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# Rhodium, palladium and platinum complexes of tris(pyridylalkyl)amine and tris(benzimidazolymethyl)amine $N_4$ -tripodal ligands

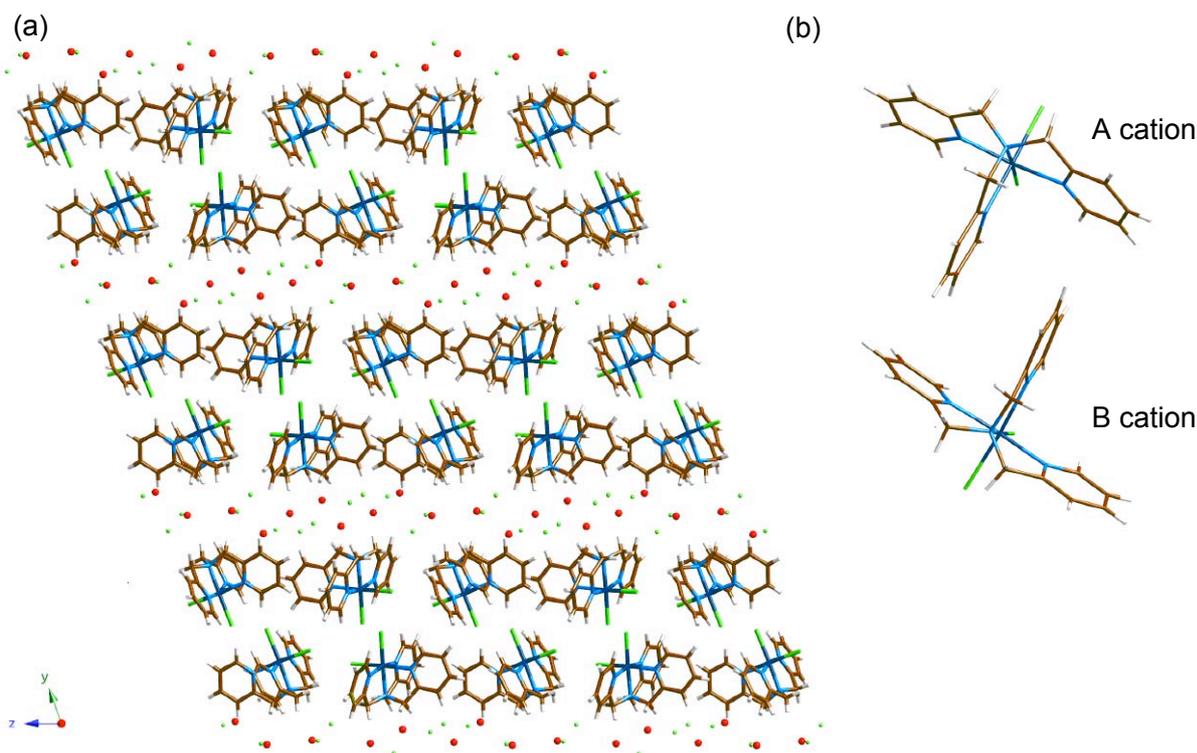
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## A. Additional discussion and views of crystal structure

The following common structural motifs or “*crystal structure rules*” are noted from examination of the ten new crystal structures:

