

Crystal engineering: the effects of π - π interactions in copper(I) and silver(I) complexes of 2,7-diazapyrene

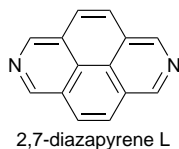
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The ligand 2,7-diazapyrene (L) is used to construct three- and two-dimensional arrays with Cu^I and Ag^I ions: $\{[\text{Cu}^{\text{I}}\text{L}_2]\text{PF}_6\}_\infty$ shows an adamantoid network with three interpenetrating networks, while $\{[\text{Ag}^{\text{I}}\text{L}_2(\text{MeCN})_2]\text{BF}_4\}_\infty$ forms linear chains of $[\text{AgL}]_\infty$ units linked by apparent π - π stacking and Ag \cdots Ag interactions between adjacent diazapyrene ligands to form two-dimensional sheets.

Crystal engineering and the design of solid-state architectures has become an area of increasing interest over recent years.¹⁻⁴ Much study has been centred upon the use of supramolecular contacts, particularly hydrogen-bonding, between suitable molecules to generate multi-dimensional arrays or networks.¹⁻³ In comparison, the design of inorganic networks has been less well developed.⁴⁻⁸ We have been investigating the effect of ligand functionality upon the construction of two- and three-dimensional arrays and, in particular, adamantoid or super-diamondoid networks based upon copper(I) complexes.⁸ We were interested in monitoring the effects of ligand bulk and the potential of π - π stacking interactions in controlling network geometry. With this in mind we chose the ligand 2,7-diazapyrene (L)⁹ as a potentially useful building block in the construction of multi-dimensional architectures. We report herein the first structurally characterised examples of metal complexes with L.



The reaction of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ with L in MeCN-PhCN afforded unusual triangular-shaped red crystals suitable for X-ray analysis. The crystal structure shows† the complex $\{[\text{CuL}_2]\text{PF}_6\}_\infty$ to form a three-dimensional adamantoid network in which each Cu^I centre is co-ordinated in a tetrahedral geometry to four diazapyrene ligands, Cu-N 2.044(9)Å. The spaces within each adamantoid network are filled by two other adamantoid networks and the three interpenetrating arrays related to each other by a 90° rotation (Fig. 1). This form of interpenetration contrasts with that observed for other copper(I) adamantoid networks which are related to each other by simple translation.^{5,6,8} Adjacent lattices interact with each other *via* face-to-face π - π interactions between 2,7-diazapyrene ligands which are arranged so that the N \cdots N axes of the ligand are at 90° to one another. The distance between aromatic rings is 3.469 Å, compared with a value of 3.450 Å for the free ligand which we have structurally characterised.¹⁰ The positive charge of the metallo-ligand lattice is balanced by PF₆⁻ counter anions which were found to be disordered around a threefold axis. The counter anion site was also found to be partially occupied with three-quarters of the PF₆⁻ anion sites filled.†

The three independent interpenetrating lattices observed for $\{[\text{CuL}_2]\text{PF}_6\}_\infty$ contrasts with the four observed for $\{[\text{Cu}(4,4'\text{-bipy})_2]\text{BF}_4\}_\infty$ ⁵ and five for $\{[\text{Cu}(\text{bpe})_2]\text{BF}_4\}_\infty$ [bpe = 1,2-*trans*-(4-pyridyl)ethene].⁸ 2,7-Diazapyrene is a slightly shorter linker than 4,4'-bipy, giving a Cu \cdots Cu distance of 10.904 Å along the edges of each adamantoid unit in $\{[\text{CuL}_2]\text{PF}_6\}_\infty$ compared to 11.166 Å for $\{[\text{Cu}(4,4'\text{-bipy})_2]\text{BF}_4\}_\infty$.⁵ Although the decrease in the number of interpenetrating lattices might in principle be explained by the decrease in the length of the linking ligand, this seems unlikely given such a small decrease in Cu \cdots Cu distance. Increased π - π interactions between adjacent lattices should encourage more

