

# Self-assembly of coordination polymeric chains: crystal structures of silver(I) complexes with 3,6-bis(diphenylphosphino)pyridazine and 2,6-bis(diphenylphosphino)pyridine

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Site-specific metal–ligand interactions lead to self-assembly of coordination polymeric chains in the crystal structures of silver(I) complexes with 3,6-bis(diphenylphosphino)pyridazine and 2,6-bis(diphenylphosphino)pyridine.

The design of solid-state architectures has become an area of increasing interest in recent years.<sup>1–6</sup> Much attention has centered upon the use of supramolecular contacts, particularly hydrogen bonding, between suitable molecules to generate multidimensional arrays or networks.<sup>1,3,4</sup> In comparison, the design of inorganic networks is less well developed though catching up fast in recent years.<sup>7–11</sup>

The self-assembly of coordination polymeric chains presents an interesting challenge. We reasoned that, with judicious design, it should be possible to assemble linear chains in a single process involving simple mixing of metals and ligands. Such a strategy requires the design of a ligand with two or more coordination sites that are juxtaposed in such a way that they cannot all coordinate to the same metal ion, and interaction between the ligand and a linear sequence of metal ions must occur in a logical fashion to form a polymeric chain.

With this in mind, we decided to conduct a test case with N,P-donor ligands with suitable binding sites and idealized  $C_{2v}$  molecular symmetry. The substituted pyridazine ligand 3,6-bis(diphenylphosphino)pyridazine ( $L^1$ ), which was synthesized in



an earlier study,<sup>13</sup> is constrained by its connectivity to act as a tetranucleating ligand, presenting a pair of N,P-bridging sites to a linear arrangement of four metal ions. Here we report the self-assembly reaction of  $L^1$  with  $[Ag(MeCN)_4]ClO_4$  to generate a zigzag polymeric chain in the silver(I) complex  $\{[Ag_2(MeCN)_2(\mu-L^1)]_n[ClO_4]_{2n}\}$  **1**. In contrast, the use of the related ligand 2,6-bis(diphenylphosphino)pyridine ( $L^2$ )<sup>14</sup> in the same reaction gave  $\{[Ag(MeCN)_2(\mu-L^2)]_n[ClO_4]_n\}$  **2** with a different metal:ligand molar ratio and exhibiting a simple linear chain.

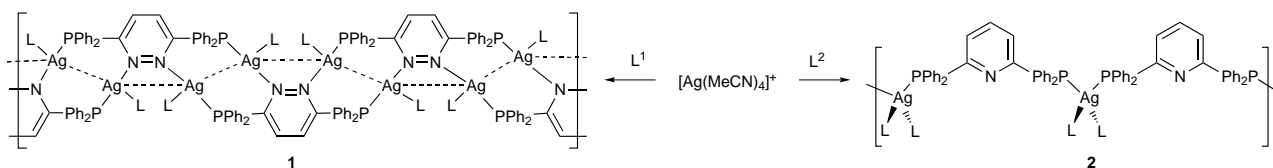
The reaction of  $[Ag(MeCN)_4]ClO_4$ <sup>15</sup> with  $L^1$  in MeCN at room temperature (Scheme 1) leads to the rapid formation of a colorless solution from which  $\{[Ag_2(MeCN)_2(\mu-L^1)]_n[ClO_4]_{2n}\}$  **1** was isolated.‡ Elemental analysis results are consistent with the stoichiometric formula  $Ag_2(MeCN)_2(L^1)(ClO_4)_2$ . Slow diffusion of diethyl ether into an acetonitrile solution afforded

colorless crystals of **1**, the structure of which was determined by single crystal X-ray analysis.§

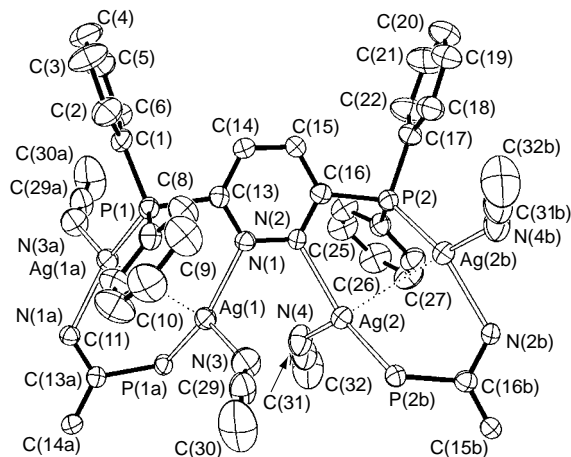
As anticipated, the  $L^1$  ligand bridges between metal centers *via* coordination by its P,N-donor sets (Fig. 1). Each silver(I) center is bound to a P atom from one  $L^1$  ligand and a N atom from the other, resulting in the formation of a polymeric zigzag chain running in the direction of the *c* axis (Scheme 1, left); note that the centers of eight-membered  $(PCNAg)_2$  rings are located at successive inversion centers. The highly distorted trigonal-planar coordination sphere about each  $Ag^I$  atom is completed by an acetonitrile ligand that stabilizes the resulting 16-electron configuration, so that the repeating structural unit is  $Ag_2(MeCN)_2(\mu-L^1)$ . The sums of the three bond angles at  $Ag(1)$  and  $Ag(2)$  are  $358.3$  and  $357.8^\circ$ , respectively. The intermolecular  $Ag(1)\cdots Ag(1a)$  and  $Ag(2)\cdots Ag(2b)$  distances are  $3.005(2)$  and  $3.184(2)$  Å, respectively, which are in agreement with those  $[3.162(1)–3.223(1)$  Å] in  $[Ag\{HC(Ph)_2\}_3]_2Cl[ClO_4]_2 \cdot 2MeCN$ ,<sup>16</sup> and those  $[2.943(2)–3.014(2)$  Å] in  $[Ag_3(dppp)_2(MeCN)_2(ClO_4)_2]^+ [dppp = \text{bis(diphenylphosphino)phenylphosphine}]$ ,<sup>17</sup> but much shorter than that  $[3.641(2)$  Å] in  $\{[AgL^3(MeCN)_2]\}_n[BF_4]_n$  ( $L^3 = 2,7\text{-diazapyrene}$ ).<sup>9</sup> The  $Ag(1)\cdots Ag(2)$  contact is  $3.535(2)$  Å.

