

Supporting Information for

Coordination properties of cyclam (1,4,8,11-tetraazacyclotetradecane) endowed with two methylphosphonic acid pendant arms in the 1,4-positions

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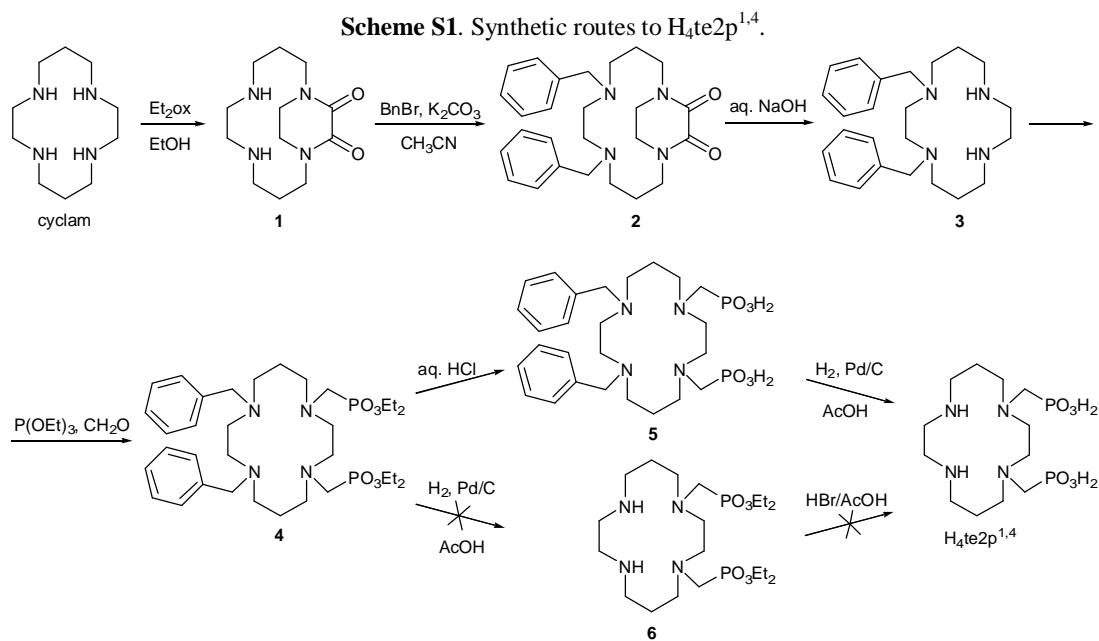


Fig. S1. Molecular structures of all three independent complex units found in the crystal structure of $\{trans-[Ni(H_2L)]\}_3 \cdot 5H_2O$. Hydrogen atoms attached to carbon atoms are omitted for the sake of clarity. Thermal ellipsoids show 30 % probability level.

