An alternative to interpenetration whereby nets with large windows may achieve satisfactory space filling

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A coordination polymer in which copper acetate dimers are bridged by 3-connecting tpt ligands reveals an alternative means to interpenetration whereby frameworks with very large holes may achieve efficient space filling, namely, by forming π–π associations between tpt units of sheets X and $X + 2$ inside the holes of sheet $X + 1$.

The promise of ultimately being able to generate by deliberate design new solid materials with useful tailor-made properties provides much of the driving force for the present interest in coordination polymers. An outstanding feature of many coordination polymers is the presence of a number of independent networks which participate in mutual interpenetration, whereby favourable non-bonded interactions can be maximised and more efficient 3D packing achieved.[1] In a very loose and general sense it can be said that the larger the windows in a 2D or 3D net the more likely is interpenetration to occur and the larger is the number of independent nets passing through a particular window likely to be. The coordination polymer we describe below which consists of hexagonal grid (6,3) sheets is unusual in that interpenetration does not occur despite the fact that the hexagonal holes within the sheets are much larger than those present in numerous other (6,3) sheet systems which do participate in interpenetration.[1] The system we describe reveals an alternative means to interpenetration whereby a network with large holes can maximise favourable non-bonded interactions and achieve efficient space filling.

The vast majority of coordination polymers so far investigated have involved single metal centres linked together in a variety of ways by bridging ligands. Relatively little work has focussed on 2D and 3D networks in which bridging ligands link together metal clusters[2] with their interesting electronic, magnetic and catalytic properties. The copper acetate dimer, which we make use of here, is one of the simplest imaginable cluster species with the potential to provide an effectively linear link between donors; indeed, a number of 1D polymeric chains are known.[3] In order to generate 2D and 3D coordination polymers it is obvious that bridging ligands providing the nodes for the network will be required to have connectivity three or higher. We know of only two examples in which metal acetate dimers are connected into 2D or 3D networks.[4,5]

We report here the 2D (6,3) sheet polymer formed when copper acetate dimer units are linked together by the μ_3 bridging ligand 2,4,6-tri(4-pyridyl)-1,3,5-triazine, tpt, which has previously been shown to afford a number of high symmetry 3D coordination polymers.[6] Reaction of $Cu_2(O_2CCH_3)_4(H_2O)_2$ in methanol with tpt in benzyl alcohol yields green crystals of composition $[\{Cu_2(O_2CCH_3)_4\}_3(tpt)_2]\cdot 2MeOH$ (**1**),† whose structure was determined by single crystal X-ray diffraction.‡

Giant hexagonal grid sheets are present, a ring from which is shown in Fig. 1. As can be seen, the tpt units provide the 3-connecting nodes of the net and copper acetate dimers link node to node, the separation between which is *ca.* 18 Å. This generates very large holes.

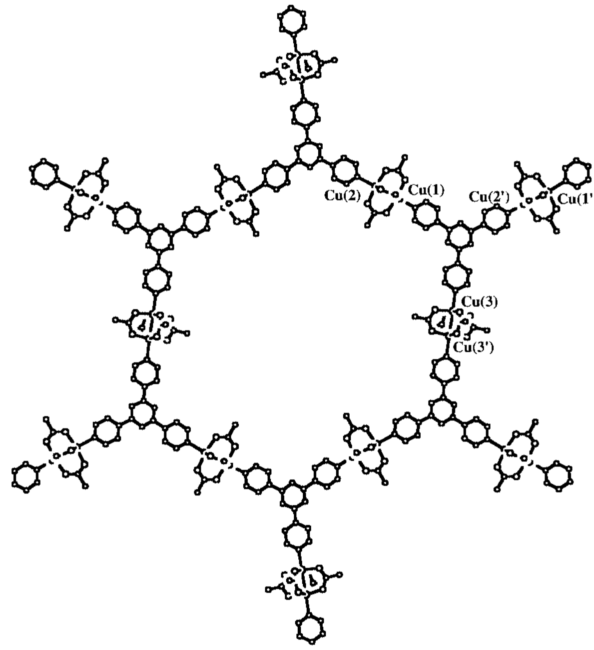

Fig. 1 A single hexagonal window in the (6,3) sheets of **1**. The ring 'diagonals' are *ca.* 34–37 Å.

