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Extended networks *via* hydrogen bond cross-linkages of [M(bipy)] (M = Zn^{2+} or Fe^{2+}; bipy = 4,4′-bipyridyl) linear co-ordination polymers

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Both co-ordinative and hydrogen bonds contribute to networking in a series of polymeric compounds based on [M(bipy)] (bipy = 4,4′-bipyridyl) linear chains, which, through metal-co-ordinated water molecules and solvated bipy bases, have been shown to be cross-linked by single or double hydrogen-bond bridges of the type $M-H_2O \cdots bipy \cdots H_2O-M$, producing extended frames.

The crystal engineering of two- and three-dimensional co-ordination polymers[1,2] is currently of great interest due to the potential properties of these materials, such as electrical conductivity,[3] magnetism,[4] host–guest chemistry[5] and catalysis.[6] Recently, many efforts have been devoted to the investigation of new synthetic strategies and use of novel ligands. Two main lines of studies are followed, based on the different nature of the interactions responsible for networking, which concern: (*i*) frames comprised of metal centres and bi- or poly-hapto ligands connected *via* co-ordinative bonds, and (*ii*) networks derived, as in the supramolecular chemistry of proper organic molecules,[7] by the assembly of mono-[8] or poly-nuclear[9] metal complexes *via* hydrogen bonds. In the latter class different constructive principles have been envisaged, implying interactions of the building units either directly or mediated by suitable spacers.[10]

Obviously, networks can be, in principle, assembled by the concurrent action of both extended co-ordinative and hydrogen bonds, though species like these have not yet attracted great attention.[11] Herein we report on a family of co-ordination polymers obtained from the self-assembly of hydrated metal ions with the linear bidentate ligand 4,4′-bipyridyl (bipy), namely $[Zn(H_2O)_4(bipy)][NO_3]_2 \cdot bipy$ **1**, $[Zn(H_2O)_4(bipy)][NO_3]_2 \cdot 2bipy \cdot 3H_2O$ **2**, $[Zn(H_2O)_4(bipy)][O_3SCF_3]_2 \cdot 2bipy$ **3** and $[Fe(H_2O)_3(ClO_4)(bipy)][ClO_4] \cdot 1.5bipy \cdot H_2O$ **4**. Interesting co-ordination polymers assembled with bipy have been reported, showing various structural motifs, including two-dimensional layers of squares,[1,6] squares,[12] interwoven and hexagonal sheets[13] and three-dimensional nets topologically related to α-plonium[14] and diamond.[15] Moreover, bipy has been employed as a spacer for the self-assembly by hydrogen bonds of cubane-like $[Mn(CO)_3(\mu\text{-}OH)]_4$ units.[9] All the compounds described here contain linear co-ordination polymers interacting *via* hydrogen bonds to produce two- or three-dimensional networks.

We have reacted hydrated metal ions with bipy under mild conditions in the hope of obtaining complexes retaining some of the original aqua ligands, capable of hydrogen bonding. Indeed, compounds **1**–**4** have been isolated, as crystals suitable for X-ray analysis,† from the mixtures obtained at room temperature by slow diffusion of an ethanolic solution of bipy into a water solution of the Zn^{2+} or Fe^{2+} salt, in molar ratios of 2 : 1.‡

The main structural feature common to all these compounds is the presence of linear co-ordinative −M−bipy−M−bipy− chains (see Fig. 1), all running in a parallel direction [mean M−N bond lengths 2.14(3) Å]. In the three zinc species **1**–**3** the repeating units are tetragonal $Zn(H_2O)_4$ units [mean Zn−O bond length 2.12(2) Å], while in compound **4** one water molecule is replaced by a co-ordinated ClO_4^- anion [mean Fe−O (H_2O) bond length 2.10(2) Å, Fe−O (ClO_4^-) 2.245(8) Å]. Solvated bipy molecules intercalate between these chains. Hydrogen bonds $OH \cdots N$ ($O \cdots N$ range 2.68–2.80 Å), involving water molecules co-ordinated to metal atoms of adjacent chains and the unco-ordinated bipy bases (acting as spacers) form long $M-H_2O \cdots$