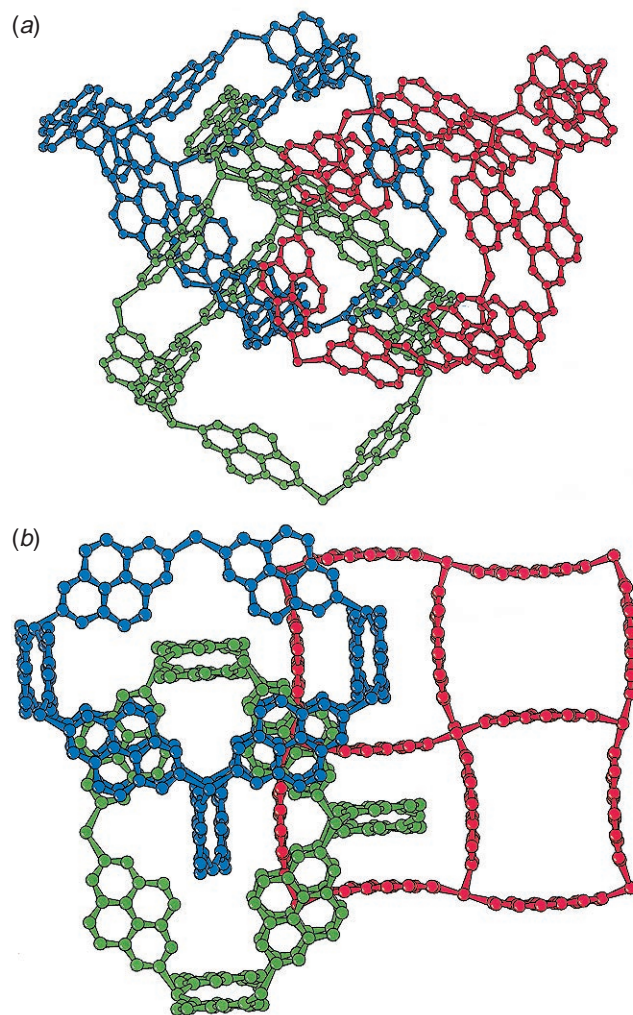


Fig. 1 Two views of the structure of $\{[\text{CuL}_2]\text{PF}_6\}_\infty$ (L = 2,7-diazapyrene) showing three interlocking adamantoid cages. PF₆⁻ anions omitted for clarity.

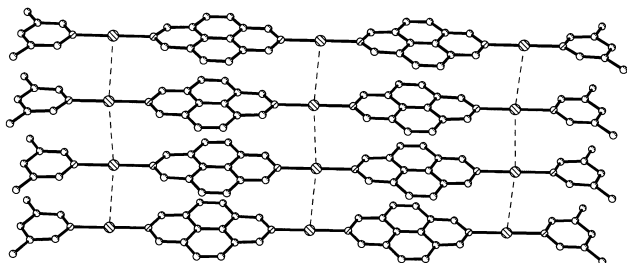


Fig. 2 View of the structure of $\{[\text{AgL}(\text{MeCN})_2]\text{BF}_4\}_\infty$ (L = 2,7-diazapyrene); MeCN molecules and BF_4^- anions have been omitted for clarity

efficient packing which would be expected to lead to increased numbers of independent lattices rather than the decrease observed here. Thus, the decrease in the number of interpenetrating lattices in $\{[\text{CuL}_2]\text{PF}_6\}_\infty$ can be rationalised by the greater lateral steric bulk of L reducing the volume within any given adamantoid lattice that can be filled by other symmetry related lattices. This represents the identification of another factor controlling the degree of interpenetration in adamantoid lattices.^{8,11}

