

**On the Complexation of Metal Cations by “Pure” Diethylenetriamine-N,N,N',N'',N''-Pentakis-
(Methylenephosphonic) Acid**

Supplementary Information

Table S1. Experimental chemical shifts for the Zn²⁺/DTPMP system from ¹H- and ³¹P-NMR measurements

pH	δHa	δHb	δHc	δHd	δPa	δPb
1.93	3.545	3.75	3.42	3.160	9.720	15.250
1.96	3.535	3.74	3.40	3.145	9.660	15.350
2.14	3.525	3.73	n.d.	3.120	9.680	15.660
2.33	3.515	3.72	n.d.	3.085	9.670	15.950
2.74	3.490	3.69	3.31	3.040	9.740	16.400
3.26	3.460	3.65	3.27	3.010	10.050	16.850
3.99	n.d. ^{a)}	3.6	3.23	3.015	10.350	17.100
4.54	n.d.	n.d.	3.22	3.010	10.020	16.950
5.45	n.d.	n.d.	3.21	3.000	9.570	15.930
6.02	n.d.	n.d.	3.22	2.930	9.080	15.970
6.61	n.d.	3.68	3.21	2.865	8.440	15.970
8.05	n.d.	3.71	3.20	2.840	7.570	15.410
9.77	n.d.	3.72	3.20	2.815	7.330	15.290
10.58	n.d.	3.7	3.20	2.735	7.310	15.290

^{a)}not detected.

$c_{\text{Zn}^{2+}} = 2.5 \text{ mmol dm}^{-3}$, $c_{\text{L}} = 5 \text{ mmol dm}^{-3}$ in $\text{NaCl}_{(\text{aq})}$ at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$.

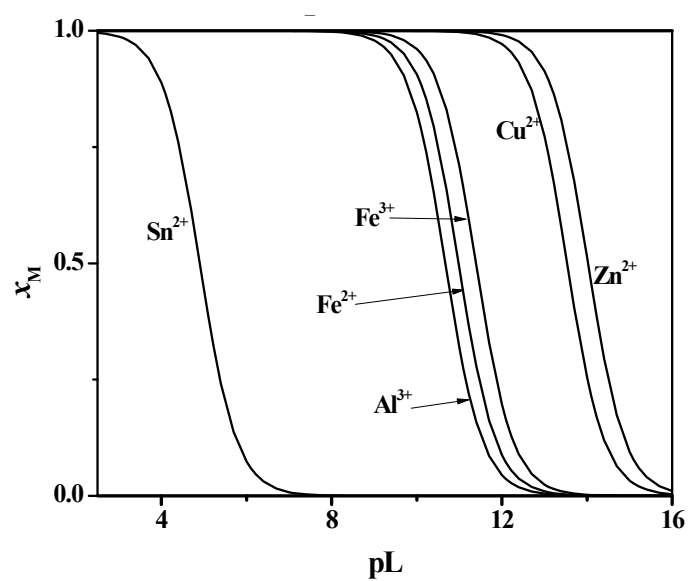


Figure S1. Sequestration diagrams of the investigated metal cations by DTPMP, in $\text{NaCl}_{(\text{aq})}$ at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$, at $\text{pH} = 8.1$.

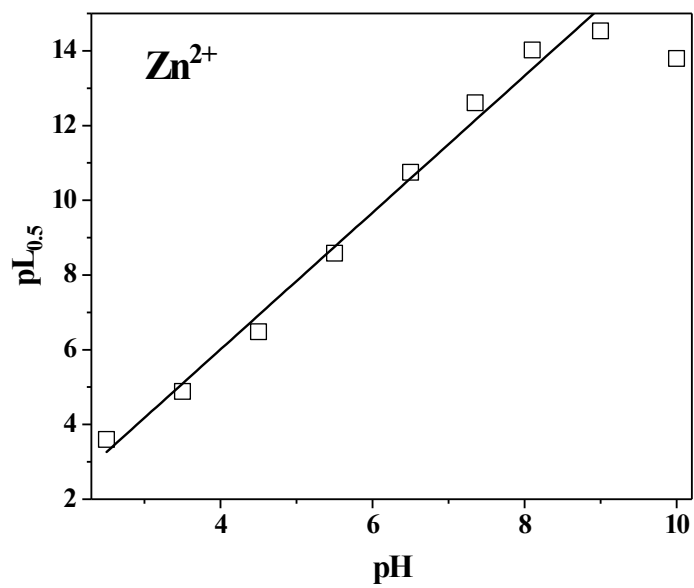


Figure S2. Dependence on pH of the sequestering ability (as pL_{0.5}) of DTPMP toward Zn²⁺, in NaCl_(aq) at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$.

