

Bis{4-[*N,N*-bis(2-cyanoethyl)amino]-pyridine- κN^1 }silver(I) perchlorate, with the perchlorate anion located in the cation cavity

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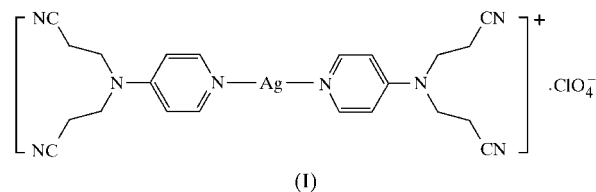
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The title complex, bis[3,3'-(pyridine-4-imino- κN^1)dipropanenitrile]silver(I) perchlorate, $[\text{Ag}(\text{CEAP})_2]\text{ClO}_4$ {CEAP is 4-[*N,N*-bis(2-cyanoethyl)amino]pyridine, $\text{C}_{11}\text{H}_{12}\text{N}_4$ }, has been prepared and characterized. The unit cell consists of two crystallographically non-equivalent molecules. Cation cavities are constructed by $[\text{Ag}(\text{CEAP})_2]^+$ cations through hydrogen bonds, and the ClO_4^- anions are incorporated into the cavities in μ_4^- and $\mu_2-\text{ClO}_4^-$ bridging modes through C—H \cdots O hydrogen bonds.

Comment

Recently, a series of compounds with zeolite-like molecule-sized channels, pores and cavities have been attracting considerable attention (Bowes & Ozin, 1996; Kitazawa *et al.*, 1992; Martin & Leafblad, 1998). These compounds can bind many molecules into their cavities, which gives them unique properties [*viz.* as catalysts, as ion-exchangers, for molecular separation sorption, *etc.* (Behrens *et al.*, 1997; Fujita *et al.*, 1994; Hoelderich *et al.*, 1988)]. The cavities are created by organic components and coordination polymers. Clearly, molecular recognition and self-organization are important factors in the sorbing of the guest (Ducharme & Wuest, 1988; Endo *et al.*, 1995; Geib *et al.*, 1991), and hydrogen-bonding interactions are very important for molecular recognition in a wide variety of crystal-packing configurations (Bishop *et al.*, 1993; Hunter, 1994; Smith, 1998; Zaworotko, 1994). Silver is an important element, with abundant catalytic properties. Absorbed oxygen on a silver surface is well known in the catalysis of epoxide formation and oxidative coupling of methane (Epling *et al.*, 1997; Minahan & Hoflund, 1996; Serafin *et al.*, 1998). Silver complexes have also been well documented as catalysts in reactions such as enantioselective

alkylation of imine ester (Ferraris *et al.*, 2002) and hetero-Diels–Alder reactions (Hague *et al.*, 2001). In this paper, we report the synthesis of the title compound, (I), which shows a two-dimensional layer structure.



