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Communication

Taming the Dragon: Complexation of Silver Fulminate with Nitrogen-Rich Azole Ligands

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ABSTRACT: The almost ancient and very sensitive silver fulminate (SF), which was involved in the establishment of fundamental chemical concepts, was desensitized for the first time with different nitrogen-rich triazoles and tetrazoles, yielding SF complexes $[Ag_x(CNO)_x(N\text{-Ligand})_y]$ (x = 1−4; y = 1−3). These were accurately characterized (X-ray diffraction, scanning electron microscopy, IR, elemental analysis, differential thermal analysis, and thermogravimetric analysis) and investigated concerning their energetic character. The highly energetic coordination compounds suddenly show, in contrast to SF, sensitivities in a manageable range and are therefore safer to handle. In particular, compounds $[Ag_4(CNO)_4(BTRI)]$ [**3**; BTRI = 4,4′-bis(1,2,4-triazole)] and $[Ag_4(CNO)_4(2,2\text{-dtp})]$ [**8**; 2,2-dtp = 1,3-di(tetrazol-1-yl)propane] show values in the range of desired lead styphnate alternatives with similar energetic performances. The crystal structure experiments reveal silver cluster formation in all complexes with distinct argentophilic interactions close to 2.77 Å. Furthermore, it was possible to synthesize **8** in a one-pot reaction, avoiding the isolation of highly sensitive SF.

During a time when alchemy turned into chemistry and attempts were made to transmute elements into gold and silver, the first fulminates were born. The history of fulminates dates back at least to the 17th century, when the unintentional synthesis of mercury fulminate (MF) by Kunckel led to a severe explosion.[1] This incident demonstrates the highly sensitive nature that all fulminates have in common and that is affected by the type of bonding (ionic vs covalent) within the compounds.[2] The explosive characteristics are also responsible for the compounds' designation, which is derived from the Latin word "fulminare", which means "to strike with lightning".[3] Since the first isolation of MF, the most common compound of this class, by Howard in 1799, several famous chemists have investigated fulminates (e.g., Liebig, Gay-Lussac, Kekulé, Pauling, Huisgen, Beck, and many more), which has led to breakthrough discoveries such as the concept of isomerism.[4] Besides the acquisition of fundamental comprehensions and its use for military applications, MF has played a crucial role for peaceful purposes. It enabled, for the first time, the detonation of safely manageable dynamite at the end of the 19th century, thus facilitating civil engineering in general as well as allowing megaprojects such as construction of the Panama Canal (Figure 1A).[1,5]

Except for MF, the only other readily accessible metal fulminate, starting from the corresponding metal, nitric acid, and ethanol, is represented by its silver salt. Silver fulminate (SF) is an extremely dangerous primary explosive (especially toward electrostatic discharge) that can even explode during filtration or underwater and that is therefore too sensitive for almost any application (this corresponds with our experiences!).[6] To the best of our knowledge, the only application of SF is in "bang snaps", also called "snap dragons" (Figure 1B). Small amounts of SF, which coats tiny stones that are wrapped in thin paper, instantly detonate when dropped.

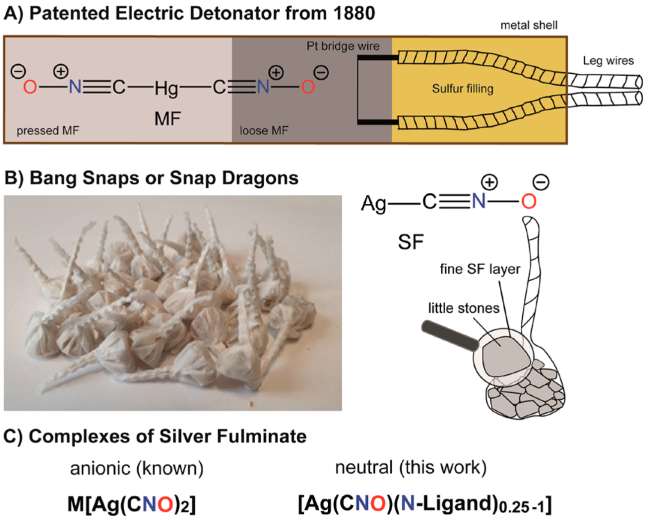

Figure 1. (A) MF in detonators for dynamite initiation. (B) SF for bang snaps. (C) Complexation of SF.

Nevertheless, it was intensively examined by Liebig, who was able to handle up to 100 g of this compound. This not only led

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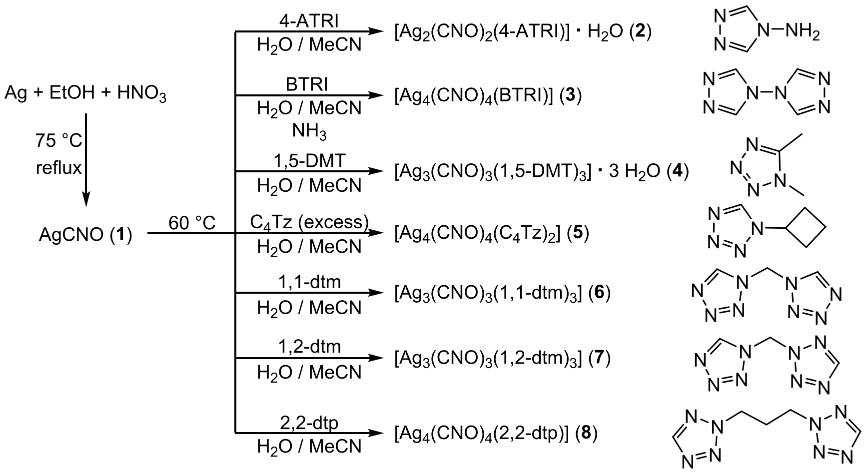
Scheme 1. Synthesis of SF and Its Conversion to Practical ECCs[a]



[a]Overview of the azole ligands used: 4-ATRI, 4-amino-1,2,4-triazole; BTRI, 4,4′-bis(1,2,4-triazole); 1,5-DMT, 1,5-dimethyltetrazole; C_4Tz, 1-cyclobutyltetrazole; 1,1-dtm, di(tetrazol-1-yl)methane; 1,2-dtm, (tetrazol-1-yl)(tetrazol-2-yl)methane; 2,2-dtp, 1,3-di(tetrazol-2-yl)propane.

