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Extension of a π-stacked N_2S ligand to form bi- and tri-nuclear silver(I) complexes†

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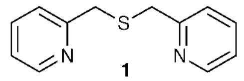
Reactions of tri- and penta-dentate thio-substituted oligopyridines with Ag(I) yielded two differently coded bi- and tri-nuclear structures containing strong intraligand π stacking of the heterocycles.

The design and construction of helicates from ligand threads and metal-ion induced self assembly has been much investigated.[1,2] However, alternatives to helicates exist, such as side-by-side arrangements which represent limiting non-helical structures formed by metal centres fixed between adjacent ligand threads.[1] These have been theoretically predicted and discussed in detail[2] but their observation is rare.[3] Such side-by-side structures offer the same opportunities for the development and understanding of the underlying construction principles of supramolecular chemistry. Both arrangements are driven by coding requirements, namely, the need to match ligand domains to the coordination preferences of the transition metal centres. Typically domains have been linked by non-coordinating species.[1] Incorporation of thioether donors into the linkers decreases the distance between the potential ligand domains thus bringing the metal centres closer together. Compressed conformations of this nature are more likely to favour side-by-side rather than helical arrangements about metal centres. With such an array of donors, ambiguity in coding may arise because of a mismatch of the number of donor atoms to metal-acceptor sites or a mis-allocation of the ligand domains to the metal centres. In such circumstances, the metal centres are required to compensate for this ambiguity. Hence, coordinatively flexible metal ions such as Ag(I) rather than Cu(I) are more likely to succeed in complex formation.

As part of our investigation of thio-substituted oligopyridines we found that the tridentate ligand **1** formed a side-by-side dimeric silver complex $[Ag_2(\mathbf{1})_2]^{2+}$ with strong intraligand π stacking of the pyridine rings. The coordinatively flexible Ag(I) ions adopted a three-coordinate planar geometry to code as a [3 + 3] rather than a [4 + 2] complex. It was of interest to see if on extending the ligand from the tridentate **1** to the related pentadentate **2** the same important features of intraligand π stacking and coding information were retained on complex formation.



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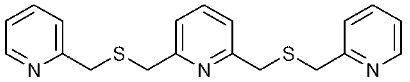

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Equimolar reaction of **1**[4] with $AgNO_3$ in MeCN, followed by treatment with NH_4PF_6, led to isolation of a cream complex in 46% yield, which analysed with a 1:1 ligand:metal ratio and gave ^1H and ^{13}C NMR spectra consistent with a symmetrical but dynamic complex.‡ The ^1H NMR spectra measured in CD_3CN and d_6-acetone remained unchanged down to the temperature limit for each solvent. Reaction of a related ligand di-2-pyridyl sulfide with Ag(I) produces a binuclear dimer containing two ligands.[5] This work would suggest **1** may not be ideally suited to forming mononuclear Ag(I) complexes. Electrospray mass spectrometry under normal operating conditions showed parent ions with appropriate isotope patterns for $\{[Ag_2(\mathbf{1})_2]PF_6\}^+$ at *m/z* 790.8 and $[Ag_2(\mathbf{1})_2]^{2+}$ at *m/z* 323.5. In addition using the Onsager equation,[6] dilution conductivity measurements in MeCN confirmed the presence of a 2:1 electrolyte‡ indicating the dimer remains intact in solution.

X-Ray crystal structure analysis§ showed the dimer is constructed from two ligands related by a crystallographic two-fold axis at the mid-point between the two Ag atoms. Each ligand experiences strong π-stacking interactions (3.41 Å) leading to an *endo-syn* conformation where the pyridine rings are tilted by 16.4° with respect to each other. The Ag atoms adopt a distorted trigonal planar geometry (Fig. 1), which links the two symmetry-related ligands by N,S chelation from one ligand and N′ donation from the other, giving rise to a folded side-by-side arrangement. This is in contrast to the centrosymmetric dimer of di-2-pyridyl sulfide in which the four-coordinate Ag atoms are bound in a NNS′ fashion with an O from a NO_3^- ion completing the coordination sphere.[5] In $[Ag_2(\mathbf{1})_2]^{2+}$ the Ag ions are separated by a short Ag··Ag distance of 3.052 Å which lies in the middle of the range (2.86–3.22 Å) found for similar systems.[3,5,7] The Ag(I) ions diverge by 0.159 Å from the trigonal planes which are tilted at 61.0° with respect to each other. As a consequence of the packing, chains of alternating intra- and inter-molecular (3.56 Å) π-stacked rings run along the *c* axis.

