## **Supporting Information:**

## A Comparison of the Selectivity of Extraction of $[PtCl_6]^{2^-}$ by Mono-, Bi- and Tripodal Receptors that Address its Outer Co-ordination Sphere

Rebecca J. Warr,<sup>†</sup> Katherine J. Bell,<sup>†</sup> Anastasia Gadzhieva,<sup>†</sup> Rafel Cabot,<sup>†</sup> Ross J. Ellis,<sup>‡</sup> Jy Chartres,<sup>‡</sup> David K. Henderson,<sup>‡</sup> Eleni Lykourina,<sup>†</sup> A. Matthew Wilson,<sup>‡</sup> Jason B. Love,<sup>‡</sup> Peter A. Tasker,<sup>\*,‡</sup> and Martin Schröder<sup>\*,†,#</sup>

<sup>†</sup> School of Chemistry, University of Nottingham, Nottingham, NG7 2RD, (UK)

<sup>‡</sup> School of Chemistry, University of Edinburgh, Edinburgh, EH9 3JJ, (UK)

<sup>#</sup> School of Chemistry, University of Manchester, Manchester, M13 9PL (UK)

**Contents:** 

Section 1. Additional extraction data.

Section 2. Additional information on crystal structures and contact distances

defining intermolecular H-bonds.

Section 3. <sup>1</sup>H nmr data for all protons in titration of L<sup>4</sup>•HCl with [(Oct<sub>4</sub>N)<sub>2</sub>PtCl<sub>6</sub>].

Section 4. Listing of CIF files.

**1. Additional extraction data.** The results presented in Figures S1-S6 demonstrate that extractants differing only in having 3,4-dimethoxy substitution rather than 3,5-dimethoxy substitution on the benzene rings show very similar loadings of  $[PtCl_6]^{2^-}$ .



**Figure SI1**. Plot of percentage of the total platinum extracted as  $[PtCl_6]^{2-}$  from aqueous 0.6 M HCl into CHCl<sub>3</sub> as a function of the [L]:[Pt] ratio for the tripodal ureas:  $L^1$  (3,4-methoxy substituted) and  $L^2$  (3,5-methoxy substituted).



**Figure SI2.** Plot of percentage of the total platinum extracted as  $[PtCl_6]^{2-}$  from aqueous 0.6 M HCl into CHCl<sub>3</sub> as a function of the [L]:[Pt] ratio for the tripodal amides:  $L^3$  (3,4-methoxy substituted) and  $L^4$  (3,5-methoxy substituted).



**Figure SI3.** Plot of percentage of the total platinum extracted as  $[PtCl_6]^{2-}$  from aqueous 0.6 M HCl into CHCl<sub>3</sub> as a function of the [L]:[Pt] ratio for the bipodal ureas:  $L^6$  (3,4-methoxy substituted) and  $L^7$  (3,5-methoxy substituted).



**Figure SI4.** Plot of percentage of the total platinum extracted as  $[PtCl_6]^{2-}$  from aqueous 0.6 M HCl into CHCl<sub>3</sub> as a function of the [L]:[Pt] ratio for the bipodal amides:  $L^8$  (3,4-methoxy substituted) and  $L^9$  (3,5-methoxy substituted).



**Figure SI5.** Plot of percentage of the total platinum extracted as  $[PtCl_6]^{2-}$  from aqueous 0.6 M HCl into CHCl<sub>3</sub> as a function of the [L]:[Pt] ratio for the monopodal ureas: L<sup>11</sup> (3,4-methoxy substituted) and L<sup>12</sup> (3,5-methoxy substituted).



**Figure SI6.** Plot of percentage of the total platinum extracted as  $[PtCl_6]^{2-}$  from aqueous 0.6 M HCl into CHCl<sub>3</sub> as a function of the [L]:[Pt] ratio for the monopodal amides:  $L^{13}$  (3,4-methoxy substituted) and  $L^{14}$  (3,5-methoxy substituted).