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† Crystal data. Compound **1**: $C_{20}H_{24}N_6O_{10}Zn$, $M = 573.82$, triclinic, $P\bar{1}$ (no. 2), $a = 10.629(4)$, $b = 11.391(5)$, $c = 12.450(5)$ Å, $\alpha = 65.44(1)$, $\beta = 79.37(1)$, $\gamma = 66.89(1)^\circ$, $U = 1260.6(9)$ Å^3, $Z = 2$, $D_c = 1.512$ Mg m^{-3}, $F(000) = 592$, $\mu = 1.039$ mm^{-1}, colourless crystal 0.30 × 0.12 × 0.05 mm, final R and $wR2$ 0.0474 and 0.0863 for 2549 significant $[I > \sigma(I)]$ independent data. Compound **2**: $C_{30}H_{38}N_8O_{13}Zn$, $M = 784.5$, triclinic, $P\bar{1}$ (no. 2), $a = 11.030(3)$, $b = 11.335(3)$, $c = 15.285(3)$ Å, $\alpha = 77.15(2)$, $\beta = 85.42(2)$, $\gamma = 78.13(2)^\circ$, $U = 1822.1(8)$ Å^3, $Z = 2$, $D_c = 1.429$ Mg m^{-3}, $F(000) = 816$, $\mu = 0.747$ mm^{-1}, colourless crystal 0.12 × 0.12 × 0.12 mm, final R and $wR2$ 0.0804 and 0.2334 for 4181 significant $[I > 2\sigma(I)]$ independent data. Compound **3**: $C_{32}H_{32}F_6N_6O_{10}S_2Zn$, $M = 904.13$, triclinic, $P\bar{1}$ (no. 2), $a = 7.405(3)$, $b = 10.749(3)$, $c = 13.694(4)$ Å, $\alpha = 103.53(2)$, $\beta = 101.61(3)$, $\gamma = 105.59(3)^\circ$, $U = 979.3(6)$ Å^3, $Z = 1$, $D_c = 1.533$ Mg m^{-3}, $F(000) = 462$, $\mu = 0.823$ mm^{-1}, colourless crystal 0.20 × 0.17 × 0.10 mm, final R and $wR2$ 0.0573 and 0.1518 for 2118 significant $[I > 2\sigma(I)]$ independent data. Compound **4**: $C_{50}H_{56}Cl_4Fe_2N_{10}O_{24}$, $M = 1434.55$, triclinic, $P\bar{1}$ (no. 2), $a = 9.024(2)$, $b = 11.446(6)$, $c = 16.376(5)$ Å, $\alpha = 74.42(3)$, $\beta = 82.91(2)$, $\gamma = 70.19(3)^\circ$, $U = 1531.9(10)$ Å^3, $Z = 1$, $D_c = 1.555$ Mg m^{-3}, $F(000) = 738$, $\mu = 0.736$ mm^{-1}, orange-yellow crystal 0.25 × 0.15 × 0.10 mm, final R and $wR2$ 0.0727 and 0.1611 for 1929 significant $[I > 2\sigma(I)]$ independent data. The data collections were performed on an Enraf-Nonius CAD4 diffractometer at 293 K, using Mo-Kα radiation ($\lambda = 0.710\,69$ Å), by the ω-scan method, within the limits $3 < \theta < 25^\circ$ (**1**, **2** and **4**) and $3 < \theta < 26^\circ$ (**3**). Empirical absorption corrections (ψ scan) were applied in all cases [transmission factors in the ranges 1.0–0.85 (**1** and **3**), 1.0–0.82 (**2**), 1.0–0.87 (**4**)]. The structures were solved by direct methods (SIR 92[16]) and refined by full-matrix least-squares on F^2 (SHELXL 93[17]). Anisotropic thermal factors were assigned to all the non-hydrogen atoms, but in **2** the anions and the solvated water molecules were treated isotropically. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/511.

