Short Communication

Propellants, Explosives, Pyrotechnics

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First Structural Characterization of Solvate-Free Silver 5-Nitrotetrazolate and its Comparison with other Energetic Silver Compounds in Structure and Property

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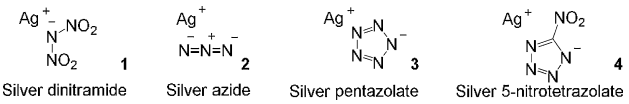
Abstract: The structure of solvate-free silver 5-nitrotetrazolate has been confirmed by single-crystal X-ray diffraction for the first time since it was prepared in 1978. Its structure and energetic performance were compared with other well-known silver energetic compounds, viz silver dinitramide, silver azide, and silver pentazolate. Its high thermal stability and very sensitive property make it a good candidate as a primary explosive.

Keywords: Silver 5-nitrotetrazolate · Single crystal · Primary explosive

1 Introduction

Energetic silver compounds attract extensive attention for their high energetic performance [1]. The most well-known energetic silver compounds generally exhibit very simple components (Scheme 1), such as silver dinitramide (**1**), silver azide (**2**), silver pentazolate (**3**), and so on [2]. However, it is a big challenge to get crystal structures of solvate-free silver compounds because of the extremely good coordination ability of silver. Furthermore, these silver compounds always exhibit extremely low solubility in most organic solvents. It is common to spend decades, even hundreds of years to get their solvate-free crystal structures.



Scheme 1. Representative silver energetic compounds.

Silver 5-nitrotetrazolate (**4**), which was first prepared in 1978, has been proven to be an excellent 5-nitrotetrazolate (NT) transfer reagent [3]. Prof Klapötke and his coworkers performed a lot of work with the starting materials of silver 5-nitrotetrazolate, including the preparation of the organic and inorganic salts, the functionalization of NT, and so on [4]. Thus, silver 5-nitrotetrazolate plays a very important role in the preparation of new high-performance energetic materials. However, although numerous researchers tried to get its solvate-free crystal structure, only three compounds containing other moieties, viz $AgNTC_2N_2H_8$, $Ag_5NT_4NO_3$, and $Ag_5NT_4ClO_4$, were reported [5].

After more than 50 years since it was first reported, we present here the solvate-free crystal structure of silver 5-nitrotetrazolate. The other characterizations, such as IR and element analysis, were also performed to confirm its structure. In addition, a comparison study on structure and performance between the above mentioned famous silver energetic compounds was conducted.

2 Experimental Section

2.1 Attention

Silver 5-nitrotetrazolate is a sensitive primary explosive. Safety protections are strongly encouraged when treating with this compound.

2.2 Synthesis

2.2.1 AgNT Powder

Sodium 5-nitrotetrazolate (1.37 g, 10 mmol) was dissolved in 20 ml water, and silver nitrate (1.70 g, 10 mmol) dissolved in water was slowly added. After stirring for 10 min at room temperature, the white solid was collected by filtra-

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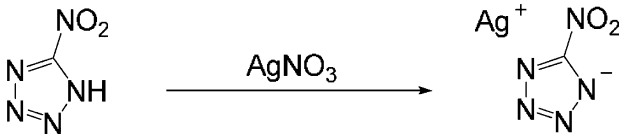
tion, washed with water, and dried in air to obtain AgNT (2.15 g, 97.7% yield).

2.2.2 AgNT Crystal

5-Nitrotetrazole (0.07 g, 0.5 mmol) was dissolved in DCM (20 ml), which was then put on the bottom of a tube. Silver nitrate (0.09 g, 0.5 mmol) dissolved in water (15 ml) was softly put on the dichloromethane. After a few days, crystals (0.08 g, 72.7% yield) were generated (Scheme 2). IR (KBr):



Scheme 2. Preparation of Silver 5-nitrotetrazolate.

1551 1493 1455 1426 1321 1203 1171 1039 832 810 659 cm^{-1}. Elemental analysis calculated for $CAgN_5O_2$ (221.93): C 5.41, N 31.56%; found C 5.20, N 31.77%.

