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Homologous families of chloride-rich 4,4′-bipyridinium salt structures†

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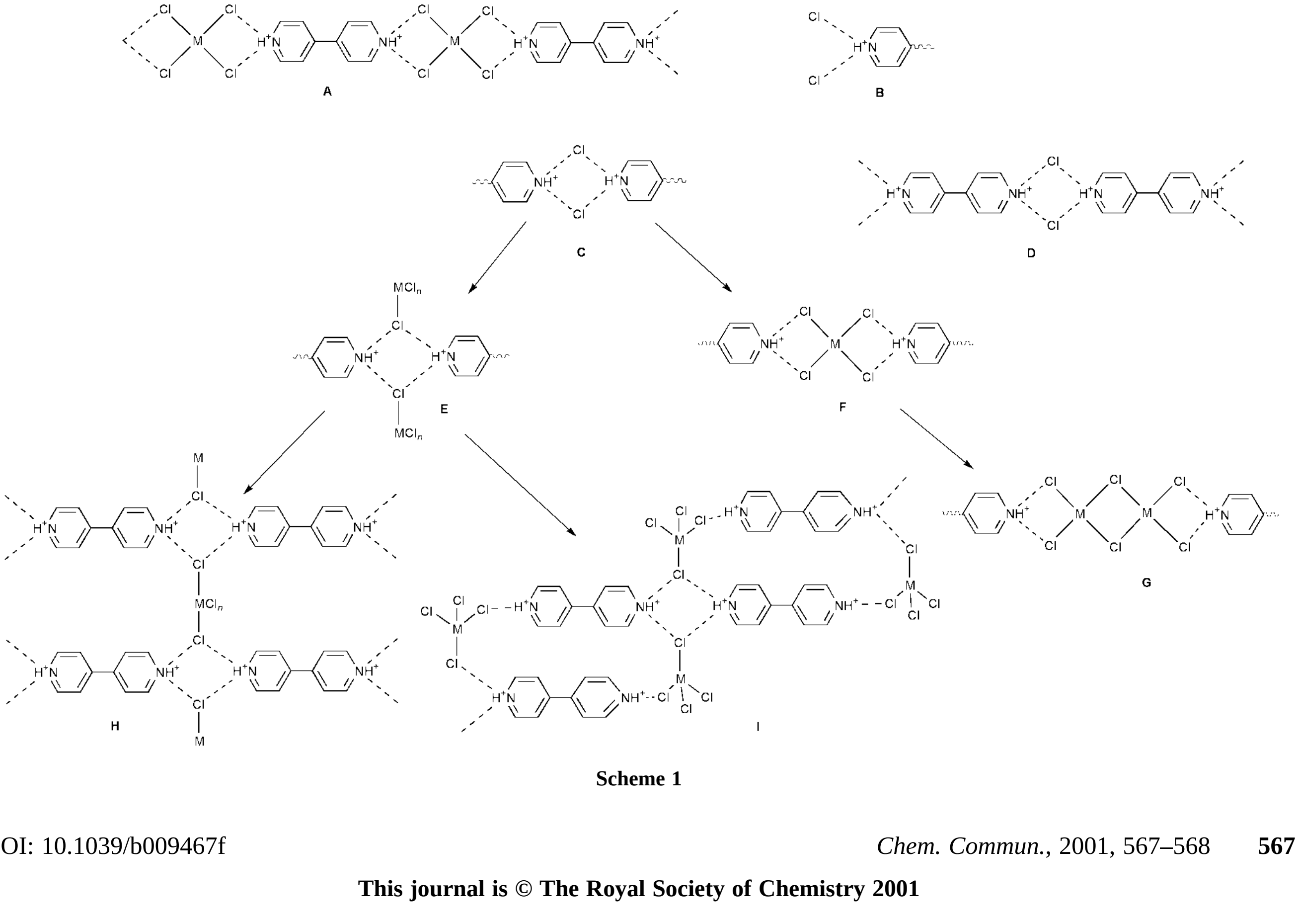
New layer and three-dimensional 4,4′-bipyridinium salts of Cl^-, $[MCl_6]^{2-}$ (M = Os, Pt) and $[FeCl_5]^{2-}$ contain $NH\cdots(Cl)_2\cdots HN$ interactions which form hydrogen bonded ribbons which in turn give one-, two-, or three-dimensional periodic networks; two related families of homologous motifs are present in these salts together with those of square planar, polymeric and tetrahedral $[MCl_4]^{2-}$ (M = Pt, Pd, Mn, Cd, Pb, Co, Zn, Hg), planar $[Cu_2Cl_6]^{2-}$ and square pyramidal $[SbCl_5]^{2-}$ dianions.