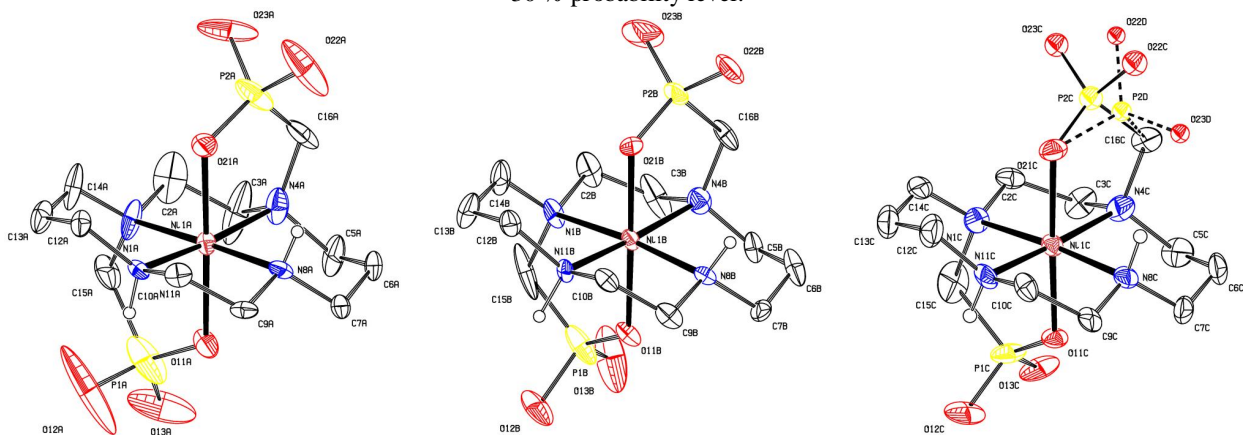
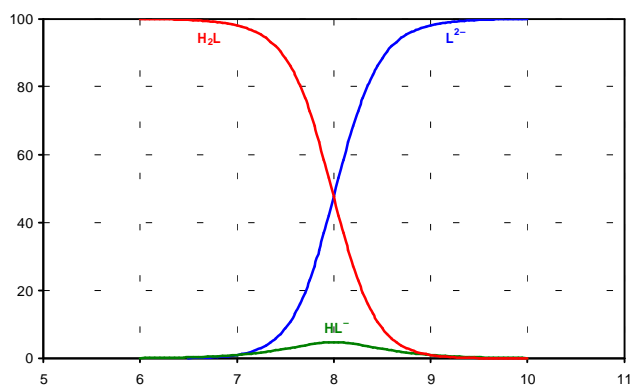
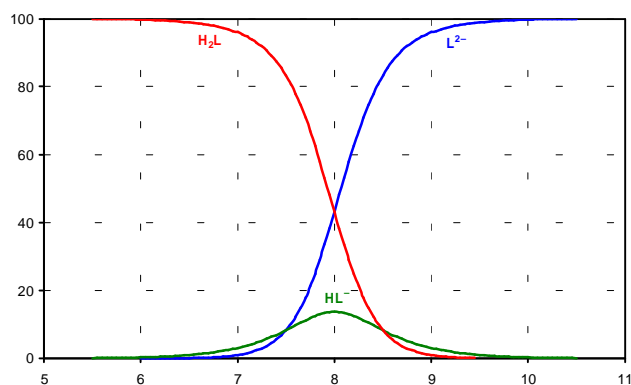


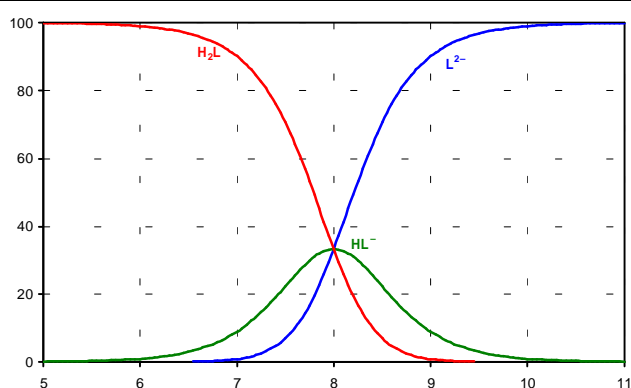
Fig. S2. Theoretical distribution diagrams showing abundances of differently protonated species of a model acid H_2A



