Solvent Extraction

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Outer-Sphere Coordination Chemistry: Selective Extraction and Transport of the $[PtCl_6]^{2-}$ Anion**

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Selectivity in the transport of platinum group metal ions by solvent extraction in industrial processes depends critically upon control of the metal coordination chemistry through the formation of either inner-sphere complexes with dialkyl sulfides or hydroxyoximes,[1] or through formation of outer-sphere organic-soluble salts with hydrophobic trialkylamine and related reagents of the Alamine type.[1,2] The latter rely upon control of partition coefficients and solubilities such that anion exchange can be used to transfer the chlorometallate to a water-immiscible solvent in a pH-dependent equilibrium [Eq. (1)].[2]

$$n\,R_3N_{(org)} + n\,H^+ + MCl_x^{n-} \rightleftharpoons [(R_3NH)_nMCl_x]_{(org)} \quad (1)$$

Although the solvent extraction of base metals such as Cu and Zn usually involves the formation of inner-sphere coordination complexes,[3] the very slow ligand exchange for the $[PtCl_6]^{2-}$ ion[4] makes it necessary to address and recognise the outer coordination sphere of this species to form neutral anion–ligand packages. Selectivity continues to be a challenge in the development of supramolecular recognition of anions[5] and is a pervasive problem in extractive metallurgy because the generation of electrolytes of high purity is essential for efficient electrolytic reduction to produce metals.[6] Thus, an understanding of the nature and disposition of electrostatic and supramolecular hydrogen-bonding interactions to chlorometallates is essential to the design of selective extractants for these anions. DFT calculations and NMR spectroscopic studies of the solvation and ion pairing of $[PtCl_6]^{2-}$ suggest that hydrogen-bonding solvate molecules, such as methanol, address the triangular faces of the hexachloro octahedron,[7] whereas formation of trifurcated hydrogen-bonds to faces or bifurcated hydrogen-bonding to edges of the hexachloro octahedron has been predicted on the basis of the location of maximum electron density in the anion;[8] such interactions have indeed been observed in solid-state structures of chlorometallates.[9]

We report herein a new approach to the selective complexation and extraction of hexachlorometallates in the presence of chloride ions using tripodal ionophores incorporating multiple hydrogen-bond donors linked to a protonatable bridgehead N center. Such a design can not only address the threefold symmetry of the outer coordination sphere of $[PtCl_6]^{2-}$ by presenting neutral hydrogen-bond donors to the faces or edges of the hexachloro octahedron (Figure 1), but also provides a positive charge to ensure the solubility of a neutral 2:1 $[LH^+]$:$[PtCl_6]^{2-}$ complex in water-immiscible solvents. Our target in this work was to design useful solvent extractants for the recovery of Pt^{IV} from acidic chloride streams, whereby loading and stripping of the organic phase are controlled by a "pH-swing" mechanism [Eqs. (2) and (3)].

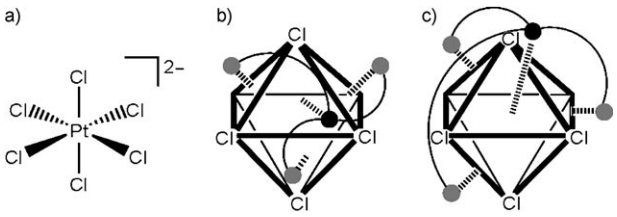

Figure 1. The structure of $[PtCl_6]^{2-}$ (a) and proposed modes of binding to tripodal multiple hydrogen-bond ionophores through interactions with the faces (b) or the edges (c) of the hexachloro octahedron. The protonated amine of the receptor is shown as a black sphere and the neutral hydrogen-bond donors as gray spheres.

$$2\,L_{(org)} + 2\,H^+ + [PtCl_6]^{2-} \rightleftharpoons [(LH)_2PtCl_6]_{(org)} \quad (2)$$

$$[(LH)_2PtCl_6]_{(org)} + 2\,NaOH \rightleftharpoons Na_2[PtCl_6] + 2\,L_{(org)} + 2\,H_2O \quad (3)$$

Such a protocol could then be implemented for the recovery of platinum metal anions from the highly acidic chloride streams currently used in industry. Furthermore, selective extraction of $[PtCl_6]^{2-}$ over Cl^-, which is present in substantial excess in industrial feed streams, is essential for an efficient process, and is, therefore, a key design requirement for our

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receptors. Significantly, the simple trialkylamine reagents of the Alamine type [Eq. (1)] are known to exhibit poor selectivity for $[PtCl_6]^{2-}$ over Cl^- (see below), particularly at high acid concentrations.[10] In this work we have used trioctylamine (TOA) as a model for the Alamines[10,11] to benchmark against our new reagents.

