Silver Cyanoguanidine Nitrate Hydrate: Ag(C$_2$N$_4$H$_4$)NO$_3$·½ H$_2$O, a Cyanoguanidine Compound Coordinating by an Inner Nitrogen Atom

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Abstract: Silver(I) cyanoguanidine nitrate hydrate, Ag(C$_2$N$_4$H$_4$)NO$_3$·½H$_2$O, was synthesized as the first cyanoguanidine solid-state complex in which monovalent Ag is coordinated through inner nitrogen N atoms. Its structure was characterized by single-crystal X-ray diffraction, crystallizing in the acentric orthorhombic space group $P2_12_12$ with a = 10.670(3) Å, b = 18.236(5) Å, and c = 3.5078(9) Å. The differing chemical bondings of Ag(C$_2$N$_4$H$_4$)NO$_3$·½H$_2$O and Ag(C$_2$N$_4$H$_4$)$_3$NO$_3$ were compared on the basis of first-principle calculations.

Keywords: cyanoguanidine; silver; crystal structure; chemical bonding

1. Introduction

Cyanoguanidine, also called dicyandiamide, is not only the dimer of molecular cyanamide (or carbodiimide) but also a commercially important compound that has found medicinal and industrial applications [1–4] and has long been known to crystallographers. The molecule has also been widely used as a precursor for synthesizing organonitrogen compounds [5]. It exists in two tautomeric forms, differing in the protonation and bonding of its nitrogen atoms (Figure 1). The structural conformations of both forms are planar with one tautomer displaying two terminal amine groups (Figure 1a) and the other expressing only one terminal amine group but two imine groups in the middle of the molecule (Figure 1b). The coordination chemistry of cyanoguanidine has earned significant attention owing to these differing functional groups [6–11], which readily coordinate late transition metals, forming complexes with monovalent [6] and divalent copper [7], silver [8,11], and divalent zinc [9,10], all of which have been structurally characterized. As alluded to in Figure 1, the inner N atoms as well as the terminal N atoms are able, at least in principle, to coordinate to metal atoms due to the existence of lone pairs at those N atoms. However, to the best of our knowledge, all reported metal cyanoguanidine compounds involve a coordination only with the terminal cyano N atoms of the cyanoguanidine molecules.
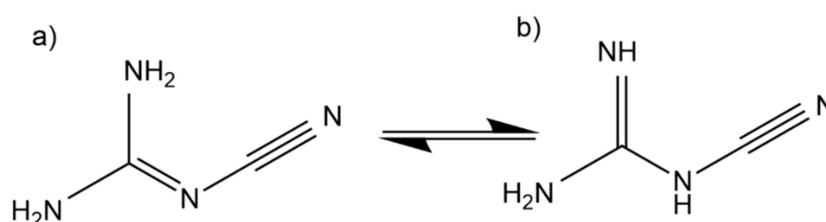
Figure 1. The two tautomeric forms of cyanoguanidine $H_4C_2N_4$ with (**a**) one tautomer displaying two terminal amine groups and (**b**) only one terminal amine group.

In an attempt to grow high-quality $Ag(C_2N_4H_4)_3NO_3$ single crystals by slow diffusion, we unexpectedly made the discovery of the title compound $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$. Here, we report the synthesis and crystal structure of this silver(I) cyanoguanidine nitrate hydrate, the first example of a metal cyanoguanidine compound coordinating with inner nitrogen atoms.