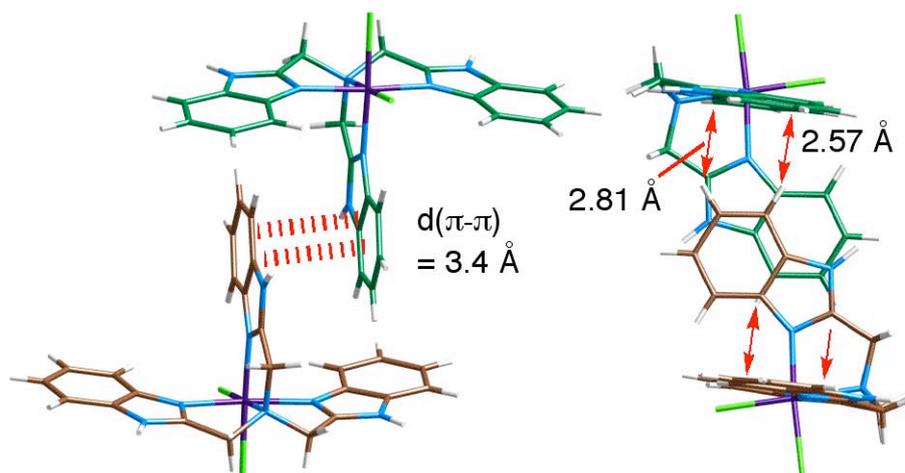
(i) **Complex cations pack into bilayers.** The crystal structures, except that of uncharged molecular  $[\text{Rh}(\text{bepa})\text{Cl}_3]$ , are *laminar*. The cations in this study are asymmetric and, in the absence of spontaneous resolution upon crystallisation, both enantiomers appear in the lattice centred about a crystallographic inversion. In all crystal structures, the hydrophobic cations pack with the chloride co-ligands pointing inward (point (iv)) into bilayers; e.g., see Figure 5 (in paper) and ESI Figs. A1 and A6–A11 (below). The packing of the cations into bilayers optimises inter-cation interactions (see points (ii)–(iv)); anions and polar solvent are excluded from the cation bilayers (see point (v)).



**ESI Fig. A1.** View of crystal structure of  $[\text{Rh}(\text{tmpa})\text{Cl}_2]\text{Cl}\cdot 3\text{H}_2\text{O}$  highlighting (a) the bilayers of complex cations in the  $xz$ -plane (with chloro co-ligands pointing ‘inwards’) that are interspersed by layers of chloride ions and lattice waters; (b) an inter-cation ‘triple embrace’.

(ii) **Complex species with orthogonal  $\pi$ -surfaces pair antiparallel by means of two edge-face, offset face-face ‘triple embraces’.**  $\kappa^4N$ -Coordination of the organic ligand, as in the octahedral Rh complexes, leads to a ‘T-shaped’ arrangement of the pyridyl or benzimidazole

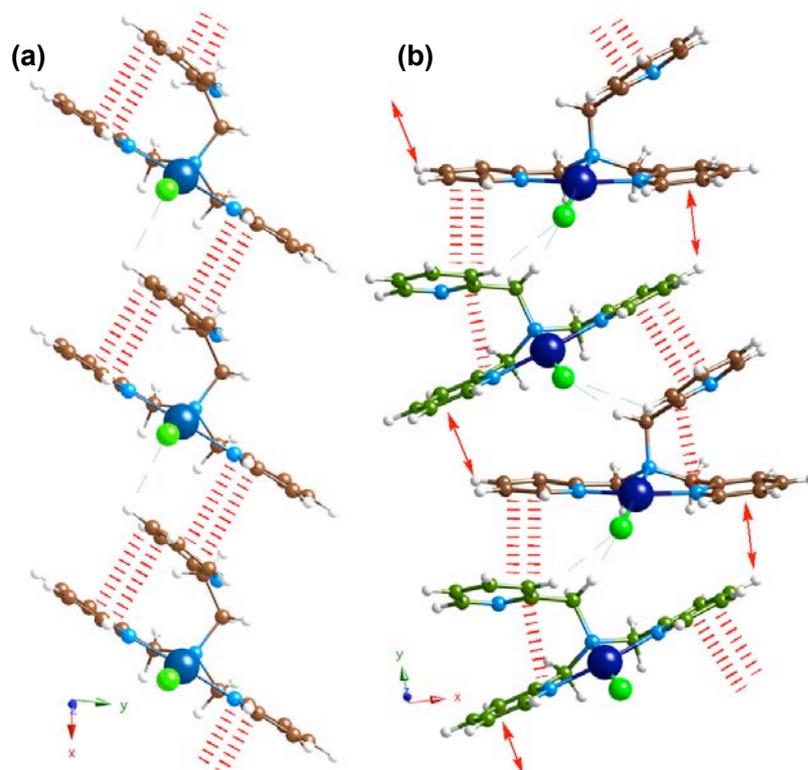
rings. A two edge–face, offset face–face ‘triple embrace’ provides the optimum interaction between two such T-shaped cations;<sup>1</sup> e.g. ESI Figure A2. The offset ( $\pi$ - $\pi$ ) face-face interaction is weaker for the pyridyl-amine ligands and stronger for the benzimidazole-amine ligands; i.e. it correlates with the  $\pi$ -surface area of the heterocyclic donors. The two cations engaged in a triple embrace lie within a single cation layer (with their inversion symmetry-related equivalents in the adjacent cation layer, thus affording the bilayer structure, point (i)).  $\kappa^3N$ -Coordination of the organic ligand, as in the Pd and Pt monomers, leaves a dangling donor leg that disrupts and prevents the triple embrace from forming.



