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Discrete Ag_6L_6 coordination nanotubular structures based on a T-shaped pyridyl diphosphine†

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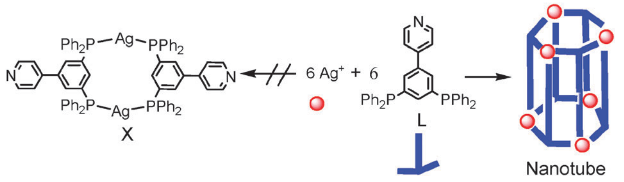
Ag_6L_6-type coordination nanotubular structures have been assembled from 6 Ag(I) ions and 6 T-shaped ligands, 4-(3,5-bis(diphenylphosphino)phenyl)pyridine; the nanotubes represent a discrete molecular architecture of a number of polymeric structures assembled from dimeric building blocks.

Inorganic nanotubes and organic nanotubular molecular structures have been well-developed due to their promising applications as one-dimensional (1D) molecular containers, such as chemical sensors, gas absorption, molecular separation, and catalysis.[1,2] In contrast, discrete coordination tubular structures remain rather uncommon even if self-assembly of other discrete coordination aggregates such as cycles,[3] cages,[4] bowls,[5] cubes,[6] and prisms,[7] have been explored in recent years. Among a handful of examples of discrete coordination tubular structures, pyridine[8] or imidazole[9]-based molecular strands have been employed to endow the structures with interesting properties, *e.g.* tunable size.[10] Herein we report self-assembly of the first phosphine-based[11] discrete M_6L_6 coordination tube with Ag(I) ions (L = 4-(3,5-bis(diphenylphosphino)phenyl)pyridine) (Scheme 1).

The T-shaped pyridyl diphosphine, L was designed and synthesised from 4-(3,5-difluorophenyl)-pyridine, by reaction with two equivalents of $KPPh_2$ in THF. The ^{31}P NMR spectra showed a single resonance at −6.46 ppm. Reactions examined with different ratios of Ag/L from 2 : 1 to 0.5 : 1 showed the Ag/L ratio to play a key role in the tubular structure formation (see supporting information†). With an L/$AgBF_4$ ratio of 1.5 : 1 or 0.5 : 1, RT ^{31}P NMR spectra showed a doublet of broad peaks, owing to the silver–phosphorus coupling, revealing some degree of coordination of the ligand to silver in solution and some dynamic behaviour. As the L : $AgBF_4$ ratio approaches 1 : 1, the ^{31}P NMR spectrum of the mixture reveals a sharp doublet of doublets centred at 9.84 ppm in $CDCl_3$–$MeNO_2$ (v : v = 3 : 1), revealing the coupling of the separate isotopes of ^{107}Ag and ^{109}Ag with $^{1}J(^{109}Ag–^{31}P)$ = 311 Hz. The upfield shift of *ca.* 16.2 ppm of the phosphorus peak in the product from the free ligand, L, indicated clearly the formation of a Ag–P coordination bond and the formation of a single isomeric product. Discrete Ag_6L_6 architectures with other anions such as SbF_6^-, PF_6^- and ClO_4^- could also be obtained. These analogous complexes gave essentially similar ^{31}P NMR spectra consisting of doublet of doublets. That of **Ag_6L_6–SbF_6** is centred at 14.84 ppm with $^{1}J(^{109}Ag–^{31}P)$ = 333 Hz in CD_2Cl_2–CD_3NO_2 (v : v = 3 : 1) (Fig. 1), that of **Ag_6L_6–PF_6** centred at 9.33 ppm with $^{1}J(^{109}Ag–^{31}P)$ = 408 Hz in $CDCl_3$–CD_3CN (v : v = 2 : 1) and that of **Ag_6L_6–ClO_4** centred at 15.68 ppm with $^{1}J(^{109}Ag–^{31}P)$ = 408 Hz in $CDCl_3$–CD_3CN (v : v = 2 : 1), which all have comparable coupling constants with **Ag_6L_6–BF_4**. ^{1}H NMR study of **Ag_6L_6–SbF_6** indicates the coordinative interaction between Ag(I) and the pyridyl N atoms of L. Upon addition of Ag(I) salt, the signals of pyridyl protons (H_a and H_b) are shifted upfield to 7.98 and 6.49 ppm, respectively. The ^{1}H NMR spectrum is also indicative of the highly symmetrical arrangement of the ligands in solution and in the complex, all six ligands are magnetically equivalent. The assignment of the signals was achieved on the basis of ^{1}H–^{1}H COSY and NOESY experiments (see supporting information†). Interestingly, **Ag_6L_6–SbF_6** has two geometrically different sets of PPh_2 phenyl rings: twelve axial phenyl rings (Ph_{ax}) lying up and down the central C_3 axis of the tube and twelve equatorial phenyl rings (Ph_{eq}) lying vertical to the central axis. The signals of Ph_{eq} protons ($H_{e'}$, $H_{f'}$ and $H_{g'}$) are shifted downfield to 7.67–7.50 ppm compared with those of Ph_{ax} ones (H_e, H_f and H_g) at 7.50–7.23 ppm. These