A range of amide and urea tripodal ligands L^{1-10} derived from tris(2-aminoethyl)amine (tren) were prepared and characterized (Scheme 1; see also the Supporting Information). Ligand L^1 was designed with a long spacer between the protonatable amine bridgehead and the neutral hydrogen-bond donors to allow these to address three faces of the $[PtCl_6]^{2-}$ octahedron (Figure 2). The urea ligands L^{2-5} and L^{10} and amide ligands L^{6-9} were synthesized to access potential tri- and bifurcating hydrogen-bonding to the $[PtCl_6]^{2-}$ ion (Figure 2).

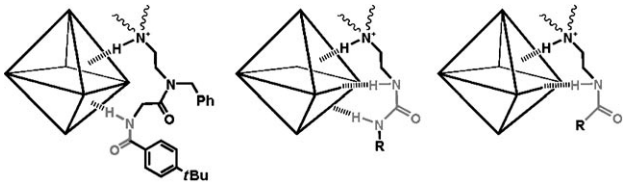


Figure 2. Binding modes of the arms of tren-based urea and amide receptors that preserve pseudo threefold symmetry (only one arm is shown for clarity).

Equilibration to form the outer-sphere complexes $[(LH)_2PtCl_6]$ [Eq. (2)] was achieved within minutes of mixing $H_2[PtCl_6]$ in aqueous 0.6 M HCl with a solution of L in $CHCl_3$ at room temperature. Prolonged mixing (> 16 h) led to a slight drop in the content of platinum in the $CHCl_3$ layer, and this observation is attributed to inner-sphere substitution processes to form insoluble complexes. Quantitative back-extraction of $[PtCl_6]^{2-}$ from the organic layer into an aqueous solution was achieved by contacting the loaded $CHCl_3$ layer with an aqueous solution containing a twofold excess of NaOH over ligand [Eq. (3)]. Results for the extraction of $[PtCl_6]^{2-}$ by the receptors are summarized in Figure 3 along with data for TOA for comparison. Ligands L^2 and L^6 afforded metal complex salts that precipitated out of solution and are therefore not discussed.

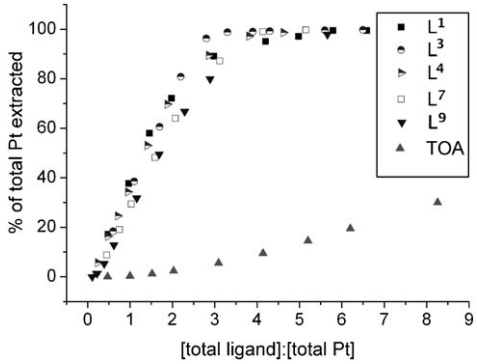
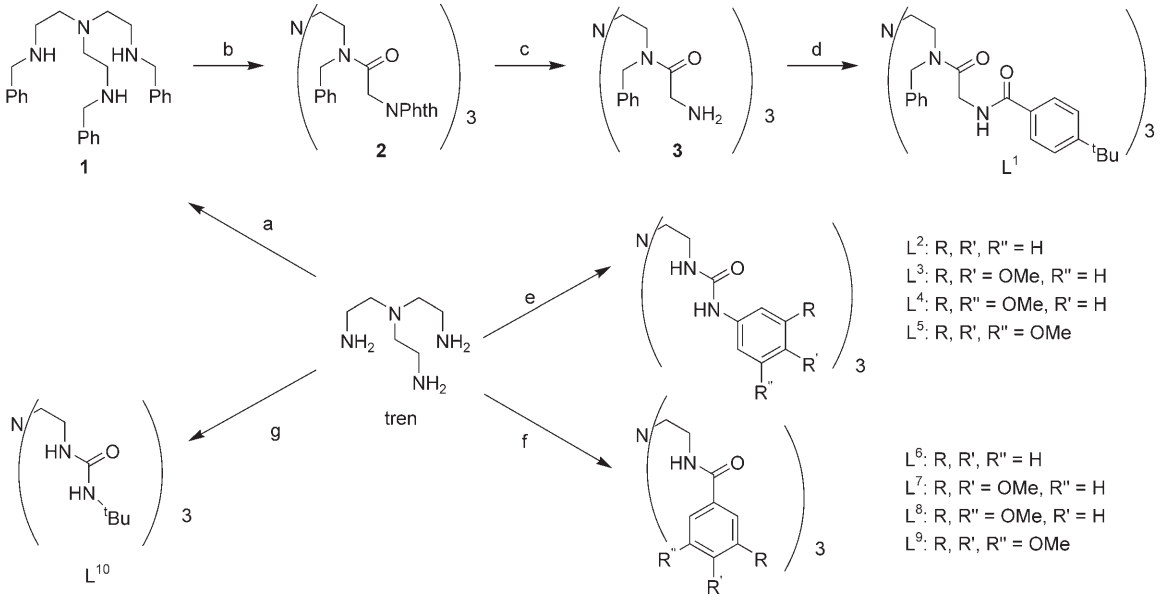