2. Results and Discussion

2.1. Structure Description

The crystal structure was analyzed by single-crystal XRD. $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ crystallizes in the orthorhombic space group $P2_12_12$ (No. 18) with $a = 10.670(3)$ Å, $b = 18.236(5)$ Å, and $c = 3.5078(9)$ Å, as well as four formula units per cell (Figure 2a). The Ag atom is coordinated by two terminal N3 atoms, one inner N2 atom, and two O atoms of the nitrate group, O1 and O2, in a distorted square-pyramidal environment (Figure 2b). One of the Ag–N3 bonds is 2.283(8) Å (symmetry code: $1-x$, $1-y$, $1+z$), which is lengthwise consistent with those given in the literature [8], while the other Ag–N3 bond of 2.543(8) Å (symmetry code: $1-x$, $1-y$, z) is somewhat longer and also weaker than the preceding one. The Ag–N2, Ag–O1, and Ag–O2 distances are 2.277(7) Å, 2.444(7) Å, and 2.733(8) Å, respectively, and within the expected distance range of Ag–N and Ag–O single bonds [8,12,13]. The elongated Ag–N3 bond probably results from further coordinative interactions of the type Ag···N and Ag···O (Ag–N2, Ag–N3, and Ag–O1) [8]. As we have discussed in the previous section, the cyanoguanidine molecule exists in two tautomeric forms (Figure 1), and here the C2–N4 and C2–N5 bond lengths come very close to 1.32 Å, a result strongly suggestive of the first form with two terminal amine groups (Figure 1a), the N4–C2–N5 angle also being almost 120°. Additional selected bond lengths and angles are given in Table 1.
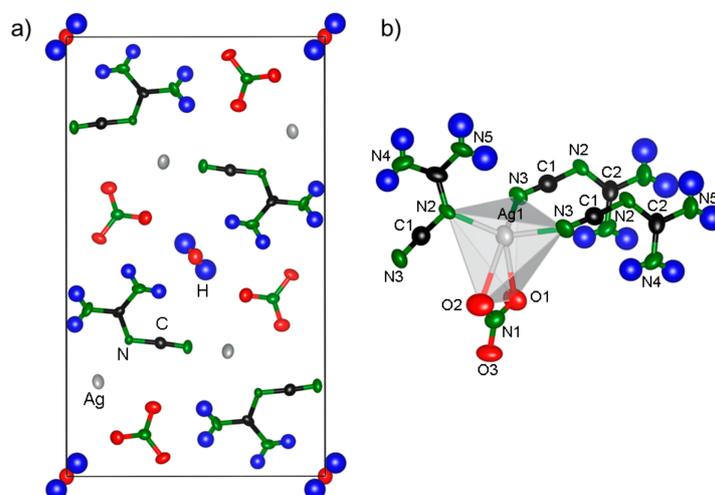

Figure 2. (**a**) Crystal structure of $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ and (**b**) coordination environment of Ag.

Table 1. Selected bond lengths and angles in $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$.

Bond Length (Å)	Bond Angle (°)
Ag1–N2 2.277(7)	O2–N1–O3 120.9(8)
Ag1–N3 ($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$) 2.283(8)	O2–N1–O1 119.1(7)
Ag1–O1 2.444(7)	O3–N1–O1 119.9(8)
Ag1–N3 ($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$) 2.543(8)	C1–N2–C2 116.2(7)
O1–N1 1.257(10)	C2–N4–H4A 120(4)
O2–N1 1.244(9)	C2–N4–H4B 114(4)
O3–N1 1.242(9)	H4A–N4–H4B 120(4)
N2–C1 1.316(10)	C2–N5–H5A 127(5)
N2–C2 1.357(12)	C2–N5–H5B 117(5)
N3–C1 1.152(10)	H5A–N5–H5B 115(4)
N4–C2 1.324(12)	N3–C1–N2 176.5(11)
N4–H4A 1.004(13)	N5–C2–N4 120.4(9)
N4–H4B 1.002(13)	N5–C2–N2 116.6(9)
N5–C2 1.324(10)	N4–C2–N2 122.9(7)
N5–H5A 1.008(13)	H1–O1W–H1 105(2)
N5–H5B 1.009(13)	
O1W–H1 (x, y, z) 0.976(13)	
O1W–H1($1-x$, $1-y$, $1-z$) 0.976(13)	

The cyanoguanidine unit may act both as an acceptor (cyanimine, $=N–C\equiv N$) and as a donor (amine, $–NH_2$), resulting in four different hydrogen bonding modes. The first is a contact between the amine group and nitrate (N4–H4B⋯O1, N4–H4B⋯O3, N4–H4B⋯N1), the second an interaction between the amine group and neighboring nitrate (N5–H5A⋯O3, N5–H5B⋯O2), and the third an interaction between a nitrate O atom and a water O atom (O1W–H1⋯O1). Finally, there is hydrogen bonding between the amine group and a water O atom (N4–H4A⋯O1W). The entire complex is linked by hydrogen bonds forming a three-dimensional structure (Figure 3). The hydrogen bonds are listed in Table 2.