Scheme 1 Self-assembly of the L_6Ag_6 tubular structures.

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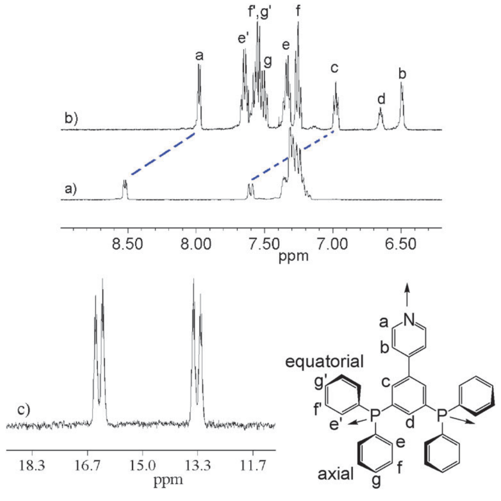

Fig. 1 (a) ^{1}H NMR of L, (b) ^{1}H NMR and (c) ^{31}P{^{1}H} NMR of **Ag_6L_6–SbF_6** in CD_2Cl_2–CD_3NO_2.

NMR results clearly indicate that only one isomer was quantitatively constructed in solution when L and Ag^+ are mixed in a ratio of 1 : 1.

ESI-TOF mass spectrometry for **Ag_6L_6–SbF_6** showed a signal at *m*/*z* 2366.01, which is assigned to the doubly charged species $L_6Ag_6(SbF_6)_4{}^{2+}$,[12] giving further evidence of the formation of a L_6Ag_6 tubular structure in solution as no ion of higher molecular mass was obtained.

Thus discrete architectures have been obtained in solution when the ratio of Ag : L is 1 : 1 with $BF_4{}^-$, $ClO_4{}^-$, $PF_6{}^-$ or $SbF_6{}^-$ as counterions indicated by combined NMR and ESI-MS results. Precluding the formation of a common dinuclear, cyclic structural motif $[Ag_2(\text{diphosphine})_2]^{2+}$ (Scheme 1, X),[13] possible candidate structures to meet the criteria of these results are tubular structures with D_{3d} symmetry (Ag_6L_6), D_{4d} (Ag_8L_8) or D_{5d} ($Ag_{10}L_{10}$), *etc.* Since such tubular structures are highly positively-charged, anions are reasonably residing in the cavity.[4] An Ag_6L_6 structure with D_{3d} symmetry may be expected to form, because its cavity size is suitable for these counterions. To prove the effect of anion size, the ^{31}P NMR spectrum of a solution of $AgBPh_4$/L = 1 : 1 in $CDCl_3$–MeCN–MeOH was tested, which shows a broad peak at *ca.* 8.5 ppm, suggesting the tubular structure is not formed for bigger $BPh_4{}^-$. Thus, anions with suitable size are important for the tube formation.

^{19}F NMR and ^{31}P NMR spectra of **Ag_6L_6–BF_4** and **Ag_6L_6–PF_6** indicate that there is no chemical shift difference between the free and encapsulated counteranions in solution. ^{19}F NMR of the former shows the signals of $BF_4{}^-$ at *ca.* 153 ppm, corresponding to ^{10}B/^{11}B–^{19}F coupling from RT to 200 K. ^{31}P NMR of the latter shows the characterised multiplet of $PF_6{}^-$ at −13.57 ppm with $^1J(^{31}P–^{19}F) = 955$ Hz. These behaviours may be well explained by the Ag_6L_6 tubular structure. In contrast to cage structures,[14] the tubes are open at both ends, resulting in fast exchange between the free and capsulated anions on the NMR timescales without structural dissociation.