The way in which efficient 3D packing is achieved without resort to interpenetration is most simply understood by considering the hypothetical stacking of idealised planar (6,3) nets in a manner which parallels that observed in the less regular real system. Any pair of neighbouring sheets are arranged in this idealised situation with half the nodes of one vertically above or below the mid-points of the hexagonal holes of the other, the remaining nodes of both sheets being located vertically above and below each other. By stacking the sheets in this manner to generate the ABCABC... sequence shown in Fig. 2(*a*) all nodes become equivalent (a real example of this arrangement is β rhombohedral graphite). As can be seen in Fig. 2(*a*) three types of columns of nodes perpendicular to the sheets are thereby generated. One type contains nodes from A sheets and B sheets but not from C sheets, which contribute only holes to these particular columns. If we refer to these columns as A/B columns, equal numbers of equivalent A/C and B/C columns are also present. One such column, the central one, is highlighted by the dashed line in Fig. 2(*a*). If the separation between sheets is *d*, the spacings between nodes in any one of the columns follows the sequence *d*, 2*d*, *d*, 2*d*, *d*, 2*d*... as can be seen in Fig. 2(*a*).

By making each of the initially planar trigonal nodes pyramidal in the appropriate direction and to the appropriate degree it is possible to contract each of the 2*d* separations within columns to *d*, as represented in Fig. 2(*b*). The individual sheets thereby acquire an undulating character and the overall structure becomes much more compact, the volume being reduced in the idealised case by close to one third. Pyramidalisation of the 3-connecting nodes allows new attractive node-to-node con-

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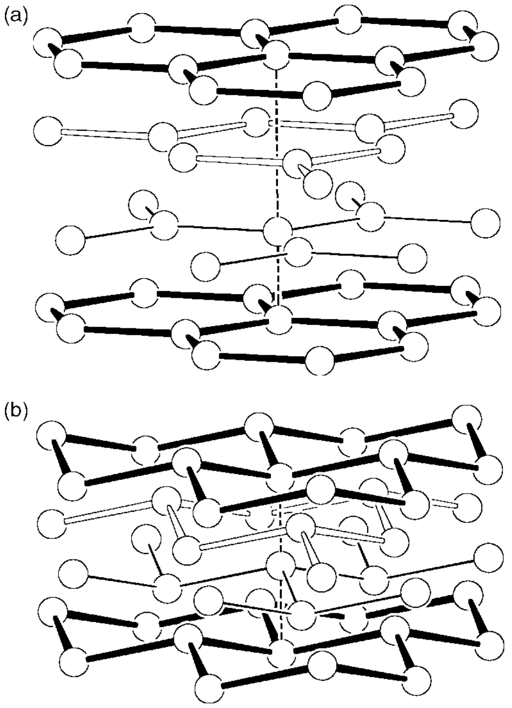

Fig. 2 (*a*) Four idealised planar (6,3) sheets stacked in the ABCA... pattern. (*b*) Hypothetical 'pyramidalisation' of the 3-connecting nodes that were planar in (*a*).

tacts to be made, which, it is interesting to note, involve nodes belonging to sheets that are not immediate neighbours. In effect the holes in any sheet are occupied by nodes belonging to the sheets on each side that come together to make favourable contact with each other around the centre of the hole. This can be easily seen by noting the effect of converting planar nodes in Fig. 2(*a*) to pyramidal nodes in Fig. 2(*b*) whereby the contact, highlighted by the dashed line, between the central node of the upmost sheet and the central node of the sheet depicted with thin bonds becomes shortened from 2*d* to *d*; this contact can be seen to be made through the ring of the intermediate sheet (shown with open bonds).

