

A New One-Dimensional Coordination Polymer of Silver(I) with Bridging 2-(2-Aminoethyl)pyridine and Nitrate Ligands: $[\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-aepy})_2]_n$

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A new silver(I) nitrate complex of 2-(2-aminoethyl)pyridine (aepy), $[\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-aepy})_2]_n$, has been synthesized and characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffractometry. Two silver(I) ions are doubly bridged by two bidentate aepy ligands forming dimeric building block $[\text{Ag}_2(\mu\text{-aepy})_2]$ units with a $\text{Ag}\cdots\text{Ag}$ distance of 3.0587(17) Å. These dimeric units are further doubly bridged by two nitrate ligands into a one-dimensional polymeric chain. The nitrate ligand exhibits an uncommon bidentate bridging mode of Ag-ONO-Ag . The title complex features a hydrogen bonded two-dimensional supramolecular framework formed *via* $\text{N-H}\cdots\text{O}$ hydrogen bonds, involving the uncoordinated O atom of the nitrate ligand and amine hydrogen atoms of aepy. The thermal stability of the title complex was investigated using thermogravimetry and differential thermal analysis.

Key words: 2-(2-Aminoethyl)-pyridine, Nitrate, Silver(I), One-Dimensional Coordination Polymer, Crystal Structure

Introduction

Coordination polymers based on silver(I) are attracting considerable attention [1–5], since the coordination sphere of silver(I) is very flexible and can adopt various coordination numbers between two and six and various geometries from linear through trigonal to tetrahedral, trigonal pyramidal, or octahedral [6, 7]. Furthermore, the flexibility of silver(I) may lead to different molecular architectures in the presence of chelating and bridging ligands.

This work is an extension our continuing research on the synthesis and characterization of mixed-ligand metal complexes of substituted pyridine ligands especially containing hydroxyl [8–12] and aminoalkyl groups [13–20]. In this paper, we describe the synthesis, spectroscopic, thermal and structural characterization of a new one-dimensional coordination polymer of silver(I) with bridging 2-(2-aminoethyl)pyridine (aepy) and nitrate ligands, namely $[\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-aepy})_2]_n$.

Results and Discussion

Synthesis and properties

The aim of the work was to prepare a glycine complex of silver(I) with the aepy ligand. However, the reaction of AgNO_3 with aepy in the presence of glycine accidentally resulted in the formation of the title complex $[\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-aepy})_2]_n$ in high yield (75%). The analytical data (C, H and N contents) are consistent with the proposed formulation of the complex, which is also confirmed by single crystal X-ray studies. The title complex is soluble only in warm water, non-hygroscopic and stable in air.

Crystal structure

A view of the building block $[\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-aepy})_2]_n$ is shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. The complex is a one-dimensional coordination polymer as illustrated in Fig. 2. The complex crystallizes in the triclinic space

Table 1. Selected bond lengths and angles, and the hydrogen bonding geometry for $[\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-aepy})_2]_n$.^a

Bond lengths [Å] and angles [°]				
Ag1–N1	2.1790(19)	N1–Ag1–O1	91.13(6)	
Ag1–N2 ⁱ	2.1748(19)	N1–Ag1–N2 ⁱ	167.80(7)	
Ag1–O1	2.6720(16)	N2 ⁱ –Ag1–O1	100.65(6)	
Ag1–O2 ⁱⁱ	2.7558(17)	N2 ⁱ –Ag1–O2 ⁱⁱ	83.72(6)	
Ag1–Ag1 ⁱ	3.0587(17)	N1–Ag1–O2 ⁱⁱ	94.71(6)	
		O1–Ag1–O2 ⁱⁱ	82.78(5)	
<i>Hydrogen bonds</i>				
D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(D–H...A)
N2–H10...O3	0.89	2.33	3.176(3)	160
N2–H9...O3 ⁱⁱⁱ	0.89	2.29	3.103(3)	152
C1–H1...O1 ⁱⁱ	0.95	2.42	3.365(3)	171
C3–H3...O3 ^{iv}	0.95	2.40	3.157(3)	137
C6–H6...O1 ⁱ	0.99	2.44	3.260(3)	140

^a Symmetry operations: ⁱ $1-x, -y, 1-z$; ⁱⁱ $-x, -y, 1-z$; ⁱⁱⁱ $1-x, -y, 2-z$; ^{iv} $1-x, 1-y, 2-z$.

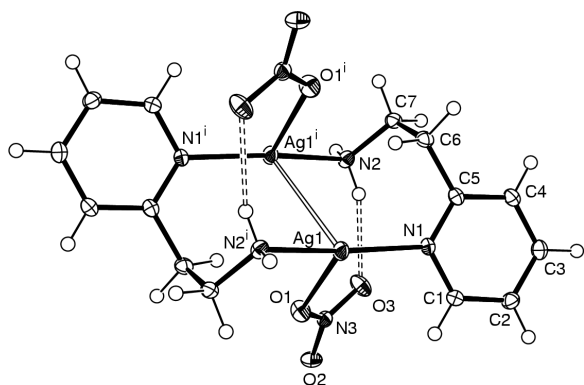


Fig. 1. A view of the building-block unit in $[\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-aepy})_2]_n$ with the atom labelling scheme and 50% thermal ellipsoids (arbitrary spheres for the H atoms). Hydrogen bonds are indicated by dashed lines. Symmetry code (i) $= 1-x, -y, 1-z$.

group $P\bar{1}$. The two silver(I) ions are doubly bridged by two bidentate aepy ligands, forming the dimeric building block units, which are further bridged by two nitrate ligands, thus resulting in an infinite linear chain propagating along the a axis.

