

Bis(cyanoguanidine)silver(I) nitrate–  
cyanoguanidine (1/1)

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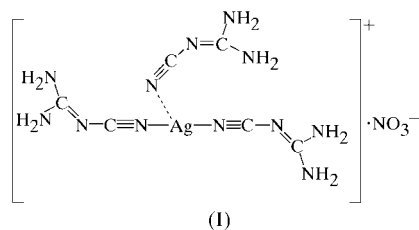
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In the title compound,  $[\text{Ag}(\text{C}_2\text{H}_4\text{N}_4)_2](\text{NO}_3)\cdot\text{C}_2\text{H}_4\text{N}_4$ , the Ag atom is surrounded by three cyanoguanidine (cngc) molecules. Two monodentate cngc molecules form strong covalent Ag–N bonds of 2.210 (7) and 2.266 (6) Å through their nitrile N atoms. The third cngc molecule is located in a vacant crystal site and is only weakly coordinated to the Ag atom as a solvate molecule. Inter- and intramolecular hydrogen bonds play an important role in the crystal packing.

## Comment

Cyanoguanidine, which is the dimeric form of cyanamide ( $\text{H}_2\text{NCN}$ ), is a commercially important compound and a versatile precursor for the syntheses of organonitrogen compounds. The coordination chemistry of cngc has been intensively studied because of its differing functional groups. It readily coordinates to the later transition metals, and coordination typically occurs through the nitrile N atom. Complexes with copper(II) (Chiesi *et al.*, 1971; Batsanov *et al.*, 1997; Begley *et al.*, 1993), copper(I) (Batsanov *et al.*, 1996), zinc(II) (Pickardt & Kühn, 1996; Harrison *et al.*, 2001), cadmium(II) and mercury(II) (Pickardt & Kühn, 1996*a,b*), and nickel(II) (Meyer *et al.*, 2000) have been reported, but no crystal structure of a silver–cngc complex has been known until now. We report here the structure of such a complex, *viz.* the title compound, (I).



A labelled displacement ellipsoid plot of the coordination motifs of (I) is shown in Fig. 1, and bond distances and angles are given in Table 1. The Ag atom is surrounded by three cngc molecules, two of which behave as monodentate ligands through nitrile N atoms. The Ag–N21 and Ag–N11 distances

are 2.210 (7) and 2.266 (6) Å, respectively, and the N11–Ag1–N21 angle is almost linear [175.5 (2)°], which is a common geometry in two-coordinate  $\text{Ag}^{\text{I}}$  complexes. The interactions of the Ag atom with two N31 atoms, *viz.* one of 2.596 (7) Å within the asymmetric unit and the other of 2.681 (7) Å (symmetry code:  $x, -1 + y, z$ ), are longer than the sum of the covalent distances and much weaker than the interactions with atoms N21 and N11. Thus, the third cngc molecule is almost uncoordinated and is essentially located in a vacant crystal site. Typical Ag–N distances are 2.11–2.16 Å for two-coordinate silver in  $\text{AgN}(\text{CN})_2$  (Britton, 1990) and silver–pyrazolate complexes (Mohamed & Fackler, 2002), 2.22 Å for three-coordinate silver in  $\text{AgC}(\text{CN})_3$  (Konnert & Britton, 1966), and 2.23 Å for four-coordinate silver in  $\text{AgC}(\text{CN})_2\text{NO}$  (Chow & Britton, 1974) and silver–1,10-decanedinitrile complexes (Carlucci *et al.*, 1999). The elongated two-coordinate Ag–N distances are probably caused by the effects of four further  $\text{Ag}\cdots\text{N}$  interactions [two with N31, as mentioned above, and two with N11, *viz.* 2.795 (7) and 2.860 (7) Å; symmetry codes:  $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$  and  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ , respectively]. The Ag atom is coplanar with the three surrounding N atoms but not with the three cngc molecules. The Ag–N11–C12 [140.2 (5)°] and Ag–N21–C22 [167.6 (6)°] angles are smaller than those expected for a transition-metal–nitrile interaction (180°) because of the hydrogen bonding (N16–H $\cdots$ N31 and N35–H $\cdots$ N21; Fig. 2 and Table 2). Such a distortion of the coordination geometry has also been observed in  $[\text{Cu}(\text{OAc})_2(\text{cngc})_2]_2$  (Begley *et al.*, 1993).