Reaction of **2**[8] with $AgNO_3$ in a 1:1 molar ratio in MeCN gave an off-white powder which analysed as $[Ag_3(\mathbf{2})_2](NO_3)_3$. Subsequently, the same compound was obtained in 76% yield using a 2:3 molar ratio.‡ A ^1H NMR spectrum measured in CD_3CN was consistent with a symmetrical structure. Previously, **2** was found to act as a pentadentate ligand in the monomeric complex $[Co(\mathbf{2})Cl]^+$.[8] Such a coordination preference is seemingly inconsistent with the analytical data for the Ag(I) complex.

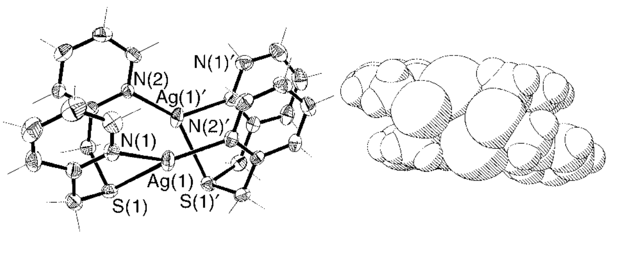

Fig. 1 Views of the binuclear $[Ag_2(\mathbf{1})_2]^{2+}$ cation, with the non-coordinating PF_6^- anions omitted: (left) Perspective view with thermal ellipsoids drawn at the 50% level. Selected distances (Å) and angles (°): Ag(1)–N(1) 2.263(3), Ag(1)–S(1) 2.5997(11), Ag(1)–N(2)′ 2.190(3); N(2)′–Ag(1)–N(1) 137.61(11), N(2)′–Ag(1)–S(1) 140.92(7), N(1)–Ag(1)–S(1) 79.77(8); (right) Space–filling view emphasising the π stacking of the ligands.

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† Dedicated to Dr Charles R. Clark on the occasion of his 60th birthday.

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The trinuclear nature of the complex was confirmed by X-ray structural analysis (Fig. 2).§ The structure consists of three non-equivalent Ag(I) ions held in a linear chain (Ag··Ag··Ag 175.3°) by two folded ligands arranged in a side-by-side fashion 11.6 Å wide and 8.3 Å long. This linear silver core is particularly rare in both helicate[9] and side-by-side structures[10] where to date in helicate formation Cu(I) predominates.[11] The Ag(I) ions adopt [4 + 4 + 2] coordination rather than the anticipated [3 + 3 + 4], with Ag··Ag distances of 3.204 and 3.232 Å, respectively, lying at the long end of the range for similar systems.[3,5,7] The four-coordinate Ag(I) ions have distorted-tetrahedral geometries (NSN′S′) while the two-coordinate Ag(I) ion has a bent structure (NN′). In addition, two NO_3^- anions interact weakly with the two-coordinate Ag(I) centre [Ag(3)··O(23) 2.698 Å, Ag(3)··O(31) 2.712 Å]. The folding of the ligand is determined by strong intramolecular π stacking, as in $[Ag_2(\mathbf{1})_2]^{2+}$. The pyridine rings are separated from each other with values in the range 3.29–3.72 Å and are inclined with respect to each other with values in the range 13.4–26.0°.

Both pentadentate ligands have the same chirality, which causes the S donors attached to the four coordinate Ag(I) ions to be diametrically opposite each other. This contrasts with the structure of $[Ag_2(\mathbf{1})_2]^{2+}$ in which the S donors are adjacent. In the trinuclear complex, such an arrangement would require the two ligands to have opposite chirality. Chains of alternating enantiomers are arranged head-to-head and form intermolecular π-stacked chains (3.42 and 3.61 Å) along the diagonal axes [1 1 0] and [1 1 0].

