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Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(C-C)$ = 0.011 Å
R factor = 0.040
wR factor = 0.096
Data-to-parameter ratio = 11.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

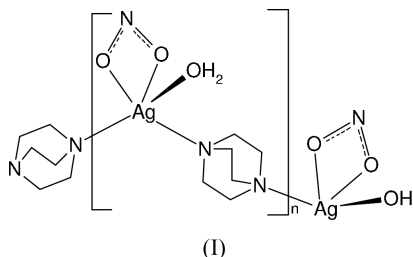
catena-Poly[[aquanitritosilver(I)]- μ -1,4-diazabicyclo[2,2,2]octane- $\kappa^2N:N'$]

The title compound, $[Ag(NO_2)(C_6H_{12}N_2)(H_2O)]_n$, is a polymeric 1,4-diazabicyclo[2,2,2]octane- Ag^I complex. Each Ag atom is five-coordinated by two N atoms from two different 1,4-diazabicyclo[2,2,2]octane ligands, two O atoms of one nitrite anion and another O atom of a coordinated water molecule, forming a severely distorted square-pyramidal coordination environment. In the crystal structure, molecules are connected by intermolecular O—H...O hydrogen bonds, forming a three-dimensional network.

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Comment

Crystal engineering and the design of solid-state architectures of coordination polymers have become very attractive fields in recent years (Smith *et al.*, 1996; Kristiansson, 2001; Wei *et al.*, 1998; Zheng *et al.*, 2001). Assembly of such extended supramolecular architectures by selecting the chemical structure of organic ligands and the coordination geometry of metal ions may yield a large number of new networks exhibiting interesting topologies and potential properties as new materials (Zhu *et al.*, 2003; Zheng *et al.*, 2003; Khlobystov *et al.*, 2001). The primary reason for the interest in such complexes is their ability to afford functional solid materials with potentially controllable properties, as well as fascinating molecular structures. The recent development of supramolecular chemistry has made it possible to select building units for assembly into structures with specific network topologies (Nomiya *et al.*, 2000). Crystal engineering of coordination polymeric networks based on multidentate ligands represents a growing area of coordination and supramolecular chemistry. We have focused our attention on the assembly of metal ions with bridging ligands, since they can adopt diverse coordination modes according to the different geometric needs of the metal ions. As reported previously, the bridging bidentate ligand 1,2-diaminoethane gives two- or three-dimensional frameworks, depending on the metal ions and counter-anions (You, Yang *et al.*, 2004; You & Zhu, 2004). We have now extended this work to include a 1,4-diazabicyclo[2,2,2]octane ligand in place of 1,2-diaminoethane.



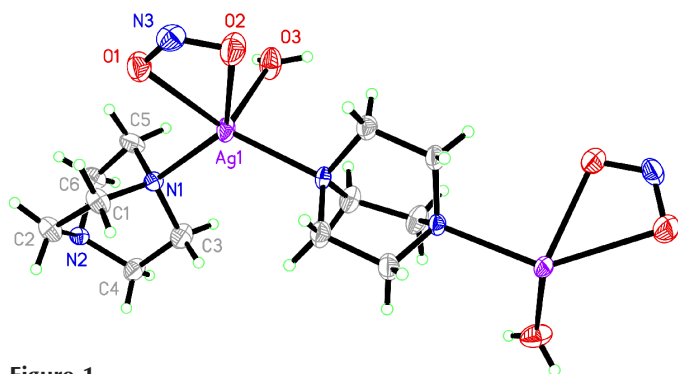


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are related by the symmetry code $(-y, x, z - \frac{1}{4})$.

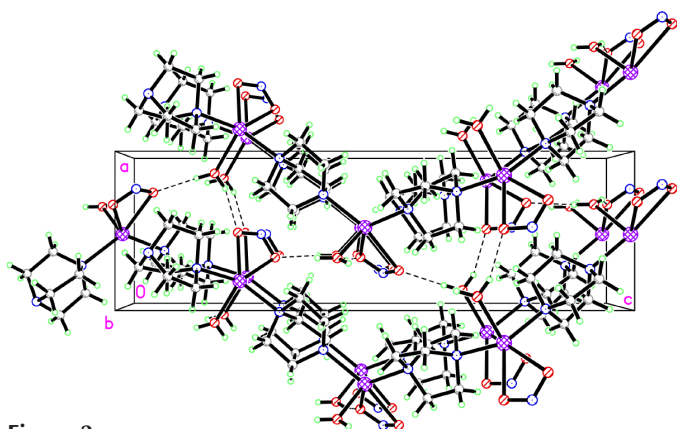


Figure 2

The crystal packing of (I), viewed along the *b* axis. Broken lines show intermolecular hydrogen bonds.

