Direct synthesis and structural characterisation of tri- and tetra-nuclear silver metallaknotanes by self-assembly approach†‡

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The combination of ligands based on two quinoline units acting as primary coordinating sites connected by tetra- or penta-ethyleneoxy fragments behaving as secondary interaction sites leads spontaneously in a one-pot reaction to the formation of tri- and terta-nuclear metalla-organic knots in the presence of silver cation.

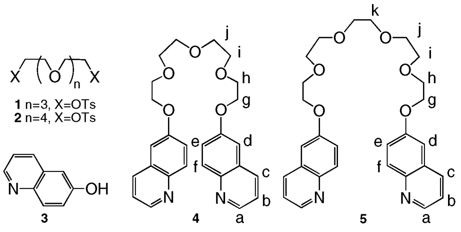
Chemical topology is a fascinating area of research and for some four decades, this topic is attracting considerable interest.[1,2] Molecular knots, for which their graphs present crossings, are non-trivial topological objects.[3–9] One of the challenges in this domain is to find viable synthetic strategies for preparing these peculiar molecules in acceptable yields. Elegant multi step strategies based on covalent[3] or metal templating processes[4b,5,6c] or on donor–acceptor interactions have been reported.[6a,b] Purely organic knots have been also prepared under self-assembly conditions using the formation of imine junctions.[7]

Here, we report on the spontaneous formation of two metalloorganic molecular knots under self-assembly conditions and their structural studies in the crystalline phase and in solution.

For the design of coordination units, we have proposed to combine primary and secondary coordinating sites.[10,11] In particular, we have previously successfully demonstrated the validity of this concept for the formation of discrete heterometallic complexes and infinite linear[10] and helical[11] coordination networks. Following on that, we have prepared a series of quinoline based ligands such as **4** and **5** (Scheme 1).[12] The latter are bis monodentate ligands bearing two 6-quinolyl groups at their extremities as primary coordinating sites. The linkage between the two coordinating groups is ensured by oligoethyleneoxy units (tetra for **4** and penta for **5**). This spacer, owing to its conformational flexibility, may adopt a curved arrangement (pseudo-crown ether), thus offering a semicircular disposition of oxygen atoms capable of surrounding the metal cation and behaving as secondary interaction sites with metal cations. The connection between the quinolyl groups and oligoethyleneoxy spacers at the position 6 is achieved by two ether junctions. Few other examples of quinoline based ligands of that type have been reported.[13] As metal centre, Ag^+ cation was chosen because of its loose demand in terms of its coordination geometry (spherical) and because of the reversible nature of its interactions with N and O atoms. As the counter ion, XF_6^- (X = As or Sb) was used because of their rather weakly coordinating propensity.

The synthesis of compounds **4** and **5** was straightforward and achieved in 68 and 51% yield respectively by condensing the ditosylate derivatives **1** and **2** with 6-hydroxyquinoline **3** in CH_3CN in the presence of K_2CO_3.§

For both ligands **4** and **5**, upon slow diffusion at r.t. of a EtOH solution (3 mL) containing $AgAsF_6$ or $AgSbF_6$ (5 mg, 16.8 mmol) into a $CHCl_3$ solution (1 mL) of **4** (6.68 mmol) or **5** (6.1 mmol), respectively, colourless air-stable crystals were obtained after one week and were studied by X-ray diffraction on single-crystals.¶ For the preparation of the tri- and tetra-nuclear complexes in large amounts see the experimental section.§ To our surprise, the structural investigation revealed that both ligands **4** and **5**, when combined with silver cation lead, in the crystalline phase, to the formation of metallo-organic molecular knots, however with different nuclearity. Indeed, ligand **5** bearing the longer pentaethyleneoxy spacer generates in the presence of $AgAsF_6$ a trimetallic knot (Fig. 1). The crystal (monoclinic, space group *C*2/*c*) is composed of three ligands **5**, 3 Ag^+ cations, 3 AsF_6^- anions and $CHCl_3$ solvent molecules. The charge on the tricationic knot-type complex (Fig. 3(a)) is neutralized by 3 AsF_6^- anions. No specific interactions between the cationic complex and the anionic partner are observed. The $CHCl_3$ solvent molecules occupy the empty spaces, again without any specific interactions with knots or anions. The knotted architecture is generated upon interconnection of 3 ligands **5** and 3 Ag^+ cations. The organic ligand **5** adopts two distinct conformations (Fig. 1). For both conformers, the pentaethyleneoxy spacer



