A New Type of Interpenetration Involving Enmeshed Independent Square Grid Sheets. The Structure of Diaquabis-(4,4′-bipyridine)zinc Hexafluorosilicate

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$Zn(4,4'\text{-bipy})_2SiF_6{\cdot}2H_2O$ (4,4′-bipy = 4,4′-bipyridine) consists of two perpendicular and equivalent stacks of infinite, essentially square grid $[Zn(H_2O)_2(4,4'\text{-bipy})_2]_n^{2n+}$ sheets, which interpenetrate so that any particular sheet has an infinite number of perpendicular ones enmeshed or concatenated with it.

Of the many known infinite 2D and 3D structures very few show the interesting feature of mutual interpenetration of independent infinite frameworks. An essential aspect of these structures is that rings belonging to one framework are intimately inter-locked with rings from the other(s) in the same sort of topological relationship as that between adjacent links in a chain. Regimented repeating catenane[1] associations are generated in such lattices. Materials with this unusual feature not only are of fundamental structural interest as special geometrical types but also they may show unusual derived properties.

Most known cases of interpenetration involve varying numbers of diamond-related frameworks, *viz.* two-fold interpenetration,[2] three-fold,[3] five-fold[4] and six-fold.[5] In the case of Cu^I[4,4′4″,4‴-tetracyanotetraphenylmethane]-$BF_4{\cdot}x PhNO_2$[6] interpenetration did not occur despite the fact that the diamond-related cationic framework appeared to leave spaces more than large enough to allow it. Only one example of interpenetrating 3D frameworks not derived from diamond is known to us, namely, the silicate mineral neptunite, in which two independent three-connected nets interpenetrate.[7,8] Rare examples of interpenetrating sheet structures are provided by $Ag[C(CN)_3]$,[9] benzene-1,3,5-tricarboxylic acid[10] and certain of its inclusion compounds[11] all of which involve sheets resembling hexagonal mesh chicken wire and Hittorfs violet phosphorus.[12] We report here a new type of interpenetration involving planar, essentially square grid sheets each of which has an infinite number of perpendicular ones enmeshed in it.

Crystals of $Zn(4,4'\text{-bipy})_2SiF_6{\cdot}2H_2O$ were isolated from aqueous mixtures containing $ZnSiF_6$ and 4,4′-bipyridine (4,4′-bipy) in 1:2 molar proportions. The structure was determined by single crystal X-ray diffraction.† The unit cell is represented in Fig. 1.

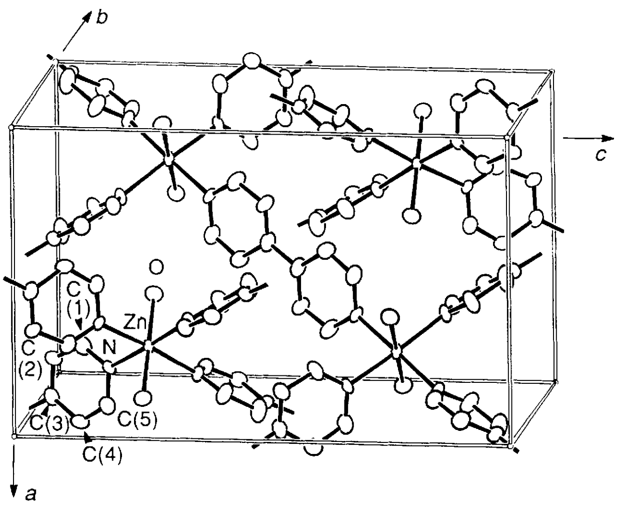

Fig. 1 The tetragonal unit cell of $Zn(4,4'\text{-bipyridine})_2SiF_6{\cdot}2H_2O$. The anions have been omitted for clarity. Selected bond distances (Å) and angles (°): Zn–O 2.132(4), Zn–N 2.158(5), O–Zn–N 87.9(2), N–Zn–N′ 89.2(2), N–Zn–N″ 175.7(2).

