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**Supplementary Material Available:** Tables of atomic coordinates, thermal parameters, and bond angles and distances (4 pages); tables of structure factors (12 pages). Ordering information is given on any current masthead page.

## Mechanism of Formation of Coordination Polymers: A Structural Model for Polymer Chain Growth

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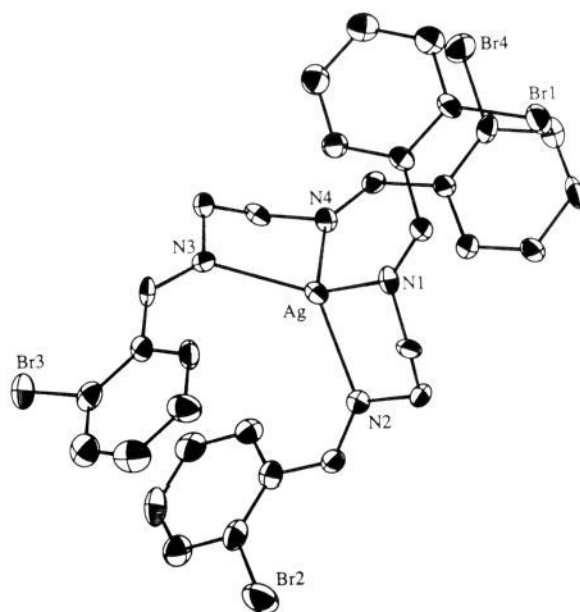
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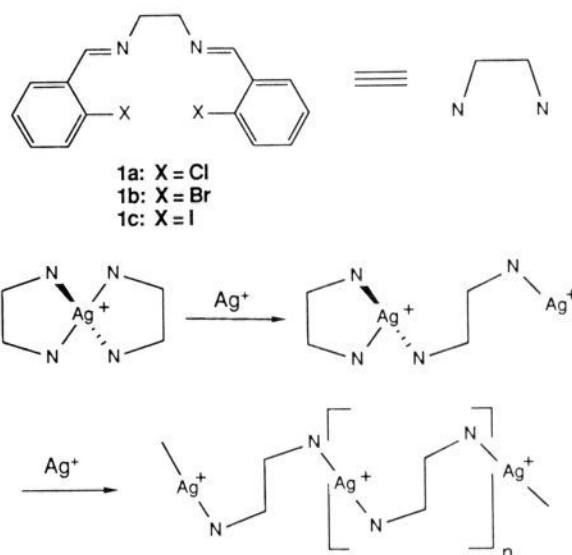
Although coordination polymers composed of metal ions linked by organic bridges have an extensive history, synthesis of well-defined materials is often problematical.<sup>1</sup> Knowledge of potential chain growth processes required in the synthesis of these materials should facilitate the rational design of metal-containing polymers with potentially useful properties.<sup>2</sup> We have recently demonstrated<sup>3</sup> that crystalline polymers derived from the ligands<sup>4</sup> **1** and silver ion can be prepared from soluble precursors (see Scheme I). We now report the isolation and crystallographic characterization of a dimeric silver complex which has structural parameters that suggest it is an intermediate in the chain growth process. This work provides the first evidence for a well-defined chain-growth step in the formation of coordination polymers.

Soluble complexes of the formula [Ag(**1**)<sub>2</sub>]OTf<sup>5</sup> are readily isolated by cooling methanol solutions containing stoichiometric quantities of AgOTf and **1**.<sup>6</sup> The structure of [Ag(**1b**)<sub>2</sub>]OTf as a methanol solvate was determined by single-crystal X-ray diffraction<sup>7</sup> (Figure 1). Each ligand is coordinated to silver by two imine nitrogens to afford a four-coordinate complex with a dis-



**Figure 1.** ORTEP representation of [Ag(**1b**)<sub>2</sub>]<sup>+</sup>. Selected bond distances (Å) are as follows: Ag–N1, 2.349 (9); Ag–N2, 2.327 (8); Ag–N3, 2.325 (8); Ag–N4, 2.330 (8). Selected bond angles (deg) are as follows: N1–Ag–N2, 76.1 (3); N3–Ag–N4, 76.6 (3); N1–Ag–N3, 133.8 (3); N1–Ag–N4, 120.4 (3); N2–Ag–N3, 127.0 (3); N2–Ag–N4, 131.6 (3).

### Scheme I



torted tetrahedral geometry. The average silver–nitrogen bond length of 2.33 (1) Å is long<sup>8</sup> and consistent with the lability of these complexes in solution.<sup>9</sup> In contrast the average silver–nitrogen distance in polymeric [Ag(**1a**)]OTf is 2.15 (2) Å.<sup>3</sup>

Interaction of stoichiometric quantities of the ligand **1c** and AgOTf affords the dimeric complex [Ag<sub>2</sub>(**1c**)<sub>3</sub>]OTf[OTf]·THF in 95% yield by crystallization from THF solution upon addition of Et<sub>2</sub>O.<sup>10</sup> Crystallographic investigation reveals a novel dimeric structure in which the silver ions are linked by a bridging ligand and a bidentate trifluoromethanesulfonate counterion (Figure 2).<sup>11</sup>

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(9) For example, room temperature 300 MHz <sup>1</sup>H NMR data shows only averaged resonances for mixtures of [Ag(**1**)<sub>2</sub>]OTf and **1**.

