

**Silver(I) complexation of linked 2,2'-dipyridylamine derivatives.  
Synthetic, solvent extraction, membrane transport and X-ray  
structural studies**

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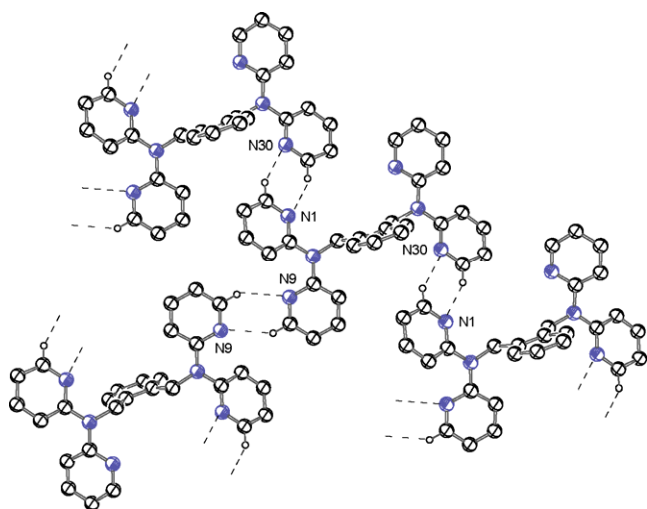
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**Additional X-ray data**

## Structure of 2



**Figure S1.** A Schematic representation of the two dimensional sheets of **2** formed via CH $\cdots$ N and  $\pi$ - $\pi$  interactions.

## Structure of 3

*Specific details:* The structure crystallised in the Monoclinic space group  $C2$  with  $\beta$  very close to  $90^\circ$  ( $90.094(3)^\circ$ ) and proved to be a twin with a two-fold rotation about  $a$ , thus emulating Orthorhombic symmetry.<sup>1</sup> The twinning was accounted for by the use of the appropriate twin law in SHELXL-97<sup>2</sup> resulting in a significant decrease in the R factor. The major twin fraction refined to an occupancy of 0.56 and subsequently no absorption correction was carried out.

## Structure of [Ag<sub>2</sub>(2)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]

**Table S1.** Selected bond lengths and angles (Å, °)

Ag(1)	N(41) <sup>1</sup>	2.2767(17)	Ag(1)	N(21)	2.2999(16)
Ag(1)	O(62)	2.5301(19)	Ag(1)	O(61)	2.5662(19)
N(41) <sup>1</sup>	Ag(1)		N(21)		144.98(5)
N(41) <sup>1</sup>	Ag(1)		O(62)		123.26(7)
N(21)	Ag(1)		O(62)		90.39(7)
N(41) <sup>1</sup>	Ag(1)		O(61)		94.74(6)
N(21)	Ag(1)		O(61)		116.81(6)
O(62)	Ag(1)		O(61)		49.16(5)

Symmetry Operator

(1) -x, -y, -z

## Structure of [Ag(3)(NO<sub>3</sub>)]

**Table S2.** Selected bond lengths and angles ( Å, °)

Ag(1)	N(21)	2.2507(15)	Ag(1)	N(41)	2.2625(15)
N(21)	Ag(1)		N(41)		145.85(5)
N(21)	Ag(1)		O(61)		122.55(6)
N(41)	Ag(1)		O(61)		90.26(6)

### Structure of [Ag<sub>3</sub>(5)<sub>2</sub>(H<sub>2</sub>O)<sub>0.5</sub>](PF<sub>6</sub>)<sub>3</sub>·1.5H<sub>2</sub>O

*Specific details:* The structure shows some dynamic disorder of the hexafluorophosphate anions. In two cases this disorder was modelled over two positions for the four fluorine atoms in the equatorial plane; in one case the low occupancy fluorine atoms of the disordered hexafluorophosphate anions are refined with isotropic displacement parameters, while in the second they were refined anisotropically. The disorder of the third hexafluorophosphate anion was not modelled. Hydrogen atoms for the coordinated and non-coordinated water molecules (half occupancy) could not be located in the Fourier difference map.

