

Control of hydrogen bond network dimensionality in tetrachloroplatinate salts†

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Received (in Cambridge, UK) 27th November 2000, Accepted 16th January 2001

First published as an Advance Article on the web 5th February 2001

Tetrachloroplatinate salts of 4,4-bipiperidinium, piperazinium and *N*-protonated isonicotinic acid or isonicotinamide show two-dimensional NH...Cl hydrogen bonds related in a rational way to the one-dimensional ribbon polymer network of [4,4'-H₂bipy][PtCl₄].

In the synthesis of crystal structures by design, the assembly of molecular units in predefined arrangements is a key goal.¹ Directional intermolecular interactions are the primary tools in achieving this goal and hydrogen bonding is currently the best among them.² We have shown³ that the chelate hydrogen bond moiety **A** (Scheme 1) is a useful supramolecular synthon^{1a,c} for the construction of crystal structure of perhalometallate salts of the 4,4'-bipyridinium dication. In these salts the motif **B** is observed, most clearly in [4,4'-H₂bipy][PtCl₄] **1** but also in cases where the MCl₄ species forms a chain polymer [4,4'-H₂bipy][MCl₄] (M = Mn, Cd, Pb).^{3c} In **1** the NH...Cl hydrogen bond network is one-dimensional (although there are longer CH...Cl contacts^{3c}) and the crystal structure can be viewed as arising from close packing of the **B**-type ribbons.³ To control the crystal structure more completely it is critical to be able to raise the dimensionality of the hydrogen bond networks in such structures in a rational and planned manner. In so doing we will probe the range of cations able to form **B**-type ribbons.

In the first instance we employed cations with two rather than one NH unit per charge starting with the saturated analogue of [4,4'-H₂bipy]²⁺, 4,4-bipiperidinium ([4,4'-H₂bipy]²⁺, **C**). On treatment of an aqueous solution of K₂[PtCl₄] with 4,4'-bipiperidine hydrochloride a crystalline salt [4,4'-H₂bipy][PtCl₄] **2** is formed.‡ The crystal structure of **2** has an

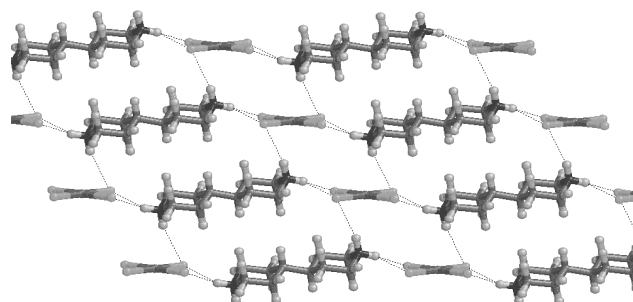
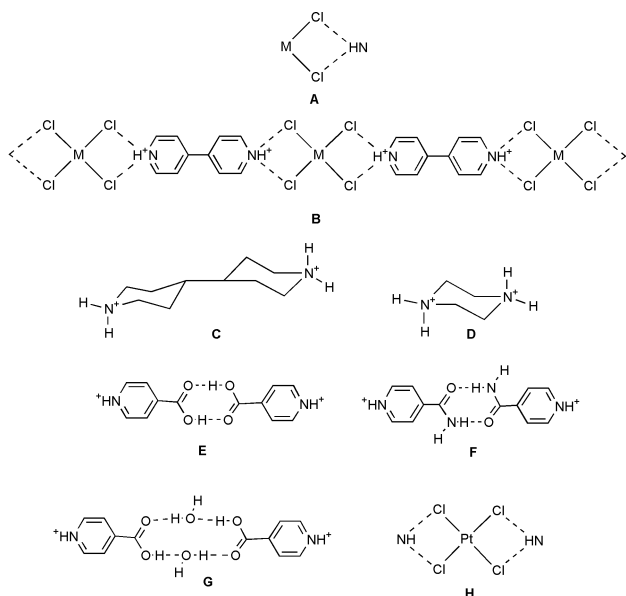


