

# Controlled aggregation of supramolecular boxes

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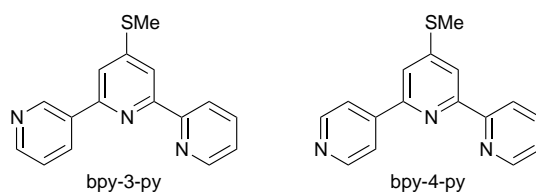
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Supramolecular boxes are prepared and their aggregation controlled by self-assembly; the crystal structure of a polymeric assembly of silver(I) cage units of 4-thiomethyl-6-(4-pyridyl)-2,2'-bipyridine is reported.

The controlled design of complex molecular architectures represents a considerable synthetic challenge. The supramolecular synthetic approach has been used to assemble large molecular aggregates<sup>1–3</sup> and extension to polymeric systems has impacted on the field of crystal engineering.<sup>4,5</sup> Sophisticated macromolecular targets will require the ability to assemble small supramolecular units which may be further aggregated in a controlled fashion. To achieve this we are targeting metallosupramolecular species which contain binding sites on their exterior. Recently, we reported the construction of metallosupramolecular cage species by interacting metal ions with simple dinucleating ligands.<sup>2</sup> These cyclophane analogues were prepared in a single-step assembly process without the need for ancillary ligands which block coordination sites on the metal centre. The metal centres incorporated into the box framework did not use all of their coordination sites in the construction process and we reasoned that these unused coordination sites (which are filled with solvent molecules) might be used to aggregate the box structures. To achieve our sophisticated assemblies, an additional ligating site must be incorporated within the system in such a way that it does not interfere with the box assembly process. Our cage design utilises dinucleating ligands which contain bipyridyl and pyridyl binding sites. Thiomethyl substituents may readily be introduced onto the outside of such ligands.<sup>6</sup> Although thiomethyl groups on the back of oligopyridyl units have not previously been observed to coordinate to metal ions, the chemistry of thioether ligands is well established.<sup>7</sup> Indeed Reid and coworkers recently reported a polymeric 3D coordination array generated by ligating silver(I) to a ligand containing two monodentate thioether sites.<sup>8</sup> The thiomethyl unit is a less effective donor than the pyridine groups and therefore should not compete with or disrupt the box formation while the hard/soft principle might allow the problem of controlled and selective aggregation to be addressed.

The ligand 4-thiomethyl-6-(3''-pyridyl)-2,2'-bipyridine (bpy-3-py) forms discrete box structures with copper(I) and cad-

mium(II) and thioether coordination is not observed with these metals.<sup>2</sup> Switching to the softer silver(I) ion might allow access to this bonding mode. Reaction of the ligand with silver(I) salts gives colourless solutions from which salts of formula  $\{Ag(bpy-3-py)X\}_n$  may be isolated (X = counter-ion). Unfortunately we have so far been unable to obtain material suitable for X-ray structural characterisation from this reaction.



Modelling indicated that the related ligand 4-thiomethyl-6-(4''-pyridyl)-2,2'-bipyridine (bpy-4-py) should give analogous box structures and so we have examined the ligation of silver(I) to this ligand. The ligand was prepared in good yield (72%) in a one-pot Potts<sup>6</sup> reaction of 3,3-bis(methylthio)-1-(2''-pyridinyl)prop-2-en-1-one with the potassium enolate of 4-acetylpyridine, followed by ring closure with ammonium acetate.

Warming methanolic solutions of the ligand with 1 equiv. of silver(I) salts leads to the rapid formation of colourless solutions from which white salts of formula  $[Ag_2(bpy-4-py)_2][PF_6]_2$  were isolated on the addition of methanolic ammonium hexafluorophosphate. Mass spectrometric analysis (FAB) showed the presence of dinuclear  $M_2L_2$  and  $M_2L_2X$  peaks consistent with this formulation. Recrystallisation of the salt from acetonitrile solution by the slow diffusion of diethyl ether afforded colourless crystals, the structure of which has been determined† and which is shown in Fig. 1.

As anticipated the bpy-4-py ligand bridges between metal centres. Each silver(I) centre is bound to a bipyridyl unit from one ligand and a pyridyl from the other, resulting in the formation of a dimeric  $M_2L_2$  box species. The metal–ligand bond lengths and angles are unremarkable and the intermetallic Ag...Ag distance is 6.686(2) Å. The pyridyl and bipyridyl binding domains are twisted with respect to each other [dihedral

