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Water molecules insert into N—H···Cl—M hydrogen bonds while M—Cl···X—C halogen bonds remain intact in dihydrates of halopyridinium hexachloroplatinates

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The crystal structures of the 3-halopyridinium hexachloroplatinate(IV) dihydrates (HPyX-3)$_2$[PtCl$_6$]·2H$_2$O [(1), X = Br; (2a), (2b), X = I] comprise networks in which the molecular components are linked *via* N—H···O and O—H···Cl—Pt hydrogen bonds and Pt—Cl···X—C halogen bonds (X = Br, I). The iodo derivative has been isolated in two polymorphic forms. Of particular interest to the understanding of the utility of the hydrogen bonds and M—X···X'—C halogen bonds that propagate the networks in anhydrous salts of this type is that the water molecules insert exclusively into the putative N—H···Cl—Pt hydrogen bonds, while the Pt—Cl···X'—C halogen bonds remain undisrupted by the presence of water molecules.

1. Introduction

Inorganic crystal engineering is an emerging field of research focused on the synthesis of molecular crystals containing metal ions (Brammer, 2004; Braga, 2000) in order to develop new materials with a variety of properties, functions and applications (Braga, 2003; Janiak, 2003; Kesanli & Lin, 2003; Coronado *et al.*, 2000; Desiraju, 2003). Broadly speaking, two classes of compounds have been studied: those commonly referred to as coordination polymers or metal-organic frameworks (Blake *et al.*, 1999; James, 2003; Zaworotko, 2001) and those based on molecules or ions linked *via* hydrogen bonds or other weak non-covalent interactions (for some examples, see Brammer, 2003; Beatty, 2001; Hosseini, 2003; Dance & Scudder, 2000; Braga & Grepioni, 1999; Aakeröy *et al.*, 1999; Brammer *et al.*, 2000). The report focuses on compounds that fall into the latter class.

In comparison to classical organic crystal engineering (Desiraju, 1995) the introduction of metal ions into crystalline materials in the form of metal complexes with ligands capable of directional supramolecular interactions with neighbouring molecules provides an opportunity to tune the nature of these interactions through the influence of the metal (Dance, 1996). A striking example is provided by the modification of the properties of halogen atoms (X) that arise from metal coordination (M—X), as compared to halogens in organic compounds (C—X). Thus, the great polarity of the M—X bond affords strong directional interactions with hydrogen-bond donors (*e.g.* N—H and O—H groups), while the analogous organic C—X group exhibits a weak and geometrically less well defined interaction (Brammer *et al.*, 2001). These hydrogen-bonding interactions (N—H···Cl$_n$Pt, n = 1–3) have been successfully used in the synthesis of new ionic organic inorganic hybrid solids (Lewis & Orpen, 1998; Gillon *et al.*,

Table 1
Experimental details.

	(1)	(2a)	(2b)
Crystal data			
Chemical formula	$2C_5H_5BrN\cdot Cl_6Pt\cdot 2H_2O$	$2C_5H_5IN\cdot Cl_6Pt\cdot 2H_2O$	$2C_5H_5IN\cdot Cl_6Pt\cdot 2H_2O$
M_r	761.84	855.82	855.82
Cell setting, space group	Monoclinic, $P2(1)/n$	Monoclinic, $P2/n$	Triclinic, $P\bar{1}$
a, b, c (Å)	10.634 (1), 9.131 (1), 11.030 (1)	7.968 (2), 7.320 (2), 18.243 (4)	7.395 (2), 11.002 (2), 13.727 (3)
α, β, γ (°)	90.00, 108.076 (2), 90.00	90.00, 100.300 (4), 90.00	97.453 (3), 95.101 (3), 103.968 (3)
V (Å^3)	1018.08 (16)	1046.9 (4)	1066.2 (4)
Z	2	2	2
D_x (Mg m^{-3})	2.485	2.715	2.666
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	6242	3570	5122
θ range (°)	2.3–28.0	2.3–27.4	2.6–27.9
μ (mm^{-1})	11.61	10.42	10.23
Temperature (K)	150 (5)	150 (5)	150 (5)
Crystal form, colour	Prismatic, brown	Block, brown	Prismatic, yellow
Crystal size (mm)	$0.30 \times 0.25 \times 0.21$	$0.27 \times 0.26 \times 0.13$	$0.21 \times 0.19 \times 0.17$
Data collection			
Diffractometer	Bruker Smart 1000 CCD	Bruker Smart 1000 CCD	Bruker Smart 1000 CCD
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
T_{min}	0.128	0.165	0.223
T_{max}	0.194	0.344	0.275
No. of measured, independent and observed reflections	11 279, 2399, 2095	11 268, 2446, 1849	11 690, 4758, 3859
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.030	0.055	0.034
θ_{max} (°)	27.8	28.0	28.0
Range of h, k, l	$-13 \Rightarrow h \Rightarrow 13$	$-10 \Rightarrow h \Rightarrow 10$	$-9 \Rightarrow h \Rightarrow 9$
	$-11 \Rightarrow k \Rightarrow 11$	$-9 \Rightarrow k \Rightarrow 9$	$-14 \Rightarrow k \Rightarrow 14$
	$-14 \Rightarrow l \Rightarrow 14$	$-23 \Rightarrow l \Rightarrow 24$	$-17 \Rightarrow l \Rightarrow 17$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.024, 0.069, 1.00	0.039, 0.097, 1.07	0.059, 0.194, 1.03
No. of reflections	2399	2446	4758
No. of parameters	112	105	208
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 1.4669P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0412P)^2 + 6.7663P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1051P)^2 + 42.8734P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001	<0.0001	<0.0001
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.30, −0.74	2.16, −1.21	4.28, −3.71

Computer programs used: *SMART* 5.040 (Bruker AXS Inc., 2003*a*), *SAINT* 6.458/6/03 (Bruker AXS Inc., 2003*b*), *SHELXTL*5.1 (Bruker AXS Inc., 1998).