The related silver(I) complex $\{[\text{AgL}(\text{MeCN})_2]\text{BF}_4\}_\infty$ was obtained by reaction of L with AgBF_4 in 1 : 1 or 2 : 1 ligand-to-metal ratios. The structure of the complex shows† linear chains of alternating Ag^{I} ions and L (Fig. 2). These chains are linked together *via* face-to-face π - π interactions between 2,7-diazapyrene ligands in which the ligand N...N axes are parallel to each other with a separation of 3.380 Å: a separation of 3.450 Å is observed in the X-ray structure of the metal-free L.¹⁰ This π - π interaction also enforces the formation of apparent $\text{Ag}\cdots\text{Ag}$ interactions of 3.641(2) Å. Bonding between adjacent chains is further strengthened by MeCN ligands which bridge adjacent Ag centres, Ag-N 2.871(4), 2.926(4) Å, to form two-dimensional sheets. The enforced formation of $\text{Ag}\cdots\text{Ag}$ interactions in this structure is in sharp contrast to the analogous complex $\{[\text{Ag}(4,4'\text{-bipy})]\text{BF}_4\}_\infty$ in which Ag^{I} ions on adjacent linear chains are staggered thereby precluding the formation of $\text{Ag}\cdots\text{Ag}$ interactions or π - π stacking between bipyridyl ligands.¹²

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Footnotes

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† Stoe Stadi-4 four-circle diffractometer, graphite-monochromated Mo-K α radiation, ω - θ scans, $\theta_{\text{max}} = 25^\circ$. Both structures were solved using direct methods¹³ and all non-H atoms were located using subsequent difference-Fourier methods.¹⁴ In both cases hydrogen atoms were placed in calculated positions and were allowed to ride on their parent atoms.

Crystal data for $\{[\text{CuL}_2]\text{PF}_6\}_\infty$: $\text{C}_{28}\text{H}_{16}\text{CuF}_6\text{N}_4\text{P}$, $M = 616.96$, cubic, space group $I\bar{4}3d$ (no. 220), $a = 19.505(7)$ Å, $U = 7421(5)$ Å³, $Z = 12$, $F(000) = 3720$, $D_c = 1.657$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.020$ mm⁻¹. A red triangular crystal ($0.28 \times 0.27 \times 0.23$ mm). Numerical absorption corrections were applied to the data ($T_{\text{min}} 0.7004$, $T_{\text{max}} 0.7487$), 603 unique reflections [$R_{\text{int}} = 0.096$], of which 485 had $I \geq 2\sigma(I)$, were used in all calculations. A correction for crystal decay (4%) was applied during data reduction. The PF_6^- anion was found to be disordered around a threefold axis and the equatorial F atoms were split over four sites of occupancy 0.15, 0.11, 0.22, 0.52. In order to balance charges the occupancy of the PF_6^- anion was required to be 0.25 (rather than 0.333 on a threefold site), see

main text. This was further justified by the improvements which resulted in the overall refinement model, for example R_1 decreased from 0.068 to 0.063. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.052P)^2 + 51.4P]$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$ was adopted. At final convergence¹⁴ $R_1 [I > 2\sigma(I)] = 0.0629$, wR_2 (all data) = 0.1509 for 104 parameters, $S = 1.20$, $(\Delta\sigma)_{\text{max}} = 0.003$, $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³.

For $\{[\text{AgL}(\text{MeCN})_2]\text{BF}_4\}_\infty$: $\text{C}_{18}\text{H}_{14}\text{AgBF}_4\text{N}_4$, $M = 481.01$, monoclinic, space group $C2/c$ (no. 15), $a = 21.660(7)$, $b = 11.380(2)$, $c = 7.263(3)$ Å, $\beta = 100.93(3)^\circ$, $U = 1757.8(10)$ Å³, $Z = 4$, $F(000) = 952$, $D_c = 1.818$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.198$ mm⁻¹. A pale yellow plate ($0.23 \times 0.15 \times 0.05$ mm). Absorption corrections based upon ψ -scans were applied to the data ($T_{\text{min}} 0.8202$, $T_{\text{max}} 0.9336$), 1283 unique reflections [$R_{\text{int}} = 0.030$], of which 1283 had $F_o \geq 4\sigma(F_o)$, were used in all calculations. The methyl carbon of the acetonitrile solvent molecule was found to be disordered over two equally occupied sites. The weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.0246P)^2 + 8.19P]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$ was adopted. At final convergence¹⁴ $R_1 [I > 2\sigma(I)] = 0.0393$, wR_2 (all data) = 0.0809 for 148 parameters, $S = 1.04$, $(\Delta\sigma)_{\text{max}} = 0.002$, $\Delta\rho_{\text{max}} = 0.58$ e Å⁻³.

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 182/472.

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