**ESI Fig. A2.** The ‘triple embrace’ between antiparallel cation pairs in the crystal structure of  $[\text{Rh}(\text{tbima})\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}\cdot\text{dmsO}$

**(iii) Complex species with two or more non-orthogonal  $\pi$ -surfaces form strands linked by inter-ion oblique edge–face or offset face–face interactions.** The  $[\text{M}(\kappa^3N\text{-L})\text{Cl}_x]$  species can not form triple embraces and are weakly associated into strands by (a) offset face–face ( $\pi$ - $\pi$  stacking) interactions when the complex species have two almost parallel heterocyclic rings or (b) edge–face ( $\sigma$ - $\pi$ ) interactions between oblique heterocyclic rings. Offset face-face associated strands are observed in the crystal structures of  $[\text{Rh}(\text{bepa})\text{Cl}_3]$ ,  $[\text{Pd}(\text{pmea})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$  and  $[\text{Pt}(\text{tmpa})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$ , e.g., ESI Figure A3. Oblique edge-face associations appear in the crystal structures of  $[\text{Pd}(\text{tmpa})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$  and  $[\text{Pt}(\text{tmpa})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$ .

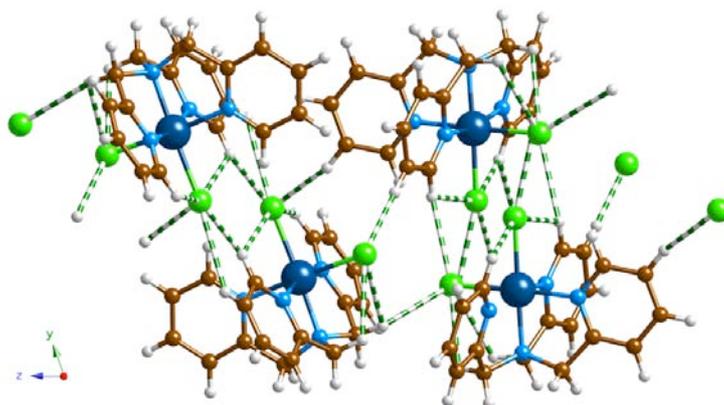
<sup>1</sup> C. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885; M. L. Scudder, H. A. Goodwin, and I. G. Dance, *New J. Chem.*, 1999, **23**, 695.



**ESI Fig. A3.** (a) View of the crystal structure of  $[\text{Pd}(\text{pmea})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$  showing the offset face–face interactions (3.2–3.3 Å; indicated by hashed red lines) within and between neighbouring cations in a layer. (b) View of the crystal structure of  $[\text{Pt}(\text{tmpa})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$  showing the offset face–face (3.3–3.5 Å) and edge–face ( $\text{C–H}\dots\text{C}_{\text{ring}} \sim 3.2$  Å; indicated by double-headed arrows) interactions between the adjacent A (brown) and B cations (green) within a cation layer