2000; Angeloni & Orpen, 2001; Dolling *et al.*, 2001; Mareque Rivas & Brammer, 1998; Brammer *et al.*, 2002)

Recently we and others have reported the synthesis of ionic crystals in which the components are linked *via* strong hydrogen bonds (N—H$\cdots$X—M) and M—X$\cdots$X'—C halogen–halogen interactions (X = Cl, Br; X' = Cl, Br, I; M = transition metal), as illustrated in Fig. 1 (Brammer *et al.*, 2003; Willett *et al.*, 2003). The impetus for our work in this area has been to establish the potential utility of the M—X$\cdots$X'—C interaction as a supramolecular synthon (Desiraju, 1995). The interaction can be viewed in terms of a Lewis acid–Lewis base interaction wherein the M—X group serves as the Lewis base (employing a lone pair on the halide ligand) and the C—X' group serves as a Lewis acid (*via* its vacant σ^* orbital). Thus, such interactions can be considered to be analogous to N$\cdots$X—C and O$\cdots$X—C halogen bonds, typified by the work

of Metrangolo & Resnati (2001) and Corradi *et al.* (2000); see also Lommerse *et al.* (1996).

In our earlier report we examined systems based upon [CoCl$_4$]$^{2-}$ anions and 3-halopyridinium cations (HPyX-3, X = Cl, Br, I). Here we report systems based upon [PtCl$_6$]$^{2-}$ anions and 3-halopyridinium cations (HPyX-3, X = Br, I). Of particular interest to our understanding of the utility of the hydrogen bonds and halogen bonds that propagate the networks in anhydrous salts of this type is to what extent the water molecules disrupt these two key types of interaction. The current systems are all dihydrates of the general formula (HPyX-3)$_2$[PtCl$_6$]$\cdot$2H$_2$O and thus allow this question to be explored. We report here that the water molecules insert exclusively into the N—H$\cdots$Cl—Pt hydrogen bonds while permitting the Pt—Cl$\cdots$X'—C halogen bonds to remain undisrupted.

2. Experimental

2.1. Crystal syntheses

All reagents (purchased from Aldrich or Lancaster) and solvents were used as received. Crystals were obtained at room temperature (293 K) *via* slow evaporation in small vials sealed with perforated Parafilm®. The very small amount of material obtained (typically few single crystals per sample) did not permit bulk analyses to be performed. However, unit-cell dimensions for single crystals from repeated syntheses were found to match those of the reported compounds.

2.1.1. (HPyBr-3)$_2$[PtCl$_6$]·2H$_2$O (1). 3-Bromopyridine, PyBr-3 (60 mg, 0.38 mmol), was dissolved in 37% aqueous HCl (60 mg) diluted with MeOH (1 ml). This solution was added to a saturated solution of K$_2$PtCl$_6$ in 37% aqueous HCl (1 ml) in a sample tube. Small brown prismatic crystals suitable for X-ray diffraction formed in low yield after 10 weeks.

2.1.2. (HPyI-3)$_2$[PtCl$_6$]·2H$_2$O (2a). 3-Iodopyridine, PyI-3 (60 mg, 0.29 mmol), was dissolved in 37% aqueous HCl (60 mg) diluted with MeOH (1 ml). This solution was added to a saturated solution of K$_2$PtCl$_6$ in 37% aqueous HCl (1 ml) in a sample tube. Small brown prismatic crystals suitable for X-ray diffraction formed in low yield after 10 weeks.

2.1.3. (HPyI-3)$_2$[PtCl$_6$]·2H$_2$O (2b). 3-Iodopyridine, PyI-3 (30 mg, 0.145 mmol), was dissolved in 37% aqueous HCl (180 mg) diluted with MeOH (1 ml). This solution was added to a saturated solution of K$_2$PtCl$_6$ in 37% aqueous HCl (1 ml) in a sample tube. Small yellow prismatic crystals suitable for X-ray diffraction formed in low yield after 10 weeks.

2.2. Crystallography

X-ray data were collected on a Bruker SMART 1000 diffractometer using Mo $K\alpha$ radiation. Crystal structures were solved and refined against all F^2 values using the *SHELXTL* suite of programs (Bruker AXS Inc., 1998). A summary of the data collection, and structure refinement information is provided in Table 1.[1] Data were corrected for absorption using empirical methods (*SADABS*) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles (Sheldrick, 1995; Blessing, 1995). Non-H atoms were refined anisotropically and H atoms associated with the halopyridinium cations were placed in calculated positions with idealized geometries. H atoms of the water molecules in the structure of (1) were located from the difference map and refined with no positional constraints. Those in structures (2a) and (2b) were modeled using the program *HYDROGEN* included in *WinGX* version 1.64.05 (Farrugia, 1999) based on combined geometric and force-field calculations on the basis of hydrogen-bonding interactions (Nardelli, 1999). In order to examine the effectiveness of this approach for calculating H-atom positions, we were able to compare the directly located positions with those calculated using the *HYDROGEN* program for (1). The angles between

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE5008). Services for accessing these data are described at the back of the journal.

the observed and calculated H-atom positions are 15.5 and 45.7°. These are relatively large discrepancies compared with most test cases presented by Nardelli (1999). However, the qualitative picture of hydrogen bonding remains unchanged in that the water molecules provide a hydrogen-bonding link between the cations and anions.

