

Control of interpenetrating copper(I) adamantoid networks: synthesis and structure of $\{[\text{Cu}(\text{bpe})_2]\text{BF}_4\}_n$

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Lengthening of linking bipyridyl ligands in interlocking copper(I)-heterocycle adamantoid arrays increases the volume of the adamantoid cages and consequently the number of observed interpenetrating networks: factors influencing the observed structures of these interpenetrating complexes are described in the context of the structure of $\{[\text{Cu}(\text{bpe})_2]\text{BF}_4\}_n$ [bpe = 1,2-*trans*-(4-pyridyl)ethene].

The construction of solid-state architectures and crystal engineering has become an area of increasing interest over recent years.^{1–4} Much study has been centred upon the use of supramolecular contacts and in particular hydrogen-bonding between suitable organic molecules to generate multi-dimensional arrays and networks.^{1–3} The design of inorganic networks is much less well developed^{4–8} but recent examples have helped to extend the understanding of this developing area. The construction of adamantoid or super-diamondoid arrays is a common feature amongst some of these infinite three-dimensional networks^{4–7} and are often based upon linear bridging ligands bound to tetrahedral metal ions such as Cu^{I} or Ag^{I} .^{5,6} Interpenetration of independent networks is often encountered in adamantoid networks as the crystal avoids the formation of large cavities within the crystalline lattice.^{4–7,9,10} The number of independent interpenetrating networks can vary in these three-dimensional polymers¹⁰ from two to as many as eight and nine.^{11–13} However, the factors that control the observed degrees of interpenetration in these systems remain largely unknown and/or unproven, and to this end we have begun studies into how ligand functionality can be used to control overall structure of three-dimensional arrays.

Red kite-shaped crystals of a complex product were grown over a period of days at the interface of layered solutions of 1,2-*trans*-(4-pyridyl)ethene (bpe) in MeCN and $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ in CH_2Cl_2 . A single-crystal X-ray structure determination‡ confirmed the product to be a three-dimensional polymer, $\{[\text{Cu}(\text{bpe})_2]\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2\}_n$, in which each Cu^{I} centre is coordinated in a tetrahedral geometry to four bpe ligands [Cu–N 2.003(5)–2.084(6) Å] which are in turn bound to four other Cu^{I} centres. The three-dimensional structure (Fig. 1) builds through the formation of edge-sharing adamantoid units. The Cu···Cu distances across the edge of each adamantoid unit ranges from 13.33 to 13.82 Å to create large cavities within this first three-dimensional lattice. These cavities are filled with four other $\{[\text{Cu}(\text{bpe})_2]^+\}_n$ lattices which are positioned such that they interpenetrate each other to fill the spaces left by each other. All five independent lattices are polycatenated with channels throughout the structure parallel to the direction of translation for the five networks and within the adamantoid units (Fig. 2): these channels accommodate BF_4^- counter ions and CH_2Cl_2 solvent molecules.

This structure is related to that observed for $\{[\text{Cu}(4,4'\text{-bipy})_2]\text{PF}_6\}_n$ ⁵ and $\{[\text{Ag}(4,4'\text{-bipy})_2]\text{CF}_3\text{SO}_3\}_n$ ⁶ in which four independent adamantoid networks are formed. Thus, by lengthening the linking bipyridyl ligand *via* insertion of a *trans* C=C double bond between the pyridyl units the length of the edges of the adamantoid units are extended from 11.16 Å for $\{[\text{Cu}(4,4'\text{-bipy})_2]\text{PF}_6\}_n$ ⁵ to 13.55 Å (average) in the structure of $\{[\text{Cu}(\text{bpe})_2]\text{BF}_4\}_n$ reported here. This increase in length of the adamantoid unit edge in $\{[\text{Cu}(\text{bpe})_2]\text{BF}_4\}_n$ creates a larger cavity within the structure which is filled by the inclusion of one