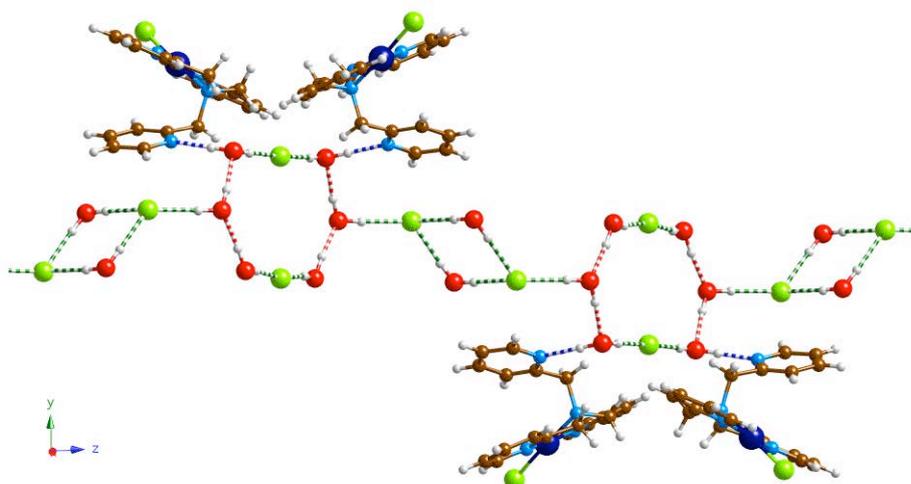
**(iv) Metal-bound chloride co-ligands point ‘inward’ to within the hydrophilic cation bilayer.** The inward orientation of the chloride co-ligands facilitates formation of multiple, weak  $\text{C–H}\dots\text{Cl}$  interactions in the range 2.6–3.2 Å ( $\text{H}\dots\text{Cl}$  distances).<sup>2</sup> That the chloride co-ligands form these interactions, and not hydrogen bonds with lattice solvent/water (see point (v)), attests to the predominantly covalent nature of the  $\text{M–Cl}$  bond in these 2<sup>nd</sup>- and 3<sup>rd</sup>-row transition metal complexes. These interactions are found in the crystal structures of all complexes; e.g., see ESI Figure A4.

<sup>2</sup> G. R. Desiraju, *Chem. Comm.*, 2005, 2995; G. R. Desiraju, *Acc. Chem. Res.*, 2002, **35**, 565; M. J. Calhorda, *Chem. Comm.*, 2000, 801.



**ESI Figure A4.** Edge-on view of part of a dual layer of A (left-side) and B (right-side) cations in the crystal structure of  $[\text{Rh}(\text{tmpa})\text{Cl}_2]\text{Cl}\cdot 3\text{H}_2\text{O}$  emphasizing the weak inter-/intra-cation C–H...Cl hydrogen bonds (indicated by green-white cross-hatched lines)

**(v) Counter-ions and polar lattice solvent associate into hydrophilic layers.** These layers are interspersed between the bilayers of hydrophobic cation pairs, e.g. Figure 5 (in paper) and additional ESI Figures below. Hydrogen bonding between lattice water and chloride anion is optimised in such layers resulting in, for example,  $(\text{Cl}\dots\text{H}_2\text{O})_2$  diamonds, unusual  $[\text{Cl}\dots(\text{H}_2\text{O})_2]_\infty$  chains, containing linked  $[\text{Cl}\dots(\text{H}_2\text{O})_4]$  pentagons (ESI Figure A1b), and novel  $\{[\text{Cl}\dots(\text{H}_2\text{O})]_2\dots[\text{Cl}\dots(\text{H}_2\text{O})_3]_2\}$  strands, formed by linking  $(\text{Cl}\dots\text{H}_2\text{O})_2$  diamonds and  $[\text{Cl}\dots(\text{H}_2\text{O})_3]_2$  octagons (ESI Fig. A5), in the hydrophilic layers within the crystal structures of



**ESI Fig. A5.** View of the crystal structure of  $[\text{Pt}(\text{tmpa})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$  showing a  $\{[\text{Cl}\dots\text{H}_2\text{O})_2\dots[\text{Cl}\dots(\text{H}_2\text{O})_3]_2\}$  strand and the A cations from the two adjacent cation layers that hydrogen bond with it; hydrogen bonds are cross-hatched: Cl...H green-white, N...H blue-white, and O...H red-white