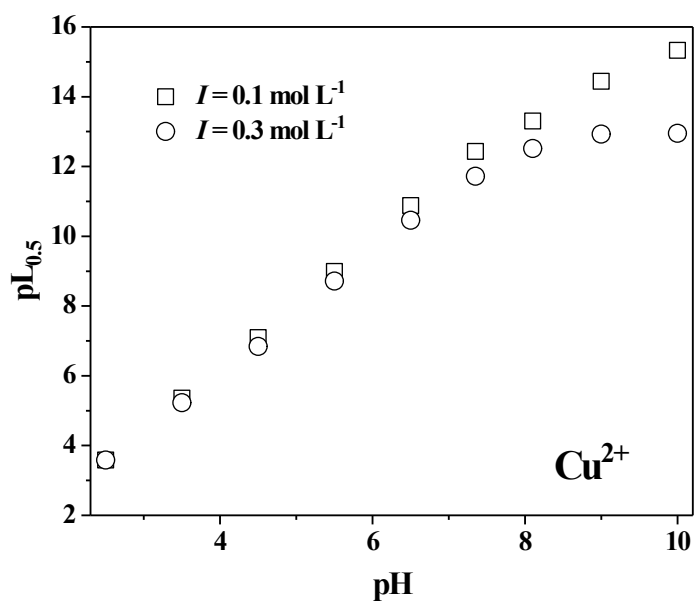


Figure S3. Dependence on pH of the sequestering ability (as $pL_{0.5}$) of DTPMP toward Cu^{2+} , in $\text{NaCl}_{(\text{aq})}$ at $I = 0.1$ and 0.3 mol dm^{-3} and $T = 298.15 \text{ K}$.

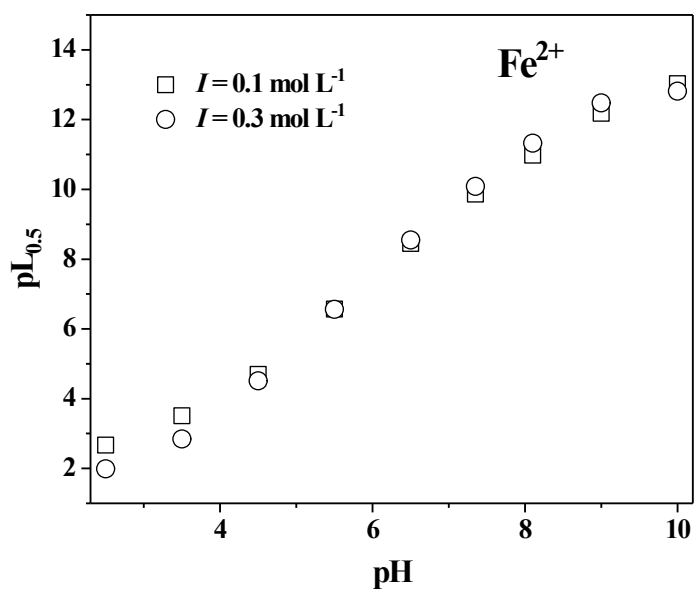


Figure S4. Dependence on pH of the sequestering ability (as $pL_{0.5}$) of DTPMP toward Fe^{2+} , in $\text{NaCl}_{(\text{aq})}$ at $I = 0.1$ and 0.3 mol dm^{-3} and $T = 298.15 \text{ K}$.

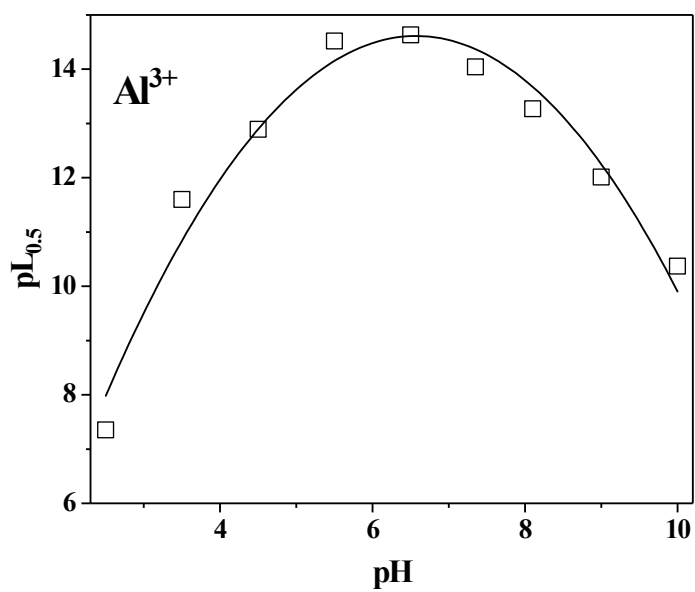


Figure S5. Dependence on pH of the sequestering ability (as $pL_{0.5}$) of DTPMP toward Al^{3+} , in $NaCl_{(aq)}$ at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$.

