The 'Trinity' helix: synthesis and structural characterisation of a C_3-symmetric tris-bidentate ligand and its coordination to Ag(I)†

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The synthesis and structural characterisation of a novel C_3-symmetric tris-bidentate ligand, **L**, featuring a triphenylamine core appended by pyridylimine coordination sites is reported: ^{1}H NMR compleximetric titration studies with Ag(I) and ESMS indicate the presence of $[Ag_3L_2]^{3+}$ species in solution, consistent with the formation of a trinuclear double helicate complex: the Trinity helix.

Current interest within supramolecular chemistry involves the development of strategies to control the outcome of metal-assisted self-assembly processes.[1] In this respect, ligands have been tailored to recognise intrinsic geometric preferences of particular metal ions, or to enforce structural constraints upon coordinated ions. Fine tuning of these ligand systems has resulted in the isolation of many structural types including grids,[2] boxes,[3] cylinders,[4] molecular polyhedra[5] and helicates.[6] Amongst these, however, the helical topography has attracted the most interest because of their prevalence and importance in nature, the ready information they provide about self-assembly processes, and because of their aesthetic beauty.[6c]

Ligands employed in the synthesis of metallo-helicates are predominantly based upon C_2-symmetric polypyridyl or related backbones, and consist of bi- or tri-dentate binding sites linked in series.[6] Recently, we have employed more synthetically facile Schiff's-base ligand types in the formation of metallo-helicates[7] and have latterly extended this approach to incorporate anion binding, reporting the first dinuclear anion helicate.[8] Whilst great advances continue to be made, a possible limitation to the development of the field is the reliance upon linearly disposed binding sites. We redress this situation here and describe the synthesis of a C_3-symmetric ligand, **L**, consisting of three pyridylimine binding sites, and report its coordination to Ag(I), to form $[Ag_3L_2]^{3+}$. We believe this to be the first report dealing specifically with the use of a rigid trigonal ligand in the formation of helical complexes.

L

L1 $n = 2, x = 2$
**L2** $n = 1, x = 3$
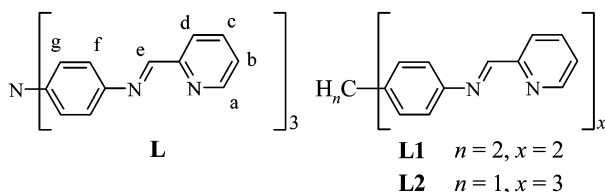
The tris-bidentate ligand, **L**, incorporates the binding features found in the bis-bidentate ligand, **L1**, which forms dinuclear double and triple helicates.[7,9] We first developed C_3-symmetric ligands based around a tetrahedral central carbon, by using a trianilinomethane scaffold, obtained through the reduction of parafuschin[10] and subsequent condensation with pyridine-2-carbaldehyde, **L2**. Whilst coordination to Ag(I) was successful,[11] the sensitivity of this scaffold toward oxidation (visibly noticeable through formation of deep-purple coloured solutions) led us to develop the more robust ligand, **L**, based around a triphenylamine core. **L** was synthesised in two steps *via*

N_2H_4–Pd/C mediated reduction of tris-4-nitrotriphenylamine followed by condensation of the resulting tri-amine with pyridine-2-carbaldehyde.‡ Recrystallisation from toluene gave orange crystals suitable for a single crystal X-ray diffraction study§[12] from which its structure was determined (ESI†). The ligand structure is as anticipated with three pyridylimine arms radiating from the amine core. The ligand is chiral due to the propeller nature of these arms, although the crystal is racemic as both Δ and Λ enantiomers are present. The ligand forms a number of self-complementary H-bond (C–H···N) interactions, and C–H···π contacts, which create a 3D network containing channels running down the crystallographic *b*-axis which are occupied by disordered toluene molecules (ESI).

Treatment of a $CHCl_3$ solution of **L** with a MeCN solution of $AgPF_6$ (2 : 3) led to the formation of a deep red solution from which an orange solid precipitated following the addition of NH_4PF_6.¶ Partial microanalytical data indicate an $[Ag_3L_2](PF_6)_3$ formulation and ESMS revealed a cluster of peaks centred around m/z 479.762, with an isotopic distribution pattern consistent with $[Ag_3L_2]^{3+}$ ions in solution (ESI). Furthermore, the ^{1}H NMR spectrum is particularly well resolved and relatively simple and indicates the presence of a single species that retains a high degree of symmetry on the NMR timescale, Fig. 1. Coordination of Ag(I) is apparent as all protons shift to some degree. Most noticeable amongst these are the pyridyl protons, *b* and *c*, and the imine proton, *e*, which shift downfield by *ca*. 0.25 ppm. The pyridyl proton, *d*, shifts by a similar amount upfield, whilst *a* shifts marginally downfield by *ca*. 0.02 ppm. The protons *g* and *f*, of the central phenyl rings, shift upfield and downfield by *ca*. 0.06 and 0.10 ppm, respectively. These observations are again consistent with the presence of $[Ag_3L_2]^{3+}$ in solution. It should be noted that there is no indication of any ligand dissociation nor of any fluxional processes operating under these conditions, which is in direct contrast to the behaviour observed for similar systems based upon linear C_2 symmetric ligands.[6c,9a,13]