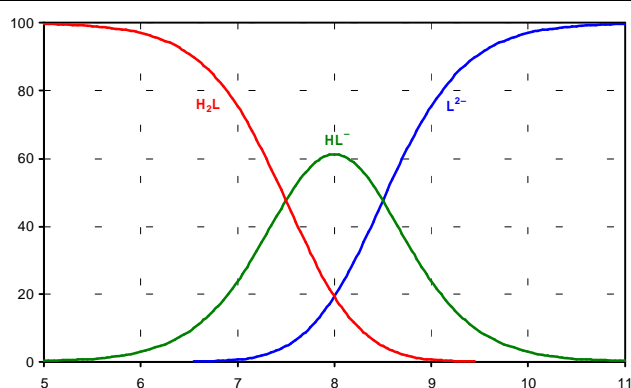
a) $pK(H_2A) = 9, pK(HA^-) = 7$



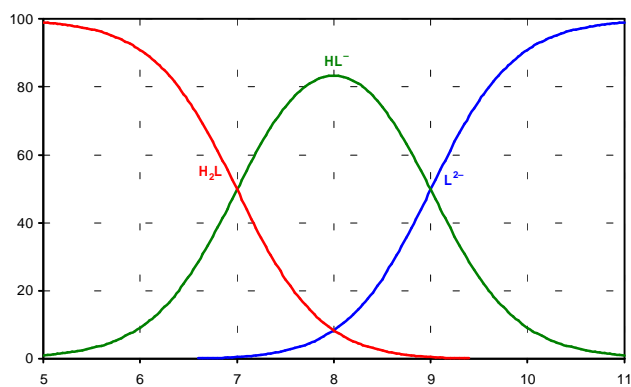
b) $pK(H_2A) = 8.5, pK(HA^-) = 7.5$



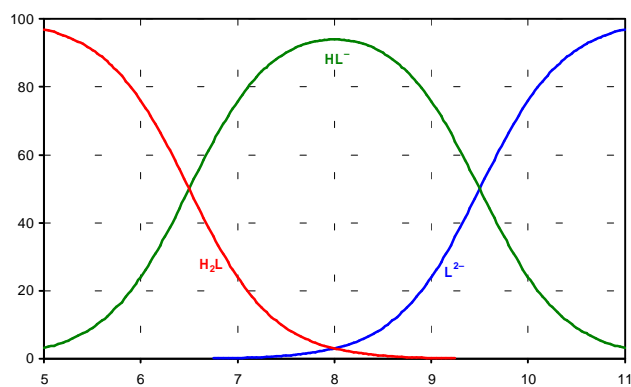
c) $pK(H_2A) = 8, pK(HA^-) = 8$



d) $pK(H_2A) = 7.5, pK(HA^-) = 8.5$



e) $pK(H_2A) = 7, pK(HA^-) = 9$



f) $pK(H_2A) = 6.5, pK(HA^-) = 9.5$

On series of distribution diagrams, one can see simulated theoretical situations, where following equilibria:



are taken into account. For all cases, $\log b_2 = pK(H_2A) + pK(HA^-) = 16$

The “reverse order” of pK_a 's of the model compound H_2A

The “reverse order” of the constants originates in an easier proton release from HA^- species comparing to H_2A species. When a difference of the corresponding pK_a 's is high it is connected with a very low abundance of the HA^- species in the solution (Fig. S2a) and, thus, the protonation constant corresponding to the monoprotated species cannot be determined as a limit for potentiometrically determinable species is usually suggested to be 10–15% in abundance. The “reverse order” of protonation constants can be mathematically determined if the difference between values of the constants is lower than ~ 1 (Fig. S2b), when the abundance of HA^- species reaches the detection limit. If values of the constants are equal (Fig. S2c), it means, that the concentration of all species is equal (33.3%) just at $pH = pK_a$. In the other cases, a “normal order” of consecutive pK_a 's is suggested, and thus, the maximal abundance of HA^- species still increases with increasing difference between values of the constants (Figs S2d–f).

Explanation of the “reverse order” of protonation constants of H_4te2p ^{1,4}

Comparing to the previous model, the “reverse order” obviously originates in easier proton release from HL^{3-} species comparing to H_2L^{2-} species. It is connected with a very low abundance of the HL^{3-} species in the solution and, thus, the protonation constant corresponding to the monoprotated species cannot be determined at all. The “reverse order” of dissociation constants is relatively common for the cyclam derivatives,^{1,2,3} and was even observed for cyclam itself.⁴ It can be explained by an intramolecular hydrogen bonds rearrangement (and weakening) after release of the first proton from the H_2L^{2-} species. Such hypothesis is supported by a shape of ¹H NMR spectra acquired at different pH values (Fig. S3).