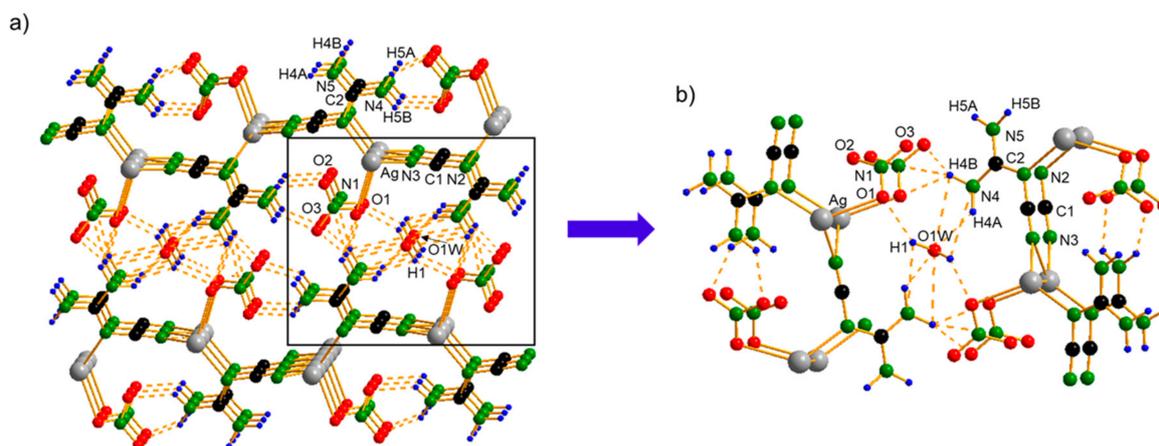**Figure 3.** (**a**) The three-dimensional hydrogen-bond network in $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ along *c* and (**b**) a selection of hydrogen bonds along *a*.

2.2. Chemical Bonding Analysis

As the discovery of $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ was a consequence of preparing yet another silver cyanoguanidine nitrate, $Ag(C_2N_4H_4)_3NO_3$ [8], questions of chemical equilibrium as regards the energetic competition between the two phases pop up, so their structural and bonding character was analyzed in more detail. As shown in Figure 2b, the Ag atom in $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ is surrounded by two amine and one imine N atoms of the $H_4C_2N_4$ molecule and also two O atoms

of the nitrate anion, while the Ag atom in $Ag(C_2N_4H_4)_3NO_3$ is surrounded by five amine N atoms. Additionally, a comparison of the bond lengths (Figure 4) indicates that the Ag–N bonds are shorter in $Ag(C_2N_4H_4)_3NO_3$ than the Ag–N and Ag–O bonds in $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$.

