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

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Abstract: A series of tripodal receptors designed to recognise the outer coordination sphere of the hexachlorometallate anion $[PtCl_6]^{2-}$, and thus show selectivity for ion-pair formation over chloride binding, has been synthesised and characterised. The tripodal ligands contain urea, amido or sulfonamido hydrogen-bond donors, which are aligned to bind to the regions of greatest electron density along the faces and edges of the octahedral anion. The ligand structure incorporates a protonatable bridgehead nitrogen centre that provides a positive charge to ensure the solubility of a neutral 2:1 $[LH]^+/[PtCl_6]^{2-}$ complex in water-immiscible solvents. The extraction of $[PtCl_6]^{2-}$ from acidic chloride solutions was evaluated by using a pH-swing mechanism to control the loading and stripping of the metallate anion. The ligands L^1–L^3, L^5–L^9, L^{11}–L^{13} and L^{15} showed extremely high loading (up to 95% in some cases) and high selectivity for $[PtCl_6]^{2-}$ over chloride ions (present in a 60-fold excess) compared with trioctylamine, a model Alamine reagent, which, under identical conditions, only extracted 10% of the Pt^{IV} anions. Generally, extraction was observed to be greater for urea-containing ligands than their amido analogues, and a quantitative recovery of platinum from feed solutions was achieved. The formation of neutral $([LH]^+)_2[PtCl_6]^{2-}$ packages in organic media is supported by single-crystal X-ray structure determinations of $[(L^2H)_2PtCl_6]\cdot 2\,CH_3CN$, $[(L^8H)_2PtCl_6\text{-}(MeOH)_2]$, $[(L^{12}H)_2PtCl_6]\cdot 2\,CH_3CN$ and $[(L^{14}H)_2PtCl_6]$, which confirm the presence of significant hydrogen bonding between the anion and urea or amido moieties of the protonated ligand and the anion. The structure of $[(L^1H)(H_3O)PtCl_6]\cdot C_6H_6\cdot CH_3CN$ shows hydrogen bonding of a H_3O^+ cation to the receptor and confirms that other stoichiometries are also possible, indicating that speciation in solution may be more complex.

Keywords: amides · anions · hydrogen bonds · ionophores · platinum

Introduction

Selectivity in the transport of platinum-group metal ions by solvent extraction in industrial processes critically depends upon control of the metal coordination chemistry through the formation of either inner-sphere complexes with dialkyl sulfides or hydroximes,[1] or outer-sphere organic-soluble salts with hydrophobic trialkylamine and related reagents of the Alamine type.[1,2] The outer-sphere salts rely upon control of the 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]

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

Although the solvent extraction of base metals such as copper and zinc usually involves the formation of inner-

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sphere and coordination complexes,[3] the very slow ligand exchange for the hexachloroplatinate anion, $[PtCl_6]^{2-}$,[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 in 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-bonded solvate molecules, such as methanol, address the triangular faces of the hexachloro octahedron,[7] whereas formation of trifurcated hydrogen bonds to the faces, or bifurcated hydrogen bonding to the 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]

Our target in this work was to design useful solvent extractants for the recovery of the platinum(IV) anion from acidic chloride streams, whereby loading and stripping of the organic phase are controlled by a "pH-swing" mechanism [Eqs. (2) and (3)].

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

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

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 extractions of $[PtCl_6]^{2-}$ over Cl^-, which is present in substantial excess in industrial feed streams, is essential for an efficient process. 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) at high acid concentrations.[10]

We report herein a new approach to the selective complexation and extraction of hexachlorometallates in the presence of chloride ions by using tripodal ionophores incorporating multiple hydrogen-bond donors linked to a protonatable bridgehead nitrogen centre.[11] Such a design not only addresses the 3-fold 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.

Results and Discussion

Synthesis and characterisation of ligands L^1–L^{15}: A range of extractants derived from tris(2-aminoethyl)amine (tren) were prepared and characterised (Scheme 1). These C_3-symmetric ionophores incorporate a variety of hydrogen-bond-donor moieties including urea, amide and sulfonamide. It is essential that the ligands and their $[PtCl_6]^{2-}$ complexes are soluble in water-immiscible organic solvents, so a variety of solubilising R groups were therefore included in the ligand structure to aid solubility. 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 the faces of the $[PtCl_6]^{2-}$ octahedron (Figure 2). The ligands L^2–L^{15} were synthesised to access potential tri- and bifurcating hydrogen-bonding modes to the $[PtCl_6]^{2-}$ ion (Figure 2).

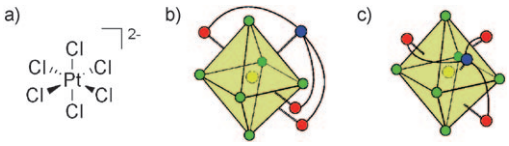
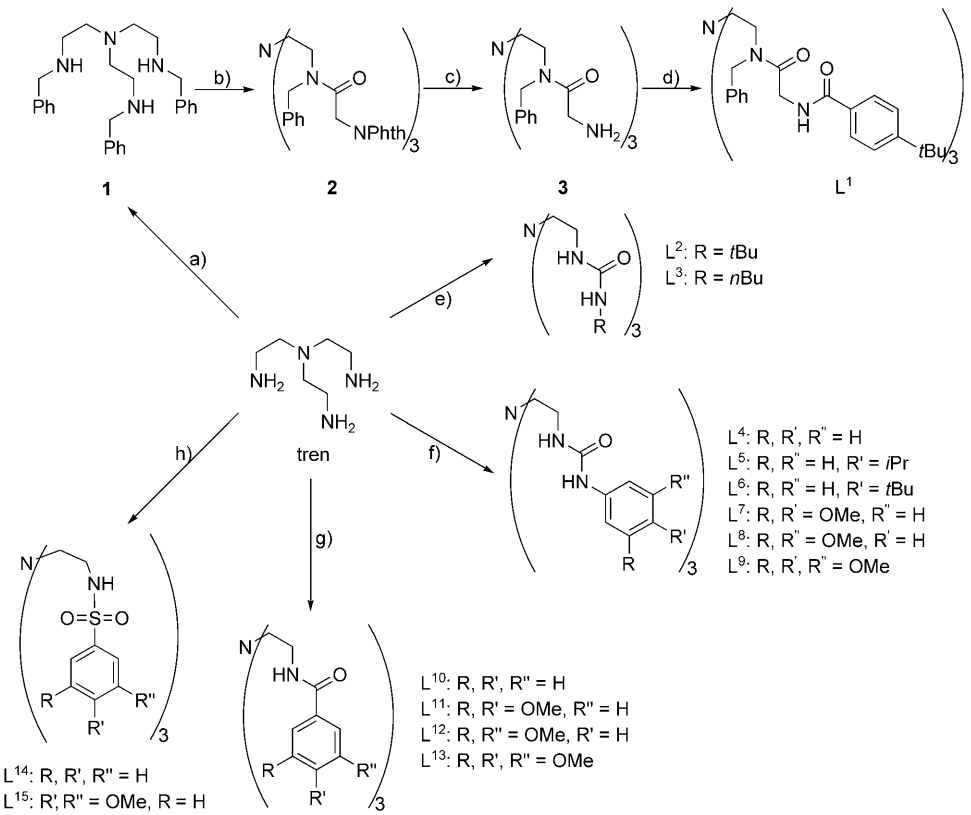


Figure 1. The structure of $[PtCl_6]^{2-}$ (a) and proposed modes of binding to tripodal, multiple hydrogen-bond ionophores through interactions with the edges (b) or the faces (c) of the hexachloro octahedron. The protonated amine of the receptor is shown as a blue sphere and the neutral hydrogen-bond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

Receptor L^1 was synthesised in four steps from commercially available tren. A Schiff base condensation of the amine tren with three equivalents of benzylaldehyde, followed by borohydride reductions of the imines to amines gave the Schiff base adduct **1**, which was subsequently reacted with 2-phthalimidoacetyl chloride.[12,13] Treatment of this product with hydrazine yielded the free amine **3**. Treatment of **3** with *tert*-butylbenzoyl chloride gave receptor L^1 as a white powder (Scheme 1). The urea-based receptors L^2–L^9 were readily obtained as white powders by the treatment of tren with the appropriate isocyanate in dry THF (Scheme 1).[14,15] Amido and sulfonamido receptors L^{10}–L^{15} were synthesised by treating tren with the appropriate benzoyl or sulfonyl chloride in the presence of sodium hydroxide to yield white powders (Scheme 1).[16,17] Purification by column chromatography was required for some receptors. Single crystals suitable for X-ray crystallographic analysis were obtained for receptors L^4, L^5, L^6, L^{12}, L^{13} and L^{14}. The molecular structures of L^4, L^{12} and L^{14} are shown in Figure 3. Crystallographic data for all structures and views of the structures of L^5, L^6 and L^{13} appear in the Supporting Information.

Single-crystal X-ray structures of L^4, L^{12} and L^{14}: Single crystals of the receptor L^4 were obtained as colourless laths by vapour diffusion of diethyl ether into a solution of the receptor in methanol. The receptor crystallises in the monoclinic space group $P2_1/c$ with four molecules in the unit cell (Table S1 in the Supporting Information). The molecular structure shows an intramolecular, bifurcated hydrogen-bond between the urea moieties on adjacent arms N2–H2A···O2 (H···A = 2.12 Å) and N3–H3A···O2 (H···A = 2.06 Å) (Figure 3a). The extended structure reveals that there are bifurcated intermolecular hydrogen bonds be-



Scheme 1. Synthesis of receptors L^1–L^{15}: 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) *tert*-butyl or *n*-butyl isocyanate, THF, RT;[14] f) phenyl, 4-*i*Pr-phenyl, 4-*t*Bu-phenyl, 3,4-dimethoxyphenyl, 3,5-dimethoxyphenyl or 3,4,5-trimethoxyphenyl isocyanate, THF, RT;[15] g) benzoyl, 3,4-dimethoxybenzoyl, 3,5-dimethoxybenzoyl, 3,4,5-trimethoxybenzoyl chloride, NaOH, H_2O, CH_2Cl_2 or Et_2O, RT;[16,17] h) phenyl or 3,4-dimethoxyphenyl sulfonyl chloride, Et_2O, H_2O, NaOH, RT.[16] (PhthCl = 2-phthalimidoacetyl chloride).

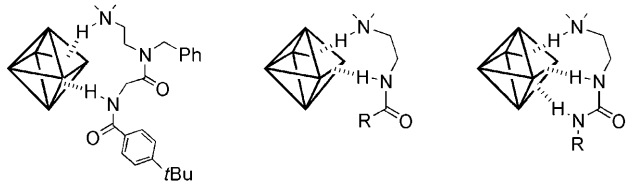


Figure 2. Possible binding modes of the arms of tren-based urea and amide receptors that preserve pseudo-threefold symmetry (only one arm is shown for clarity).

tween the urea moieties on adjacent molecules of the receptor between N4–H4A···O3 and N5–H5A···O3, and also between N6–H6A···O1 and N7–H7A···O1, which leads to a chain of molecules linked by hydrogen bonds. Details of all hydrogen bonds in L^4 are given in Table 1.

Single crystals of L^{12} were obtained by slow evaporation of a concentrated solution of the receptor in methanol. The receptor crystallises in the triclinic space group $P\bar{1}$ with two receptors in the unit cell (Table S1 in the Supporting Information). The structure contains intramolecular hydrogen bonds between amide moieties on adjacent arms of the tripod N2–H2A···O7 (H···O = 2.04 Å) (Figure 3b). The extended structure shows intermolecular N3–H3A···O1 hydrogen bonds (H···O = 2.25 Å) giving rise to a chain-like structure. Hydrogen-bonding details for L^{12} are given in Table 2.

Single crystals of L^{14} were grown by diffusion of *n*-hexane into a concentrated solution of the receptor in methanol. The receptor crystallised in the orthorhombic space group *Pbca* with eight molecules in the unit cell (Table S1 in the Supporting Information). The molecular structure (Figure 3c) shows intramolecular N4–H4A···O2 hydrogen bonding (H···O = 2.28 Å), which encourages the three arms to be orientated in a tripodal, rather than a splayed, geometry, with regular spacing between each arm. Disorder in the phenyl group C19–C24 was modelled over two half-occupied sites for each atom, distance restraints were applied and the structure was refined with isotropic displacement parameters for the disordered region. The extended structure showed intermolecular N2–H2A···O3 (H···A = 2.60 Å) hydrogen bonds between the sulfonamide moieties on adjacent molecules of L^{14}, and these interactions lead to a chain of alternating molecules linked by hydrogen bonds. Hydrogen-bond details are given in Table 3.

These structural data confirm that the breaking of intra- and intermolecular hydrogen bonds in these metal-free receptors is required for complexation and binding to metal anion(s).