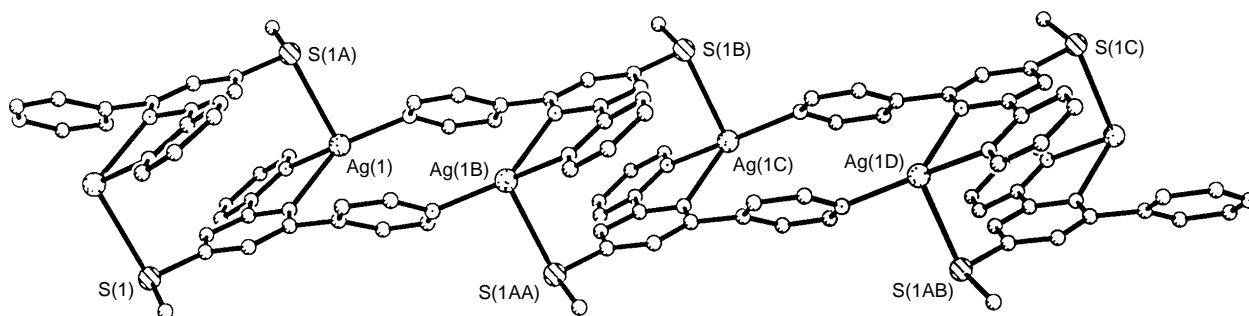


Fig. 1 Crystal and molecular structure of the cation  $[Ag_2(bpy-4-py)_2]_n^{2n+}$

angle 47.4(4)°] and a cavity between the pyridyl units of the two ligands results. This twisting is anticipated and is similar to that observed in the box complexes of bpy-3-py. The twisting results in the aromatic rings defining an aryl-lined cavity. The centroid-centroid distance between the two monodentate pyridyl rings, which define the cavity, is 4.00 Å. The box structure is, as would be anticipated from the ligand connectivity, slightly flatter than those formed with bpy-3-py.<sup>2</sup>

Each silver(I) ion is four coordinate and its coordination sphere is completed by coordination to a thioether unit from an adjacent box. This interaction links the boxes together into a polymeric array. The elongated Ag-S bonds [2.940(3) and 2.961(3) Å] are approximately 0.3 Å longer than those observed in other thioether silver(I) complexes.<sup>8</sup> The coordination of the thioether groups brings the aryl rings of adjacent boxes into close contact. The central pyridyl rings, bearing the thiomethyl substituents, are coplanar and offset, with a centroid-centroid distance of 3.86 Å. This may represent a weak  $\pi$ -stacking contribution to the aggregation process.

This form of supramolecular architecture may be contrasted with the elegant solid-state cavity-containing arrays of Robson and coworkers and Fujita *et al.*<sup>5</sup> In their approach they allow the repeat cavity unit to propagate through the structure with each cavity sharing a corner and/or side with the adjacent units. Our structure is somewhat different. The repeat cavity unit is assembled independently and the units are then linked *via* sulfur bridges. The cavities share neither edges nor corners with their adjacent neighbours.

While the crystallographic study confirms the aggregation in the solid state this is not the case in solution. The <sup>1</sup>H NMR spectra of CD<sub>3</sub>CN solutions of the salts showed the expected eight resonances in the aromatic region and the presence of a single thiomethyl resonance. The thiomethyl resonance appears at a similar chemical shift in both the complex ( $\delta$  2.69) and the free ligand ( $\delta$  2.66), indicating that the aggregation process is not occurring in acetonitrile solution. This is unsurprising as the donor solvent is expected to compete effectively with the weakly coordinating thiomethyl group.

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## Footnotes and References

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† Crystal data for [Ag<sub>2</sub>(bpy-4-py)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>·MeCN: C<sub>34</sub>H<sub>29</sub>Ag<sub>2</sub>F<sub>12</sub>N<sub>7</sub>P<sub>2</sub>S<sub>2</sub>, *M* = 1105.44, triclinic, space group *P*1̄, *a* = 10.9196(2), *b* = 14.3306(3), *c* = 15.0364(3) Å,  $\alpha$  = 113.967(1),  $\beta$  = 104.25(1),  $\gamma$  = 100.635(1)°, *U* = 1973.47(7) Å<sup>3</sup>, *Z* = 2, *T* = 230(2) K,  $\mu$  = 1.274 mm<sup>-1</sup>; final *R*1, *wR*2 and *S* are 0.071, 0.169 and 1.167 for 532 parameters. Data were collected using a Siemens SMART CCD area-detector diffractometer. Refinement was by full-matrix least squares on *F*<sup>2</sup> for all data using SHELXL-96.<sup>9</sup> CCDC 182/571.

- 1 J.-M. Lehn, *Supramolecular Chemistry—Concepts and Perspectives*, VCH, Weinheim, 1995; D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1155.
- 2 M. J. Hannon, C. L. Painting and W. Errington, *Chem. Commun.*, 1997, 307.
- 3 D. P. Funeri, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1997, **3**, 99; P. N. W. Baxter, J.-M. Lehn, J. Fischer and M.-T. Youinou, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2284.
- 4 B. F. Robson, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle and J.-M. Lehn, Pergamon, Oxford, 1997, vol. 6; M. J. Zarorotko, *Chem. Soc. Rev.*, 1994, **23**, 284.
- 5 B. F. Abrahams, S. R. Batten, H. Hamit, B. F. Hoskins, D. M. Michail and R. Robson, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1690; B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature*, 1994, **369**, 727; M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.
- 6 K. T. Potts, M. J. Cipullo, P. Ralli and G. Theodoridis, *J. Org. Chem.*, 1982, **47**, 3027; E. C. Constable, *Prog. Inorg. Chem.*, 1994, **42**, 67.
- 7 *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987.
- 8 J. R. Black, N. R. Champness, W. Levason and G. Reid, *J. Chem. Soc., Chem. Commun.*, 1995, 1277.
- 9 G. M. Sheldrick, SHELXL-96, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1996.

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