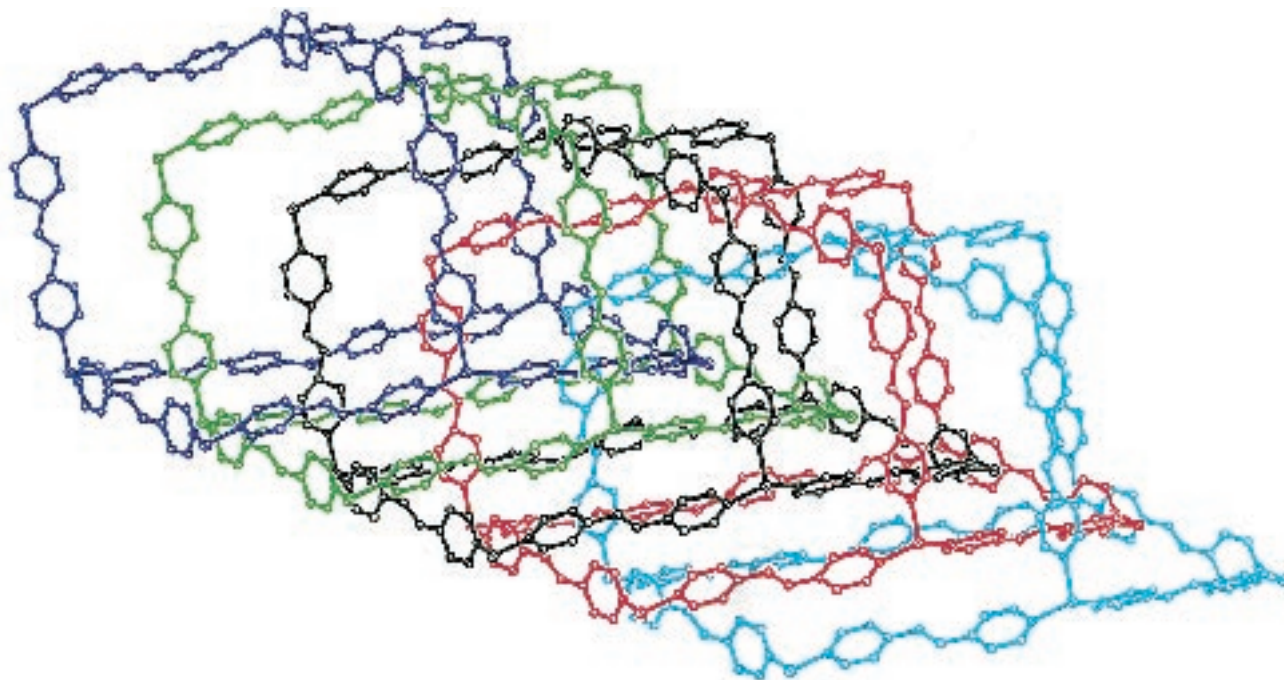


Fig. 1 View of the structure of $\{[\text{Cu}(\text{bpe})_2]\text{BF}_4\}_n$ showing five interlocking adamantoid cages

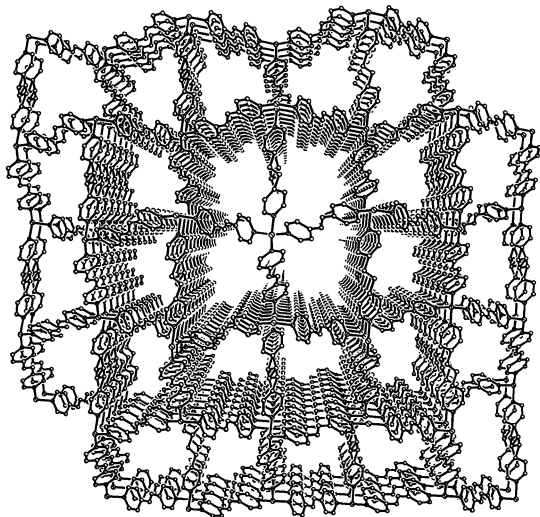


Fig. 2 View of the structure of {[Cu(bpe)₂]BF₄}_n

extra independent {[Cu(bpe)₂]⁺}_n lattice. Also, CH₂Cl₂ fills the extra volume created within the counter anion channels. Thus, by altering the ligand length, the degree of interpenetration has been increased from four independent lattices for {[Cu(4,4'-bipy)₂]PF₆}_n⁵ and {[Ag(4,4'-bipy)₂]CF₃SO₃}_n⁶ to five independent arrays, representing control over the degree of interpenetration. There are only two previous examples of systems with five independent interpenetrating arrays, firstly the hydrogen-bonded array of adamantane-1,3,5,7-tetracarboxylic acid⁹ and secondly the polymer involving Cu^I and 1,4-dicyanobenzene for which the nature of interpenetration was not fully discussed.⁴

The separations between adjacent adamantoid cages in {[Cu(bpe)₂]BF₄}_n is controlled further by face-to-face π-π stacking interactions of 3.659 and 3.855 Å between sets of bpe ligands marked *a* and *b*, respectively, in Fig. 1. Other seemingly adjacent bpe ligands have larger gaps between them along the other sides of the adamantoid cages [*c* in Fig. 1]. Nonetheless, π-π stacking is clearly important in the overall control of this extended structure and the presence of this interaction along the direction in which the adamantoid cages propagate may reveal how such long-range structure is formed during crystallisation. Interestingly, the related complex {[Ag{NC(C₆H₄)₂CN}₂]PF₆}_n has nine independent adamantoid networks¹³ despite only a relatively small increase in the M...M distance of 16.42 Å, compared with 13.55 Å (average) in the present study. This higher degree of interpenetration in {[Ag{NC(C₆H₄)₂CN}₂]PF₆}_n is enabled by the closer approach of adjacent lattices in this complex: this is not allowed in {[Cu(bpe)₂]BF₄}_n due to steric repulsion between pyridyl groups coordinated to Cu centres from adjacent cages.