Synthesis of complexes of $[PtCl_6]^{2-}$: The outer-sphere complexes of $[PtCl_6]^{2-}$ with L^1–L^{15} were prepared by the treatment of two equivalents of the appropriate receptor in methanol or acetonitrile with one equivalent of hexachloroplatinic acid, $[H_2PtCl_6]$, in acetonitrile. When necessary, dissolution of the receptor was aided by heating. The acid $[H_2PtCl_6]$ served not only as a source of the $[PtCl_6]^{2-}$ anion, but also to protonate the tertiary nitrogen of the tren-based receptors to yield the charge-neutral ion-pair $[(LH)_2PtCl_6]$. Alternatively, an aqueous hydrochloric acid solution of K_2PtCl_6 was used as the source of metalloanion. Elemental analysis, mass spectrometry and ^1H NMR spectroscopy of the $[PtCl_6]^{2-}$ complexes established the general formation of 2:1 ligand-to-anion complexes. The ^1H NMR spectra of all complexes showed characteristic downfield shifts of the NH

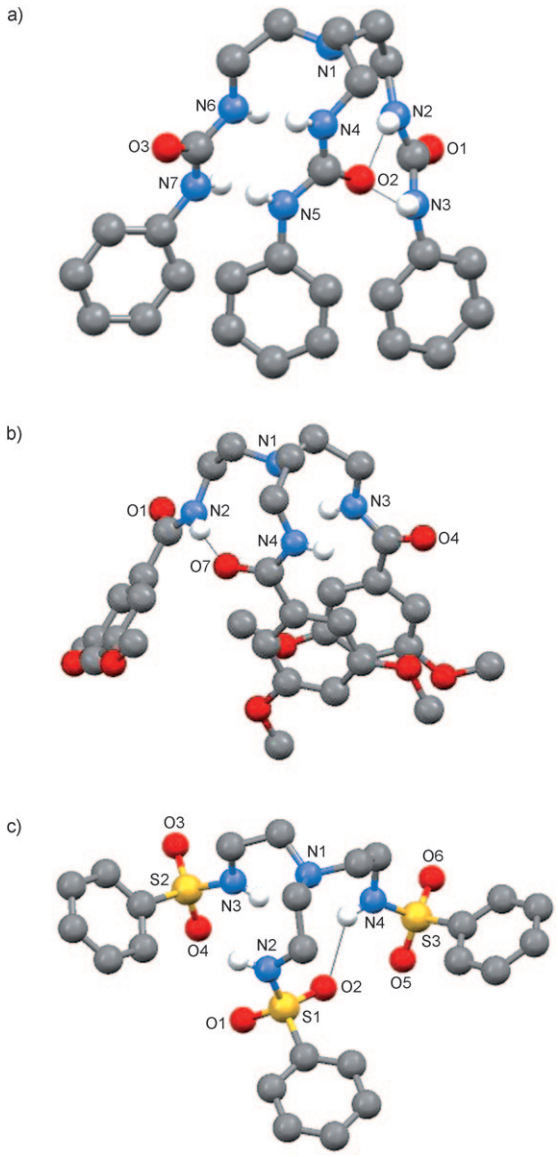


Figure 3. View of the molecular structures of a) L^4, b) L^{12} and c) L^{14} showing intramolecular hydrogen bonding. All hydrogen atoms (except NH) have been omitted for clarity.

Table 1. Intra- and intermolecular hydrogen bonds for L^4.

D–H···A	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠(DHA) [°]
N2–H2A···O2	0.88	2.12	2.901	147
N3–H3A···O2	0.88	2.06	2.837	147
N4–H4A···O3[a]	0.88	1.97	2.808	159
N5–H5A···O3[a]	0.88	2.22	2.999	147
N6–H6A···O1[b]	0.88	2.16	2.924	145
N7–H7A···O1[b]	0.88	2.02	2.846	156

[a] Symmetry transformation used to generate equivalent atoms: $-x+1$, $-y+1$, $-z+2$. [b] $-x$, $-y+1$, $-z+1$.

protons, indicative of the presence of hydrogen-bonding interactions (Figure 4). Also observed was the development of a broad peak further downfield, which was assigned to protonation of the tertiary amine position. Single crystals suitable for X-ray crystallographic analysis were obtained for $[(L^1H)(H_3O)PtCl_6]\cdot C_6H_6\cdot CH_3CN$, $[(L^2H)_2PtCl_6]\cdot 2\,CH_3CN$, $[(L^8H)_2PtCl_6(MeOH)_2]$, $[(L^{12}H)_2PtCl_6]\cdot 2\,CH_3CN$ and $[(L^{14}H)_2PtCl_6]$.

Table 2. Intra- and intermolecular hydrogen bonds for L^{12}.

D–H···A	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠(DHA) [°]
N2–H2A···O7	0.88	2.04	2.910	170
N3–H3A···O1[a]	0.88	2.25	2.913	132

[a] Symmetry transformation used to generate equivalent atoms: $-x$, $-y+1$, $-z+1$.

Table 3. Intra- and intermolecular hydrogen bonds for L^{14}.

D–H···A	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠(DHA) [°]
N4–H4A···O2	0.88	2.28	2.988	138
N2–H2A···O3[a]	0.88	2.60	3.081	116

[a] Symmetry transformation used to generate equivalent atoms: $-x+1/2$, $y-1/2$, z.

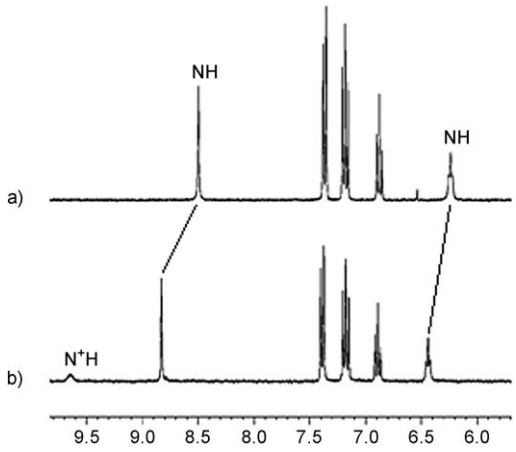


Figure 4. ^{1}H NMR spectra ([D$_6$]DMSO, 300 MHz) of a) L^4 and b) $[(L^4H)_2PtCl_6]$.

X-ray crystal structures of $[(L^1H)(H_3O)PtCl_6]\cdot C_6H_6\cdot CH_3CN$, $[(L^2H)_2PtCl_6]\cdot 2\,CH_3CN$, $[(L^8H)_2PtCl_6(MeOH)_2]$, $[(L^{12}H)_2PtCl_6]$ and $[(L^{14}H)_2PtCl_6]$

$[(L^1H)PtCl_6(H_3O)]\cdot C_6H_6\cdot CH_3CN$: Colourless plates were grown by diffusion of benzene into a solution of the complex in acetonitrile. $[(L^1H)PtCl_6(H_3O)]\cdot C_6H_6\cdot CH_3CN$ crystallises in the triclinic space group $P\bar{1}$ with one $[(L^1H)(H_3O)PtCl_6]$ molecule and a molecule each of benzene and acetonitrile in the asymmetric unit. The receptor is protonated at the bridgehead nitrogen N1 to give $(L^1H)^+$. In addition, a hydroxonium cation is also present in the structure and combined with the receptor cation to form a charge-neutral complex with the $[PtCl_6]^{2-}$ anion (Figure 5a). Two of the three receptor arms participate in hydrogen bonding with the anion: N3 forms a bifurcated bond with Cl4 and Cl5 (N3–H3C···Cl4, H···Cl = 2.75 Å; N–H3C···Cl5, H···Cl = 2.72 Å) and N5 forms a single hydrogen bond to Cl5 (N5–

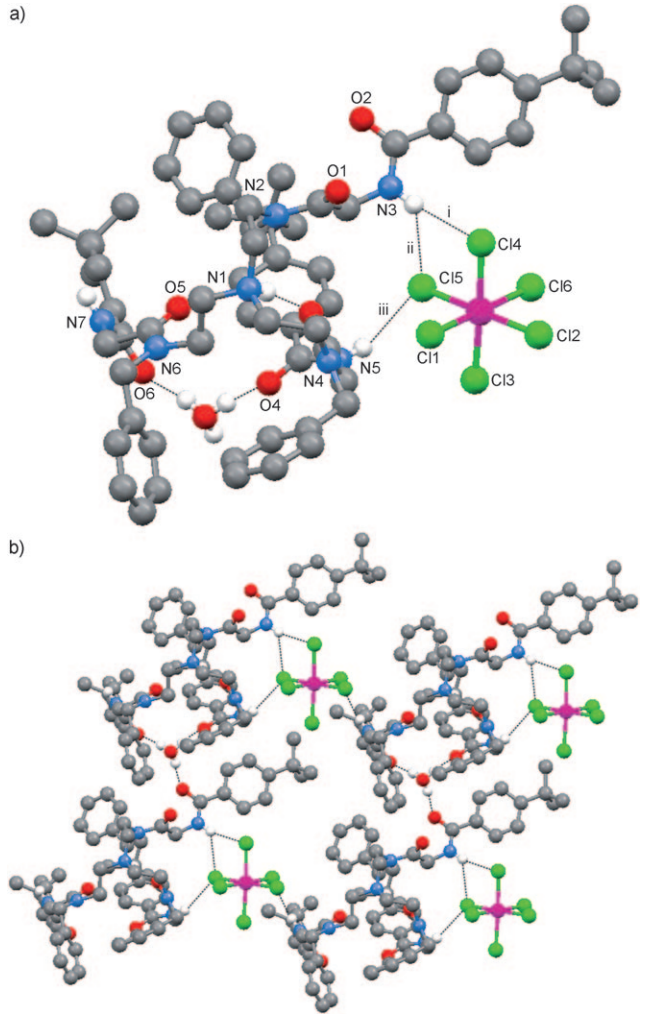


Figure 5. a) Molecular and b) extended structure of $[(L^1H)(H_3O)PtCl_6]\cdot C_6H_6\cdot CH_3CN$ showing hydrogen bonding between the receptors and $[PtCl_6]^{2-}$ anion. All hydrogen atoms (except NH) have been omitted for clarity, as have the solvent molecules. Hydrogen-bond lengths: i) NH···Cl 2.75, ii) NH···Cl 2.72 and iii) NH···O 2.53 Å.

H5C···Cl5, H···Cl = 2.53 Å). There is also an intramolecular hydrogen bond (N1−H1C···O3) and significant hydrogen bonding between the receptor and hydroxonium cation. The extended structure reveals that an arm of each tripodal ligand forms a single hydrogen bond to a different $[PtCl_6]^{2-}$ unit N7−H7C···Cl6 (H···Cl = 2.61 Å) to form a hydrogen-bonded polymeric lattice (Figure 5b, Table 4).

$[(L^2H)_2PtCl_6]\cdot 2CH_3CN$: Yellow tablets were grown by slow evaporation of a solution of the complex in acetonitrile. The complex crystallises in the triclinic space group $P\bar{1}$ with one $[(L^2H)_2PtCl_6]$ molecule and two molecules of acetonitrile in the unit cell. The $[PtCl_6]^{2-}$ anion lies on a centre of inversion and the two receptor cations are related by the inversion centre. Both urea receptors are protonated at the tertiary bridgehead position (N1) to give an $(L^2H)^+$ cation resulting in the complex having a net charge of zero. There is significant hydrogen bonding between the anion and the urea moieties of the receptor (Figure 6a). A bifurcated hydrogen bond is observed between N2−H2A···Cl1 (H···Cl = 2.80 Å) and N2−H2A···Cl3 (H···Cl = 2.80 Å) with further hydrogen-bond interactions between N3−H3A···Cl3 (H···Cl = 2.66 Å) and N4−H4A···Cl2 (H···Cl = 2.79 Å). The extended structure shows a hydrogen-bond chain arrangement of the type ···{$(L^2H)^+$···$[PtCl_6]^{2-}$···$(L^2H)^+$}···{$(L^2H)^+$···$[PtCl_6]^{2-}$···$(L^2H)^+$}··· with two arms of each $(L^2H)^+$ cation interacting with the anion; the third arm participates in hydrogen bonding with an adjacent molecule of $(L^2H)^+$ to form an extended ribbon-like structure (Figure 6b, Table 5).

Table 4. Hydrogen bonds for $[(L^1H)(H_3O)PtCl_6]\cdot C_6H_6\cdot CH_3CN$.