To investigate the solution chemistry of $[Ag_3L_2]^{3+}$ further and to better understand the processes leading to its formation we performed a compleximetric titration experiment, tracking the progress of complex formation through observing shifts within the ^{1}H NMR spectra.[2a] To this end, a 1.06×10^{-5} M CD_3CN–$CDCl_3$ (4 : 1) solution of **L** was treated with successive
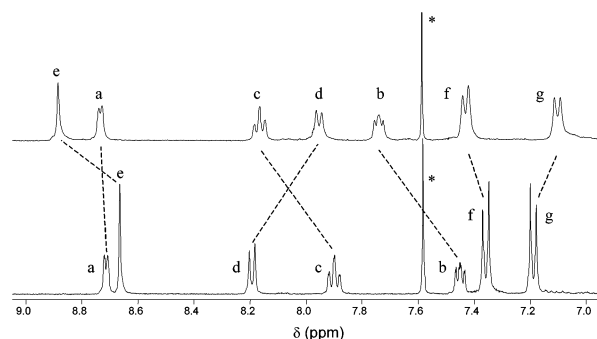
Fig. 1 ^{1}H NMR spectra of **L** (bottom) and $[Ag_3L_2](PF_6)_3$ (top) with assignments (400 MHz, CDCN–CDCl$_3$ 298 K). * residual CHCl$_3$.

additions of a 0.25 M solution of AgPF$_6$ within the same solvent regime (equating to sequential *ca.* 0.12 mol equivalents of Ag(I) with each addition), Fig. 2. Several points of note can be taken from this experiment. Firstly, the final spectrum is identical to that obtained above. Secondly, those protons that undergo the largest shifts (*b*, *c*, *d*, *e*) do so before the addition of 1.5 equivalents, whereupon no further appreciable shifting is observed up to and beyond 2.5 equivalents. Thirdly, a slight inflection point may be discerned within the plots of those protons undergoing marginal shifts (*a*, *f*, *g*) at *ca.* 1 : 1 stoichiometry.
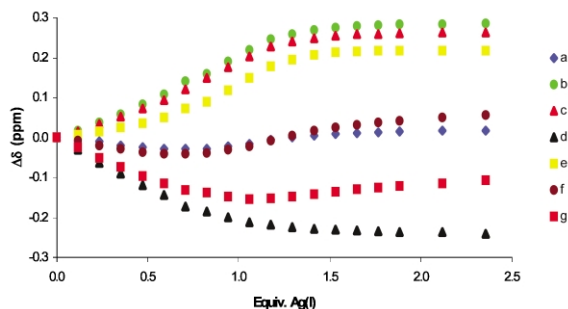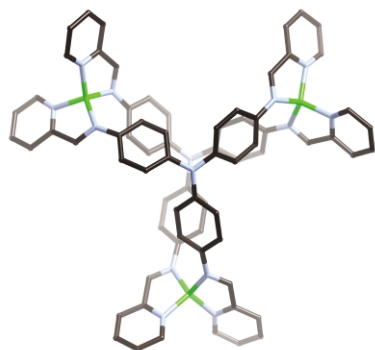

Fig. 2 Compleximetric titration of **L** (1.06 × 10^{-5} M) with AgPF$_6$ (0.25 M) showing $\Delta\delta$ of assigned protons with successive additions {400 MHz, CDCN–CDCl$_3$ (4 : 1) 298 K}.

These observations may be rationalised in the following way: successive additions firstly lead to [Ag$_2$L$_2$]$^{2+}$, a dinuclear species at 1 : 1 stoichiometry. The presence of this species may account for the inflection within the plots for *a*, *f*, and *g*, as these protons begin to feel through-space effects of the neighbouring strand. This species, potentially a dinuclear double helicate, has two vacant coordination sites. Further addition of Ag(I) binds the two vacant sites together to give the tri-nuclear product: [Ag$_3$L$_2$]$^{3+}$, which is robust in the presence of excess Ag(I) and non-fluxional as the ^{1}H NMR spectrum is well resolved.