The present study on {[Cu(bpe)₂]BF₄·0.5CH₂Cl₂}_n reveals direct evidence of control over the fascinating phenomenon of interpenetration and highlights the factors (namely, ligand length, π-π and steric interactions) which will allow design of further supramolecular architectures *via* control of separations between adjacent interlocking cages.

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Footnotes

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‡ Crystal data for [Cu(bpe)₂]BF₄·0.5CH₂Cl₂, C₂₄H₂₁BClCuF₄N₄, *M* = 557.25, triclinic, space group *P*1̄ (no. 2), *a* = 7.310(3), *b* = 13.144(5),

c = 13.800(4) Å, α = 83.46(3), β = 82.88(4), γ = 84.71(3)°, *U* = 1303.0(8) Å³, *Z* = 2, *F*(000) = 566, *D_c* = 1.420 g cm⁻³, μ(Mo-Kα) = 0.989 mm⁻¹. Red kite-shaped crystal (0.29 × 0.23 × 0.12 mm). Stoe Stadi-4 four-circle diffractometer, graphite monochromated Mo-Kα radiation, ω-2θ scans with ω-scan width of 1.1°. Numerical absorption corrections were applied to the data (*T_{min}* = 0.828, *T_{max}* = 0.900), 4593 unique reflections (2θ_{max} = 50°, *R_{int}* = 0.0489), of which 3763 had *F_o* ≥ 4σ(*F_o*), were used in all calculations. The position of the Cu atom was deduced by Patterson synthesis¹⁴ and all the remaining non-H atoms were located from subsequent difference-Fourier methods.¹⁵ Atom C(16), an ethylene carbon on one of the bipyridyl groups, and three of the F-atoms of the BF₄⁻ anion are each disordered into two equal components. Full-matrix least-squares procedures were used for refinement and all non-F and C atoms [except for C(11), C(12), C(13), C(14), C(15), (one pyridyl unit), and C(1s) from the CH₂Cl₂ solvent molecule] were refined with anisotropic displacement parameters; hydrogen atoms were placed geometrically for all non-disordered carbon atoms and thereafter allowed to ride on their parent C-atoms with *U_{iso}*(H) = 1.2 *U_{eq}*(C). The weighting scheme *w*⁻¹ = [σ²(*F_o*)² + (0.1131*P*)² + 8.1717*P*], *P* = 1/3[max(*F_o*², 0) + 2*F_c*²], gave satisfactory agreement analyses. Final *R*₁ [*F_o* ≥ 4σ(*F_o*)] = 0.0892, *wR*₂ (all data) = 0.2553 for 234 refined parameters, *S* = 1.095, (Δ/σ)_{max} = 0.03, Δρ_{max} = 1.50 e Å⁻³ [in the proximity of the C(1s) and Cl atoms]. 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 182/432.

References

- G. R. Desiraju, in *Crystal Engineering: Design of Organic Solids*, Elsevier, Amsterdam, 1989.
- The Crystal as a Supramolecular Entity*, ed. G. R. Desiraju, Wiley, 1995.
- G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
- R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, *Supramolecular Architecture*, ACS publications, 1992, ch. 19.
- L. R. MacGillivray, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1994, 1325.
- L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1994, 2755.
- S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1992, **114**, 8719; S. B. Copp, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1993, 1078; S. B. Copp, K. T. Holman, J. O. S. Sangster, S. Subramanian and M. J. Zaworotko, *J. Chem. Soc., Dalton Trans.*, 1995, 2233.
- D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. Hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030; B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1966, **35**, 1690; J. Black, N. R. Champness, W. Levason and G. Reid, *Inorg. Chem.*, 1996, **35**, 4432; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562; B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; D. M. L. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 574; P. C. M. Duncan, D. M. L. Goodgame, S. Menzer and D. J. Williams, *Chem. Commun.*, 1996, 2127.
- O. Ermer, *J. Am. Chem. Soc.*, 1988, **110**, 3747.
- D. B. Amabilino and J. F. Stoddart, *Chem. Rev.*, 1995, **95**, 2725.
- B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins and R. Robson, *Chem. Commun.*, 1996, 1313.
- L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Chem. Commun.*, 1996, 1393.
- K. A. Hirsch, D. Venkataraman, S. R. Wilson, J. S. Moore and S. Lee, *J. Chem. Soc., Chem. Commun.*, 1995, 2199.
- SHELXS-96: G. M. Sheldrick, Universität Göttingen, 1996.
- SHELXL-96: G. M. Sheldrick, Universität Göttingen, 1996.

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