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Combination of weak covalent, hydrogen bonding, and Ag $\cdots$ π interactions in the formation of a 3D porous network $Ag(pypd)_2(ClO_4)\cdot CH_2Cl_2$ by the ambidentate ligand 1-(4′-pyridyl)pyridin-4-one

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An interesting diversity of linkage types — weak covalent, hydrogen bonding, and Ag $\cdots$ π interactions — is shown to be involved in the 3D porous network formed by the title compound.

We recently reported[1] the ability of the ambidentate, extended-reach ligand 1-(4′-pyridyl)pyridin-4-one (pypd)[2] to form heterometallic networks. The advantage of using N,O donor ligands of this type is not limited to the use of combinations of metals as node points as there is also the potential for exploiting the differing capacities of the two donor groups for other types of bonding interaction, such as hydrogen bonding — a feature clearly adumbrated in the structure of the ethanoic acid adduct of pypd.[1] Although 'conventional' O–H $\cdots$ O/N and N–H $\cdots$ O/N hydrogen bonding has been extensively employed in the creation of molecular arrays,[3] the utilisation of cooperative, weaker interactions has received far less attention. The importance of involving such additional interactions in the formation of porous 3D coordination polymer networks is well-illustrated by the structure of the complex $Ag(pypd)_2(ClO_4)\cdot CH_2Cl_2$ **1**.

A single crystal X-ray structural analysis of crystals of **1**,† obtained by a conventional 'layering' method from pypd and silver perchlorate in 2 : 1 mole ratio in ethanol and dichloromethane respectively, revealed the formation of a complex of stoichiometry $Ag(pypd)_2(ClO_4)\cdot CH_2Cl_2$. The silver atom is bound to the nitrogen atom of the pyridyl ring of two crystallographically independent pypd ligands [Ag–N, 2.174(5) and 2.195(5) Å] in a distinctly non-linear geometry [N–Ag–N 155.7(2)°]. The pyridyl and pyridone rings within each pypd ligand are twisted with respect to each other about their central C–N bond by *ca.* 30°, a value less than that observed (*ca.* 40°) in the simple hydrogen-bonded ethanoic acid adduct of the ligand.[1] The pyridone oxygen atoms adopt two differing roles, with one of them, O(22), making a T-type linkage[4] to the silver atom of an adjacent $Ag(pypd)_2$ unit, at a weaker bonding distance of 2.559(5) Å, whereas the other, O(10), acts as the acceptor for two C–H $\cdots$ O hydrogen bonds from the *ortho* pyridyl carbon atoms C(2) and C(14) of a third $Ag(pypd)_2$ unit. The combination of these interactions gives rise to the formation of a covalent/H-bonded two-dimensional sheet polymer, the basic building unit of which is illustrated in Fig. 1. The contiguous, trapezium-shaped macrocycles within this array have edge Ag $\cdots$ Ag lengths of 11.9 and 14.1 Å.

Adjacent sheets stack essentially in register along the crystallographic *c* direction to form a 3D porous net (Fig. 2). These sheets are linked by a combination of: (i) π–π stacking of both head-to-tail and head-to-head arrangements of the pypd ligands, (ii) by additional, longer range, O(22) $\cdots$ Ag links (2.99 Å) and (iii) Ag $\cdots$ π interactions to an orthogonally oriented pyridyl ring of adjacent sheets. These latter two interactions are illustrated in Fig. 3, which depicts the relevant component parts of three adjacent layers A, B, and C. As can be seen from this Figure, a pseudo square-pyramidal geometry exists at each silver centre. Longer range orthogonal O $\cdots$ Ag approaches are fairly commonplace as are Ag $\cdots$ π interactions involving phenyl ring systems. Analogous interactions involving pyridyl rings, however, appear to be relatively rare and we have found only three comparable examples in the literature[5–7] and in only one of them[5] was the Ag $\cdots$ π interaction

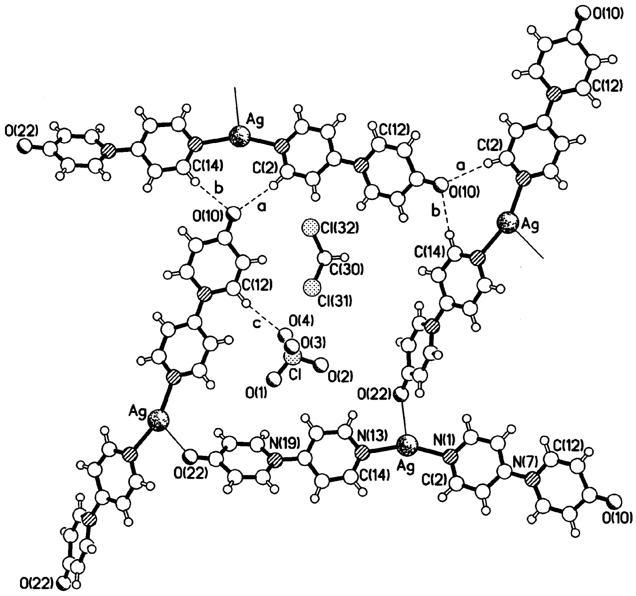

Fig. 1 One of the trapezoidal-shaped building units in the sheets within the 3D network of **1**. Hydrogen bonding geometries [C $\cdots$ O], [H $\cdots$ O] (Å), [C–H $\cdots$ O] (°): (a) 3.34, 2.41, 164; (b) 3.27, 2.35, 161; (c) 3.36, 2.42, 166.