## Section 2. Additional information on crystal structures and contact distances defining intermolecular H-bonds.

**Proligand L<sup>11</sup>:** The extended structure shows inter-molecular hydrogen-bonding in L<sup>11(a)</sup> with N2—H2A<sup>...</sup>O2 (H<sup>...</sup>A = 2.121 Å) and N3—H3A<sup>...</sup>O2 (H<sup>...</sup>A = 2.092 Å) (Figure 2). The molecules of L<sup>11(a)</sup> have an alternating orientation and form a chain with each molecule of L<sup>11(a)</sup> being linked to the next through bifurcated hydrogen-bonds between the urea moieties. There are analogous inter-molecular interactions between the L<sup>11(b)</sup> molecules with N7—H7A<sup>...</sup>O4 (H<sup>...</sup>A = 2.056 Å) and N8—H8A<sup>...</sup>O4 (H<sup>...</sup>A = 2.140 Å). Further data are included in Table S1.

 $[(\mathbf{L}^{11}\mathbf{H})_2\mathbf{PtCl}_6]$ : The complex crystallises in the monoclinic space group P2<sub>1</sub>/c with one  $[PtCl_6]^{2-}$  anion lying on a centre of inversion and two receptor cations related by the inversion centre. The  $\mathbf{L}^{11}$  molecules are protonated at the bridgehead position (N1) to give the receptor a +1 charge and for each  $[PtCl_6]^{2-}$  anion present there are two  $(\mathbf{L}^{11}\mathbf{H})^+$  cations ensuring that the structure has a net charge of zero and confirming the expected 2: 1  $(\mathbf{L}^{11}\mathbf{H})^+$  to  $[PtCl_6]^{2-}$  stoichiometry of the complex. Disorder around the NMe fragment involving N1, C1 and C2 was modelled over two half-occupied sites with distance restraints and was refined with isotropic atomic displacement parameters.

The structure determination reveals extensive hydrogen-bonding between the urea moieties of  $(\mathbf{L}^{11}\mathrm{H})^+$  and  $[PtCl_6]^{2-}$  and also between the  $(\mathbf{L}^{11}\mathrm{H})^+$  cations. Each  $[PtCl_6]^{2-}$  anion accepts three hydrogen-bonds from two  $(\mathbf{L}^{11}\mathrm{H}^+)$  cations giving a total of six

NH<sup>...</sup>Cl interactions per anion with N4—H4A<sup>...</sup>Cl2 (H<sup>...</sup>A = 2.604 Å), N4—H4A<sup>...</sup>Cl3 (H<sup>...</sup>A = 2.745 Å) and N5—H5A<sup>...</sup>Cl2 (H<sup>...</sup>A = 2.729 Å) (Figure 3). The N4—H4A donor group is located between the Cl2 and Cl3 atoms and the N5—H5A group is located approximately in the centre of a triangular face defined by Cl1, Cl2 and Cl3. These correspond to areas of highest electron density surrounding  $[PtCl_6]^{2-}$  and are locations predicted to be targeted by NH groups.<sup>15</sup>

There are also intra- and inter-ligand NH<sup>...</sup>O interactions N1—H1D<sup>...</sup>O2 (H<sup>...</sup>A = 2.103 Å), N2—H2A<sup>...</sup>O1 (H<sup>...</sup>A = 2.069 Å) and N3—H3A<sup>...</sup>O1 (H<sup>...</sup>A = 2.141 Å). The extended structure shows that one urea group in each ( $\mathbf{L}^{11}$ H<sup>+</sup>) cation hydrogen-bonds to [PtCl<sub>6</sub>]<sup>2-</sup> while the other forms hydrogen-bonds to an adjacent ( $\mathbf{L}^{11}$ H<sup>+</sup>) molecule to give ...( $(\mathbf{L}^{11}$ H<sup>+</sup>)...[PtCl<sub>6</sub>]<sup>2-...</sup>( $\mathbf{L}^{11}$ H<sup>+</sup>))...(( $\mathbf{L}^{11}$ H<sup>+</sup>)...[PtCl<sub>6</sub>]<sup>2-...</sup>( $\mathbf{L}^{11}$ H<sup>+</sup>))..... The details of the hydrogen-bonds present in this structure are given in Table S2.