Fig. 1 Structure of the NH...Cl hydrogen bonded layer in crystalline [4,4'-H₂bipy][PtCl₄] **2**. The NH...Cl hydrogen bonds are indicated. Hydrogen bond lengths and angles include: in-ribbon NH...Cl 2.79 Å, N-H...Cl 132°, Pt-Cl...HN 89°; NH...Cl 2.45 Å, N-H...Cl 147°, Pt-Cl...HN 98°. Between ribbons: NH...Cl 2.55 Å, N-H...Cl 158°, Pt-Cl...HN 74°.

hydrogen bonded ribbon motif analogous to that of **1** (see Fig. 1). In addition to the chelate hydrogen bond of type **A** in the **B**-like ribbon, which is formed by the equatorial hydrogen at the nitrogens of the [4,4'-H₂bipy]²⁺ cation, a second NH...Cl interaction links parallel ribbons by NH...Cl bonds. The **B**-like ribbons are not flat as they are in **1** because of the chair form of the saturated bipiperidinium rings and the inter-ribbon distance is rather larger than in **1** (4.0 Å in **2** compared with 3.5 Å in **1**) as a consequence of the thicker cation in **2**. The chelate hydrogen bond is rather asymmetric in **2**, presumably because one of the chloride ligands involved is also forming a hydrogen bond to the axial NH hydrogen. It is this chloride which forms the longer NH...Cl contact in the **A**-type interaction. The net result is that the NH...Cl hydrogen bond network is two-dimensional. Although, as in **1**, each ribbon is surrounded by six near neighbours the ribbons in **2** are tilted with respect to the hydrogen bonded layers they form so that all ribbons within a layer are parallel but ribbons in adjacent layers are not parallel.

To probe the generality of the NH₂ hydrogen bond donor approach, we also prepared the piperazinium (**D** in Scheme 1) salt, [C₄H₁₂N₂][PtCl₄] **3** by a similar route.‡ In the crystal structure§ of **3** (Fig. 2) a two-dimensional NH...Cl hydrogen bond network results in which the **B**-like ribbons are more distorted from planarity than in **2**. Thus the type **A** chelate interaction is not planar (see Fig. 3) and is formed by the *axial* NH groups of the piperazinium (*cf.* **2** in which the equatorial NH groups are used). The NH...Cl bonds between **B**-type ribbons are only slightly longer than those within the rows (2.61 *cf.* 2.56 Å) and are also of the chelate type.

Clearly the replacement of the bipyridinium moieties of **1** by bipiperidinium or piperazinium does not prevent the formation of a **B**-type motif. We therefore sought to test other aspects of this motif for robustness by replacing part of the covalent framework of the bipyridinium cation with supramolecular units. Thus protonated isonicotinic acid and isonicotinamide were used in preparation of salts of [PtCl₄]²⁻ from acidic (HCl) aqueous solution in the expectation that supramolecular dications **E** and **F** would replace bipyridinium. In the case of **F**, additional NH hydrogen bond donor capability is available parallel to the plane of the supramolecular dication. In this way



Scheme 1

† Electronic supplementary information (ESI) available: syntheses of **2–5**. See <http://www.rsc.org/suppdata/cc/b0/b009515j/>

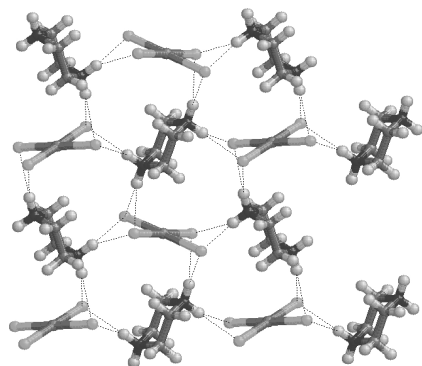


Fig. 2 The NH...Cl hydrogen bonded layer in crystalline [piperazinium][PtCl₄] **3**. The NH...Cl hydrogen bonds are indicated. Hydrogen bond lengths and angles include: in-ribbon (across page): NH...Cl 2.56 Å, N-H...Cl 141°, Pt-Cl...HN 87°. Between ribbons: NH...Cl 2.61 Å, N-H...Cl 141°, Pt-Cl...HN 69°.

