Bis(nitrilotriacetamide-$\kappa^4N,O,O′,O″$)silver(I) nitrate

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In the centrosymmetric cation of the title compound, [Ag(C$_6$H$_{12}$N$_4$O$_3$)$_2$]NO$_3$, the Ag^I ion, lying on a threefold rotoinversion axis, is coordinated by two N atoms and six O atoms from two nitrilotriacetamide ligands, forming a distorted dodecahedral environment. In the crystal, cations and anions are linked through N—H···O hydrogen-bonding interactions, leading to a three-dimensional network structure.

3D view

Chemical scheme
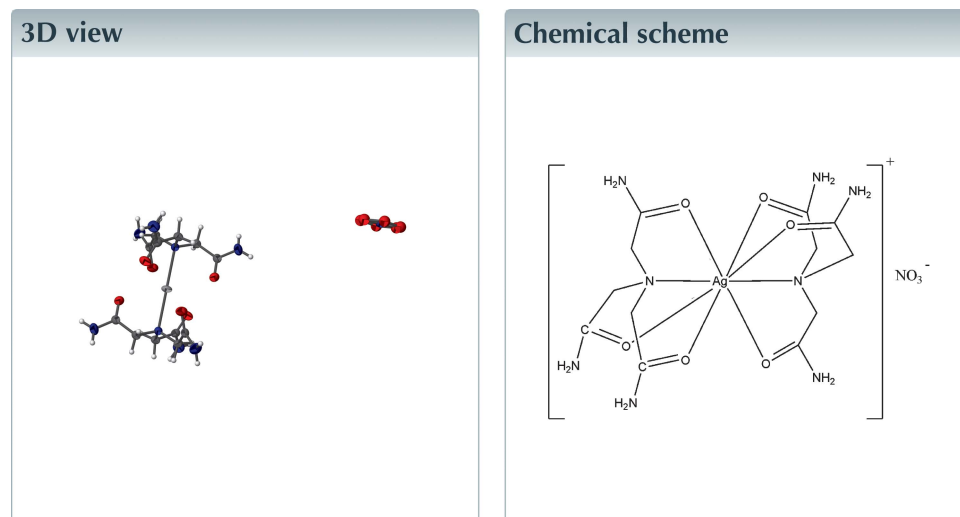
Structure description

Nitrilotriacetamide (NTA) as a ligand is able to coordinate through various coordination sites. Synthetic aspects of the coordination chemistry of transition metals with nitrilotriacetamide ligands were given in detail some time ago (Smith *et al.*, 1992, 1995). A silver complex of the derivative nitrilotris(*N*-benzylacetamide) as a ligand was reported by Kang *et al.* (2007) where the Ag^I ion is coordinated by the tetradentate ligand and by a bidentate nitrate anion. The resulting coordination environment is distorted octahedral. As an extension of the structural characterization of silver compounds with mixed ligands derived from NTA and nitrate, we report here on the synthesis and crystal structure of a new mononuclear silver(I) compound, [Ag(C$_6$H$_{12}$N$_4$O$_3$)$_2$]$^+$·NO$_3^-$.

The Ag^I atom of the cation (Fig. 1) is located on a site with point group symmetry $\bar{3}$. (Wyckoff position 1*a*) and is linearly coordinated by the central N atoms of two symmetry-related NTA ligands at distances of 2.417 (2) Å. In comparison with a true twofold coordination by N atoms (Ag—N ≃ 2.15 Å), the Ag—N bonds are elongated. The overall coordination sphere is supplemented by six symmetry-related O atoms from the two NTA ligands [Ag—O = 2.7774 (14) Å], leading to a distorted dodecahedral coordination environment. The nitrate anion is disordered around a $\bar{3}$ axis and is not involved in coordination to the silver cation.
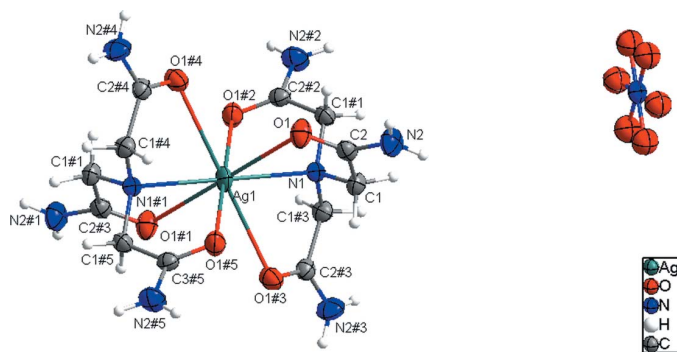
Figure 1
The molecular entities in the complex title salt. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (1) $-x, -y, -z$; (2) $-y, x - y, z$; (3) $y, -x + y, -z$; (4) $x - y, x, -z$; (5) $-x + y, -x, z$.]