3. Results

Reaction of K$_2$[PtCl$_6$] with 3-bromo- or 3-iodopyridine (Py*X*-3, *X* = Br, I) under acidic conditions yields compounds
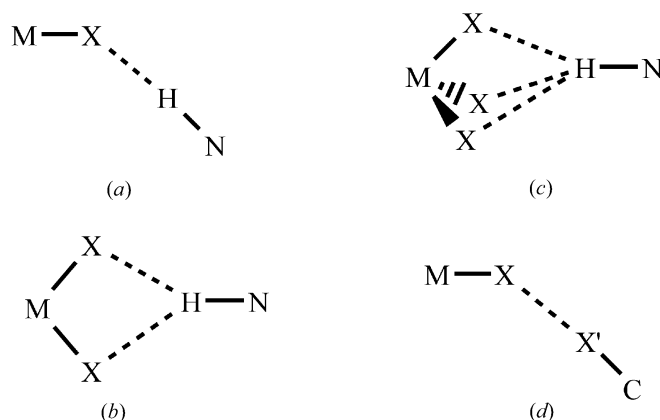
Figure 1
Examples of hydrogen bonds [(*a*), (*b*) and (*c*)] and halogen bonds (*d*) used in linking perhalometallate ions *via* organic cations (*X* = Cl, Br; *X'* = Cl, Br, I; *M* = transition metal).
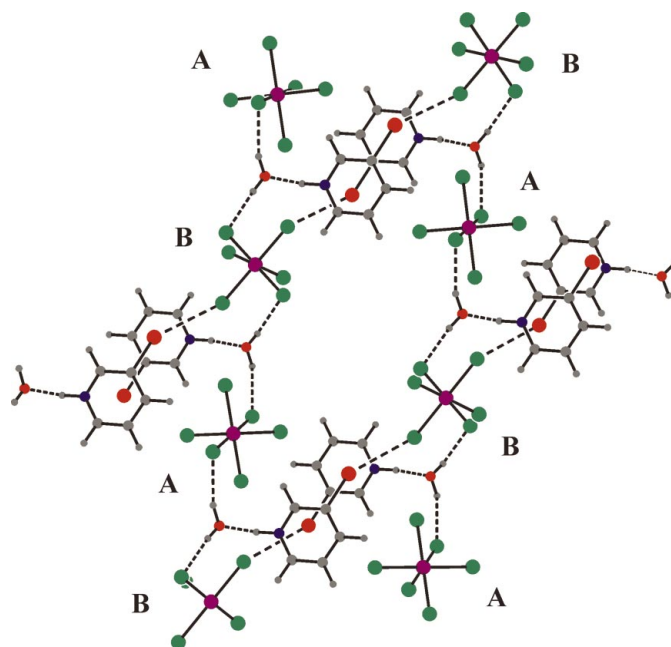
Figure 2
Structure of (1) showing O—H···Cl(Pt) and N—H···O hydrogen bonds, and Pt—Cl···Br—C halogen bonds that link the molecular components within one layer of the three-dimensional network. Anions *A* and *B* are crystallographically equivalent, but have different orientations relative to the layer shown and form additional interactions to complete the three-dimensional network (see text).

(HPyBr-3)$_2$[PtCl$_6$]·2H$_2$O (1) and (HPyI-3)$_2$[PtCl$_6$]·2H$_2$O (2a) and (2b), respectively. The structures (2a) and (2b) are two polymorphic forms. The crystal structures contain 3-halopyridinium cations, hexachloroplatinate dianions and water molecules linked via a network of hydrogen bonds [N—H···O and O—H···Cl(Pt)] and halogen–halogen interactions Pt—Cl···(Br,I)—C. The descriptions of the crystal structures that follow are based upon a consideration of such interactions that lie within the sum of van der Waals radii for the pair of interacting atoms (H···O 2.6, H···Cl 2.95, Cl···Br 3.6, Cl···I 3.73 Å; Bondi, 1964). All reported hydrogen-bond geometries are based upon H-atom positions that have been adjusted along their bond vector to positions consistent with their expected nuclear positions (C—H 1.083, N—H 1.01, O—H 0.96 Å; Allen, 1986).

3.1. Structure of (HPyBr-3)$_2$[PtCl$_6$]·2H$_2$O (1)

The structure of (1) is shown in Fig. 2 and comprises rows of [PtCl$_6$]$^{2-}$ anions linked via hydrogen bonding to the water molecules [(Pt)Cl···H—O—H···Cl(Pt): (O)H···Cl 2.26, 2.39 Å; O—H···Cl 163.7, 158.8°]. Bridges between these hydrogen-bonded chains are then provided by the 3-bromopyridinium cations which are each linked via an N—H···O hydrogen bond to a water molecule [(N)H···O 1.68 Å; N—H···O 170.1°] and interact with an anion from the neighbouring row via Pt—Cl···Br—C halogen bonds [(Pt)Cl···Br(C) 3.521 Å; (Pt)Cl···Br 157.1°, Cl···Br—C 145.7°]. Anions A and B (Fig. 2) are crystallographically

equivalent (asymmetric unit contains half an anion), each forming four O—H···Cl hydrogen bonds and two Pt—Cl···Br—C halogen bonds. However, anion A forms only two hydrogen bonds within the layer shown, while anion B forms two hydrogen bonds and two halogen bonds within this layer. The network is propagated in the third dimension through the formation of the two additional hydrogen bonds by anion B and two additional hydrogen bonds and two halogen bonds by anion A. Secondary C—H···Cl(Pt) interactions [(C)H···Cl(Pt) 2.68–2.74 Å, Pt—Cl···H 88.8–107.2°] and dipole-assisted stacking interactions of the pyridinium rings [interplanar separation 3.74 Å, inter-ring centroid–centroid distance 4.89 Å (see Hunter & Sanders, 1990; Janiak, 2000)] also contribute to the overall packing of the crystal structure.