D−H···A	d(D−H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠(DHA) [°]
N3−H3A···Cl4	0.86	2.75	3.546	156
N3−H3A···Cl5	0.86	2.72	3.274	124
N5−H5A···Cl5	0.80	2.53	3.299	166
N7−H7A···Cl6[a]	0.85	2.61	3.436	165
N1−H1A···O3	0.85	1.87	2.684	159
N1−H1A···N2	0.85	2.55	2.950	110
O1S−H1S···O6	0.83	1.71	2.526	172
O1S−H2S···O2[b]	0.84	1.74	2.568	170
O1S−H3S···O4	0.82	1.65	2.460	167

[a] Symmetry transformation used to generate equivalent atoms: x, $y-1$, z. [b] $x-1$, y, z.

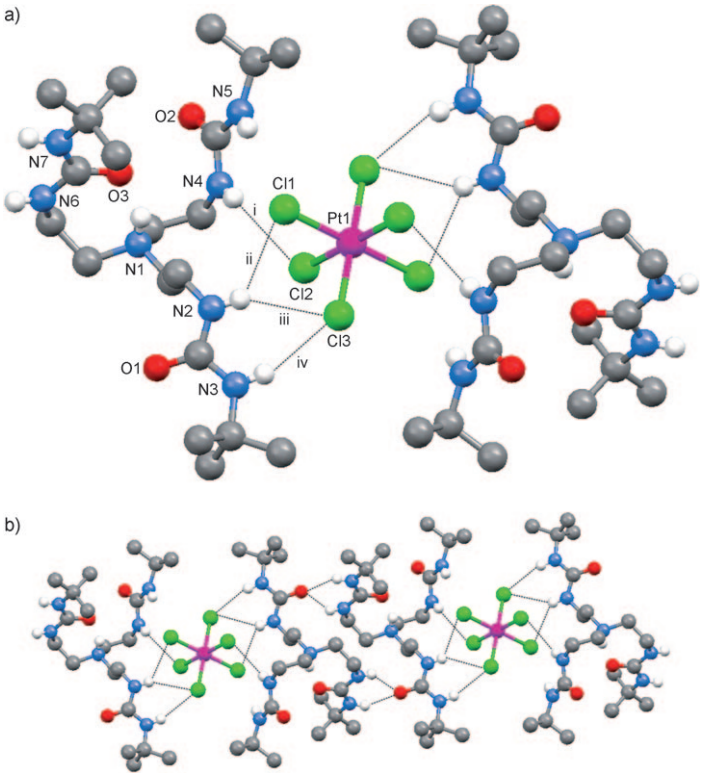


Figure 6. a) Molecular and b) extended structure of $[(L^2H)_2PtCl_6]\cdot 2\,CH_3CN$ showing hydrogen bonding between the receptors and the $[PtCl_6]^{2-}$ anion. All hydrogen atoms (except NH) have been omitted for clarity, as have the solvent molecules. NH···Cl hydrogen-bond lengths: i) 2.79, ii) 2.80, iii) 2.80 and iv) 2.66 Å.

Table 5. Hydrogen bonds for $[(L^2H)_2PtCl_6]$.

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	∠(DHA) [°]
N2–H2A···Cl1	0.86	2.80	3.4390	132
N2–H2A···Cl3	0.86	2.80	3.5778	150
N3–H3A···Cl3	0.86	2.66	3.4951	163
N4–H4A···Cl2	0.86	2.79	3.3629	125
N6–H6A···O1[a]	0.86	2.10	2.832	143
N7–H7A···O1[a]	0.86	2.18	2.951	149

[a] Symmetry transformation used to generate equivalent atoms: $-x+1$, $-y+1$, $-z$.

$[(L^8H)_2PtCl_6(MeOH)_2]$: The complex crystallises as pale-yellow tablets from a concentrated solution in methanol and 2 M hydrochloric acid. The space group is triclinic $P\bar{1}$ with one $[(L^8H)_2PtCl_6]$ molecule and two molecules of methanol in the unit cell. The structure determination reveals one $[PtCl_6]^{2-}$ anion lying on a centre of inversion and two receptor cations related by that centre (Figure 7a). Both urea receptors are protonated at the bridgehead nitrogen (N1) to give an overall charge-neutral complex. One of the three urea arms of each receptor is involved in hydrogen bonding with the $[PtCl_6]^{2-}$ anion, and hydrogen bonding is observed between N6–H6A···Cl2 (H···Cl = 2.57 Å) as well as through the methanol molecules (N7–H7A···O1S, O1S–H1S···Cl1 and O1S–H1S···Cl2). The remaining two urea arms participate in intra- and intermolecular hydrogen bonding with other cations, which results in an extensive hydrogen-bonding network (Figure 7b, Table 6).

Table 6. Hydrogen bonds for $[(L^8H)_2PtCl_6(MeOH)_2]$.

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	∠(DHA) [°]
N1–H1C···O1	0.93	1.90	2.762	153
N4–H4A···O7	0.88	2.00	2.849	161
N6–H6A···Cl2	0.88	2.57	3.3742	152
N7–H7A···O1S	0.88	2.05	2.874	156
O1S–H4S···Cl2	0.84	2.53	3.2178	140
O1S–H4S···Cl1	0.84	2.93	3.6062	139
N2–H2A···O4[a]	0.88	2.15	2.965	153
N3–H3A···O4[a]	0.88	2.28	3.086	153

$[(L^{12}H)_2PtCl_6]\cdot 2\,CH_3CN$: The complex crystallises as pale-yellow columns from a concentrated solution in acetonitrile in the triclinic space group $P\bar{1}$ with one $[(L^{12}H)_2PtCl_6]$ molecule and two molecules of acetonitrile in the unit cell. The structure determination reveals one $[PtCl_6]^{2-}$ anion lying on a centre of inversion and two receptor cations related by the inversion centre (Figure 8a). Both amide receptors are protonated at the bridgehead nitrogen (N1) to give an overall charge-neutral complex. One of the three amide NH donors of $(L^{12}H)^+$ forms hydrogen bonds to $[PtCl_6]^{2-}$ to form a bifurcated interaction: N2–H2A···Cl1 (H···Cl = 2.95 Å) and N2–H2A···Cl2 (H···Cl = 2.83 Å). The remaining two amide groups form hydrogen bonds to another $(L^{12}H)^+$ cation to give a chain arrangement ···{$(L^{12}H)^+$···$[PtCl_6]^{2-}$···$(L^{12}H)^+$}···{$(L^{12}H)^+$···$[PtCl_6]^{2-}$···$(L^{12}H)^+$}··· (Figure 8b). In addition to the NH···Cl hydrogen bonds, there is an intraligand hydrogen bond N3–H3A···O1 (H···O = 2.13 Å) and an interligand hydrogen bond N4–H4A···O4 (H···O = 2.15 Å) (Table 7). The structure also contains two molecules of acetonitrile, which are disordered over two sites with 0.65:0.35 occupancy. The atoms were refined with isotropic displacement parameters.

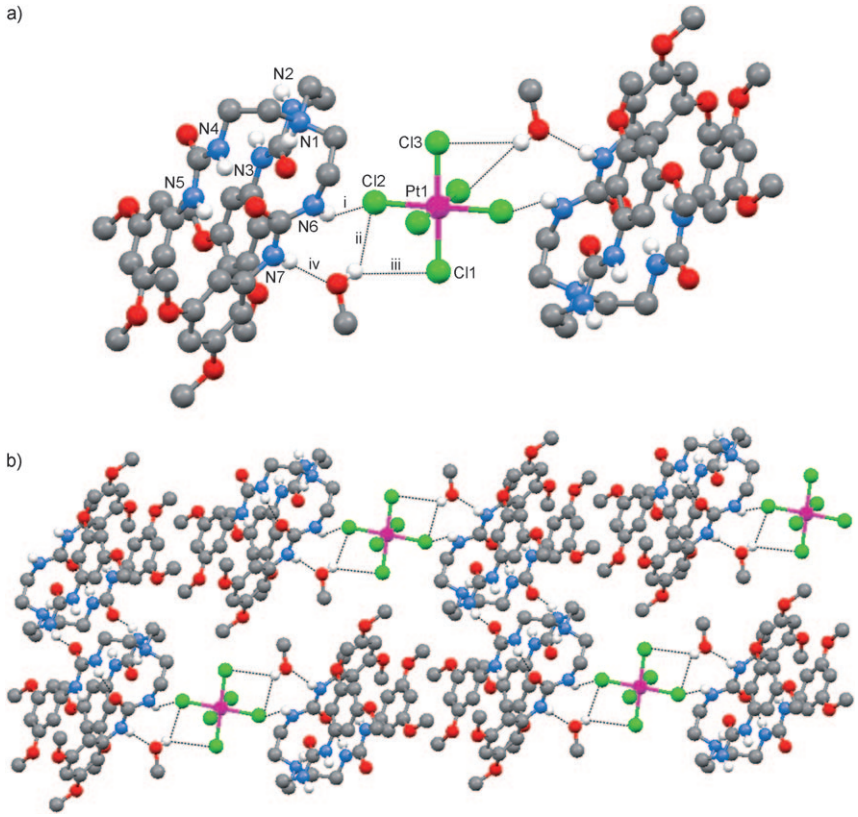


Figure 7. a) Molecular and b) extended structure of $[(L^8H)_2PtCl_6(MeOH)_2]$ showing hydrogen bonding between the receptors and the $[PtCl_6]^{2-}$ anion. All hydrogen atoms (except NH) have been omitted for clarity. Hydrogen-bond lengths: i) NH···Cl 2.57, ii) OH···Cl 2.53, iii) OH···Cl 2.93 and iv) NH···O 2.05 Å.

$[(L^{14}H)_2PtCl_6]$: The complex crystallises as pale-yellow laths in the monoclinic space group

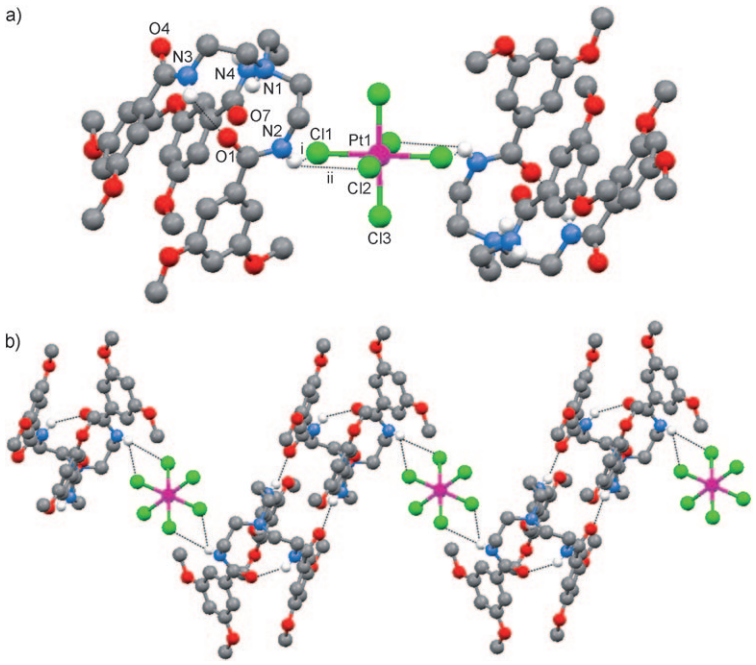


Figure 8. a) Molecular and b) extended structure of $[(L^{12}H)_2PtCl_6]\cdot 2\,CH_3CN$ showing hydrogen bonding between the receptors and the $[PtCl_6]^{2-}$ anion. All hydrogen atoms (except NH) have been omitted for clarity, as have the solvent molecules. NH···Cl hydrogen-bond lengths: i) 2.95 and ii) 2.83 Å.

Table 7. Hydrogen bonds for $[(L^{12}H)_2PtCl_6]\cdot 2\,CH_3CN$.

D–H···A	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠(DHA) [°]
N2–H2A···Cl2	0.86	2.83	3.438	129
N2–H2A···Cl1	0.86	2.95	3.618	136
N3–H3A···O1	0.86	2.13	2.868	144
N4–H4A···O4[a]	0.86	2.15	2.950	155

[a] Symmetry transformation used to generate equivalent atoms: $-x+1$, $-y$, $-z+1$.

$P2_1/c$. The structure determination shows one $[PtCl_6]^{2-}$ anion lying on a centre of inversion with both sulfonamide receptors protonated at their bridgehead nitrogen atom (N1) to give an overall charge-neutral complex (Figure 9a). Disorder involving the atoms C3–C8 in one of the terminal phenyl rings was modelled by allowing two half-occupied sites for each atom. Distance restraints were applied and the disordered atoms were refined with isotopic atomic displacement parameters for the disordered region.