The 3D arrangement is a deformed version of the idealised structure shown in Fig. 2(*b*). The 3-connecting nodes in this real case are tpt units which remain internally approximately planar despite the fact they constitute pyramidal centres in the sense that lines drawn between triazine centroids make angles significantly less than 120°. The bending required to produce this pyramidalisation occurs mainly not within tpt units but between them; the most pronounced bending is seen at Cu(2) which is located 0.503 Å out of the plane of the coordinated pyridine ring. The node-to-node contacts indicated by a vertical dashed line in the idealised situation shown in Fig. 2(*b*), in the real system are π–π stacks of tpt units. Not only are the individual sheets distorted from hexagonal regularity but the columns are no longer perpendicular to the sheets; in addition the centres of the tpt triazine rings in the columns do not fall on a straight line nor are the average tpt planes perpendicular to the direction of the column. An outstanding feature of some highly symmetrical coordination polymers of tpt reported earlier[6] has been the appearance of tight pairs of tpt units with their triazine rings in close face-to-face π contact, one rotated 60° relative to the other around a 3-fold axis passing through the mid-points of both rings and perpendicular to them; these are examples of Piedfort pairs.[7] In the present structure there appears to be a dominant, structure-determining driving force for each tpt unit to become π-associated not with a single partner but with one on each side to generate an extended π stack. The closest non-hydrogen contacts between tpt units in the columns are not triazine-to-triazine but rather triazine-to-pyridine and the high symmetry of the Piedfort pairs is lost. The closest atom-to-atom contact on one side of a tpt unit to a tpt unit of an adjacent sheet is 3.327 Å, whilst on the other side the closest contact of 3.352 Å is to a tpt unit two sheets removed.

The methanol of solvation is hydrogen bonded to a particular one of the acetate units in the Cu(1)··Cu(2) dimer (O··O, 2.876 Å).

The variation of magnetic susceptibility of **1** with temperature is very much like that of the antiferromagnetically coupled parent complex $Cu_2(O_2CCH_3)_4(H_2O)_2$. Fitting of the data to the Bleaney–Bowers equation[8] for an isolated Cu^{II} dimer yielded parameter values $g = 2.0$, $J = -153$ cm^{-1}, $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}, fraction monomer = 0.02 (*cf.* $Cu_2(O_2CCH_3)_4(H_2O)_2$ $J = -148$ cm^{-1}). Thus there are negligible or very weak dimer–dimer interactions propagated by the tpt group. Related linear chains linked by pyrazines behave similarly.[9]

In conclusion, the structure reported here reveals an alternative means to interpenetration whereby large holes in the individual 2D sheets may be satisfactorily occupied by tpt nodes from the sheets on opposite sides which are attracted together to form π–π associations inside the hole.

Notes and references

† A buffer layer of benzyl alcohol (5 ml) was carefully layered over a solution of tpt (25 mg, 0.080 mmol) in benzyl alcohol (10 ml), and a layer of $Cu(O_2CCH_3)_2 \cdot H_2O$ (38 mg, 0.19 mmol) in methanol (10 ml) was carefully placed on top of the buffer layer. Green crystalline **1** formed after 3 days (23 mg, 0.013 mmol, 41%). (Found: C, 41.44; H, 3.29; N, 9.79. Calc for $Cu_6C_{62}H_{68}N_{12}O_{26}$: C, 41.47; H, 3.89; N, 9.52%).

‡ *Crystal data* for **1**: $Cu_6C_{62}H_{68}N_{12}O_{26}$, $M = 1778.52$, green plate, crystal dimensions $0.03 \times 0.1 \times 0.17$ mm, monoclinic, $P2_1/n$ (no. 14), $a = 7.976(1)$, $b = 30.996(5)$, $c = 15.559(2)$ Å, $\beta = 104.47(1)°$, $U = 3724.5(9)$ Å^3, $T = 150$ K, $Z = 2$, $\mu(Cu_{K\alpha}) = 2.60$ mm^{-1}, 8827 reflections collected, 7634 unique ($R_{int} = 0.0618$), 4340 observed ($I > 2\sigma(I)$), 482 parameters, $R_1 = 0.0739$ ($I > 2\sigma(I)$), $wR_2 = 0.1952$ (all data), $S = 1.020$. CCDC reference number 182/1631. See http://www.rsc.org/suppdata/cc/b0/b002193h/ for crystallographic files in .cif format.

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