

Self-assembly of Silver(I) Helicates

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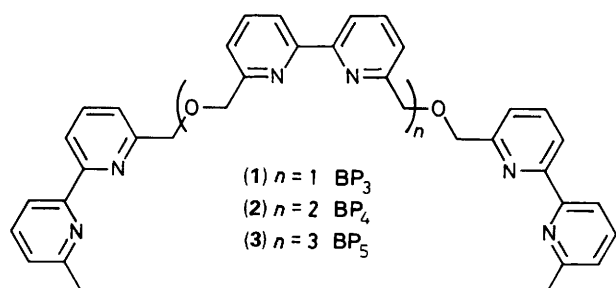
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Treatment of the oligobipyridine ligands containing three, four, and five bipyridine units with silver triflate (trifluoromethanesulphonate) yields the trinuclear, tetranuclear, and pentanuclear silver helicates.

Self-assembly is a process by which organized supramolecular structures are spontaneously generated from their component molecular parts in high yield and specificity. Prominent biological examples¹ are double-helix formation of nucleic acids² and self-assembly of viral protein coats.³ A system based on oligobipyridine ligands has been designed, where co-ordination of copper(I) ions spontaneously produces complexes of double helical geometry, the *helicates*.^{4,5} In order to delineate the features of the driving force leading to helicate self-assembly, it is of importance to determine whether all metal ions that tetrahedrally co-ordinate two bipyridines will act as templates.

We have now found that complexation of the silver(I) ion functions perfectly in helix self-assembly. This is interesting in that silver(I) binding to bipyridine (bipy) is much less strong and selective than that of Cu^I. The formation constant for Ag(bipy)₂⁺ is approximately one-half⁶ that for Cu(bipy)₂⁺ and the 60% larger Ag^I ion⁷ is known to prefer two over four co-ordination, often producing polymers with chelating ligands.⁸ It has been reported that related ligands did not produce double-helices when they were allowed to react with Ag^I, but rather formed mononuclear, near-planar complexes.⁹

The present complexes were synthesized in one step in the following manner: to an acetonitrile suspension of the bipyridine ligand (1), (2), or (3),^{4,5} in the dark, was added a 10% excess of silver(I) triflate (trifluoromethanesulphonate) in acetonitrile. After all the ligand had dissolved, the product was precipitated with ether, yielding a white powder. Three compounds have been obtained, trinuclear [Ag₃(BP₃)₂]X₃, tetranuclear [Ag₄(BP₄)₂]X₄, and pentanuclear [Ag₅(BP₅)₂]X₅, (X = CF₃SO₃).‡ In all three cases similar



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‡ Selected spectroscopic data: for [Ag₃(BP₃)₂](CF₃SO₃)₃: ¹H NMR (CD₃CN): δ 2.35 (s, CH₃), 3.90–4.15 (m, CH₂–O–CH₂), 6.81 (d, bipy), 6.95 (d, bipy), 7.40–8.05 (m, bipy). FAB MS: m/z 1783.1 {[Ag₃(BP₃)₂(CF₃SO₃)₂]⁺}, isotope pattern consistent.

For [Ag₄(BP₄)₂](CF₃SO₃)₄: ¹H NMR (CD₃CN): δ 2.30 (s, CH₃), 3.75–4.10 (m, CH₂–O–CH₂), 6.75 (t, bipy), 6.92 (d, bipy), 7.35–8.05 (m, bipy). FAB MS: m/z 2435.2 {[Ag₄(BP₄)₂(CF₃SO₃)₃]⁺}, isotope pattern consistent.

For [Ag₅(BP₅)₂](CF₃SO₃)₅: ¹H NMR (CD₃CN): δ 2.30 (s, CH₃), 3.70–4.15 (m, CH₂–O–CH₂), 6.70 (t, bipy), 6.90 (d, bipy), 7.40–8.05 (m, bipy). FAB MS: m/z 3089.9 {[Ag₅(BP₅)₂(CF₃SO₃)₄]⁺}, isotope pattern consistent.

characteristic proton NMR patterns are observed upon complexation that, by analogy with the Cu^I results,^{4,5} point to double helical structures in which two molecular strands are wrapped around three, four, and five metal ions respectively. A schematic representation of the trihelicate is given in Figure 2(a). The ¹H NMR spectrum of [Ag₅(BP₅)₂]X₅ is shown in Figure 1. The signals of the methylene groups α to the ether oxygen shift upfield by about 1 ppm and split into overlapping AB patterns, which unlike the Cu^I case are not fully resolved. The CH₃ signal also shifts upfield by about 0.3 ppm. The

