Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Silver(I) complexes of 2-(2-aminoethyl)pyridine: nitrate and perchlorate salts of bis[μ-2-(2-aminoethyl)pyridine-κ^2N:N']disilver(I)

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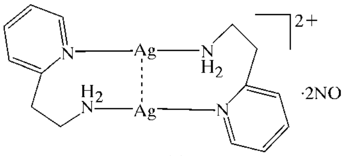
Received 9 March 2005
Accepted 20 April 2005
Online 13 May 2005

2-(2-Aminoethyl)pyridine (2-aep, $C_7H_{10}N_2$) acts as a bridging ligand in bis[μ-2-(2-aminoethyl)pyridine-κ^2N:N']disilver(I) dinitrate, $[Ag_2(2\text{-aep})_2](NO_3)_2$, and bis[$\mu$-2-(2-aminoethyl)pyridine-κ^2N:N']disilver(I) diperchlorate, $[Ag_2(2\text{-aep})_2](ClO_4)_2$. Both salts contain the dinuclear $[Ag_2(2\text{-aep})_2]^{2+}$ cation, which possesses a crystallographic inversion center. The Ag···Ag distance is 3.1163 (5) Å for the nitrate and 3.0923 (3) Å for the perchlorate salt, and may indicate a weak d^{10}–d^{10} interaction in each case. Essentially linear coordination of the Ag^I atom is perturbed by weak coordination to the anionic O atoms. These latter interactions organize the dinuclear cations into one-dimensional polymeric chains in the crystals of the two salts.

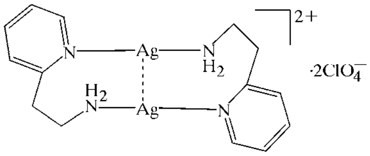
Comment

The design of coordination polymers requires knowledge of the geometrical and ligand atom preferences of the metal ion as well as the structural features of the ligand (Khlobystov *et al.*, 2001). Ag^I, well known for its preference for linear coordination, can bind with bidentate ligands to form one-dimensional polymeric chains as well as ligand-bridged dinuclear complexes. The observed stereochemistry and crystal structures are influenced by several factors, *viz.* (i) metal–metal interaction indicated by an Ag···Ag distance in the range 2.8–3.4 Å, (ii) coordination shell expansion leading to coordination number 3 or higher, which may be accomplished through the coordination of an additional ligand or anions, (iii) non-covalent interactions with anions and (iv) π–π stacking interactions, between aromatic groups.

We recently reported some Ag^I complexes with various isomers of aminomethylpyridines (amp; Sailaja & Rajasekharan, 2000, 2003), which illustrate the above factors. To study further the effect of anions on the structures through self-assembly processes, we have synthesized two complexes of Ag^I with 2-(2′-aminoethyl)pyridine (2-aep) having nitrate and perchlorate as anions, *viz.* $[Ag_2(2\text{-aep})_2](NO_3)_2$, (I), and $[Ag_2(2\text{-aep})_2](ClO_4)_2$, (II). Even though 2-aep is the next higher homologue of 2-amp, the structures of the present Ag^I complexes are entirely different.



(I)



(II)

In both (I) and (II), the cationic part consists of a 12-membered ring, with an inversion center, made up of two Ag atoms bridged by two 2-aep ligands in a head-to-tail fashion (Figs. 1 and 2, and Tables 1 and 2). The Ag atoms are coordinated to the pyridine and amine groups from two different ligands in a nearly linear mode. The conformation of the 12-membered ring is such that there is a close contact between the two Ag atoms [3.1163 (5) Å for (I) and 3.0923 (3) Å for (II)]. There are additional weak interactions with two anionic O atoms [Ag···O = 2.7091 (18) and 2.8290 (19) Å for (I), and 2.8476 (15) and 2.9529 (15) Å for (II)]. These interactions, coming from two different anions, lead to the formation of anion-bridged one-dimensional chains of the dinuclear cations (Figs. 3 and 4). The chains are linked by a hydrogen bond between one H atom of the NH$_2$ group and a free O atom of the anions [N2···O3($x + 1, y, z + 1$) = 3.124 (3) Å and 146 (2)° for (I); N2···O3($-x + 1, -y + 1, -z$) = 3.162 (2) Å and