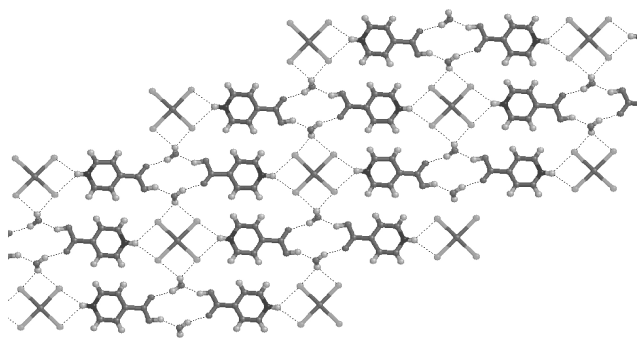


Fig. 3 The hydrogen bonded layer in crystalline [HNC₅H₄CO₂H-4]₂[PtCl₄]·2H₂O **4**. The NH...Cl, OH...Cl and OH...O hydrogen bonds are indicated. Hydrogen bond lengths and angles include: in-ribbon NH...Cl 2.45 Å, N-H...Cl 145°, Pt-Cl...HN 97°; NH...Cl 2.63 Å, N-H...Cl 134°, Pt-Cl...HN 92°; HOH...O(1) 1.90 Å, O-H...O 163°, H...O-C 133°; OH...OH₂ 1.74 Å, O-H...OH₂ 147°. Between ribbons: OH...Cl 2.63 Å, O-H...Cl 141°, Pt-Cl...HO 85°; OH...Cl 2.77 Å, O-H...Cl 145°, Pt-Cl...HO 82°.

the salts [HNC₅H₄CO₂H-4]₂[PtCl₄]·2H₂O **4** and [HNC₅H₄CONH₂-4]₂[PtCl₄] **5** were prepared[‡] and characterised by single crystal X-ray diffraction analyses.[§]

Both **4** and **5** contain B-type ribbons (see Fig. 3 and 4) with supramolecular dications in the chain as anticipated. However the incorporation of water in **4** was unexpected and instead of the R₂,2(8) cyclic dimer (**E**), the dihydrate variant (**G**) of this structure, is formed. Thus an R₄,4(12) supramolecular motif is incorporated in the B-type ribbon of **4** (see Fig. 3). As a result of water incorporation there is a pair of extra hydrogen bond donors present in the supramolecular dication **G** compared with **E**. In contrast **5** has the expected motif containing the classic amide dimer R₂,2(8) unit (see Fig. 4). As in **4** there are

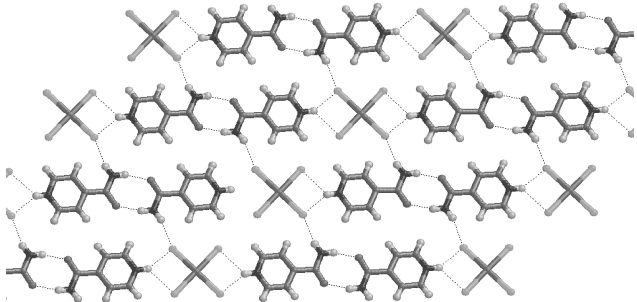


Fig. 4 The hydrogen bonded layer in crystalline [HNC₅H₄CONH₂-4]₂[PtCl₄] **5**. The NH...Cl and NH...O hydrogen bonds are indicated. Hydrogen bond lengths and angles include: in-ribbon NH...Cl 2.47 Å, N-H...Cl 146°, Pt-Cl...HN 97°; NH...Cl 2.60 Å, N-H...Cl 133°, Pt-Cl...HN 80°; NH...O 2.03 Å, N-H...O 161°, NH...O-C 124°. Between ribbons: NH...Cl 2.58 Å, N-H...Cl 156°, Pt-Cl...HN 144°.

additional acidic hydrogens (OH in **4** and NH in **5**) available to cross-link the ribbons. In **4** the spare OH is inclined at 59° to the plane of the ribbon, while in **5** the spare NH bond is near coplanar with the ribbon. As a consequence the resultant cross-linked ribbons are of pleated and planar form in **4** and **5**, respectively.