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

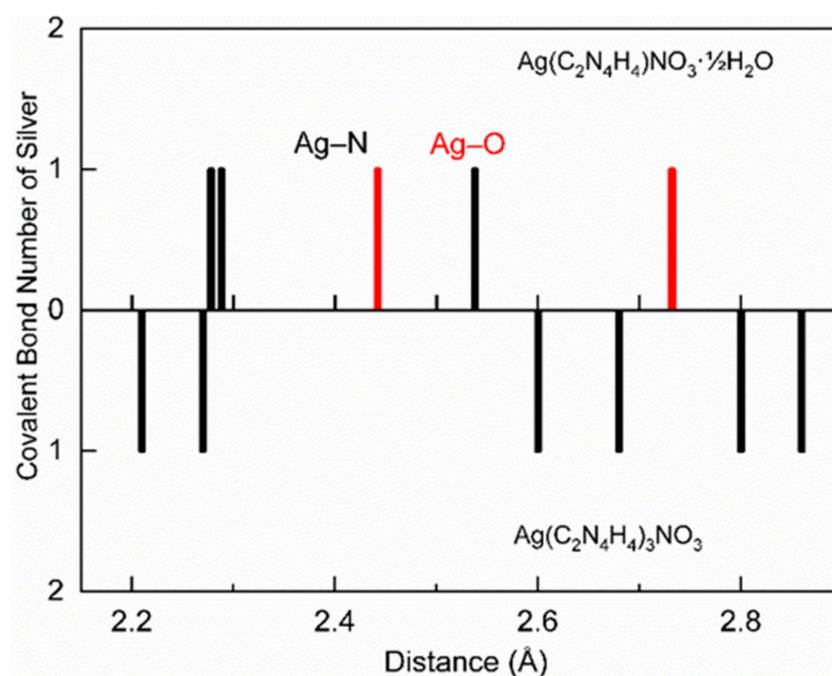| D−H	d(D−H)	d(H·A)	<DHA	d(D·A)	A	Symmetry Code
N4−H4A	1.004(13)	2.13(6)	136(6)	2.939(11)	O1W	
N4−H4B	1.002(13)	2.29(5)	135(6)	3.075(10)	O1	$-x+\frac{1}{2}, y+\frac{1}{2}, -z+1$
N4−H4B	1.002(13)	2.13(5)	148(8)	3.028(10)	O3	$-x+\frac{1}{2}, y+\frac{1}{2}, -z+1$
N4−H4B	1.002(13)	2.54(4)	156(8)	3.477(11)	N1	$-x+\frac{1}{2}, y+\frac{1}{2}, -z+1$
N5−H5A	1.008(13)	2.20(5)	149(7)	3.107(10)	O3	$x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$
N5−H5B	1.009(13)	2.32(6)	137(5)	3.132(11)	O2	$x-\frac{1}{2}, -y+\frac{1}{2}, -z$
O1W−H1	0.976(13)	2.15(6)	146(9)	3.007(10)	O1	$-x+\frac{1}{2}, y+\frac{1}{2}, -z$

Figure 4. Bond-length histogram of $Ag(H_4C_2N_4)NO_3 \cdot \frac{1}{2}H_2O$ (top) and $Ag(H_4C_2N_4)_3NO_3$ (bottom).

In order to quantitatively probe the relative stability of these phases, crystal orbital Hamilton population (COHP) analyses were performed to study the bonding mechanisms, as shown in Figure 5. Note that the integrated COHP (ICOHP) up to the Fermi level measures covalency, with more negative ICOHP values corresponding to stronger bonding interactions. Figure 5 reveals that the enhanced stability of $Ag(C_2N_4H_4)_3NO_3$, compared with $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$, appears to arise from the increased strength of the two short Ag–N bonds in $Ag(C_2N_4H_4)_3NO_3$ (ICOHP = −1.58 eV for Ag–N1 and −1.31 eV for Ag–N5), which are significantly stronger than the two short Ag–N bonds in $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ (−1.08 eV for Ag–N2 and −1.14 eV for Ag–N3). Furthermore, we note that the inner Ag–N2 mode in $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ is weaker than the terminal Ag–N3 interaction despite being slightly shorter. It seems, therefore, that the inner N coordination mode is less strongly bonding than equivalent terminal N bonds, thus explaining the preferential formation of $Ag(C_2N_4H_4)_3NO_3$ over $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ and the absence of other metal cyanoguanidines that coordinate with inner N atoms.
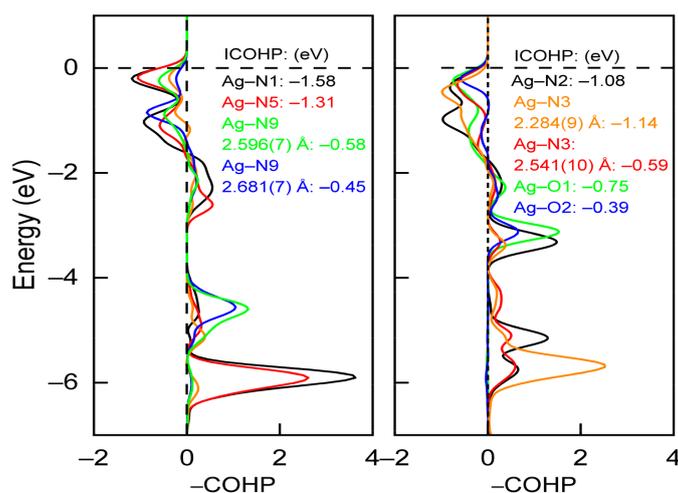
Figure 5. COHP analysis of various bonds in $Ag(C_2N_4H_4)_3NO_3$ (left) and $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ (right).