The coordination geometry around the silver(I) ion is four-coordinate with a AgN_2O_2 pattern. The intra-dimer $\text{Ag}\cdots\text{Ag}^i$ [$i = 1-x, -y, 1-z$] separation is 3.0587(17) Å and much smaller than the van der Waals' radius sum for silver(I) (3.40 Å), showing a significant interactions between the silver(I) ions. It compares well to those in other dimeric silver(I) complexes with nitrogen coordinated ligands: $[\text{Ag}_2(\text{NO}_3)_2(\text{tp})_2]$ [3.117(1) Å] (tp = triazolopyrimidine) [21], $[\text{Ag}_2(\text{dppy})_3](\text{ClO}_4)_2$ [3.072(1) Å] [22] (dppy = 2-(diphenylphosphino)pyridine and $[\text{Ag}_2\text{-}$

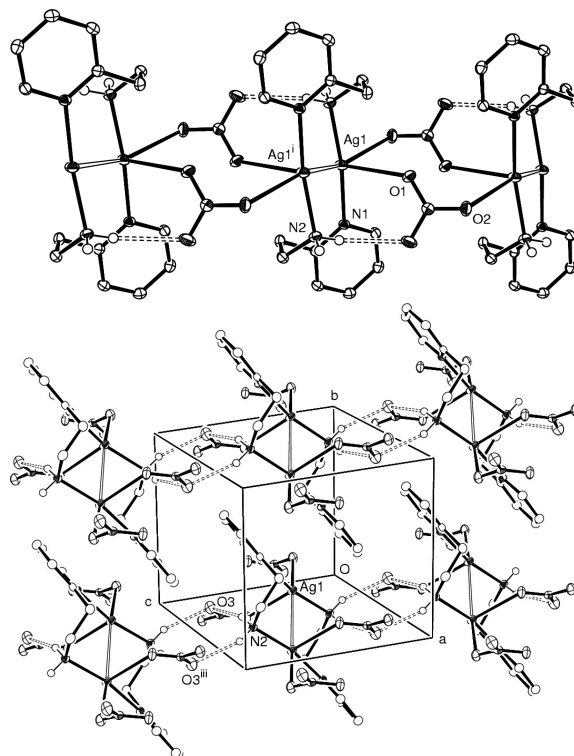


Fig. 2. Top: A fragment of the one-dimensional chain in $[\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-aepy})_2]_n$. Hydrogen bonds are indicated by dashed lines. All C–H hydrogen atoms are omitted for clarity. Symmetry code (i) $= 1-x, -y, 1-z$. Bottom: Packing of chains of $[\text{Ag}_2(\mu\text{-NO}_3)_2(\mu\text{-aepy})_2]_n$ forming a hydrogen-bonded two-dimensional framework. Symmetry code (iii) $1-x, -y, 2-z$.

$(\text{tren}(\text{mim})_3)]_n(\text{NO}_3)_{2n}\cdot n\text{H}_2\text{O}$ [2.9337(10) and 3.0533(11) Å] ($\text{tren}(\text{mim})_3$ = tris{2-[2-(l-methyl)-imidazolyl]-methyliminoethyl}amine) [23]. Although the closed shell d^{10} configuration of silver(I) appears to cancel any intermetallic bonding in silver(I) complexes, there are many examples of dimeric or polymeric silver(I) complexes with definite $\text{Ag}\cdots\text{Ag}$ attractive forces known as argentophilic interactions [24].

The Ag–N distances are identical and much shorter than the Ag–O distances, indicating the much stronger interaction of aepy compared to the nitrate anion. The three N–O bond distances in the nitrate anion are almost identical of *ca.* 1.253(3) Å. One of the O atoms remains uncoordinated. In most of the reported silver(I)-nitrate complexes, the nitrate ligand usually acts as a monodentate or bidentate chelating ligand. Although the bridging mode involving only one O atom of the nitrate ion

(Ag–O–Ag) was reported in [Ag(im-mpy)(μ -NO₃)] where im-mpy is 2-(3-pyridyl)-4,4,5,5-tetramethyl-2-imidazolin-1-ol [25], the bidentate bridging (Ag–ONO–Ag) found in [Ag₂(μ -NO₃)₂(μ -aepy)₂]_n is rather uncommon. It was reported that the nitrate ligands in [Ag₂(μ -NO₃)₂(μ -C₅H₅NS)]_n (C₅H₅NS = pyridinium-4-thiolate) interestingly exhibit both bridging modes [16] and the Ag–O distances in the Ag–O–Ag group are noticeably shorter than those of the bidentate bridging group.

