Solution state coordination polymers featuring wormlike macroscopic structures and cage–polymer interconversions†

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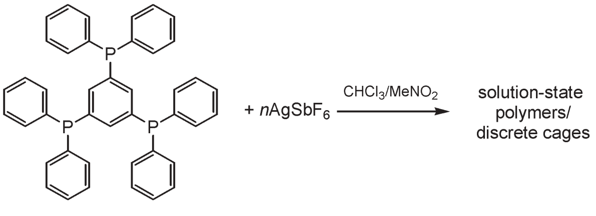
In the absence of coordinating solvents and anions, silver salts and triphosphines form viscous, thixotropic coordination polymers in solution, which aggregate into unusual wormlike macroscopic structures and undergo cage–polymer interconversions depending on the stoichiometry and presence of templating anions.

Coordination polymers exhibit many properties which are different to those of covalent polymers,[1,2] arising from the reversible nature of the coordination bond, the formation of crystalline frameworks, and the rich geometric, electronic and optical characteristics of metal ions. In recent years coordination polymers have been studied very extensively in the crystalline state.[1] Studies of the solutions from which such crystalline coordination polymers are obtained have generally revealed small cyclic or cage complexes, which must undergo ring-opening to give the crystalline polymer.[3] Although coordination polymers in solution, or as gels,[2] have not been studied to the same extent, interesting properties such as responsiveness to chemical stimuli,[2a,b] the ability to template macroporous materials[2c] and catalytic behaviour[2d] show there is great potential in this area for new and interesting materials.

Here we report a rare link between crystalline and solution-based coordination polymers. In particular, a versatile silver-triphosphine system which is known to form polymers in the crystalline state,[4] is also found to form polymers *in solution* under certain conditions. Furthermore, the polymers formed exhibit some interesting characteristics such as unusual wormlike macroscopic structures and polymer–cage interconversions as a function of stoichiometry and templating anions.



L

The titration of AgSbF$_6$ against triphosphine ligand **L** in chloroform–nitromethane solution was monitored by ^{31}P NMR as shown in Table 1.‡ At an Ag/**L** ratio of 3 : 2, the sharp spectrum shows ^{109}Ag– and ^{107}Ag–^{31}P coupling (δP = 16.2 ppm, $^1J_{109\text{Ag}-31\text{P}}$ = 605 Hz), the magnitude of which corresponds to AgP$_2$ coordination centres.[5] Together with the high symmetry and lack of viscosity this suggests that discrete Ag$_3$**L**$_2$ cages are formed (similar to [Ag$_3$**L**$_2$(OTf)$_3$] described recently[4a]). However, increasing the proportion of **L** up to a ratio of 1 : 1 resulted in a broad featureless spectrum as well as a striking increase in viscosity of the solution (to give solution **A**), suggesting polymerization had occurred. On further increasing the proportion of **L** up to a ratio of 2 : 3 the solution then returns to a non-viscous state and the ^{31}P NMR spectrum shows signals at δP = 12.0 ppm, with coupling to silver ($^1J_{109\text{Ag}-31\text{P}}$ = 363 Hz) which indicates that AgP$_3$ centres are formed. Signals due to free phosphine groups (δP = −2.8) are also visible in the spectrum. The signals in the 2 : 3 spectrum are broad suggesting some dynamic behaviour, possibly interchange between the coordinated and free phosphine sites. The structure suggested in the table for these finally-formed complexes, is based on related disilver complexes which have been structurally characterized,[6] and is consistent with the NMR spectrum.

Overall, during the titration it seems that the initially-formed Ag$_3$**L**$_2$ cages undergo ring-opening polymerization as the Ag : **L** ratio is altered to 1 : 1. Further addition of **L** to the polymer then breaks it up into discrete Ag$_2$**L**$_3$ complexes with coordinatively saturated silver ions.

