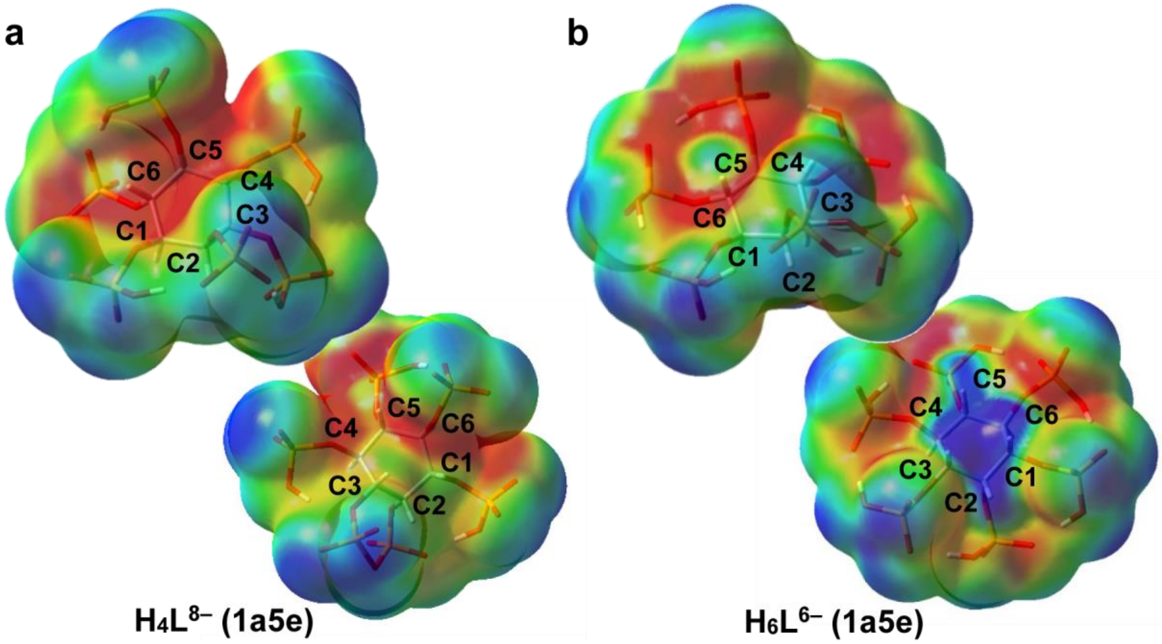
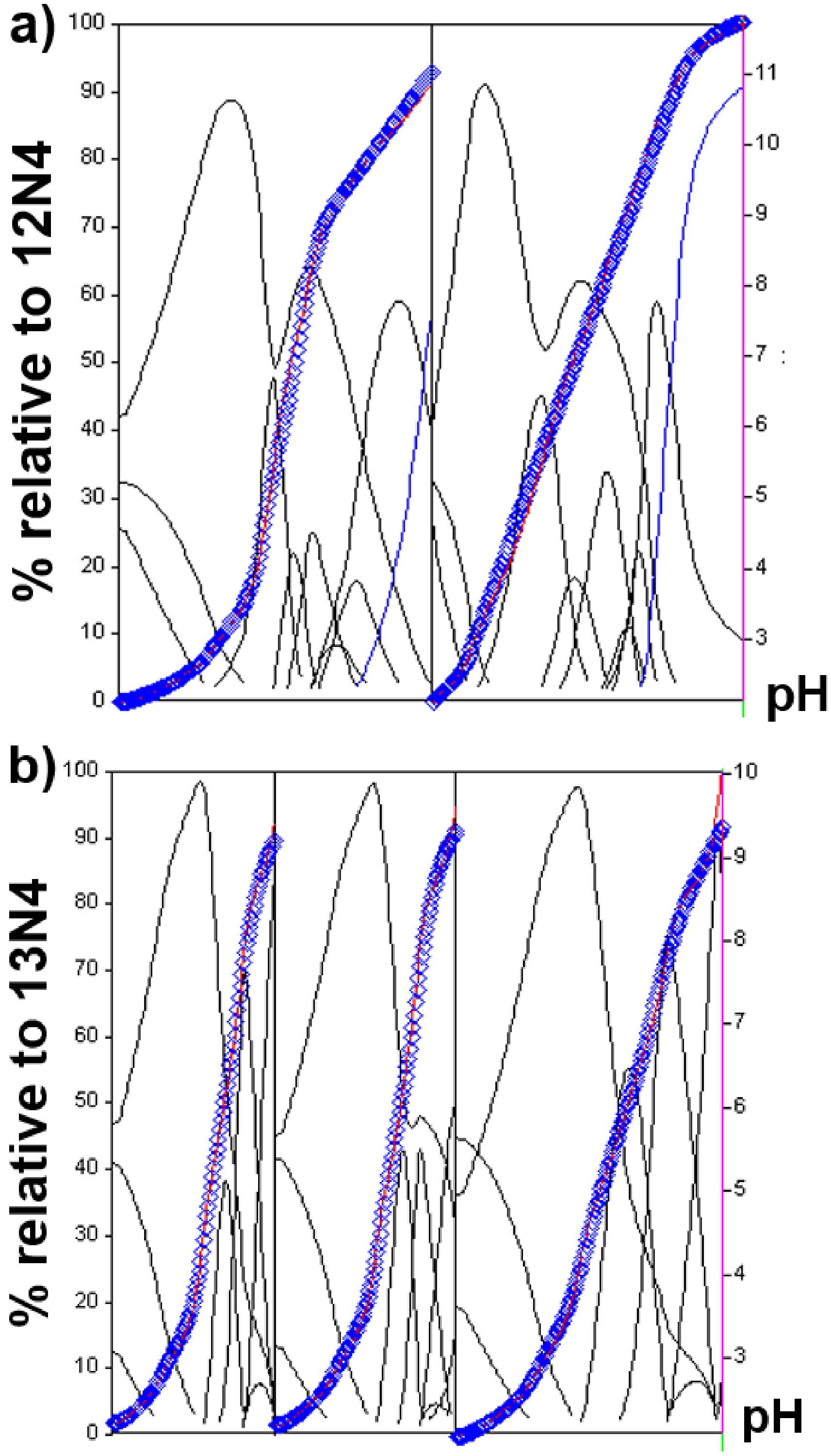
