

# Cation-controlled formation of $[\{MCl_4\}_n]^{2n-}$ chains in $[4,4'\text{-H}_2\text{bipy}][MCl_4]$ ( $M = \text{Mn}, \text{Cd}$ ): an alternative to the $A_2MCl_4 <100>$ layer perovskite structure†

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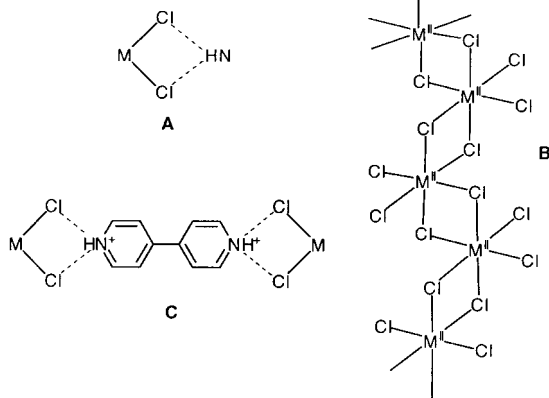
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The *cis*- $MCl_2 \cdots HN^+$  chelated hydrogen bond synthon has been exploited in preparation of crystalline  $[4,4'\text{-H}_2\text{bipy}][MCl_4]$  ( $M = \text{Mn}$  **2** and  $\text{Cd}$  **3**), which shows a one-dimensional substructure of the form  $[\{MCl_4\}_n]^{2n-}$  consisting of a kinked chain of doubly edge sharing  $MCl_6$  octahedra. These chains are cross-linked by hydrogen bonding to the  $[4,4'\text{-H}_2\text{bipy}]^{2+}$  ions.

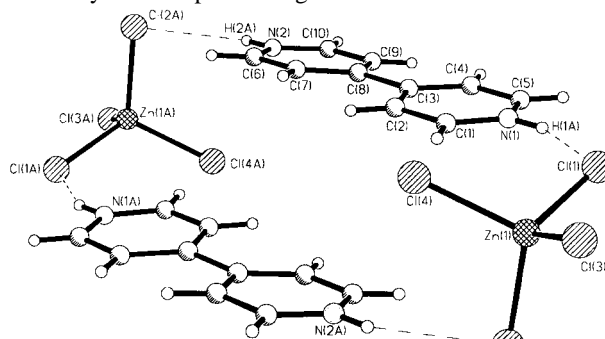
The  $<100>$  layer perovskites  $A_2MX_4$  ( $A =$  ammonium cation  $NH_3R^+$  or  $A_2 = NH_3(CH_2)_nNH_3^{2+}$ , etc.;  $M = \text{Cr}^{II}, \text{Mn}^{II}, \text{Cu}^{II}, \text{Cd}^{II}, \text{Pb}^{II}$ , etc.;  $X = \text{Cl}$  or other halide) have attracted sustained interest because of their magnetic, electronic and other physical properties and the possibility of tuning both geometry and properties by variation of the organic cation.<sup>1</sup> The hydrogen bond donor properties of the ammonium ions serve to promote the formation of two-dimensional  $[\{MCl_4\}_n]^{2n-}$  sheets, whose structure may be formally derived from that of cubic perovskite. We have previously shown that the *cis*- $MCl_2 \cdots HN^+$  supramolecular synthon **A** may be used to construct a hydrogen bonded



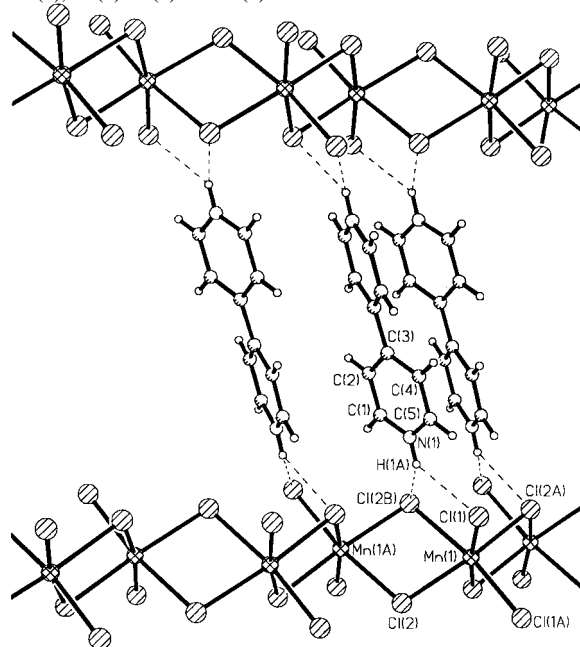
polymeric ribbon structure  $[\{4,4'\text{-H}_2\text{bipy}\}[MCl_4]]_n$  for  $M = \text{Pt}^{2+}$  while a hydrogen bonded dimeric ring motif is formed for  $M = \text{Co}$ .<sup>3</sup> Here, we show that a third family of structures exists of stoichiometry  $[4,4'\text{-H}_2\text{bipy}][MCl_4]$  in which the tetrachlorometallate anions polymerise to form a one-dimensional chain. This form contrasts both with the two other structure types and with the layer perovskite structures seen for primary ammonium salts of the same dianions.