3. Materials and Methods

3.1. Synthesis

$Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ was prepared by mixing aqueous solutions of $AgNO_3$ (339.7 mg, 2 mmol in 20 mL; Alfa, Kandel, Rheinland-Pfalz, Germany) and $H_4C_2N_4$ (504.0 mg, 2 mmol in 20 mL; Alfa, Kandel, Rheinland-Pfalz, Germany). This reaction yielded a large amount of white precipitate that was isolated by filtration and washed with water before being dried under vacuum. The product was then recrystallized by dissolving 0.5 g in 20 mL water and stirring for 1 h. Colorless, transparent needle-like crystals were obtained after water evaporation. It should be noted that attempts to grow high-quality single crystals by evaporation were hindered by the preferential formation of yet another silver cyanoguanidine compound, $Ag(C_2N_4H_4)_3NO_3$ [8], whose crystal structure was clarified many years ago. In order to help understand this preferential formation, electronic structure calculations were performed as detailed below.

3.2. Single-Crystal Diffraction

A selected crystal was mounted on a glass fiber. Intensity data were collected with a Bruker SMART APEX CCD detector (Bruker AXS GmbH, Karlsruhe, Germany) equipped with an Incoatec microsource (Mo-Kα radiation, $\lambda = 0.71073$ Å, multilayer optics). The software package SHELXL-2014 (Version 2014/7, George M. Sheldrick, Göttingen, Germany) [14,15] was used to solve and refine the crystal structure. Full details concerning the structure determination are available in CIF format and have been deposited under the CCDC entry number 1973094. Further crystallographic details can be found in the Supplementary Materials. Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/Community/csd-communications/ or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

3.3. Chemical Bonding Analysis

The chemical bonding analysis was performed using the LOBSTER package (Version 3.2.0, Richard Dronskowski, Aachen, Germany) [16–19], starting from a static self-consistency calculation using the entire *k*-mesh with the symmetry switched off. For bonding analysis, the "pbevaspfit2015" basis set including 1s orbitals for hydrogen, 2s and 2p orbitals for nitrogen, carbon, and oxygen, and the 5s, 4p, and 4d orbitals for silver was employed.

4. Conclusions

The first silver(I) cyanoguanidine nitrate in which silver is coordinated by inner imine nitrogen atoms was prepared by mixing aqueous solutions of $AgNO_3$ and $H_4C_2N_4$. LOBSTER calculations were used to compare the chemical bonding interactions of $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$ and $Ag(C_2N_4H_4)_3NO_3$ such as to explain the limited stability of $Ag(C_2N_4H_4)NO_3 \cdot \frac{1}{2}H_2O$. ICOHP analysis reveals that the inner N interaction in $Ag(C_2N_4H_4)_3NO_3 \cdot \frac{1}{2}H_2O$ is somewhat weaker than equivalent terminal N bonding modes, thereby explaining the propensity for terminal N bonding in metal cyanoguanidines.

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