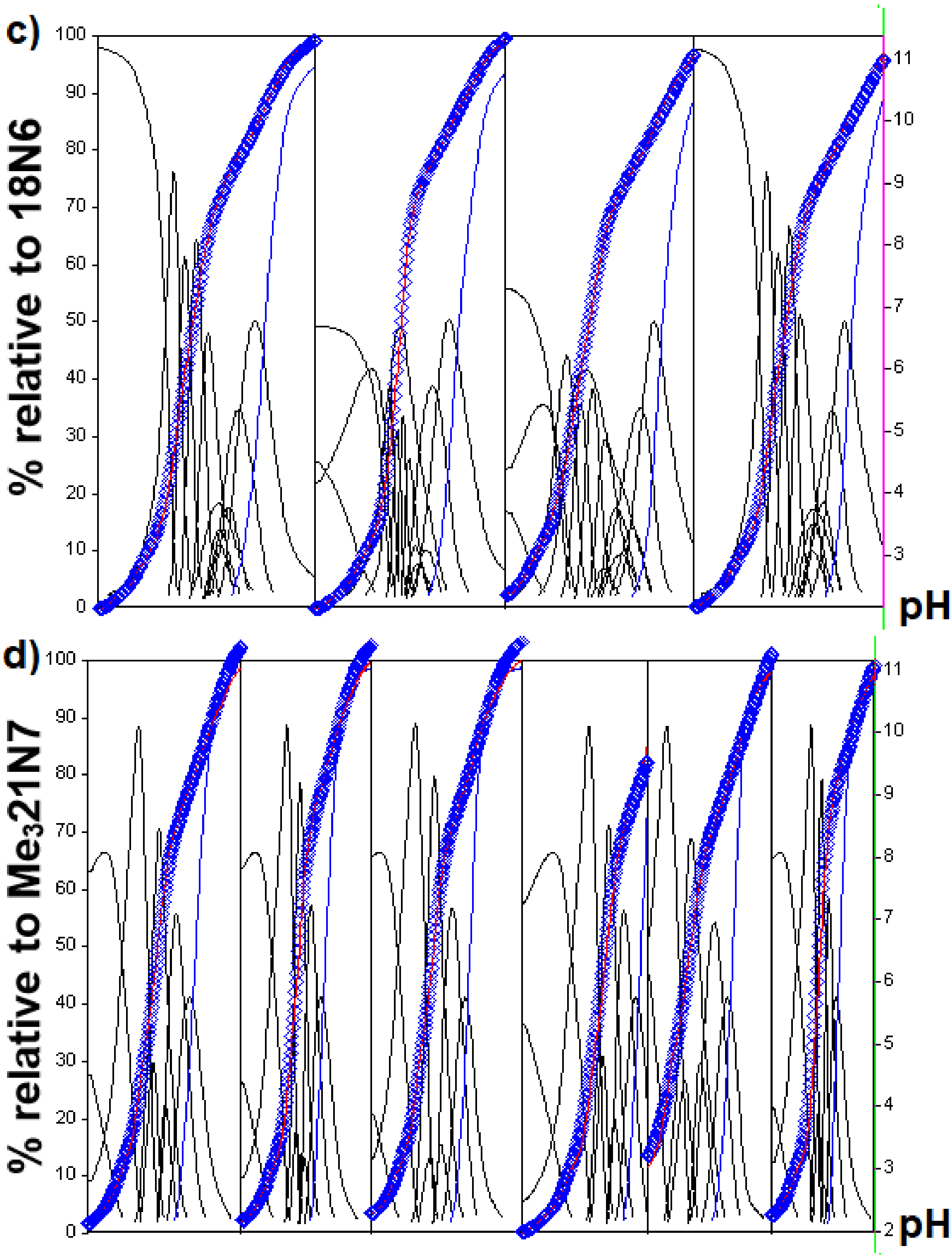


