Infinite Square-grid $[Cd(CN)_2]_n$ Sheets linked together by either Pyrazine Bridges or Polymerisable 1,4-bis(4-pyridyl)butadiyne Bridges arranged in an Unusual Criss-cross Fashion

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The compounds $Cd(CN)_2{\cdot}pyz$ (pyz = pyrazine) and $Cd(CN)_2{\cdot}bpb$ [bpb = 1,4-bis(4-pyridyl)butadiyne] contain square-grid $[Cd(CN)_2]_n$ sheets linked together by either pyrazine bridges or bpb bridges which criss-cross in an unusual fashion producing face-to-face stacks of pyrazine rings and collections of bpb units in which every one is sandwiched between six others, three on each side; butadiyne C_4 moieties are brought thereby into close proximity (closest C···C contact 3.36 Å) and the initially colourless $Cd(CN)_2{\cdot}bpb$ crystals acquire a deep blue-purple colour on exposure to light indicating diacetylene polymerisation within the crystal.

The much studied Hofmann-type clathrates contain square-grid sheets consisting of alternating octahedral and square-planar metal centres linked together by cyano bridges.[1] Derived three-dimensional (3D) nets providing cavities in which a range of guest species can be accommodated have been generated by linking the sheets together with α,ω-diaminoalkane bridges between octahedral centres.[2] We report here two new types of 3D topology involving square-grid $[Cd(CN)_2]_n$ sheets in which all metal centres are six-connecting and are linked to adjacent sheets by bridging ligands which criss-cross in an unusual way.

A hot aqueous solution containing $Cd(CN)_2$ and pyrazine (pyz) gave, upon cooling, crystals of $Cd(CN)_2{\cdot}pyz$ whose structure was determined by X-ray crystallography.† The extended structure is represented in Fig. 1 and consists of infinite $[Cd(CN)_2]_n$ sheets bound together by pyrazine bridges. Within each sheet all cadmium centres are coplanar. Each sheet appears, in projection, as a square grid with every cadmium linked to four others by cyano bridges. The sheets are corrugated with all the troughs parallel, running perpendicular to the page in Fig. 1 (along the *c* axis). All cadmium centres have an approximately octahedral environment consisting of two *cis* cyano nitrogens [at 2.41(1) Å], two *cis* cyano carbons [at 2.29(1) Å] and two pyrazine nitrogens [at 2.448(6) Å] located on opposite sides of the $[Cd(CN)_2]_n$ sheets. The troughs of one sheet are vertically above and below the crests of the two adjacent sheets. As can be seen in Fig. 1 the cyano-derived N_2C_2 donor sets are inclined to the Cd_n plane in one of two ways. The bridging pyrazines, which coordinate approximately normal to these inclined N_2C_2 planes, thereby form a criss-cross pattern, stacking face-to-face. Each C_4N_2 ring is rotated around its pseudo-sixfold axis approximately one sixth of a revolution relative to its two neighbours so that when the stack is viewed along the *c* axis (into the page in Fig. 1) carbon atoms and nitrogen atoms almost overlay each other. The pyrazine planes are parallel with a separation of 4.00 Å.

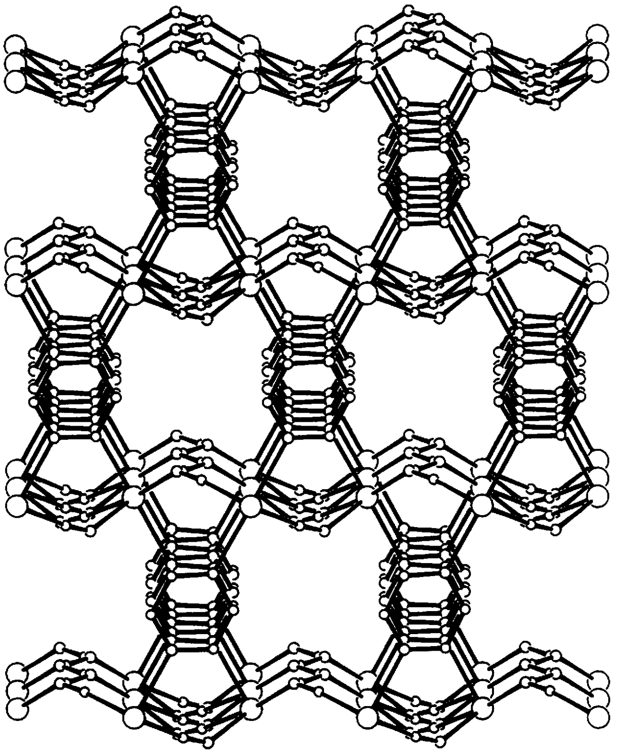

Fig. 1 The extended framework structure of $Cd(CN)_2{\cdot}pyz$

Whilst the work described here was being carried out a material formulated as $Cd(pyz)Cd(CN)_4{\cdot}C_6H_6$ was reported which, on the basis of vibrational spectra, was assigned a Hofmann-Td-type clathrate structure.[3]

