In situ ligand synthesis and construction of an unprecedented three-dimensional array with silver(I): a new approach to inorganic crystal engineering

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Reaction of 1,2-*trans*-(4-pyridyl)ethene with $AgBF_4$ results in the formation of a three-dimensional network based upon a cyclobutane-linked tetrapyridyl ligand, 1,2,3,4-tetrakis(4-pyridyl)cyclobutane, linked by Ag^I ions; the *in situ* formation of the ligand represents a potential new direction for inorganic crystal engineering.

Inorganic supramolecular chemistry and the construction of polymeric arrays is an area of great current interest.[1–5] The design of different network topologies *via* ligand design and the use of different transition-metal coordination numbers has resulted in a wide variety of structural motifs.[1–5] More subtle effects on network topology such as anion control[4] and the use of the π–π stacking have received growing attention.[5] During our research into polymeric arrays formed by silver(I) complexes of bipyridyl ligands we have observed a common structural motif of linear chains of alternating Ag ions and linking ligands.[2,4–6] In complexes where the ligand has significant π–π stacking ability, adjacent chains may tend to adopt an arrangement to maximise both π–π stacking and Ag–Ag interactions (Fig. 1).[4–6] However, the reaction of $AgBF_4$ with 1,2-*trans*-(4-pyridyl)ethene revealed an unexpected *in situ* cyclisation to yield the ligand 1,2,3,4-tetrakis(4- pyridyl)cyclobutane which is incorporated within a three-dimensional metal–complex polymeric array.

A crystalline sample from the reaction of $AgBF_4$ and 1,2-*trans*-(4-pyridyl)ethene was prepared in MeCN and CH_2Cl_2 in the presence of light. Colourless blocks, suitable for single-crystal X-ray analysis were grown following diffusion of the two solvents over the period of *ca.* one month.†

An X-ray structural determination‡ revealed that the ligand had undergone a [2 + 2] cyclisation to form a tetrapyridyl-substituted cyclobutane ring (Fig. 2). The complex exists as a three-dimensional cationic polymer in which each Ag^I centre is coordinated in a tetrahedral geometry to four pyridyl groups [Ag–N 2.302(4), 2.360(4) Å] each from different 1,2,3,4-tetrakis(4-pyridyl)cyclobutane ligands. The lattice grows so that channels are generated which accommodate the BF_4^- counter anions and MeCN solvent molecules (Fig. 3). These channels are intriguing in that the silver–pyridyl–cyclobutane–pyridyl–silver chain forms a helix which winds around the channel. The handedness of these helices alternates along adjacent channels providing the lattice with no overall chirality. Somewhat suprisingly and unusually for such three-dimensional networks, the lattice fills space efficiently without requiring interpenetration of independent lattices. We believe that this non-interpenetrating lattice with helical channels is a previously unobserved network topology.

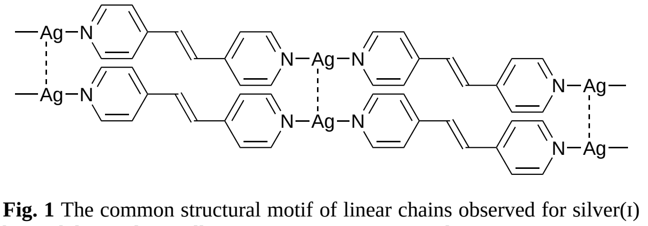

Fig. 1 The common structural motif of linear chains observed for silver(I) bipyridyl complexes allowing Ag···Ag contacts andπ–π interactions

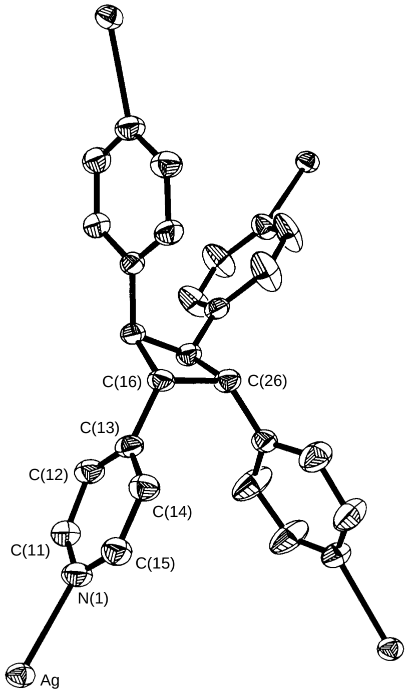

Fig. 2 View of the structure of 1,2,3,4-tetrakis(4-pyridyl)cyclobutane with Ag^I coordinated to each pyridyl group