The configuration of the ligand is different in  $L^{11}$  and  $(L^{11}H)_2PtCl_6]$ . In  $L^{11}$  the two pendant arms have a parallel orientation with a bifurcated intra-ligand hydrogenbond between the urea moieties on the pendant arms. The arms are aligned less in  $[(L^{11}H)_2PtCl_6]$  and there are no intra-ligand hydrogen-bonds between the urea moieties.

It was thought that a bipodal receptor would form fewer hydrogen-bonds to  $[PtCl_6]^{2-}$  than a tripodal urea receptor because there are fewer NH donor groups available. The structure  $[(L^{11}H)_2PtCl_6]$  shows that two out of four functionalised arms interact with the anion and there are six NH<sup>...</sup>Cl hydrogen-bonds to each  $[PtCl_6]^{2-}$ . This suggests that the number of functionalised pendant arms does not play a significant part in determining the number of hydrogen-bonds that are formed to  $[PtCl_6]^{2-}$  in the solid state. This is true also for the other structures.  $[(\mathbf{L}^{13}\mathbf{H})_2\mathbf{PtCl_6}]$ : The  $\mathbf{L}^{13}\mathbf{H}^+$  units present in the structure are protonated at the tertiary amine position (N1) giving them a +1 charge and as the  $(\mathbf{L}^{13}\mathbf{H})^+$ :  $[\mathbf{PtCl_6}]^{2-}$  ratio is 2: 1 the crystal has a net charge of zero. The structure also contains four molecules of disordered MeCN in the unit cell. These have been omitted in Figure 4.

There are N—H<sup>...</sup>Cl—Pt interactions between both amide NH groups in ( $L^{13}H^+$ ) and two separate molecules of [PtCl<sub>6</sub>]<sup>2-</sup> with N2—H2A<sup>...</sup>Cl2 (H<sup>...</sup>A = 2.464 Å) and N3— H3A<sup>...</sup>Cl3 (H<sup>...</sup>A = 2.581 Å). There is a centre of inversion at Pt1 resulting in each [PtCl<sub>6</sub>]<sup>2-</sup> anion accepting one hydrogen-bond from four different ( $L^{13}H^+$ ) cations. The H3A atom hydrogen-bonds to Cl3 but the H3A<sup>...</sup>Cl1 distance (H<sup>...</sup>A = 2.990 Å) is slightly too long to be classed as a close interaction. The H3A atom is located between the Cl1 and Cl3 atoms but is slightly out of the plane defined by Pt1, Cl1 and Cl3. There are also inter-ligand interactions N1—H1<sup>...</sup>O5 (H<sup>...</sup>A = 2.038 Å) and N1—H1<sup>...</sup>O1 (H<sup>...</sup>A = 2.569 Å). Further information on the hydrogen-bonds present are given in Table S3.

 $[(\mathbf{L}^{23}\mathbf{H})_{2}\mathbf{PtCl_{6}}]$ : Orange blocks of  $[(\mathbf{L}^{23}\mathbf{H})_{2}\mathbf{PtCl_{6}}]$  obtained by slow evaporation of an aqueous methanolic solution of  $\mathbf{L}^{23}$ ,  $\mathbf{H}_{2}\mathbf{PtCl_{6}}$  and HCl have the triclinic space group P-1. The NH unit of the protonated tertiary amine nitrogen atom forms a H-bond to the neighbouring amide oxygen atom to form a 6-membered "proton chelate". The chelated proton does not make close contacts with  $[\mathbf{PtCl_{6}}]^{2-}$  ions but the chelate ring structure determines which polarised N-H and C-H bonds are available to address the outer coordination sphere of a chloridoplatinate through N—H…Cl and C—H…Cl H-bonding interactions. A polymeric structure results in which chloridoplatinate shows twelve long