Scheme 1

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† This paper is dedicated to Professor Andrew B. Holmes FRS on the occasion of his 65th birthday.

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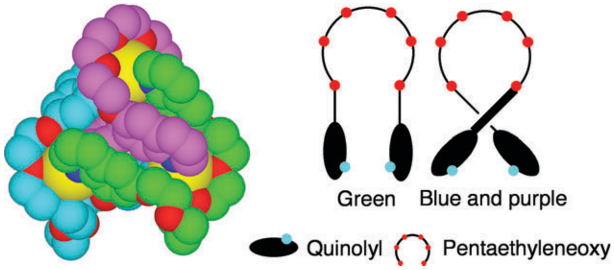

Fig. 1 Structures (left) of (**5**-Ag)$_3$ trinuclear knot type complex and schematic representations of the two conformations adopted by **5** (right). The three strands forming the knot are differentiated by colour. Only one enantiomer is presented. Silver cation is coloured in yellow; H atoms, AsF_6 anions and $CHCl_3$ solvent molecules are omitted for clarity.

adopts a loop type arrangement suitable for interactions with Ag^+ cation and the N atoms of the two quinolyl groups are oriented in convergent manner. Among the three Ag^+ cations, two are crystallographically non-equivalent. One of them is on a C_2 axis of symmetry. All three Ag^+ cations are surrounded by two N and two O atoms. The organic ligands and metallic centres are interconnected through the N atoms belong to two consecutive ligands **5** and Ag^+ cations ($d_{Ag–N}$ of 2.20 Å for the loop type conformer, 2.19 and 2.17 Å for the other conformer). The cation also interacts with two out of the 6 O atoms belonging to the pentaethynenoxy fragment of the neighbour ligands ($d_{Ag–O}$ of 2.62 Å for the loop type conformer, 2.60 and 2.62 Å for the other conformer). The coordination geometry around the metal cation is a distorted tetrahedron (XAgX angles: NAgN = 157.2°, OAgO = 64.0°, NAgO = 97.2° and 101.9° for the loop type conformer and NAgN = 148.0°, OAgO = 64.4°, NAgO = 99.3° and 104.3° for the other conformer). The quinolyl groups are arranged in two groups of three units with opposite orientation (Fig. 1). The shortest C···C distance is in the range of 3.72–3.81 Å. The trinuclear knot is the simplest one that can be formed. As one could anticipate owing to the absence of chiral information within the backbone of the ligand **5**, the crystal (centric group space) contains both P and M enantiomers.[9]

For the ligand **4** bearing the shorter tetraethyleneoxy space, the reaction with $AgSbF_6$ affords a tetrametallic knot (Fig. 3(a)). The crystal (monoclinic, space group $P2/c$) is composed of four ligands **4**, 4 Ag^+ cations, 4 SbF_6^- anions and $CHCl_3$ solvent molecules (Fig. 2). Again no specific interactions between the anions nor the solvent molecules and the tetranuclear is observed. The knotted complex is formed through mutual connection between 4 ligands **4** and 4 Ag^+ cations (Fig. 3(b)). In contrast with the case of **5** mentioned above, the ligand **4** adopts a single conformation (Fig. 2) displaying also a loop type arrangement of the spacer. The two quinolyl groups are again oriented in convergent fashion. All four Ag^+ cations are crystallographically non-equivalent. Again they are bonded to two N and two O atoms. The connectivity between ligands and cations is ensured by Ag–N bonds between quinolyl groups belonging to consecutive and silver cations ($d_{Ag–N}$ in the range of 2.18–2.24). The cation also further interacts with two adjacent O atoms belonging to the spacer of the neighbour ligands ($d_{Ag–O}$ in the range of 2.60–2.96 Å). The metal cation adopts again a distorted Td coordination geometry (NAgN and OAgO angles in the range of: 146.5–154.5° and 87.0–121.9°). The quinolyl groups are arranged in pairwise and opposite fashion (Fig. 2). The shortest C···C distance is in the range of 3.53–3.74 Å. Both enantiomers of the tetranuclear knot are present in the crystal.