The unit cell of (I) consists of two types of basic units (*a* containing Ag1 and *b* containing Ag2) that have the same chemical composition but crystallographically non-equivalent conformations (Fig. 1). Each unit contains an $[\text{Ag}(\text{CEAP})_2]^+$ cation {CEAP is 4-[*N,N*-bis(2-cyanoethyl)amino]pyridine} and a ClO_4^- anion, which form a vaulted structure. In the cation, each Ag atom is coordinated by two pyridine N atoms, with Ag—N distances in the range 2.138 (3)–2.142 (3) Å and an N—Ag—N angle of 179.10 (13)° in unit *a* and 177.12 (13)° in unit *b* (Table 1). The bond distances and angles are all within the ranges typically observed in Ag complexes (Furuta *et al.*, 1999; Ozutsumi *et al.*, 1997; Smith *et al.*, 1999). The Cl—O distances in the two units are in the range 1.396 (3)–1.460 (3) Å, which is also within the range of typical values (Riera *et al.*, 1998). The main difference between units *a* and *b* is the dihedral angle of the ligands. In unit *a*, which consists of the Ag1 complex and the Cl1 perchlorate ion, the angle between the planes of the two pyridine rings of the ligand is 45.8 (2)°. However, in unit *b*, which consists of the Ag2 complex and the Cl2 perchlorate ion, the pyridine rings are nearly coplanar and the angle between their planes is 16.7 (2)°. The complex packing consists of parallel layers. In one layer, all arc-centers of the vaulted cations have the same positions and stack above or below the plane. The two adjacent layers form a zip-like structure, and they are connected by C—H \cdots N hydrogen bonds (C4—H4 \cdots N4ⁱ, C40—H40A \cdots N4 and C35—H35 \cdots N16^v; see Table 2 for geometric details and symmetry codes). Neighboring layers slide laterally with respect to each other, and the sliding of the layers and the vaulted structure of the $[\text{Ag}(\text{CEAP})_2]^+$ cations make hydrogen-bond formation easy. Each layer contains many chains composed of alternate basic units, and the unit–unit distance (l_{u-u} in Fig. 2) in a chain is 8.893 (3) Å. All chains in the layer are parallel, with a chain–chain distance (l_{c-c} in Fig. 2) of 19.020 (2) Å. Neighboring chains also slide over each other, and they are connected by C—H \cdots N hydrogen bonds, with a C10 \cdots N11(1 - *x*, 1 - *y*, 2 - *z*) distance of 3.362 (6) Å. In a chain, the supramolecular cavities of the host are constructed by adjacent units connected by C—H \cdots N hydrogen bonds. The length (l_c in Fig. 2) and width (l_{u-u} in Fig. 2) of the cavity are 11.274 (2) and 8.893 (3) Å, respectively. All ClO_4^- anions are located as guests in the cavities and are connected with the $[\text{Ag}(\text{CEAP})_2]^+$ cations by C—H \cdots O interactions. In unit *a*,

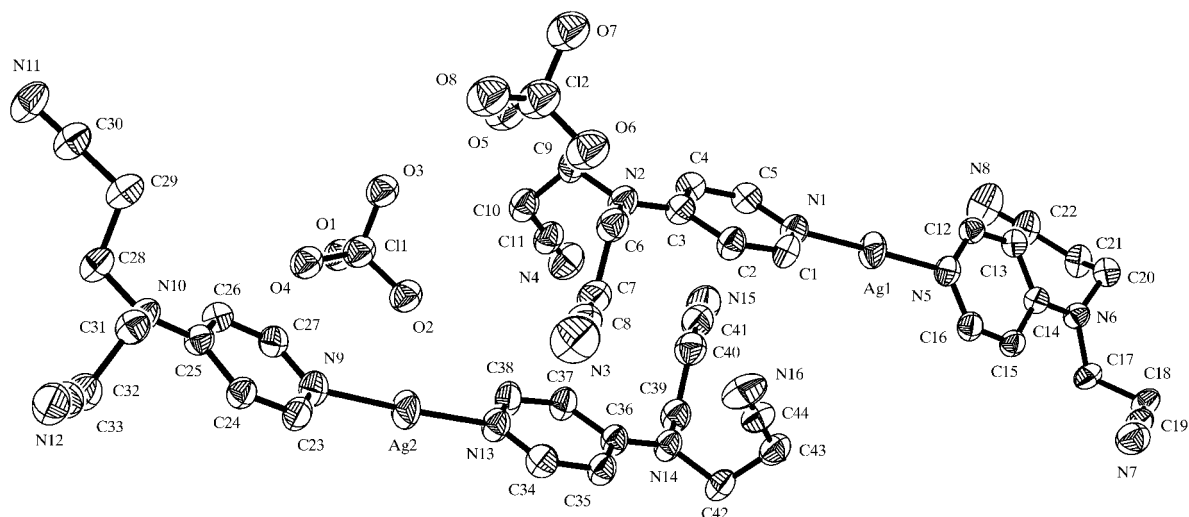


Figure 1
The molecular structure of (I), with displacement ellipsoids shown at the 50% probability level.