In the search for reliable strategies for crystal synthesis by design a key goal is the identification and exploitation of robust synthons[1] to control the relative orientation of the molecular components of the solid. While such local interactions (such as hydrogen bonds) may be necessary they may not be sufficient to afford control over the crystal structure or even the periodic network formed by synthons. Various possibilities may exist in which the same synthons are present but different although related structures form. In this paper we explore the relationships between the structures formed by complex salts containing similar molecular components and having closely related hydrogen bond-based synthon networks.

We have shown that chlorometallate anions and other metal chloride complexes are good hydrogen bond acceptors.[2] This has enabled preparation of three classes of tetrachlorometallate salts of stoichiometry $[4,4'\text{-}H_2bipy][MCl_4]$.[3] For square planar anions $[MCl_4]^{2-}$ (M = Pt, Pd), linear hydrogen bonded ribbons of type **A** are formed (see Scheme 1). When M = Pb, Mn or Cd the $[MCl_4]^{2-}$ moiety is polymerised and the zig-zag edge-sharing octahedral chains formed are cross-linked by hydrogen bonds to form **A**-type periodic motifs. The third family of structures has tetrahedral anions $[MCl_4]^{2-}$ (M = Zn, Co, Hg). Here we report that the simplest chlorine-containing salt of $[4,4'\text{-}H_2bipy]^{2+}$, $[4,4'\text{-}H_2bipy]Cl_2$ **1** itself, has a structure which presages the $NH\cdots Cl$ motifs in a large number of more complex chlorometallate salts. These more complex structures may be regarded as part of homologous families of structures formally derived from that of the chloride salt.

Treatment of metal chloride salts with aqueous HCl solutions of 4,4′-bipyridine led to isolation of crystalline salts **2–4**‡ whose single crystal structures were determined.§ Crystals of **2** and **3** are strictly isostructural and, as expected, have metal ions in essentially regular octahedral coordination. Compound **4** contains the rare trigonal bipyramidal $[FeCl_5]^{2-}$ ion, which has not apparently previously been obtained from aqueous media.[4] Presumably its isolation in this case is due to its stabilisation in the solid state through the network of hydrogen bonds formed (see below). The bipyridinium ions $[4,4'\text{-}H_2bipy]^{2+}$ in **1–4** have normal geometries.

All of these structures contain motif **B**, in a doubled form, **C**, as do the $[4,4'\text{-}H_2bipy]$ salts of the tetrahedral $[MCl_4]^{2-}$ anions (M = Zn, Co, Hg) **5–7**.[3c] The dimensions of units **B** are given in Table 1 for **1–4** and **5–7**[3c] and $[4,4'\text{-}H_2bipy][PtCl_4]$ **8**.[3c] They show some variation in geometry, notably for **5–7**, in which one of the $NH\cdots Cl$ contacts is *ca.* 3 Å. In **1**, ribbons of type **D** are formed because interaction **C** is present at both ends of the bipyridinium ion. The same **D**-type ribbons are present in the



Scheme 1

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† Electronic supplementary information (ESI) available: synthesis details for **1–4**, crystal refinement details and colour structures for **1**, **2** and **4**. See http://www.rsc.org/suppdata/cc/b0/b009467f/

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Table 1 Selected hydrogen bond[ab] lengths, angles and Cl···Cl distances in crystals of [4,4′-H$_2$bipy]Cl$_2$ **1** and [4,4′-H$_2$bipy][MCl$_6$] **2**, **3**, [4,4′-H$_2$bipy][MCl$_5$] **4**, [4,4′-H$_2$bipy][MCl$_4$] **5**–**8**† (see ref. 3*c*)