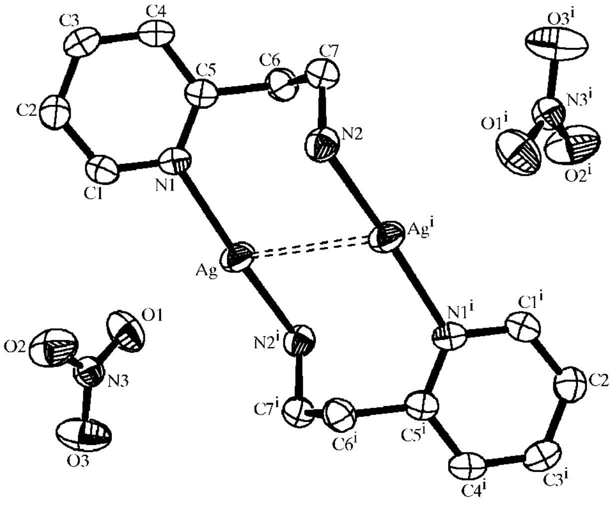


Figure 1
An *ORTEP-3* view (Farrugia, 1997) of $[Ag_2(2\text{-aep})_2](NO_3)_2$. Displacement ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, -y + 1, -z + 2$.]

DOI: 10.1107/S0108270105012448

134 (2)° for (II)], the other H atom being hydrogen bonded to another free O atom of the anion within the chain itself [N2···O3($-x$, $-y + 1$, $-z + 2$) = 3.195 (3) Å and 158 (2)° for (I); N2···O4 = 3.099 (2) Å and 164 (3)° for (II)]. With regard to the formation of the chains, (I) and (II) are exactly analogous to [Ag_2(8-aminoquinoline)$_2$](NO_3)$_2$, (III) (Schmidbaur *et al.*, 1991), which contains a ten-membered cation ring [Ag···Ag = 3.035 (1) Å, Ag···O = 2.435 (2) Å and 2.728 (1) Å, and N—Ag—N = 152.6 (1)°].

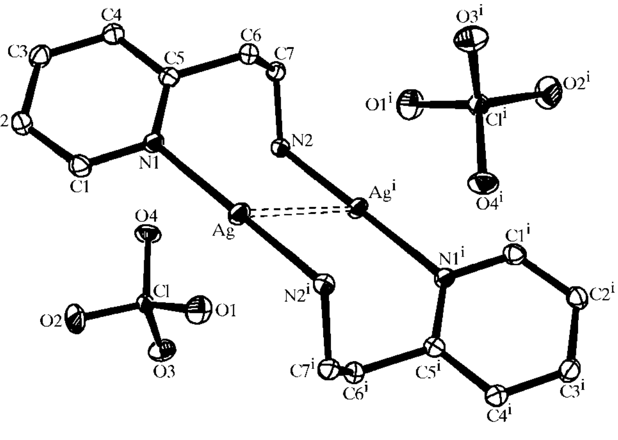


Figure 2
An *ORTEP-3* view (Farrugia, 1997) of [Ag_2(2-aep)$_2$](ClO_4)$_2$. Displacement ellipsoids are shown at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (iii) $-x + 1$, $-y + 1$, $-z + 1$.]

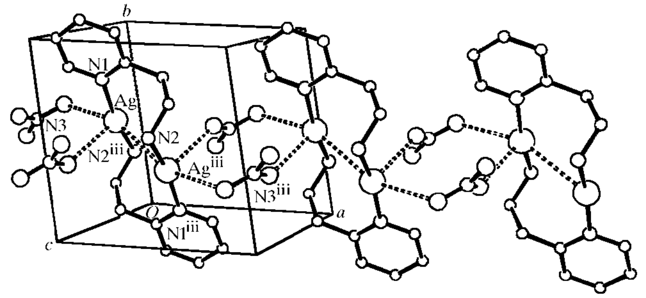


Figure 3
The polymeric chain in (I), showing weak contacts between [Ag_2(2-aep)$_2$]$^{2+}$ and NO_3^- units. Atoms are shown as circles of increasing size in the order C, N, O and Ag. H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1$, $-y + 1$, $-z + 2$.]

