Supporting Information for

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

Jana Havlíčková, Hana Medová, Tomáš Vitha, Jan Kotek, Ivana Císařová and Petr Hermann

Department of Inorganic Chemistry, Universita Karlova (Charles University), Hlavova 2030, Prague 2, 128 40, Czech Republic. Tel: +420-2-2195-1263; Fax: +420-2-2195-1253; E-mail: modrej@natur.cuni.cz

Table of contents

Scheme S1. Synthetic routes to H₄te₂p₁₄.

Fig. S1. Molecular structures of all three independent complex units found in the crystal structure of \{\textit{trans-}[Ni(H₂L)]\}_3·5H₂O. 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; discussion of “reverse order” in protonation constants

Fig. S3. The pH-dependence of ¹H NMR spectra of free ligand H₄te₂p₁₄

Fig. S4. Calculated distribution diagram of free ligand H₄te₂p₁₄

Fig. S5. Calculated distribution diagram of Ca²⁺-H₄te₂p₁₄ system \( (c_L = c_{Ca} = 0.004 \text{ M}) \)

Fig. S6. Calculated distribution diagram of Pb²⁺-H₄te₂p₁₄ system \( (c_L = c_{Pb} = 0.004 \text{ M}) \)

Fig. S7. Calculated distribution diagram of Ni²⁺-H₄te₂p₁₄ system \( (c_L = c_{Ni} = 0.004 \text{ M}) \)

Fig. S8. Calculated distribution diagram of Zn²⁺-H₄te₂p₁₄ system \( (c_L = c_{Zn} = 0.004 \text{ M}) \)

Fig. S9. Calculated distribution diagram of Cd²⁺-H₄te₂p₁₄ system \( (c_L = c_{Cd} = 0.004 \text{ M}) \)
Scheme S1. Synthetic routes to H$_4$te$_2$p$_{1,4}$. 

**Fig. S1.** Molecular structures of all three independent complex units found in the crystal structure of \{trans-[Ni(H$_2$L)]\}_3·5H$_2$O. 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 $H_2A$

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

$H_2A \rightleftharpoons HA^- \rightleftharpoons A^{2-}$

are taken into account. For all cases, $\log \beta_2 = pK(H_2A) + pK(HA^-) = 16$.

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) $pK(H_2A) = 6.5, pK(HA^-) = 9.5$
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 monoprotonated 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 $H_4te2p^{14}$

Comparing to the previous model, the “reverse order” obviously originates in easier proton release from $HL^-$ species comparing to $H_2L^2-$ species. It is connected with a very low abundance of the $HL^-$ species in the solution and, thus, the protonation constant corresponding to the monoprotonated species cannot be determined at all. The “reverse order” of dissociation constants is relatively common for the cyclam derivatives, and was even observed for cyclam itself. 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).

Fig. S3. The $^1$H and $^{31}$P NMR spectra of the free H$_4$Te2p$_{1,4}$ at different pD (25 °C, D$_2$O/DCl/NaOD, pD of the sample was measured by calibrated electrode, and after acquiring of spectra re-adjusted to the next point)

<table>
<thead>
<tr>
<th>pD</th>
<th>$^1$H NMR</th>
<th>$^{31}$P NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.29</td>
<td><img src="image" alt="H NMR 13.29" /></td>
<td><img src="image" alt="P NMR 13.29" /></td>
</tr>
<tr>
<td>12.18</td>
<td><img src="image" alt="H NMR 12.18" /></td>
<td><img src="image" alt="P NMR 12.18" /></td>
</tr>
<tr>
<td>11.02</td>
<td><img src="image" alt="H NMR 11.02" /></td>
<td><img src="image" alt="P NMR 11.02" /></td>
</tr>
<tr>
<td>9.45</td>
<td><img src="image" alt="H NMR 9.45" /></td>
<td><img src="image" alt="P NMR 9.45" /></td>
</tr>
<tr>
<td>6.81</td>
<td><img src="image" alt="H NMR 6.81" /></td>
<td><img src="image" alt="P NMR 6.81" /></td>
</tr>
<tr>
<td>3.77</td>
<td><img src="image" alt="H NMR 3.77" /></td>
<td><img src="image" alt="P NMR 3.77" /></td>
</tr>
<tr>
<td>1.46</td>
<td><img src="image" alt="H NMR 1.46" /></td>
<td><img src="image" alt="P NMR 1.46" /></td>
</tr>
<tr>
<td>0.39</td>
<td><img src="image" alt="H NMR 0.39" /></td>
<td><img src="image" alt="P NMR 0.39" /></td>
</tr>
</tbody>
</table>
**Fig. S4.** Calculated distribution diagram of free ligand H$_4$Te$_2$p$_{1.4}$ ($c_L = 0.004$ M)

![Fig. S4. Calculated distribution diagram of free ligand H$_4$Te$_2$p$_{1.4}$ ($c_L = 0.004$ M)](image)

**Fig. S5.** Calculated distribution diagram of Ca$^{2+}$-H$_4$Te$_2$p$_{1.4}$ system ($c_L = c_{Ca} = 0.004$ M)

![Fig. S5. Calculated distribution diagram of Ca$^{2+}$-H$_4$Te$_2$p$_{1.4}$ system ($c_L = c_{Ca} = 0.004$ M)](image)
Fig. S6. Calculated distribution diagram of Pb$^{2+}$-H$_2$Te$_2$p$_{1,4}$ system ($c_L = c_{Pb} = 0.004$ M)

Fig. S7. Calculated distribution diagram of Ni$^{2+}$-H$_2$Te$_2$p$_{1,4}$ system ($c_L = c_{Ni} = 0.004$ M)
**Fig. S8.** Calculated distribution diagram of Zn$^{2+}$-H$_2$te$_2$p$_{1,4}$ system ($c_L = c_{Zn} = 0.004$ M)

**Fig. S9.** Calculated distribution diagram of Cd$^{2+}$-H$_2$te$_2$p$_{1,4}$ system ($c_L = c_{Cd} = 0.004$ M)