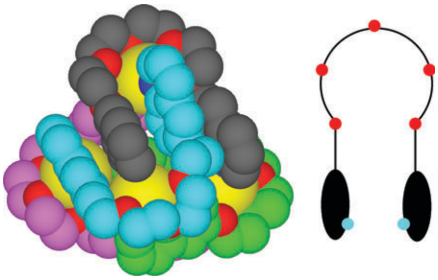

Fig. 2 Structures (left) of (**4**-Ag)$_4$ tetranuclear silver knot and schematic representations of the conformation adopted by **4** (right). The four strands forming the knot are differentiated by colour. Only one enantiomer is presented. H atoms, SbF_6 anions and $CHCl_3$ solvent molecules are omitted for clarity.

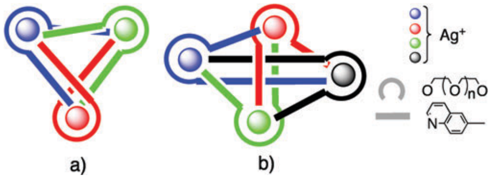

Fig. 3 Schematic representations of the trinuclear and tetranuclear knots obtained upon combining silver cation with ligands **5** and **4**, respectively. The strands are differentiated by colour for clarity.

It is interesting to note that for both metalloknotanes, the metal centres are serving as connecting nodes (Fig. 3). Thus in contrast with the examples reported by Sauvage *et al.*[14] and Stoddart *et al.*,[15] the removal of metal cations disrupts the connectivity of the architecture. In other terms, if one considers the Ag–N bonds as the other X–Y (X = C, N, O; Y = C) links, both systems may be described as knotted strings with closed graphs.

The stability of the two knotted structures was investigated in acetone by ^{1}H NMR. Whereas the trinuclear system appeared to be unstable, the tetranuclear knot was found to survive in solution. However, DOSY experiments showed *ca.*

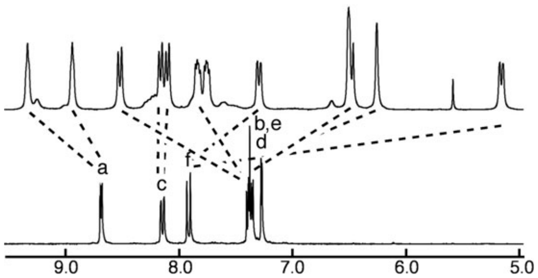

Fig. 4 Portions (5.0–9.5 ppm range) of the ^{1}H NMR spectra of **4** (bottom) and the tetranuclear silver knot (top) in deuterated acetone. The formation of the knotted structure breaks the symmetry of the ligand and doubles the number of signals for the quinolyl part.

5–10% decomplexation. The NMR study revealed the lowering of symmetry upon the formation of the complex (Fig. 4).

In conclusion, the combination of silver cation with bis-monodentate ligands **4** and **5**, bearing two quinolyl groups interconnected by penta- and tetra-ethyleneoxy spacers, leads in a one-pot reactions to the formation of trinuclear and tetranuclear silver metalloknotanes respectively. Whereas the tetranuclear complex was stable both in the crystalline phase and in solution in acetone, the trinuclear assembly was only obtained in the solid state. Extension to other analogous ligands and metal cations is currently under way. In particular, the stabilisation of this type of knots in solution is currently under investigation.

