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$_2$O ···· M. H$_2$O–M, producing extended frames.

The crystal engineering of two- and three-dimensional co-ordination polymers is currently of great interest due to the potential properties of these materials, such as electrical conductivity, magnetism, host-guest chemistry and catalysis. 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, by the assembly of mono- or poly-nuclear 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.

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. Here 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$_2$O)$_4$(bipy)][(N$_2$O)$_2$bipy 1, [Zn(H$_2$O)$_2$(bipy)]- [N$_2$O$_2$]-2bipy·3H$_2$O 2, [Zn(H$_2$O)$_2$(bipy)][O$_2$SCF$_3$]-2bipy 3 and [Fe(H$_2$O)$_2$Cl(bipy)]([ClO$_4$]-1.5bipy·H$_2$O 4. Interesting co-ordination polymers assembled with bipy have been reported, showing various structural motifs, including two-dimensional layers of squares, 1,8 squares, 12 interwoven and hexagonal sheets 8 and three-dimensional nets topologically related to α-plonium 8 and diamond. Moreover, bipy has been employed as a spacer for the self-assembly by hydrogen bonds of cubane-like [Mn(μ-O)(μ-Cl)H$_2$O]$_n$ units. 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, 1,8 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 2:1:1. 1,8

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polymers, grids with respect to the square meshes of the co-ordination
11.29 to 11.44 Å, while those involving hydrogen bonds are
X which have proven to be useful in guest exchange and catalysis.

Three-dimensional properties of this class of compounds,
ment differs in compounds
bipy
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-
(H2O)2X2(bipy)]-bipy · (M = Mn(II), X = NCS-); [M = Cu(II),
X = ClO4-], 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 · · · · M contacts via co-ordinate bonds range from
11.29 to 11.44 Å, while those involving hydrogen bonds are
longer, in the range 15.68–15.78 Å. The enlargement of the
grids with respect to the square meshes of the co-ordination
polymers [M(bipy)3X+]n,14,32,33 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

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 com-
ounds. 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–O · · ·
(NO3)2 · · · H–O–Zn bridges which link the next nearest layers
[Zn · · · · Zn contacts of 7.83 and 7.98 Å and H–O · · · O (NO3–)]
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 supra-
molecular interactions of low-dimensional co-ordination
polymers, like those described here, can play a significant role in
the self-assembly of novel nanoporous materials.§ Further
work is in progress.

§ An interesting one-dimensional complicated polymer, built with flex-
able 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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