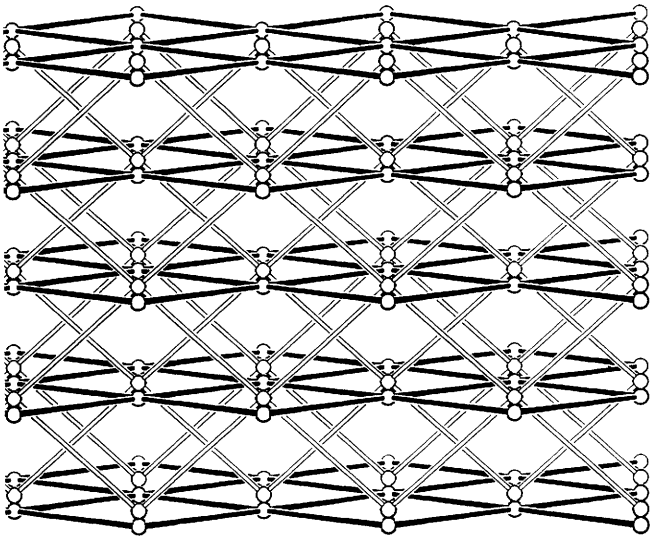

Fig. 2 View of the interpenetrating perpendicular $[Zn(4,4'\text{-bipyridine})_2]_n^{2n+}$ sheets, which lie parallel to [110] and $[\bar{1}10]$. Zn centres only are shown. Each 'rod' connecting neighbouring Zn centres is of the type $Zn{\cdot}NC_5H_4{\cdot}C_5H_4N{\cdot}Zn$ of length 11.436(2) Å. Lines of intersection of pairs of perpendicular sheets are parallel to [001].

The zinc centre is in an essentially octahedral environment with two *trans* water ligands and four pyridine nitrogen donors. The two rings of each 4,4′-bipyridine unit are coplanar. The four pyridine units associated with each zinc are arranged in propeller fashion, all four being inclined to the mean plane through the four nitrogens at a dihedral angle of 53.2°.

Each bipyridine unit is attached to two zinc centres [Zn · · · Zn separation 11.436(2) Å] to form infinite sheets of

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† *Crystal data:* $[Zn(4,4'\text{-bipyridine})_2(H_2O)_2][SiF_6]$, $C_{20}H_{20}F_6N_4O_2SiZn$, M = 555.9, tetragonal, space group *P4/ncc* (No. 130), a = 10.815(2), c = 17.006(3) Å, U = 1989 Å^3, $F(000)$ = 1128, Z = 4, D_c = 1.856 g cm^{-3}, D_m = 1.85(1) g cm^{-3}, μ(Mo-K$\bar{\alpha}$) = 13.64 cm^{-1}. Intensity data were collected on an Enraf-Nonius CAD-4F single crystal automatic diffractometer employing the ω–2θ scan method; absorption corrections were applied. The structure was refined using a full-matrix least-squares refinement procedure (SHELX-76), with anisotropic thermal parameters assigned to all non-hydrogen atoms. All hydrogen atoms were observed in the difference map; those on the bipyridine ligand were constrained at geometrical estimates, while the parameters of the hydrogen atom bonded to the oxygen were refined. At convergence R = 0.058 and R_w = 0.064 for the 660 observed reflections [$I \geqslant 3\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

composition $[Zn(H_2O)_2(4,4'\text{-bipy})_2]_n^{2n+}$ with an approximately square grid structure. The zinc centres within a sheet are all coplanar and form a grid of edge-shared rhombuses with angles of 96.07(1) and 83.93(1)°. Parallel sheets stacked on top of each other [separation 7.648(2) Å] are laterally displaced so that zinc centres of the first sheet, viewed in the horizontal plane, are vertically above those of the 3rd, 5th, 7th *etc.* sheets while being vertically above the mid-points of the Zn_4 rhombuses of the 2nd, 4th, 6th *etc.* sheets. An equivalent stack of sheets is found in planes perpendicular to the first, giving rise to the unprecedented interpenetration pattern represented in Fig. 2. The line of intersection of any particular pair of perpendicular interpenetrating sheets is collinear with the long diagonals of the concatenated Zn_4 rhombuses.

The SiF_6^{2-} ions are hydrogen bonded to four metal-coordinated water molecules, which surround the anion at the corners of a square [O···F distance 2.683(5) Å]. Each coordinated water molecule is associated equally in this way with two SiF_6^{2-} units.

The average volume per non-hydrogen atom of 14.6 Å^3 is remarkably small for a crystalline solid containing significant organic material and reflects the efficiency of the 3D packing provided by this mode of interpenetration.

It is difficult to see why it should not be possible to assemble essentially this structure with a number of cations other than Zn^{2+}. Given the potential of the delocalised electron system of the 4,4′-bipyridine to 'conduct' electrons some of these possibilities may show interesting electrical properties.

With great pleasure we acknowledge support from the Selby Scientific Foundation.

Received, 22nd June 1990; Com. 0/02813D

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