The symmetrical nature of the ^1H NMR spectrum was at odds with the unsymmetrical [4 + 4 + 2] coding. Thus in solution either the complex is symmetrical or is undergoing rapid dynamic processes which may include equilibria between species of differing nuclearities. Electrospray mass spectrometry showed peaks which could be assigned to a number of species including a parent ion $\{[Ag_3(\mathbf{2})_2](NO_3)_2\}^+$ at *m/z* 1154.8, $\{[Ag_2(\mathbf{2})_2](NO_3)\}^+$ at *m/z* 983.9, $\{[Ag_2(\mathbf{2})](NO_3)\}^+$ at *m/z* 630.9 and $[Ag(\mathbf{2})]^+$ at *m/z* 459.9. However using the Onsager equation,[6] dilution conductivity measurements in $MeNO_2$ strongly indicated a 1:1 electrolyte‡ suggesting the trimer does not maintain its integrity in solution. Results from variable-temperature ^1H NMR spectra measured in d_6-acetone–10% CF_3CO_2D were inconclusive. They showed no changes other than significant broadening and collapse of peaks down to 188K.

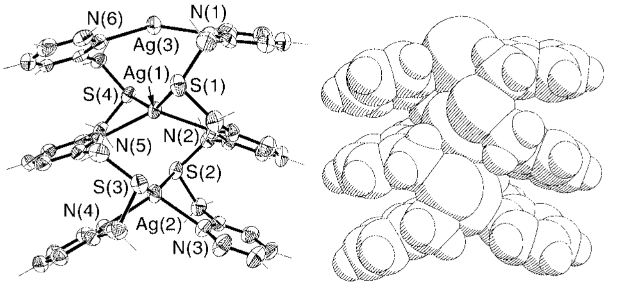

Fig. 2 Views of the trinuclear $[Ag_3(\mathbf{2})_2]^{3+}$ cation with NO_3^- anions, two weakly coordinating and one non–coordinating, omitted: (left) Perspective view with thermal ellipsoids drawn at the 50% level. Selected distances (Å) and angles (°): Ag(1)–N(2) 2.408(6), Ag(1)–N(5) 2.491(6), Ag(1)–S(4) 2.609(2), Ag(1)–S(1) 2.667(2), Ag(2)–N(4) 2.332(6), Ag(2)–N(3) 2.357(6), Ag(2)–S(2) 2.584(2), Ag(2)–S(3) 2.652(2), Ag(3)–N(1) 2.213(7), Ag(3)–N(6) 2.228(6); N(2)–Ag(1)–N(5) 133.8(2), N(2)–Ag(1)–S(4) 121.7(2), N(5)–Ag(1)–S(4) 75.9(2), N(2)–Ag(1)–S(1) 75.5(2), N(5)–Ag(1)–S(1) 114.7(2), S(4)–Ag(1)–S(1) 146.35(7), N(4)–Ag(2)–N(3) 112.7(2), N(4)–Ag(2)–S(2) 126.6(2), N(3)–Ag(2)–S(2) 79.0(2), N(4)–Ag(2)–S(3) 77.2(2), N(3)–Ag(2)–S(3) 111.5(2), S(2)–Ag(2)–S(3) 149.44(7), N(1)–Ag(3)–N(6) 150.6(2); (right) Space–filling view emphasising the extensive π stacking of the ligands.

We have shown that side-by-side structures can offer the diversity found in helicate structures. The intramolecular π stacking of the ligands was maintained in both complexes despite the ambiguity of coding being resolved in different ways to give different structural arrangements of side-by-side complexes.