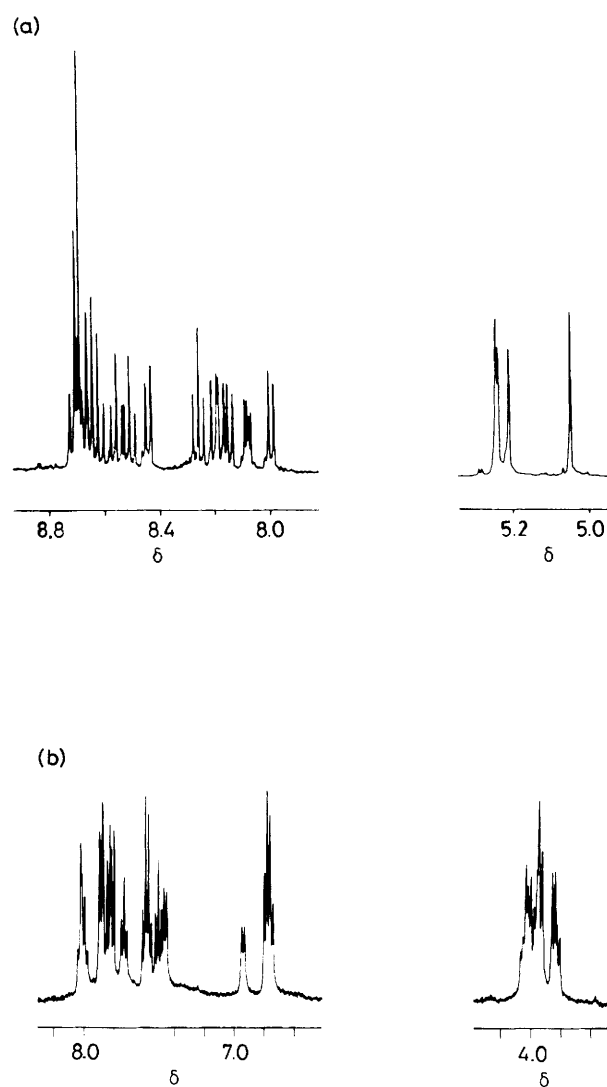


Figure 1. ¹H NMR (400 MHz) spectra of (a) BP₅ in [2H₆]acetone + 10% CF₃CO₂D, and (b) [Ag₅(BP₅)₂](CF₃SO₃)₅ in CD₃CN. The CH₃ signals at δ 2.6 and 2.3, respectively, are not shown.

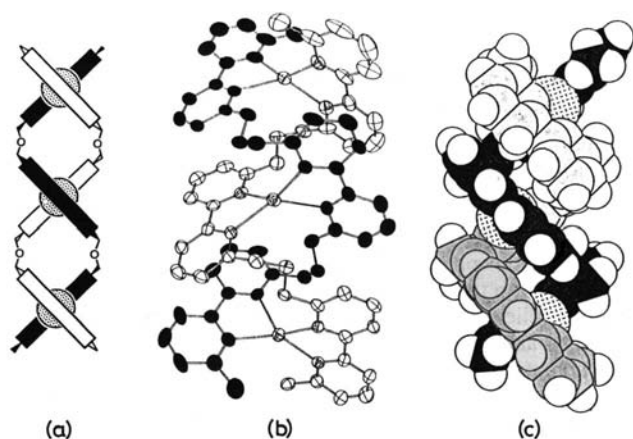


Figure 2. Views from the structural study of $[\text{Ag}_3(\text{BP}_3)_2](\text{CF}_3\text{SO}_3)_3$: (a) schematic representation of a trinuclear double helicate; (b) ORTEP plot, the spheres represent 20% probability; (c) MOLDRW plot with radii criteria, giving a space filling model.

pyridine resonances give a complicated overlapping pattern, from 6.6 to 8.1 ppm.

X-Ray quality crystals of $[\text{Ag}_3(\text{BP}_3)_2](\text{CF}_3\text{SO}_3)_3$ were obtained by vapour diffusion of diethyl ether into acetonitrile solutions. The structure analysis,[§] of which two views are shown in Figure 2, clearly demonstrates a trinuclear double helix 9.8 Å wide and 20 Å long. The Ag–N distances vary from 2.26(1) to 2.42(1) Å with a distorted tetrahedral geometry around Ag^{I} . The intrapyridine N–Ag–N angles vary from

70.3(3) to 72.6(4)° and the interpyridine N–Ag–N angles from 114.8(3) to 138.7(4)°. The bipyridines themselves are not planar and dihedral angles between the pyridine moieties range from 4.6–21.4°. These variations produce a helix that is not regular, but bent. The Ag–Ag–Ag angle is 141.82(2)° and the two silver to silver distances differ by 0.485 Å.

Physicochemical studies on these compounds have yielded interesting preliminary results. Formation of the helices is apparently a co-operative reaction as the product is uniquely formed when silver is titrated into ligand solutions. No by-products are found. Further, when the silver double helix is heated with excess ligand, the NMR peak corresponding to the complex disappears and the free ligand peak increases, before coalescence is reached. This indicates that dissociation occurs while ligand exchange is still slow on the NMR time scale. Further studies are in progress in order to gain more insight into the thermodynamic and kinetic features of the self-assembly process.

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§ *Crystal data*: $\text{C}_{75}\text{H}_{64}\text{Ag}_3\text{F}_9\text{N}_{12}\text{O}_{13}\text{S}_3$, $M = 1932.2$, triclinic, space group $P\bar{1}$, $a = 17.125(6)$, $b = 17.654(6)$, $c = 13.522(4)$ Å, $\alpha = 102.39(2)$, $\beta = 98.59(2)$, $\gamma = 91.59(2)^\circ$, $U = 3940.3$ Å³, $Z = 2$, $D_c = 1.63$ g cm⁻³, monochromated Cu-K α radiation, $\lambda = 1.5405$ Å, $\mu = 75.464$ cm⁻¹. Data were collected on a Philips PW 1100/16 diffractometer. A total of 9003 reflections were measured in the range $3 < \theta < 52.5^\circ$ and $\pm h \pm k + l$, and 5880 reflections with $I > 3\sigma$ were used in the refinement. An empirical absorption correction was made 0.58 min., 1.21 max. There was no crystal decay. The structure was solved by the Patterson method and refined by full-matrix least-squares and ΔF map techniques. The weighting scheme was $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = \sigma^2_{\text{counts}} + (pI)^2$, $p = 0.08$ and the final residuals were $R = 0.070$, $R_w = 0.097$, G.O.F. = 1.88. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.