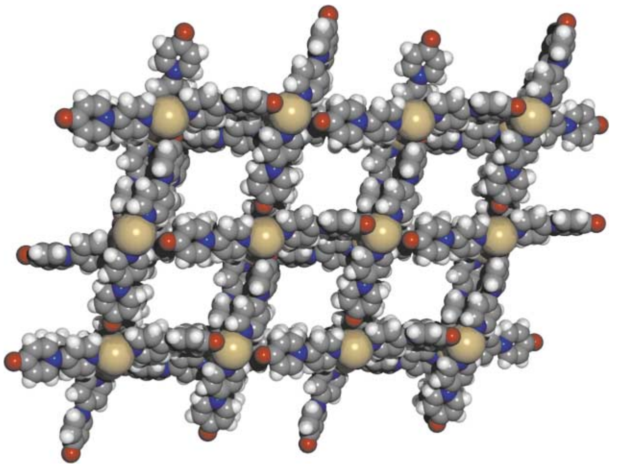

Fig. 2 Space-filling representation of part of the 3D net structure of **1**. The atom colours are: Ag buff, N blue, O red, C grey, H white.

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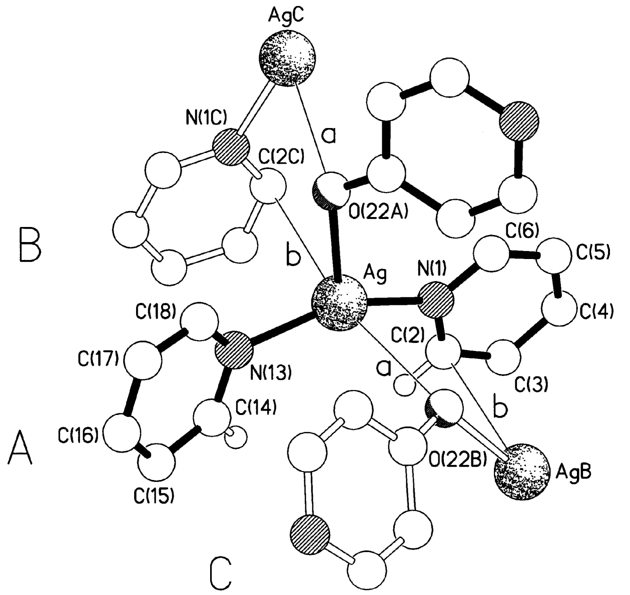

Fig. 3 The weak covalent O ··· Ag and non-covalent Ag ··· π interactions between three layers (A, B, and C) in the structure of **1**. The intersheet linkages are: (a) 2.99 Å, and (b) 3.21 Å.

identified. The network channels have a free pathway diameter of *ca.* 6 Å but contain ordered perchlorate counter ions and dichloromethane solvent molecules (Fig. 1); the anion participates in a C–H ··· O hydrogen bond to one of the walls of the channel (c in Fig. 1).

This network demonstrates the ability to form, *via* the cooperative action of disparate types of weak, non-covalent forces, a relatively robust porous material capable of retaining both anions and volatile solvent species.

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Notes and references

† Crystal data for **1**: $[C_{20}H_{16}N_4O_2Ag][ClO_4]\cdot CH_2Cl_2$, M = 636.61, monoclinic, $P2_1/c$ (no. 14), a = 14.8073(9), b = 19.2390(14), c = 8.4894(7) Å, β = 92.937(6)°, V = 2425.5(3) Å^3, Z = 4, D_c = 1.743 g cm^{-3}, μ(Mo-Kα) = 1.21 mm^{-1}, T = 293 K; 4257 independent measured reflections, F^2 refinement, R_1 = 0.056, wR_2 = 0.119, 2778 independent observed, absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \le 50°$], 317 parameters. CCDC reference number 182733. See http://www.rsc.org/suppdata/dt/b2/b202938n/ for crystallographic data in CIF or other electronic format.

1 D. M. L. Goodgame, D. A. Grachvogel and D. J. Williams, *Inorg. Chem.*, 2001, **40**, 6180.
2 F. Arndt, *Chem. Ber.*, 1932, **65**, 92.
3 *e.g.* S. Nagasoto, Y. Sunatsuki, S. Ohsato, T. Kido, N. Matsumoto and M. Kojima, *Chem. Commun.*, 2002, 14.
4 For a recent example of this type of interaction in network formation see: S. Ferlay, S. Koenig, M. W. Hosseini, J. Pansanel, A. De Cian and N. Kyritsakas, *Chem. Commun.*, 2002, 218.
5 M. Hedrich and H. Hartl, *Acta Crystallogr., Sect. C*, 1983, **39**, 1649.
6 T. Soma and T. Iwamoto, *Acta Crystallogr., Sect. C*, 1997, **53**, 1819.
7 S. Sailaja and M. V. Rajasekharan, *Inorg. Chem.*, 2000, **39**, 4586.