**Table S3.** Selected bond lengths and angles ( Å, °)

Ag(1)	N(31')	2.151(3)	Ag(1)	N(31)	2.156(3)
Ag(2)	N(41)	2.166(3)	Ag(2)	N(41')	2.175(3)
Ag(3)	N(21)	2.195(3)	Ag(3)	N(21')	2.204(3)
Ag(3)	O(60)	2.579(5)	C(1')	C(2')	1.383(5)
N(31')	Ag(1)		N(31)		163.80(12)
N(41)	Ag(2)		N(41')		172.77(11)
N(21)	Ag(3)		N(21')		150.40(12)
N(21)	Ag(3)		O(60)		94.88(19)
N(21')	Ag(3)		O(60)		103.18(17)

### Structure of [Ag<sub>2</sub>(2)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>

*Specific details:* The tetrafluoroborate counter-ion was disordered over two positions with occupancies of 0.68 and 0.32. All disordered fluorine atoms were refined with anisotropic displacement parameters.

**Table S4.** Selected bond lengths and angles ( Å, °)

Ag(1)	N(21) <sup>1</sup>	2.223(2)		
Ag(1)	N(41)	2.233(2)		
N(21) <sup>1</sup>	Ag(1)	N(41)	152.84(7)	

### Symmetry Operator

(1) -x, -y, -z

### Structure of $[\text{Ag}_2(\mathbf{2})_2]_3(\text{PF}_6)_6 \cdot 2\text{CH}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$

*Specific details:* A chlorine atom (Cl61) of a disordered dichloromethane molecule is modelled over two positions and the minor component refined with isotropic displacement parameters.

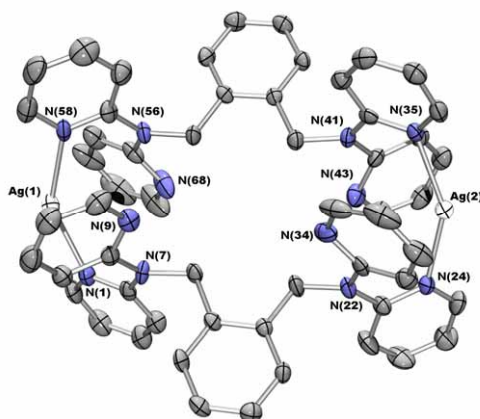
**Table S5.** Selected bond lengths and angles ( $\text{\AA}$ ,  $^\circ$ )

Ag(1)	N(21)	2.221(5)	Ag(1)	N(41) <sup>1</sup>	2.222(5)
Ag(2)	N(21')	2.250(5)	Ag(2)	N(41') <sup>1</sup>	2.253(5)
Ag(3)	N(41'') <sup>1</sup>	2.213(5)	Ag(3)	N(21'')	2.232(5)
N(21)	Ag(1)		N(41) <sup>1</sup>		146.11(14)
N(21')	Ag(2)		N(41') <sup>1</sup>		147.49(15)
N(41'') <sup>1</sup>	Ag(3)		N(21'')		150.23(15)