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Notes and references

‡ *Selected data*: for $[Ag_2(\mathbf{1})_2](PF_6)_2$: δ_H(300 MHz; CD_3CN) 8.42 (d, 4H, ^3J 7.5 Hz), 7.72 (dt, 4H, ^3J 7.5, ^4J 1.8 Hz), 7.33 (d, 4H, ^3J 7.8 Hz), 7.27 (m, 8H), 4.03 (s, 8H). Anal. Calc. for $C_{24}H_{24}N_4S_2Ag_2P_2F_{12}$: C, 30.73; H, 2.58; N, 5.97; S, 6.84. Found: C, 30.47; H, 2.47; N, 6.25; S, 6.72%. Slope of the linear variation of $\Lambda_0 - \Lambda_{eq}$ *vs.* $\sqrt{C_{eq}}$ (MeCN): $[Ag_2(\mathbf{1})_2](PF_6)_2$ 365 ± 85 Ω^{-1} $L^{1/2}$ equiv.$^{-1/2}$, standard: $[Cu(H_2O)_6](ClO_4)_2$ 353 ± 19 Ω^{-1} $L^{1/2}$ equiv.$^{-1/2}$. Colourless crystals were grown from slow evaporation of an acetonitrile solution.

For $[Ag_3(\mathbf{2})_2](NO_3)_3$: δ_H(300 MHz; CD_3CN) 8.55 (d, 4H, ^3J 4.8 Hz), 7.88 (dt, 4H, ^3J 7.8, ^4J 1.8 Hz), 7.58 (t, 2H, ^3J 7.5 Hz), 7.53 (d, 4H, ^3J 7.8 Hz), 7.38 (m, 4H), 7.18 (d, 4H, ^3J 7.5 Hz), 4.19 (s, 8H), 4.02 (s, 8H). Anal. Calc. for $C_{38}H_{38}N_9S_4Ag_3O_9$: C, 37.51; H, 3.15; N, 10.36; S, 10.54. Found: C, 37.45; H, 3.36; N, 10.32; S 10.23%. Slope of the linear variation of $\Lambda_0 - \Lambda_{eq}$ *vs.* $\sqrt{C_{eq}}$ ($MeNO_2$): $[Ag_3(\mathbf{2})_2](NO_3)_3$ 272 ± 11 Ω^{-1} $L^{1/2}$ equiv.$^{-1/2}$, standard: (NEt_4ClO_4 277 ± 42 Ω^{-1} $L^{1/2}$ equiv.$^{-1/2}$. Colourless crystals were grown from slow diffusion of diethyl ether in an acetonitrile solution.

§ *Crystal data*: $[Ag_2(\mathbf{1})_2](PF_6)_2$: $C_{12}H_{12}AgF_6N_2PS$, M = 469.14, monoclinic, space group $P2/n$ (no. 13), a = 13.657(4), b = 8.278(3), c = 14.071(4) Å, β = 103.063(4)°, U = 1549.7(8) Å^3, T = 173(2) K, Z = 4, μ(Mo-Kα) = 1.599 mm^{-1}, 19 328 reflections measured, 3176 independent reflections (R_{int} = 0.032), [2720, $I \geqslant 2\sigma(I)$], R_1 = 0.0353, 0.0426 (all data), wR_2 = 0.0899, 0.0940 (all data).

$[Ag_3(\mathbf{2})_2](NO_3)_3 \cdot 1.5CH_3CH_2OCH_2CH_3$: $C_{44}H_{53}Ag_3N_9O_{10.5}S_4$, M = 1317.72, monoclinic, space group $P2_1/n$ (no. 14), a = 18.749(7), b = 12.780(5), c = 21.716(8) Å, β = 99.729(4)°, U = 5128(3) Å^3, T = 170(2) K, Z = 4, μ(Mo-Kα) = 1.362 mm^{-1}, 63 340 reflections measured, 10 233 independent reflections (R_{int} = 0.11), [5676, $I \geqslant 2\sigma(I)$], R_1 = 0.0588, 0.1380 (all data), wR_2 = 0.1196, 0.1512 (all data). A disordered diethyl ether solvent molecule was refined isotropically without H-atoms. CCDC 182/1584. See http://www.rsc.org/suppdata/cc/a9/a910342m/ for crystallographic files in .cif format.

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