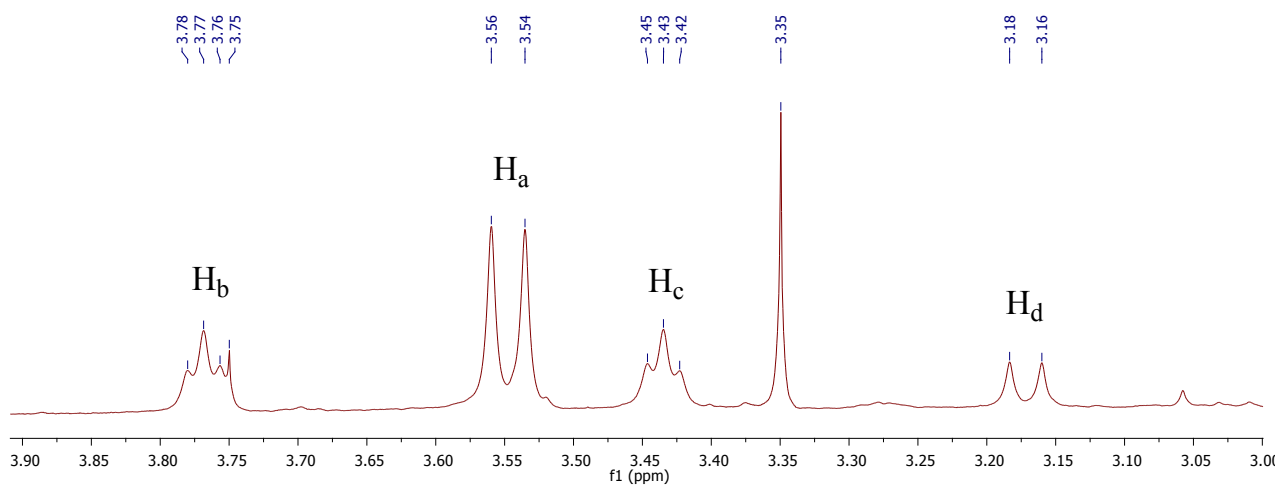


Figure S6. $^1\text{H-NMR}$ (500 MHz) spectrum of DTPMP, in $\text{NaCl}_{(\text{aq})}$ at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$.

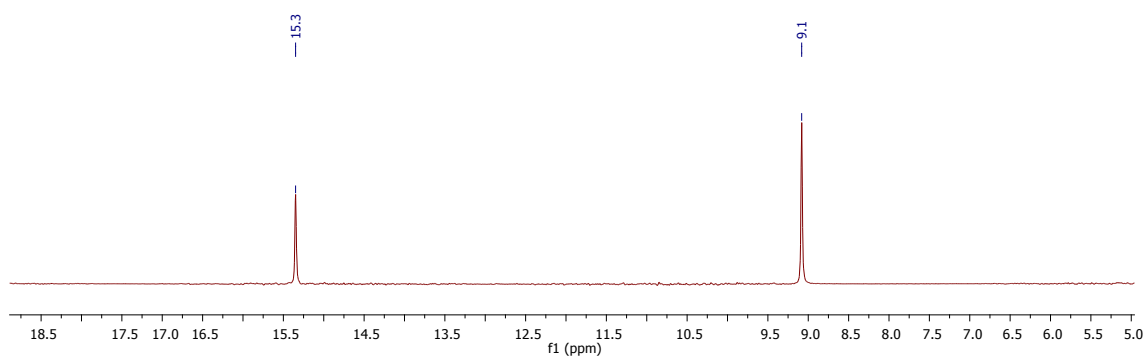


Figure S7. ^{31}P -NMR (202.4 MHz) spectrum of DTPMP, in $\text{NaCl}_{(\text{aq})}$ at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$.