### Symmetry Operator

(1) -x, -y, -z

### Structure of $[\text{Ag}_2(\mathbf{2})_2(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$



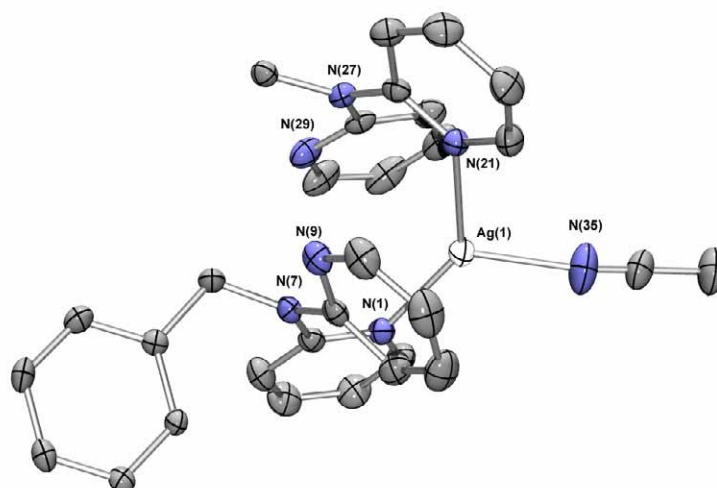
**Figure S2.** An ORTEP<sup>3</sup> representation of the cation in  $[\text{Ag}_2(\mathbf{2})_2(\text{ClO}_4)_2] \cdot 2\text{H}_2\text{O}$  with 50 % probability ellipsoids. Hydrogen atoms, disordered solvent and anions removed for clarity.

*Specific details:* One of the coordinated perchlorate anions is disordered and is modelled over two positions of 0.6 and 0.4 occupancy with isotropic displacement parameters. Large peaks of residual density were modelled as disordered isotropic water molecules over five positions with a total occupancy of two per silver complex. The hydrogen atoms could not be located in the Fourier difference map.

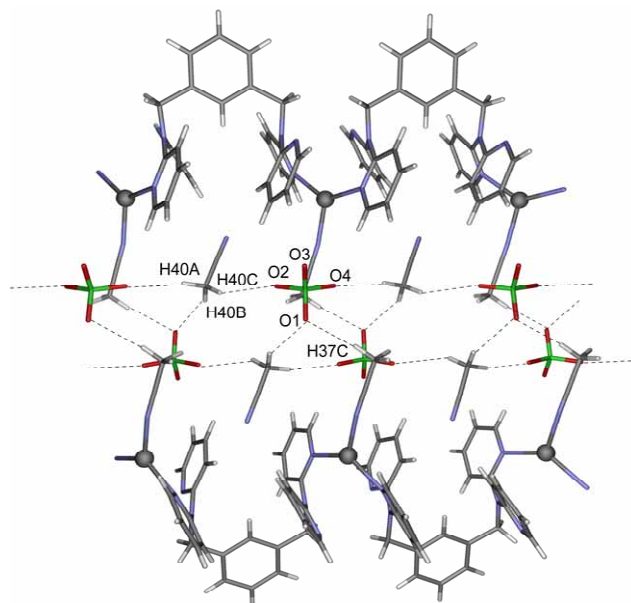
**Table S6.** Selected bond lengths and angles ( Å, °)

Ag(1)	N(1)	2.259(6)	Ag(1)	N(58)	2.268(6)
Ag(1)	O(8)	2.334(15)	Ag(1)	O(10)	2.407(12)
Ag(2)	N(24)	2.236(6)	Ag(2)	N(35)	2.262(5)
Ag(2)	O(3)	2.386(5)	N(1)	C(6)	1.337(9)
N(1)	Ag(1)	N(58)			142.31(19)
N(1)	Ag(1)	O(8)			107.5(4)
N(58)	Ag(1)	O(8)			109.8(4)
N(1)	Ag(1)	O(10)			120.1(3)
N(58)	Ag(1)	O(10)			97.4(3)
O(8)	Ag(1)	O(10)			18.3(4)
N(24)	Ag(2)	N(35)			147.45(19)
N(24)	Ag(2)	O(3)			113.4(2)
N(35)	Ag(2)	O(3)			99.0(2)

**Structure of  $\{[\text{Ag}(3)(\text{CH}_3\text{CN})](\text{ClO}_4)\cdot\text{CH}_3\text{CN}\}_n$**



**Figure S3.** An ORTEP<sup>3</sup> representation of the cation in  $\{[\text{Ag}(3)(\text{CH}_3\text{CN})](\text{ClO}_4)\cdot\text{CH}_3\text{CN}\}_n$  with 50 % probability ellipsoids. Hydrogen atoms, disordered solvent and anions removed for clarity.