$[\text{Pd}(\text{pmea})\text{Cl}]\text{Cl}\cdot \text{H}_2\text{O}$ ,  $[\text{Pd}(\text{tmpa})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$  and  $[\text{Pt}(\text{tmpa})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$ , respectively. One way of looking at the lamellar crystal structures could be that the cation bilayers arise from exclusion of the weakly associated cation pairs from the hydrophilic layers in order to optimise the stronger lattice water and chloride ion hydrogen bonding. However, separate cation bilayers and anion layers are also found in the structure of  $[\text{Rh}(\text{pmea})\text{Cl}_2][\text{PF}_6]\cdot \text{CH}_3\text{CN}$ , in which the anions and lattice solvent do not form hydrogen bonds. Lattice water does not form hydrogen bonds with the

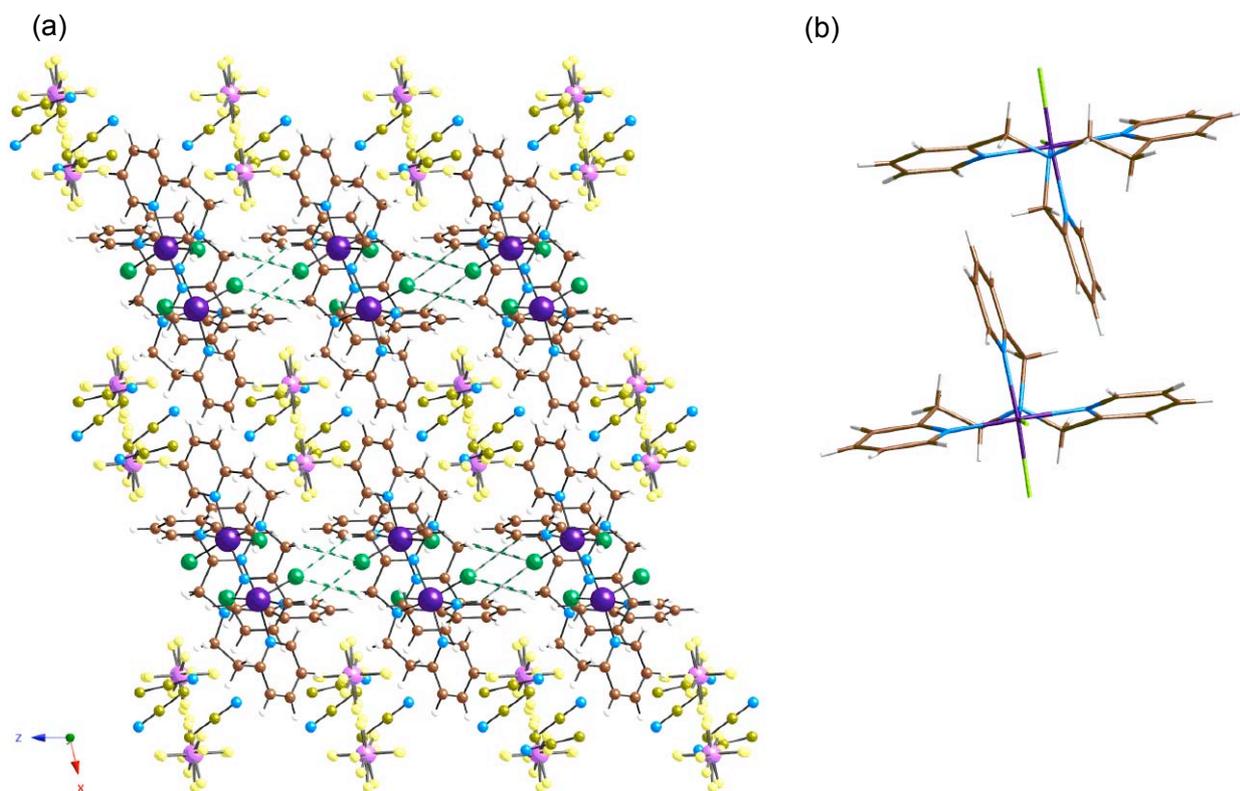
metal-bound chloride co-ligands (consistent with the loss of negative charge upon covalent coordinate bonding with a metal ion and the positioning of these co-ligands (point (iv)).