In the crystal structure, N—H⋯O hydrogen-bonding interactions (including a trifurcated hydrogen bond) between the amino functions as donor groups and the weakly bound amide O atoms and nitrate O atoms as acceptor groups consolidate the molecular packing within the three-dimensional network structure (Fig. 2, Table 1).

Synthesis and crystallization

The NTA ligand was prepared according to a literature method (Smith *et al.*, 1995). The title compound was synthesized by adding an aqueous solution of $AgNO_3$ (340 mg, 2 mmol) to a solution of the ligand (752 mg, 4 mmol) in water (20 ml). The mixture was stirred for 30 min at room temperature. The solution was then filtered and the filtrate was allowed to stand in air for one week. Colourless crystals were formed at the bottom of the vessel on slow evaporation of the solvent at room temperature (yield: 41.5%). Selected IR data (cm^{-1}): 3416 (*vs*), 1677 (*vs*), 1358 (*m*), 605 (*m*), 1617 (*w*), 1264 (*w*).
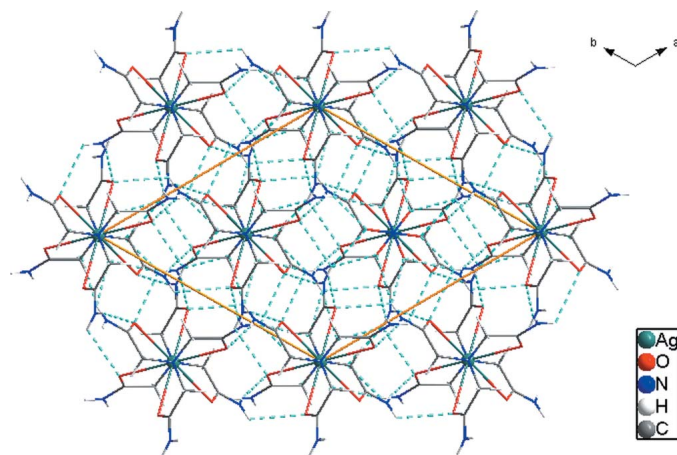

Figure 2
The packing diagram for the title compound, viewed along the *c* axis, with hydrogen bonds drawn as dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2B⋯O1^i	0.86	2.15	2.969 (2)	159
N2—H2A⋯O2^{ii}	0.86	2.42	3.256 (4)	163
N2—H2A⋯O2^{iii}	0.86	2.22	2.880 (4)	133
N2—H2A⋯O1^{iv}	0.86	2.59	3.058 (2)	115

Symmetry codes: (i) $-x + y + \frac{2}{3}, -x + \frac{1}{3}, z + \frac{1}{3}$; (ii) $y + \frac{1}{3}, -x + y + \frac{2}{3}, -z + \frac{2}{3}$; (iii) $x - \frac{2}{3}, y - \frac{1}{3}, z - \frac{1}{3}$; (iv) $y + \frac{2}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ag(C_6H_{12}N_4O_3)_2]NO_3$
M_r	546.27
Crystal system, space group	Trigonal, $R\bar{3}$
Temperature (K)	291
a, c (Å)	11.6518 (16), 12.590 (3)
V (Å^3)	1480.3 (5)
Z	3
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.09
Crystal size (mm)	0.30 × 0.26 × 0.24
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2005)
T_{min}, T_{max}	0.736, 0.780
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4800, 761, 748
R_{int}	0.017
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.023, 0.059, 1.12
No. of reflections	761
No. of parameters	48
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.46, −0.31

Computer programs: *APEX2* and *SAINT* (Bruker, 2005), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The N atom of the nitrate group is located on a position with point group symmetry $\bar{3}$. (Wyckoff position 1*b*). Hence the unique O atom of the nitrate group is equally disordered around the $\bar{3}$ axis and was treated with half-occupancy.