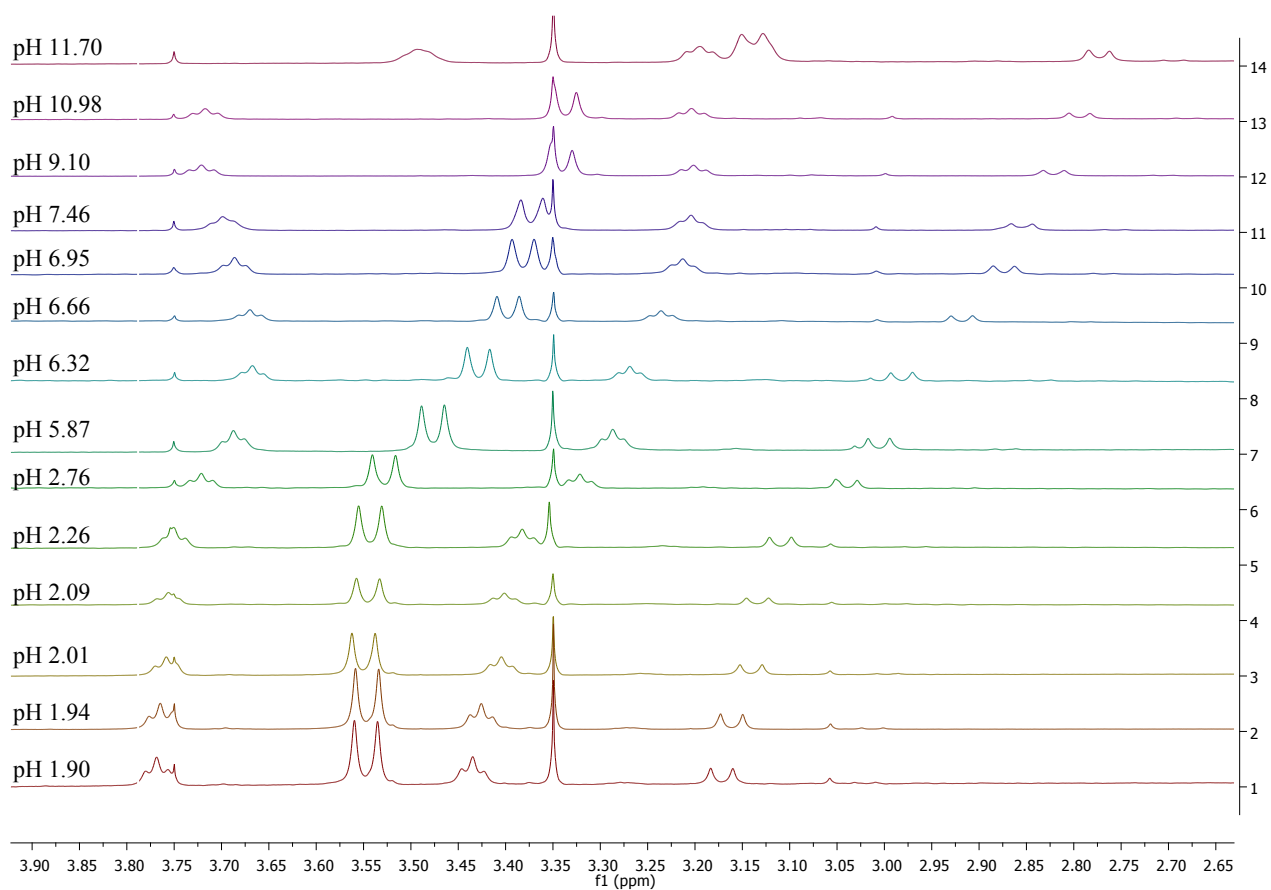


Figure S8. Superimposed $^1\text{H-NMR}$ (500 MHz) spectra of DTPMP at different pHs (increasing from down to top), in $\text{NaCl}_{(\text{aq})}$ at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$. $c_L = 5.0 \text{ mmol dm}^{-3}$.