Higher concentrations of a 1 : 1 mixture (100 mg mol^{-1}) of AgSbF$_6$ and **L** resulted in a still more viscous, gel-like phase **B**.‡ **B** could be inverted in an NMR tube with no evidence of flow after 1 h, although when inverted in larger sample vials it began to flow slowly after several seconds. On evaporation of the solvent under reduced pressure, a white powder was obtained, which reformed viscous solutions/gels upon redissolution.

Heating the gel-like phase **B** gave a reversible gel-sol transition. However it was not sharp, occurring from 35–58 °C (at heating at a rate of *ca.* 2 °C min^{-1}). This suggests that the gel-like phase **B** can be regarded as 'weak gel',[7] or even just a very viscous solution, with steadily decreasing viscosity as temperature increases. **B** is also visibly thixotropic. Shaking by hand for 1 min or less led to a free-flowing liquid, which once again 'gelled' on standing for several minutes. Rheometry also revealed non-Newtonian behaviour, in particular shear-thinning, *i.e.* a sharp drop in viscosity occurred on increasing the shear rate from 20 to 100 s^{-1} (Fig. 1). In broad terms, these rheological characteristics are consistent with entangled chains which become disentangled with increasing shear rate, or over time at constant shear rate[8] (see also below).

The formation of polymers in solution only occurred in non-coordinating solvents and with poorly-coordinating (fluoro) anions. For example, AgPF$_6$ yielded similar results to AgSbF$_6$, and AgBF$_4$ caused separation of a gel-like viscous phase from a

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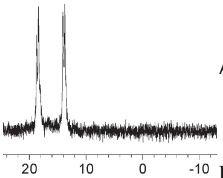
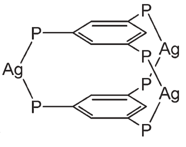
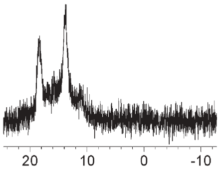
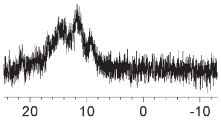
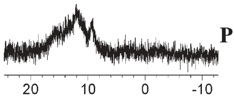
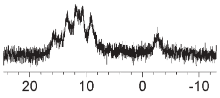
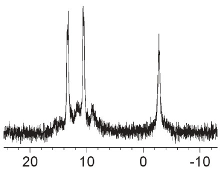
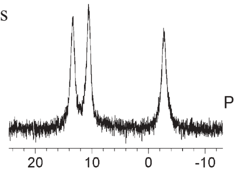
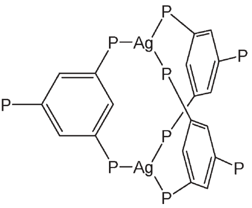
Table 1 Visual observations of viscosities correlated with ^{31}P NMR spectra and interpretation of structures present as a function of increasing ratio of **L** to AgSbF$_6$ (19.1 mg mol^{-1}, CHCl$_3$: MeNO$_2$ = 1.6 : 1, P = PPh$_2$, charges and anions are omitted for clarity)

Ag : **L**	Viscosity	^{31}P NMR	Structures present
3 : 2	Non-viscous		 **Discrete Ag$_3$L$_2$ complexes**
4 : 3	Non-viscous		Ring-opening polymerisation
11 : 10	Non-viscous		
1 : 1	Viscous		**Polymer (solution A)**
10 : 11	Low-viscosity		Break-up of polymer
3 : 4	Non-viscous		
2 : 3	Non-viscous		 **Discrete Ag$_2$L$_3$ complexes**

supernatant with low viscosity. Strikingly, however, silver salts with oxo-anions such as AgOTf or AgNO$_3$ behaved very differently, giving normal, non-viscous solutions from which solids would precipitate at high concentrations. The ^{31}P NMR spectra of the SbF$_6^-$, PF$_6^-$ or BF$_4^-$ polymers all show only very broad peaks. However, the spectrum of the analogous OTf$^-$ solution (see ESI),† whilst also broad, clearly shows some sharp signals with recognizable ^{107}Ag– and ^{109}Ag–^{31}P couplings. The sharpness of the signals and magnitudes of these couplings indicate that stable AgP$_2$ coordination centres are formed. Whilst more than one species appear to be present in the OTf$^-$ system, the well-defined Ag–P couplings and the lack of viscosity are consistent with discrete polyhedral cage structures.[4] Furthermore, we have previously established that cage structures can be templated by oxo-anions[4e–g] (since they are more strongly coordinating than fluoro-anions they can stabilise cages by weakly bridging between Ag(I) centres).