The py ligand is essentially planar. There are no $\pi \cdots \pi$ stacking interactions (minimum ring-centroid separation = 4.23 Å). The packing of the chains is presented in Fig. 2. The amine hydrogen atoms of the aepy ligand form intra- and intermolecular hydrogen bonds with the uncoordinated O atoms of the adjacent nitrate ligands. Some of the ring hydrogen atoms of aepy are also involved in relatively weak C–H \cdots O interactions with the O atoms of the nitrate ligands. The individual polymeric chains are thus connected by the N–H \cdots O hydrogen bonds into a hydrogen bonded two-dimensional supramolecular framework.

Infrared spectra

The absorption band of the amine hydrogens of the aepy ligand is observed as strong and broad band centered at *ca.* 3326 cm^{−1}, and is significantly shifted to the lower frequency region, compared to the free ligand (3365 cm^{−1}) in agreement with its participation in coordination. The broadness of the band is due to the strong hydrogen bonding of the NH₂ groups.

The absorption bands with various intensity between 1595 and 1436 cm^{−1} correspond to the ν (CC) and ν (CN) vibrations of the aromatic ring of the aepy ligand. A very strong band at 1383 cm^{−1} together with a medium band at 825 cm^{−1} characterizes the nitrate ligand.

Thermal behaviour

The thermal stability of the title complex was investigated using thermogravimetry (TG) and differential thermal analysis (DTA) in a static atmosphere of air. The complex melts at 192 °C with decomposition. The first decomposition stage between 190 and 220 °C corresponds to exothermic removal of the two aepy molecules in a single stage with a sharp DTA peak at 214 °C. The experimental mass loss of 41.6% agrees well with the calculated mass loss of 41.8%. The decomposition of the nitrate anions occurs in the temperature range 278–430 °C, with a violently exothermic

Table 2. Crystallographic data for [Ag₂(μ -NO₃)₂(μ -aepy)₂]_n.

	[Ag ₂ (μ -NO ₃) ₂ (μ -aepy) ₂] _n
Empirical formula	C ₁₄ H ₂₀ N ₆ O ₆ Ag ₂
<i>M_r</i>	584.10
<i>T</i> [K]	120(2)
Radiation, λ [Å]	0.71073
Crystal system	triclinic
Space group	<i>P</i> 1
Unit cell dimensions	
<i>a</i> [Å]	7.5870(3)
<i>b</i> [Å]	7.8092(2)
<i>c</i> [Å]	8.2104(2)
α [°]	95.839(2)
β [°]	109.563(2)
γ [°]	99.5246(18)
<i>V</i> [Å ³]	445.54(2)
<i>Z</i>	1
<i>D_c</i> [g/cm ³]	2.177
μ [mm ^{−1}]	2.246
<i>F</i> (000)	288
Crystal size [mm ³]	0.22 × 0.18 × 0.06
θ Range [°]	3.52/27.54
Index range (<i>h, k, l</i>)	−9/9, −10/9, −9/9
Reflections collected	9246
Independent reflections (<i>R_{int}</i>)	2033 (0.0281)
Reflections observed (> 2 σ)	1878
Absorption correction	multi-scan
Min. and max. transmission	0.638 and 0.877
Data / parameters	2033 / 130
Goodness-of-fit on <i>F</i> ²	1.097
Final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0216
<i>wR</i> ²	0.0478
Largest diff. peak and hole [e·Å ^{−3}]	1.086 and −0.519

DTA peak at 340 °C. The observed mass loss of 21.5% in the second stage is consistent with the calculated mass loss of 21.2%. The total mass loss of all decomposition process of 63.1% (calcd. 63.0%) and microanalysis suggest that the remaining residue consists of silver metal.

Experimental Section

Materials and measurements

All reagents were purchased from commercial sources and used as supplied. IR spectra were recorded on a Shimadzu FTIR-8900 spectrophotometer as KBr pellets in the frequency range 4000–300 cm^{−1}. The elemental analyses (C, H and N) were performed on a Vario EL Elemental Analyser. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere. A sample size of 5–10 mg was used.

Synthesis of the silver(I) complex

The aepy ligand (0.12 g, 1.0 mmol) was added dropwise to a solution of AgNO₃ (0.17 g, 1.0 mmol) in a mixture of

water and isopropanol (30 cm³, 1:1) containing 1.0 mmol of glycine. The reaction mixture was stirred for 30 min at room temperature. X-ray quality colorless crystals were obtained by slow evaporation of the resulting solution at room temperature. Yield 75%. M.p. 192 °C. C₁₄H₂₀N₆O₆Ag₂ (584.10): calcd. C 28.79, H 3.45, N 14.38; found C 28.75, H 3.49, N 14.32.

X-ray crystallography

Intensity data for the title compound were collected using an Enraf Kappa CCD area detector diffractometer (Mo-K α radiation, λ = 0.71073 Å) at 120 K. The structure was solved with SHELXS-97 and refined using SHELXL-97 [27]. All non-hydrogen atoms were refined with anisotropic displacement

parameters. H atoms were included using a riding model in idealised positions. The details of data collection, refinement and crystallographic data are summarized in Table 2.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC-262658. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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