References

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full crystallographic data

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Crystal data

[Ag(C$_6$H$_{12}$N$_4$O$_3$)$_2$]NO$_3$	D_x = 1.838 Mg m^{-3}
M_r = 546.27	D_m = 1.838 Mg m^{-3}
Trigonal, $R\bar{3}$	D_m measured by not measured
a = 11.6518 (16) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
c = 12.590 (3) Å	Cell parameters from 761 reflections
V = 1480.3 (5) Å^3	θ = 1.0–27.5°
Z = 3	μ = 1.09 mm^{-1}
$F(000)$ = 834	T = 291 K
	Cuboid, colorless
	0.30 × 0.26 × 0.24 mm

Data collection

Bruker APEXII CCD diffractometer	761 independent reflections
Radiation source: fine-focus sealed tube	748 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.017
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	θ_{max} = 27.5°, θ_{min} = 3.5°
	$h = -15 \rightarrow 15$
T_{min} = 0.736, T_{max} = 0.780	$k = -15 \rightarrow 14$
4800 measured reflections	$l = -16 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)]$ = 0.023	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ = 0.059	
S = 1.12	H-atom parameters constrained
761 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 1.4406P]$ where $P = (F_o^2 + 2F_c^2)/3$
48 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max}$ = 0.46 e Å^{-3}
	$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Ag1	0.0000	0.0000	0.0000	0.03254 (13)	
O1	0.17358 (13)	−0.06869 (14)	0.09278 (10)	0.0376 (3)	
N1	0.0000	0.0000	0.19194 (18)	0.0229 (4)	
N2	0.29870 (16)	−0.01709 (18)	0.24078 (15)	0.0418 (4)	
H2A	0.3432	−0.0526	0.2178	0.050*	
H2B	0.3155	0.0195	0.3024	0.050*	
C1	0.13626 (15)	0.05180 (16)	0.23128 (13)	0.0279 (3)	
H1A	0.1341	0.0411	0.3078	0.033*	
H1B	0.1879	0.1458	0.2158	0.033*	
C2	0.20369 (15)	−0.01821 (15)	0.18150 (13)	0.0269 (3)	
N3	1.0000	0.0000	0.5000	0.0288 (7)	
O2	0.9536 (3)	0.0759 (3)	0.5023 (2)	0.0452 (6)*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.04075 (16)	0.04075 (16)	0.01610 (17)	0.02038 (8)	0.000	0.000
O1	0.0383 (6)	0.0522 (8)	0.0289 (6)	0.0275 (6)	−0.0018 (5)	−0.0065 (5)
N1	0.0229 (6)	0.0229 (6)	0.0230 (10)	0.0114 (3)	0.000	0.000
N2	0.0368 (8)	0.0525 (9)	0.0434 (9)	0.0278 (7)	−0.0116 (7)	−0.0045 (7)
C1	0.0266 (7)	0.0311 (7)	0.0252 (7)	0.0140 (6)	−0.0047 (6)	−0.0037 (6)
C2	0.0226 (7)	0.0271 (7)	0.0280 (7)	0.0102 (6)	0.0012 (6)	0.0042 (6)
N3	0.0328 (10)	0.0328 (10)	0.0209 (15)	0.0164 (5)	0.000	0.000

Geometric parameters (Å, º)

Ag1—N1[i]	2.417 (2)	N2—H2A	0.8593
Ag1—N1	2.417 (2)	N2—H2B	0.8591
Ag1—O1[ii]	2.7774 (14)	C1—C2	1.522 (2)
Ag1—O1[i]	2.7774 (14)	C1—H1A	0.9700
Ag1—O1[iii]	2.7774 (14)	C1—H1B	0.9700
Ag1—O1[iv]	2.7774 (14)	N3—O2[vi]	1.247 (3)
Ag1—O1	2.7774 (14)	N3—O2[vii]	1.247 (3)
Ag1—O1[v]	2.7774 (14)	N3—O2[viii]	1.247 (3)
O1—C2	1.229 (2)	N3—O2[ix]	1.247 (3)
N1—C1[v]	1.4737 (17)	N3—O2[x]	1.247 (3)
N1—C1	1.4737 (17)	N3—O2	1.247 (3)
N1—C1[ii]	1.4738 (17)	O2—O2[viii]	1.248 (3)
N2—C2	1.330 (2)	O2—O2[vi]	1.248 (3)

