On the Extraction of HCl and H2PtCl6 by Tributyl Phosphate: A Mode of Action Study

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Electronic Supplement

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**S1. Extraction of HCl by TBP in toluene – water content analysis.**

**Volume changes**

To track volume changes between the aqueous and organic phases, all measurements reported have been adjusted using a metal tracer in the aqueous phase. All data (adjusted and raw) are reported herein. By placing a non-extractable metal in the aqueous phase (in this case Nickel) and measuring its concentration (by ICP-OES, details in the main text) in the aqueous phase pre and post extraction of HCl by TBP, the change in volume of the aqueous phase was determined. This percentage change in volume can then be assumed to have moved to the organic phase, therefore permitting the concentration of the components in the organic phase to be adjusted by this percent.

| Measured Ni in aqueous phase pre-extraction (ppm) | 7.180 |
|--------------------------------------------------|-------|
| Initial [HCl] in aqueous phase (mol/L)           |       |
| Ni measured in aqueous phase after extraction (ppm) |       |
| Difference in Ni measured after extraction (ppm) |       |
| Difference in Ni measured after extraction (%)   |       |
| 2                                                | 7.630 | 0.450  | 6.022  |
| 3                                                | 7.263 | 0.083  | 1.115  |
| 4                                                | 7.910 | 0.730  | 9.778  |
| 5                                                | 7.263 | 0.083  | 1.115  |
| 6                                                | 7.368 | 0.188  | 2.512  |
| 7                                                | 7.231 | 0.051  | 0.686  |
| 8                                                | 7.301 | 0.121  | 1.624  |
| 9                                                | 7.824 | 0.644  | 8.618  |
| 10                                               | 7.878 | 0.698  | 9.352  |
| 11                                               | 7.562 | 0.382  | 5.118  |
| 11.5                                             | 7.634 | 0.454  | 6.075  |

**Table S1.** Concentration of Ni measured in aqueous phase after 1M TBP extraction of HCl, as a function of [HCl].
| Initial [HCl] in aqueous phase (mol/L) | Raw measurements [H₂O] measured in organic phase by KF titration (mol/L) | Adjusted for volume changes [H₂O] measured in organic phase by KF titration (mol/L) |
|---------------------------------------|-------------------------------------------------|-------------------------------------------------|
|                                       | 0.5 M TBP in organic phase | 1 M TBP in organic phase | 0.5 M TBP in organic phase | 1 M TBP in organic phase |
| 2                                     | 0.068                          | 0.390                          | 0.072                          | 0.414                          |
| 3                                     | 0.066                          | 0.293                          | 0.067                          | 0.297                          |
| 4                                     | 0.063                          | 0.278                          | 0.070                          | 0.305                          |
| 5                                     | 0.058                          | 0.291                          | 0.059                          | 0.294                          |
| 6                                     | 0.101                          | 0.406                          | 0.103                          | 0.417                          |
| 7                                     | 0.131                          | 0.706                          | 0.132                          | 0.710                          |
| 8                                     | 0.203                          | 0.945                          | 0.207                          | 0.960                          |
| 9                                     | 0.286                          | 1.064                          | 0.311                          | 1.156                          |
| 10                                    | 0.326                          | 1.188                          | 0.356                          | 1.300                          |
| 11                                    | 0.332                          | 1.099                          | 0.348                          | 1.155                          |
| 12                                    | 0.308                          | 1.060                          | 0.327                          | 1.124                          |

**Table S2.** Raw and corrected H₂O content extracted into toluene by 0.5 and 0.1 M TBP (data plotted in main text).
Background water concentration measurements of toluene on contact with HCl

The water content of the organic phase was measured by sampling (1 mL) of the organic phase, after physical separation from the aqueous phase, by coulometric Karl Fischer titration, using a Metrohm 831 KF Coulometer and HYDRANAL® Coulomat AG reagent. The water content of toluene was measured after contacting with 2-12 M HCl aqueous phase, with the raw data displayed below. Measurements indicate a steady concentration of water (ca. 0.012 mol L⁻¹) up to 10 M HCl, after which levels start to fall, reflecting the hygroscopic behaviour of strong acid solutions.