Figure 3. Plot of percentage of the total platinum extracted as $[PtCl_6]^{2-}$ from aqueous 0.6 M HCl into $CHCl_3$ as a function of the [L]:[Pt] ratio.

TOA is not an effective extractant at high concentrations of HCl. Although platinum uptake by a threefold excess of TOA from an aqueous solution of $H_2[PtCl_6]$ with no added HCl is around 80% of the theoretical value, it drops to around only 20% when the aqueous feed solution contains 0.6 M HCl, suggesting strong transfer of Cl^- instead of $[PtCl_6]^{2-}$ under these conditions (see the Supporting Information). As a consequence, the transport efficiency of platinum from acidic feeds in a flow sheet will be low using TOA, and chloride concentrations will build up downstream. Significantly, the



Scheme 1. Synthesis of the receptors L^1–L^{10}: a) benzaldehyde, MeOH, RT then $NaBH_4$;[12] b) 2-phthalimidoacetyl chloride, Et_3N, $CHCl_3$, 0 °C then RT; c) $NH_2NH_2{\cdot}H_2O$, EtOH, $CHCl_3$, reflux; d) *tert*-butylbenzoyl chloride, Et_3N, $CHCl_3$, 0 °C then RT; e) phenyl, 3,4-dimethoxyphenyl, 3,5-dimethoxyphenyl, or 3,4,5-trimethoxyphenyl isocyanate, THF, RT;[13] f) benzoyl, 3,4-dimethoxybenzoyl, 3,5-dimethoxybenzoyl, or 3,4,5-trimethoxybenzoyl chloride, NaOH, H_2O, CH_2Cl_2, or Et_2O, RT;[14,15] g) *tert*-butyl isocyanate, THF, RT. Full details of preparations are given in the Supporting Information.

tripodal hydrogen-bond donor ligands described herein are much more effective than the Alamine model TOA[10] in recovering $[PtCl_6]^{2-}$ in the presence of excess HCl (Figure 3 and Table 1). We note that L^3 is especially effective in this system. Loadings of greater than 90% imply that the

Table 1: Percentage of Pt extracted as $[PtCl_6]^{2-}$ into $CHCl_3$ from aqueous 0.6 M HCl in the presence of 3 molar excess of L.

Ligand	TOA	L^1	L^3	L^4	L^7	L^9
% Pt extracted	5	89	98	90	85	80

triamide/urea ligands show high selectivity for $[PtCl_6]^{2-}$ over Cl^- because the latter is present in a 60-fold excess in the aqueous feed solution. Generally, extractant strengths are observed to be greater for the urea-containing ligands than their amido analogues (Table 1).

