

# Binuclear silver(I) complexes with polydentate phosphine ligands 2-(diphenylphosphino)-6-[3-(2'-pyridyl)pyrazol-1-yl]pyridine and 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine

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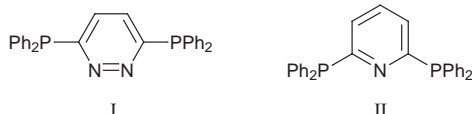
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The new polydentate, pyridine-based phosphine ligand 2-(diphenylphosphino)-6-[3-(2'-pyridyl)-pyrazol-1-yl]-pyridine ( $L^2$ ) has been synthesized. The reaction of  $L^2$  with  $[Ag(MeCN)_4][ClO_4]$  resulted in the formation of the binuclear silver(I) complex  $[Ag_2(\mu-L^2)_2(ClO_4)_2]$ , which is stabilized by significant  $\pi$ - $\pi$  stacking interactions between its inter-ligand pyridyl fragments. In contrast, the reaction of 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine ( $L^1$ ) with  $[Ag(MeCN)_4][ClO_4]$  gave the binuclear complex  $[Ag_2(\mu-L^1)_2(MeCN)_2][ClO_4]_2$ , which exhibits a weak metal-metal interaction.

## Introduction

In our previous work, we have successfully synthesized polymeric silver(I) complexes  $\{[Ag_2(MeCN)_2(\mu-L^1)]_n[ClO_4]_{2n}\}$  and  $\{[Ag(MeCN)_2(\mu-L^2)]_n[ClO_4]_n\}$  by the self-assembly reaction of polydentate phosphine ligands 3,6-bis(diphenylphosphino)pyridazine (I) and 2,6-bis(diphenylphosphino)pyridine (II) with  $[Ag(MeCN)_4][ClO_4]$ .<sup>1</sup> We have also recently reported several binuclear copper(I) complexes with 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine ( $L^1$ ), although the synthesis of this polydentate phosphine ligand was only briefly sketched.<sup>2</sup>



Here we report our subsequent study on the design of a related ligand, 2-(diphenylphosphino)-6-[3-(2'-pyridyl)pyrazol-1-yl]pyridine ( $L^2$ ), and its reaction with  $[Ag(MeCN)_4][ClO_4]$  in comparison with  $L^1$ , the synthesis of which is now described in detail.

## Experimental

### General procedure, measurement and materials

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. The solvents were purified by standard methods. The  $^1H$  and  $^{13}C\{-^1H\}$  NMR spectra were recorded on a Bruker-300 NMR spectrometer using  $SiMe_4$  as the external standard and  $CDCl_3$  as solvent. The  $^{31}P\{-^1H\}$  NMR spectra were recorded on a Bruker-500 NMR spectrometer at 202.45 MHz using 85%  $H_3PO_4$  as the external standard and  $CDCl_3$  as solvent. The compounds  $[Ag(MeCN)_4][ClO_4]$ <sup>3</sup> and 3-(2-pyridyl)pyrazole<sup>4</sup> were prepared from literature procedures.

**CAUTION:** while none of these perchlorate complexes has proved to be shock sensitive, nevertheless proper care should always be taken.<sup>5</sup>

### Preparations

**2-Chloro-6-(diphenylphosphino)pyridine.** A solution of  $LiBu^t$  in hexane (1.60 M, 36.0 mL) was added dropwise to a solution of  $Ph_2PH$  (9.30 g, 0.05 mol) in tetrahydrofuran (50 mL) at 0 °C. The resulting mixture was added dropwise to a solution of 2,6-dichloropyridine (7.40 g, 0.05 mol) in tetrahydrofuran at

-78 °C, after which the mixture was stirred for 1 h at this temperature and then allowed to warm slowly to room temperature. The solvent was removed in vacuum and water (100 mL) was added. The aqueous phase was extracted with  $CH_2Cl_2$  (3 × 50 mL) and the organic phase dried with anhydrous  $Na_2SO_4$  overnight. Most of the  $CH_2Cl_2$  was removed under vacuum and hexane (100 mL) was added to deposit a colorless solid, which upon recrystallization from  $CH_2Cl_2$ -hexane afforded an analytically pure product (yield 9.40 g, 63%). Mp: 82–83 °C.  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.49 (d,  $J = 1.2$ , 1 H, pyridyl- $H^5$ ), 7.38 (m, 10 H, phenyl), 7.20 (m, 1 H, pyridyl- $H^4$ ), 6.95 (d,  $J = 1.5$  Hz, 1 H, pyridyl- $H^3$ ).  $^{31}P\{-^1H\}$  NMR:  $\delta$  34.20 (Found: C, 68.50; H, 4.21; N, 4.51. Calc. for  $C_{17}H_{13}ClNP$ : C, 65.58; H, 4.40; N, 4.71%).