![Graph showing concentration of water measured in organic phase after contact with varying HCl concentration.](image)

**Figure S1.1** Concentration of water measured in organic (toluene) phase after contact with varying [HCl].

| Initial [HCl] in aqueous phase (mol/L) | [H₂O] measured in organic phase by KF titration (mol/L) |
|--------------------------------------|-----------------------------------------------------|
| 2                                    | 0.0124                                               |
| 3                                    | 0.0124                                               |
| 4                                    | 0.0123                                               |
| 5                                    | 0.0123                                               |
| 6                                    | 0.0119                                               |
| 7                                    | 0.0124                                               |
| 8                                    | 0.0121                                               |
| 9                                    | 0.0126                                               |
| 10                                   | 0.0116                                               |
| 11                                   | 0.0102                                               |
| 12                                   | 0.0052                                               |

**Table S2.** Concentration of water measured in organic (toluene) phase after contact with varying [HCl] (shown graphically in Fig S1.1).
S 1.2 Extraction of PtCl$_6^{2-}$ by TBP in toluene – water content analysis.

![Graph showing the concentration of water extracted by TBP during HCl and PtCl$_6^{2-}$ extraction from HCl.](image)

**Figure S1.2** Concentration of water measured in organic (toluene) phase in presence of 0.01 M Na$_3$PtCl$_6$ after contact with varying [HCl].

S2. Molecular dynamics simulations

S2.1 Aggregate formation of 1-6 TBP, 5H$_2$O, Cl$^-$ (counter ion TBPH$^+$ or H$_3$O$^+$)

A distance analysis quickly identifies how many TBP molecules assemble in the aggregate structure. Each trace represents the distance between the Q=P(TBP/TBPH$^+$) and Cl$^-$ ion, with respect to time. Upon increasing TBP number, the coordination number increases, but never exceeds four. Results are shown for the TBPH$^+$ counter ion system in Figure S2.1, and for the H$_3$O$^+$ counter ion system in Figure S2.2. In the absence of the water layer (counter ion TBPH$^+$) the coordination number for TBP never exceeds three (Figure S2.3).
Figure S2.1 Distance analysis between (n-BuO)$_3$P=O/OH$^+$···Cl$^-$ for NPT simulations containing varying [TBP], Cl$^-$ and 5 H$_2$O in (40 Å)$^3$ toluene solvent box, where the counter-ion is TBPH$^+$. Each trace represents the dynamics of an individual TBP molecule, with the red line denoting TBPH$^+$ and blue the closest coordinated neutral TBP. Vertical dotted line marks beginning of production run data used in further analysis presented in the main text.
Figure S2.2. Distance analysis between (n-BuO)$_3$P=O/OH$^-$⋯Cl$^-$ for NPT simulations containing varying [TBP] and 1 Cl (no water), in (40 Å)$^3$ toluene solvent box, where the counter-ion is TBPH$^+$. Each trace represents the dynamics of an individual TBP molecule, with the red line denoting TBPH$^+$ and blue the closest coordinated neutral TBP.
Figure S2.3 Distance analysis between (n-BuO)$_3$P=O/OH$^-$···Cl$^-$ for NPT simulations containing varying [TBP], 1 Cl$^-$ and 10 H$_2$O, in (40 Å)$^3$ toluene solvent box, where the counter-ion is TBPH$^+$. Each trace represents the dynamics of an individual TBP molecule, with the red line denoting TBPH$^+$ and blue the closest coordinated neutral TBP.
Figure S2.4 Distance analysis between (n-BuO)$_3$P=O...Cl$^-$ for NPT simulations containing varying [TBP], 1 Cl$^-$ and 5 H$_2$O, in (40 Å)$^3$ toluene solvent box, where the counter-ion is H$_3$O$^+$. Each trace represents the dynamics of an individual TBP molecule. Vertical dotted line marks beginning of production run data used in further analysis presented in the main text.