Figure S1. RHF/3-21+G* geometries for the 1a5e conformer of two InsP_6 species: H_4L^{8-} (a) and H_6L^{6-} (b), taken from a previous work.[1] The electrostatic potential is mapped on an isodensity surface (isodensity value = 0.0004 e, scale: -0.75 V (red) to -0.65 V (blue) for a, and -0.56 V (red) to -0.51 V (blue) for b).



a)
% relative to 12N4
100
90
80
70
60
50
40
30
20
10
0
11
10
9
8
7
6
5
4
3
pH
b)
% relative to 13N4
100
90
80
70
60
50
40
30
20
10
0
10
9
8
7
6
5
4
3
pH


c)
% relative to 18N6
pH
d)
% relative to Me₃21N7
pH

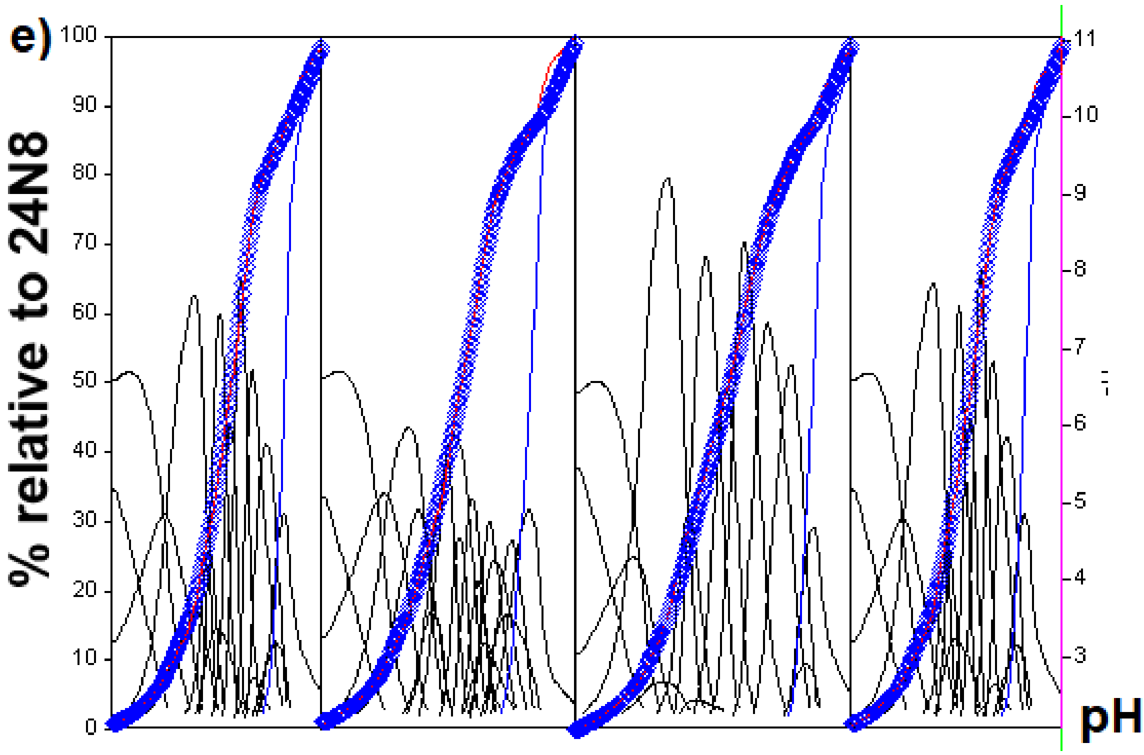


Figure S2- Potentiometric data used for final fit for the $InsP_6$:polyamine systems as shown by Hyperquad software.[2] Calculated expected pH values and formed species are also shown.

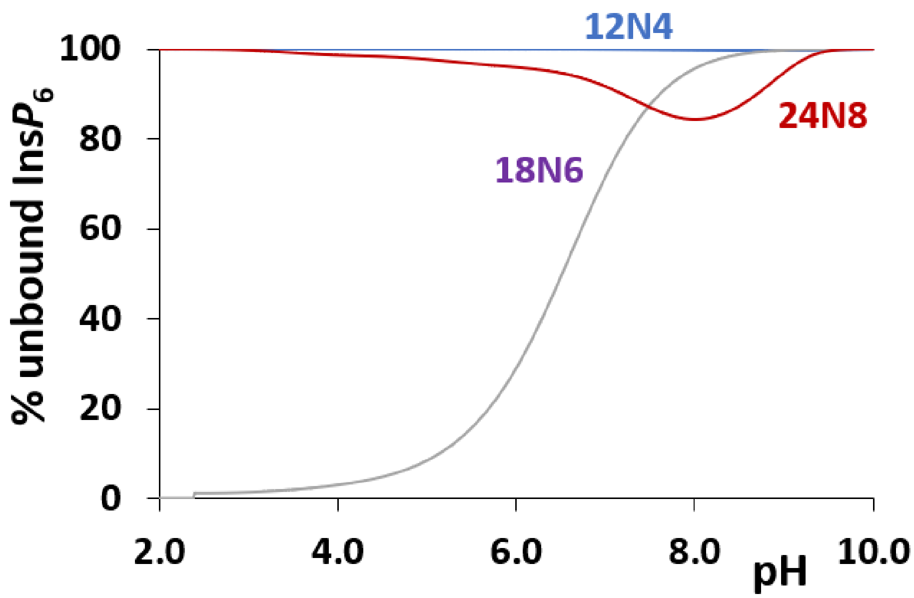


