

Bis(μ -2-cyanopyridine- $N:N'$)bis-[(2-cyanopyridine- N)silver(I)] bis(tetrafluoroborate): an anion-linked molecular ladder

Alexander J. Blake,* Neil R. Champness, James E. B. Nicolson and Claire Wilson

School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England

Correspondence e-mail: a.j.blake@nottingham.ac.uk

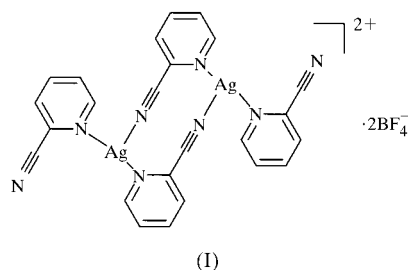
Received 3 August 2001

Accepted 22 August 2001

In the title compound, $[\text{Ag}_2(\text{C}_6\text{H}_4\text{N}_2)_4](\text{BF}_4)_2$, the Ag^{I} cations adopt distorted trigonal-planar coordination geometries. The Ag^{I} centres are linked *via* two bridging 2-cyanopyridine ligands to give a centrosymmetric dinuclear complex in which the Ag^{I} coordination environment is completed by monodentate non-bridging 2-cyanopyridine ligands. Bridging $\text{Ag}\cdots\text{F}(\text{BF}_2)\text{F}\cdots\text{Ag}$ interactions link the dinuclear cations into molecular ladders.

Comment

The title compound, (I), isolated during studies into the formation of Ag^{I} coordination polymers using pyridine and nitrile donors, exists as an air-stable colourless solid. An X-ray study confirmed the stoichiometry of the compound (Fig. 1). The Ag^{I} centres of the dinuclear $[\text{Ag}_2(\text{NCC}_5\text{H}_4\text{N})_4]^{2+}$ cation are related by an inversion centre, with each Ag^{I} atom occupying a distorted trigonal-planar environment involving one terminal and two bridging 2-cyanopyridine ligands. Thus, each Ag^{I} atom is coordinated by two pyridyl and one nitrile donor,



and sits 0.15 Å above the N_3 plane. The BF_4^- anions sit both above and below the AgN_3 plane, displaying $\text{Ag}\cdots\text{F}$ interactions of 2.7029 (15) and 2.8443 (16) Å. Taking these long-range interactions into account, the Ag^{I} cation adopts a trigonal-bipyramidal arrangement, with the F atoms of the

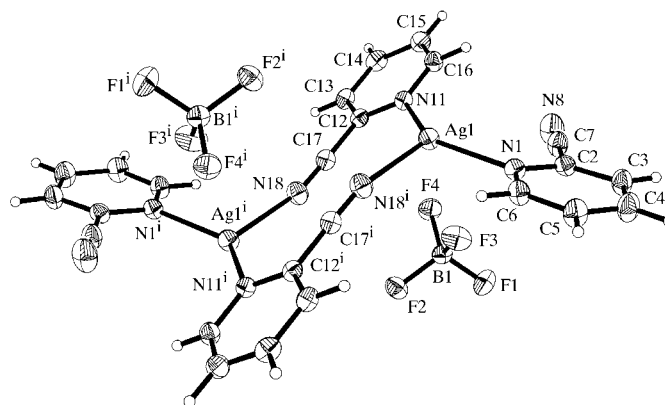


Figure 1

View of (I) showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. [Symmetry code: (i) $-x, -y, -z$.]

anion assuming apical positions; $\text{F}\cdots\text{Ag}\cdots\text{F} = 170.95(4)^\circ$ (Fig. 2). Thus, each BF_4^- anion bridges Ag^{I} centres to give a molecular ladder motif, which has been widely observed in coordination polymer chemistry (Withersby *et al.*, 1999), although not involving anion bridging as observed here. Such $\text{Ag}\cdots\text{F}(\text{BF}_2)\text{F}\cdots\text{Ag}$ interactions are within the sum of the van der Waals radii of Ag and F, and have previously been shown to be structure determining in Ag^{I} coordination polymers of 1,4-dithiane (Blake *et al.*, 2000).

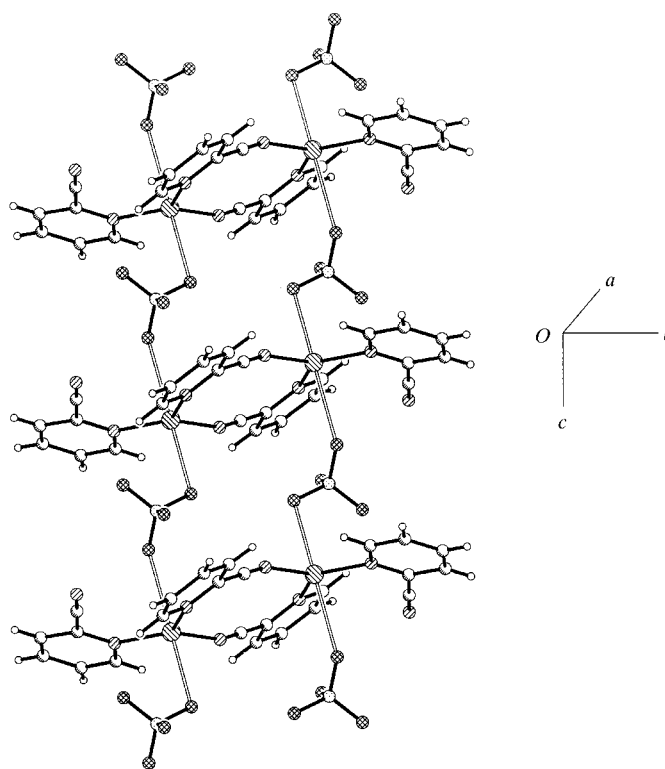


Figure 2

View of the molecular ladder formed by $\text{Ag}\cdots\text{F}$ interactions, which are represented by open lines. Left-hatched circles are Ag, right-hatched circles are N, dotted circles are B and cross-hatched circles are F atoms.

