A metal-containing synthon for crystal engineering: synthesis of the hydrogen bond ribbon polymer $[4,4'\text{-}H_2bipy][MCl_4]$ (M = Pd, Pt)

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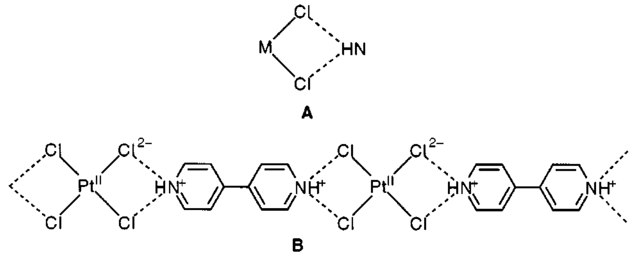
The utility of the *cis*-$MCl_2\cdots HN^+$ chelated hydrogen bond as a synthon in preparation of crystalline $[4,4'\text{-}H_2bipy][MCl_4]$ (M = Pd 1, Pt 2) is demonstrated; the structure of 2 contains anions and cations linked by hydrogen bonds to form a ribbon polymer.

Desiraju[1] and others[2] have argued persuasively that crystal engineering or synthesis may be a realistic goal for modern chemistry. The means to this goal is the identification and application of reliable synthons which can control molecular aggregation and lead to crystal structures with (partly) controlled structures, containing sheets, ribbons and other desired motifs in the pattern formed. The synthons listed[1,2] and used to date are drawn in the main from the field of organic chemistry and almost all exploit the directionality of hydrogen bonds to afford the desired control of aggregation. The ability to incorporate metals in the structure offers promise of novel functionalities (chemical, magnetic, optical or electronic) which complement those available in purely organic molecular crystals. Here, we show that the metal assisted hydrogen bond affords a new class of synthon, one which may yield both desirable structures and desirable properties.

Recently,[3] we reported a crystallographic database analysis which demonstrated the ability of metal chloride complexes to act as hydrogen bond acceptors, as others had noted in specific examples.[4] Our study showed that these metal-assisted hydrogen bonds typically showed $M–Cl\cdots H$ angles of between 90 and 120°. The geometry at the hydrogen in these systems is normal[5] with all the shorter $M–Cl\cdots HE$ (E = N, O) bonds having $E–H\cdots Cl \geqslant 140°$. These geometric preferences are compatible with the formation of acceptor chelate hydrogen bonds in which a pair of *cis*-chloride ligands at a metal form a chelate hydrogen bond with a single H–N moiety (see **A** in Scheme 1). Indeed, such an interaction in $[HNC_5H_3Ph_2][AuCl_4]$ has attracted attention.[4a]



Scheme 1

We therefore sought to establish the utility of the *cis*-$MCl_2\cdots HN$ interaction (**A** in Scheme 1) as a synthon for the preparation of a hydrogen bonded polymer (**B** in Scheme 1) incorporating both inorganic ($[MCl_4]^{2-}$) and organic ($[4,4'\text{-}H_2bipy]^{2+}$) components. The planarity and opposite charges of the component ions led us to expect the formation of planar polymeric ribbons of type **B** shown in Scheme 1.

Reaction of aqueous $[MCl_4]^{2-}$ salts (M = Pd or Pt) with $[4,4'\text{-}H_2bipy][PF_6]_2$ leads to instantaneous formation of crystalline precipitates $[4,4'\text{-}H_2bipy][MCl_4]$ (M = Pd **1**, Pt **2**).† Single crystal structure analysis‡ of **2** shows the desired structure has indeed been formed (Fig. 1). The component ions have normal, planar geometries with exact C_{2h} symmetry. The $N–H\cdots Cl$ bonds are of dimensions (N–H 0.86 Å, $H\cdots Cl$ 2.51 Å, $N\cdots Cl$ 3.219 Å; $N–H\cdots Cl$ 140°, $Pt–Cl\cdots H$ 95°) similar to those typically observed in our database study.[3] The anion$\cdots$cation$\cdots$anion$\cdots$cation$\cdots$ ribbons formed are planar (mean atomic deviation 0.038 Å) and all ribbons lie parallel to one another although they are not coplanar. The ribbons lie perpendicular to the crystallographic mirror planes and extend along $2x - z$. Each ribbon lies 5.81 Å above its face-to-face neighbour and is in closer contact with four other ribbons through edge-to-edge interactions ($CH\cdots Cl$ 2.84 Å, $Cl\cdots Cl$ 3.510 Å, Fig. 2). This apparently efficient packing is presumably facilitated by the planarity of the component ions.