The silver(I) complex  $\{[Ag(MeCN)_2(\mu-L^2)]_n[ClO_4]_n\}$  **2** was obtained from the reaction of  $[Ag(MeCN)_4]ClO_4$  with  $L^2$  in 1 : 1 molar ratio. The crystal structure of **2**§ consists of a packing of linear chains of alternating  $Ag^I$  and  $L^2$  units (Fig. 2 and Scheme 1, right) and perchlorate ions. In each coordination polymeric chain the repeating unit  $Ag(MeCN)_2(\mu-L^2)$  is held together by the P atoms of ligand  $L^2$ , whose pyridyl N atom takes no part in metal coordination. The coordination geometry of the silver(I) center is distorted tetrahedral, stabilization being achieved by linkage to two acetonitrile ligands. The Ag–N distances of  $2.332(8)$  and  $2.419(9)$  Å are much shorter than those  $[2.871(4), 2.926(4)$  Å] found in  $\{[AgL^3(MeCN)_2]\}_n[BF_4]_n$ .<sup>9</sup>

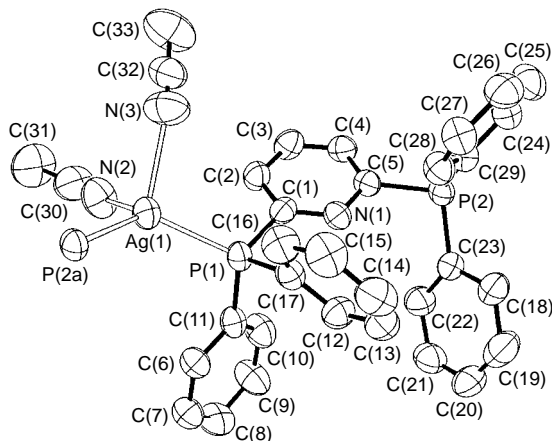
In summary, we have taken advantage of the different site-specific ligating capacities of P,N-donor ligands  $L^1$  and  $L^2$  in generating coordination polymeric chains with  $[Ag(MeCN)_4]ClO_4$ . In complex **1**, successive  $L^1$  ligands lie on alternate sides of the zigzag silver(I) chain, while in **2** the  $L^2$  ligand is repeated by the *a* translation to generate a simple linear chain. The latter case contrasts sharply with the related one-dimensional gold(I) polymer  $\{[Au_2(\mu-L^2)(C\equiv CPh)_2]\}_n$  in which the  $L^2$  ligands are arranged in a zigzag fashion along the chain.<sup>18</sup> That the silver(I) and gold(I) complexes of  $L^2$  adopt different linear polymeric structures can be attributed to the difference in number, charge and bulkiness of the respective acetonitrile and phenylacetylide



Scheme 1



**Fig. 1** Perspective view (35% thermal ellipsoids) of the cationic  $[\text{Ag}_2(\text{MeCN})_2(\mu\text{-L})]^{2+}$  unit in complex **1**. Selected bond lengths (Å) and angles ( $^\circ$ ): Ag(1)–N(1) 2.299(5), Ag(1)–N(3) 2.300(7), Ag(1)–P(1a) 2.387(2), Ag(1)–Ag(1a) 3.005(2), Ag(2)–N(4) 2.274(7), Ag(2)–N(2) 2.309(5), Ag(2)–P(2b) 2.384(2), Ag(2)–Ag(2b) 3.185(2); N(1)–Ag(1)–N(3) 89.9(2), N(1)–Ag(1)–P(1a) 147.30(13), N(3)–Ag(1)–P(1a) 121.1(2), N(1)–Ag(1)–Ag(1a) 89.15(13), N(3)–Ag(1)–Ag(1a) 135.4(2), P(1a)–Ag(1)–Ag(1a) 75.99(5), N(4)–Ag(2)–N(2) 91.7(2), N(4)–Ag(2)–P(2b) 126.6(2), N(2)–Ag(2)–P(2b) 139.50(12), N(4)–Ag(2)–Ag(2b) 142.3(2), N(2)–Ag(2)–Ag(2b) 86.89(12), P(2b)–Ag(2)–Ag(2b) 70.86(5). Symmetry codes: a,  $-x, 1-y, 2-z$ ; b,  $-1-x, 1-y, 2-z$ .