(10) Analytical data for [Ag<sub>2</sub>(**1c**)<sub>3</sub>]OTf[OTf]·THF. Anal. Calcd for C<sub>34</sub>H<sub>30</sub>N<sub>6</sub>Ag<sub>2</sub>F<sub>6</sub>O<sub>7</sub>S: C, 31.63; H, 2.46; N, 4.10. Found: C, 31.56; H, 2.33; N, 3.86.

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(5) Abbreviations: Et, ethyl; Me methyl; OTf, trifluoromethanesulfonate; THF, tetrahydrofuran.

(6) Analytical data: (a) [Ag(**1b**)<sub>2</sub>]OTf. Anal. Calcd for C<sub>33</sub>H<sub>28</sub>N<sub>4</sub>AgBr<sub>2</sub>F<sub>3</sub>O<sub>3</sub>S: C, 37.92; H, 2.70; N, 5.36. Found: C, 37.74; H, 2.86; N, 5.09. (b) [Ag(**1c**)<sub>2</sub>]OTf. Anal. Calcd for C<sub>33</sub>H<sub>28</sub>N<sub>4</sub>AgI<sub>2</sub>F<sub>3</sub>O<sub>3</sub>S: C, 32.14; H, 2.29; N, 4.54. Found: C, 32.24; H, 2.28; N, 4.40.

(7) Crystal data for [Ag(**1b**)<sub>2</sub>]OTf·MeOH: AgBr<sub>2</sub>SF<sub>3</sub>O<sub>4</sub>N<sub>4</sub>C<sub>34</sub>H<sub>18</sub>, colorless, monoclinic, P2<sub>1</sub>/c, a = 14.491 (3) Å, b = 21.005 (7) Å, c = 13.677 (3) Å, β = 108.75 (2)°, V = 3942.2 Å<sup>3</sup>, Z = 4, Mo Kα. Unique reflections (3095) were collected at ambient temperature (Nicolet R3m, 3.5° < 2θ < 40°) and used in the solution and refinement (SHELXTL program). Final refinement included phenyl rings as rigid regular hexagons, all other non-hydrogen atoms as anisotropic, and hydrogen atoms as idealized isotropic contributions. For 412 parameters, R = 0.068 and R<sub>w</sub> = 0.053, GOF = 1.29.

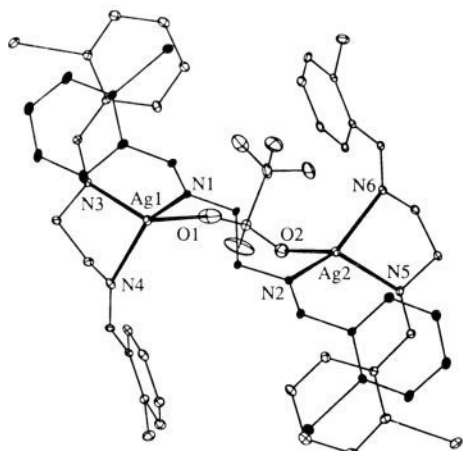


Figure 2. ORTEP representation of  $[\text{Ag}_2(\mathbf{1c})_3\text{OTf}]^+$  with atoms of the bridging ligand as solid ellipsoids.

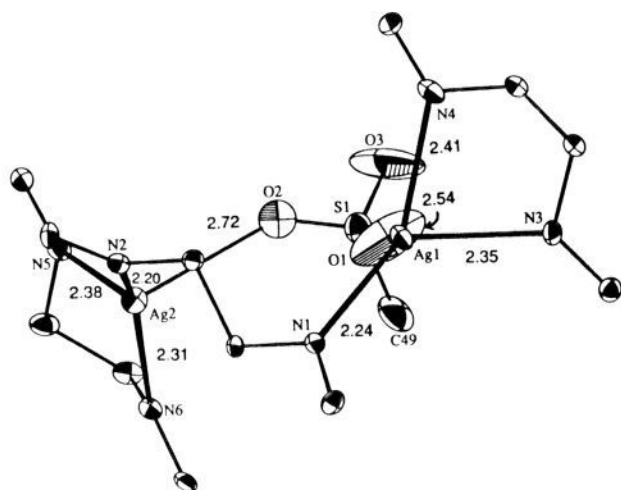


Figure 3. Inner coordination sphere of  $[\text{Ag}_2(\mathbf{1c})_3\text{OTf}]^+$  with selected bond distances ( $\pm 0.015$  Å). Selected bond angles (deg) are as follows: N1–Ag–N3, 131.0 (4); N1–Ag1–N4, 148.1 (4); N3–Ag1–N4, 76.3 (6); N1–Ag1–O1, 102.5 (9); N2–Ag2–N5, 127.9 (4); N2–Ag2–N6, 148.0 (5); N5–Ag2–N6, 76.8 (5); N2–Ag2–O2, 104.3 (7).