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- 2 J. Kotek, P. Vojtíšek, I. Čišařová, P. Hermann, P. Jurečka, J. Rohovec and I. Lukeš, *Collect. Czech. Chem. Commun.*, 2000, **65**, 1289–1316.
- 3 (a) R. Delgado, L. C. Siegfried and T. A. Kaden, *Helv. Chim. Acta*, 1990, **73**, 140–148; (b) F. Marques, L. Gano, M. P. Campello, S. Lacerda, I. Santos, L. M. P. Lima, J. Costa, P. Antunes and R. Delgado, *J. Inorg. Biochem.*, 2006, **100**, 270–280.
- 4 R. D. Hancock, R. J. Motekaitis, J. Mashishi, I. Cukrowski, J. H. Reibenspies and A. E. Martell, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 1925–1929.

Fig. S3. The ^1H and ^{31}P NMR spectra of the free $\text{H}_4\text{te}2\text{p}^{1,4}$ at different pD (25 °C, $\text{D}_2\text{O}/\text{DCI}/\text{NaOD}$, pD of the sample was measured by calibrated electrode, and after acquiring of spectra re-adjusted to the next point)

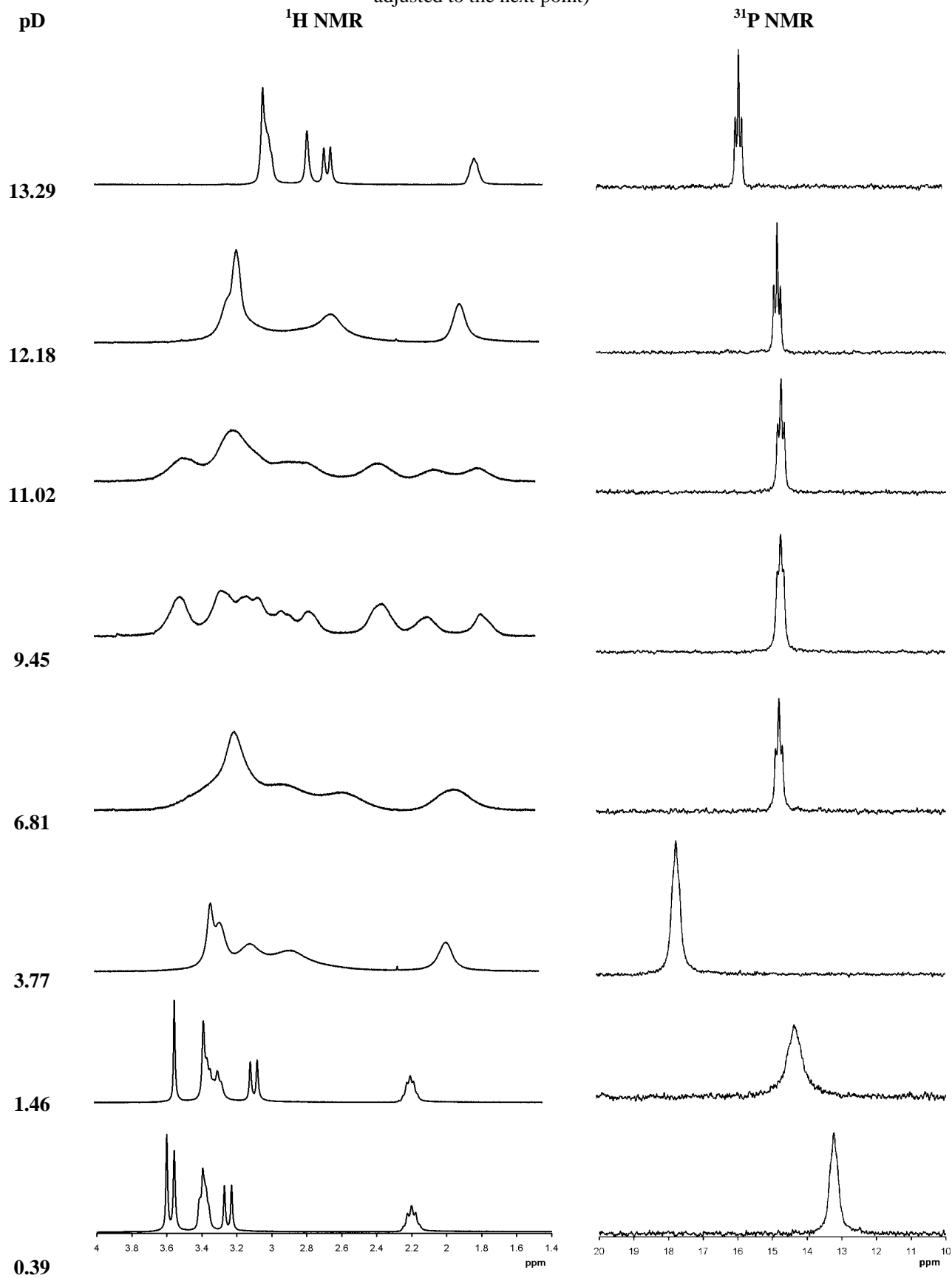


Fig. S4. Calculated distribution diagram of free ligand $H_4te2p^{1,4}$ ($c_L = 0.004$ M)

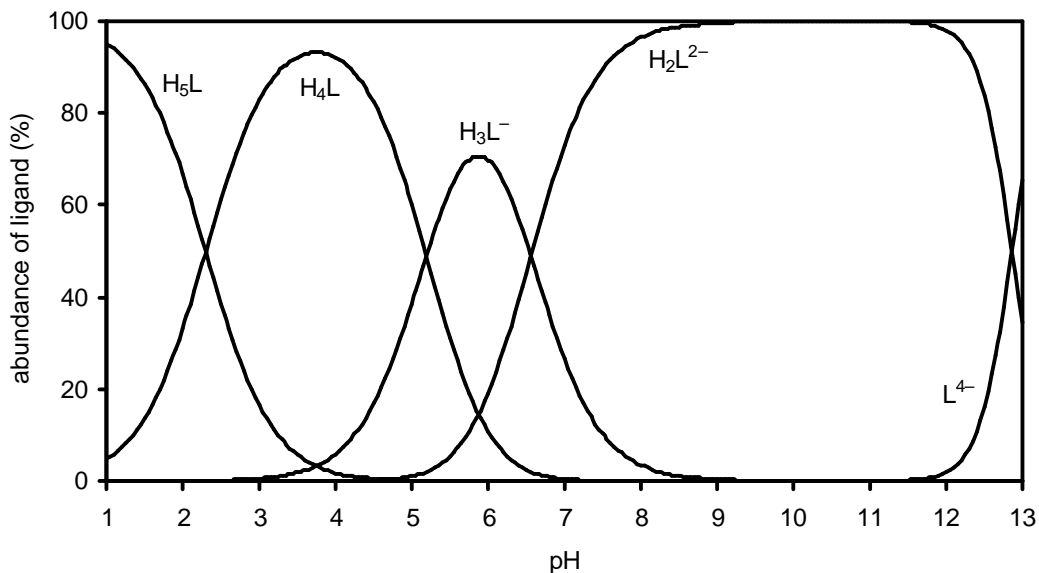


Fig. S5. Calculated distribution diagram of Ca^{2+} - $H_4te2p^{1,4}$ system ($c_L = c_{Ca} = 0.004$ M)