**2-(Diphenylphosphino)-6-[3-(2'-pyridyl)pyrazol-1-yl]pyridine  $L^2$ .** A solution of 3-(2-pyridyl)pyrazole (4.43 g, 0.03 mmol) in anhydrous 2-methoxyethyl ether (40 mL) was mixed with 1.17 g (0.03 mol) of potassium and stirred at 70 °C until the metal dissolved. To this solution was added 7.44 g (0.025 mol) of 2-chloro-6-(diphenylphosphino)pyridine in one portion. The resulting mixture was stirred at 110 °C for 7 d. The solvent was removed under reduced pressure and water (100 mL) was added. The aqueous phase was extracted with  $CH_2Cl_2$  (3 × 50 mL) and the organic phase dried with anhydrous  $Na_2SO_4$  overnight. Most of the  $CH_2Cl_2$  was removed under vacuum and hexane (100 mL) was added to give a crude product which could be purified by column chromatography using 6:1 hexane-diethyl ether as the eluent. The product was obtained as colorless microcrystals (yield 7.80 g, 64%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  8.31 (d,  $J = 0.7$ , 1 H, pyridyl- $H^6$ ), 7.80 (d,  $J = 1.7$ , 1 H, pyrazolyl- $H^3$ ), 7.62 (m, 2 H, pyridyl- $H^3$  and pyridyl- $H^5$ ), 7.31–7.39 (m, 13 H, phenyl, pyridyl- $H^4$ ,  $P$ -pyridyl- $H^3$  and  $P$ -pyridyl- $H^5$ ), 7.00 (d,  $J = 1.4$ , 1 H, pyrazolyl- $H^4$ ), 6.32 (t,  $J = 0.5$  Hz, 1 H,  $P$ -pyridyl- $H^4$ ).  $^{31}P\{-^1H\}$  NMR:  $\delta$  10.13 (Found: C, 73.78; H, 4.68; N, 13.72. Calc for  $C_{25}H_{19}N_4P$ : C, 73.88; H, 4.71; N, 13.79%).

**2-(Diphenylphosphino)-6-(pyrazol-1-yl)pyridine  $L^1$ .** The procedure was similar to that given above, except that 2.04 g (0.03 mol) of pyrazole was used instead of 3-(2-pyridyl)pyrazole. The product was obtained as colorless microcrystals (yield 6.70 g, 81%).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  8.36 (d,  $J = 0.7$ , 1 H, pyrazolyl- $H^3$ ), 7.87 (m, 1 H, pyrazolyl- $H^5$ ), 7.65 (m, 2 H, pyrazolyl- $H^4$  and pyridyl- $H^5$ ), 7.35–7.46 (m, 10 H, phenyl), 7.04 (m, 1 H, pyridyl- $H^3$ ), 6.36 (t,  $J = 0.6$  Hz, 1 H, pyridyl- $H^4$ ).  $^{31}P\{-^1H\}$  NMR:  $\delta$  9.31 (Found: C, 73.02; H, 5.08; N, 12.60. Calc. for  $C_{20}H_{16}N_3P$ : C, 72.94; H, 4.90; N, 12.76%).

**Table 1** Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

| <b>1</b>          |          | <b>2</b>         |          |
|-------------------|----------|------------------|----------|
| Ag(1)–P(1)        | 2.359(1) | Ag(1)–P(1a)      | 2.375(2) |
| Ag(1)–N(3a)       | 2.395(5) | Ag(1)–N(1)       | 2.405(6) |
| Ag(1)–N(4a)       | 2.395(5) | Ag(1)–N(3)       | 2.324(5) |
| Ag(1)–O(3)        | 2.652(5) | Ag(1)–N(4)       | 2.412(8) |
| Ag(1)⋯Ag(1a)      | 7.630(1) | Ag(1)⋯Ag(1a)     | 2.964(1) |
| P(1)–Ag(1)–N(3a)  | 120.5(1) | P(1a)–Ag(1)–N(1) | 110.7(2) |
| P(1)–Ag(1)–N(4a)  | 144.3(1) | P(1a)–Ag(1)–N(3) | 155.1(1) |
| N(3a)–Ag(1)–N(4a) | 71.3(2)  | N(1)–Ag(1)–N(3)  | 70.0(2)  |

Symmetry code: compound **1**, a, y, x,  $\frac{1}{2} - z$ ; compound **2**, a 1 - x, -y, -z.