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Notes and references

§ *Synthesis* of **4** and **5**: **3** (500 mg, 3.44 mmol) and K_2CO_3 in excess (713 mg, 5.16 mmol) were dissolved in CH_3CN (50 mL) and the mixture was stirred before **1** (865 mg, 1.72 mmol) or **2** (940 mg, 1.72 mmol) was added. The mixture was refluxed overnight and the solvent was removed under reduced pressure. The residue was suspended in CH_2Cl_2 (50 mL) and stirred before the solid was removed by filtration and the solvent was evaporated. The residue thus obtained was purified by column chromatography (CH_2Cl_2 and CH_2Cl_2/MeOH 99/1). The pure compounds **4** (68% yield) and **5** (51% yield) were obtained as brownish oils. **4**: ^1H NMR ($CDCl_3$, δ, ppm): 3.71 (m, 8H, CH_2), 4.03 (t, 4H, CH_2, J = 5.5 Hz), 4.39 (t, 4H, CH_2, J = 5.5 Hz), 7.08 (dd, 2H, arom, J = 7.5 Hz and 1.8 Hz), 7.39 (m, 6H, arom), 8.09 (dd, 2H, arom, J = 8.1 Hz and 1.7 Hz), 8.91 (dd, 2H, arom, J = 4.3 Hz and 1.7 Hz); ^1H NMR (CD_3COCD_3, δ, ppm): 3.66 (m, 8H, CH_2), 3.88 (t, 4H, CH_2, J = 4.8 Hz), 4,25 (t, 4H, CH_2, J = 4.8 Hz), 7.30 (d, 2H, arom, J = 2.7 Hz), 7.41 (m, 4H, arom), 7.94 (d, 2H, arom, J = 9 Hz), 8.18 (dd, 2H, arom, J = 9 Hz and 1.8 Hz), 8.72 (dd, 2H, arom, J = 2.7 Hz, J = 1.8 Hz); ^{13}C NMR ($CDCl_3$, δ, ppm): 68.0, 69.5, 70.6, 70.9, 109.2, 119.9, 121.6, 126.6, 129.5, 135.9, 140.3, 149.3, 154.6. Calc. for $C_{26}H_{28}N_2O_5$ (448.20): C 69.63, H 6.29, N 6.25; found: C 69.91, H 6.35, N 6.19%; **5**: ^1H NMR ($CDCl_3$, δ, ppm): 3.69 (m, 12H, CH_2), 4.03 (t, 4H, CH_2, J = 5.7 Hz), 4.40 (t, 4H, CH_2, J = 5.4 Hz), 7.10 (dd, 2H, arom, J = 7.3 Hz and 1.7 Hz), 7.39 (m, 6H, arom), 8.09 (dd, 2H, arom, J = 8.3 Hz and 1.7 Hz), 8.91 (dd, 2H, arom, J = 4.3 Hz and 1.9 Hz); ^{13}C NMR ($CDCl_3$, δ, ppm): 68.2, 69.5, 70.6, 70.9, 109.3, 119.9, 121.5, 126.6, 129.5, 135.9, 140.4, 149.3, 154.6. Calc. for $C_{28}H_{32}N_2O_6$ (492.23): C 68.28, H 6.55, N 5.69; found: C 68.41, H 6.51, N 5.63%.

Synthesis of trinuclear [**5**-Ag]$_3$·[SbF_6]$_3$ and tetranuclear [**4**-Ag]$_4$·[SbF_6]$_4$ knots: In a round flask, to a EtOH solution (1.5 mL) of $AgSbF_6$ (20 mg, 0.67 mmol) a $CHCl_3$ solution (1 mL) of either **4** (0.67 mmol) or **5** (0.67 mmol) was added. The addition of 2 mL of Et_2O to the mixture caused the precipitation of the complex which was isolated, further washed with ether and dried under vacuum (65 and 80% yields for [**5**-Ag]$_3$·[SbF_6]$_3$ and [**4**-Ag]$_4$·[SbF_6]$_4$ complexes respectively). ESMS: 601.10 ([**5**-Ag]$_3^{3+}$).