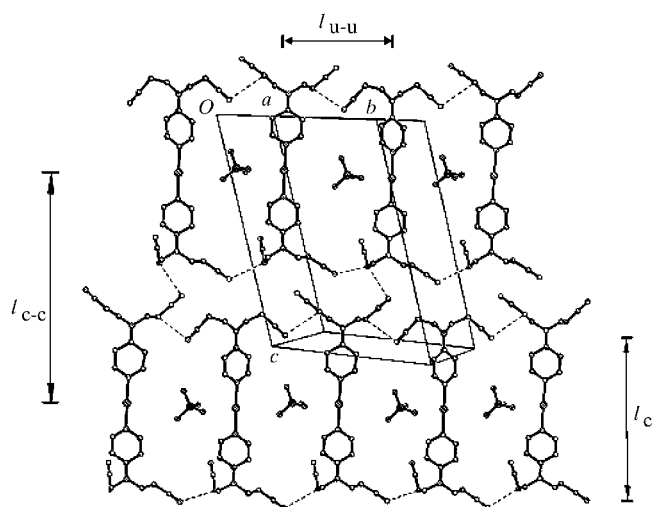


Figure 2
Supramolecular cavities in a molecular layer. H atoms have been omitted for clarity.

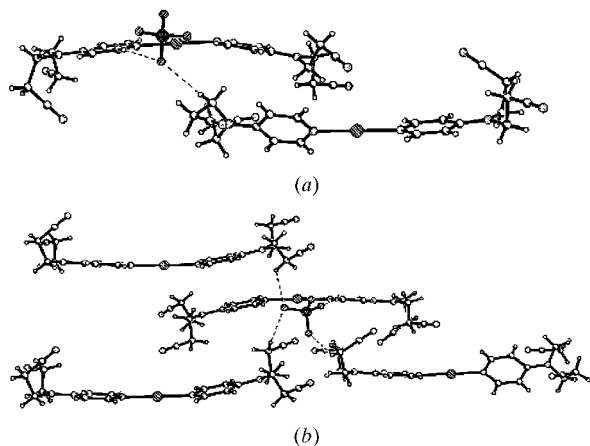


Figure 3
(a) A view of the μ_2 -ClO₄⁻ bridging mode in basic unit *b*, involving atoms Ag2 and Cl2. (b) A view of the μ_4 -ClO₄⁻ bridging mode in basic unit *a*, involving atoms Ag1 and Cl1.

the ClO₄⁻ anion bridges three [Ag(CEAP)₂]⁺ cations in two layers to form a zip-like structure through C38–H38···O2, C10–H10B···O3 and C29–H29A···O4(1 - *x*, 1 - *y*, 2 - *z*) hydrogen bonds. This anion is also connected to an adjacent zip structure through the C32–H32B···O4 hydrogen bond. Therefore, the ClO₄⁻ anion in unit *a* bridges four [Ag(CEAP)₂]⁺ cations in a μ_4 -ClO₄⁻ bridging mode. In unit *b*, the ClO₄⁻ anion bridges two [Ag(CEAP)₂]⁺ cations in a μ_2 -ClO₄⁻ bridging mode (see Fig. 3) to form a zip structure through C17–H17A···O7(1 + *x*, *y*, -1 + *z*) and C34–H34···O7(1 + *x*, *y*, *z*) hydrogen bonds. The O···H (range 2.51–2.59 Å) and C···O distances [range 3.279 (5)–3.446 (5) Å] fall into the typical ranges for C–H···O separations (Desiraju, 1991; Steiner & Desiraju, 1998).