**[Ag<sub>2</sub>(μ-L<sup>2</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] 1.** To a solution containing 0.40 g (1 mmol) of L<sup>2</sup> in CH<sub>3</sub>CN (20 mL) was added solid [Ag(MeCN)<sub>4</sub>][ClO<sub>4</sub>] (0.37 g, 1 mmol). The resulting solution was stirred at room temperature for 30 min. Subsequent diffusion of diethyl ether into the concentrated solution gave **1** as colorless crystals (yield 0.32 g, 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.31 (d, *J* = 1.0, 2 H, pyridyl-H<sup>6</sup>), 7.52 (d, *J* = 1.6, 2 H, pyrazolyl-H<sup>3</sup>), 7.50 (m, 4 H, pyridyl-H<sup>3</sup> and pyridyl-H<sup>5</sup>), 7.13–7.37 (m, 26 H, phenyl, pyridyl-H<sup>4</sup>, *P*-pyridyl-H<sup>3</sup> and *P*-pyridyl-H<sup>5</sup>), 6.47 (d, *J* = 0.7, 2 H, pyrazolyl-H<sup>4</sup>), 6.30 (t, *J* = 0.4 Hz, 2 H, *P*-pyridyl-H<sup>4</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR: δ 27.31 (Found: C, 48.75; H, 3.07; N, 9.05. Calc. for C<sub>25</sub>H<sub>19</sub>AgClN<sub>4</sub>O<sub>4</sub>P: C, 48.92; H, 3.12; N, 9.13%).

**[Ag<sub>2</sub>(μ-L<sup>1</sup>)<sub>2</sub>(MeCN)<sub>2</sub>][ClO<sub>4</sub>]<sub>2</sub> 2.** The procedure was similar to that above, except for 0.33 g (1 mmol) of L<sup>1</sup> was used instead of L<sup>2</sup>. The product was obtained as colorless crystals (yield 0.46 g, 91%). IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(C≡N) 2306.7 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.56 (d, *J* = 0.7, 2 H, pyrazolyl-H<sup>3</sup>), 8.12 (m, 2 H, pyrazolyl-H<sup>5</sup>), 8.00 (m, 4 H, pyrazolyl-H<sup>4</sup> and pyridyl-H<sup>5</sup>), 7.28 (m, 20 H, phenyl), 6.99 (m, 2 H, pyridyl-H<sup>3</sup>), 6.54 (t, *J* = 1.0 Hz, 2 H, pyridyl-H<sup>4</sup>), 2.02 (s, 6 H, methyl). <sup>31</sup>P-{<sup>1</sup>H} NMR: δ 36.92 (Found: C, 45.70; H, 3.31; N, 9.45. Calc. for C<sub>22</sub>H<sub>19</sub>ClAgN<sub>4</sub>O<sub>4</sub>P: C, 45.74; H, 3.32; N, 9.70%).

### Crystal structure determinations

**Complex 1.** C<sub>50</sub>H<sub>38</sub>Ag<sub>2</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>8</sub>P<sub>2</sub>, *M* = 1227.5, trigonal, *a* = 23.173(3), *b* = 23.173(3), *c* = 18.795(4) Å, *U* = 8742(4) Å<sup>3</sup>, *T* = 294 K, space group *P*3<sub>1</sub>(no. 165), *Z* = 6, μ(Mo-Kα) = 0.872 mm<sup>-1</sup>, 5210 reflections measured, 4258 unique (*R*<sub>int</sub> = 0.043) which were used in all calculations. The final *wR*(*F*<sup>2</sup>) was 0.088. *R*<sub>1</sub> = 0.058. Rigaku RAXIS IIC imaging-plate diffractometer was used.

