Polymeric Silver Co-ordination Compounds

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Preparation and crystallographic characterization of novel co-ordination polymers containing silver ions bridged by a flexible ligand provides evidence for a well defined pathway for polymerization of co-ordination compounds.

Polymeric substances which contain transition metals may exhibit unusual and technologically useful properties quite different to those of wholly organic materials.[1] The preparation of well defined polymer systems containing metal ions has been a major synthetic challenge to inorganic chemists.[2] We have been exploring the co-ordination chemistry of a series of neutral, potentially tetradentate ligands (see Scheme 1), prepared by Schiff base condensation of halo-substituted benzaldehydes and ethylenediamine, with a variety of transition metals.[3] Herein we report that the flexible co-ordination properties of these ligands enable preparation of crystalline co-ordination polymers containing the silver ion. Although polymeric complexes of silver are known (*e.g.* AgCN and AgSCN),[4] we report the transformation of a soluble complex into a polymeric material with identical ligand sets.

Reaction of silver triflate and the ligand L_{Cl} in a 1 : 2 molar ratio in methanol affords the soluble complex $[Ag(L_{Cl})_2]$-OTf(OTf = triflate) as colourless crystals in high yield.† The imine donor atoms of the ligand co-ordinate about the silver

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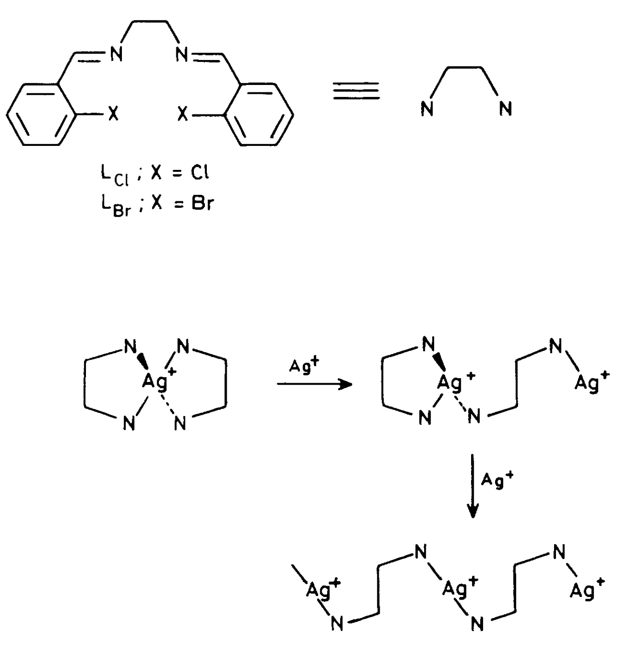
† All new compounds were characterized by i.r. and n.m.r. spectroscopy and gave satisfactory elemental analyses (C, H, and N).



Scheme 1

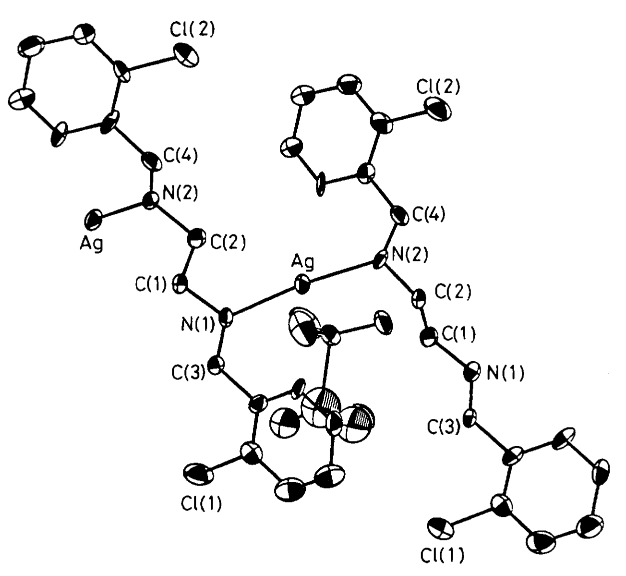


Figure 1. ORTEP representation of polymeric $[AgL_{Cl}]OTf$. Selected bond distances (Å): Ag–N(1) 2.131(15), Ag–N(2) 2.164(15), N(1)–C(3) 1.28(2), N(2)–C(4) 1.32(2), N(1)–C(3) 1.50(2), N(2)–C(2) 1.54(4), C(1)–C(2) 1.50(4). Selected bond angles (°): N(1)–Ag–N(2) 173.3(6), Ag–N(1)–C(3) 126(1), Ag–N(1)–C(1) 119(1), Ag–N(2)–C(4) 129(1), Ag–N(2)–C(2) 114(1), N(1)–C(1)–C(2) 109(2), N(2)–C(2)–C(1) 107(3), C(1)–N(1)–C(3) 115(1), C(2)–N(2)–C(4) 117(2).

atom in a bis-bidentate fashion and the complex has a distorted tetrahedral structure similar to the previously crystallographically characterized analogue $[Ag(L_{Br})_2]OTf$.[5] Dissolution of this material in tetrahydrofuran (THF) and addition of AgOTf (1 equiv.) followed by crystallization with ether affords $[Ag(L_{Cl})]OTf$ as a white powder slightly soluble in nonco-ordinating solvents.† The same material can be obtained by direct reaction of AgOTf and L_{Cl} in THF or CH_2Cl_2. Single crystals of $[Ag(L_{Cl})]OTf$ were obtained by slow diffusion of ether into a saturated solution (THF) of the complex at room temperature.

An ORTEP representation of the polymeric structure is shown in Figure 1.‡ Each silver ion is co-ordinated in a linear fashion by relatively short[6] silver–nitrogen bonds from two different ligands to form an infinite polymer in the solid state. This structure provides a rare example of homoleptic imine co-ordination about a metal centre in the absence of the additional stability imparted by chelation. The triflate anion is nonco-ordinating;[7] the shortest silver–oxygen contact is 2.84 Å. The ability of the silver ion to accommodate either a linear or tetrahedral co-ordination geometry, combined with the flexibility of the ethylene bridge of the ligand, provides a well defined pathway for ring opening polymerization (see Scheme 1). The flexibility of the ligand backbone and lability[8] of the d^{10} silver ion also enables the polymeric material to form a solution in polar solvents, presumably with depolymerization. Recrystallization of $[Ag(L_{Cl})]OTf$ from methanol affords $[Ag(L_{Cl})_2]OTf$ and free AgOTf. This demonstrates that the polymerization reaction is reversible. We are continuing to investigate the solution and solid state properties of these new materials.

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‡ *Crystal data*: $C_{17}H_{14}AgCl_2F_3N_2O_3S$, colourless, orthorhombic, $P2_1ca$, a = 12.305(3), b = 12.739(4), c = 13.229(9) Å, U = 2073(1) Å^3, Z = 4, Mo-K_α radiation, crystal dimensions 0.27 × 0.09 × 0.04 mm. Of 1443 unique reflections collected at ambient temperature (Synthex P1, $3 < 2\theta < 45°$), 1272 with $F_o \geqslant \sigma(F_o)$ were used in the solution (Patterson) and refinement. Final refinement included all atoms as anisotropic, except for the trifluoromethyl group of the triflate anion and hydrogen atoms which were included as idealized isotropic contributions. For 241 parameters, R = 0.080 and R_w = 0.064, g.o.f. = 1.65, and the highest peak in the final difference map of 1.99 e Å^3 was *ca.* 1.1 Å from Ag. 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.

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