Crystals of **Ag_6L_6–SbF_6** were grown by layering of a MeOH solution of $AgSbF_6$ into a $CHCl_3$ solution of L. The presence of $SbF_6{}^-$ in **Ag_6L_6–SbF_6** was confirmed by its characteristic IR absorption band at 660 cm^{-1} and the L/$AgSbF_6$ ratio of 1 : 1 was confirmed by microanalysis. In spite of easy efflorescence of the crystals and severe disorder of solvent molecules, X-ray structural analysis enabled us to obtain an acceptable structural model, a discrete Ag_6L_6 tubular structure (Fig. 2).‡‡ The discrete tubular architecture consists of six Ag^+ and six ligands. The ligands are connected by Ag atoms in a head-to-tail arrangement. Each Ag^+ is tricoordinate and bound by two phosphorus donors and one pyridyl nitrogen atom of three separate ligands. There exists six uniform AgP_2N centres. Two phenyl rings of each PPh_2 group are lying in the axial and equatorial position, respectively, consistent with the NMR results. Two of six $SbF_6{}^-$ counteranions are located in the tubular cavity. The tubular structure is *ca.* 2.1 nm long.

To clarify the formation mechanism of the present tubular structure, its ring-opening polymerisation (ROP) relationship with other polymeric structures is studied. The ROP relationship, established between metallacycles/cages and 1D chain or 2D polymeric structures,[15] not only has mechanistic significance, but also may guide synthesis of new polymeric or discrete structures. Potential ROP relationships exist between discrete Ag_6L_6 tubular architectures and a number of T-shaped ligand-based polymeric structures, such as 1D ladder, 2D (4,8^2) and 3D (4,12^2) networks (Fig. 3).[16,17] All these structures contain dimeric L_2M_2 subunits as a 4-connecting node which can be considered to be secondary building blocks. This point is verified experimentally by a signal of $[L_2Ag_2(SbF_6)]^+$ (*m*/*z* 1499.0) in the ESI-MS spectra of **Ag_6L_6–SbF_6**. It suggests that new structures may be synthesised based on the L_2M_2 subunits.[18]

To achieve new L_2Ag_2-based structures, coordinating anions (TFA^- or OTs^-) were introduced. ^{31}P NMR spectra of the $CDCl_3$–MeCN solutions of L : $AgCF_3CO_2$(AgTFA) or L : $AgCH_3PhSO_3$(AgOTs) = 1 : 1 indicate that the P–Ag bond is labile, with the RT resonance showing no sign of Ag coupling. Diffusion of Et_2O vapour into the solution mixtures of L and AgTFA or AgOTs yielded polymeric structures of $[Ag_2L(CF_3CO_2)_2(H_2O)]_n \supset (Et_2O)_n$ (**Ag–TFA** $\supset$ Et_2O) and

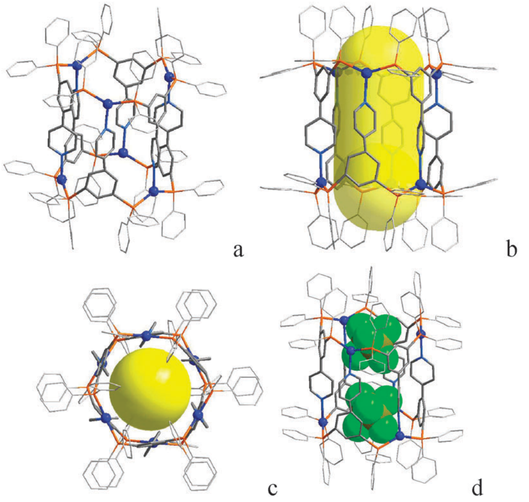

Fig. 2 X-ray structure of the nanotubular complex **Ag_6L_6–SbF_6** with anions and hydrogen atoms omitted for clarity, (a,b) side views, (c) top view, and (d) two $SbF_6{}^-$ anions located in the cavity.

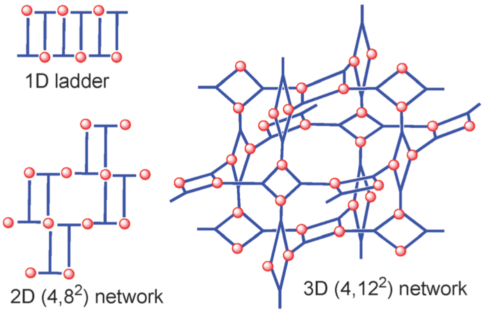

Fig. 3 Potential 1D–3D ring-opening polymers of the tubular architecture.