These results establish:

- (1) The robustness of motif **A** in its doubled form **H**; both saturated and aromatic cationic NH donors are compatible with this supramolecular synthon.
- (2) The robustness of the periodic structural motif **B** with respect to the nature of the framework to which the NH group(s) are attached, whether saturated or aromatic, molecular or supramolecular. Furthermore the metric of this motif is very flexible, the repeat distance along the B-like ribbon in **1** is 15.76 Å while in **2–5** it is 15.87, 10.15, 23.38 and 21.32 Å, respectively.
- (3) That the presence of additional hydrogen bond donors, beyond those required to form interaction **H** or to form the supramolecular dications of **4** and **5**, may be exploited to add dimensionality to the NH...Cl hydrogen bond network in a rational manner.

Financial support of the EPSRC and the Royal Society and the Leverhulme Trust (a Royal Society Leverhulme Trust Senior Research Fellowship for A. G. O.) is gratefully acknowledged.

Notes and references

[‡] *Syntheses of 2–5*. Details are given in ESI[†]. In general, stoichiometric amount of the nitrogen base (or its hydrochloride) dissolved in aqueous HCl was added to an aqueous solution of K₂PtCl₄ and crystalline samples grown from solution. For **5** this yielded a mixture of products, presumably as a result of hydrolysis of the isonicotinamide. A sample of crystalline **5** was obtained by hand selection of crystals.

[§] *Crystal structure analyses of 2–5*: Crystal data: [4,4'-H₂bipip][PtCl₄] **2**, C₁₀H₂₂Cl₄N₂Pt, *M* = 507.19, monoclinic, space group *P*2₁/*n* (no. 14), *a* = 5.9922(11), *b* = 10.766(3), *c* = 11.601(2) Å, β = 95.545(12)°, *U* = 744.9(3) Å³, *Z* = 2, μ = 10.117 mm⁻¹, *T* = 173 K, 1700 unique data, *R*₁ = 0.018. [piperazinium][PtCl₄] **3**, C₈H₁₂Cl₄N₂Pt, *M* = 425.05, orthorhombic, space group *Cmca* (no. 64), *a* = 12.0729(24), *b* = 8.6976(28), *c* = 10.1510(25) Å, *U* = 1065.9(4) Å³, *Z* = 4, μ = 14.112 mm⁻¹, *T* = 173 K, 646 unique data, *R*₁ = 0.016. [HNC₅H₄CO₂H-4]₂[PtCl₄]·2H₂O **4**, C₁₂H₁₆Cl₄N₂O₆Pt, *M* = 507.19, triclinic, space group *P*1̄ (no. 2), *a* = 6.9551(13), *b* = 8.5188(12), *c* = 8.9795(10) Å, α = 86.462(13), β = 73.017(9), γ = 66.472(10)°, *U* = 465.61(11) Å³, *Z* = 1, μ = 8.139 mm⁻¹, *T* = 173 K, 2114 unique data, *R*₁ = 0.019. [HNC₅H₄CONH₂-4]₂[PtCl₄] **5**, C₁₂H₁₄Cl₄N₂O₂Pt, *M* = 583.16, triclinic, space group *P*1̄ (no. 2), *a* = 6.8888(13), *b* = 7.7068(18), *c* = 8.2032(15) Å, α = 88.779(15), β = 72.911(19), γ = 89.466(19)°, *U* = 416.19(15) Å³, *Z* = 1, μ = 9.083 mm⁻¹, *T* = 173 K, 1900 unique data, *R*₁ = 0.018. In **2**, **4** and **5** the metal atoms lie at sites of C_i symmetry as does the dication in **2**. In **3** both cations and anions lie at sites of C_{2h} symmetry. All hydrogen atoms were located in difference maps and included in idealised positions except for OH group hydrogens in **4** which were refined without constraints. CCDC 154209–54212. See <http://www.rsc.org/suppdata/cc/b0/b009515j/> for crystallographic data in .cif or other electronic format.

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