We used a procedure similar to that described by Yoshizawa and co-workers[11] to determine the stoichiometry of the platinum-containing complex formed in the water-immiscible phase and to probe further the selectivity of $[PtCl_6]^{2-}$ over Cl^-. At low pH values, where it can be assumed that the ligand is fully protonated, the extraction of $[PtCl_6]^{2-}$ is a competitive process, as shown by Equation (4).

$$[PtCl_6]^{2-} + 2\,[(LH)Cl]_{(org)} \overset{K_{[PtCl_6]^{2-}}}{\rightleftharpoons} [(LH)_2PtCl_6]_{(org)} + 2\,Cl^- \qquad K_{[PtCl_6]^{2-}} = \frac{[(LH)_2PtCl_6]\,[Cl^-]^2}{[PtCl_6{}^{2-}]\,[(LH)Cl]^2} \tag{4}$$

Assuming no inner-sphere substitution on the timescale of the extraction, the distribution coefficient for platinum is $D_{Pt} = [(LH)_2PtCl_6]/[PtCl_6{}^{2-}]$, and from Equation (4), $\log D_{Pt}$ has values defined by Equation (5).

$$\log D_{Pt} = \log K_{[PtCl_6]^{2-}} + 2\log\left[\frac{[(LH)Cl]}{[Cl^-]}\right] \tag{5}$$

Plots of $\log D_{Pt}$ versus $\log\{[(LH)Cl]/[Cl^-]\}$ (Figure 4) for TOA, L^1, and L^4 show slopes close to 2, which is in line with formation of the anticipated 2:1 $[LH]^+:[PtCl_6]^{2-}$ assemblies in

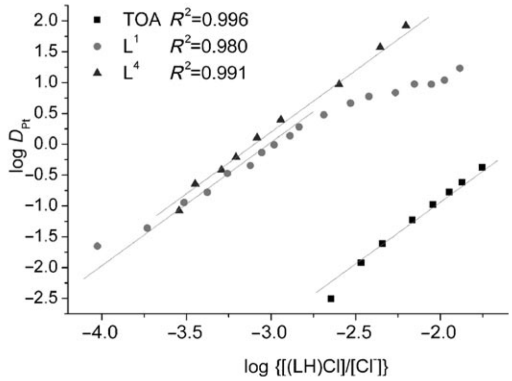


Figure 4. Plot of $\log D_{Pt}$ vs. $\log\{[(LH)Cl]/[Cl^-]\}$.

$CHCl_3$. Whilst the data for these ligands are consistent with the formation of $[(LH)_2PtCl_6]$ complexes as the extracted species, for other ligands, L^3, L^5, L^7, and L^9 in this work, and for TOA at high ligand concentrations,[11] the Yoshizawa plots show some deviation from linearity (see the Supporting Information). Such deviations may be due to the formation of outer-sphere complexes with alternative stoichiometries such as 3:1:1 $[LH]^+:[PtCl_6]^{2-}:Cl^-$ at high ligand concentrations or may involve the incorporation of a hydroxonium ion into the outer-sphere complex giving a 1:1:1 assembly $[LH]^+:[H_3O]^+:[PtCl_6]^{2-}$, which would be favored at low ligand concentrations. Alternatively, the receptors, their hydrochloride salts, and/or their platinum complexes with some solubility in the aqueous phase cannot be discounted at this stage. These caveats notwithstanding, the triamide/urea ligands L^1 and L^4 show very high selectivity for $[PtCl_6]^{2-}$ over Cl^-, the latter being present in a 60-fold excess.

The formation of a 2:1 $[LH]^+:[PtCl_6]^{2-}$ package in organic media was supported further by a single-crystal X-ray structure determination of $[(L^{10}H)_2PtCl_6]$.[16] The structure determination confirms the presence of significant hydrogen-bonding between the urea moieties of $[L^{10}H]^+$ and the $[PtCl_6]^{2-}$ ion, and, as anticipated, the bridgehead N atom in L^{10} is protonated to afford a complex with a net neutral charge (Figure 5). A bifurcated hydrogen bond is observed between