Figure S3. Percentage of unbound InsP_6 in the presence of cyclic polyamines. $[\mathrm{Ins}P_6]_{total}$ = $[\mathrm{polyamine}]_{total}$ = 1 μM, calculated from data in Tables S1 and Table 2 values.

Table S1. Protonation constant values of polyamines and InsP_6 at 25.0 °C in 0.15 M $NaClO_4$ employed for polyamine:InsP_6 interaction studies. Stepwise protonation constants are calculated in b) from overall protonation constants shown in a).

a) Overall protonation constants									
	K^H_1	β^H_2	β^H_3	β^H_4	β^H_5	β^H_6	β^H_7	β^H_8	**Details**
12N4	10.71(3)	20.41(4)	22.4(1)	24.4(2)					This work, σ = 1.6
13N4	11.02(5)	20.84(5)	23.0(1)	24.7(3)					This work, σ = 1.2
18N6	10.15	19.63	28.52	32.79	35.00	36.0			Taken from [3]
Me$_3$21N7	9.27	18.22	26.19	31.61	34.59	36.37			Taken from [4]
24N8	9.65	18.98	27.74	35.61	40.16	43.58	46.29	48.24	Taken from [5]
Ins*P*$_6$	10.43(2)	19.55(4)	29.33(2)	38.37(3)	46.18(4)	52.35(5)	57.39(6)	60.08(8)	This work, σ = 0.7