2.3 Crystal Test

A colorless needle crystal (AgNT) of dimensions 0.30×0.06×0.04 mm^3 was mounted on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ = 0.71073 Å) at 173 K. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares calculation on F^2 with SHELXL-97.

3 Results and Discussion

3.1 Crystal Structure

The molecular structure and packing diagram of silver 5-nitrotetrazolate (**4**) are shown in Figure 1. It is very interesting that there are eight different shapes of 5-nitrotetrazolate anions and silver cations in the unit cell. The packing style indicates that it exhibits a 2D structure.

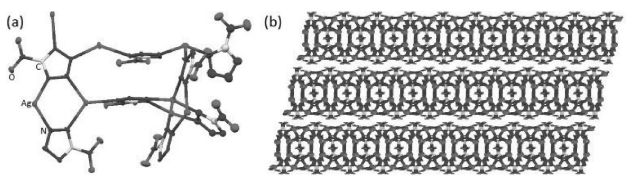


Figure 1. Crystal structure and packing diagram of silver 5-nitrotetrazolate.

To comprehensively study the structure of **4**, the structure of silver dinitramide (**1**), silver azide (**2**), and silver pentazolate (**3**) were also studied to compare with **4**. The Crystallographic data for these four compounds are provided in supporting information (Table S1). All compounds **1**, **2**, and **3** exhibit the orthorhombic crystal system, while **4** exhibits the triclicnic crystal system. These four compounds exhibit different space groups, which are Pbca, Ibam, Fddd, and P-1, respectively. The coordination environments of four anions are presented in Figure 2. The dinitramide anion is

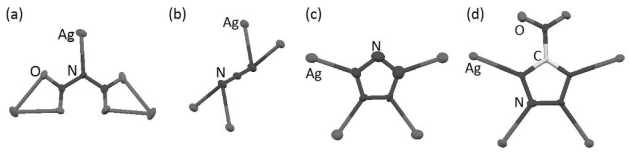


Figure 2. Coordination environments of four anions.

coordinated with three silver cations, while the other three anions are all coordinated with four silver cations. The bond lengths of Ag–O in compound **1** are 2.523–2.707 Å, and the bond lengths of Ag–N in these four compounds are 2.284, 2.559, 2.250–2.330, and 2.254–2.516 Å, respectively. There is no general rule between these bond lengths. In addition, the coordination environments of silver cations are also compared. As shown in Figure 3, in compound **1**, silver is coordinated with three anions. While for **2** and **3**, silvers are coordinated with four N_3^- and N_5^- anions. Different from **1**, **2**, and **3**, silver exhibits two coordination styles, which are tri-coordinated and tetra-coordinated (Figure 3d).

In addition, the interactions between the anions are also studied. Because there are no hydrogen atoms in the anions, the most common hydrogen-bonding interactions can not be found in the structures. However, π-π interactions can be observed in silver pentazolate and silver 5-nitrotetrazolate. As can be seen in Figure 4, there are strong π-π interactions between two face-to-face N-rich anions.

3.2 Energetic Performance

The physical and energetic performance of silver 5-nitrotetrazolate (**4**) were studied and compared with the other three silver energetic compounds (Table 1). Due to the existence of 5-nitrotetrazolate, **4** exhibits a high nitrogen content of 31.56%, but lower than that of **3** with pentazolate anion. Compound **4** also possesses a high combined nitrogen and oxygen content, which was slightly lower than that of **1** with a dinitramide anion. Due to the high stability of NT anion, **4** shows the highest thermal stability with a decomposition temperature of 275 °C. The density at room temperature was obtained using empirical formula, and the value of **4** is 3.13 g cm^{-3}. It can be predicted that compound **2** possesses the highest density, because the azide anion