Each $(L^{14}H)^+$ cation is involved in three hydrogen bonds to two separate $[PtCl_6]^{2-}$ anions with a bifurcated interaction to one $[PtCl_6]^{2-}$ anion and a single hydrogen bond to another $[PtCl_6]^{2-}$ anion. Figure 9a shows the bifurcated hydrogen-bonding interactions N4–H4B···Cl2 (H···Cl = 2.89 Å) and N4–H4B···Cl3 (H···Cl = 2.61 Å) between two $(L^{14}H)^+$ receptors and a central $[PtCl_6]^{2-}$ anion. The extended structure (Figure 9b) reveals that, in addition to the bifurcated interaction, one arm of each tripod interacts with a different $[PtCl_6]^{2-}$ unit, N2–H2C···Cl3 (H···Cl = 2.79 Å). Additionally, the extended structure shows N–H···O, N–H···N and N–H···S hydrogen bonds (Table 8).

In summary, the crystallographic studies confirm the formation of charge-neutral anion-receptor complexes through extensive intra- and intermolecular hydrogen bonding.

Potentiometry: To determine the number of protonation sites in the receptors and the pH at which they become protonated, potentiometry experiments were performed (see the Experimental Section).[18] Protonation equilibria were determined for the urea receptor L^7 and the amide receptors L^{11} and L^{13} (Table 9). Only one protonation site was observed for each receptor represented by the equilibrium $L+H^+ \rightleftharpoons LH^+$ and the pK_a values obtained were consistent with protonation of the tertiary amine bridgehead nitrogen po-

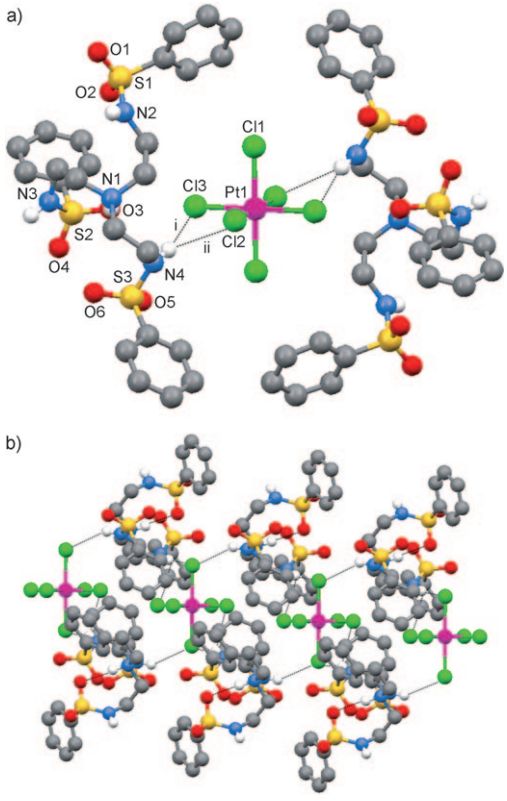


Figure 9. a) Molecular and b) extended structure of $[(L^{14}H)_2PtCl_6]$ showing hydrogen bonding between the receptors and the $[PtCl_6]^{2-}$ anion. All hydrogen atoms (except NH) have been omitted for clarity. NH···Cl hydrogen-bond lengths: i) 2.61 and ii) 2.89 Å.

Table 8. Hydrogen bonds for $[(L^{14}H)_2PtCl_6]$.

D–H···A	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠(DHA) [°]
N4–H4B···Cl3	0.88	2.61	3.460	163
N1–H1C···O3	0.93	2.08	2.957	156
N1–H1C···N3	0.93	2.53	2.991	111
N1–H1C···S2	0.93	2.79	3.584	144
N2–H2C···Cl3[a]	0.88	2.79	3.570	148
N4–H4B···Cl2[b]	0.88	2.89	3.422	121
N3–H3A···O5[c]	0.88	2.49	3.190	137
N3–H3A···O4[c]	0.88	2.60	3.214	128
N3–H3A···S3[c]	0.88	2.99	3.627	131

[a] Symmetry transformation used to generate equivalent atoms: x, $y+1$, z. [b] $-x$, $-y$, $-z$. [c] $-x$, $y+1/2$, $-z+1/2$.

Table 9. Protonation constants determined in MeCN/H_2O (50:50 v/v) (0.1 M NMe_4Cl, (298.1 ± 0.1) K).

Receptor	Equilibrium	pK_a
L^7	$L+H^+ \rightleftharpoons LH^+$	6.43(7)
L^{11}	$L+H^+ \rightleftharpoons LH^+$	5.94(2)
L^{13}	$L+H^+ \rightleftharpoons LH^+$	5.93(5)

sition.[19] The pK_a values between the urea and amido ligands differ by 0.5, indicating that the type of hydrogen-bond-donor group has relatively little effect on the basicity of the bridgehead nitrogen. The receptors L^{11} and L^{13} both have amide hydrogen-bond groups, but contain a different number of methoxy substituents. The pK_a values for these two receptors are very similar (5.94 and 5.93, respectively), indicating that the number of methoxy substituents on the terminal phenyl ring does not affect the basicity of the bridgehead nitrogen.

Solvent extraction: The solvent extractants described in this work will ideally recover platinum(IV) from acidic chloride streams, whereby loading and stripping of the organic phase are controlled by a pH-swing mechanism [Eqs. (2) and (3)]. The flowchart (Figure 10) and Equations (4)–(7) represent

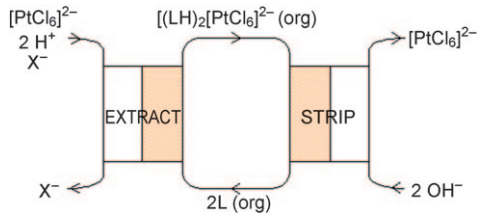


Figure 10. pH-swing-controlled transport of $[PtCl_6]^{2-}$.

the processes involved in purifying $[PtCl_6]^{2-}$. The first step is leaching in which the platinum-containing ore is dissolved in aqua regia to produce $[H_2PtCl_6]$ in an acidic, aqueous solution.[22] Separation of $[PtCl_6]^{2-}$ is achieved by mixing an organic phase containing two equivalents of a receptor (L) with an aqueous, acidic solution of $[H_2PtCl_6]$. Under acidic conditions the bridgehead nitrogen is protonated. Interaction of two tripodal ligands with the anion will lead to the formation of a neutral outer-sphere complex by means of which the chlorometallate can be transported into the organic phase in a liquid–liquid extraction process. Quantitative back extraction of $[PtCl_6]^{2-}$ from the organic layer into an aqueous solution is achieved by contacting the loaded chloroform layer with an aqueous solution that contains a two-fold excess of NaOH over ligand. Finally, an electro-refining technique such as electrowinning can be employed to recover pure metallic platinum from $[PtCl_6]^{2-}$.[21,22]

$$\text{LEACH} \quad Pt + 6HCl + 4HNO_3 \rightleftharpoons H_2PtCl_6 + 4NO_2 + 4H_2O \tag{4}$$

$$\text{EXTRACT} \quad H_2PtCl_6 + 2L \rightleftharpoons [(LH)_2PtCl_6] \tag{5}$$

$$\text{STRIP} \quad [(LH)_2PtCl_6] + 2OH^- \rightleftharpoons L + [PtCl_6]^{2-} + H_2O \tag{6}$$

$$\text{ELECTROWIN} \quad [PtCl_6]^{2-} + 4e^- \rightleftharpoons Pt + 6Cl^- \tag{7}$$

To determine the extractive ability of the series of the multiple hydrogen-bond-donor ligands L^1–L^{15} in the presence of a large excess of chloride ions, various studies of the solvent extraction of $[PtCl_6]^{2-}$ from aqueous, acidic media with the extractants were performed. The extractive behaviour of these ligands was compared with that of trioctylamine (TOA), a compound that is acknowledged to be an efficient extractant for octahedral $[MCl_6]^{2-}$ precious-metal anions.[23]

Method development: A series of experiments to assess chloride selectivity, and the effect of pH, mixing time, concentration and back extraction were conducted to determine the optimum extraction conditions.

Chloride selectivity: The presence of HCl in the processing of platinum-containing ores is necessary for the production of $[PtCl_6]^{2-}$. However, chloride ions may compete for the hydrogen-bonding sites on the receptor. The selective extraction of $[PtCl_6]^{2-}$ over Cl^-, which is present in substantial excess in industrial feed streams, is thus essential for an efficient extraction process. To assess whether our receptors would extract Cl^-, extractions that used L^8 were performed in either 0.1 or 0.6 M HCl. For both HCl concentrations studied, the results showed that the amount of Cl^- extracted increased with increasing receptor concentration. Furthermore, at higher HCl concentrations, more chloride was extracted; thus, in the presence of 0.1 M HCl the maximum amount of Cl^- extracted was 88% compared with 100% Cl^- extraction from 0.6 M HCl (Figure 11). These results confirm that under certain conditions the receptor L^8, and potentially other tripodal receptors discussed in this work, can extract Cl^- to form organic-soluble complexes.

Effect of pH: To accurately represent the conditions used in the processing of platinum-containing ores, it is necessary to perform the extractions in an acidic media. The above preliminary extraction experiments confirm that the tren-based

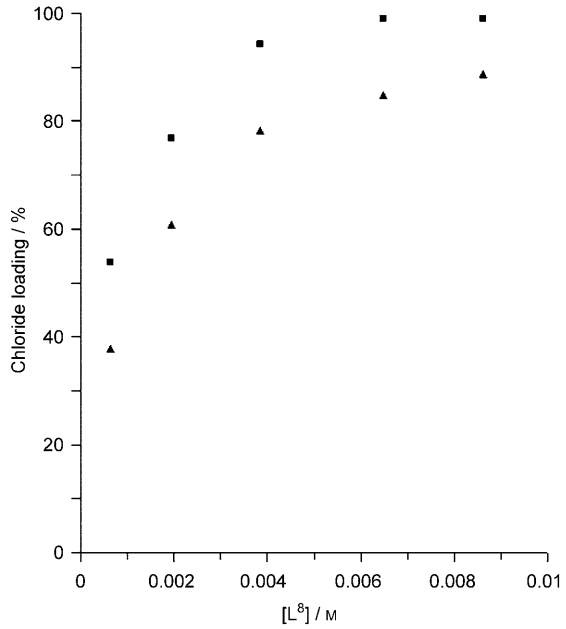


Figure 11. Plot of percentage of chloride extracted from 0.1 (▲) or 0.6 M (■) HCl into $CHCl_3$ by L^8.

receptors can potentially extract chloride ions. The effect of feed pH on the extraction of $[PtCl_6]^{2-}$ with L^8 in chloroform was studied. The percentage of platinum extracted into chloroform in the presence of a three molar excess of L^8 or TOA is given in Table 10. Interestingly and significantly,

Table 10. Percentage of platinum extracted as $[PtCl_6]^{2<M->}$ into $CHCl_3$ from aqueous HCl in the presence of a threefold molar excess of L^8 or TOA.

	HCl concentration [M]		
	0.0	0.1	0.6
% Pt extracted with L^8	63	100	98
% Pt extracted with TOA	62	57	4

TOA is not an effective extractant of platinum at high concentrations of HCl. Although uptake of $[PtCl_6]^{2-}$ by a three-fold excess of TOA from an aqueous solution of $[H_2PtCl_6]$ with no added HCl is around 60% of the theoretical value, it drops to only about 5% when the aqueous feed solution contains 0.6 M HCl, suggesting a 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 when using TOA, and chloride concentrations will build up downstream. However, in 0.6 M HCl, a three-fold excess of L^8 can extract >98% of the platinum. Most importantly, these reactions confirm the selectivity of our receptor for $[PtCl_6]^{2-}$ over Cl^- under acidic conditions. Therefore, all subsequent extractions were carried out in 0.6 M HCl.

Mixing time studies: Previous studies of the equilibrium time for $[PtCl_6]^{2-}$ extraction by long-chain alkylamines have shown that mixing periods ranging from several minutes (e.g., between 1–5 mins for Alamine 304 and *N-n*-octylaniline)[24,25] to several hours (e.g., overnight for trioctylamine)[23] may be necessary to achieve equilibrium. To determine the optimum mixing time, a chloroform phase containing L^8 and an acidic, aqueous phase containing $[H_2PtCl_6]$ were contacted at room temperature for varying periods of time. The platinum content of the organic phase was measured at regular intervals and after 4 h the maximum level of extraction was achieved, suggesting that equilibrium to the outer-sphere complex $[(L^8H)_2PtCl_6]$ had been established. Prolonged mixing (>16 h) led to a slight drop in the content of platinum in the chloroform layer; this observation was attributed to an inner-sphere substitution processes to form insoluble complexes.

Concentration studies: A series of extraction experiments were performed with the receptor L^8 and platinum stock solutions of varying concentrations (1.25, 2.5 and 6.5 mM). No significant variations in the extraction results were observed. It was concluded that concentration does not play a major role in the extraction process.