**(vi) Significant interactions between the cation bilayers and the anion/lattice solvent layers (only) occur when the complex cations have hydrogen bond donor/acceptor groups.** The three structures that exhibit cation to anion/lattice solvent interaction follow this rule; these are [Rh(tbima)Cl<sub>2</sub>]Cl·H<sub>2</sub>O·dmsO (hydrogen bonding with the benzimidazole N–H groups), [Pd(tpa~OH)-Cl]Cl·H<sub>2</sub>O·dmsO (hydrogen bonding with the pyridylmethanol OH groups) and [Pt(tmpa)Cl]Cl·2H<sub>2</sub>O (A cations only: the pendant pyridyls form hydrogen bonds with water).

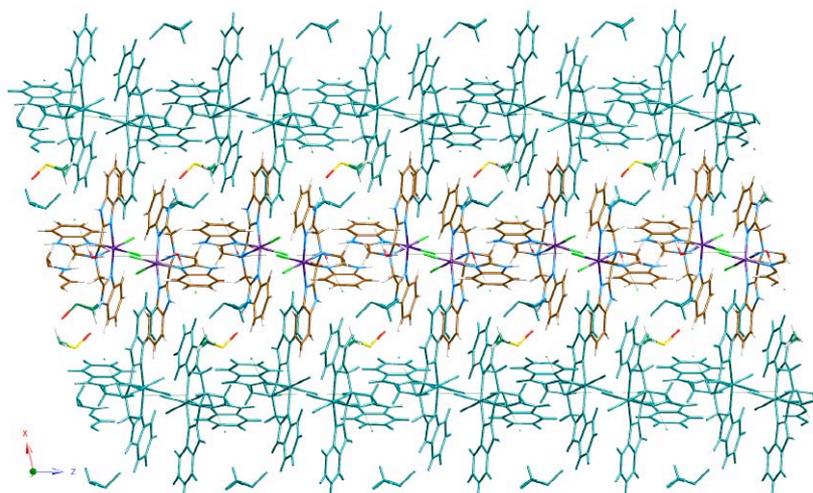
**(vii) Pendant N-heterocyclic groups form E–H...N<sub>pendant</sub> hydrogen bonds.** The [M(κ<sup>3</sup>N-L)Cl]<sup>+</sup> cations all have one pendant N-heterocyclic leg and, in each case, hydrogen bonds form: stronger C–H...N hydrogen bonds to lattice water (O...N 2.89 Å) are found in the crystal structure of [Pt(tmpa)Cl]Cl·H<sub>2</sub>O (for the A cations, ESI Figure A5) and, in the absence of this, weaker inter-ring associations (C–H...N 2.65–3.15 Å) form as in the crystal structures of [Pd(tmpa)Cl]Cl·H<sub>2</sub>O, [Pd(pmea)Cl]Cl·H<sub>2</sub>O, [Pd(tpa~OH)Cl]Cl·2H<sub>2</sub>O and [Pt(tmpa)Cl]Cl·H<sub>2</sub>O (for the B cations).

Whilst each of these seven motifs or ‘crystal structure rules’ is not out of the ordinary or unexpected in itself, *together* they should have wide applicability and some predictive power, both to the crystal structures of metal-halide complexes of polydentate amines with N-heterocyclic legs and, more generally, to the crystal structures of any species containing covalent halo-N-heterocyclic cations.

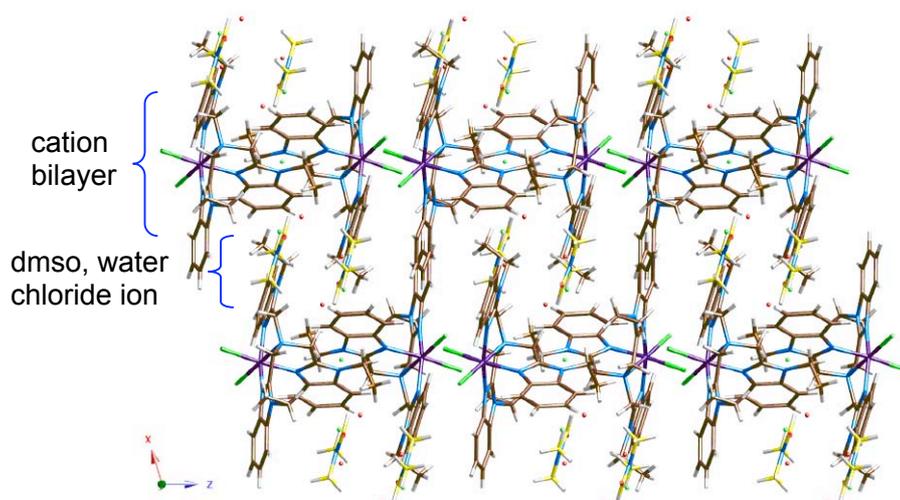
## Some additional views of crystal structure.