**Fig. 2** Perspective view (35% thermal ellipsoids) of cation  $[\text{Ag}(\text{MeCN})_2(\mu\text{-L})_2]^+$  in complex **2**. Selected bond lengths (Å) and angles ( $^\circ$ ): Ag(1)–P(1) 2.441(2), Ag(1)–N(2) 2.332(8), Ag(1)–N(3) 2.419(9), Ag(1)–P(2a) 2.423(2); P(1)–Ag(1)–N(2) 107.6(2), P(1)–Ag(1)–N(3) 102.8(3), P(1)–Ag(1)–Ag(2a) 127.5(1), N(2)–Ag(1)–N(3) 86.7(4), N(2)–Ag(1)–P(2a) 111.2(2), N(3)–Ag(1)–P(2a) 113.2(2). Symmetry code: a,  $1-x, y, z$ .

coligands, as well as the tendency for weak intermolecular interaction between adjacent gold(i) centres.<sup>19</sup>

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## Notes and References

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‡ **Preparations:** polymeric complex **1**: to a solution of  $[\text{Ag}(\text{MeCN})_4]\text{ClO}_4$  (0.19 g, 0.5 mmol) in 20 ml of MeCN was added  $\text{L}^1$  (0.23 g, 0.5 mmol). The resulting solution was stirred at room temperature for 3 h after which the colorless solution was filtered and subsequent diffusion of diethyl ether into the concentrated solution gave **1** as air-stable colorless crystals, 0.40 g (85.1%). (Found: C, 40.73; H, 3.01; N, 6.00.  $\text{C}_{32}\text{H}_{28}\text{AgCl}_2\text{N}_4\text{O}_8\text{P}_2$  requires: C, 40.66; H, 2.99; N, 5.93%).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , external standard: 85%  $\text{H}_3\text{PO}_4$ , 298 K):  $\delta$  15.9.

Polymeric complex **2**: the procedure was similar to that above, except that 0.23 g (0.5 mmol) of  $\text{L}^2$  was used instead of  $\text{L}^1$ . Recrystallization from MeCN–diethyl ether afforded **2** as colorless crystals. Yield: 0.32 g (86.5%) (Found: C, 53.99; H, 3.60; N, 5.60.  $\text{C}_{35}\text{H}_{35}\text{CuNP}_2\text{S}_2\text{O}_3\cdot\text{H}_2\text{O}$  requires: C, 53.79; H, 3.97; N, 5.70%).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , external standard: 85%  $\text{H}_3\text{PO}_4$ , 298 K):  $\delta$  10.1.

§ **Crystal data:**  $\{[\text{Ag}_2(\text{MeCN})_2(\mu\text{-L}^1)]\}_n[\text{ClO}_4]_{2n}$ ,  $\text{C}_{32}\text{H}_{28}\text{Ag}_2\text{Cl}_2\text{N}_4\text{O}_8\text{P}_2$ ,  $M = 945.16$ , triclinic, space group  $P1$  (no. 2),  $a = 12.294(2)$ ,  $b = 12.999(3)$ ,  $c = 13.679(3)$  Å,  $\alpha = 62.98(3)$ ,  $\beta = 73.74(3)$ ,  $\gamma = 74.63(3)^\circ$ ,  $U = 1845.1(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 1.342$  mm<sup>-1</sup>; Rigaku RAXIS-IIC imaging plate, 5639 observed data [ $|F_o| > 4\sigma(F_o)$ ] out of 5964 unique reflections converged (SHELXTL-PC<sup>19</sup>) to  $R(F) = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.053$  and  $R_w(F^2) = \{ \sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2 \}^{1/2} = 0.057$ .

$\{[\text{Ag}(\text{MeCN})_2(\mu\text{-L}^2)]\}_n[\text{ClO}_4]_n$ ,  $\text{C}_{33}\text{H}_{29}\text{AgClN}_3\text{O}_4\text{P}_2$ ,  $M = 736.85$ , orthorhombic, space group  $P2_12_12_1$  (no. 22),  $a = 9.465(1)$ ,  $b = 14.116(1)$ ,  $c = 25.596(2)$  Å,  $U = 3419.8(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 0.801$  mm<sup>-1</sup>; Rigaku RAXIS-IIC imaging plate, 5687 observed data out of 6025 unique reflections converged (SHELXTL-PC<sup>20</sup>) to  $R(F) = 0.065$  and  $R_w(F^2) = 0.070$ . CCDC 182/749.

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