A Wellsian 'three-dimensional' racemate: eight interpenetrating, enantiomorphic (10,3)-a nets, four right- and four left-handed

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The crystal structure of solvated [Zn(tpt)$_{2/3}$(SiF$_6$)(H$_2$O)$_2$(MeOH)] [tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine] is comprised of eight independent [Zn$_3$(tpt)$_2$]$_n$ networks with the (10,3)-a topology, four of one handedness and four of the other, which interpenetrate in a remarkable way, aspects of which were postulated by A. F. Wells almost twenty years ago.

In 1977 A. F. Wells published a survey of three-dimensional nets which we have been finding extremely valuable in developing a net-based approach to crystal engineering.[1] With remarkable insight Wells realised that the intrinsically enantiomorphic (10,3)-a net is in principle capable of participating in interpenetration not only with an independent identical net of the same handedness but also with a net of the opposite handedness. He observed that such an interpenetrating enantiomorphic pair of nets would provide 'an interesting type of structure, at present unknown, a three-dimensional racemate'. We report here just such a three-dimensional racemate in which not one but four enantiomorphic (10,3)-a pairs interpenetrate. Examples of (10,3)-a nets are rare.[2]

The building block used in this work was 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt) which we[3] and others[4] have used previously in the role of trigonal connecting unit, in our case for the generation of infinite three-dimensional networks and in the cases described in ref. 4 for the construction of molecular species. Diffusion of a methanolic solution of ZnSiF$_6$ into a solution of tpt in chloroform–1,1,2,2-tetrachloroethane gave colourless crystals of solvated [Zn(tpt)$_{2/3}$(SiF$_6$)(H$_2$O)$_2$(MeOH)] whose structure has been determined from single-crystal X-ray diffraction data collected at 120 K.†

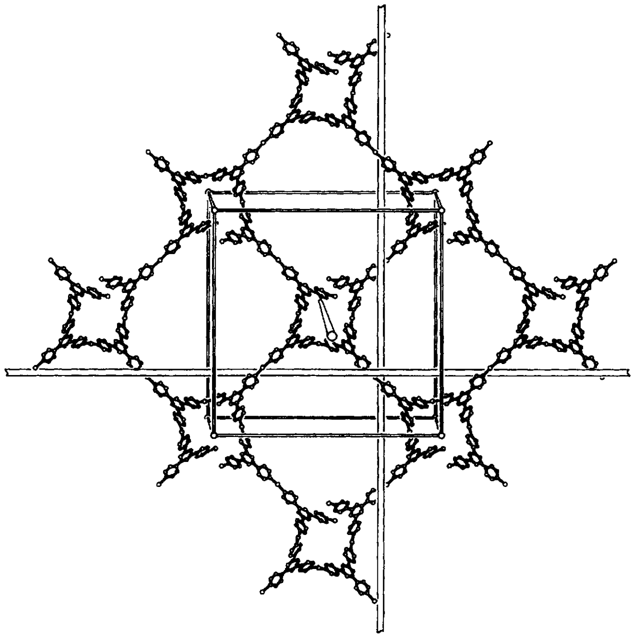

Fig. 1 The C/N/Zn framework of one of the eight cubic (10,3)-a nets present in the structure viewed slightly inclined to one of the axes. Helices, in this case left handed, running parallel to the three cubic cell axes are highlighted by 'poles' placed along their helical axes. The cubic unit cell indicated has been translated from the origin.

Each zinc, which is essentially octahedral, is coordinated by two *trans* tpt-pyridine donors in an almost linear fashion [N–Zn–N, 173.3(3)°] so that an infinite three-dimensional three-connected Zn–tpt network is formed which possesses the (10,3)-a topology. The four remaining ligands around zinc (one F-bonded SiF$_6^{2-}$, two water molecules and one methanol) can be regarded as appendages to the net.

Characteristic features of a single (10,3)-a net are fourfold helices, all of the same handedness, running parallel to the cubic cell edges. A single one of the eight (10,3)-a nets present in the structure is shown in Fig. 1 in which the fourfold helices happen to be left handed; we refer below to the net as a whole in this case as being 'left handed'.