range interactions (within 3 Å) between five of its chloride atoms: two amido N—H…Cl interactions, N5A—H5A…Cl4C (H5A…Cl4C = 2.637 Å) and N5B—H5B…Cl6C (H5B…Cl6C = 2.468 Å) and a further ten C—H…Cl interactions between 2.768 and 2.903 Å H…Cl length. A list if the X-H…Cl contacts shorter than 3 Å is given in Table S4.

[ $(L^{24}H)_2PtCl_6$ ]: Preliminary details of this structure have been published.<sup>7</sup> Figure 6 provides a comparison with those described for the first time in this work. The assembly formed by  $[L^{24}H]^+$  is fundamentally different in having only C-H...Cl interactions because it does not contain any amido N-H groups and the ammonium proton is not available as it is chelated by the amido C=O group. Four C—H groups  $\alpha$  to the ammonium nitrogen atoms form close contacts (2.641 to 2.993 Å, see Table S5). A further four interactions with aryl C—H donors are observed.

D—H <sup>…</sup> A	d(D—H) / Å	d(H <sup></sup> A) / Å	d(D···A) / Å	<(DHA) /
N4—H4A <sup></sup> O1	0.86	2.087	2.8821(14)	153.5
N5—H5A <sup></sup> O1	0.86	2.127	2.9144(14)	152.1
N2—H2A <sup></sup> O2	0.86	2.121	2.9044(14)	151.2
N3—H3A <sup></sup> O2	0.86	2.092	2.8868(14)	153.4
N9—H9A <sup></sup> O3	0.86	2.161	2.9281(14)	148.3
N10—H10A <sup></sup> O3	0.86	2.204	2.9404(14)	143.6
N7—H7A <sup></sup> O4	0.86	2.056	2.8583(14)	154.8

**Table S1.** Intra- and inter-molecular hydrogen-bonds D— $H^{...}A$  in  $L^{11}$  (D = donor, A = acceptor, d = distance)

\*symmetry codes x+1/2, y+1/2, -z+1/2, -x+3/2, y-1/2, z+1/2.

**Table S2.** Inter-molecular hydrogen-bonds in  $[(\mathbf{L}^{11}\mathbf{H})_2\text{PtCl}_6]$  (D = donor, A = acceptor, d = distance).

D—H <sup>…</sup> A	d(D—H) / Å	d(H <sup></sup> A) / Å	d(D···A) / Å	<(DHA) / °
N1—H1D <sup></sup> O2	0.93	2.103	2.912(13)	145
N2—H2A <sup>…</sup> O1	0.88	2.069	2.885(7)	154
N3—H3A <sup></sup> O1	0.88	2.141	2.937(7)	150
N4—H4A <sup>…</sup> Cl2	0.88	2.604	3.411(7)	153
N4—H4A <sup>…</sup> Cl3	0.88	2.745	3.386(9)	131
N5—H5A <sup>…</sup> Cl2	0.88	2.729	3.521(5)	151

\*symmetry codes x, -y+1/2, z-1/2, -x+1, -y+1, -z+2.

\* The NH<sup>--</sup>Cl and NH<sup>--</sup>O interactions are separated by a horizontal line.

**Table S3.** Inter-molecular hydrogen-bonds in  $[(\mathbf{L}^{13}\mathbf{H})_2\text{PtCl}_6]$  (D = donor, A = acceptor, d = distance).