$[Ag_2L(OTs)_2]_n \supset (CHCl_3)_n$ (**Ag–OTs** $\supset$ $CHCl_3$), respectively. X-ray single-crystal analyses were performed to reveal unambiguously that both **Ag–TFA** and **Ag–OTs** have 2D (4,8^2)-type networks consisting of dimeric L_2Ag_4 secondary building blocks (Fig. 4, see also supporting information†).‡ In these structures, the nodes are bridged dimeric Ag_2 species. In other words, the L_2Ag_4 subunits are doubly bridged by TFA^- and water in **Ag–TFA**, while they are doubly bridged by OTs^- anions in **Ag–OTs**. In all the tubular architecture and the polymeric structures of **Ag–TFA** and **Ag–OTs**, a divergent conformation is adopted among possible orientations of the lone pairs for *meta*-diphosphine groups (Fig. 4).[13]

The above results suggest the dimeric species existing in solution may be connected by bridging coordinating anions to form 2D polymeric structures under specific conditions. The strategy paves a way to novel 2D or 3D phosphine-based polymeric structures, only a few examples of which are available so far.[16,19] It is worth mentioning that the polymeric structures can be transformed into the discrete tubular structures in solution by introducing the anions like SbF_6^-, which is evidenced by the ^{31}P NMR spectrum of $AgSbF_6 : AgTFA : L = 1:1:2$ showing a characteristic doublet of doublets of the tubular structures.

In summary, an unprecedented phosphine-based M_6L_6 coordination tubular architecture has been quantitatively assembled based on a T-shaped pyridyl diphosphine ligand and tricoordinate Ag(I) ions. The tubular structures represent a discrete molecular architecture of a number of polymeric structures assembled from dimeric building blocks, which may guide future syntheses of novel discrete and polymeric structures. Studies along this line are going on in our lab.

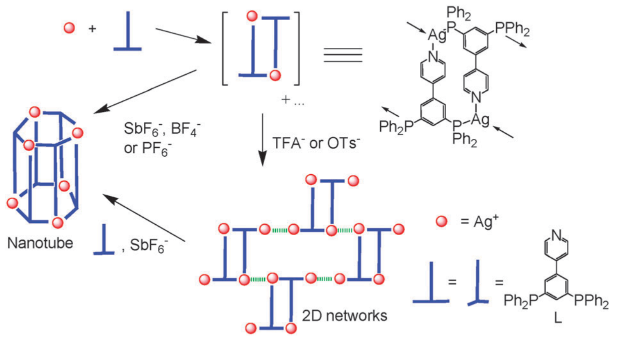

Fig. 4 Formation of the tubular architectures and 2D networks, and a divergent dimeric synthon formed by L and Ag^+ according to the orientations of the lone pairs for *meta*-diphosphine groups.

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Notes and references

‡ **Ag_6L_6–SbF_6**: $C_{210}H_{162}Ag_6F_{36}N_6P_{12}Sb_6$, monoclinic, $P2_1/n$, a = 18.4879(6), b = 34.8299(11), c = 20.2362(10) Å, β = 102.860(4)°, V = 12703.9(9) Å^3, Z = 2, d_c = 1.360 g cm^{-3}, R_1 = 0.1116, wR_2 = 0.2544 (obs. data) **Ag–TFA**: $C_{43}H_{39}Ag_2F_6NO_6P_2$, monoclinic, $P2_1/c$, a = 11.3131(6), b = 21.5140(9), c = 18.1697(8) Å, β = 90.950(5)° V = 4421.7(4) Å^3, Z = 4, d_c = 1.588 g cm^{-3}, R_1 = 0.0766, wR_2 = 0.2011 (obs. data) **Ag–OTs**: $C_{50}H_{42}Ag_2Cl_3NO_6P_2S_2$, monoclinic, $P2_1/n$, a = 10.6348(5), b = 24.7251(11), c = 19.4535(10) Å, β = 103.775(5)°, V = 4968.1(4) Å^3, Z = 4, d_c = 1.606 g cm^{-3}, R_1 = 0.0550, wR_2 = 0.1651 (obs. data)

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