The remaining coordination sites on silver are occupied by a chelating bidentate ligand; the THF solvate and noncoordinating triflate do not interact with the metal centers. Each silver ion is coordinated (Figure 3) in an approximate trigonal planar<sup>12</sup> fashion by three imine nitrogens, and the relatively long<sup>13</sup> Ag–O bonds to the bridging trifluoromethanesulfonate<sup>14</sup> serve to pull the silver ions out of these planes by 0.253 (2) Å (Ag1) and 0.314 (2) Å (Ag2). These planes are orthogonal (dihedral angle = 91.6 (4)°), and the Ag1–Ag2 distance is 5.38 Å.

Note that the average Ag–N distance of the chelating ligands is long (2.36 (4) Å) and similar to that observed in  $[\text{Ag}(\mathbf{1b})_2]\text{OTf}$ .

(11) Crystal data for  $[\text{Ag}_2(\mathbf{1c})_3\text{OTf}]\text{OTf}\cdot\text{THF}$ :  $\text{I}_6\text{Ag}_2\text{SO}_7\text{N}_6\text{F}_6\text{C}_{54}\text{H}_{50}$ , colorless, triclinic,  $P1$ ,  $a = 13.245$  (5) Å,  $b = 13.207$  (5) Å,  $c = 20.496$  (5) Å,  $\alpha = 89.35$  (3)°,  $\beta = 100.64$  (3)°,  $\gamma = 108.20$  (3)°,  $V = 3342.9$  Å<sup>3</sup>,  $Z = 2$ ,  $\text{Mo K}\alpha$ . Of 9530 reflections collected (syntax  $P1$ , ambient temperature), 7292 were unique and 5835 with  $I > 2\sigma(I)$  were used in the solution and refinement (SPD package). Final refinement included all non-hydrogen atoms as anisotropic contributions. For 744 parameters,  $R = 0.066$  and  $R_w = 0.074$ ,  $\text{GOF} = 2.35$ .

(12) Rigorously trigonal coordination about silver(I) has been observed: Francisco, R. H. P.; Mascareñas, Y. P.; Lechar, J. R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 177–178.

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The 2.22 (3) Å average Ag–N distance of the bridging ligand approaches that of the polymeric species. The pseudotrigonal planar silver environment in  $[\text{Ag}_2(\mathbf{1c})_3\text{OTf}]^+$  is intermediate between that in  $[\text{Ag}(\mathbf{1b})_2]^+$  and the linear coordination geometry observed in the polymer. Thus net chain growth would be expected upon addition of AgOTf and subsequent replacement of the long Ag–N bonds with the shorter and presumably stronger Ag–N bonds in the polymer.<sup>3</sup> Polymer formation is observed upon addition of 1 equiv of AgOTf to a  $\text{CH}_2\text{Cl}_2$  solution of  $[\text{Ag}_2(\mathbf{1c})_3\text{OTf}]\text{OTf}$  to afford  $[\text{Ag}(\mathbf{1c})]\text{OTf}$ .<sup>15</sup> These results suggest that  $[\text{Ag}_2(\mathbf{1c})_3\text{OTf}]\text{OTf}$  is indeed a reasonable model for the chain-growth process required in the formation of this class of coordination polymers.

Two factors appear to be important in the formation of extended polymers by this pathway. The metal ion must have several accessible coordination numbers and geometries to stabilize soluble precursors and allow for chain elongation. In addition the flexible backbone of the ligand is crucial in enabling transformation from chelating to bridging modes of coordination. We are continuing to pursue the solution and solid-state characterization of these materials with related ligand systems and metal ions.

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**Supplementary Material Available:** NMR spectroscopic data along with crystallographic data including tables of bond distances and angles and final positional and thermal parameters for  $[\text{Ag}(\mathbf{1b})_2]\text{OTf}\cdot\text{MeOH}$  and  $[\text{Ag}_2(\mathbf{1c})_3\text{OTf}]\text{OTf}\cdot\text{THF}$  (28 pages); tables of observed and calculated structure factors (50 pages). Ordering information is given on any current masthead page.

(15) Analytical data for  $[\text{Ag}(\mathbf{1c})]\text{OTf}$ . Anal. Calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{AgF}_3\text{O}_3\text{S}$ : C, 27.41; H, 1.89; N, 3.76. Found: C, 27.69; H, 1.84; N, 3.52.

## A Model for the Unsaturated Intermediate in Dissociative Electron-Transfer-Catalyzed Substitution Reactions of Organometallic Compounds

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Reductively induced electron transfer catalysis (ETC) has rapidly become an important reaction in organometallic substitution chemistry.<sup>1–8</sup> Virtually all papers on this subject agree

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