3.2. Crystal structure of (HPyI-3)$_2$[PtCl$_6$]·2H$_2$O (2a)

The structure of (2a) is shown in Fig. 3 and again comprises rows of [PtCl$_6$]$^{2-}$ anions linked via hydrogen bonding to the water molecules, with bridges between these hydrogen-bonded chains being provided by the 3-iodopyridinium cations through N—H···O hydrogen bonds to the water molecules [(N)H···O 1.84 Å, N—H···O 146.7°] and Pt—Cl···I—C halogen bonds involving anions from the neighbouring row [(Pt)Cl···I(C) 3.352 Å; (Pt)Cl···I 109.8°, Cl···I—C 176.1°]. In contrast to the structure of (1), all cation/water bridges link anions within the same layer giving a two-dimensional network. Additionally, while the linking cations shown in Fig. 2 lie parallel to the anion layer of (1) shown and are mutually
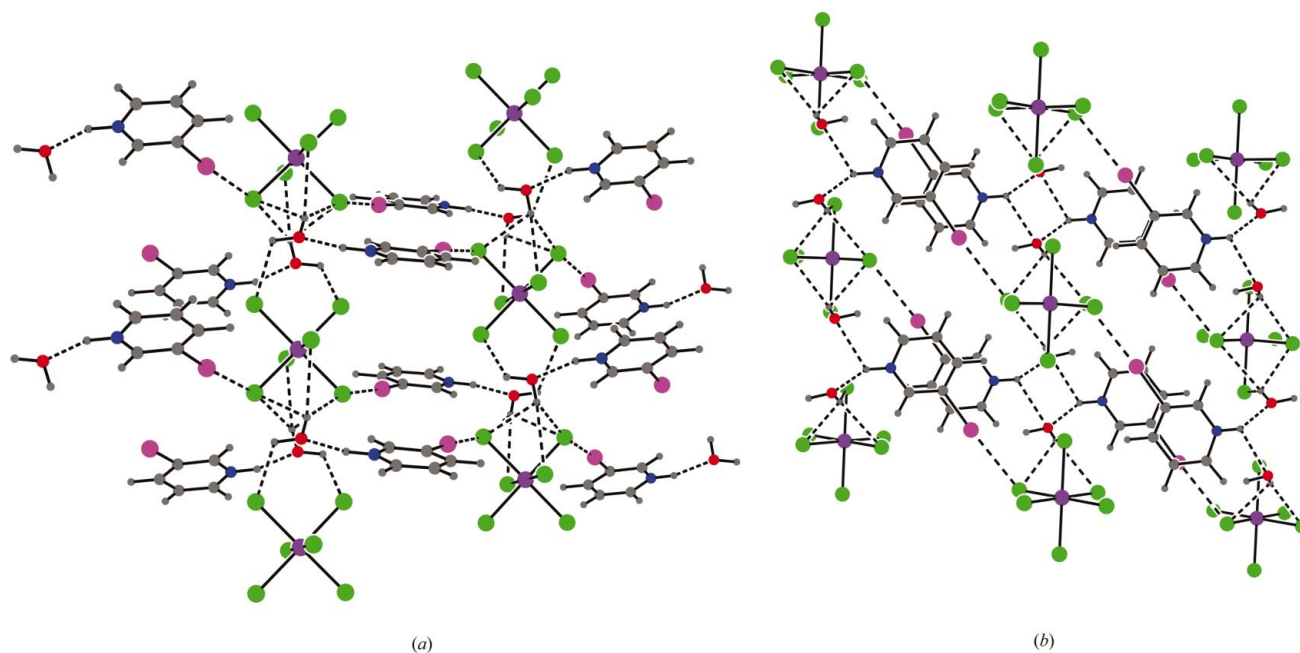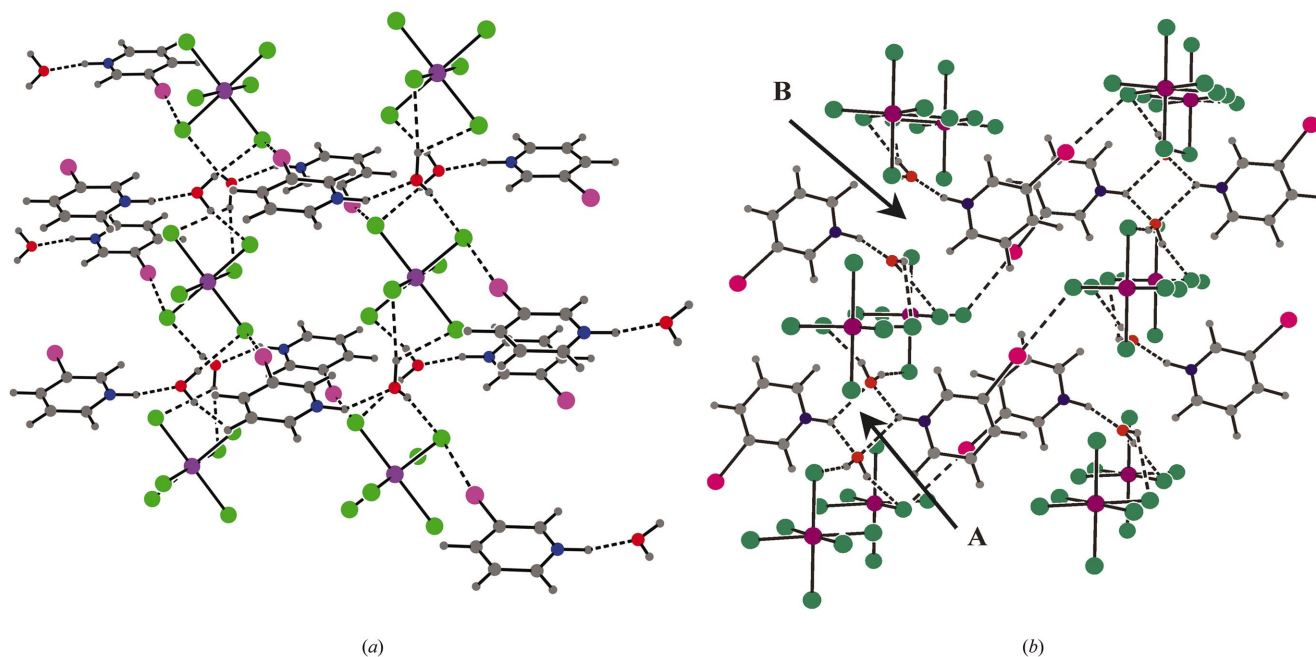