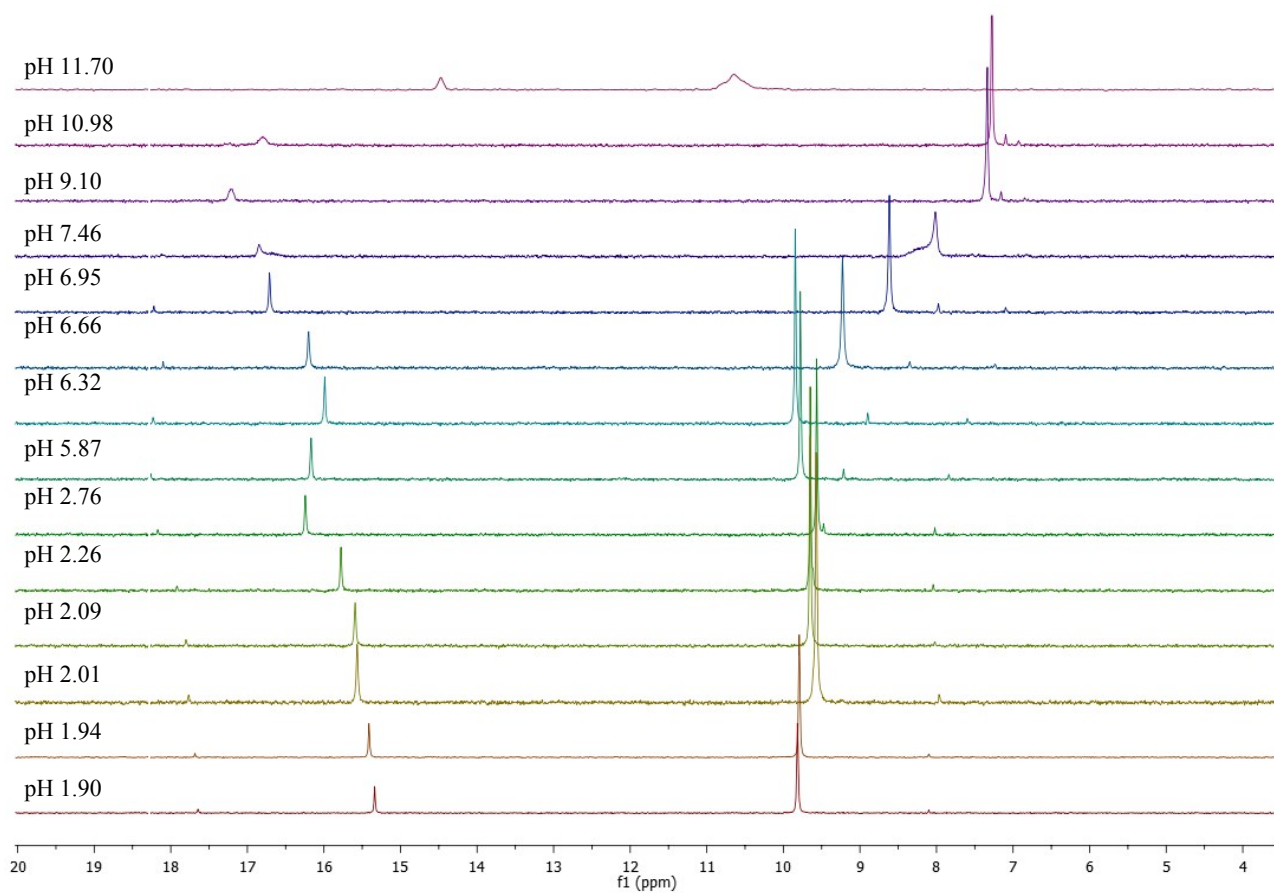


Figure S9. Superimposed ³¹P-NMR (202.4 MHz) spectra of DTPMP at different pHs (increasing from down to top), in NaCl_(aq) at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$. $c_L = 5.0 \text{ mmol dm}^{-3}$.

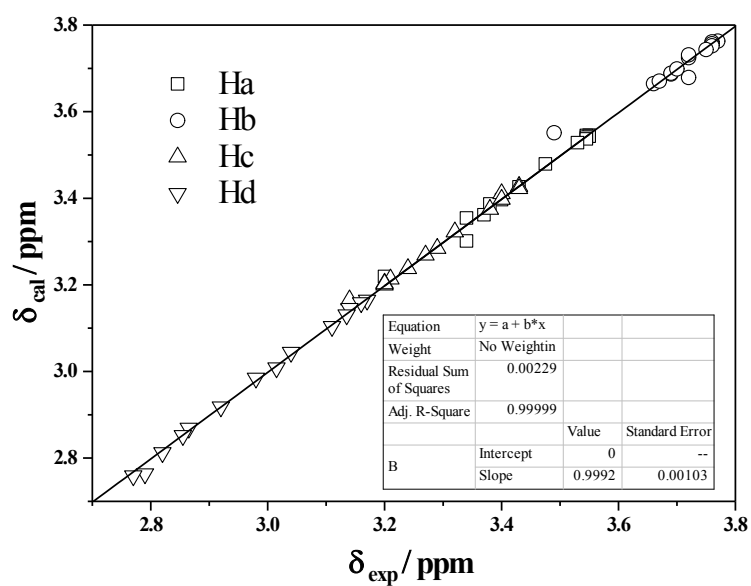


Figure S10. Calculated vs. experimental chemical shifts $^1\text{H-NMR}$ (500 MHz) of Ha, Hb, Hc, and Hd of DTPMP. Conditions: $c_{\text{DTPMP}} = 0.00510 \text{ mol dm}^{-3}$, in $\text{NaCl}_{(\text{aq})}$ at $I = 0.100 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$.

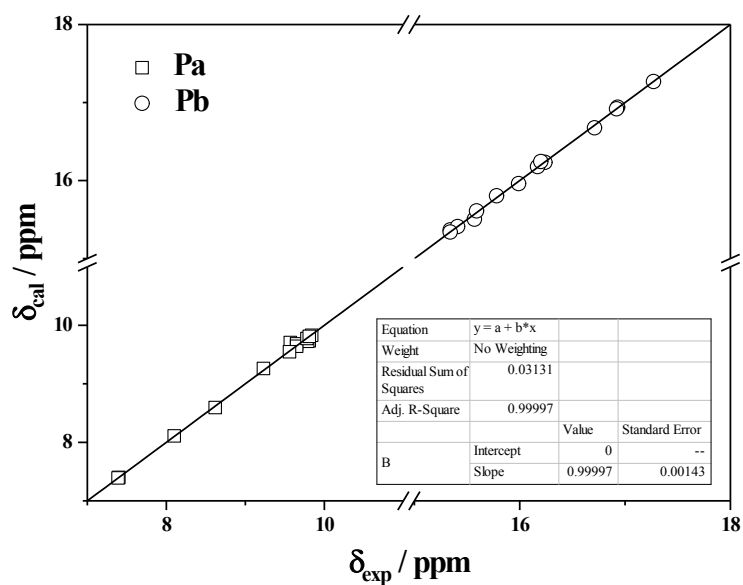


Figure S11. Calculated vs. experimental chemical shifts ^{31}P -NMR (202.4 MHz) of Pa and Pb of DTPMP. Conditions: $c_{\text{DTPMP}} = 0.00510 \text{ mol dm}^{-3}$, in $\text{NaCl}_{(\text{aq})}$ at $I = 0.100 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$.