N1—Ag1—N1^{i}	180.0	O2^{vi}—N3—O2^{vii}	180.0
C1^{v}—N1—C1	109.31 (11)	O2^{vi}—N3—O2^{viii}	119.947 (12)
C1^{v}—N1—C1^{ii}	109.30 (11)	O2^{vii}—N3—O2^{viii}	60.053 (12)
C1—N1—C1^{ii}	109.31 (11)	O2^{vi}—N3—O2^{ix}	60.053 (12)
C1^{v}—N1—Ag1	109.64 (10)	O2^{vii}—N3—O2^{ix}	119.947 (12)
C1—N1—Ag1	109.64 (10)	O2^{viii}—N3—O2^{ix}	180.0 (3)
C1^{ii}—N1—Ag1	109.64 (10)	O2^{vi}—N3—O2^{x}	119.947 (13)
C2—N2—H2A	120.4	O2^{vii}—N3—O2^{x}	60.053 (12)
C2—N2—H2B	119.6	O2^{viii}—N3—O2^{x}	119.947 (12)
H2A—N2—H2B	120.0	O2^{ix}—N3—O2^{x}	60.053 (12)
N1—C1—C2	112.41 (13)	O2^{vi}—N3—O2	60.054 (12)
N1—C1—H1A	109.1	O2^{vii}—N3—O2	119.946 (12)
C2—C1—H1A	109.1	O2^{viii}—N3—O2	60.052 (12)
N1—C1—H1B	109.1	O2^{ix}—N3—O2	119.948 (13)
C2—C1—H1B	109.1	O2^{x}—N3—O2	180.0 (2)
H1A—C1—H1B	107.9	N3—O2—O2^{viii}	59.974 (6)
O1—C2—N2	123.50 (16)	N3—O2—O2^{vi}	59.973 (6)
O1—C2—C1	122.03 (14)	O2^{viii}—O2—O2^{vi}	119.79 (5)
N2—C2—C1	114.46 (15)		
C1^{v}—N1—C1—C2	68.5 (2)	O2^{vii}—N3—O2—O2^{viii}	−4.6 (5)
C1^{ii}—N1—C1—C2	−171.88 (13)	O2^{ix}—N3—O2—O2^{viii}	180.0
Ag1—N1—C1—C2	−51.68 (13)	O2^{vii}—N3—O2—O2^{vi}	180.0
N1—C1—C2—O1	27.5 (2)	O2^{viii}—N3—O2—O2^{vi}	−175.4 (5)
N1—C1—C2—N2	−153.92 (16)	O2^{ix}—N3—O2—O2^{vi}	4.6 (5)
O2^{vi}—N3—O2—O2^{viii}	175.4 (5)		

Symmetry codes: (i) −x, −y, −z; (ii) −y, x−y, z; (iii) y, −x+y, −z; (iv) x−y, x, −z; (v) −x+y, −x, z; (vi) y+1, −x+y+1, −z+1; (vii) −y+1, x−y−1, z; (viii) x−y, x−1, −z+1; (ix) −x+y+2, −x+1, z; (x) −x+2, −y, −z+1.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2*B*⋯O1^{xi}	0.86	2.15	2.969 (2)	159
N2—H2*A*⋯O2^{xii}	0.86	2.42	3.256 (4)	163
N2—H2*A*⋯O2^{xiii}	0.86	2.22	2.880 (4)	133
N2—H2*A*⋯O1^{xiv}	0.86	2.59	3.058 (2)	115

Symmetry codes: (xi) −x+y+2/3, −x+1/3, z+1/3; (xii) y+1/3, −x+y+2/3, −z+2/3; (xiii) x−2/3, y−1/3, z−1/3; (xiv) y+2/3, −x+y+1/3, −z+1/3.