Figure 3
(a) Structure of (2a) showing O—H···Cl(Pt) and N—H···O hydrogen bonds, and Pt—Cl···I—C halogen bonds that link the molecular components within one layer of the network. Rows of anions lie along the b axis. (b) View of (2a) approximately down the b axis presenting three anion layers (horizontally) and illustrating the cation/water hydrogen-bonding arrangement and dipole-assisted cation stacking between anion layers.

stacked in pairs, the cations in (2a) are oriented perpendicular to the anion layer shown in Fig. 3. Layers within structure (2a) are more weakly linked via highly asymmetric bifurcation of the N—H···O hydrogen bond to involve water molecules in a neighbouring layer [minor component: (N)H···O 2.49 Å; N—H···O 119.1°] and through the dipole-assisted stacking of cations (see Hunter & Sanders, 1990; Janiak, 2000) associated with neighbouring layers (interplanar separations 3.47, 3.35 Å; inter-ring centroid–centroid distances 4.52, 3.86 Å, respectively). The calculated water H-atom positions suggest that the bridge formed between anions within a row is of the form $(Pt)Cl···H—O—H···Cl_3(Pt)$, i.e. involving interactions as shown in Figs. 2(a) and (c). Minor errors in the positions of the H atoms could potentially lead to some quantitative reinterpretation of specific O—H···Cl interactions, although the qualitative description, namely that water molecules interact with one cation and two anions via hydrogen bonds, would remain unchanged. Several C—H···Cl(Pt) interactions [(C)H···Cl(Pt) 2.59–2.84 Å with typical Pt—Cl···H interaction geometry far from linear (Brammer et al., 2001; Thallapally & Nangia, 2001)] also contribute to the overall packing of the crystal structure.

3.3. Crystal structure of $(HPyI-3)_2[PtCl_6]·2H_2O$ (2b)

The structure of (2b) is shown in Fig. 4 and shows many similarities but some key differences from the polymorphic form (2a). Notably, the symmetry is lower for (2b) [space group $P\bar{1}$ for (2b) versus $P2/n$ for (2a)] permitting the two independent cations and water molecules to adopt different interaction geometries. Similarly to that observed in (2a), rows of $[PtCl_6]^{2-}$ anions are linked via hydrogen bonding to the water molecules, with bridges between these hydrogen-bonded chains being provided by the 3-iodopyridinium cations through N—H···O hydrogen bonds to the water molecules [(N)H···O 1.72, 1.98 Å; N—H···O 161.3, 138.8°] and Pt—Cl···I—C halogen bonds involving anions from the neighbouring row [(Pt)Cl···I(C) 3.364, 3.422 Å; (Pt)Cl···I 116.8, 104.1°, Cl···I—C 170.9, 173.1°]. Again, as seen in (2a), all cation/water bridges link anions within the same layer giving a two-dimensional network and the cations are oriented perpendicular to the anion layer shown in Fig. 4(a). Layers within structure (2b) are again linked via bifurcation of the N—H···O hydrogen bonds to involve water molecules in a neighbouring layer. However, this arises in only one of the two independent cation/water pairings (A in Fig. 4b) and is a more symmetric bifurcation [minor component: (N)H···O 2.26 Å; N—H···O 127.7°; see (III), Fig. 5] than observed in (2a). The second cation/water pairing (B in Fig. 4b) plays an analogous structural role, but the water molecules are markedly further apart and the N—H···O hydrogen bonds can no longer be described as bifurcated [see (IV), Fig. 5]. Dipole-assisted stacking of cations associated with neighbouring layers also clearly contributes to the organization of the layers [inter-

(a)   (b)

Figure 4
(a) Structure of (2b) showing O—H···Cl(Pt) and N—H···O hydrogen bonds, and Pt—Cl···I—C halogen bonds that link the molecular components within one layer of the network. Rows of anions lie along the a axis, layers lie in the (011) plane. (b) View of (2b) approximately down the a axis showing three anion layers (horizontally) and the two types of cation/water hydrogen-bonding arrangement and dipole-assisted cation stacking between anion layers.

planar separations 4.60, 3.91 Å, inter-ring centroid–centroid distances 3.59, 3.38 Å, respectively].