In exploring the range of metals for which  $[4,4'\text{-H}_2\text{bipy}]^{2+}$  salts of  $[MCl_4]^{2-}$  ions form the dimeric ring structure we obtained crystals of  $[4,4'\text{-H}_2\text{bipy}][MCl_4]$  ( $M = \text{Zn}$  **1** and  $\text{Mn}$  **2**) by routes in which the metal halides were crystallised from aqueous solution in the presence of 4,4'-bipyridinium and chloride ions.† The zinc species§ is isostructural (Fig. 1) with its cobalt analogue and shows  $NH \cdots Cl$  hydrogen bonds of length 2.30 and 2.63 Å.<sup>3</sup> The manganese species has a quite different structure (Fig. 2) in which the metals are octahedrally

coordinated and the  $MnCl_6$  octahedra are linked into kinked chains (as in the  $ZrCl_4$  structure **B**<sup>4</sup>) which extend along the crystallographic  $c$  axis. The  $[\{MCl_4\}_n]^{2n-}$  chains are linked by  $NH \cdots Cl$  hydrogen bonding to  $[4,4'\text{-H}_2\text{bipy}]^{2+}$  into neutral sheets lying parallel to the  $ac$  plane. In these sheets synthon **A** is used at both ends of the dication (see **C** and Fig. 2). The neutral layers then pack along the  $b$  axis to form the overall

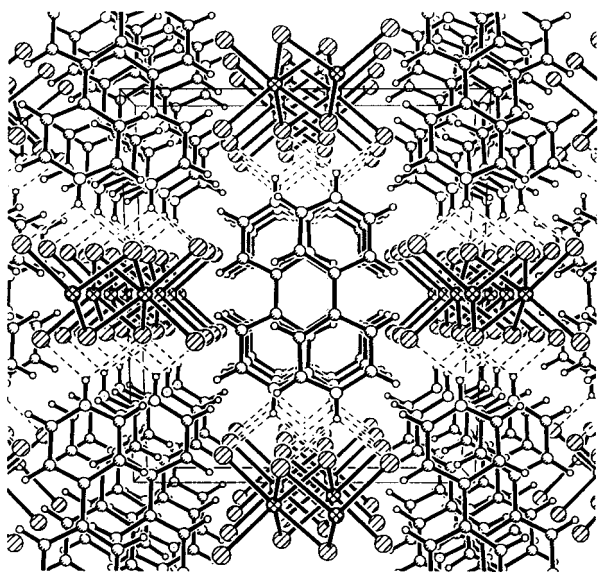


**Fig. 1** Structure of the hydrogen bonded dimeric ring in  $[4,4'\text{-H}_2\text{bipy}][ZnCl_4]$  **1**. The  $NH \cdots Cl$  hydrogen bonds are indicated. Important bond lengths (Å):  $Zn(1)-Cl(1)$  2.2934(7),  $Zn(1)-Cl(2)$  2.2977(8),  $Zn(1)-Cl(3)$  2.2526(7),  $Zn(1)-Cl(4)$  2.2546(7).



**Fig. 2** Structure of a layer of  $[MnCl_4]$  chains cross-linked by  $[4,4'\text{-H}_2\text{bipy}]$  in crystalline  $[4,4'\text{-H}_2\text{bipy}][MnCl_4]$  **2**. The  $NH \cdots Cl$  hydrogen bonds are indicated. Important bond lengths (Å):  $Mn(1)-Cl(1)$  2.4904(6) [2.5733(8)],  $Mn(1)-Cl(2)$  2.6294(6) [2.7031(7)],  $Mn(1)-Cl(2A)$  2.5946(7) [2.6672(8)]. Values in square brackets are for the isostructural  $[4,4'\text{-H}_2\text{bipy}][CdCl_4]$  **3**.