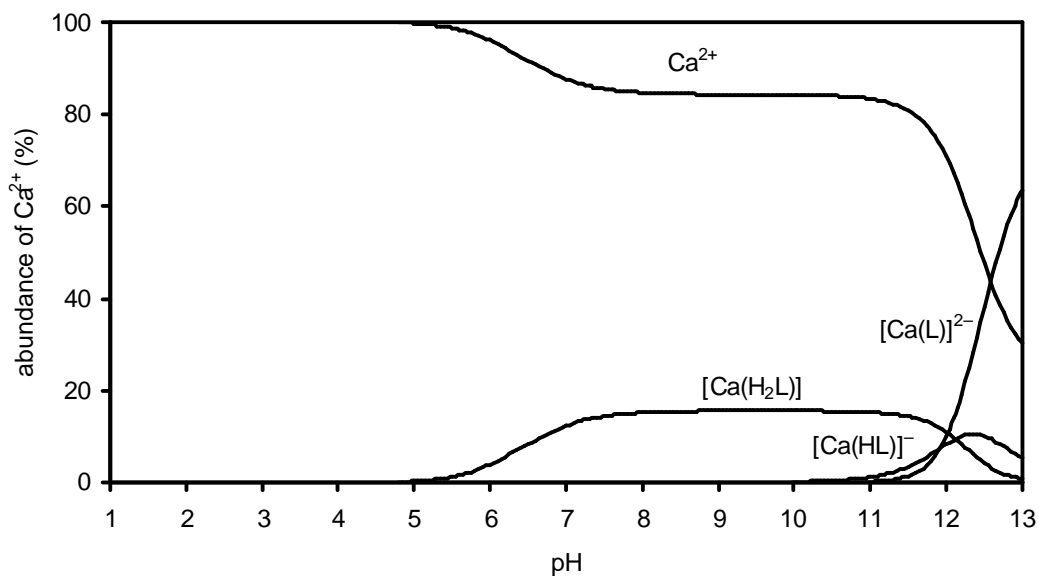


Fig. S6. Calculated distribution diagram of Pb^{2+} - $\text{H}_4\text{te2p}^{1.4}$ system ($c_L = c_{\text{Pb}} = 0.004 \text{ M}$)

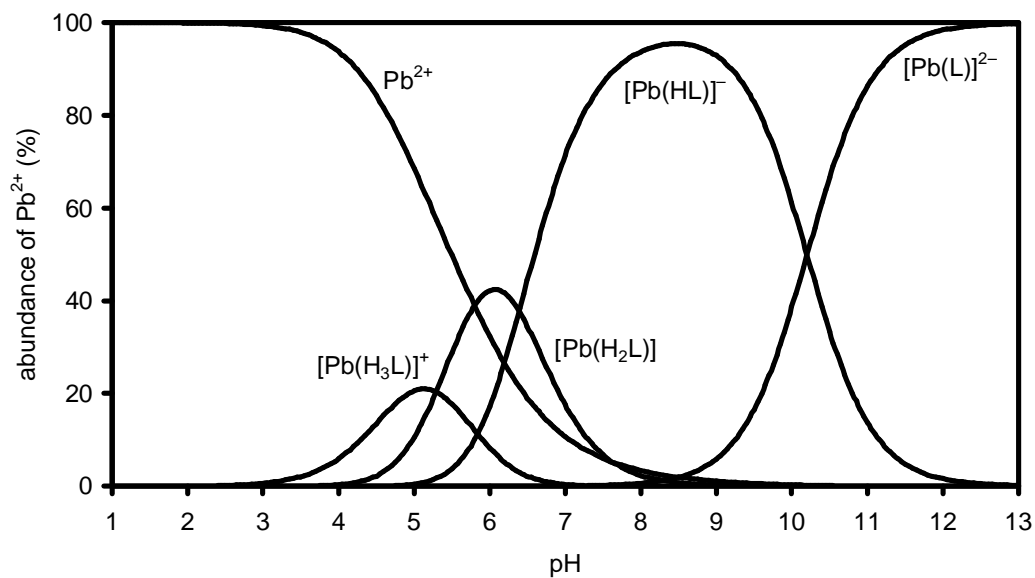


Fig. S7. Calculated distribution diagram of Ni^{2+} - $\text{H}_4\text{te2p}^{1.4}$ system ($c_L = c_{\text{Ni}} = 0.004 \text{ M}$)