The calculated water H-atom positions suggest that the bridge formed between anions within a row is of the form $(Pt)Cl\cdots H-O-H\cdots Cl_2(Pt)$ for one water molecule and $(Pt)Cl\cdots H-O-H\cdots Cl(Pt)$ for the other. Several C—H$\cdots$Cl(Pt) interactions [(C)H$\cdots$Cl(Pt) 2.61–2.86 Å with typical Pt—Cl$\cdots$H interaction geometry far from linear (Brammer *et al.*, 2001; Thallapally & Nangia, 2001)] also contribute to the overall packing of the crystal structure.

4. Discussion

4.1. The water molecules

Based upon previous studies (Brammer *et al.*, 2003; Willett *et al.*, 2003) it is anticipated that the anhydrous compounds (HPyBr-3)$_2$[PtCl$_6$] and (HPyI-3)$_2$[PtCl$_6$] would form crystals in which anions and cations were arranged in networks and linked *via* N—H$\cdots$Cl$_n$Pt (n = 1–3) hydrogen bonds and Pt—Cl$\cdots X'$—C halogen bonds (X' = Br, I). In this study the opportunity has arisen to examine the effect of inclusion of water molecules upon the anticipated interactions. By consideration of hydrogen bonds and halogen bonds in terms of Lewis acid–Lewis base interactions, one might anticipate that the water molecules should be capable in principle of expanding either the hydrogen bonding or halogen-bonding interaction *via* insertion, as shown in Fig. 6. Insertion of water molecules into hydrogen-bonded networks is well established, a common example being the expansion of the well known carboxylic acid hydrogen-bonded dimer through such insertion. Insertion into the halogen bond must also be considered since the two new interactions that would be formed are well established, namely O—H$\cdots$Cl(M) (Brammer *et al.*, 2001) and O$\cdots$Br—C or O$\cdots$I—C (Lommerse *et al.*, 1996) interactions.

Crystals of both compounds have been obtained as dihydrates, with two polymorphic forms of (HPyI-3)$_2$[PtCl$_6$]·2H$_2$O [(2*a*) and (2*b*)] being obtained under different conditions. These structures enable some insight into the role of the water molecule in these structures and in particular the interplay of the water molecule hydrogen-bond donor and acceptor functions with those of Lewis acidic functional groups of the cation (N—H and C—X', X' = Br, I) and the Lewis basic groups of the anion, *i.e.* the chloride ligands. In all three structures N—H$\cdots$Cl(Pt) hydrogen bonding is not observed and further-

more the water molecules are inserted exclusively into this putative hydrogen bond, as illustrated schematically in Fig. 6(*a*). However, the formation of the anticipated Pt—Cl$\cdots X'$—C halogen bonds (X' = Br, I) appears to be unaffected. In a related study of a hydrogen-bonded tetrachloroplatinate(II) compound, Angeloni & Orpen (2001) have observed the insertion of water molecules into the O—H$\cdots$O hydrogen bonds of a carboxylic acid dimer rather than into N—H$\cdots$Cl(Pt) hydrogen bonds linking cations and anions.

Simple inorganic hydrates have been comprehensively described and classified (Wells, 1984), and the Cambridge Structural Database (CSD; Allen, 2002) has been used to establish typical hydrogen-bonding motifs of water molecules in small biological molecules (Jeffrey & Maluszynska, 1990). A very recent study has also examined hydrogen-bonding patterns in hydrates of molecular organic compounds (Gillon *et al.*, 2003) and reflects great current interest in hydrates and solvates of pharmaceutical compounds. In the latter study three distinct hydrogen-bonding roles for water molecules have been found in molecular organic crystals:

(i) water is exclusively a donor or an acceptor forming only one hydrogen bond,

(ii) water is exclusively a donor or an acceptor forming two hydrogen bonds and

(iii) water is both a donor and an acceptor with two, three or four interactions with neighbouring molecules.

In the three structures described herein, the role of the water molecules falls into the last of these categories. In all cases the water molecules serve as hydrogen-bond donors to two separate [PtCl$_6$]$^{2-}$ anions, linking the anions in rows. Each water molecule also serves as a hydrogen-bond acceptor with either one or two cations as summarized in Fig. 5.
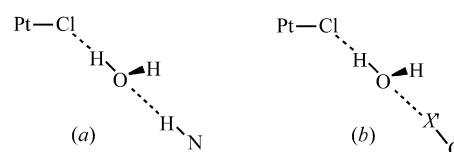
4.2. Halogen bonds

Halogen bonds (Pt—Cl$\cdots X'$—C, X' = Br, I) are formed in all three structures and provide a linkage between the cations and anions which is consistent with previous findings in the anhydrous salts of halopyridinium tetrachloro- and tetra-bromometallates (Brammer *et al.*, 2003; Willett *et al.*, 2003) and related to those observed for halopyridinium halides (Freytag *et al.*, 1999). The geometries of the halogen bonds are summarized in Table 2.