DOSY data for [**5**-Ag]$_3$·[SbF_6]$_3$ how at least three spaces in acetone solution. IR (cm^{-1}): 3080; 2929; 2878; 1624; 1560; 1508; 1458; 1387; 1325; 1236; 1121; 1056; 949; 833; 701. Calc. for [$C_{28}H_{32}N_2O_6Ag$]$_3$, [AsF_6]$_3$, [$CHCl_3$]$_{3/2}$: C 40.32; H 3.86; N 3.30; Found: C 40.35; H 3.89; N 3.27. [**4**-Ag]$_4$·[AsF_6]$_4$: ^1H NMR (acetone-d$_6$, δ, ppm, 300 MHz): 9.36 (s, 4H), 8.97 (s, 4H), 8.54 (d, 4H, J = 9.3 Hz), 8.18 (d, 4H, J = 1.8 Hz), 8.12 (d, 4H, J = 1.8 Hz), 7.87 (m, 8H), 7.34 (d, 4H, J = 1.8 Hz), 6.53 (m, 8H), 6.28 (s, 4H), 5.20 (d, 4H, J = 1.8 Hz), 3.93 (m, 16H), 3.68 (m, 16H), 3.21 (m, 8H) 2.88 (m, 16H). IR (cm^{-1}): 3446; 2916; 2868; 1624; 1593; 1508; 1469; 1387; 1388; 1325; 1238; 1119; 1092; 951; 822; 700. Calc. for [$C_{26}H_{28}N_2O_5Ag$]$_4$ [SbF_6]$_4$ [$CHCl_3$]: C 40.67; H 3.67; N 3.61; Found: C 40.72; H 3.65; N 3.58. ESMS: 557.06 ([**4**-Ag]$_4^{4+}$).

¶ *Crystallography*: Data were collected at 173(2) K on a Bruker SMART CCD Diffractometer equipped with an Oxford Cryosystem liquid-N_2 device, using graphite-monochromated Mo-Kα radiation. For all structures, diffraction data were corrected for absorption and structural determination was achieved using SHELXS97.[16]

Owing to the large R factors, the bond distances and angles cannot be discusses with high accuracy.

Crystal data for **4**-Ag: $C_{171}H_{195}Ag_6As_6Cl_9F_{36}N_{12}O_{36}$, M = 5094.18, monoclinic, space group $C2/c$, a = 29.3000(8), b = 20.1815(5), c = 18.7343(5) Å, β = 98.442(2)°, V = 10957.9(5) Å^3, T = 173(2) K, Z = 2, D_c = 1.544 g cm^{-3}, μ = 0.71073 Å, 57 564 collected reflections, 12 616 independent (R(int) = 0.0639), GooF = 1.453, R_1 = 0.1339, wR_2 = 0.3822 for $I > 2\sigma(I)$ and R_1 = 0.2084, wR_2 = 0.4315 for all data.

Crystal data for **5**-Ag: $C_{104}H_{112}Ag_4F_{24}N_8O_{20}Sb_4$, M = 3168.50, monoclinic, space group $P2_1/c$, a = 27.703(2), b = 14.8580(11), c = 28.187(2) Å, β = 92.174(4)°, V = 11593.4(16) Å^3, T = 173(2) K, Z = 4, D_c = 1.815 g cm^{-3}, μ = 0.71073 Å, 292876 collected reflections, 26844 independent (R(int) = 0.0963), GooF = 1.080, R_1 = 0.1262, wR_2 = 0.3660 for $I > 2\sigma(I)$ and R_1 = 0.1924, wR_2 = 0.3836 for all data.

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