‡ In particular, compounds **1** and **2** were obtained from the same reaction; an ethanolic solution of bipy was layered over a solution of $Zn(NO_3)_2 \cdot 6H_2O$ in water (molar ratio 2 : 1); **1** forms first on the walls after a few days, while **2** is produced successively, upon concentration of the solution by slow evaporation. Crystals of compounds **3** and **4** were obtained, together with powdery materials, in a similar manner using $Zn(O_3SCF_3)_2$ or $Fe(ClO_4)_2 \cdot 6H_2O$ respectively, but required longer times. Together with **4** crystals of the related polymeric $[Fe(H_2O)_2(ClO_4)_2(bipy)] \cdot bipy$ **5** were also obtained. The structure of the latter shows two *trans* co-ordinated ClO_4^- anions [triclinic, $P\bar{1}$, $a = 7.524(2)$, $b = 9.016(2)$, $c = 10.106(5)$ Å, $\alpha = 105.13(3)$, $\beta = 95.90(3)$, $\gamma = 109.90(2)^\circ$] and is quite similar to that of the analogous Cu^{II} compound with type **A** cross-linking (see ref. 19); so it will not be further discussed.

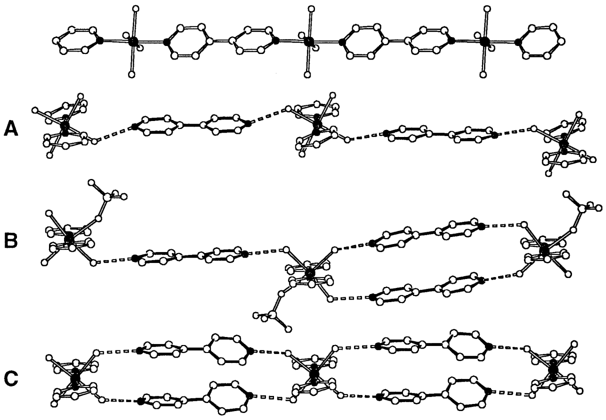

Fig. 1 The linear chain common to compounds **1**–**4**, and the different hydrogen bond cross-linkages: types **A** in **1**, **B** in **4** and **C** in **2** and **3**