The two polymorphs of (HPyI-3)$_2$[PtCl$_6$]·2H$_2$O [(2*a*) and (2*b*)] exhibit Pt—Cl$\cdots$I–C halogen bonds that are 8–10% shorter than a simple van der Waals separation, but not as short as analogous Co—Cl$\cdots$I—C halogen bonds reported for
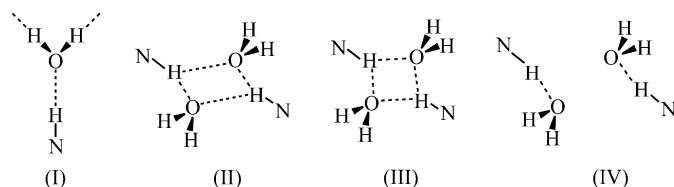
Figure 5
N—H$\cdots$O hydrogen-bonding patterns observed in structures (1), (2*a*) and (2*b*). Pattern (I) found in (1) (water molecules are well separated). Pattern (II) found in (2*a*) (O$\cdots$O separation 3.07 Å). Patterns (III) and (IV) found in (2*b*) (O$\cdots$O separations 3.00 and 4.55 Å, respectively).

Figure 6
Possible insertion of water molecules (*a*) into N—H$\cdots$Cl–Pt hydrogen bonds or (*b*) into Pt—Cl$\cdots X'$—C halogen bonds (X' = Br, I).

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Table 2
Halogen-bond geometries (Å, °).

Synthon	Compound	$Cl \cdots X'$ (R_{ClX})	$Pt—Cl \cdots X'$	$C—X' \cdots Cl$
$Pt—Cl \cdots Br—C$	(1)	3.521 (0.978)	157.1	145.7
$Pt—Cl \cdots I—C$	(2a)	3.352 (0.899)	109.8	176.1
$Pt—Cl \cdots I—C$	(2b)	3.364 (0.902)	116.8	170.9
$Pt—Cl \cdots I—C$	(2b)	3.422 (0.917)	104.1	173.1

$R_{ClX} = d_{ClX}/(r_{Cl} + r_X)$, where the $d_{ClX} = Cl \cdots X'$ distance and r_{Cl} and r_X are the van der Waals radii (Bondi, 1964) of Cl and X', respectively (see description in Lommerse et al., 1996).

(HPyI-3)$_2$[CoCl$_4$] ($d_{ClX} = 3.213, 3.430$ Å, $R_{ClX} = 0.868, 0.920$; Brammer et al., 2003), where a greater partial negative charge associated with the chloride ligands might be expected to enhance the interaction. The $Pt—Cl \cdots I—C$ geometries are consistent with the Lewis acidic behaviour by the C—I group of the cation (approximately linear $C—I \cdots Cl$) and Lewis basic behaviour of the chloride ligands of the anion (highly bent $Pt—Cl \cdots I$ angle). The bromopyridinium analogue (1), however, exhibits a $Pt—Cl \cdots Br—C$ halogen bond that is only 2% shorter than the van der Waals separation, suggesting a weaker interaction. The $C—Br \cdots Cl$ and $Pt—Cl \cdots Br$ angles lie between the Lewis acid and base geometric extremes found in (2a) and (2b), and are most likely distorted from the energetically optimum geometry for the $Pt—Cl \cdots Br—C$ interaction to accommodate other interactions within the crystal. Such geometric distortions are common in weaker intermolecular interactions as has been well studied in comparisons of weak hydrogen bonds involving C—H donors with stronger ones involving N—H or O—H donors (Steiner, 2002; Desiraju & Steiner, 1999).

Thus, the halogen bonds present structures uninterrupted by the presence of the water molecules. This is a valuable indication of the robustness of the $M—Cl \cdots X'—C$ interaction in the presence of competing interactions and lends support to the potential utility of such interactions as synthons in inorganic crystal engineering. Related, but more extensive competition reactions have been conducted by Metrangolo, Resnati and coworkers using strongly electron-accepting perfluorodiiodobenzene and perfluorodiiodoalkanes to establish the dominance of $N \cdots I—C$ and $O \cdots I—C$ halogen bonds over potentially competing $O—H \cdots N$ and $O—H \cdots O$ hydrogen bonds in organic co-crystal formation (Corradi et al., 2000).

Finally, it is interesting to note that there is also a close contact between chloride ligands of neighbouring anions in structures (2a) [(Pt)Cl$\cdots$Cl(Pt) 3.370 Å; $Pt—Cl \cdots Cl$ 165.7°] and (2b) [(Pt)Cl$\cdots$Cl(Pt) 3.366 Å; $Pt—Cl \cdots Cl$ 158.0°]. However, it is not anticipated to be attractive in nature due to the negative charge associated with the anions. The closest (Pt)Cl$\cdots$Cl(Pt) contact in (1) is 3.752 Å.

5. Conclusions

The compounds whose structures are discussed herein were obtained as a byproduct of our efforts to employ directional hydrogen bonds and/or halogen bonds in the systematic design and construction or organic inorganic hybrid crystalline materials (Brammer et al., 2002, 2003). As with any molecular crystal synthesis or crystallization from solution, solvent inclusion is a possibility if the solvent molecules are able to form suitable interactions with the other molecular components. All who are involved in crystal engineering or crystal preparation (e.g. pharmaceuticals) will have had to contend with this possibility. This study has provided an opportunity to assess the impact of water molecule inclusion in a class of halopyridinium perhalometallates in which the water molecule could interrupt (or expand) the anticipated hydrogen-bonding and/or halogen-bonding links between the cations and anions. We observe that the water molecules insert exclusively into the $N—H \cdots Cl—Pt$ hydrogen bonds while leaving the $Pt—Cl \cdots Br—C$ and $Pt—Cl \cdots I—C$ halogen bonds intact.

It is finally worth noting that two polymorphs of (HPyI-3)$_2$[PtCl$_6$]·2H$_2$O [(2a) and (2b)] were obtained under different solution conditions (different concentrations), although solution conditions have not been varied systematically to examine the range of conditions leading to each structure.