It appears that $Cd(CN)_2{\cdot}pyz$ adopts this criss-crossed structure, the topological essence of which is represented in Fig. 2(*a*), rather than the simpler, less distorted and topologically distinct α-polonium structure shown in Fig. 2(*b*), because it affords significantly more efficient packing. The estimated density if it adopted the structure in Fig. 2(*b*) is 1.60 g cm^{-3} whereas that for the structure in Fig. 2(*a*) is 2.04 g cm^{-3}. In this connection it is interesting that $Cd(CN)_2{\cdot}$quinoxaline‡ does adopt the much more open α-polonium-related structure. As can be readily visualised upon examination of Fig. 1, the benzene ring fused to the pyrazine ring in quinoxaline would clash disastrously with the cyano units in a structure of the $Cd(CN)_2{\cdot}pyz$ type making this arrangement impossible; the fused benzene ring can however be satisfactorily accommodated in a structure of the type shown in Fig. 2(*b*).

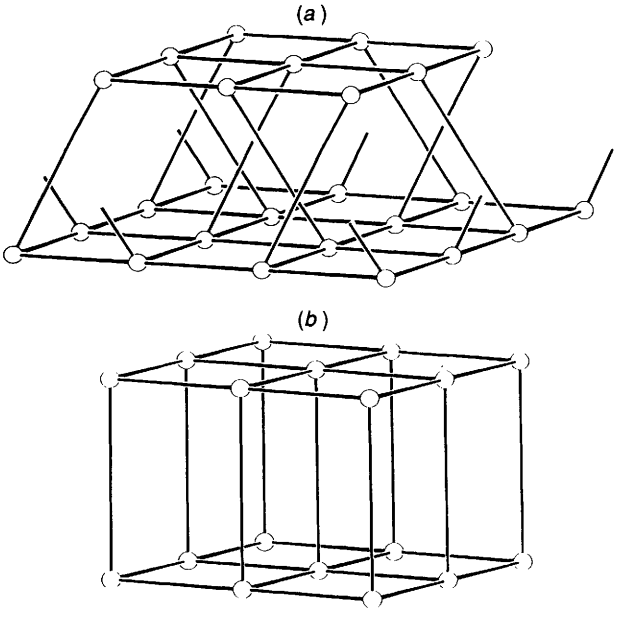

Fig. 2 Schematic representation of the connectivity in (*a*) $Cd(CN)_2{\cdot}pyz$ and (*b*) the α-polonium-related net