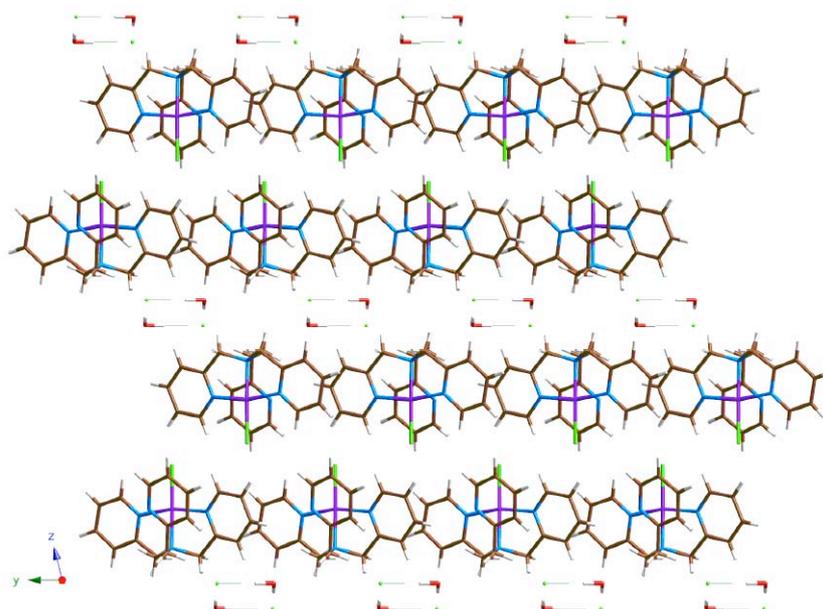
**ESI Fig. A6.** Crystal structure of  $[\text{Rh}(\text{pmea})\text{Cl}_2][\text{PF}_6]\cdot\text{MeCN}$  showing: (a) the alternating cation bilayers and lattice acetonitrile – (disordered)  $\text{PF}_6^-$  anion layers (weak  $\text{C}-\text{H}\cdots\text{Cl}$  inter-cation hydrogen bonds are indicated by green dashes); (b) a cation–cation ‘triple embrace’.



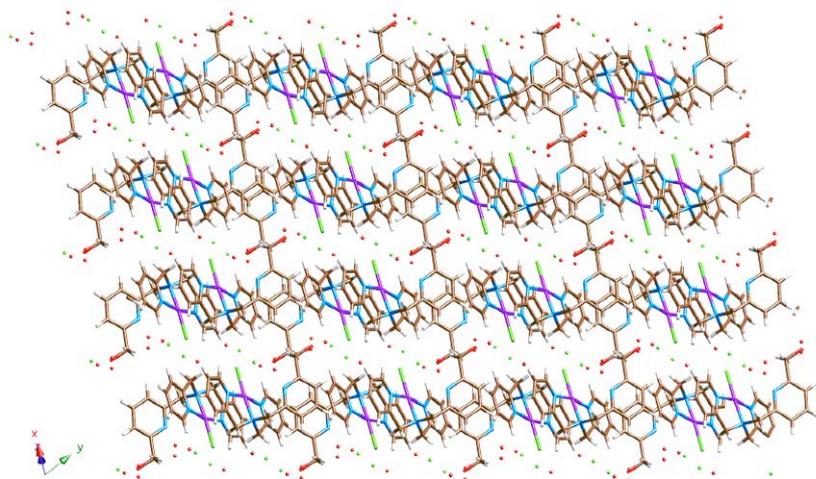
**ESI Fig. A7.** View of crystal structure of  $[\text{Rh}(\text{tbima})\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}\cdot 0.5\text{dmf}$  showing three cation bilayers. The cations, chloride counterions and dmsol molecules (green carbon atoms) and waters within a single bilayer are all interconnected by hydrogen bonding; there are no significant interactions between different bilayers. To emphasize the layer structure, all species in the two outer bilayers have been coloured teal.