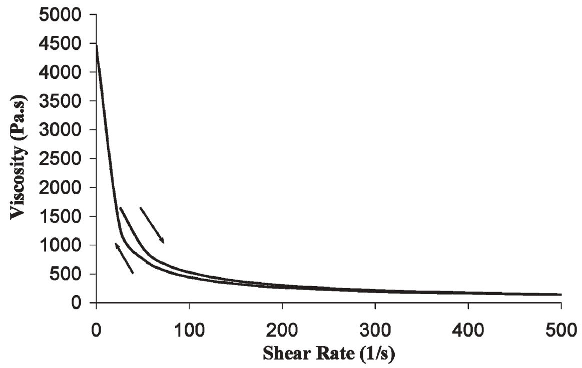


Fig. 1 Shear rate dependence of the viscosity of **B**.

The sensing of anions, and their use as triggers and templates is highly topical.[9] Coordination polymers can potentially undergo phase changes in response to anions, as described in one previous case by Lee *et al.*[2b] For the polymers described here, addition of as little as 0.1 molar equivalents of salts such as [NBu$_4$][OTf], [NBu$_4$][NO$_3$] or [NBu$_4$][*p*-MeC$_6$H$_4$SO$_3$] converted viscous solution **A** into non-viscous solutions within a few seconds (see ESI).† In contrast, addition of fluoro-anion salts [NBu$_4$][SbF$_6$], [NBu$_4$][PF$_6$] or [NBu$_4$][BF$_4$] had no visible effect on the polymers, as expected from their inability to template discrete cages.

With regard to coordinating solvents, addition of acetonitrile or DMSO up to only 2% (v/v) also converted viscous solutions (total mass of AgSbF$_6$ and **L** = 29 mg mol^{-1}) into non-viscous solutions. This is presumably simply due to terminal coordination at Ag sites.

To gain insight into the macroscopic structures of the highly viscous gel-like phases, cryogenic scanning electron microscopy (cryo-SEM) was performed on **B**. A clear image of macroscopic structure was obtained from an 'etched drop' (Fig. 2). It shows

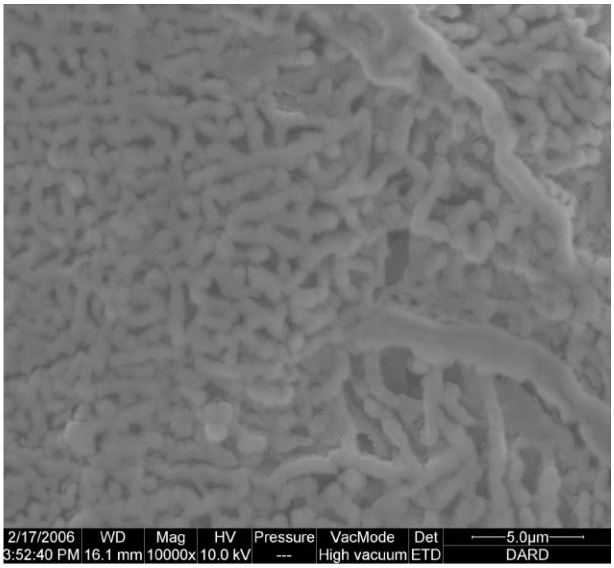


Fig. 2 Cryo-SEM image of the gel-like material **B** obtained from **L** and AgSbF$_6$ in CHCl$_3$/MeNO$_2$ showing unusual wormlike macroscopic structures *ca.* 0.5–1 μm in diameter.