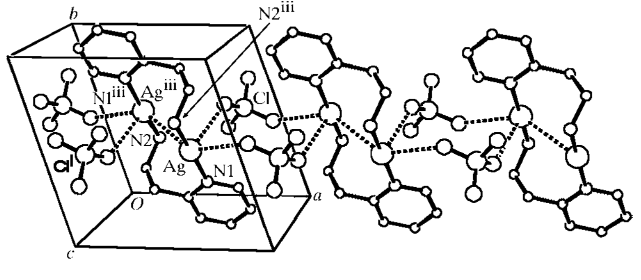


Figure 4
A polymeric chain in (II), showing weak contacts between [Ag_2(2-aep)$_2$]$^{2+}$ and ClO_4^- units. Atoms are shown as circles of increasing size in the order C, N, O, Cl and Ag. H atoms have been omitted for clarity. [Symmetry code: (iii) $-x + 1$, $-y + 1$, $-z + 1$.]

It is instructive to compare the present structure with those of Ag^I complexes of the lower homologues of 2-aep, *viz*. 2-(aminomethyl)pyridine (2-amp) and 2-aminopyridine (2-apy). Both [Ag(2-amp)]NO_3, (IV) (Swarnabala & Rajasekharan, 1997), and [Ag(2-amp)]ClO_4, (V) (Sailaja & Rajasekharan, 2000), form one-dimensional ligand-bridged chains. Weak coordination with the anion is observed in the structures but there is no Ag—Ag bonding. In the case of 2-apy, complexes with Ag^I carboxylates have been characterized (You & Zhu, 2004). Generally, the aromatic amine group does not coordinate because of its low basicity. However, the structure of [Ag_2(2-apy)$_2$](CF_3COO)$_2$, (VI), contains an eight-membered dication ring with three-coordinate Ag and a close Ag···Ag contact. An important feature of two-coordinate Ag^I complexes in the solid state is coordination to anions. The range of interactions extends from weak non-covalent to covalent character, as seen from the following data [Ag—O (Å) and N—Ag—N (°)] for the above-mentioned compounds: 2.709 (2) and 167.92 (6) for (I), 2.848 (2) and 171.48 (6) for (II), 2.435 (2) and 152.6 (1) for (III), 2.72 (3) and 164.9 (2) for (IV), 2.732 (3) and 171.0 (1) for (V), and 2.384 (3) and 134.0 (1) for (VI). The deviation of the N—Ag—N group from linearity correlates with the strength of the Ag—O interaction. In (VI), where the Ag—O bond is the strongest, the coordination geometry is close to trigonal planar.

The nature of d^{10}–d^{10} interactions in Ag^I complexes has been reviewed elsewhere (Sailaja & Rajasekharan, 2003). Even though there is no need to propose an Ag···Ag contact in dibridged structures, the interaction between two Ag^+ complex ions at distances less than two times the van der Waals radius of Ag (1.72 Å; Bondi, 1964) is, no doubt, an attractive one.

Experimental

For the preparation of [Ag_2(2-aep)$_2$](NO_3)$_2$, 2-aep (0.12 ml, 1.0 mmol) was added slowly with constant stirring to an acetonitrile solution (5 ml) of $AgNO_3$ (0.169 g, 1.00 mmol). The white precipitate which formed was filtered off and dried. It was redissolved in acetonitrile and the solution was allowed to evaporate at low temperature (288 K) to yield colorless crystals suitable for X-ray data collection (yield 0.18 g, 0.62 mmol, 62%). Analysis calculated for $C_{14}H_{20}Ag_2N_6O_6$: C 28.78, H 3.45, N 14.48%; found: C 29.37, H 3.53, N 13.99%. IR (KBr disk, cm^{-1}): 3258, 1595, 1477, 1375, 1035, 991, 825, 765, 588. For the preparation of [Ag_2(2-aep)$_2$](ClO_4)$_2$, 2-aep (0.12 ml, 1.0 mmol) was added slowly with constant stirring to an aqueous solution (10 ml) of $AgClO_4 \cdot H_2O$ (0.225 g, 1.00 mmol). The white precipitate which formed was filtered off and dried. It was redissolved in acetonitrile and the solution was allowed to evaporate at low temperature (288 K) to produce colorless crystals suitable for X-ray data collection (yield 0.20 g, 0.60 mmol, 60%). Analysis calculated for $C_{14}H_{20}Ag_2Cl_2N_4O_8$: C 25.52, H 3.06, N 8.50%; found: C 24.76, H 2.98, N 7.95%. IR (KBr disk, cm^{-1}): 3308, 1595, 1477, 1437, 1392, 1305, 1039, 765, 520.