	1	**2** (M = Os)	**3** (M = Pt)	**4** (M = Fe)	**5** (M = Zn)	**6** (M = Co)	**7** (M = Hg)	**8** (M = Pt)
Cl···HN/Å	2.49, 2.51	2.59	2.59	2.54, 2.54	2.30,[c] 2.63, 3.04	2.32,[c] 2.63, 3.06	2.28,[c] 2.74, 2.93	2.40
M–Cl···HN/°	—	127	126	131, 135	116,[c] 91, 91	116,[c] 91, 91	112,[c] 88, 86	92
MCl···H–N/°	131, 132	143	144	137, 137	156,[c] 139, 123	156,[c] 140, 123	162,[c] 136, 125	136
Cl···Cl/Å	3.744	3.107	3.044	3.461	4.267	4.264	4.250	3.250

[a] Only Cl···HN contacts < 3.15 Å are listed.[2] Other hydrogen bonds (notably Cl···HC)[5] are omitted for brevity. [b] Values quoted for hydrogen bonds are based on hydrogen atom positions determined by X-ray diffraction. [c] Two-centre interaction, not involved in **C**-type interaction.

structures of **2**, **3** and **4** albeit in a form in which the chloride is also bonded to a metal ion (*i.e.* as in **E**). Ribbons **A** are present in [4,4′-H$_2$bipy][MCl$_4$] for M = Pt, Pd, Mn, Cd and Pb,[3c] in which the pair of Cl$^-$ ions in **D** are replaced by a planar MCl$_4$ moiety (see **F**). In [4,4′-H$_2$bipy][Cu$_2$Cl$_6$][6] (see **G**) the planar anion contains two square planar metals and takes the place of the two chlorides in **D**. Therefore, **G** may be regarded as the next higher homologue in the sequence **D**, **F**, **G**.

In **2**–**4** ribbons of type **D** are cross-linked by the metal ions (see **E** and **H**) so that *trans* chlorides at the metal belong to different ribbons. In the isostructural salts **2** and **3** these chains are parallel and coplanar and therefore neutral layers are formed (see Fig. 1). These contain a (4,4) network[7] with motif **E** at the nodes and equal numbers of organic (bipyridyl) and inorganic (metal) connections. In **4** the trigonal bipyramidal [FeCl$_5$]$^{2-}$ dianions link ribbons inclined at 55° to one another and a three-dimensional structure results in which there are two sets of criss-cross **D**-type ribbons (see Fig. 2) with every second ribbon parallel and coplanar. The network formed here is of the rare CdSO$_4$ type in which nodes of square-planar connectivity (here motif **E**) are linked in a three-dimensional manner.[8,9] Salts **5**–**7** also contain motif **C** but as part of a double-stranded chain (see **I**) in which only one end of the dication is engaged in a **C**-type interaction, the other forming a short, two-centre hydrogen bond with just one chloride ligand (see ref. 3*c* for further details on this interaction). Finally, it is striking that of the two known polymorphs[10] of the [4,4′-H$_2$bipy] salt of the square pyramidal anion [SbCl$_5$]$^{2-}$ one has layers of form **H** and the other contains ribbons of type **A**.

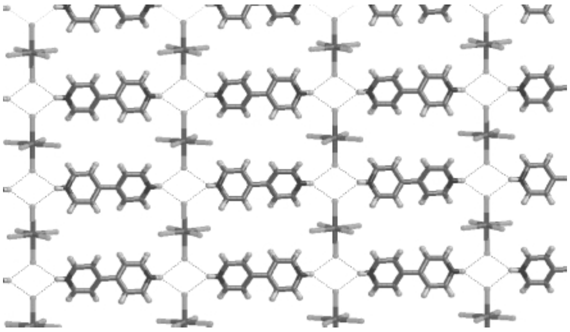

Fig. 1 A hydrogen bonded layer present within the crystal structure of [4,4′-H$_2$bipy][OsCl$_6$] **2**. Compound **3** is isostructural with **2**.