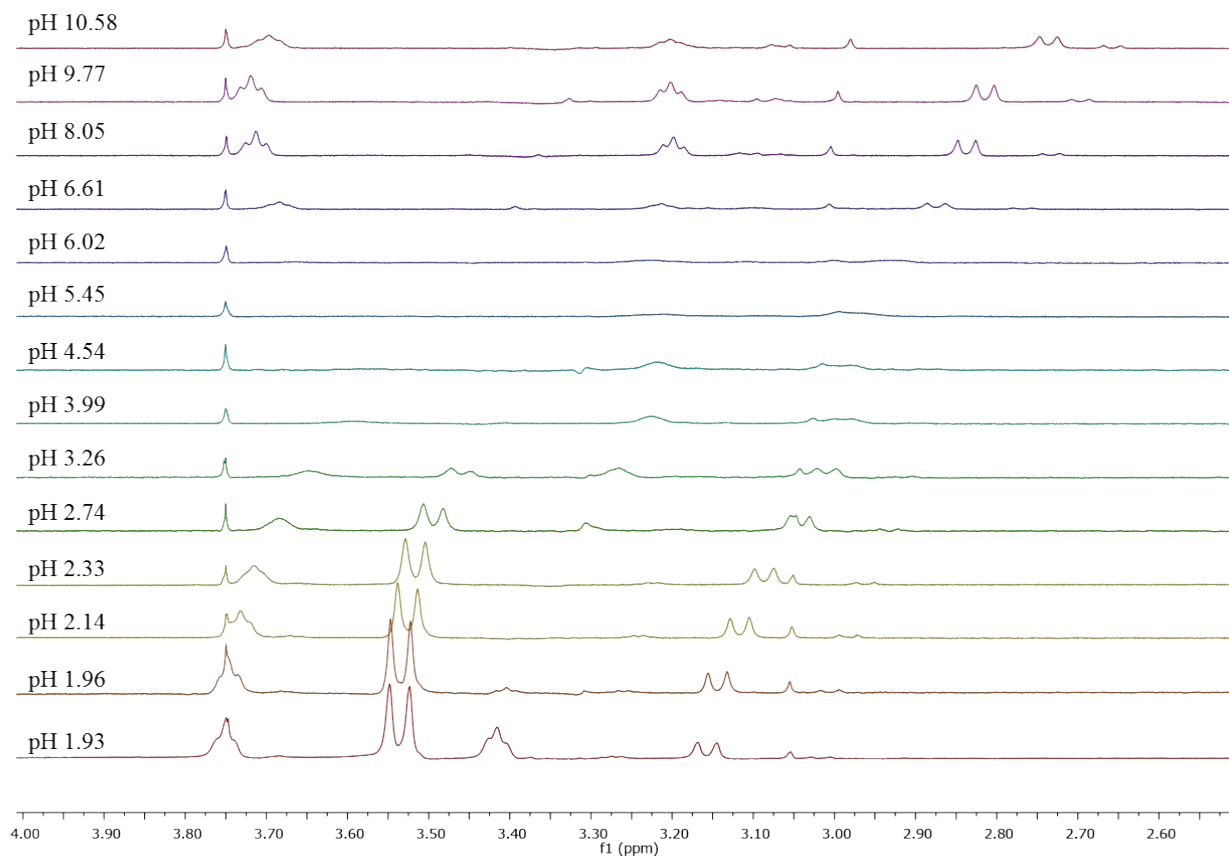


Figure S12. Superimposed ^1H -NMR (500 MHz) spectra of $\text{Zn}^{2+}/\text{DTPMP}$ solutions at different pHs (increasing from down to top), in $\text{NaCl}_{(\text{aq})}$ at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$. $c_L = 5.0 \text{ mmol dm}^{-3}$; $c_M = 2.5 \text{ mmol dm}^{-3}$.