D—H <sup>…</sup> A	d(D—H) / Å	d(H <sup></sup> A) / Å	d(D <sup></sup> A) / Å	<(DHA) / °
N2—H2A <sup></sup> Cl2	0.880	2.464	3.310	161.61
N3—H3A <sup></sup> Cl3	0.880	2.581	3.365	148.84
N1—H1 <sup></sup> O5	0.845	2.038	2.751	141.67
N1—H1 <sup></sup> O1	0.845	2.569	3.154	127.26

\*symmetry codes -x+1, -y+1, -z+1, -x,-y+1,-z+2.

\*A horizontal line separates the NH<sup>...</sup>Cl and NH<sup>...</sup>O interactions

**Table S4.** Inter-molecular interactions in  $[(L^{23}H)_2PtCl_6]$  (D = donor, A = acceptor, d = distance).

D—H <sup>…</sup> A	d(D—H) / Å	d(H <sup></sup> A) / Å	d(D <sup></sup> A) / Å	<(DHA) / °
N5B-H5B <sup></sup> Cl6C	0.881	2.468	3.324	163.98
N5A-H5A <sup></sup> Cl4C	0.881	2.637	3.513	173.20

C9B-H9B2 <sup></sup> Cl6C	0.990	2.768	3.321	115.77
C3A-H3A1 <sup></sup> Cl3C	0.990	2.832	3.713	148.65
C17B-H17F <sup></sup> Cl4C	0.979	2.834	3.557	131.32
C17B-H17E <sup></sup> Cl5C	0.980	2.842	3.615	136.36
C18A-H18B <sup></sup> Cl1C	0.979	2.850	3.881	167.44
C17A-H17B <sup></sup> Cl6C	0.980	2.861	3.794	159.28
C15B-H15D <sup></sup> Cl3C	0.991	2.862	3.817	162.06
C13B-H13F <sup></sup> Cl3C	0.981	2.889	3.556	126.15
C11A-H11A <sup></sup> Cl5C	0.990	2.893	3.781	149.64
C12B-H12B <sup></sup> Cl3C	1.000	2.903	3.536	121.99

**Table S5.** Inter-molecular interactions in  $[(\mathbf{L}^{24}\mathbf{H})_2\mathbf{PtCl}_6]$  (D = donor, A = acceptor, d = distance).

D—H <sup>…</sup> A	d(D—H)/ Å	d(H <sup></sup> A) / Å	d(D <sup></sup> A) / Å	<(DHA) / °
C45—H45B…Cl4	0.990	2.938	3.438	113.33
C16—H16A…Cl2	0.989	2.864	3.664	138.50
C47—H47…Cl2	0.950	2.946	3.762	144.81
C52—H52B…Cl5	0.990	2.993	3.923	178.51
C23—H23B…Cl6	0.990	2.647	3.437	136.90
C22—H22…Cl6	0.950	2.883	3.788	156.76
C23—H23B…Cl6	0.990	2.861	3.561	128.34
C22—H22···Cl3	0.950	2.814	3.487	128.72
C32—H32…Cl3	0.951	2.820	3.710	156.42

Section 3. <sup>1</sup>H nmr data for all protons in titration of L<sup>4</sup>•HCl with [(Oct<sub>4</sub>N)<sub>2</sub>PtCl<sub>6</sub>]



**Figure SI7.** <sup>1</sup>H NMR titration of  $L^4$ •HCl (10 mM) with [(Oct<sub>4</sub>N)<sub>2</sub>PtCl<sub>6</sub>] in CDCl<sub>3</sub>. Chemical shift changes for the hydrogen atoms (*a*-*g*) in the host are presented on arbitrary scales to show their different behaviour upon increasing concentration of the guest anion. The dotted lines mark the 2:1 host : guest ratio (0.5 eq. of guest added).

## Section 4. Listing of CIF files.

SI File: ic6b00848\_si\_001.pdf SI File: ic6b00848\_si\_002.cif SI File: ic6b00848\_si\_003.cif SI File: ic6b00848\_si\_004.cif SI File: ic6b00848\_si\_005.cif