Back-extraction studies: Back extractions were performed to establish the use of a pH-swing mechanism to control the uptake and release of the $[PtCl_6]^{2-}$ anion and also to determine the amount of platinum present in the organic phase in a mass balance equation. Yoshizawa and co-workers have reported solvent extraction experiments with TOA and $[PtCl_6]^{2-}$ in toluene.[23] They investigated the stripping of $[PtCl_6]^{2-}$ from an organic phase containing $[(TOA+H)_2PtCl_6]$ by using an aqueous solution of NaOH, which proceeded by deprotonation of the tertiary amine in $(TOA+H)^+$; this removed the electrostatic attraction between the receptor and the anion. An alternative approach in which HCl was used was also investigated in this work.

Experiments were performed to assess if $[PtCl_6]^{2-}$ recovery from the organic phase containing $[(LH)_2PtCl_6]$ was possible by addition of NaOH and to identify the volume required for such a process. In the presence of two equivalents of OH^-, quantitative back extraction of $[PtCl_6]^{2-}$ was achieved and a mixing time of 30 min was found to be sufficient.

Platinum extraction: The extraction potential of the receptors L^1–L^{15} for $[PtCl_6]^{2-}$ was determined for each receptor under optimised conditions. Ligands L^4, L^{10} and L^{14} afforded metal complex salts that precipitate from solution or do not extract into the organic phase. A key requirement for the success of this solvent extraction process is the solubility of the resultant $[PtCl_6]^{2-}$ complex in the organic phase, therefore, these complexes were not studied further. Results for the extraction of $[PtCl_6]^{2-}$ by the receptors L^1–L^3, L^5–L^9, L^{11}–L^{13} and L^{15} are summarised in Figure 12 along with data for TOA for comparison.

In the presence of 0.6 M HCl, all of the tren-based urea and amide receptors that were studied show increased ex-

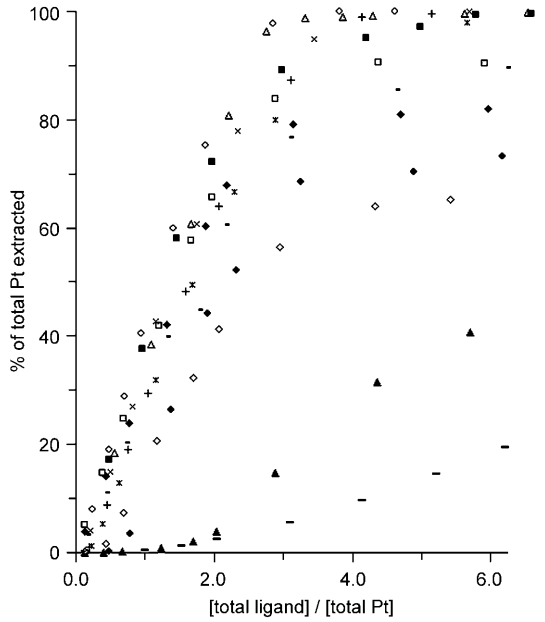


Figure 12. Plot of percentage of the total platinum extracted as $[PtCl_6]^{2-}$ from aqueous 0.6 M HCl into $CHCl_3$ as a function of the [L]/[Pt] ratio. ■: L^1, ▲: L^2, ●: L^3, ◆: L^5, □: L^6, △: L^7, ○: L^8, ◇: L^9, +: L^{11}, ×: L^{12}, ∗: L^{13}, −: L^{15} and ——: TOA.

traction compared with TOA, confirming that the presence of hydrogen-bond-donor groups leads to a more effective extraction of $[PtCl_6]^{2-}$ (Figure 12 and Table 11). The maximum extraction occurs at $[L]/[PtCl_6]^{2-}$ ratios greater than or equal to three, indicating that a slight excess of receptor is required; this may suggest that there is competition from Cl^- anions. Loadings of greater than 90%, however, imply that the triamide/urea ligands show high selectivity for $[PtCl_6]^{2-}$ over Cl^- ions 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 11).

Table 11. Percentage of platinum extracted as $[PtCl_6]^{2<M->}$ into $CHCl_3$ from aqueous 0.6 M HCl in the presence of three-fold molar excess of L.

Ligand	Pt extracted [%]	Ligand	Pt extracted [%]
L^1	89	L^9	56
L^2	15	L^{11}	85
L^3	67	L^{12}	89
L^5	76	L^{13}	80
L^6	84	L^{15}	76
L^7	98	TOA	5
L^8	98		

Yoshizawa plot: A procedure similar to that described by Yoshizawa and co-workers[23] was used 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, in which it can be assumed that the ligand is fully protonated, the extraction of $[PtCl_6]^{2-}$ is a competitive process given by Equation (8), in which $K_{[PtCl_6]^{2-}}$ is given by Equation (9):

$$PtCl_6^{2-} + 2[(LH)Cl]_{(org)} \overset{K_{[PtCl_6]^{2-}}}{\rightleftharpoons} [(LH)_2PtCl_6]_{(org)} + 2Cl^- \quad (8)$$

$$K_{[PtCl_6]^{2-}} = \frac{[(LH)_2PtCl_6][Cl^-]^2}{[PtCl_6^{2-}][(LH)Cl]^2} \quad (9)$$

Assuming that no inner-sphere substitution occurs on the timescale of the extraction, the distribution coefficient for platinum is given by Equation (10), in which D_{Pt} is defined by Equation (11):

$$D_{Pt} = \frac{[(LH)_2PtCl_6]}{[PtCl_6^{2-}]} \quad (10)$$

$$\log D_{Pt} = \log K[PtCl_6^{2-}] + 2\log\left\{\frac{[(LH)Cl]}{[Cl^-]}\right\} \quad (11)$$

Plots of $\log D_{Pt}$ versus $\log\{[(LH)Cl]/[Cl^-]\}$ for TOA and six of the receptors show slopes close to two (Figure 13), in accordance with the anticipated formation of 2:1 $[LH]^+/[PtCl_6]^{2-}$ assemblies in chloroform. For the other ligands used in this work, and for TOA at high ligand concentrations,[23] the Yoshizawa plots show some deviation from linearity (see the Supporting Information). This 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 to give a 1:1:1 assembly $[LH]^+/[H_3O]^+/[PtCl_6]^{2-}$, which would be favoured at low ligand concentrations (see the discussion of the crystal structure of $[(L^1H)(H_3O)PtCl_6]$ above). Alternatively, the possibility that the receptors, their hydrochloride salts

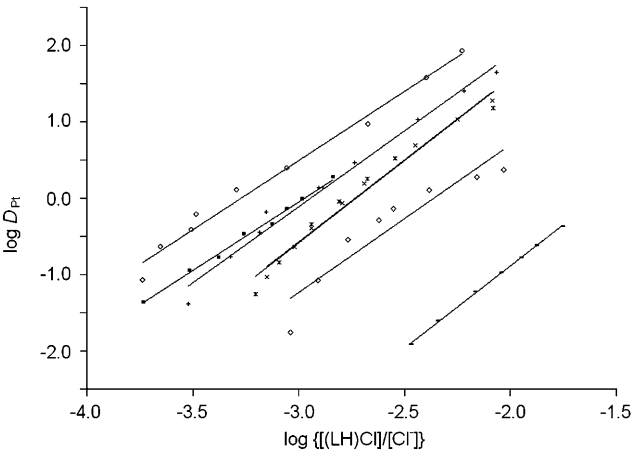


Figure 13. Plot of $\log D_{Pt}$ versus $\log\{[(LH)Cl]/[Cl^-]\}$ for the extraction of $[PtCl_6]^{2-}$ with a range of tripodal hydrogen-bonding receptors. ■: L^1 ($y = 1.7988x + 5.3463$, $R^2 = 0.9947$), ○: L^8 ($y = 1.8106x + 5.9276$, $R^2 = 0.9854$), ◇: L^9 ($y = 1.9342x + 4.5674$, $R^2 = 0.8776$), +: L^{11} ($y = 1.9886x + 5.8554$, $R^2 = 0.985$), ×: L^{12} ($y = 2.1462x + 5.8588$, $R^2 = 0.9596$); ∗: L^{13} ($y = 2.1508x + 5.8797$, $R^2 = 0.9885$), −: TOA ($y = 2.1473x + 3.4067$, $R^2 = 0.9992$).

and/or their platinum complexes have some solubility in the aqueous phase cannot be discounted at this stage. These caveats notwithstanding, the majority of the triamide/urea ligands show very high selectivity for $[PtCl_6]^{2-}$ over Cl^-, the latter being present in a 60-fold excess.

Recycling of the receptor: Recycling experiments were conducted on receptor L^8. A ^1H NMR spectrum of L^8, recorded after one extraction cycle indicated that the structure of the receptor was preserved during the extraction process. The recycled ligand was put through a series of subsequent extraction phases with minimal loss in observed efficiency.

Deviations: Although many of the ligands described extract in a similar manner, there are certain deviations from theory that must be accounted for and which emphasise the complexity of these systems. One deviation already discussed is the variation away from a gradient of two in the Yoshizawa plots (Figure 13). One of these ligands, L^9, also shows a reduced ability to select $[PtCl_6]^{2-}$ over chloride, presumably because the formation of the outer-sphere complex $[(L^9H)_2(PtCl_6)]$ is disfavoured. This is unexpected because there are only minor structural differences between L^9 and the related urea-based ligands, L^4–L^8, highlighting the delicate interactions inherent to the systems. Other sources of deviations from theory include the interesting binding modes displayed in the crystal structures of complexes L^1 and L^8. The former clearly displays the inclusion of a H_3O^+ moiety, giving a 1:1:1 assembly of $[LH]^+/[H_3O]^+/[PtCl_6]^{2-}$, which may account for deviations in the Yoshizawa plot at high values of $\log\{[(LH)Cl]/[Cl^-]\}$. The crystal structure of $[(L^8H)PtCl_6(MeOH)_2]$ (Figure 7) shows methanol molecules hydrogen bonded to and interacting with both the metal anion and protonated receptor. These examples illustrate the flexibility of these systems in the way they bind and indicate that the speciation of the outer-sphere complexes in solution may not be as simple as originally proposed.

Conclusion

The efficacy of our tripodal urea and amide 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 (>95%) from acidic chloride solutions for the new receptors, coupled with the quantitative stripping and release of metallate anions by base, provides the basis for a very efficient process for the separation and concentration of platinum with minimal reagent consumption (two equivalents of NaOH) and generation of two molar equivalents of NaCl as a byproduct. Significantly, our receptors show selectivity for $[PtCl_6]^{2-}$ over Cl^-. Receptors containing urea moieties extracted slightly more $[PtCl_6]^{2-}$ than analogous amide receptors. Solution and solid-state studies support the formation of $([LH]^+)_2[PtCl_6]^{2-}$ packages in organic media. Future and current work is focused on the variation in the disposition and nature of hydrogen-bonding groups in the pendant arms of the reagents to allow the selectivity of receptors to be tuned to accomplish the separation of chlorometallates with second coordination spheres with different geometries.

Experimental Section

Methods and materials: All solvents and reagents were commercially available from Aldrich or Fisher. ^1H and ^{13}C NMR spectra were obtained on Bruker ARX 250, DPX 360 or DPX 300 spectrometers. The chemical shifts (δ) are reported in parts per million (ppm) relative to the residual protio solvent signal in $CDCl_3$ ($\delta=7.26$ (^1H) and 77.0 ppm (^{13}C)), $[D_6]$DMSO ($\delta=2.50$ (^1H) and 39.5 ppm (^{13}C)), CD_3OD ($\delta=3.31$ (^1H) and 49.0 ppm (^{13}C)) or $[D_2]C_2H_2Cl_4$ ($\delta=5.91$ (^1H) and 74.2 ppm (^{13}C)). Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS50TC instrument in a 3-nitrobenzyl alcohol (NOBA) matrix. Electrospray (ES) mass spectra were recorded on a VG Autospec instrument. ICP-OES was carried out by using a Perkin–Elmer Optima 5300DV spectrometer and ICP-MS was carried out by using a Thermo-Fisher Scientific X-Series^{II} spectrometer. For pH measurements, an AR50 (Fisher Scientific) pH meter was used.