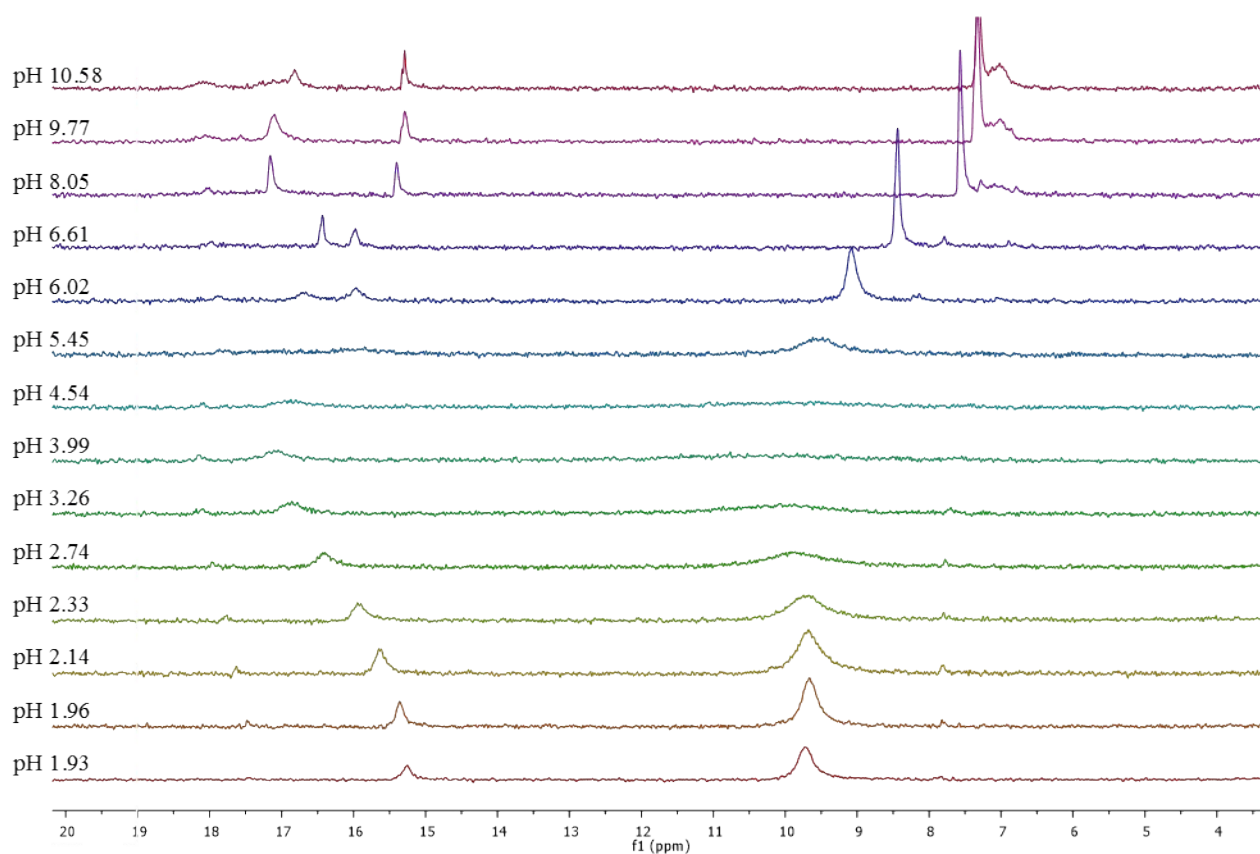


Figure S13. Superimposed ³¹P-NMR (202.4 MHz) spectra of Zn²⁺/ DTPMP solutions at different pHs (increasing from down to top), in NaCl_(aq) at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$. $c_L = 5.0 \text{ mmol dm}^{-3}$; $c_M = 2.5 \text{ mmol dm}^{-3}$.