The hydrogen bonds are listed in Table 2. The cngc molecule is a hydrogen-bonding ligand that may act both as a donor (amino,  $\text{NH}_2$ ) and as an acceptor (cyanimino,  $=\text{N}-\text{C}\equiv\text{N}$ ). The N–H donor systems from both amino groups have close contacts to the nitrate anion [the hydrogen bond labelled ( $\sigma$ ) in Fig. 2], and there is also hydrogen bonding between the imino and amino N atoms of neighbouring molecules [labelled ( $\eta$ ) in Fig. 2]. In addition, there is intramolecular hydrogen bonding between amino and nitrile N atoms [labelled ( $\chi$ ) in Fig. 2]. The three above-mentioned hydrogen-bonding modes have been reviewed for cngc coordination compounds by Batsanov *et al.* (1997). Overall, the hydrogen

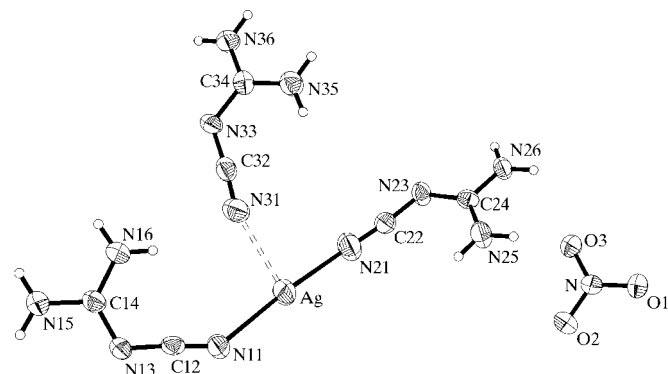
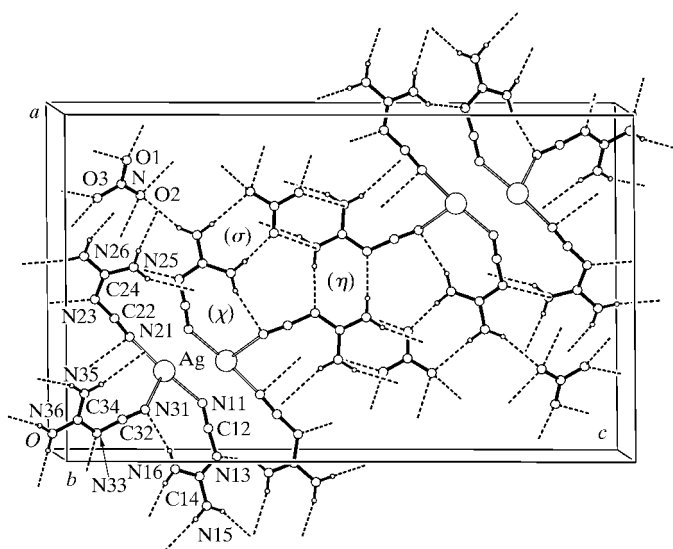


Figure 1

View of the asymmetric unit of the title compound, with displacement ellipsoids scaled at the 50% probability level for non-H atoms.



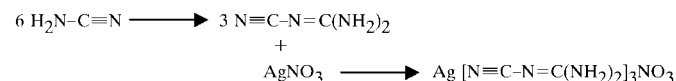
**Figure 2**  
Crystal packing for the title compound, showing the inter- and intramolecular hydrogen bonding and hydrogen-bonding types.

bonding promotes the two-dimensional sheet structure and stabilizes the crystal architecture.

All three cng molecules are planar within crystallographic resolution, and the maximum distances from the least-squares plane are 0.025 (N11–N16 ligand), 0.008 (N21–N26 ligand) and 0.013 Å (N31–N36 ligand). The individual coordination does not severely affect the structural parameters of cng (Fernanda *et al.*, 1993). The shortest Ag...Ag distance along *b* is 3.648 (1) Å, parallel to the  $2_1$  axis. The structure as a whole consists of layers stacked along the *b* direction, which is also the direction of fast crystal growth.

## Experimental

The title compound was prepared by mixing AgNO<sub>3</sub> (34.0 mg, 0.2 mmol) and H<sub>2</sub>NCN (cyanamide; Aldrich; 50.4 mg, 1.2 mmol) in diethyl ether (10 ml). This reaction yielded a colourless solution. Slow addition of hexane caused the complex to crystallize as long colourless needles (see *Scheme* below). These were separated by filtration, washed with diethyl ether and hexane, and dried in a desiccator over P<sub>2</sub>O<sub>5</sub>. An IR spectrum indicated a nitrile unit (major absorption at 2150 cm<sup>-1</sup>) and a series of N–H groups in the range 3200–3450 cm<sup>-1</sup>; the elemental analysis agrees with the title composition.