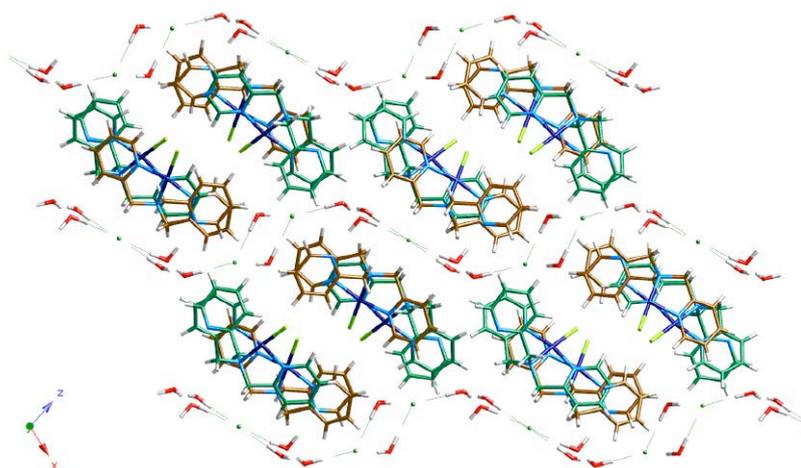
**ESI Fig. A8.** Crystal structure of  $[\text{Rh}(\text{Et-tbima})\text{Cl}_2]\text{Cl}\cdot\text{dmsO}\cdot\text{H}_2\text{O}$ : view down the  $y$ -axis revealing the bilayer structure. The cation pairs of one layer (in the  $yz$ -plane) are 'interdigitated' with those of the adjacent layer; dmsO, water and chloride ion lie within layers interspersed between the 'fingers' of the cation bilayers. Cation carbon atoms are brown; those of dmf are yellow.



**ESI Fig. A9.** Crystal structure of  $[\text{Pd}(\text{pmea})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$ . View down  $y$ -axis depicting the cation bilayers interspersed by layers of discrete  $[\text{H}_2\text{O}\dots\text{Cl}]_2$  'diamonds'.



**ESI Fig. A10.** Crystal structure of  $[\text{Pd}(\text{tpa}\sim\text{OH})\text{Cl}]\text{Cl}\cdot\text{H}_2\text{O}$ . View  $(h, k, l: 1, 0, -1)$  emphasizing the bilayers of cations and the intervening layers of chloride counterions and lattice waters. Each pyridyl-methanol group interjects into the chloride–water layer such that it is ideally placed to form hydrogen bonds with a water molecule and a chloride ion. To facilitate this inter-layer hydrogen bonding, the cations orientate with the chloride co-ligand outwards toward the adjacent hydrophilic chloride-water layer, rather than centrally to within a cation bilayer as in the other crystal structures; nonetheless, the Pd-bound chloride co-ligands are orientated away from the lattice waters and do not form strong hydrogen bonds. The pyridylmethanol group is disordered over two positions that are only slightly shifted from each other: for clarity only one position is shown; each of the two half-occupied sites for each water and chloride is shown.



**ESI Fig. A11.** Crystal structure of  $[\text{Pt}(\text{tmpa})\text{Cl}]\text{Cl}\cdot 2\text{H}_2\text{O}$ . View down  $y$ -axis emphasizing the cation bilayers, parallel to the plane defined by the  $y$ -axis and the  $xz$ -diagonal, which are interspersed by layers of hydrogen bonded chains of chloride counterions and lattice waters. The two crystallographically independent  $[\text{Pt}(\text{tmpa})\text{Cl}]^+$  cations are distinguished by the colours of their carbon atoms: A cations brown; B cations deep green.