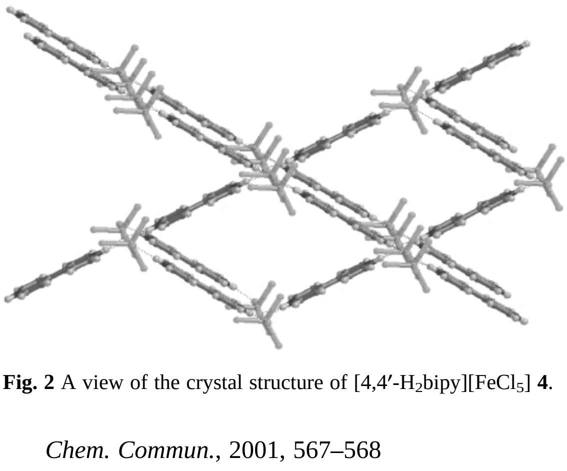

Fig. 2 A view of the crystal structure of [4,4′-H$_2$bipy][FeCl$_5$] **4**.

Indeed, all of the perchlorometallate [4,4′-H$_2$bipy] salts whose structures are known to us (as judged by the content of the current release of the Cambridge Structural Database[11] and as reported or cited here) incorporate motif **C**.

The recurrence of motif **C**, in periodic motif **D** and the derived **F–I** in this range of structures (and various analogous bromide salts)[3] implies that **C** is a robust feature of such salts.

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Notes and references

‡ Full synthesis details and crystal refinement details for **1**–**4** are given as ESI.† *Synthesis* of **2**–**4**: a stoichiometric amount of 4,4′-bipy dissolved in aqueous HCl was added to an aqueous solution of the metal chloride in air, and crystalline samples grown from solution. In the case of **4** this yielded a mixture of iron(III) containing products, presumably as a result of aerial oxidation of the ferrous chloride used. A sample of crystalline **4** was obtained by hand selection of crystals.

§ *Crystal data*: for [4,4′-H$_2$bipy]Cl$_2$ **1**: C$_{10}$H$_{10}$Cl$_2$N$_2$, M = 229.1, monoclinic, space group *C*2/*c* (no. 15), a = 12.687(4), b = 12.0981(19), c = 7.0707(17) Å, β = 112.565(18)°, U = 1002.2(4) Å^3, Z = 4, μ = 0.605 mm^{-1}, T = 173 K, 1151 unique data, *R*1 = 0.026. For [4,4′-H$_2$bipy][OsCl$_6$] **2**: C$_{10}$H$_{10}$Cl$_6$N$_2$Os, M = 561.10, orthorhombic, space group *Ibam* (no. 72), a = 7.3602(10), b = 12.8184(18), c = 15.606(2) Å, U = 1472.3(3) Å^3, Z = 4, μ = 9.734 mm^{-1}, T = 173 K, 883 unique data, *R*1 = 0.024. For [4,4′-H$_2$bipy][PtCl$_6$] **3**: C$_{10}$H$_{10}$Cl$_6$N$_2$Pt, M = 565.99, orthorhombic, space group *Ibam* (no. 72), a = 7.4757(17), b = 12.837(2), c = 15.362(2)Å, U = 1474.2(5) Å^3, Z = 4, μ = 10.590 mm^{-1}, T = 173 YK, 884 unique data, *R*1 = 0.017. For [4,4′-H$_2$bipy][FeCl$_5$] **4**; C$_{10}$H$_{10}$Cl$_5$N$_2$Fe, M = 391.30, orthorhombic, space group *Ama2* (no. 40), a = 16.651(2), b = 11.6816(15), c = 7.2764(10) Å, U = 1415.3(3) Å^3, Z = 4, μ = 1.990 mm^{-1}, T = 173 K, 1671 unique data, *R*1 = 0.029. CCDC 154205–154208. See http://www.rsc.org/suppdata/cc/b0/b009467f/ for crystallographic data in .cif or other electronic format.

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