X-ray crystallography: Crystallographic data and structure refinement parameters for ligands L^4, L^5, L^6, L^{12}, L^{13} and L^{14}, and complexes $[(L^1H)PtCl_6(H_3O)]\cdot C_6H_6\cdot CH_3CN$, $[(L^2H)_2PtCl_6]\cdot 2\,CH_3CN$, $[(L^8H)_2PtCl_6(MeOH)_2]$, $[(L^{12}H)_2PtCl_6]\cdot 2\,CH_3CN$ and $[(L^{14}H)_2PtCl_6]$ are summarised in the Supporting Information. Crystals were mounted on a dual-stage glass fibre and diffraction measurements were collected at 150(2) K on a Bruker APEX CCD diffractomer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) and ω scans. Structures were solved by direct methods by using the SHELXS-97 programme.[26] CCDC-707579 (L^4), 707580 (L^5), 707581 (L^6), 707582 (L^{12}), 707583 (L^{13}), 707584 (L^{14}), 707585 ($[(L^1H)(H_3O)PtCl_6]\cdot C_6H_6\cdot CH_3CN$), 653924 ($[(L^2H)_2PtCl_6]$), 707586 ($[(L^8H)_2PtCl_6(MeOH)_2]$), 707587 ($[(L^{12}H)_2PtCl_6]\cdot 2\,CH_3CN$) and 707588 ($[(L^{14}H)_2PtCl_6]$) contain 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.

Potentiometry experiments: All pH-metric measurements ($pH=-\log[H^+]$) employed for the determination of the protonation constants were carried out in solutions of NMe_4Cl (0.10 M) in MeCN/H_2O (50:50 v/v) at (298.1 ± 0.1) K under a nitrogen atmosphere. A Hamilton glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free aqueous solutions of NaOH and determining the equivalence point by Gran's method,[27] which allows one to determine the standard potential E° and the ionic product of H_2O ($pK_w=14.99(1)$). At least three measurements were performed for each system in the pH range 2.5–11.0. In all experiments, the ligand concentration was approximately 1×10^{-4} M. The computer program HYPERQUAD[28] was used to calculate the equilibrium constants from electromotive force (emf) data.

General experimental procedure for extractions: Analytical grade $CHCl_3$ was used to prepare the ligand solutions without further purification. Water used to prepare the solutions of $[H_2PtCl_6]$ was purified by using a commercial filtration system and reported to a resistance of approximately 18 Ω. The acid $[H_2PtCl_6]\cdot 6H_2O$, which was purchased from Aldrich, was dried over P_2O_5 to obtain a yellow solid. Calibration curves for ICP-OES and ICP-MS were prepared by dilution of commercially available standards.

Solutions of the ligand were prepared at varying concentrations between 0.0005 and 0.01 M by weighing aliquots of ligand stock solution (0.01 M in $CHCl_3$) into 5 cm^3 volumetric flasks and diluting to the mark with $CHCl_3$. Solutions of $[H_2PtCl_6]$ were prepared by weighing $[H_2PtCl_6]\cdot 6H_2O$ (0.03 g) into a 50 cm^3 volumetric flask and diluting to the mark with water, 0.1 M HCl or 0.6 M HCl.

Extractions were prepared by charging 100 cm^3 Schott flasks, fitted with a magnetic stir bar, with solutions of the ligand (5 cm^3) and $[H_2PtCl_6]$

(5 cm^3). The extractions were stirred at 25 °C for 4 h, after which time the phases were separated. Aqueous samples for ICP-OES analysis were prepared by weighing the aqueous phase (2 cm^3) into 5 cm^3 volumetric flasks and diluting to the mark with water; samples for ICP-MS analysis were diluted by a thousand fold using 0.6 M HCl as the diluent. The organic phases (4.0 cm^3) were transferred into glass snap-top vials fitted with magnetic stir bars by using a volumetric glass pipette. An aliquot of aqueous NaOH (0.06 M) was added to these vials so that there were two molar equivalents of OH^- relative to the amount of ligand in the sample, as well as sufficient water to make the final aqueous volume 4 cm^3. The two phases were contacted for 30 min then separated. Samples for ICP-OES analysis were prepared by weighing the aqueous phase (2 cm^3) into 5 cm^3 volumetric flasks and diluting to the mark with water. To determine the concentration of Pt in the stock solution by ICP-OES or ICP-MS analyses, samples were prepared by weighing in the same manner as the above aqueous extraction samples.

Compound L^1: A solution of *tert*-butylbenzoyl chloride (2.70 g, 13.8 mmol) in $CHCl_3$ (100 cm^3) was added to a solution of **3** (2.45 g, 4.17 mmol) in $CHCl_3$ (200 cm^3) containing Et_3N (2.04 cm^3, 14.6 mmol) at 0 °C over a period of 2 h. The reaction mixture was allowed to warm to room temperature and was then stirred for 16 h. The solvent was removed in vacuo and the residue was purified by column chromatography by eluting with 2–5 % MeOH/CH_2Cl_2 to give the product L^1 as a colourless glass (4.4 g, 99 %). The ^{1}H NMR spectrum of this material was extremely complex, showing severe splitting and broadening of the signals because of the large number and slow rotation of the amide rotamers. This was clarified by acquiring the ^{1}H NMR spectrum at 80 °C in [D$_6$]DMSO, resulting in broad but separate signals for each set of non-equivalent protons with the correct integration of signals. High-resolution FAB mass spectrometry of this material was also consistent with the proposed structure. ^{1}H NMR (360 MHz, [D$_6$]DMSO, 80 °C): δ = 8.17 (br s, 3H; N*H*), 7.79 (d, 6H, ^3J(H,H) = 11.2 Hz; H_{Ar} *ortho* to the amide), 7.45 (d, ^3J(H,H) = 11.2 Hz, 6H; H_{Ar} *ortho* to the *t*Bu group), 7.27 (br s, 15H; H_{Ar}), 4.58 (br s, 6H; ArCH_2), 4.20 (br s, 6H; NCOCH_2), 3.35 (br s, 6H; NCH$_2$CH_2NCO), 2.63 (br s, 6H; NCH_2CH$_2$NCO), 1.31 ppm (s, 27H; CH_3); ^{13}C NMR (90 MHz, [D$_6$]DMSO, 110 °C): δ = 168.3, 165.8, 153.6, 137.0, 131.2, 127.8, 126.6, 126.4, 124.2, 51.7 (br), 49.2 (br), 44.9, 40.6, 33.9, 30.3 ppm; IR (solid): $\tilde{\nu}$ = 2956 (C=C), 1633 cm^{-1}(C=O); HRMS (FAB): *m*/*z* calcd for $C_{66}H_{81}N_7O_6$: 1068.63211; found: 1068.63445; elemental analysis calcd (%) for $C_{66}H_{81}N_7O_6$: C 74.20, H 7.64, N 9.18; found: C 73.60, H 6.97, N 8.87.

General procedure A: Urea synthesis: Tren (0.20 cm^3, 1.35 mmol) was dissolved in dry THF (30 cm^3) under N_2. A solution of the appropriate isocyanate (4.20 mmol) dissolved in THF (30 cm^3) was added dropwise with stirring at room temperature. The reaction was stirred at room temperature for 2 h. If a white precipitate formed, it was collected by filtration and dried in vacuo. Alternatively, the solvent was removed and the product was purified by column chromatography.

General procedure B: Amide and sulfonamide synthesis: Tren (0.40 cm^3, 2.70 mmol) was dissolved in water (20 cm^3) containing NaOH (0.33 g, 8.25 mmol). A solution of the appropriate benzoyl chloride (7.66 mmol) dissolved in diethyl ether (10 cm^3) was added slowly and the reaction was stirred at room temperature for 2 days. The off-white solid that formed was collected by filtration, washed with a portion of Et_2O (10 cm^3) and dried in vacuo.

Compound L^2:[14] Compound L^2 was prepared by the treatment of tren with *tert*-butyl isocyanate by following procedure A. Yield 98 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.79 (br, 3H; N*H*), 5.00–4.80 (m, 3H; N*H*), 3.13 (br, 6H; CH_2), 2.46 (br, 6H; CH_2), 1.33 ppm (s, 27H; CH_3); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 160.6, 56.4, 50.7, 29.7 ppm; IR (KBr): $\tilde{\nu}$ = 3350 (N–H), 1650 cm^{-1} (C=O); MS (ES$^+$): *m*/*z*: 444 [*M*+H]$^+$, 467 [*M*+Na]$^+$; elemental analysis calcd (%) for $C_{21}H_{45}N_7O_3$: C 56.86, H 10.22, N 22.10; found: C 56.50, H 10.24, N 20.58.

Compound L^3: Compound L^3 was prepared by the treatment of tren with butyl isocyanate by following procedure A. Yield: 96 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00 (br t, 3H; N*H*), 5.54 (br t, 3H; N*H*), 3.17–3.10 (m, 6H; CH_2), 2.53 (br, 6H; CH_2), 1.98 (br, 6H; CH_2), 1.53–1.30 (m, 12H; CH_2), 0.92 ppm (t, ^3J(H,H) = 7.2 Hz, 3H; CH_3); ^{13}C NMR (68 MHz, $CDCl_3$): δ = 160.8, 55.7, 40.4, 39.9, 32.7, 21.4, 13.8 ppm; IR (KBr): $\tilde{\nu}$ = 3354 (N–H), 1652 cm^{-1} (C=O); MS (ES$^+$): *m*/*z*: 444 [*M*+H]$^+$; elemental analysis calcd (%) for $C_{21}H_{45}N_7O_3$: C 56.86, H 10.22, N 22.10; found: C 56.77, H 10.22, N 21.96.

Compound L^4:[15] Compound L^4 was prepared by the treatment of tren with phenyl isocyanate by following procedure A. Yield: 95 %; ^{1}H NMR (270 MHz, CD_3OD): δ = 7.26 (d, ^3J(H,H) = 7.6 Hz, 6H; H_{Ar}), 7.21–7.16 (m, 6H; H_{Ar}), 6.95 (t, ^3J(H,H) = 8.1 Hz, 3H; H_{Ar}), 3.54–3.48 (m, 6H; CH_2), 2.68 ppm (t, ^3J(H,H) = 5.4 Hz, 6H; CH_2); ^{13}C NMR (68 MHz, [D$_6$]DMSO): δ = 156.3, 141.4, 128.9, 121.6, 118.1, 55.5, 37.4 ppm; IR (KBr): $\tilde{\nu}$ = 3334 (NH), 1650 cm^{-1} (C=O); MS (ES$^+$): *m*/*z*: 504 [*M*+H]$^+$, 526 [*M*+Na]$^+$; elemental analysis calcd (%) for $C_{27}H_{33}N_7O_3$: C 64.40, H 6.60, N 19.47; found: C 64.29, H 6.78, N 19.11.

Compound L^5: Compound L^5 was prepared by the treatment of tren with 4-*iso*-propylphenyl isocyanate by following procedure A. Yield: 69 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (s, 3H; N*H*), 6.97 (s, 12H; H_{Ar}), 6.10 (t, ^3J(H,H) = 4.9 Hz, 3H; N*H*), 3.13 (br, 6H; CH_2), 2.80 (septet, ^3J-(H,H) = 6.9 Hz, 3H; *i*PrC*H*), 2.23 (br, 6H; CH_2), 1.19 ppm (d, ^3J(H,H) = 6.9 Hz, 18H; *i*PrCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.9, 141.5, 138.6, 123.8, 118.5, 54.5, 48.6, 44.8, 24.5 ppm; IR (solid): $\tilde{\nu}$ = 3100 (N–H), 1640 (C=O), 1601 cm^{-1} (C=C); MS (ES$^+$): *m*/*z*: 630.41 [*M*+H]$^+$; elemental analysis calcd (%) for $C_{36}H_{51}N_7O_3$: C 68.65, H 8.16, N 15.57; found: C 68.05, H 8.11, N 15.43.

Compound L^6: Compound L^6 was prepared by the treatment of tren with 4-*tert*-butylphenyl isocyanate by following procedure A. Yield: 59 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (br, 3H; N*H*), 7.14 (d, ^3J(H,H) = 8.6 Hz; 6H; H_{Ar}), 7.03 (d, ^3J(H,H) = 7.7 Hz, 6H; H_{Ar}), 6.18 (br, 3H; N*H*), 3.16 (br, 6H; CH_2), 2.27 (br, 6H; CH_2), 1.25 ppm (s, 27H; CH_3); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 156.3, 144.9, 138.3, 125.9, 117.2, 54.3, 48.4, 34.2, 31.9 ppm; IR (solid): $\tilde{\nu}$ = 2997 (N–H), 1640 (C=O), 1590 cm^{-1} (C=C, Ar); MS (ES$^+$): *m*/*z*: 672.46 [*M*+H]$^+$; elemental analysis calcd (%) for $C_{39}H_{57}N_7O_3$: C 69.71, H 8.55, N 14.59; found: C 69.23, H 8.47, N 14.35.