**Complex 2.** C<sub>44</sub>H<sub>38</sub>Ag<sub>2</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>8</sub>P<sub>2</sub>, *M* = 1155.4, monoclinic, *a* = 9.663(1), *b* = 11.557(1), *c* = 21.344(7) Å, β = 99.88(3)°, *U* = 2348.0(9) Å<sup>3</sup>, *T* = 294 K, space group *P*2<sub>1</sub>/*c* (no. 14), *Z* = 2, μ(Mo-Kα) = 1.077 mm<sup>-1</sup>, 5409 reflections measured, 3726 unique (*R*<sub>int</sub> = 0.034) which were used in all calculations. The final *wR*(*F*<sup>2</sup>) was 0.092. *R*<sub>1</sub> = 0.055. Siemens P4/PC four-circle diffractometer was used.

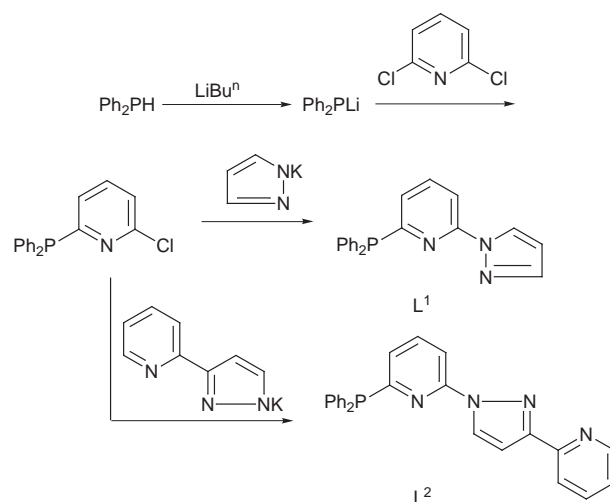
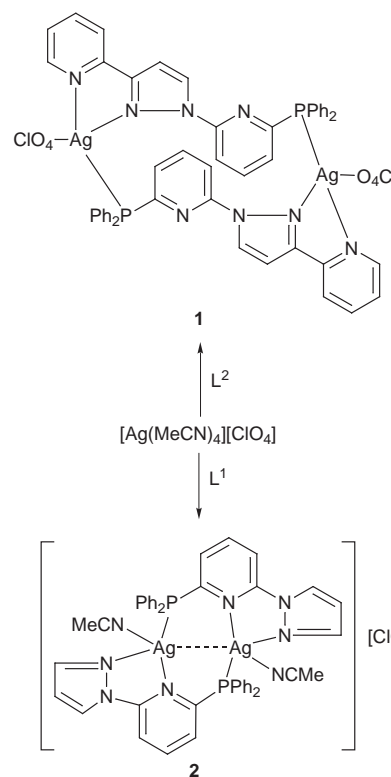
Selected bond distances and angles are presented in Table 1.

CCDC reference number 186/1087.

See <http://www.rsc.org/suppdata/dt/1998/2927/> for crystallographic files in .cif format.

### Results and discussion

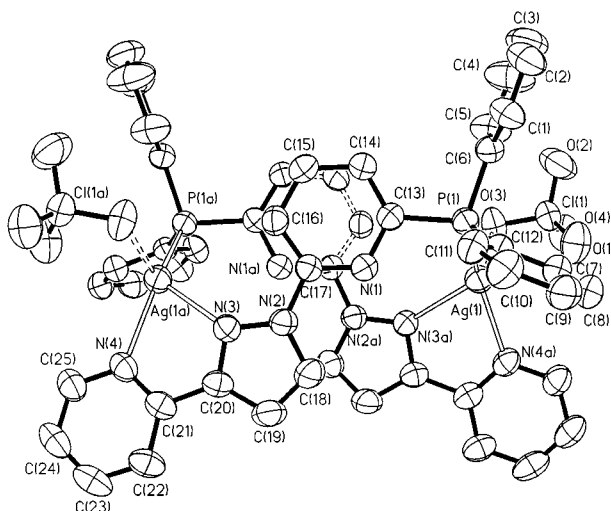
The P,N-polydentate ligands 2-(diphenylphosphino)-6-[3-(2'-pyridyl)pyrazol-1-yl]pyridine (L<sup>2</sup>) and 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine (L<sup>1</sup>), which possess rigid, narrow bites, have been synthesized in good yields in two steps. Reaction of Ph<sub>2</sub>PLi (prepared "in situ" from Ph<sub>2</sub>PH and LiBu<sup>n</sup>) with 2,6-dichloropyridine at low temperature gave the mono-substituted product 2-chloro-6-(diphenylphosphino)pyridine, which in turn reacted with potassium 3-(2-pyridyl)pyrazolate or potassium