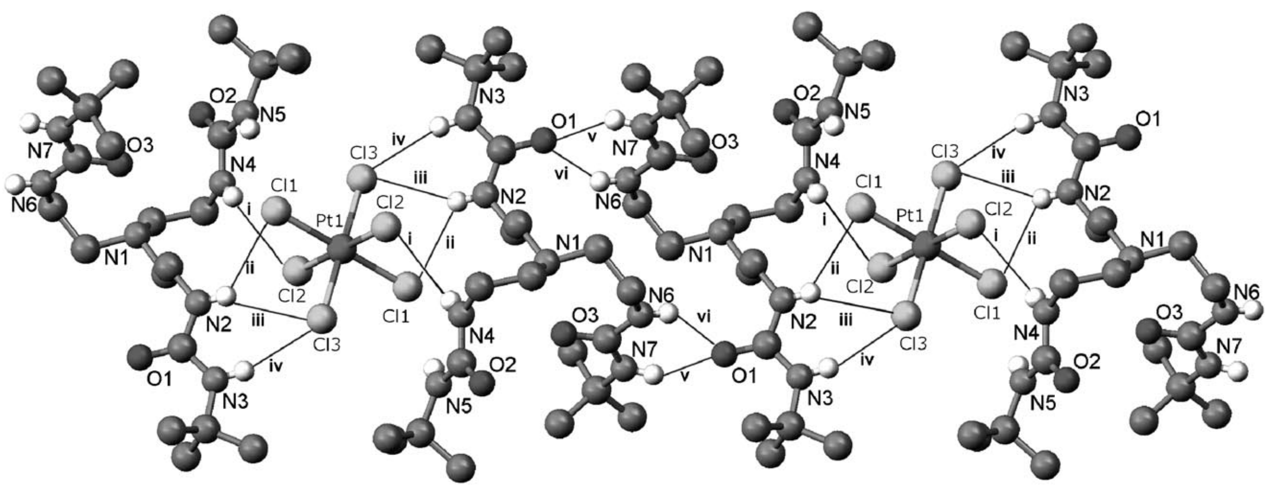


Figure 5. View of the structure of $[(L^{10}H)_2PtCl_6]$. Hydrogen-bond lengths: i) 2.791, ii) 2.799, iii) 2.805, iv) 2.664, v) 2.180, vi) 2.096 Å.

N2–H2A···Cl1 [2.799 Å] and N2–H2A···Cl3 [2.805 Å] with further hydrogen-bond interactions between N3–H3A···Cl3 [2.664 Å] and N4–H4A···Cl2 [2.791 Å]. Although there are extensive hydrogen-bonding interactions between $[L^{10}H]^+$ and $[PtCl_6]^{2-}$, only two of the three arms of the receptor interact with one $[PtCl_6]^{2-}$ ion; the third arm participates in hydrogen-bonding with an adjacent molecule of $[L^{10}H]^+$ to form an extended ribbon structure (Figure 5). This ribbon structure accounts for the low solubility of this complex in chloroform, which excluded this ligand from the extraction experiments. Although the results for the solid-state structure cannot be translated directly to the structure in solution, they do confirm the success of our strategy and illustrate many of the design features that we sought in addressing the molecular recognition and selectivity of hexachlorometallate anions through coordination at the outer sphere.

Significantly, the efficacy of our tripodal amide and urea ligands in a "pH-swing" controlled process to recover platinum from acid chloride feed solutions has been established. The very high $[PtCl_6]^{2-}$ loading from acidic chloride solutions for the new receptors reported herein, coupled with the quantitative stripping and release of metallate anion by base, provides the basis for a very efficient process for the separation and concentration of platinum with minimal reagent consumption (2 equivalents of NaOH) and generation of 2 mol equivalents of NaCl as a by-product. Variation of the disposition and nature of hydrogen-bonding groups in the pendant arms of the reagents should allow the selectivity of receptors to be tuned to accomplish the separation of chlorometallates having second coordination spheres with different geometries (e.g., $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$), sizes (e.g., $[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$), or net charges (e.g., $[PtCl_6]^{2-}$ and $[IrCl_6]^{3-}$).

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[16] Crystal data for $[(L^{10}H)_2PtCl_6]$: $M_r = 1379.2$, triclinic, $a = 8.8396(5)$, $b = 13.2745(7)$, $c = 14.4379(8)$ Å, $\alpha = 93.865(2)$, $\beta = 97.368(2)$, $\gamma = 95.263(2)°$, $V = 1667.7(3)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$, $Z = 1$, $\rho_{calcd} = 1.373$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.397$ mm^{-1}, 7540 unique reflections ($R_{int} = 0.013$) used in all calculations. Final R_1 [7536 $F \geq 4\sigma(F)$] = 0.0202 and wR_2(all F^2) was 0.0536. The dataset for $[(L^{10}H)_2PtCl_6]$ was collected on a Bruker APEX CCD diffractometer. The structure was solved by direct methods using SHELXS97[18] and refined by full-matrix least-squares on F^2 using SHELXL97.[19] CCDC-653924 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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