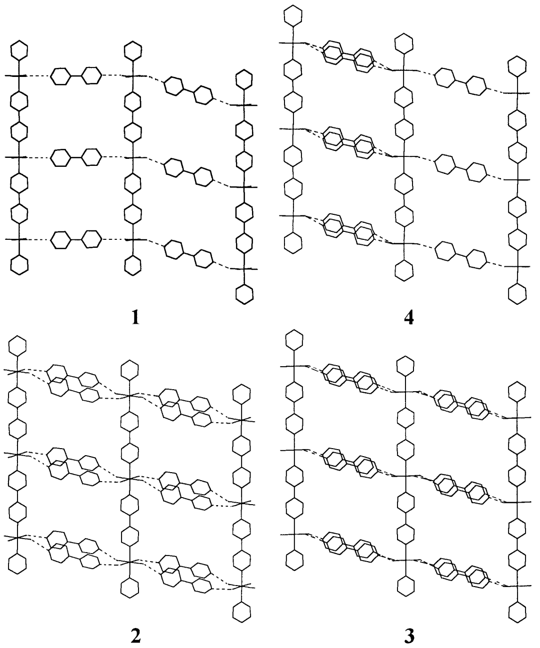

Fig. 2 A schematic view of the two-dimensional layer in compounds **1**–**4**

bipy$\cdots$H$_2$O–M bridges, which generate, in all cases, two-dimensional layers of rhombic meshes. However, this arrangement differs in compounds **1**–**4** (see Fig. 1): in **1** 'single' bridges of the above type cross-link the chains (type **A**), and only two *trans* co-ordinated water molecules on each metal are involved in these interactions. In **2** and **3** the metal centres on adjacent chains are joined by two such parallel bridges, *i.e.* 'double' bridges cross-link the chains (type **C**), and all four co-ordinated water molecules participate to these interactions. Finally, in **4** an intermediate situation is observed, with alternating 'single' and 'double' bridges (type **B**). While two examples of type **A** cross-linking have been recently reported, namely [M(H$_2$O)$_2$X$_2$(bipy)]·bipy (M = Mn^{2+}, X = NCS$^-$;[18] M = Cu^{2+}, X = ClO$_4^-$ [19]), the other types are unprecedented. The pairs of parallel bipy spacers in **2**–**4** show stacking interactions of 3.6–3.7 Å.

The rhombic meshes of the two-dimensional layers, shown in Fig. 2, present acute angles ranging from 75.3 to 90.0°. In these layers the M$\cdots$M contacts *via* co-ordinate bonds range from 11.29 to 11.44 Å, while those involving hydrogen bonds are longer, in the range 15.08–15.78 Å. The enlargement of the grids with respect to the square meshes of the co-ordination polymers [M(bipy)$_2$]X$_2$[1,6,12,14] can have some influence on the dimension-controlled properties of this class of compounds, which have proven to be useful in guest exchange and catalysis.[6]

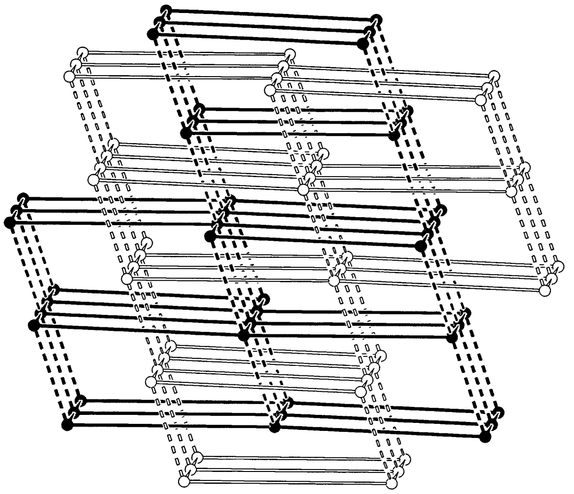

Fig. 3 A schematic view down the *b* axis, of the two interpenetrating three-dimensional networks in compound **1** (rods = two-dimensional layers with type **A** cross-linking, broken rods = hydrogen bonds involving the anions)

Also of interest are further supramolecular interactions of these layers. Other hydrogen bonds, involving the co-ordinated water molecules and the anions, are observed in all the compounds. In **3** and **4**, however, these hydrogen bonds are not effective in extending the dimensions of the networks, while in **1** and **2** three-dimensional arrays are produced. The net observed in **2** is quite intricate and difficult to rationalize, due to the presence of additional solvated water molecules participating in the hydrogen-bond system. On the other hand, the array in **1** is more simple: the two co-ordinated *trans* water molecules not involved in the in-layer hydrogen bonds give Zn–H$_2$O$\cdots$(NO$_3^-$)$_2\cdots$H$_2$O–Zn bridges which link the next nearest layers [Zn$\cdots$Zn contacts of 7.83 and 7.98 Å and H$_2$O$\cdots$O (NO$_3^-$) hydrogens bonds from 2.69 to 3.00 Å], forming a system of two identical interpenetrating three-dimensional nets topologically related to α-polonium (Fig. 3).

Though a structural control of systems involving hydrogen-bonded water molecule is quite difficult, we think that supramolecular interactions of low-dimensional co-ordination polymers, like those described here, can play a significant role in the self-assembly of novel nanoporous materials.§,[20] Further work is in progress.

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§ An interesting one-dimensional complicated polymer, built with flexible bidentate ligands and cross-linked *via* hydrogen bonds involving co-ordinated water molecules and free ligands, has been recently reported.[20]

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