S2.2 Aggregate formation of (TBP:HCl:H$_2$O)$_{3.5}$ (counter ion TBPH$^+$ or H$_3$O$^+$)

A distance analysis quickly identifies how many TBP molecules assemble in the aggregate structure. Each trace represents the distance between the O=P(TBP/TBPH$^+$) to one of the Cl$^-$ ions, with respect to time. All TBP molecules bind to the (Cl$^-$.H$_2$O)$_{3.5}$ core, but it is evident from the distance analysis plots that the system is more dynamic when the counter ion is H$_3$O$^+$ (Figures S2.5 and S2.6). Also in this section is a plot of the root-mean square deviation obtained during the production run of each system (Figure S2.7).
Figure S2.5 Distance analysis between O=P(TBP) and one Cl\textsuperscript{-}, for NPT simulations performed on (TBP.H\textsubscript{2}O.HCl)\textsubscript{3-s}, within a (40 Å\textsuperscript{3}) toluene solvent box (TBPH\textsuperscript{+} counter-ion). Vertical dotted line marks beginning of production run data used in further analysis presented in the main text.
Figure S2.6 Distance analysis between O=P(TBP) and one Cl\textsuperscript{-}, for NPT simulations performed on (TBP.H\textsubscript{2}O.HCl\textsubscript{3}s, within a (40 Å\textsuperscript{3}) toluene solvent box (H\textsubscript{3}O\textsuperscript{+} counter-ion). Vertical dotted line marks beginning of production run data used in further analysis presented in the main text.
Figure S2.7: RMSD plots obtained from NPT simulations of \((\text{TBP.HCl})_{3.5}\) within 40 Å³ toluene solvent box; counter-ion TBPH⁺ (left column), or H₃O⁺ (right column).
S2.3 Aggregate formation of $\text{(TBP)}_4\text{H}_2\text{O}\cdot \text{Cl}_4$ (counter ion TBPH$^+$ or H$_3$O$^+$)

These simulations were performed to ascertain whether stable aggregates could be formed that comprise more than four TBP molecules. Each trace in the plots given below represents the distance between the Q=P(TBP/TBPH$^+$) to one of the four Cl$^-$ ions, with respect to time. From this it is apparent that it is unusual for more than four TBP molecules to bind to the hydrated chloride core at any one time.

**Figure S2.8** Distance analysis between Q=P(TBP) and one Cl$^-$, for NPT simulations performed on $\text{(TBP)}_4\text{H}_2\text{O}\cdot \text{Cl}_4$, within a (40 Å)$^3$ toluene solvent box (TBPH$^+$ counter-ion).
Figure S2.9 Distance analysis between O=P(TBP) and one Cl⁻, for production run NPT simulations performed on (TBP)₄, 6 or 7(H₂O:Cl)₄, within a (40 Å)³ toluene solvent box (H₃O⁺ counter-ion).

S2.4 Force field parameterisation, PtCl₆²⁻

The OPLS-AA force field does not include parameters for transition metals. Leinke et al.¹ have described force field parameters for PtCl₆²⁻ using CHARMM, however it was found that benchmarking simulations (comprising a single PtCl₆²⁻ ion in a TIP3P water box of size 40 Å³ and two H₂O⁺ ions included to ensure a neutral box) could not reproduce comparable PtCl₆²⁻…H₂O g(r) plots in LAMMPS, with over-binding of H₂O molecules observed. As a simple alternative in this work PtCl₆²⁻ has been treated as a rigid octahedral unit (rPt-Cl = 2.42 Å, k = 150 kcal mol⁻¹ Å⁻², ∠Cl-Pt-Cl = 90 or 180°, k = 45 kcal mol⁻¹ deg⁻²), with the 2⁻ charge shared equally between all six Cl atoms, which were also described using the Van der Waal radius for an individual chloride ion. The platinum site was treated as a dummy atom, with zero charge and radius, leaving the chloride Van der Waal well depth (ε, 0.71) and collision diameter (σ, 4.02) as parameters, which were varied until the PtCl₆²⁻…H₂O g(r) plots (Figure S2.10) gave reasonable correlation to distances obtained from a M06/6-31G(d), LANL2DZ optimisation of a [PtCl₆(TBPH)₂(H₂O)₈] system [Figure S2.10, rPt…OH₂ = 4.4 Å (average value)].
**Figure S2.10:** $g(r)$ plots obtained for PtCl$_6^{2-}$.2H$_2$O$^+$ in a (40 Å)$^3$ TIP3P water box, using Cl$^-$ parameters $q = -0.333$, $\varepsilon = 0.71$ and $\sigma = 4.02$.