Compound L^7: Compound L^7 was prepared by the treatment of tren with 3,4-dimethoxyphenyl isocyanate by following procedure A. The product was purified by column chromatography on silica gel by using 5 % MeOH and 95 % CH_2Cl_2. Yield: 86 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (s, 3H; N*H*), 6.91 (s, 3H; H_{Ar}), 6.57 (d, ^3J(H,H) = 8.6 Hz, 3H; H_{Ar}), 6.49 (d, ^3J(H,H) = 9.0 Hz, 3H; H_{Ar}), 6.14 (br t, 3H; NH), 3.76 (s, 9H; OCH_3), 3.68 (s, 9H; OCH_3), 3.08 (br, 6H; CH_2), 2.35 ppm (br, 6H; CH_2); ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 156.3, 149.9, 144.4, 135.2, 112.9, 110.2, 104.7, 56.1, 55.4, 54.5, 37.2 ppm; IR (solid): $\tilde{\nu}$ = 3299 (N–H), 2935 (C–H), 2834 (C–H), 1627 (C=O), 1205 cm^{-1} (C–O); MS (ES$^+$): *m*/*z*: 684.33 [*M*+H]$^+$; elemental analysis calcd (%) for $C_{33}H_{45}N_7O_9$: C 57.97, H 6.63, N 14.34; found: C 58.07, H 6.69, N 14.36.

Compound L^8: Compound L^8 was prepared by the treatment of tren with 3,5-dimethoxyphenyl isocyanate by following procedure A. The product was purified by column chromatography on silica gel by using 10 % MeOH and 90 % CH_2Cl_2. Yield: 81 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39 (s, 3H; N*H*), 6.44 (s, 6H; H_{Ar}), 6.10 (br t, 3H; N*H*), 6.06 (s, 3H; H_{Ar}), 3.64 (s, 18H; OCH_3), 3.22 (br, 6H; CH_2), 2.38 ppm (br, 6H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.0, 156.3, 142.9, 96.0, 93.5, 56.5, 55.4, 48.4 ppm; IR (solid): $\tilde{\nu}$ = 3333 (N–H), 2942 (C–H), 2836 (C–H), 1647 (C=O), 1148 cm^{-1} (C–O); MS (ES$^+$): *m*/*z*: 684.34 [*M*+H]$^+$; elemental analysis calcd (%) for $C_{33}H_{45}N_7O_9$: C 57.97, H 6.63, N 14.34; found: C 57.74, H 6.61, N 14.10.

Compound L^9: Compound L^9 was prepared by the treatment of tren with 3,4,5-trimethoxyphenyl isocyanate by following procedure A. The product was purified by column chromatography on silica gel by using 7 % MeOH and 93 % $CHCl_3$. Yield: 74 %; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.50 (s, 3H; N*H*), 6.72 (s, 6H; H_{Ar}), 6.12 (t, ^3J(H,H) = 6.4 Hz, 3H; N*H*), 3.68 (s, 18H; OCH_3), 3.57 (s, 9H; OCH_3), 3.18–3.16 (m, 6H; CH_2), 2.57 ppm (t, ^3J(H,H) = 5.3 Hz, 6H; CH_2); ^{13}C NMR (75 MHz, [D$_6$]DMSO): 156.2, 154.3, 138.2, 132.8, 96.0, 60.8, 56.1, 54.5, 37.4 ppm; IR (solid): $\tilde{\nu}$ = 3336 (N–H), 1650 (C=O), 1603 (C=C, Ar), 1122 cm^{-1} (C–O); MS (ES$^+$): *m*/*z*: 774 [*M*+H]$^+$.

Compound L^{10}:[16] Compound L^{10} was prepared by the treatment of tren with benzoyl chloride by following procedure B. Yield: 74 %; ^{1}H NMR

(300 MHz, $CDCl_3$): $\delta = 7.60$ (d, $^3J(H,H) = 6.0$ Hz, 3H; H_{Ar}), 7.33 (t, $^3J(H,H) = 9.0$ Hz; 6H; H_{Ar}), 7.18 (br, 3H; N*H*), 7.07 (t, $^3J(H,H) = 9.0$ Hz, 6H; H_{Ar}), 3.60–3.55 (m, 6H; CH_2), 2.76 ppm (t, $^3J(H,H) = 6.0$ Hz; 6H; CH_2); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 167.5$, 134.2, 131.5, 128.8, 127.5, 53.7, 37.7 ppm; IR (solid): $\bar{\nu} = 3345$ (NH), 3286 (NH), 1536 cm^{-1} (C=O); MS (ES^+): *m/z*: 459 $[M+H]^+$; elemental analysis calcd (%) for $C_{27}H_{30}N_4O_3$: C 70.72, H 6.59, N 12.22; found: C 70.86, H 6.61, N 12.24.

Compound L^{11}:[17] Compound L^{11} was prepared by the treatment of tren with 3,4-dimethoxybenzoyl chloride by following procedure B. The product was purified by column chromatography on silica gel by using 7% MeOH and 93% CH_2Cl_2. Yield: 66%; ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.37 (br, 3H; N*H*), 7.28 (s, 3H, H_{Ar}), 7.12 (d, $^3J(H,H) = 8.4$ Hz, 3H; H_{Ar}), 6.31 (d, $^3J(H,H) = 8.4$ Hz, 3H; H_{Ar}), 3.81 (s, 9H; OCH_3), 3.79 (s, 9H; OCH_3), 3.69–3.55 (m, 6H; CH_2), 2.77 ppm (t, $^3J(H,H) = 5.2$ Hz, 6H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.5$, 154.9, 153.2, 147.8, 126.6, 120.8, 110.9, 109.3, 56.1, 53.7, 39.7 ppm; IR (solid): $\bar{\nu} = 3291$ (N–H), 2936 (C–H), 2836 (C–H), 1628 (C=O), 1264 cm^{-1} (C–O); MS (ES^+): *m/z*: 639.30 $[M+H]^+$; elemental analysis calcd (%) for $C_{33}H_{42}N_4O_9$: C 62.06, H 6.63, N 8.77; found: C 61.97, H 6.55, N 8.69.

Compound L^{12}: Compound L^{12} was prepared by the treatment of tren with 3,5-dimethoxybenzoyl chloride by following procedure B. Yield: 74%; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.57$ (t, $^3J(H,H) = 5.4$ Hz, 3H; N*H*), 6.87 (s, 6H; H_{Ar}), 6.38 (s, 3H; H_{Ar}), 3.63 (s, 18H; OCH_3), 3.64–3.55 (m, 6H; CH_2), 2.66 ppm (t, $^3J(H,H) = 5.1$ Hz, 6H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.5$, 161.7, 105.5, 103.8, 55.8, 53.7, 39.7 ppm; IR (solid): $\bar{\nu} = 3304$ (N–H), 2938 (C–H), 2837 (C–H), 1637 (C=O), 1151 cm^{-1} (C–O); MS (ES^+): *m/z*: 639.30 $[M+H]^+$; elemental analysis calcd (%) for $C_{33}H_{42}N_4O_9$: C 62.06, H 6.63, N 8.77; found: C 61.98, H 6.81, N 8.59.

Compound L^{13}: Compound L^{13} was prepared by the treatment of tren with 3,4,5-trimethoxybenzoyl chloride by following procedure B. The product was purified by column chromatography on silica gel by using 5% MeOH and 95% CH_2Cl_2. Yield: 73%; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.77$ (t, $^3J(H,H) = 4.6$ Hz, 3H; N*H*), 7.00 (s, 6H; H_{Ar}), 3.78 (s, 3H; OCH_3), 3.63 (s, 6H; OCH_3), 3.44 ppm (br, 6H; CH_2), 2.61 (br, 6H; CH_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.5$, 153.2, 141.6, 129.0, 105.6, 60.8, 56.1, 55.7, 39.7 ppm; IR (solid): $\bar{\nu} = 3304$ (N–H), 2939 (C–H), 2836 (C–H), 1636 (C=O), 1120 cm^{-1} (C–O); MS (ES^+): *m/z*: 729 $[M+H]^+$; elemental analysis calcd (%) for $C_{36}H_{48}N_4O_{12}$: C 59.33, H 6.64, N 7.69; found: C 59.21, H 6.58, N 7.71.

Compound L^{14}:[16] Compound L^{14} was prepared by the treatment of tren with phenyl sulfonyl chloride by following procedure B. The product was recrystallised from MeOH. Yield: 82%; ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.95–7.90 (m, 6H; H_{Ar}), 7.90–7.51 (m, 9H; H_{Ar}), 6.02 (br, 3H; N*H*), 2.97 (br, 6H; NCH_2), 2.66 ppm (br, 6H; NCH_2); ^{13}C NMR (68 MHz, $CDCl_3$): $\delta = 140.5$, 133.3, 129.0, 54.5, 41.4 ppm; IR (KBr): $\bar{\nu} = 3297$ (NH), 1619 (C=C, Ar), 1350 (SO_2), 1150 cm^{-1} (SO_2); MS (ES^+): *m/z*: 567 $[M+H]^+$, 590 $[M+Na]^+$; elemental analysis calcd (%) for $C_{24}H_{30}N_4O_6S_3$: C 50.87, H 5.34, N 9.89; found: C 50.85, H 5.34, N 9.73.

Compound L^{15}: Compound L^{15} was prepared by the treatment of tren with 3,4-dimethoxyphenyl sulfonyl chloride in THF for 48 h by following procedure B. The product was purified by column chromatography on silica with 5% MeOH and 95% CH_2Cl_2. Yield: 24%; ^1H NMR (270 MHz, $CDCl_3$): $\delta = 7.54$ (dd, $^3J(H,H) = 8.5$, $^4J(H,H) = 2.1$ Hz, 3H; H_{Ar}), 7.42 (d, $^4J(H,H) = 2.1$ Hz, 3H; H_{Ar}), 6.96 (d, $^3J(H,H) = 8.5$ Hz, 3H; H_{Ar}), 6.01 (t, $^3J(H,H) = 6.2$ Hz, 3H; N*H*), 3.93 (s, 18H; OCH_3), 2.93 (brs, 6H; $NHCH_2$), 2.51 (brs, 6H; NCH_2); ^{13}C (68 MHz, $CDCl_3$): $\delta = 152.5$, 149.2, 131.4, 121.0, 110.8, 109.7, 60.4, 54.1, 41.0 ppm; MS (ES^+): *m/z*: 769 $[M+Na]^+$, 747 $[M+H]^+$; IR ($CHCl_3$,): $\bar{\nu} = 3286$ (N–H), 2841 (C–H), 1590 (C=C), 1509 (C=C), 1326 (S=O), 1263 (C–O), 1184 (S=O), 1140 cm^{-1} (C–O); elemental analysis calcd (%) for $C_{30}H_{42}N_4O_{12}S_3$: C 47.91, H 5.67, N 7.50; found: C 47.94, H 5.66, N 7.23.

[(L^1H)$_2$PtCl$_6$]: A solution of L^1 (0.53 g, 0.50 mmol) in MeOH (1 cm^3) was added to a solution of $[H_2PtCl_6]$ (0.013 g, 0.025 mmol) in MeOH (1 cm^3). MeOH (1 cm^3) and concentrated HCl (6 drops) were added. The pale-orange solid that resulted after 3 days was filtered off, washed with cold MeOH and dried under high vacuum (0.047 g,74%). ^1H NMR (360 MHz, $[D_2]C_2H_2Cl_4$): $\delta = 7.82$–7.80 (m, 12H; H_{Ar}), 7.67 (br, 6H; CON*H*), 7.36–7.33 (m, 12H; H_{Ar}), 7.24–7.09 (m, 30H; H_{Ar}), 6.75 (br, 2H; NH^+), 4.35 (br, 12H; CH_2), 3.91 (br, 12H; CH_2), 3.60 (br, 24H; CH_2), 1.18 ppm (br, 54H; CH_3); ^{13}C NMR (90 MHz, $[D_2]C_2H_2Cl_4$, 80 °C): $\delta = 172.5$, 168.0, 155.7, 135.4, 131.1, 129.4, 128.3, 127.5, 127.4, 125.7, 54.4, 51.8, 42.5, 42.0, 35.0, 31.3 ppm; IR (solid): $\bar{\nu} = 3359$ (N–H), 1632 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{132}H_{164}Cl_6N_{14}O_{12}Pt$: C 62.26, H 6.49, N 7.70; found: C 62.86, H 6.41, N 7.74.

[(L^2H)$_2$PtCl$_6$]: A solution of L^2 (0.02 g, 0.04 mmol) in MeCN (2 cm^3) was added to $[H_2PtCl_6]$ (0.01 g, 0.02 mmol) in MeCN (1 cm^3). An orange precipitate immediately formed, which was collected by filtration and dried in vacuo (0.013 g,52%). ^1H NMR (270 MHz, $[D_6]$DMSO): $\delta = 10.05$ (br, 2H; NH^+), 6.05 (br, 6H; N*H*), 4.31 (br, 6H; N*H*), 3.31 (br, 12H; CH_2), 3.20 (br, 12H; CH_2), 1.25 (s, 54H; CH_3); IR (solid): $\bar{\nu} = 3342$ (N–H), 1632 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{42}H_{92}Cl_6N_{14}O_6Pt$: C 38.89, H 7.15, N 15.12; found: C 38.82, H 7.09, N 15.03.