entangled wormlike aggregates *ca.* 0.5–1 μm in diameter and with continuous sections up to 10 μm long clearly visible. Entanglement of these wormlike features can account for the thixotropy and shear-thinning behaviour observed (see above). Similar sized features have been identified in gels (for example those based on dendrimers[10a]) and in dried xerogels (*e.g.* bis(urea)s and their complexes[10b]) but they were in contrast straight-edged fibres. TEM images of dried coordination polymer gels have also been reported,[2b] showing entangled curled-up fibres, but they were only a few nanometers in diameter. Although wormlike morphologies are well known to form in water–surfactant phases at high salt concentrations,[11] these features are also only a few nanometers in diameter. The thick worm-like structures seen here could result from aggregation of linear coordination chains or potentially the curling-up of 2-D coordination sheets, both types of structures having been identified in crystalline polymers of **L** with silver triflate.[4a,b]

In summary, at the correct stoichiometry and in the absence of coordinating solvents and anions, viscous silver–phosphine coordination polymers are observed to form in solution for the first time. The polymers adopt unusual, thick wormlike macroscopic structures and undergo polymer–cage interconversions depending on the ratio of metal to ligand and the presence of templating anions.

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Notes and references

‡ Reagents were purchased and used as supplied. **L** was prepared following the literature procedure.[12] Typical preparative procedure: Solutions of $AgSbF_6$ (36.8 mg, 0.11 mmol) in $MeNO_2$ (2.1 ml) and 1,3,5-tris(diphenylphosphino)benzene (**L**, 67.6 mg, 0.11 mmol) in $CDCl_3$ (3.4 ml) were mixed in a sample vial. **A** was obtained as a viscous solution. ^{31}P NMR ($MeNO_2$/$CDCl_3$): δ 10.5 (broad). Similarly **B** was prepared from solutions of $AgSbF_6$ (91.4 mg, 0.27 mmol) in $MeNO_2$ (1.0 ml) and **L** (167.8 mg, 0.27 mmol) in $CHCl_3$ (1.6 ml) and was a highly viscous, gel-like phase.

^{31}P NMR spectra were recorded at 121.5 MHz and 27 °C, are referenced to external H_3PO_4 (*aq*) 85%, and were taken in $MeNO_2$/$CDCl_3$ (1:1.6) with concentration of 0.030 mol l^{-1} (based on Ag/**L**). δ SbF_6^- 8–20 ppm (broad); PF_6^- 8–20 ppm (broad); BF_4^- 8–20 ppm (broad); OTf^- 14.4 ppm ($^1J_{109Ag-31P}$ = 562 Hz), 10.6 ppm ($^1J_{109Ag-31P}$ = 492 Hz) plus other peaks.

Cryo-scanning eectron microscopy was performed by Mr David McCall, at The Queen's University of Belfast Department of Applied Science, Faculty of Agriculture & Food Science, Newforge Lane, Belfast. The cryo-SEM samples were prepared in EMITECH. A drop of the gel was placed in a stub and was quickly cooled to −220 °C with under-cooled nitrogen as slush. The sample was then introduced into the microscope cooling pre-chamber, which was then evacuated, and allowed to warm to −95 °C for 5 min. At this temperature the upper part of the drop was fractured with a cool knife and etched for 2 min. The pre-chamber was cooled to −120 °C and the sample was sputtered *in situ* with 1.5 nm of Au/Pd. Finally, it was transferred into the microscope chamber where the temperature was kept below −130 °C to avoid the formation of ice crystals. The samples were imaged with a FET Quanta 200 SEM.

Rheological analysis was carried out at the Materials Ireland Research Centre, University of Limerick, National Technological Park, Limerick, Ireland, using the Haake Rotovisco 1 with parallel plates (PP35 Ti) at 25 °C. Sample volumes of 1.5–2 ml were used. The experiment was performed in an atmosphere controlled chamber to reduce solvent evaporation. Steady state flow and time curves were performed.

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