That this synthon may have some general applicability is indicated by the similarity of the structure of **2** and those of $[4,4'\text{-}H_2bipy][Cu_2(\mu\text{-}X)_2X_4]$ (X = Cl **3**;[6] X = Br **4**[7]). In crystalline **3** and **4**, which were prepared for rather different reasons, hydrogen bonded ribbon motifs are present. In contrast, the structure[8] of $[4,4'\text{-}H_2bipy][CoCl_4]$ is markedly different with the tetrahedral $[CoCl_4]^{2-}$ units forming two-centre

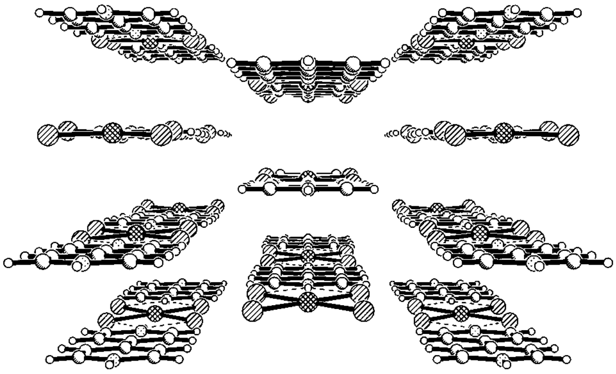


Fig. 2 The crystal structure of $[4,4'\text{-}H_2bipy][PtCl_4]$ **2**.

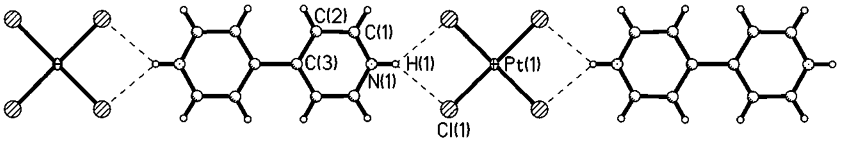


Fig. 1 Structure of one polymeric ribbon in crystalline $[4,4'\text{-}H_2bipy][PtCl_4]$ **2**.

Cl···HN interactions in a dimeric cyclic [4,4-H_2bipy]$_2$[$CoCl_4$]$_2$ motif.

The utility of the *cis*-MCl_2···HE (E = O, N) synthon, the effect of the charges and geometry of the component species, the consequent structures formed and their properties are under investigation.

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Notes and References

† *Synthesis* of [4,4′-H_2bipy][MCl_4] (M = Pd **1**, Pt **2**): addition of a colourless solution of [4,4′-H_2bipy][PF_6]$_2$ (156 mg, 0.347 mmol) in H_2O (10 cm^3) to a brown solution of $Na_2PdCl_4 \cdot 1/3H_2O$ (101 mg, 0.335 mmol) in H_2O (6 cm^3) caused the formation of a light brown insoluble precipitate of **1**. The product was washed with H_2O and dried *in vacuo*, yield 121 mg (88%). Orange crystalline compound **2** was prepared similarly from [4,4′-H_2bipy][PF_6]$_2$ and K_2[$PtCl_4$], yield 83%. Both complex salts gave satisfactory microanalytical data.

‡ *Crystal structure analysis* of [4,4′-H_2bipy][$PtCl_4$] **2**. The crystal structure of **2** was determined from data collected on a Siemens SMART diffractometer (λ = 0.6978 Å) at 160 K on station 9.8 at the Daresbury SRS. The structure was refined by least-squares against all F^2 data corrected for absorption, and hydrogen atoms were located in difference maps. *Crystal data*: [4,4′-H_2bipy][$PtCl_4$], $C_{10}H_{10}Cl_4N_2Pt$, M = 495.09, monoclinic, space group $I2/m$ (no. 15), a = 6.6172(3), b = 11.6264(6), c = 8.0962(5) Å, β = 91.266(2)°, U = 622.76(6) Å^3, Z = 2, μ = 12.10 mm^{-1}, 512 unique data, $R1$ = 0.034. CCDC 182/946.

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