As a result of the $\text{Ag}^+ \cdots \text{FBF}_3^-$ interactions, two nitrile donors per cation remain uncoordinated, which is surprising considering the preference of Ag^+ for two- or four-coordinate environments and for *N*-donor ligands (Blake *et al.*, 1999). However, the absence of coordinate bonds formed between Ag^+ and these pendant nitrile donors reinforces the significance of the $\text{Ag}^+ \cdots \text{FBF}_3^-$ interactions. The pendant nitrile groups are directed toward an aromatic H atom of a pyridyl ring of an adjacent cation. However, the distances and angles associated with this interaction (Table 2) are at the limit of what can be considered a $\text{CN} \cdots \text{H}(\text{C})$ interaction (Desiraju & Steiner, 1999; Dhurjati *et al.*, 1991; Reddy *et al.*, 1993). An elongated π - π -stacking interaction between pendant 2-cyanopyridine ligands on adjacent complexes is also observed, with a centroid-centroid separation of 4.080 Å and a plane-centroid separation of 3.697 Å (Janiak, 2000).

Experimental

The title compound was prepared by adding a solution of AgBF_4 (0.01 mg, 0.05 mmol) in MeNO_2 (5 ml) to a solution of 2-cyanopyridine (0.011 mg, 0.1 mmol) in MeNO_2 (5 ml). Vapour diffusion of diethyl ether into the reaction solution afforded colourless sphenoidal crystals after *ca* 3 d.

Crystal data

$[\text{Ag}_2(\text{C}_6\text{H}_4\text{N}_2)_4](\text{BF}_4)_2$
 $M_r = 805.80$
 Monoclinic, $P2_1/c$
 $a = 8.3265$ (7) Å
 $b = 25.364$ (2) Å
 $c = 7.0865$ (6) Å
 $\beta = 113.427$ (1)°
 $V = 1373.3$ (2) Å³
 $Z = 2$

$D_x = 1.949$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4803 reflections
 $\theta = 2.4$ – 28.6 °
 $\mu = 1.51$ mm⁻¹
 $T = 150$ (2) K
 Sphenoid, colourless
 $0.33 \times 0.22 \times 0.14$ mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Siemens, 1996)
 $T_{\text{min}} = 0.641$, $T_{\text{max}} = 0.717$
 13 628 measured reflections

3224 independent reflections
 3035 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 29.0$ °
 $h = -11 \rightarrow 11$
 $k = -32 \rightarrow 32$
 $l = -9 \rightarrow 9$

Table 1

Selected geometric parameters (Å, °).

Ag1–N1	2.2778 (19)	Ag1–F2 ⁱⁱ	2.7029 (15)
Ag1–N11	2.2455 (19)	Ag1–F3	2.8443 (16)
Ag1–N18 ⁱ	2.318 (2)		
N1–Ag1–N11	138.04 (7)	N11–Ag1–F2 ⁱⁱ	83.84 (6)
N1–Ag1–N18 ⁱ	97.74 (7)	N11–Ag1–F3	87.63 (6)
N1–Ag1–F2 ⁱⁱ	106.71 (6)	N18 ⁱ –Ag1–F2 ⁱⁱ	92.30 (6)
N1–Ag1–F3	77.80 (6)	N18 ⁱ –Ag1–F3	94.86 (6)
N11–Ag1–N18 ⁱ	122.80 (7)	F2 ⁱⁱ –Ag1–F3	170.95 (4)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y, z - 1$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.058$
 $S = 1.30$
 3224 reflections
 199 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.014P)^2 + 1.214P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.52 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.43 \text{ e } \text{Å}^{-3}$

Table 2

Hydrogen interaction geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C4–H4 \cdots N8 ⁱⁱⁱ	0.95	2.56	3.184 (3)	124

Symmetry code: (iii) $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$.

All H atoms were included at geometrically calculated positions and constrained to ride at a distance of 0.95 Å from their parent C atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT and SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2001).

The authors thank EPSRC for provision of a diffractometer and the University of Nottingham for a studentship (JEBN).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1494). Services for accessing these data are described at the back of the journal.

References

- Blake, A. J., Brooks, N. R., Champness, N. R., Cunningham, J. W., Hubberstey, P. & Schröder, M. (2000). *CrystEngComm*, Article 6.
- Blake, A. J., Champness, N. R., Hubberstey, P., Li, W.-S., Withersby, M. A. & Schröder, M. (1999). *Coord. Chem. Rev.* **183**, 117–138.
- Bruker (1997). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1998). SMART. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2001). SAINT. Version 6.02a. Bruker AXS Inc., Madison, Wisconsin, USA.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. Oxford University Press.
- Dhurjati, M. S. K., Sarma, J. A. R. P. & Desiraju, G. R. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1702–1703.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Reddy, D. S., Goud, B. S., Panneerselvam, K. & Desiraju, G. R. (1993). *J. Chem. Soc. Chem. Commun.* pp. 663–664.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
- Siemens (1996). SADABS. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2001). PLATON. University of Utrecht, The Netherlands.
- Withersby, M. A., Blake, A. J., Champness, N. R., Hubberstey, P., Li, W.-S. & Schröder, M. (1999). *Inorg. Chem.* **38**, 2259–2266.