**Scheme 1****Scheme 2**

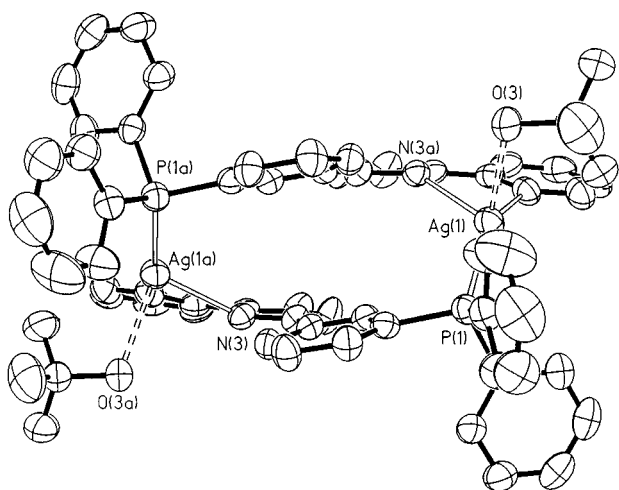
pyrazolate to furnish the desired phosphine ligands (Scheme 1). The composition of the intermediate 2-chloro-6-(diphenylphosphino)pyridine, L<sup>2</sup> and L<sup>1</sup> were all confirmed by elemental analysis, <sup>1</sup>H NMR and <sup>31</sup>P-{<sup>1</sup>H} NMR spectroscopy.

Treatment of L<sup>2</sup> with 1 equivalent of [Ag(MeCN)<sub>4</sub>][ClO<sub>4</sub>] resulted in the formation of [Ag<sub>2</sub>(μ-L<sup>2</sup>)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] **1**, in which the two L<sup>2</sup> ligands are arranged in a head-to-tail configuration and one of the two pyridyl nitrogen atoms in each does not participate in metal co-ordination (Scheme 2).

A perspective view of the binuclear complex **1**, which has molecular symmetry 2, is displayed in Fig. 1 with atom numbering. The adopted cyclic structure results from stabilization through π-π stacking of a pair of pyridyl moieties from different phosphine ligands. As anticipated, L<sup>2</sup> bridges between two metal centers. Each silver(I) center is bound to a pyridyl-pyrazole unit from one ligand and a phosphorus atom from the other, resulting in the formation of a dimeric M<sub>2</sub>L<sub>2</sub> species (Fig. 2). The pseudo-tetrahedral co-ordination sphere of each metal center is completed by a weakly co-ordinated perchlorate ligand



**Fig. 1** Perspective view (35% thermal ellipsoids) of the molecular structure of  $[\text{Ag}_2(\mu\text{-L}^2)_2(\text{ClO}_4)_2]$  **1** with atom labelling scheme (H atoms have been omitted for clarity). A crystallographic  $C_2$  axis runs vertically and bisects a line joining the silver atoms. Symmetry code: a  $y, x, \frac{1}{2} - z$ .

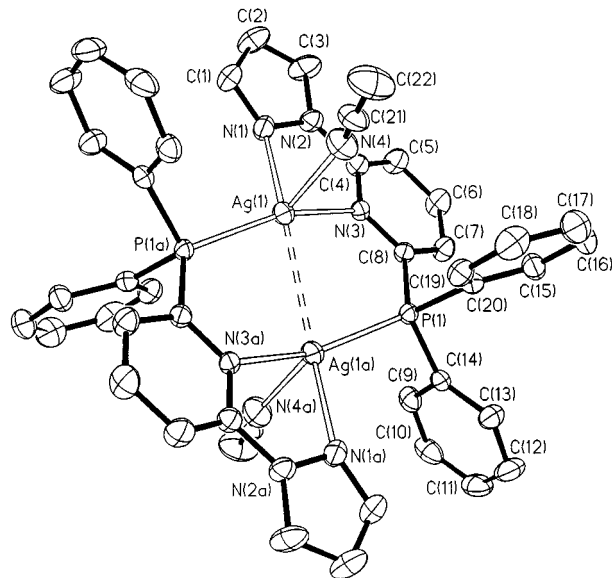


**Fig. 2** View of the molecular structure of **1** showing the  $\pi$ - $\pi$  separation between pyridyl fragments of the pair of co-ordinated  $\text{L}^2$  ligands.