b) Stepwise protonation constants									
	K^H_1	K^H_2	K^H_3	K^H_4	K^H_5	K^H_6	K^H_7	K^H_8	**Details**
12N4	10.73	9.69	2.0	2.0					Calculated
13N4	11.02	9.82	2.2	1.7					Calculated
18N6	10.15	9.48	8.89	4.27	2.21	1.0			Calculated
Me$_3$21N7	9.27	8.95	7.97	5.42	2.99	1.78			Calculated
24N8	9.65	9.33	8.76	7.87	4.55	3.42	2.71	1.95	Calculated
Ins*P*$_6$	10.43	9.12	9.78	9.04	7.81	6.17	5.04	2.69	Calculated

Table S2. Effective formation constants for 1:1 adduct formation of polyamines and InsP_6 at 25.0 °C in 0.15 M $NaClO_4$. Protons are associated either to the polyamine (A) or InsP_6 (L) considering the relative basicity of the interacting species. ξ is the product of the charges of the interacting species.[6]

Polyamine	**Equilibrium**	**log *K***	**log *K*/ξ**
12N4	$H_2A^{2+} + H_2L^{10-} \rightleftharpoons [(H_2A)(H_2L)]^{8-}$	3.99	0.20
	$H_2A^{2+} + H_3L^{9-} \rightleftharpoons [(H_2A)(H_3L)]^{7-}$	3.26	0.18
	$H_2A^{2+} + H_4L^{8-} \rightleftharpoons [(H_2A)(H_4L)]^{6-}$	3.45	0.22
13N4	$H_2A^{2+} + H_2L^{10-} \rightleftharpoons [(H_2A)(H_2L)]^{8-}$	6.00	0.30
	$H_2A^{2+} + H_3L^{9-} \rightleftharpoons [(H_2A)(H_3L)]^{7-}$	4.46	0.25
	$H_2A^{2+} + H_4L^{8-} \rightleftharpoons [(H_2A)(H_4L)]^{6-}$	4.51	0.28
18N6	$H_2A^{2+} + H_4L^{8-} \rightleftharpoons [(H_2A)(H_4L)]^{6-}$	3.70	0.23
	$H_3A^{3+} + H_4L^{8-} \rightleftharpoons [(H_3A)(H_4L)]^{5-}$	3.71	0.15
	$H_3A^{3+} + H_5L^{7-} \rightleftharpoons [(H_3A)(H_5L)]^{4-}$	4.94	0.24
	$H_3A^{3+} + H_6L^{6-} \rightleftharpoons [(H_3A)(H_6L)]^{3-}$	6.53	0.36
	$H_3A^{3+} + H_7L^{5-} \rightleftharpoons [(H_3A)(H_7L)]^{2-}$	7.96	0.38
	$H_4A^{4+} + H_7L^{5-} \rightleftharpoons [(H_4A)(H_7L)]^{-}$	9.12	0.46
	$H_4A^{4+} + H_8L^{4-} \rightleftharpoons [(H_4A)(H_8L)]$	10.23	0.64
$Me_3$21N7	$H_3A^{3+} + H_6L^{6-} \rightleftharpoons [(H_3A)(H_6L)]^{3-}$	1.82	0.10
24N8	$H_2A^{2+} + H_4L^{8-} \rightleftharpoons [(H_2A)(H_4L)]^{6-}$	5.04	0.32
	$H_3A^{3+} + H_4L^{8-} \rightleftharpoons [(H_3A)(H_4L)]^{5-}$	5.44	0.23
	$H_4A^{4+} + H_4L^{8-} \rightleftharpoons [(H_4A)(H_4L)]^{4-}$	5.75	0.18
	$H_4A^{4+} + H_5L^{7-} \rightleftharpoons [(H_4A)(H_5L)]^{3-}$	4.68	0.17
	$H_4A^{4+} + H_6L^{6-} \rightleftharpoons [(H_4A)(H_6L)]^{2-}$	4.63	0.19
	$H_4A^{4+} + H_7L^{5-} \rightleftharpoons [(H_4A)(H_7L)]^{-}$	4.22	0.21
	$H_5A^{5+} + H_7L^{5-} \rightleftharpoons [(H_5A)(H_7L)]$	4.29	0.17

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