But what does [Ag$_3$L$_2$]$^{3+}$ look like? Based upon the above evidence we propose, and molecular modelling supports, that [Ag$_3$L$_2$]$^{3+}$ is a helicate complex, Fig. 3. The helical nature of the complex is reflected in each arm, as they cross over the Ag–Ag axis. Helical complexes based upon C_2-symmetric ligand types may exist in either a helical form (*rac*-isomer) or as a metallo-cyclophane (*meso*-isomer, the ligands do not cross the M–M axis), and may interconvert between each (as evidenced by their fluxional behaviour in solution).[6c] Whilst this is an option here, the three-armed nature of the complex ensures that a helical species must exist even if the *meso*-isomer is formed *i.e.* it is impossible to coordinate three arms without at least two arms crossing the Ag–Ag axis (ESI).

In conclusion, we have shown for the first time that a rigid C_3-symmetric ligand readily forms helical species on coordina-

tion to Ag(I). This approach represents a significant move away from the traditionally employed C_2-symmetric ligands that dominate the field of metallo-helicate chemistry and provides valuable insight into metal directed self-assembly processes.[14] We are currently extending this series further.

Notes and references

‡ Full synthetic details will be given elsewhere. Selected data for **L**: Found C, 72.22; H, 4.55; N, 16.31; [C$_{36}$H$_{27}$N$_7$]·2.25 H$_2$O requires C, 72.28; H, 5.30; N, 16.39%. ^{1}H NMR (400 MHz; 4 : 1 CD$_3$CN–CDCl$_3$): δ 8.71 (3 H, d, J = 4.0 Hz, H$_a$), 8.66 (3 H, s, H$_e$), 8.19 (3 H, d, J = 8.0 Hz, H$_d$), 7.89 (3 H, dd, J = 8.0, 6.0 Hz, H$_c$), 7.45 (3 H, dd, J = 6.0, 4.0 Hz, H$_b$), 7.35 (6 H, d, 7.0 Hz, H$_f$), 7.19 (6 H, d, J = 7.0 Hz, H$_g$). ν_{max}/cm^{-1} 1625(s), 1581(s), 1499(s), 1319(s). ESMS m/z 558.24 [L]$^+$.
§ Crystal data for **L**·(toluene)$_{0.5}$ C$_{39.5}$H$_{31}$N$_7$, M = 603.71, orange prism (0.25 × 0.20 × 0.08), triclinic $P\bar{1}$, a = 10.1332(8) Å, b = 11.0554(8) Å, c = 16.6857(13) Å, α = 70.954(2)°, β = 75.751(2)°, γ = 74.992(2)°, V = 1679.7(2) Å^3, T = 153(2) K, Z = 2, D_{calc} = 1.194 g cm^{-3}, μ(Mo–Kα) = 0.073 mm^{-1}, Bruker SMART APEX CCD diffractometer, Mo–Kα radiation (λ = 0.71073 Å). 3144 independent reflections, 2049 observed (I > 2σ(I)). R_1 = 0.0987, wR_2 = 0.2723 for observed reflections. CCDC 205745. See http://www.rsc.org/suppdata/cc/b3/b302652c/ for crystallographic data in .cif or other electronic format.
¶ Selected data for [Ag$_3$L$_2$][PF$_6$]$_3$: Found: C, 46.09; H, 3.06; N, 10.60. [Ag$_3$(C$_{36}$H$_{27}$N$_7$)$_2$][PF$_6$]$_3$ requires C, 45.86; H, 3.53; N, 10.40%. ^{1}H NMR (400 MHz; 4 : 1 CD$_3$CN–CDCl$_3$): δ 8.81 (6 H, s, H$_e$), 8.72 (6 H, d, J = 5.0 Hz, H$_a$), 8.13 (6 H, dd, J = 7.5, 6.0 Hz, H$_c$), 7.96 (6 H, d, J = 7.5 Hz, H$_d$), 7.70 (6 H, dd, J = 6.0, 5.0 Hz, H$_b$), 7.32 (12 H, d, J = 8.5 Hz, H$_f$), 7.01 (12 H, d, J = 8.5 Hz, H$_g$). ESMS, m/z 479.762 [Ag$_3$L$_2$]$^{3+}$.

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Fig. 3 Proposed structure of [Ag$_3$L$_2$]$^{3+}$ showing the helical nature of each strand.