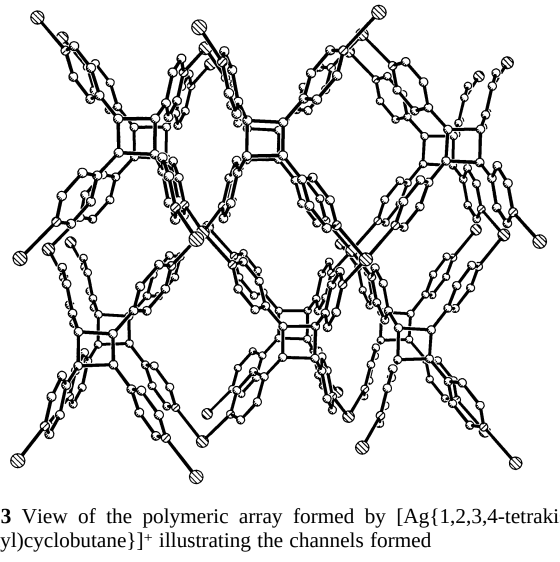

Fig. 3 View of the polymeric array formed by $[Ag\{1,2,3,4\text{-tetrakis(4-pyridyl)cyclobutane}\}]^+$ illustrating the channels formed

Dimerisation of substituted alkenes is most commonly achieved by UV photolysis.[7,8] Interestingly, UV photolytic dimerisation of 1,2-*trans*-(4-pyridyl)ethene in MeOH or C_6H_6 affords two isomers of the ligand, but cyclisation does not occur in the absence of a UV source.[8] Furthermore, 1,2-*trans*-(4-pyridyl)ethene does not dimerise in the solid state, and this has been attributed to an unfavourable arrangement of the ligands within the crystalline lattice.[8] Interestingly, the reaction reported herein produces only a single isomer of the tetrapyridyl ligand (confirmed by NMR studies of the bulk product) consistent with the reaction proceeding in the solid state as outlined by Schmidt *et al.*,[7] and contrary to the reported UV photolytic dimerisation of 1,2-*trans*-(4-pyridyl)ethene in solution which would be expected to give two isomers of the cyclised ligand.[8] Significantly, no dimerisation product was observed in the reaction of Ag^I with 1,2-*trans*-(4-pyridyl)ethene in the absence of light. This indicates a key role of the Ag^I ions in the light-induced dimerisation process, but does not confirm whether the ligand cyclisation occurs in the solid state or in solution.

In conclusion, the reaction of Ag^I with 1,2-*trans*-(4-pyridyl)ethene represents the first example of the formation of an inorganic three-dimensional lattice *via* the *in situ* generation of a ligand, and the first structurally characterised network incorporating 1,2,3,4-tetrakis(4-pyridyl)cyclobutane. We are currently probing the mechanism of cyclodimerisation reactions and the wider applications of this approach to inorganic crystal engineering.

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Footnotes and References

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† *Experimental*: {[Ag(1,2,3,4-tetrakis(4-pyridyl)cyclobutane]BF_4}$_\infty$. A solution of $AgBF_4$ (50 mg, 0.26 mmol) in MeCN (10 cm^3) was layered over a solution of 1,2-*trans*-(4-pyridyl)ethene (bpe) (95 mg, 0.52 mmol) in CH_2Cl_2 (10 cm^3). The two layers were allowed to diffuse and colourless block crystals were grown over a period of *ca.* one month. The sample was exposed to daylight throughout the experiment. Yield (63 mg, 44%). Satisfactory spectroscopic and analytical data were obtained.

‡ *Crystal data* for {[Ag(1,2,3,4-tetrakis(4-pyridyl)cyclobutane]$BF_4\cdot3$MeCN}$_\infty$: $C_{30}H_{29}AgBF_4N_7$, M = 682.28, orthorhombic, space group *Fddd* (no. 70), a = 10.292(2), b = 29.887(6), c = 38.593(8) Å, U = 11871(4) Å^3, T = 150 K, Z = 16, F(000) = 5536, D_c = 1.527 g cm^{-3}, μ(Mo-Kα) = 0.738 mm^{-1}. Colourless crystal (0.48 × 0.36 × 0.36 mm). Stoe Stadi-4 four-circle diffractometer, graphite-monochromated Mo-Kα radiation, ω–2θ scans, data collection range (θ_{max} = 25.0°). An absorption correction based upon ψ-scans was applied to the data (T_{min} 0.645, T_{max} 0.768), 2631 unique reflections, of which 2220 had $F_o > 4\sigma(F_o)$, were used in all calculations. The structure was solved using direct methods[9] and all non-H atoms were located using subsequent difference-Fourier methods.[10] The BF_4^- counter anion was found to be disordered into two equally occupied sites. The two carbon atoms of one acetonitrile solvent molecule were found to be disordered over two equally occupied sites. Hydrogen atoms were placed in calculated positions and were allowed to ride on their parent atoms. All atoms except H, F, B and the disordered carbon atoms of a MeCN solvent molecule were refined with anisotropic thermal parameters. The weighting scheme {$w^{-1} = [\sigma^2(F_o^2) + (0.0756P)^2 + 175.39P]$, $P = [\max(F_o^2,0) + (2F_c^2)/3]$ was adopted. At final convergence[10] R_1 [$I > 2\sigma(I)$] = 0.054 wR_2 (all data) = 0.147 for 195 parameters, S = 1.041, $(\Delta/\sigma)_{max}$ = −0.002, $\Delta\rho_{max}$ = 0.598 e Å^{-3}. CCDC 182/497.

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