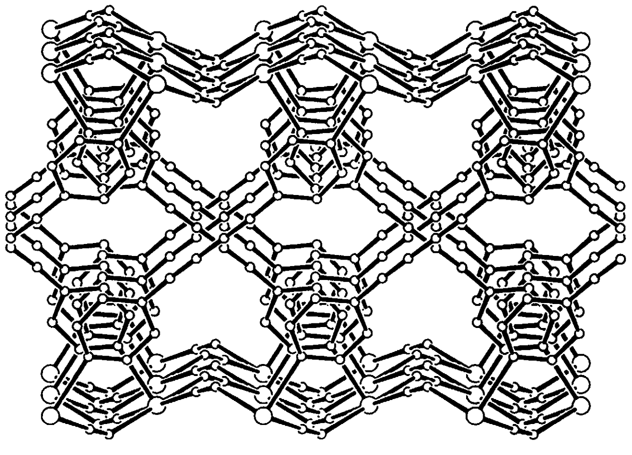

Fig. 3 Extended framework structure of Cd(CN)$_2$·bpb

Crystals of Cd(CN)$_2$·bpb [bpb = 1,4-bis(4-pyridyl)butadiyne[4]] were obtained from aqueous Bu^{t}OH solutions containing Cd(CN)$_2$ and bpb. When grown in the dark the crystals were colourless but on exposure to daylight they rapidly acquired a dark blue-purple colour, almost certainly as a result of diacetylene polymerisation within the crystal, a common solid-state phenomenon with a range of diacetylenic derivatives which has been studied intensively.[5] This solid-state polymerisation also proceeds in the X-ray beam which meant that diffraction data for the structure determination had to be collected on several different crystals each of which was continuously degenerating during the data collection.[§] Fig. 3 represents the extended framework structure which contains corrugated [Cd(CN)$_2$]$_n$ sheets very similar to those in Cd(CN)$_2$·pyz except that the cyano-derived N_2C_2 coordination environment now has a *trans* arrangement. Sheets are linked by somewhat bent but basically linear bpb bridges which are markedly inclined to the sheets. Again, troughs of one corrugated sheet are vertically above and below the crests of its immediate neighbours. The bridging ligands are now so long [Cd···Cd separation in Cd–bpb–Cd = 16.771(2) Å] that they connect Cd centres associated with troughs displaced sideways one trough further than was the case in Cd(CN)$_2$·pyz as can be seen by comparing Figs. 1 and 3. The butadiyne C_4 moieties are brought into moderately close proximity, the closest C···C contact being 3.36 Å. The photo-generated deeply coloured solid product may well provide the unique situation in which infinite polyunsaturated carbon chains with a conjugated delocalised electronic π system are sandwiched between [Cd(CN)$_2$]$_n$ sheets. We are presently examining the structure and properties of the photo-product.

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Footnotes

[†] The space groups *Cccm* and *Ccc*2 are consistent with the diffraction data recorded for Cd(CN)$_2$·pyz. Refinements were carried out in both space groups which yielded similar results; the details reported here refer to those obtained in the non-centrosymmetric space group.

Crystal data for Cd(CN)$_2$·pyz: $C_6H_4CdN_4$, M = 244.55, orthorhombic, space group *Ccc*2 (no. 37), a = 7.428(1), b = 13.278(2), c = 8.005(3) Å, V = 795.45 Å^3, $F(000)$ = 464, Z = 4, D_c = 2.04 g cm^{-3}, D_m = 2.00(2) g cm^{-3}, μ(Mo-Kα) = 26.49 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 applied to all non-hydrogen atoms; at convergence R = 0.025 and R_w = 0.024 for the 347 observed reflections [$I \geqslant 3\sigma(I)$]. The assignment of the C and N of the cyanide group, made on the basis of X-ray data, was consistent with expected Cd–C and Cd–N bonds, but only a neutron diffraction study would remove all uncertainty on this point.

[‡] X-Ray diffraction data for Cd(CN)$_2$·quinoxaline contain weak classes of reflections which have complicated the structure solution. The crystal data below refer to a monoclinic cell ($P2_1/n$) but these and the intensity data indicate the true cell to be almost certainly of higher symmetry (*C*-centred orthorhombic). Intractable problems concerning space group ambiguities exist which have yet to be resolved. No matter which of the alternative space groups is employed essentially identical solutions for the Cd(CN)$_2$·quinoxaline framework are obtained which correspond to the α-polonium net. Investigation of the structure is continuing. *Crystal data* based on the monoclinic cell: $C_{10}H_6CdN_4$, M = 296.6, space group $P2_1/n$ (no. 14), a = 9.673(3), b = 11.209(3), c = 9.679(3) Å, β = 107.44(3)°, V = 1001.2 Å^3, Z = 4, D_c = 1.97 g cm^{-3}, D_m = 1.91 g cm^{-3}.

[§] *Crystal data* for Cd(CN)$_2$·bpb; $C_{16}H_8CdN_4$, M = 368.52, monoclinic, space group *C*2/*c* (no. 15), a = 24.555(8), b = 7.239(2), c = 8.348(3) Å, β = 106.16(4)°, V = 1425.10 Å^3, Z = 4, D_c = 1.72, D_m = 1.72(1) g cm^{-3}, μ(Mo-Kα) = 1.52 mm^{-1}, $F(000)$ = 728. Owing to crystal deterioration, intensity data were collected from four separate crystals and combined. Intensity data were measured at 295(1)K with Mo-Kα radiation (graphite crystal monochromator) using an Enraf-Nonius CAD-4F diffractometer and the ω–2θ scan method; absorption corrections were applied. A full-matrix least-squares refinement method (SHELX-76) was employed with anisotropic thermal parameters applied to all the non-hydrogen atoms; at convergence R = 0.1066 for 821 reflections [$I \geqslant 3\sigma(I)$]; unit weights were used.

For Cd(CN)$_2$·pyz and Cd(CN)$_2$·bpb, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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