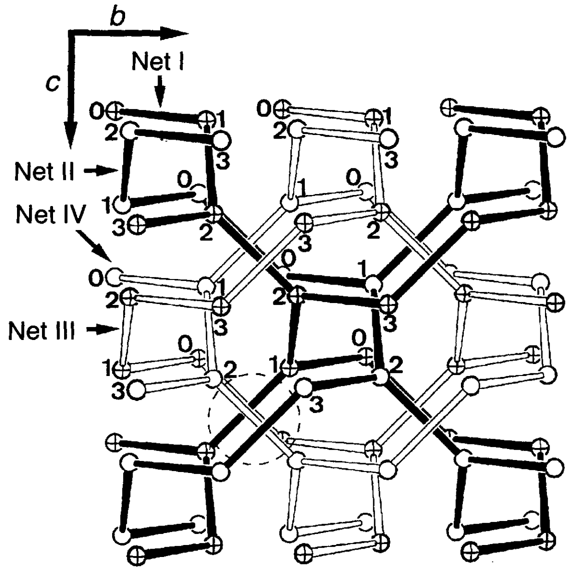

Fig. 2 A view slightly displaced from *a* showing the three-dimensional relationship between four idealised (10,3)-a nets of the same handedness (here left). Only trigonal centres are represented. Numbers represent heights in quarters of a unit cell. Net I, heavy connections + cross-hatched circles; net II, heavy connections + open circles; net III, open connections + cross-hatched circles; net IV, open connections + open circles.

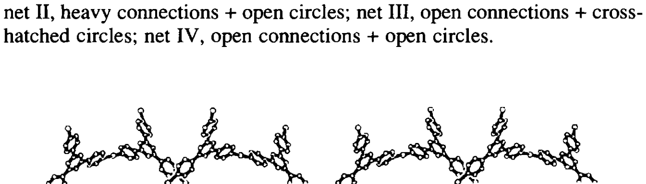

Fig. 3 A double helix; the two helices shown are from independent three-dimensional nets

The structure contains, in all, four right- and four left-handed (10,3)-a nets. The relationships between four nets with the same handedness can be most easily appreciated in terms of the geometrically idealised representation shown in Fig. 2 in which each net (here left-handed) is in its most symmetrical configuration with strictly 120° angles (minor deformations from this ideal are present in the real structure). Nets II, III and IV, according to this idealised description, are generated from net I by half-cell translations along *a*, *b* and *c* respectively. As a consequence, double helices consisting of net I paired with net II can be seen running almost perpendicular to the page along *a* in Fig. 2. A further consequence is that in the *a* direction, as well as net I/net II double helices there are also net III/net IV double helices. Likewise, in the *b* direction are found net I/net III and net II/net IV double helices and in the *c* direction net I/net IV and net II/net III double helices. A double helix in isolation, showing the C/N/Zn skeleton, is represented in Fig. 3.

One such collection of four independent nets, all of the same handedness, is interpenetrated by an analogous collection of four independent nets with the opposite handedness with the relative dispositions as shown in Fig. 4. In essence, the double helical columns of either quartet of nets occupy those regions of the other quartet where the double helical columns are interconnected by criss-crossing links; such regions can be seen in Fig. 2, one of them highlighted by a broken line circle.