The title compound, (I), is a polymeric 1,4-diazabicyclo[2,2,2]octane- Ag^{I} complex (Fig. 1). The smallest repeat unit for the complex contains a 1,4-diazabicyclo[2,2,2]octane ligand, an Ag^{I} cation, a nitrite anion and a coordinated water molecule. The Ag atom is in a severely distorted square-pyramidal coordination environment, whose basal plane is composed of two N atoms from two different 1,4-diazabicyclo[2,2,2]octane ligands and two O atoms of a nitrite anion. The O atom of the coordinated water molecule occupies the apical position. The substantial distortion of the square pyramid is revealed by the bond angles between apical and basal donor atoms, showing an average deviation of 11.2° from the ideal 90° angle in a regular square pyramid. On the other hand, the bond angles between the donor atoms in basal positions deviate severely from the ideal 90° (Table 1). Thus, the coordination configuration of the Ag atom is a severely distorted square pyramid. The bond angle $\text{N}2^{\text{i}}-\text{Ag}1-\text{N}1$ of $121.09(17)^\circ$ [symmetry code: (i) $y - 1, 1 - x, \frac{1}{4} + z$] is much larger than that of the $\text{O}1-\text{Ag}1-\text{O}2$ angle, $47.95(19)^\circ$, which is due to the strain created by the four-membered chelate ring, *viz.* $\text{Ag}1/\text{O}1/\text{N}3/\text{O}2$. Atom Ag1 is displaced from the least-squares plane defined by the basal donor atoms in the direction of the apical atom O3 by $0.413(5) \text{ \AA}$.

The question of whether the coordination polyhedron around the $\text{Ag}1$ atom should be described as a distorted

square pyramid or a distorted trigonal bipyramid can be answered by determining the structural index τ (Addison *et al.*, 1984). The value of τ for Ag1 is 0.103, indicating that the coordination configuration of the Ag atom in the complex is better described as distorted square pyramidal.

In the crystal structure, the Ag-N bonds link the 1,4-diazabicyclo[2,2,2]octane molecules and the Ag atoms into a helical chain along the *c* axis. Adjacent chains are linked by intermolecular O-H...O hydrogen bonds, forming a three-dimensional network (Table 2 and Fig. 2).

Experimental

1,4-Diazabicyclo[2,2,2]octane (0.1 mmol, 11.2 mg) and AgNO_2 (0.1 mmol, 15.4 mg) were dissolved in a 30% aqueous ammonia solution (10 ml). The mixture was stirred at room temperature for 20 min to give a colourless clear solution. The solution was kept in air and, after slow evaporation of the solvent over a period of a week, large colourless block-shaped crystals were formed at the bottom of the vessel. The crystals were isolated, washed three times with water and dried in a vacuum desiccator using anhydrous CaCl_2 (yield 71.1%). Analysis found: C 25.2, H 5.0, N 14.9%; calculated for $\text{C}_6\text{H}_{14}\text{AgN}_3\text{O}_3$: C 25.4, H 5.0, N 14.8%.

Crystal data

$[\text{Ag}(\text{NO}_2)(\text{C}_6\text{H}_{12}\text{N}_2)(\text{H}_2\text{O})]$
 $M_r = 284.07$
 Tetragonal, $P4_3$
 $a = 6.706(3) \text{ \AA}$
 $c = 21.834(16) \text{ \AA}$
 $V = 981.9(10) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.922 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 4594 reflections
 $\theta = 3.6\text{--}26.5^\circ$
 $\mu = 2.03 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Block, colourless
 $0.48 \times 0.43 \times 0.37 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.402, T_{\text{max}} = 0.473$
 5148 measured reflections

1478 independent reflections
 1448 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -7 \rightarrow 7$
 $k = -7 \rightarrow 7$
 $l = -25 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.096$
 $S = 1.29$
 1478 reflections
 124 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.58 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 590 Friedel pairs
 Flack parameter = 0.07(7)

Table 1

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

$\text{Ag}1-\text{N}2^{\text{i}}$	2.345 (5)	$\text{Ag}1-\text{O}3$	2.586 (5)
$\text{Ag}1-\text{N}1$	2.353 (5)	$\text{Ag}1-\text{O}2$	2.598 (6)
$\text{Ag}1-\text{O}1$	2.511 (5)		
$\text{N}2^{\text{i}}-\text{Ag}1-\text{N}1$	121.09 (17)	$\text{O}1-\text{Ag}1-\text{O}3$	110.2 (2)
$\text{N}2^{\text{i}}-\text{Ag}1-\text{O}1$	134.2 (2)	$\text{N}2^{\text{i}}-\text{Ag}1-\text{O}2$	91.09 (19)
$\text{N}1-\text{Ag}1-\text{O}1$	92.92 (17)	$\text{N}1-\text{Ag}1-\text{O}2$	140.39 (17)
$\text{N}2^{\text{i}}-\text{Ag}1-\text{O}3$	95.37 (18)	$\text{O}1-\text{Ag}1-\text{O}2$	47.95 (19)
$\text{N}1-\text{Ag}1-\text{O}3$	98.0 (2)	$\text{O}3-\text{Ag}1-\text{O}2$	101.4 (2)

Symmetry code: (i) $y - 1, 1 - x, \frac{1}{4} + z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3–H1 \cdots O2 ⁱⁱ	0.84 (3)	2.06 (4)	2.899 (9)	176 (9)
O3–H2 \cdots O1 ⁱⁱⁱ	0.83 (7)	2.08 (5)	2.854 (7)	154 (10)

Symmetry codes: (ii) $-y, x, z - \frac{1}{4}$; (iii) $x - 1, y, z$.

Water H atoms were located in a difference Fourier map and refined isotropically, with the O–H and H \cdots H distances restrained to 0.84 (1) and 1.37 (2) Å, respectively. All remaining H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C–H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. An unassigned maximum residual density was observed 1.0 Å from atom H3A. The minimum residual density was observed 0.2 Å from atom Ag1.

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

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