[(L^3H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to $[(L^2H)_2PtCl_6]$ and precipitated as a yellow powder. Yield = 55%; ^1H NMR (270 MHz, $[D_6]$DMSO): $\delta = 10.07$ (br, 2H, NH^+), 6.26 (t, $^3J(H,H) = 5.4$ Hz, 6H; N*H*), 6.18 (t, $^3J(H,H) = 5.0$ Hz, 6H; N*H*), 3.32 (br, 12H; CH_2), 3.23 (br, 12H; CH_2), 1.41–1.20 (m, 36H; CH_2), 0.88 (t, $^3J(H,H) = 7.0$ Hz, 18H; CH_3); IR (solid): $\bar{\nu} = 3364$ (N–H), 1640 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{42}H_{92}Cl_6N_{14}O_6Pt$: C 38.89, H 7.15, N 15.12; found: C 38.94, H 6.94, N 14.97.

[(L^4H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to $[(L^2H)_2PtCl_6]$ and precipitated as a yellow powder. Yield = 51%; ^1H NMR (300 MHz, $[D_6]$DMSO): $\delta = 9.61$ (br, 2H; NH^+), 8.80 (s, 6H; N*H*), 7.40 (d, $^3J(H,H) = 8.7$ Hz, 12H; H_{Ar}), 7.19 (t, $^3J(H,H) = 8.4$ Hz, 12H; H_{Ar}), 6.92 (t, $^3J(H,H) = 7.3$ Hz, 6H; H_{Ar}), 6.45 (t, $^3J(H,H) = 5.6$ Hz, 6H; N*H*), 3.51–3.45 (m, 12H; CH_2), 3.36–3.38 ppm (m, 12H; CH_2); IR (solid): $\bar{\nu} = 3358$ (N–H), 1650 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{54}H_{68}Cl_6N_{14}O_6Pt + 1.4\ H_2O$: C 44.97, H 4.95, N 13.60; found: C 44.97, H 4.71, N 13.56.

[(L^5H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for $[(L^2H)_2PtCl_6]$ and precipitated as a yellow powder. Yield = 58%; ^1H NMR (270 MHz, $[D_6]$DMSO): $\delta = 9.71$ (br, 2H; NH^+), 8.72 (s, 6H; N*H*), 7.30 (d, $^3J(H,H) = 8.4$ Hz, 12H; H_{Ar}), 7.04 (d, $^3J(H,H) = 8.6$ Hz, 12H; H_{Ar}), 6.43 (t, $^3J(H,H) = 5.4$ Hz, 6H; N*H*), 3.52 (br, 12H; CH_2), 2.80–2.72 (m, 6H; *i*Pr*CH*), 1.18 ppm (d, 36H; *i*PrCH_3); IR (solid): $\bar{\nu} =$ 3347 (N–H), 1660 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{72}H_{104}Cl_6N_{14}O_6Pt$: C 51.80, H 6.28, N 11.75; found: C 51.80, H 6.17, N 11.71.

[(L^6H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for $[(L^2H)_2PtCl_6]$ and precipitated as a yellow powder. Yield = 54%; ^1H NMR (270 MHz, $[D_6]$DMSO): $\delta = 9.74$ (br, 2H; NH^+), 8.74 (s, 6H; N*H*), 7.30 (d, $^3J(H,H) = 8.8$ Hz, 12H; H_{Ar}), 7.19 (d, $^3J(H,H) = 8.9$ Hz; 12H; H_{Ar}), 6.44 (t, $^3J(H,H) = 5.4$ Hz, 6H; N*H*), 3.51 (br, 12H; CH_2), 3.46 (br, 12H; CH_2), 1.24 ppm (s, 54H; CH_3); IR (solid): $\bar{\nu} = 3333$ (N–H), 1651 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{78}H_{116}Cl_6N_{14}O_6Pt$: C 53.42, H 6.67, N 11.18; found: C 53.32, H 6.53, N 11.08.

[(L^7H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for $[(L^2H)_2PtCl_6]$, but no precipitate formed so the reaction was repeated in $[D_3]$MeCN to study complexation in solution. ^1H NMR (270 MHz, $[D_3]$MeCN): $\delta = 9.65$ (br, 2H; NH^+), 7.73 (s, 6H; N*H*), 6.93 (s, 6H; H_{Ar}), 6.83 (br, 6H; H_{Ar}), 6.59 (br, 6H; H_{Ar}), 6.19 (br, 6H; N*H*), 3.65 (s, 36H; OCH_3), 3.56 (br, 12H; CH_2), 3.40 ppm (br, 12H; CH_2); ^{195}Pt NMR (500 MHz, $[D_3]$MeCN): $\delta = 247$ ppm.

[(L^8H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for $[(L^2H)_2PtCl_6]$, but no precipitate formed so the reaction was repeated in $[D_3]$MeCN to study complexation in solution. ^1H NMR (270 MHz, $[D_3]$MeCN): $\delta = 9.12$ (br, 2H; NH^+), 6.56 (br, 12H; H_{Ar}), 6.15 (br, 6H; H_{Ar}), 3.67 (br, 36H; OCH_3), 3.55 ppm (br, 6H; CH_2) (CH_2 peak obscured by broad H_2O signal); MS (ES^+): *m/z*: 981 $[(L^{8-}-2H)PtCl_3]^-$, 1089 $[(L^8H)PtCl_6]^-$, 1772 $[L^8(L^8H)PtCl_6]^-$.

[(L^9H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for $[(L^2H)_2PtCl_6]$ and precipitated as a yellow powder. Yield = 57%; ^1H NMR (300 MHz, $[D_6]$DMSO): $\delta = 9.87$ (br, 2H; NH^+), 8.81 (t, $^3J(H,H) = 5.2$ Hz, 6H; N*H*), 7.81 (d, $^3J(H,H) = 7.10$ Hz, 12H; H_{Ar}), 7.54

(t, ^3J(H,H) = 7.3 Hz, 6H; H_{Ar}), 7.47 (t, ^3J(H,H) = 7.1 Hz, 12H; H_{Ar}), 3.72 ppm (d, ^3J(H,H) = 5.5, 12H; CH_2) (CH_2 peak obscured by broad H_2O signal); elemental analysis calcd (%) for $C_{54}H_{62}Cl_6N_8O_6Pt$: C 48.88, H 4.71, N 8.44; found: C 49.15, H 4.63, N 8.37.

[(L[10]H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for [(L^{2}H)$_2$PtCl$_6$] and precipitated as a yellow powder. Yield = 55%; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.87 (br, 2H; N*H*$^+$), 8.81 (t, ^3J(H,H) = 5.2 Hz, 6H; N*H*), 7.81 (d, ^3J(H,H) = 7.10 Hz, 12H; H_{Ar}), 7.54 (t, ^3J(H,H) = 7.3 Hz, 6H; H_{Ar}), 7.47 (t, ^3J(H,H) = 7.1 Hz, 12H; H_{Ar}), 3.72 ppm (d, ^3J(H,H) = 5.5, 12H; CH_2) (CH_2 peak obscured by broad H_2O signal); IR (solid): $\tilde{\nu}$ = 3371 (N–H), 3221 (N–H), 1637 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{54}H_{62}Cl_6N_8O_6Pt$: C 48.88, H 4.71, N 8.44; found: C 49.15, H 4.63, N 8.37.

[(L[11]H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for [(L^{2}H)$_2$PtCl$_6$], but no precipitate formed so the reaction was repeated in [D$_3$]MeCN to study complexation in solution. ^{1}H NMR (300 MHz, [D$_3$]MeCN): δ = 9.83 (br, 2H; N*H*$^+$), 7.87 (br, 6H; N*H*), 7.31 (d, ^3J(H,H) = 6.6 Hz, 6H; H_{Ar}), 7.18 (s, 6H; H_{Ar}), 6.73 (d, ^3J(H,H) = 6.4 Hz, 6H; H_{Ar}), 3.81 (s, 18H; OC*H*$_3$), 3.65 (s, 18H; OC*H*$_3$), 2.39 (br, 6H; C*H*$_2$), 2.07 ppm (br, 6H; C*H*$_2$); IR (solid): $\tilde{\nu}$ = 3340 (N–H), 1634 cm^{-1} (C=O).

[(L[12]H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for [(L^{2}H)$_2$PtCl$_6$]. Crystals precipitated from the solution over 24 h. Yield = 58%; ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 9.68 (br, 2H; N*H*$^+$), 8.79 (t, ^3J(H,H) = 4.9 Hz, 6H; N*H*), 7.00 (s, 12H; H_{Ar}), 6.68 (s, 6H; H_{Ar}), 3.78 (s, 36H; OC*H*$_3$), 3.70 (br, 12H; C*H*$_2$), 3.50 ppm (br, 12H; C*H*$_2$); ^{195}Pt NMR (500 MHz, [D$_3$]MeCN): δ = 244 ppm; IR (solid): $\tilde{\nu}$ = 3368 (N–H), 1641 (C=O), 1592 (C=C), 1155 cm^{-1} (C–O); MS (ES$^-$): *m/z*: 936 [(L^{12-}–2H)PtCl$_3$]$^-$, 972 [(L^{12}–H)PtCl$_4$]$^-$, 1044 [(L^{12}H)PtCl$_6$]$^-$, 1378 [(L^{12}H)(PtCl$_5$)$_2$]$^-$, 1682 [L^{12}(L^{12}H)PtCl$_6$]$^-$; elemental analysis calcd (%) for $C_{66}H_{86}Cl_6N_8O_{18}Pt$: C 46.98, H 5.14, N 6.64; found: C 47.05, H 5.11, N 6.57.

[(L[13]H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for [(L^{2}H)$_2$PtCl$_6$], but no precipitate formed so the reaction was repeated in [D$_3$]MeCN to study complexation in solution. ^{1}H NMR (300 MHz, [D$_3$]MeCN): δ = 9.96 (br, 2H; N*H*$^+$), 8.34 (br, 6H; N*H*), 7.03 (s, 6H; H_{Ar}), 6.73 (d, ^3J(H,H) = 6.4 Hz, 6H; H_{Ar}), 4.01 (br, 12H; C*H*$_2$), 3.90 (br, 12H; C*H*$_2$), 3.73 (s, 36H; OC*H*$_3$), 3.72 ppm (s, 18H; OC*H*$_3$); ^{13}C NMR (75 MHz, [D$_3$]MeCN): δ = 170, 153, 128, 117, 105, 60, 56, 55, 36 ppm; IR (solid): $\tilde{\nu}$ = 3364 (N–H), 1650 cm^{-1} (C=O).

[(L[14]H)$_2$PtCl$_6$]: Yield = 52%; ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.70 (br, 2H; N*H*$^+$), 7.96 (br, 6H; N*H*), 7.82 (d, ^3J(H,H) = 8.0 Hz, 12H; H_{Ar}), 7.61–7.71 (m, 18H; H_{Ar}), 3.68 (br, 12H; C*H*$_2$), 3.07 ppm (br, 12H; C*H*$_2$); ^{13}C NMR (101 MHz, CDCl$_3$): δ = 139.5, 132.8, 129.4, 126.6, 51.9, 37.0 ppm; IR (solid): $\tilde{\nu}$ = 3248 (N–H), 1329 cm^{-1} (S=O).

[(L[15]H)$_2$PtCl$_6$]: This compound was prepared in a similar manner to that described for [(L^{2}H)$_2$PtCl$_6$] and precipitated as an orange-yellow powder. Yield = 46%; ^{1}H NMR (270 MHz, CDCl$_3$): δ = 8.19 (s, 2H; N*H*$^+$), 7.51 (dd, ^3J(H,H) = 8.5, ^4J(H,H) = 2.2 Hz, 6H; H_{Ar}), 7.38 (d, ^4J(H,H) = 2.2 Hz, 6H; H_{Ar}), 6.91 (d, ^3J(H,H) = 8.5 Hz, 6H; H_{Ar}), 6.80 (br, 6H; N*H*), 3.94–3.87 ppm (m, 60H; OC*H*$_3$, NHC*H*$_2$); IR (CDCl$_3$): $\tilde{\nu}$ = 3009 (C–H, Ar), 2935 (C–H), 2855 (C–H), 1590 (C=C), 1510 (C=C), 1331 (S=O), 1264 (C–O), 1185 (S=O), 1157 cm^{-1} (C–O); elemental analysis calcd (%) for $C_{48}H_{62}Cl_6N_8O_{12}PtS_6$: C 37.36, H 4.05, N 7.26; found: C, 38.07, H 4.19, N 7.33.

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