**Figure S2.11:** Lowest energy minimised conformation determined for [PtCl$_6$(TBPH)$_2$(H$_2$O)$_8$] using M06/6-31G(d), LANL2DZ for Pt

**S2.5 Aggregate formation of 4-6 TBP, 0-10 H$_2$O and PtCl$_6^{2-}$ (counter ions TBPH$^+$ or H$_3$O$^+$)**

**Figure S2.12:** Distance analysis between Pt...O=P(TBP/TBPH$^+$), for NPT simulations containing varying [TBP] and 1 PtCl$_6^{2-}$, (no water present) within (40 Å)$^3$ toluene solvent box. Each trace represents the dynamics of an individual TBP molecule, with the red and blue lines denoting counter ions TBPH$^+$. 
Figure S2.13: Radial distribution plots between \((n\text{-BuO})_3P=O\text{OH}^+\cdots\text{PtCl}_6^{2-}\) for simulation containing 4 TBP and 1 PtCl\(_6^{2-}\), in \((40 \text{ Å})^3\) toluene solvent box, where the counter-ions are TBPH\(^+\), with \(g(r)\) shown in black and \(\text{int}[g(r)]\) in red.

Figure S2.14: Density profile for simulation containing 4 TBP and 1 PtCl\(_6^{2-}\) in \((40 \text{ Å})^3\) toluene solvent box (not represented), where counter-ions are TBPH\(^+\).
Figure S2.15: Distance analysis between \((n\text{-BuO})_3P=O/\text{OH}^+\cdots\text{PtCl}_6^{2-}\) for NPT simulations containing varying [TBP], 1 PtCl\(_6^{2-}\) and 5 H\(_2\)O, in (40 Å)\(^3\) toluene solvent box. Each trace represents the dynamics of an individual TBP molecule, with the red and blue lines denoting counter ions TBPH\(^+\).

Figure S2.16: Distance analysis between \((n\text{-BuO})_3P=O/\text{OH}^+\cdots\text{PtCl}_6^{2-}\) for NPT simulations containing varying [TBP], 1 PtCl\(_6^{2-}\) and 10 H\(_2\)O, in (40 Å)\(^3\) toluene solvent box. Each trace represents the dynamics of an individual TBP molecule, with the red and blue lines denoting counter ions TBPH\(^+\). Vertical dotted line marks beginning of production run data used in further analysis presented in the main text.
Figure S2.17: Distance analysis between (n-BuO)$_3$P=O···Cl$^-$ for NPT simulation containing 4 TBP, 1 PtCl$_6^{2-}$ and 5 H$_2$O, in (40 Å)$^3$ toluene solvent box, where the counter-ions are H$_3$O$^+$. 

Figure S2.18: Distance analysis between (n-BuO)$_3$P=O···PtCl$_6^{2-}$ for NPT simulation containing 4 TBP, 1 PtCl$_6^{2-}$ and 10 H$_2$O, in (40 Å)$^3$ toluene solvent box, where the counter-ions are H$_3$O$^+$. Vertical dotted line marks beginning of production run data used in further analysis presented in the main text.

References

(1) Lienke, A.; Klatt, G.; D. J. Robinson; K. R. Koch; Naidoo, K. J. Inorg. Chem. 2001, 40, 2352-2357.