Experimental

The synthesis of the title compound, (I), was performed in the dark. A solution of AgNO₃ (170 mg, 1 mmol) in CH₃OH (10 ml) was added to a stirred solution of 4-[*N,N*-bis(2-cyanoethyl)amino]pyridine (400 mg, 2 mmol) in CH₃OH (20 ml) at room temperature; the reaction mixture was stirred for 1 h and filtered. A solution of NaClO₄ (122.5 mg, 1 mmol) in CH₃OH (5 ml) was added to the clear filtrate and stirred for 15 min. The reaction mixture was filtered again, and colorless single crystals of (I) suitable for X-ray analysis were obtained after several days by slow evaporation of the filtrate. Analysis calculated for C₂₂H₂₄AgClN₈O₄: C 43.47, H 3.98, N 18.44%; found: C 43.35, H 4.01, N 18.40%.

Crystal data

[Ag(C₁₁H₁₂N₄)₂]ClO₄
M_r = 607.81
 Triclinic, *P*1̄
a = 9.221 (2) Å
b = 14.457 (2) Å
c = 19.897 (2) Å
 α = 76.39 (1)°
 β = 84.20 (1)°
 γ = 88.06 (1)°
V = 2564.6 (7) Å³

Z = 4
D_x = 1.574 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 2238 reflections
 θ = 2.7–22.3°
 μ = 0.94 mm⁻¹
T = 293 (2) K
 Block, colorless
 0.3 × 0.3 × 0.2 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	8825 independent reflections
φ and ω scans	6422 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Bruker, 2000)	$R_{\text{int}} = 0.018$
$T_{\text{min}} = 0.762$, $T_{\text{max}} = 0.827$	$\theta_{\text{max}} = 25.0^\circ$
13 111 measured reflections	$h = -11 \rightarrow 11$
	$k = -17 \rightarrow 11$
	$l = -24 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 1.1404P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.103$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.83 \text{ e } \text{\AA}^{-3}$
8825 reflections	$\Delta\rho_{\text{min}} = -0.98 \text{ e } \text{\AA}^{-3}$
601 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ag1—N1	2.139 (3)	Cl2—O7	1.454 (4)
Ag1—N5	2.139 (3)	Cl2—O5	1.460 (3)
Ag2—N9	2.138 (3)	Cl1—O2	1.429 (3)
Ag2—N13	2.142 (3)	Cl1—O3	1.444 (3)
Cl2—O6	1.396 (3)	Cl1—O4	1.452 (3)
Cl2—O8	1.426 (3)	Cl1—O1	1.460 (3)
N1—Ag1—N5	179.10 (13)	N9—Ag2—N13	177.12 (13)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C4—H4 \cdots N4 ⁱ	0.93	2.59	3.365 (6)	142
C10—H10A \cdots N11 ⁱⁱ	0.97	2.52	3.362 (6)	145
C10—H10B \cdots O3	0.97	2.57	3.346 (5)	137
C10—H10B \cdots N15 ⁱ	0.97	2.57	3.267 (6)	129
C17—H17A \cdots O7 ⁱⁱⁱ	0.97	2.52	3.305 (5)	138
C29—H29A \cdots O4 ⁱⁱ	0.97	2.51	3.307 (5)	140
C29—H29B \cdots N8 ⁱ	0.97	2.68	3.329 (6)	125
C32—H32B \cdots O4 ^{iv}	0.97	2.61	3.279 (5)	127
C32—H32B \cdots N7 ^v	0.97	2.83	3.474 (6)	125
C34—H34 \cdots O7 ^{vi}	0.93	2.59	3.405 (5)	147
C35—H35 \cdots N16 ^v	0.93	2.54	3.382 (6)	151
C38—H38 \cdots O2	0.93	2.53	3.446 (5)	168
C40—H40A \cdots N4	0.97	2.59	3.380 (6)	138
C43—H43A \cdots N3 ^v	0.97	2.62	3.457 (7)	145

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, 2-z$; (iii) $1+x, y, z-1$; (iv) $2-x, 1-y, 2-z$; (v) $2-x, 2-y, 1-z$; (vi) $1+x, y, z$.

The positions of all H atoms were fixed geometrically (C—H = 0.93–0.97 \AA).

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve

structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1118). Services for accessing these data are described at the back of the journal.

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