† Electronic supplementary information (ESI) available: synthesis details for **1**, **2** and **3**. See <http://www.rsc.org/suppdata/cc/1999/2287/>



**Fig. 3** The crystal structure of [4,4'-H<sub>2</sub>bipy][MnCl<sub>4</sub>] **2** viewed along the *c* axis, parallel to the metal chains. The NH...Cl hydrogen bonds are indicated.

structure (Fig. 3). There is very weak intrachain antiferromagnetic coupling of the paramagnetic Mn<sup>II</sup> centres with negligible interchain coupling (Mn...Mn distances along the chain are 4.011 Å).<sup>¶</sup>

Despite the wide variety of cations for which [MnCl<sub>4</sub>]<sup>2-</sup> salts have been structurally characterised, only two structure types have been observed: tetrahedral [MnCl<sub>4</sub>]<sup>2-</sup> units or sheets of corner sharing {MnCl<sub>6</sub>} octahedra in a <100> layer perovskite structure. As such these [MnCl<sub>4</sub>]<sup>2-</sup> salts are representative of a much larger set of salts of tetrahalometallate dianions of the transition and post-transition metals.<sup>1</sup> For example, of 24 [CdCl<sub>4</sub>]<sup>2-</sup> salts in the Cambridge Structural Database<sup>5</sup> all but one<sup>6</sup> (which has a chain structure of corner linked trigonal bipyramidal CdCl<sub>5</sub> units) also show only isolated tetrahedral (10 examples) or <100> layer perovskite structures (13 examples). In organic-inorganic layer perovskites it is generally thought that the hydrogen bonding capability of the organic (primary ammonium) cations promotes the observed structures. Indeed in general, in these structures each NH<sub>3</sub> makes three strong NH...Cl hydrogen bonds. We reasoned that the different hydrogen bonding capabilities of the [4,4'-H<sub>2</sub>bipy]<sup>2+</sup> cation might provide a general route to the new chain structure type for those metals which are readily able to form octahedral {MCl<sub>6</sub>} moieties in their +II oxidation state. Given the behaviour of the [CdCl<sub>4</sub>]<sup>2-</sup> salts noted above, cadmium was chosen as a representative example. Treatment of aqueous cadmium chloride with [4,4'-H<sub>2</sub>bipy]<sup>2+</sup> does indeed lead to formation of a salt [4,4'-H<sub>2</sub>bipy][CdCl<sub>4</sub>] **3** in which the new structure type is adopted.<sup>‡</sup> Compound **3** is isostructural with its manganese analogue.<sup>§</sup> As in **2** synthon A is present [NH...Cl] 2.54 and 2.60 Å in **3** for Cl(1) and Cl(2), respectively; cf. 2.51, 2.58 in **2**] as well as two CH...Cl bonds per chlorine (2.71–2.85 Å in **3**, 2.70–2.85 Å in **2**).

It is noteworthy that the same polymeric {MCl<sub>4</sub>}<sub>n</sub> substructure has been observed in neutral MCl<sub>4</sub> species (e.g. ZrCl<sub>4</sub>)<sup>4</sup> and in monoanionic form (e.g. in [Hpy][SbCl<sub>4</sub>])<sup>7</sup> but not previously in dianionic species. Such chains are a substructure of the familiar CdCl<sub>2</sub> structure.<sup>8</sup> Presumably the [4,4'-H<sub>2</sub>bipy]<sup>2+</sup> cation plays a vital role in stabilising the chain structure. As noted above, despite the wide variety of cations employed in salts of [MCl<sub>4</sub>]<sup>2-</sup> (M = Mn or Cd) the new structure type has not previously been observed. The chain structure has as many bridging (four per metal) and terminal (two per metal) chlorines as does the layer perovskite form of the [{MCl<sub>4</sub>}]<sub>n</sub><sup>2n-</sup> polymer. However the perovskite structure has nearly linear M–Cl–M bridges (angles typically 160–165°) compared with the much more normal M–Cl–M angles in **2** and **3** [100.29(2) and 99.38(2)°, respectively]. The more open