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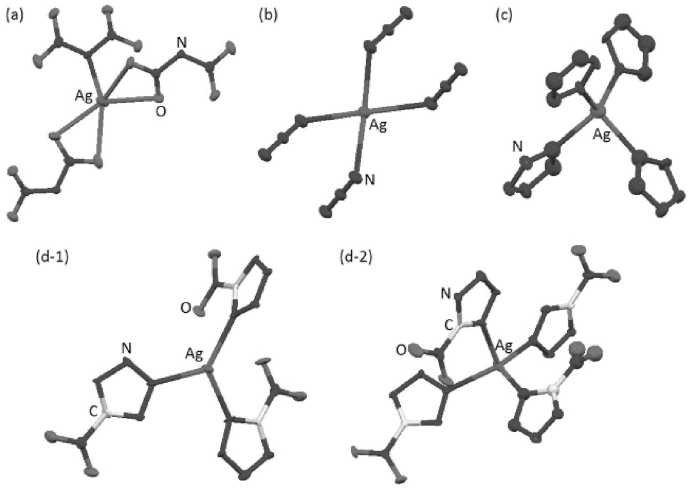

Figure 3. Coordination environments of silvers in four silver compounds.

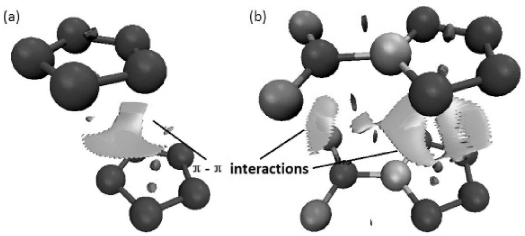

Figure 4. π-π interactions between two face to face anions in compounds **3** and **4**.

Table 1. Physical and energetic properties of 4 compared with 1, 2, 3 and Pb(N3)2.

	N[a] [%]	N + O[b] [%]	T_d[c] [°C]	d[d] [g cm-3]	OB[e] [%]	IS[f] [J]	FS[g] [N]
1	19.65	49.57	120	3.56	26.3	> 40	≥ 240
2	28.03	28.03	252	4.95	−5.3	–	–
3	39.37	39.37	98	2.96	−4.5	–	–
4	31.56	45.98	275	3.13	−3.6	< 1	< 5
$Pb(N_3)_2$[h]	28.86	28.86	315	4.80	−11.0	0.1–1	6–12

[a] Content of nitrogen. [b] Content of combined nitrogen and oxygen. [c] Decomposition temperature. [d] Crystal density at 298 K. $d_{298K} = d_T/(1 + a_v(298\text{-}T))$; $a_v = 1.5 \times 10^{-4}$ K^{-1}. [e] Oxygen balance based on CO_2. [f] Impact sensitivity. [g] Friction sensitivity. [h] Ref [6].

exhibits the lowest molecular weight, in other words, compound **2** exhibits the highest content of silver. The oxygen balance of these four compounds were also studied. Due to the existence of dinitramide anion, compound **1** has a very high oxygen balance of 26.3 %, which indicates its potential application as energetic oxidizers. Mechanical sensitivity is a important parameter to evaluate the safety property of an energetic compound. It is found that compound **4** is very sensitive to external stimuli and should be classified into primary explosive.

Due to the very sensitive performance that **4** exhibits, it was compared with the traditional explosive $Pb(N_3)_2$. On the whole, they show very similar physical and energetic performance. However, silver exhibits much lower toxicity than lead, thus compound **4** can be a good candidate as primary explosive. In addition, it must be noted that an explosion happened when we handled compound **4**. Please try to avoid metal spoons and safety protections are strongly encouraged.

4 Conclusion

In summary, the crystal structure and energetic performance of silver 5-nitrotetrazolate were demonstrated. It is the first solvate-free crystal structure since silver 5-nitrotetrazolate was prepared in 1978. AgNT crystallizes in the triclicnic space group P-1 with sixteen molecules per unit cell and a density of 3.184 g cm^{-3} at 173 K. π-π interactions between 5-nitrotetrazolate anions were studied. AgNT exhibits very high decomposition temperature at 275 °C. Furthermore, it also exhibits very high mechanical sensitivity with impact sensitivity lower than 1 N and friction sensitivity lower than 5 N, making it a strong candidate as primary explosive. In addition, the crystal structures and physical and energetic properties of silver dinitramide, silver azide, and silver pentazolate were also studied to compare with silver 5-nitrotetrazolate. These compounds exhibit very different crystal structures and energetic performance, which indicates their different possible applications. We believe this work can give new sight into silver 5-nitrotetrazolate and the energetic silver compounds.

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