bound through a single O atom. The metal-ligand bond lengths and angles are unremarkable and the non-bonded  $\text{Ag}\cdots\text{Ag}$  distance is 7.630 Å. The inter-ligand  $\pi$ - $\pi$  stacking interaction distance between the pyridyl units is 3.759 Å, which is a little longer than that (3.380 Å) in  $\{\text{AgL}(\text{MeCN})_2\}_n[\text{BF}_4]_n$  ( $\text{L} = 2,7$ -diazapyrene).<sup>6</sup> The  $\text{Ag}-\text{O}$  distance of 2.625(5) Å is shorter than those [2.762(13)-3.489(12) Å] found in  $[\text{Ag}_3(\text{dppp})_2(\text{MeCN})_2(\text{ClO}_4)_2][\text{ClO}_4]$  [dppp = bis(diphenylphosphinomethyl)phenylphosphine].<sup>7</sup>

In contrast, reaction of 2-(diphenylphosphino)-6-(pyrazol-1-yl)pyridine with 1 equivalent of  $[\text{Ag}(\text{MeCN})_4][\text{ClO}_4]$  resulted in the formation of  $[\text{Ag}_2(\mu\text{-L}^1)_2(\text{MeCN})_2][\text{ClO}_4]_2$  **2**, in which the two  $\text{L}^1$  ligands are in a head-to-tail configuration and the two metal atoms have a weak metal-metal interaction as revealed by X-ray crystallography.

A perspective view of the centrosymmetric binuclear cation of complex **2** is displayed in Fig. 3. Each  $\text{Ag}(t)$  atom exhibits distorted tetrahedral geometry with ligation by two N atoms from one phosphine ligand and one P atom from the other, and further stabilization was accomplished by the co-ordination of an acetonitrile ligand. The structure is isostructural to  $[\text{Cu}_2(\mu\text{-L}^1)_2(\text{MeCN})_2][\text{ClO}_4]_2$ ,<sup>2b</sup> although the two compounds are not isomorphous. The  $\text{Ag}\cdots\text{Ag}$  separation of 2.964(1) Å is much shorter than the  $\text{Cu}\cdots\text{Cu}$  separation [3.625(1) and 3.587(1) Å] in the analogous copper(I) complex, which is an unusual result.



**Fig. 3** Perspective view (35% thermal ellipsoids) and atom labelling scheme of the centrosymmetric  $[\text{Ag}_2(\mu\text{-L}^1)_2(\text{MeCN})_2]^{2+}$  cation in **2** (H atoms have been omitted for clarity). Symmetry code: a  $1 - x, -y, -z$ .

This value, however, is in agreement with those [2.943(2)-3.014(2) Å] in  $[\text{Ag}_3(\text{dppp})_2(\text{MeCN})_2(\text{ClO}_4)_2][\text{ClO}_4]$ ,<sup>7</sup> but shorter than those found in  $\{\text{Ag}_2(\text{MeCN})_2(\mu\text{-L})_n\}_n[\text{ClO}_4]_{2n}$  [ $\text{L} = 3,6$ -bis(diphenylphosphino)pyridazine] [3.005(2), 3.184(2) Å],<sup>1</sup>  $[\text{Ag}\{\text{HC}(\text{PPh}_2)_3\}_2\text{Cl}][\text{ClO}_4]_2 \cdot 2\text{MeCN}$  [3.162(1)-3.223(1) Å],<sup>8</sup> and  $[\text{Ag}_2(\text{dppm})_2(\text{NO}_3)_2]$  (3.085 Å),<sup>9</sup> indicating the possibility of a weak metal-metal interaction in this binuclear complex.

## Conclusion

We have taken advantage of the different site-specific ligating behavior of the newly-designed polydentate P,N-ligands  $\text{L}^2$  and  $\text{L}^1$  to generate binuclear complexes with  $[\text{Ag}(\text{MeCN})_4][\text{ClO}_4]$ . The adopted structure of **1** is favored by significant inter-ligand  $\pi$ - $\pi$  stacking interactions involving one pyridyl group of  $\text{L}^2$ , while a weak metal-metal interaction in **2** is imposed by simultaneous tight binding of  $\text{L}^1$  to two metal centers.

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