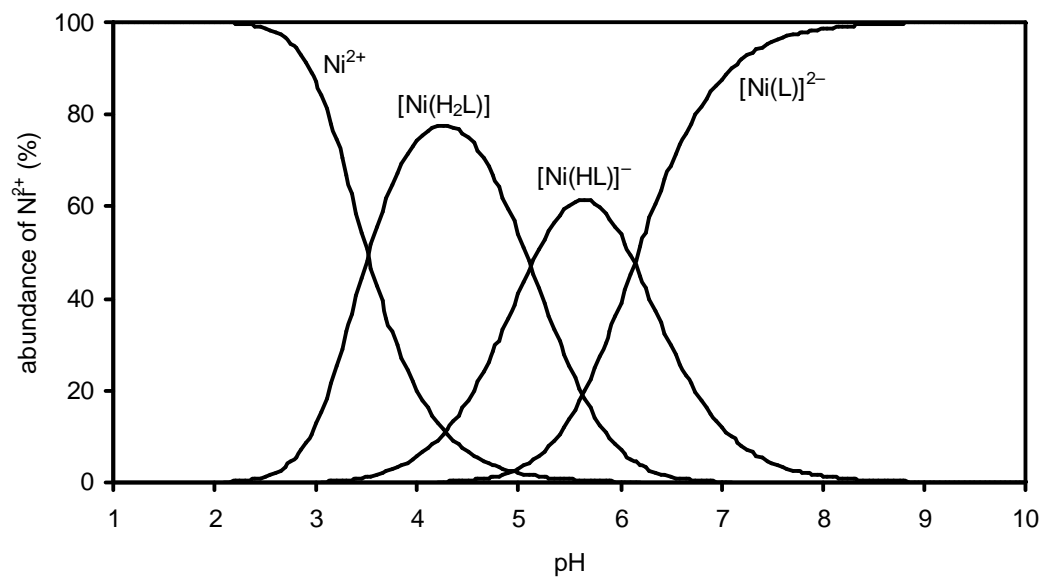


Fig. S8. Calculated distribution diagram of Zn^{2+} - $\text{H}_4\text{te2p}^{1.4}$ system ($c_L = c_{\text{Zn}} = 0.004 \text{ M}$)

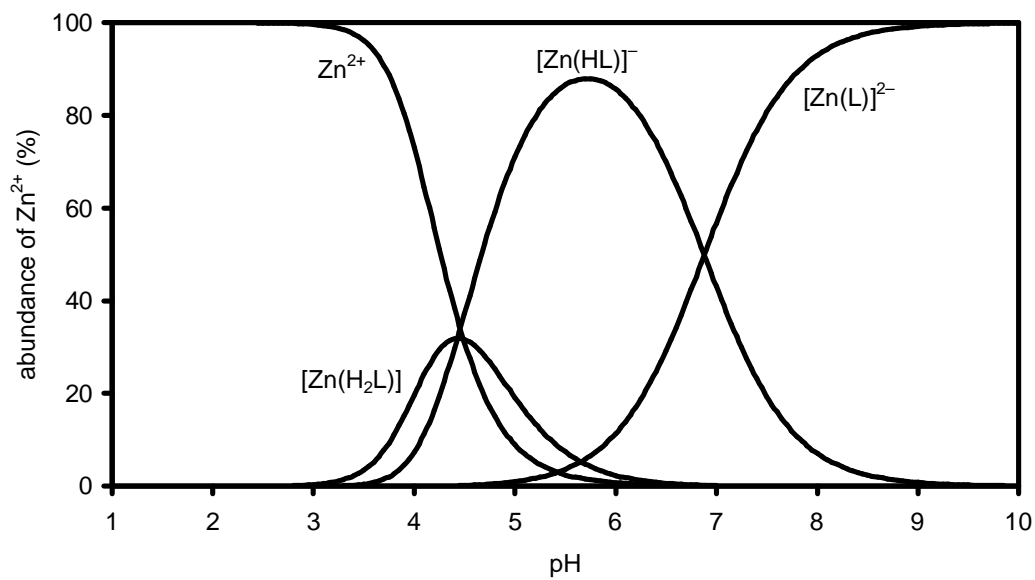


Fig. S9. Calculated distribution diagram of Cd^{2+} - $\text{H}_4\text{te2p}^{1.4}$ system ($c_L = c_{\text{Cd}} = 0.004 \text{ M}$)