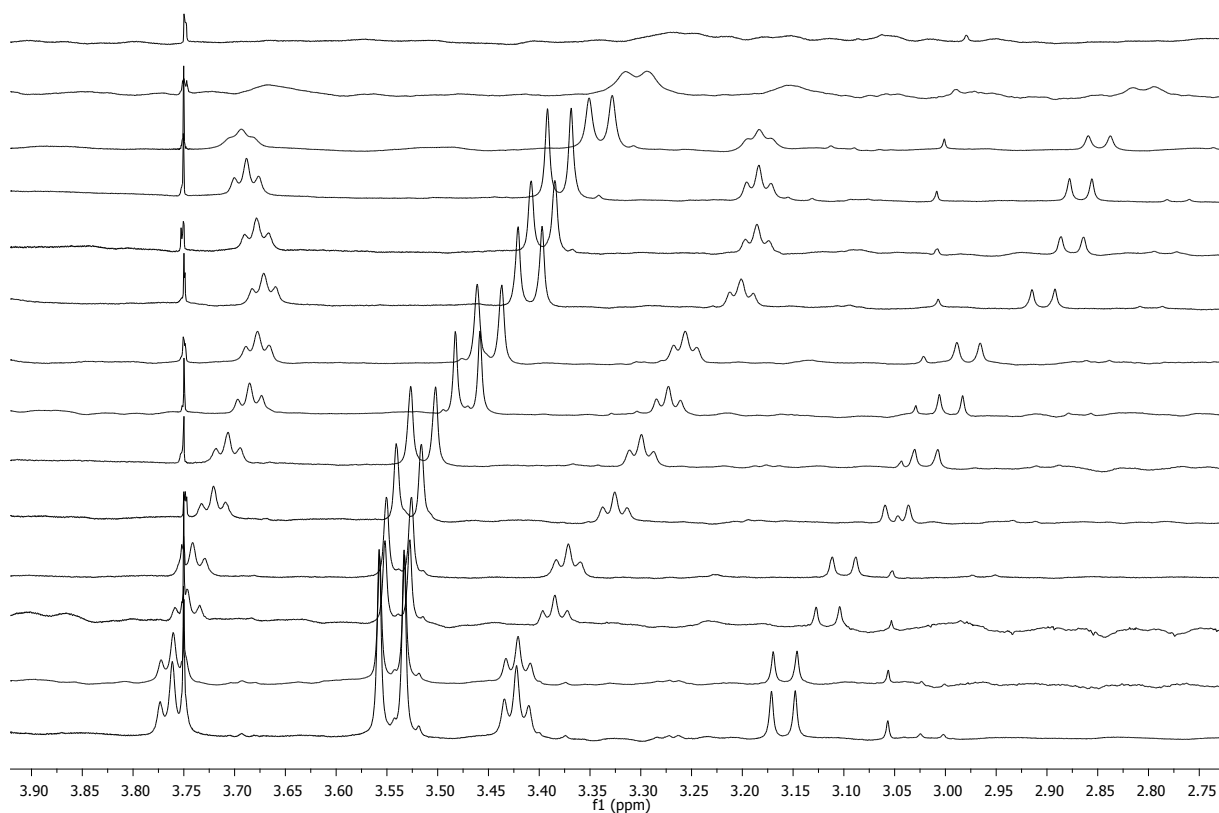


Figure S14. Superimposed $^1\text{H-NMR}$ (500 MHz) spectra of $\text{Ca}^{2+}/\text{DTPMP}$ solutions at different pHs (increasing from down to top), in $\text{NaCl}_{(\text{aq})}$ at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$. $c_L = 5.0 \text{ mmol dm}^{-3}$; $c_M = 2.5 \text{ mmol dm}^{-3}$.

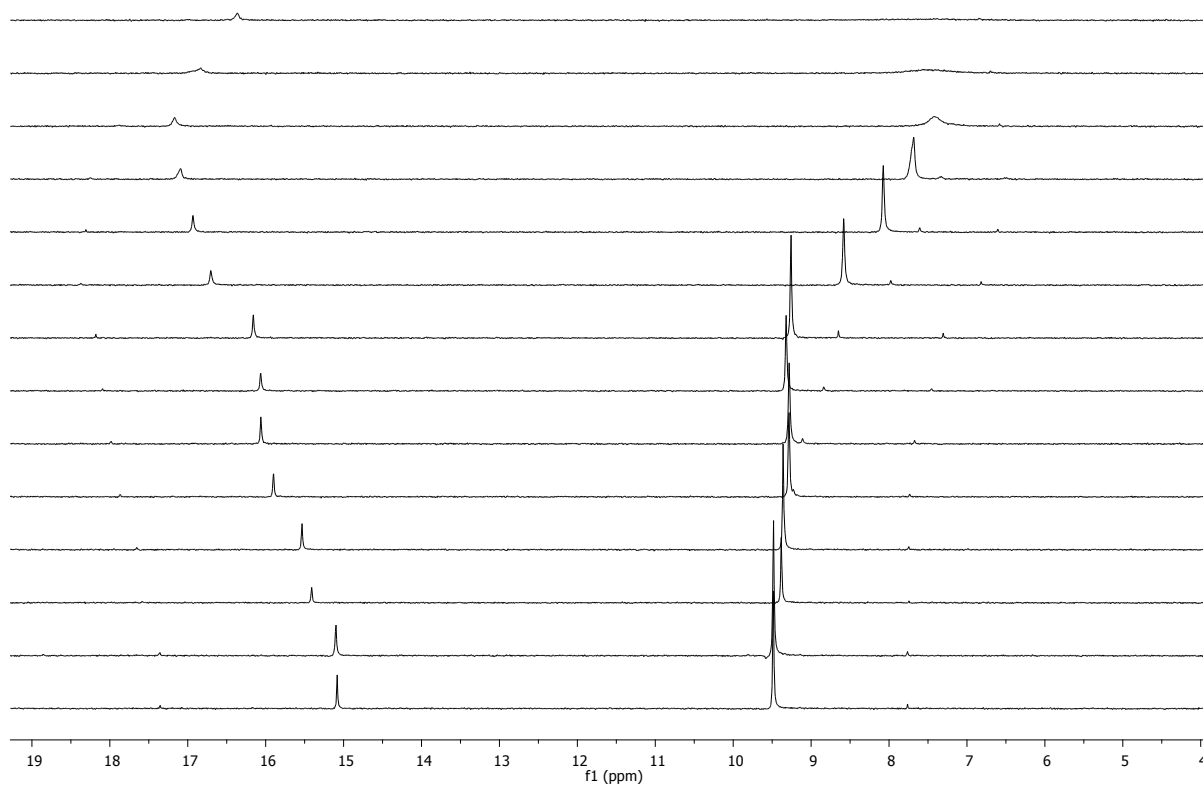


Figure S15. Superimposed ³¹P-NMR (202.4 MHz) spectra of Ca²⁺/ DTPMP solutions at different pHs (increasing from down to top), in NaCl_(aq) at $I = 0.1 \text{ mol dm}^{-3}$ and $T = 298.15 \text{ K}$. $c_L = 5.0 \text{ mmol dm}^{-3}$; $c_M = 2.5 \text{ mmol dm}^{-3}$.