perovskite structure apparently requires greater strain at the μ-Cl site. This strain is presumably compensated by formation of stronger NH...Cl hydrogen bonds (usually six per metal, as in A<sub>2</sub>MX<sub>4</sub> structures with A = primary ammonium) than for the chain structure in **2** and **3** where there are just two NH groups per metal. Notably [Hpy]<sub>2</sub>[MnCl<sub>4</sub>]<sup>9</sup> contains tetrahedral manganese centres implying that it is not merely the number of NH hydrogen bond donors that influences the polymerisation of the MnCl<sub>4</sub> moieties. The willingness of the metal to be octahedrally coordinated must also be important. Thus the [4,4'-H<sub>2</sub>bipy][MCl<sub>4</sub>] (M = Co or Zn) salts contain [MCl<sub>4</sub>] tetrahedra rather than polymeric anions. Notably the same is true of [NH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>NH<sub>3</sub>]<sup>2+</sup> (n = 2, 3) salts of tetrachlorometallate anions: only those cases where M = Zn or Co have tetrahedral dianions. In other cases, e.g. M = Cr, Mn, Fe, Ni, Cd or Cu the <100> layer perovskite structure, with octahedral (or distorted octahedral) coordination of the metal, is adopted.

The ability of [4,4'-H<sub>2</sub>bipy]<sup>2+</sup> to control the aggregation of other metal anions, such as metal-oxo species has been noted.<sup>10</sup> In the present case it seems that the hydrogen bonding capability of [4,4'-H<sub>2</sub>bipy]<sup>2+</sup> may provide access to a new family of chain polymers of perhalometallate anions which may offer intriguing and potentially useful properties.

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## Notes and references

<sup>‡</sup> Syntheses of [4,4'-H<sub>2</sub>bipy][MCl<sub>4</sub>] (M = Zn **1**, Mn **2** or Cd **3**). Details are available as electronic supplementary information.

<sup>§</sup> Crystal structure analyses of [4,4'-H<sub>2</sub>bipy][MCl<sub>4</sub>] **1–3**: Crystal data: [4,4'-H<sub>2</sub>bipy][ZnCl<sub>4</sub>] **1**: C<sub>10</sub>H<sub>10</sub>Cl<sub>4</sub>N<sub>2</sub>Zn, *M* = 365.37, monoclinic, space group *P*2<sub>1</sub>/*c* (no. 14), *a* = 7.6507(12), *b* = 19.765(4), *c* = 9.5012(18) Å, β = 108.826(15)°, *U* = 1359.9(4) Å<sup>3</sup>, *Z* = 4, μ = 2.569 mm<sup>-1</sup>, *T* = 173 K, 3112 unique data, *R*<sub>1</sub> = 0.026. [4,4'-H<sub>2</sub>bipy][MnCl<sub>4</sub>] **2**: C<sub>10</sub>H<sub>10</sub>Cl<sub>4</sub>N<sub>2</sub>Mn, *M* = 354.94, monoclinic, space group *C*2/*c* (no. 15), *a* = 15.526(2), *b* = 12.660(3), *c* = 6.914(2) Å, β = 114.90(2)°, *U* = 1232.6(5) Å<sup>3</sup>, *Z* = 4, μ = 1.912 mm<sup>-1</sup>, *T* = 173 K, 1389 unique data, *R*<sub>1</sub> = 0.020. [4,4'-H<sub>2</sub>bipy][CdCl<sub>4</sub>] **3**: C<sub>10</sub>H<sub>10</sub>Cl<sub>4</sub>N<sub>2</sub>Cd, *M* = 412.40, monoclinic, space group *C*2/*c* (no. 15), *a* = 15.612(3), *b* = 12.746(2), *c* = 7.0261(12) Å, β = 114.984(3)°, *U* = 1267.3(4) Å<sup>3</sup>, *Z* = 4, μ = 2.542 mm<sup>-1</sup>, *T* = 173, 1448 unique data, *R*<sub>1</sub> = 0.025. In **2** and **3** the metal atoms and the cations lie at sites of *C*<sub>2</sub> symmetry. All hydrogen atoms were located in difference maps and included in idealised positions. X-Ray powder diffraction experiments on bulk samples of **1**, **2** and **3** were consistent with the presence of pure phases with the structures noted above.

CCDC 182/1438. See <http://www.rsc.org/suppdata/cc/1999/2287/> for crystallographic files in .cif format.

<sup>¶</sup> The magnetic susceptibility of microcrystalline **2** was measured between room temperature and 2 K and shows antiferromagnetic exchange coupling. The molar susceptibility was assumed to be produced by a system of non-interacting linear chains, and the molar susceptibility for these chains calculated according to Fisher's model (M. E. Fisher, *Am. J. Phys.*, 1964, **32**, 343). A satisfactory fit was obtained with Weiss constant θ = -0.024 K, *J* = -0.1 cm<sup>-1</sup> and *g* = 1.99.

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