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Compound (I)

Crystal data

$[Ag_2(C_7H_{10}N_2)_2](NO_3)_2$
$M_r = 584.10$
Triclinic, $P\overline{1}$
$a = 7.5983\ (9)$ Å
$b = 7.8834\ (10)$ Å
$c = 8.2843\ (10)$ Å
$\alpha = 96.126\ (10)^\circ$
$\beta = 108.370\ (10)^\circ$
$\gamma = 101.011\ (10)^\circ$
$V = 454.80\ (10)$ Å^3
$Z = 1$
$D_x = 2.133$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.0$–10.7°
$\mu = 2.20$ mm^{-1}
$T = 298\ (2)$ K
Needle, colorless
$0.60 \times 0.24 \times 0.24$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.545$, $T_{\max} = 0.590$
2109 measured reflections
2070 independent reflections
1945 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\max} = 27.5^\circ$
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$
3 standard reflections every 250 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.047$
$S = 1.07$
2070 reflections
136 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 0.2512P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0382 (15)

Table 1

Selected geometric parameters (Å, °) for (I).

Ag—N2$^{\rm i}$	2.1671 (18)	Ag—O1	2.8290 (19)
Ag—N1	2.1747 (17)	Ag—Ag$^{\rm i}$	3.1163 (5)
Ag—O2$^{\rm ii}$	2.7091 (18)		
N2$^{\rm i}$—Ag—N1	167.92 (6)	O2$^{\rm ii}$—Ag—O1	85.98 (6)
N2$^{\rm i}$—Ag—O2$^{\rm ii}$	101.16 (6)	N2$^{\rm i}$—Ag—Ag$^{\rm i}$	80.41 (5)
N1—Ag—O2$^{\rm ii}$	90.65 (6)	N1—Ag—Ag$^{\rm i}$	104.28 (5)
N2$^{\rm i}$—Ag—O1	83.20 (7)	O2$^{\rm ii}$—Ag—Ag$^{\rm i}$	80.51 (5)
N1—Ag—O1	95.26 (6)	O1—Ag—Ag$^{\rm i}$	156.25 (4)

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

Compound (II)

Crystal data

$[Ag_2(C_7H_{10}N_2)_2](ClO_4)_2$
$M_r = 658.98$
Triclinic, $P\overline{1}$
$a = 7.9933\ (5)$ Å
$b = 8.0990\ (5)$ Å
$c = 8.4726\ (5)$ Å
$\alpha = 98.294\ (1)^\circ$
$\beta = 97.990\ (1)^\circ$
$\gamma = 110.495\ (1)^\circ$
$V = 497.67\ (5)$ Å^3
$Z = 1$
$D_x = 2.199$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5208 reflections
$\theta = 2.5$–28.3°
$\mu = 2.29$ mm^{-1}
$T = 100\ (2)$ K
Needle, colorless
$0.30 \times 0.27 \times 0.18$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.514$, $T_{\max} = 0.662$
5743 measured reflections
2336 independent reflections
2304 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 28.3^\circ$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.048$
$S = 1.13$
2336 reflections
144 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 0.2891P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.69$ e Å^{-3}

Table 2

Selected geometric parameters (Å, °) for (II).

Ag—N1	2.1458 (15)	Ag—O1	2.9529 (15)
Ag—N2$^{\rm iii}$	2.1498 (16)	Ag—Ag$^{\rm iii}$	3.0923 (3)
Ag—O2$^{\rm iv}$	2.8476 (15)		
N1—Ag—N2$^{\rm iii}$	171.48 (6)	O2$^{\rm iv}$—Ag—O1	80.22 (5)
N1—Ag—O2$^{\rm iv}$	99.77 (5)	N1—Ag—Ag$^{\rm iii}$	101.34 (4)
N2$^{\rm iii}$—Ag—O2$^{\rm iv}$	76.42 (5)	N2$^{\rm iii}$—Ag—Ag$^{\rm iii}$	86.09 (4)
N1—Ag—O1	82.61 (5)	O2$^{\rm iv}$—Ag—Ag$^{\rm iii}$	141.05 (3)
N2$^{\rm iii}$—Ag—O1	104.00 (5)	O1—Ag—Ag$^{\rm iii}$	70.56 (3)

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

For compound (I), data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *Xtal3.5* (Hall *et al.*, 1995). For compound (II), data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000). For both compounds, structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

This work was supported by CSIR, India. TKP thanks CSIR for a fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1131). Services for accessing these data are described at the back of the journal.

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