**Figure S4.** A Schematic representation of the two dimensional sheets of  $\{[Ag(3)(CH_3CN)] \cdot (CH_3CN) \cdot (ClO_4)\}_n$  formed via  $CH \cdots O$  interactions.

**Table S7.** Selected bond lengths and angles ( $\text{\AA}$ ,  $^\circ$ )

Ag(1)	N(35)	2.2311(19)	Ag(1)	N(1)	2.2336(15)
Ag(1)	N(21)	2.2941(14)			
N(35)	Ag(1)		N(1)	Ag(1)	121.40(7)
N(35)	Ag(1)		N(21)	Ag(1)	102.57(7)
N(1)	Ag(1)		N(21)	Ag(1)	135.93(5)

**Structure  $\{[Ag(3)](PF_6) \cdot CH_3OH\}_n$**

*Specific details:* The structure shows some dynamic disorder of the hexafluorophosphate anion and symmetry imposed disorder of the coordinated methanol molecule.

**Table S8.** Selected bond lengths and angles ( $\text{\AA}$ ,  $^\circ$ )

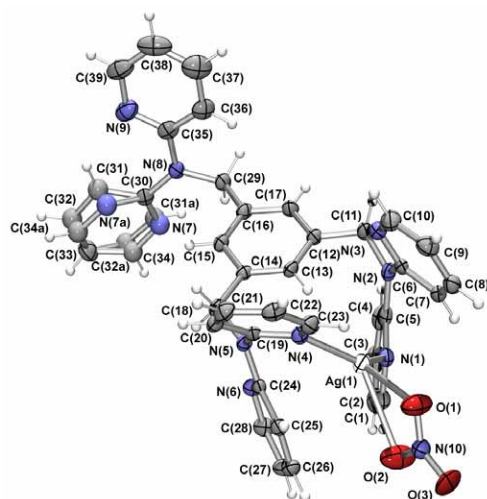
Ag(1)	N(21) <sup>1</sup>	2.235(4)	Ag(1)	N(21)	2.235(4)
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Ag(1)	O(40)	2.591(7)	Ag(1)	O(40) <sup>1</sup>	2.591(7)
N(21) <sup>1</sup>	Ag(1)		N(21)		142.5(2)
N(21) <sup>1</sup>	Ag(1)		O(40)		98.3(2)
N(21)	Ag(1)		O(40)		113.8(2)
N(21) <sup>1</sup>	Ag(1)		O(40) <sup>1</sup>		113.8(2)
N(21)	Ag(1)		O(40) <sup>1</sup>		98.3(2)
O(40)	Ag(1)		O(40) <sup>1</sup>		63.2(4)

Symmetry Operator

(1) -x, y, -z+1/2

### Structure of [Ag(6)(NO<sub>3</sub>)]



**Figure S5.** An ORTEP<sup>3</sup> representation of [Ag<sub>6</sub>(NO<sub>3</sub>)] with 50 % probability ellipsoids.

*Specific details:* The N(7) containing pyridyl ring is disordered over two positions and was modelled isotropically with 50 % occupancy for each position.

**Table S9.** Selected bond lengths and angles ( Å, °)

N(1)	Ag(1)	2.263(2)	N(4)	Ag(1)	N(1)	139.18(8)
N(4)	Ag(1)	2.249(2)	N(4)	Ag(1)	O(1)	103.35(9)
O(1)	Ag(1)	2.436(2)	N(1)	Ag(1)	O(1)	117.12(9)

### References

1. S. Parsons, *Acta Cryst.* 2003, **D59**, 1995.
2. Sheldrick, G. M., *SHELX-97: Programs for Crystal Structure Analysis*, University of Göttingen, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1997.
3. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **30**, 565.