### Crystal data

[Ag(C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>)<sub>2</sub>](NO<sub>3</sub>)·C<sub>2</sub>H<sub>4</sub>N<sub>4</sub>  
*M<sub>r</sub>* = 422.16  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*  
*a* = 15.526 (4) Å  
*b* = 3.6482 (9) Å  
*c* = 25.797 (6) Å  
 $\beta$  = 92.519 (6)°  
*V* = 1459.8 (6) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.921 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 9648 reflections  
 $\theta$  = 2.6–28.3°  
 $\mu$  = 1.42 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Needle, colourless  
 0.15 × 0.05 × 0.02 mm

### Data collection

Bruker APEX CCD diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996)  
*T*<sub>min</sub> = 0.746, *T*<sub>max</sub> = 0.989  
 9648 measured reflections  
 3609 independent reflections

1818 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.095  
 $\theta_{\text{max}}$  = 28.3°  
*h* = −20 → 20  
*k* = −4 → 4  
*l* = −34 → 22

### Refinement

Refinement on *F*<sup>2</sup>  
*R*(*F*) = 0.065  
*wR*(*F*<sup>2</sup>) = 0.206  
*S* = 0.87  
 3609 reflections  
 245 parameters

Only coordinates of H atoms refined  
*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>)]  
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.78 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ag–N21	2.210 (7)	C22–N23	1.301 (9)
Ag–N11	2.266 (6)	N23–C24	1.336 (8)
Ag–N31	2.596 (7)	C24–N26	1.314 (8)
N11–C12	1.155 (9)	C24–N25	1.318 (8)
C12–N13	1.302 (9)	N31–C32	1.144 (9)
N13–C14	1.328 (8)	C32–N33	1.323 (9)
C14–N16	1.322 (9)	N33–C34	1.350 (8)
C14–N15	1.344 (9)	C34–N36	1.307 (9)
N21–C22	1.159 (9)	C34–N35	1.345 (9)
N21–Ag–N11	175.5 (2)	C22–N23–C24	119.7 (6)
N21–Ag–N31	93.8 (2)	N26–C24–N25	118.3 (6)
N11–Ag–N31	90.1 (2)	N26–C24–N23	117.5 (6)
C12–N11–Ag	140.2 (5)	N25–C24–N23	124.1 (6)
N11–C12–N13	175.4 (7)	C32–N31–Ag	137.0 (6)
C12–N13–C14	117.1 (6)	N31–C32–N33	175.7 (8)
N16–C14–N13	124.8 (7)	C32–N33–C34	120.2 (6)
N16–C14–N15	117.1 (7)	N36–C34–N35	119.3 (7)
N13–C14–N15	118.1 (6)	N36–C34–N33	118.1 (6)
C22–N21–Ag	167.6 (6)	N35–C34–N33	122.6 (6)
N21–C22–N23	173.5 (7)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N15–H11...O2 <sup>i</sup>	0.80 (6)	2.29 (6)	3.079 (9)	169 (7)
N15–H12...O2 <sup>ii</sup>	0.79 (5)	2.31 (6)	3.075 (8)	165 (6)
N16–H13...N31	0.80 (4)	2.37 (5)	3.113 (9)	156 (7)
N16–H14...O1 <sup>i</sup>	0.78 (7)	2.18 (7)	2.954 (8)	169 (7)
N25–H21...O2 <sup>iii</sup>	0.79 (4)	2.29 (4)	3.067 (8)	170 (7)
N25–H21...O3 <sup>iii</sup>	0.79 (4)	2.29 (6)	3.363 (8)	154 (6)
N25–H22...N13 <sup>iii</sup>	0.78 (6)	2.40 (6)	3.073 (8)	145 (6)
N26–H23...O3 <sup>iii</sup>	0.79 (4)	2.29 (6)	3.014 (8)	154 (6)
N26–H24...N23 <sup>v</sup>	0.79 (4)	2.34 (5)	3.048 (8)	151 (7)
N35–H31...O3 <sup>v</sup>	0.79 (5)	2.28 (5)	3.071 (8)	176 (3)
N35–H32...N21 <sup>iii</sup>	0.79 (2)	2.68 (4)	3.427 (10)	160 (7)
N36–H33...O1 <sup>v</sup>	0.79 (6)	2.18 (6)	2.962 (8)	172 (7)
N36–H34...N33 <sup>vi</sup>	0.79 (5)	2.29 (6)	3.075 (9)	176 (9)

Symmetry codes: (i) *x* − 1, 1 + *y*, *z*; (ii)  $\frac{1}{2}$  − *x*,  $\frac{1}{2}$  + *y*,  $\frac{1}{2}$  − *z*; (iii) *x*, 1 + *y*, *z*; (iv) 1 − *x*, 1 − *y*, −*z*; (v) 1 − *x*, 2 − *y*, −*z*; (vi) −*x*, 2 − *y*, −*z*.

All H atoms were found from Δ*F* maps and were refined freely, with all N–H bond distances restrained to be equal within an effective standard uncertainty of 0.02 Å (SADI instruction in *SHELXL97*; Sheldrick, 1997). H atoms were assigned a common isotropic displacement parameter.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXL97* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1551). Services for accessing these data are described at the back of the journal.

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