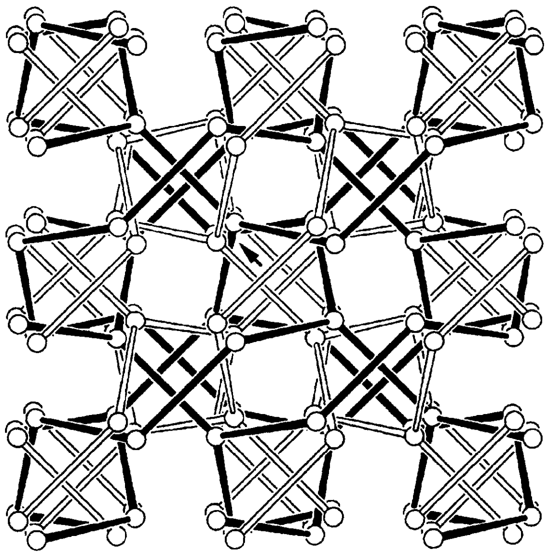

Fig. 4 A representation of all eight nets in the structure. Circles represent centres of triazine rings. Heavy lines represent a quartet of left handed nets analogous to the idealised quartet described in Fig. 2 but including the real deformations. The right-handed quartet of nets is represented by 'open' lines. One of the discrete $(tpt)_2$ pairs is highlighted by an arrow.

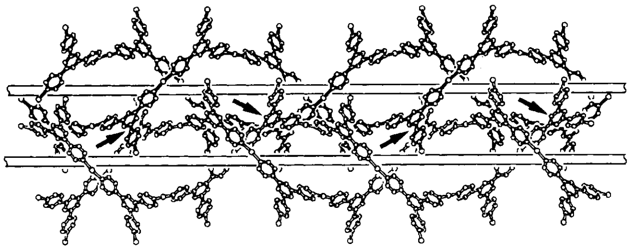

Fig. 5 A pair of parallel double helices of the opposite handedness making a number of π contacts indicated by arrows

The mode of interpenetration is such that tpt units appear in the structure in discrete, closely spaced, face-to-face pairs [triazine–triazine inter-plane separation 3.365(8) Å], the members of each pair belonging to nets of opposite handedness and being positioned around a $\bar{3}$ site. One such pair is highlighted by an arrow in Fig. 4. Every double helix is associated by multiple tpt–tpt π interactions of this type with four parallel double helices of the opposite handedness as can be seen in Fig. 4. Fig. 5, showing the C/N/Zn framework, illustrates this tpt–tpt π-pairing between adjacent double helices, only two of which are shown for clarity.

The structure described here is the fourth type we have discovered of a highly symmetrical, cubic infinite network derived from tpt[3] whose coordination polymers we are continuing to explore.

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Footnote

† Colourless crystals of solvated $[Zn(tpt)_{2/3}(SiF_6)(H_2O)_2(MeOH)]$ were prepared by carefully layering a buffer zone of chloroform (5 ml) on top of a solution of tpt (25 mg) in 1,1,2,2-tetrachloroethane (10 ml) and then carefully layering a solution of $ZnSiF_6\cdot 6H_2O$ (20 mg) in methanol (10 ml) on top of that. Crystals grew over a period of a week or so. The crystals were sensitive to solvent loss upon exposure to the atmosphere. Anal: Calc. for $Zn_3(C_{18}H_{12}N_6)_2(SiF_6)_3(H_2O)_6\cdot C_2H_2Cl_4$: C, 29.93; H, 2.52; N, 11.04; Cl, 9.31. Found: C, 29.53; H, 2.54; N, 10.92; Cl, 9.2% (sample dried *in vacuo*). Crystals were transferred directly from solution to oil and cooled to 120 K on an Enraf-Nonius CAD-4FMachS diffractometer. *Crystal data* for $[Zn(tpt)_{2/3}(SiF_6)(H_2O)_2(MeOH)]\cdot$solvate: cubic, space group $Fd\bar{3}c$ (no. 228), a = 42.672(15) Å, U = 77701(47) Å^3, Z = 96, T = 120 K, $2\theta_{max}$ = 150°, Cu-Kα radiation, λ = 1.5418 Å, ω–2θ scan, 3499 reflections collected, 3262 independent reflections, all reflections included in the refinement. Corrections applied for Lorentz, polarization and absorption[5] effects, μ(Cu-Kα) = 37.04 cm^{-1}. Structure solved using direct methods (SHELXS-86[6]) and refined using a full-matrix least-squares refinement based on F^2 (SHELXL-93[7]). $R1$ $[I > 2\sigma(I)]$ = 0.0826, $wR2$ $[I > 2\sigma(I)]$ = 0.2130. Residual electron density = 0.623 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/69.

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