References

Aakeröy, C. B., Beatty, A. M. & Leinen, D. S. (1999). Angew. Chem. Int. Ed. **38**, 1815–1819.
Allen, F. H. (1986). Acta Cryst. B**42**, 515–522.
Allen, F. H. (2002). Acta Cryst. B**58**, 380–388.
Angeloni, A. & Orpen, A. G. (2001). Chem. Commun. pp. 343–344.
Beatty, A. M. (2001). CrystEngComm, **3**, 243–255.
Blake, A. J., Champness, N. R., Hubberstey, P., Li, W., Withersby, M. A. & Schröder, M. (1999). Coord. Chem. Rev. **183**, 117–138.
Blessing, R. H. (1995). Acta Cryst. A**51**, 33–38.
Bondi, A. (1964). J. Phys. Chem. **68**, 441–451.
Braga, D. (2000). J. Chem. Soc. Dalton Trans. pp. 3705–3713, and subsequent papers in issue 21, which is entirely devoted to inorganic crystal engineering.
Braga, D. (2003). Chem. Commun. pp. 2751–2754.
Braga, D. & Grepioni, F. (1999). J. Chem. Soc. Dalton Trans., pp. 1–8.
Brammer, L. (2003). Perspectives in Supramolecular Chemistry, Vol. 7: Crystal Design – Structure and Function, edited by G. R. Desiraju, pp. 1–75. New York: Wiley.
Brammer, L. (2004). Chem. Soc. Rev. In the press.
Brammer, L., Bruton, E. A. & Sherwood, P. (2001). Cryst. Growth Des. **1**, 277–290.
Brammer, L., Mareque Rivas, J. C., Atencio, R., Fang, S. & Pigge, F. C. (2000). J. Chem. Soc. Dalton Trans. pp. 3855–3867.
Brammer, L., Mínguez Espargallas, G. & Adams, H. (2003). CrystEngComm, **5**, 343–345.
Brammer, L., Swearingen, J. K., Bruton, E. A. & Sherwood, P. (2002). Proc. Natl. Acad. Sci. USA, **99**, 4956–4961.
Bruker AXS Inc. (1998). SHELXTL 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker AXS Inc. (2003a). SMART 5.040. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker AXS Inc. (2003b). SAINT 6.458/6/03. Bruker AXS Inc., Madison, Wisconsin, USA.

Coronado, E., Clemente-León, M., Galán-Mascarós, J. R., Giménez-Saiz, C., Gómez-García, C. J. & Martínez-Ferrero, E. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3955–3961.

Corradi, E., Meille, S. V., Messina, M. T., Metrangolo, P. & Resnati, G. (2000). *Angew. Chem. Int. Ed.* **39**, 1782–1786.

Dance, I. (1996). *Perspectives in Supramolecular Chemistry*, Vol 2: *The Crystal as a Supramolecular Entity*, edited by G. R. Desiraju, pp. 137–233. New York: Wiley.

Dance, I. & Scudder, M. (2000). *J. Chem. Soc. Dalton Trans.* pp. 1587–1594.

Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.

Desiraju, G. R. (2003). Editor. *Perspectives in Supramolecular Chemistry*, Vol. 7: *Crystal Design – Structure and Function.* Chichester, UK: Wiley.

Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*, IUCr Monographs on Crystallography 9. Oxford University Press.

Dolling, B., Gillon, A. L., Orpen, A. G., Starbuck, J. & Wang, X. (2001). *Chem. Commun.* pp. 567–568.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Freytag, M., Jones, P. G., Ahrens, B. & Fischer, A. K. (1999). *New J. Chem.* **23**, 1137–1139.

Gillon, A. L., Feeder, N., Davey, R. J. & Storey, R. (2003). *Cryst. Growth Des.* **3**, 663–673.

Gillon, A. L., Lewis, G. R., Orpen, A. G., Rotter, S., Starbuck, J., Wang, X., Rodríguez-Martín, Y. & Ruiz-Pérez, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3897–3905.

Hosseini, M. W. (2003). *Coord. Chem. Rev.* **240**, 157–166.

Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.

James, S. L. (2003). *Chem. Soc. Rev.* **32**, 276–288.

Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.

Janiak, C. (2003). *Dalton Trans.* pp. 2781–2804.

Jeffrey, G. A. & Maluszynska, H. (1990). *Acta Cryst.* B**46**, 546–549.

Kesanli, B. & Lin, W. (2003). *Coord. Chem. Rev.* **246**, 305–326.

Lewis, G. R. & Orpen, A. G. (1998). *Chem. Commun.* pp. 1873–1874.

Lommerse, J. P. M., Stone, A. J., Taylor, R. & Allen, F. H. (1996). *J. Am. Chem. Soc.* **117**, 3108–3116.

Mareque Rivas, J. C. & Brammer, L. (1998). *Inorg. Chem.* **37**, 4756–4757.

Metrangolo, P. & Resnati, G. (2001). *Chem. Eur. J.* **7**, 2511–2519.

Nardelli, M. (1999). *J. Appl. Cryst.* **32**, 563–571.

Sheldrick, G. M. (1995). *SADABS*. University of Göttingen, Germany; based upon the method of Blessing (1995).

Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.

Thallapally, P. K. & Nangia, A. (2001). *CrystEngComm*, **3**, 114–119.

Wells, A. F. (1984). *Structural Inorganic Chemistry*, 5th ed., ch. 15. Oxford University Press.

Willett, R. D., Awwadi, F., Butcher, R., Haddad, S. & Twamley, B. (2003). *Cryst. Growth Des.* **3**, 301–311.

Zaworotko, M. J. (2001). *Chem. Commun.* pp. 1–9.