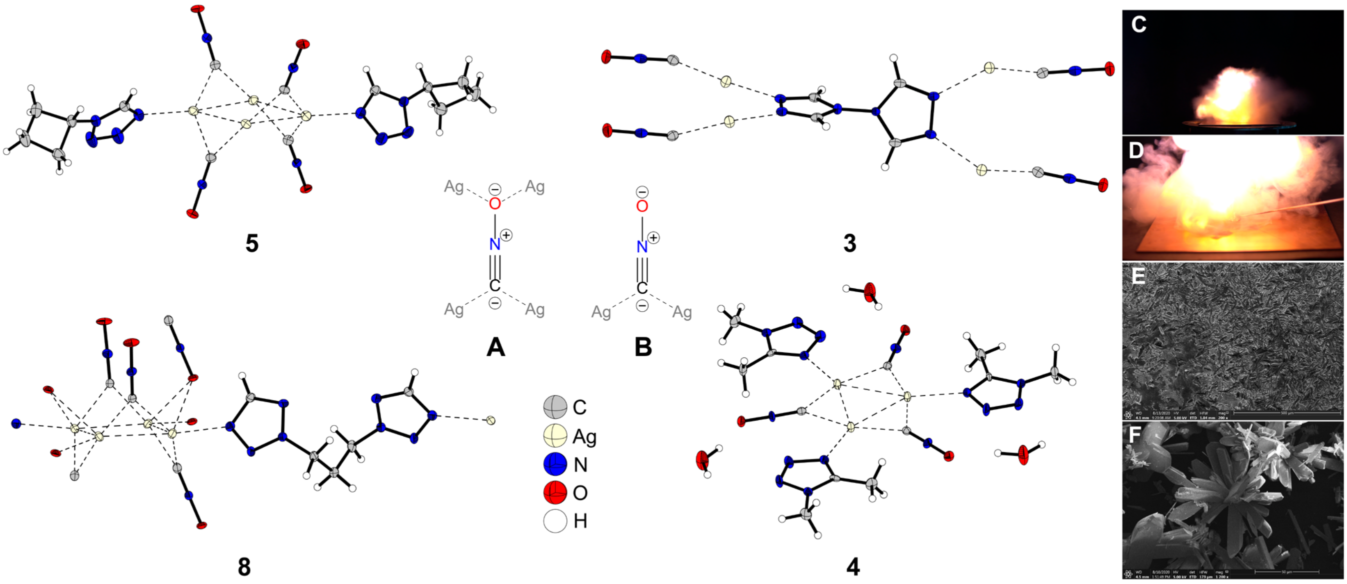


Figure 2. Different bridging modes **A** and **B** of the fulminate anion and molecular units of **3**−**5** as well as the extended molecular unit of **8**. Ellipsoids are set to the 50% probability level.[29] Physicochemical properties: (C) detonation of the ECC **3** during the hot plate test; (D) deflagration of **3** during the hot needle test; (E) SEM image of decomposed AgCNO (200× enlargement); (F) SEM image of complex **8** (1200× enlargement).

to the perfection of his well-known carbon, hydrogen, and nitrogen analysis but also proved his exceptional abilities and great skills.[7] He was also the first one who investigated simple fulminato complexes such as $K[Ag(CNO)_2]$ (Figure 1C).

Soon, several more compounds followed, which were discovered by Nef,[8] Wöhler and Martin,[9] and Wieland.[10] Despite their explosive and sensitive character, all of these complexes had in common that they did not receive much attention regarding their coordination behavior at that time. More detailed examinations on the complexing nature of the CNO^- anion were carried out by Beck, whose work with metal fulminates was extensive.[11] For the first time, it was also possible to obtain nonexplosive and thermally stable fulminato complexes by using large-volume cations.[12] Completely unknown in the literature are fulminate complexes with nitrogen-donor ligands, and especially rare are single-crystal X-ray diffraction (XRD) investigations of fulminate compounds. In recent years, the concept of energetic coordination compounds (ECC) gained increasing interest among scientists worldwide, and various reports set the stage for their future applications.[13−18] Herein, we report the first-ever SF complexes based on nitrogen-rich azole ligands. Following the concept of ECC, highly sensitive SF was combined with (highly) endothermic nonacidic triazole and tetrazole ligands. The incorporation reveals practicable ECC with very diverse and interesting coordination spheres compared to pure SF. Therefore, AgCNO was synthesized according to our preferred literature procedure, which starts with elementary silver, nitric acid, and absolute ethanol.[19] SF was further reacted with readily obtained azole ligands.[20−22] The reaction conditions are highly dependent on the ligand systems used, and all compounds were obtained as colorless solids with satisfactory to very good yields (56−89%). All ECC can be stored at ambient conditions and do not show any evidence for

Table 1. Summary of the Compounds' Thermal Stability[a], Sensitivities toward Various External Stimuli, and Results of Hot Plate (HP) and Hot Needle (HN) Tests Compared to SF and LS

compound	T_{endo} (°C)[b]	T_{exo} (°C)[c]	IS (J)[d]	FS (N)[e]	ESD (mJ)[f]	BDIS (mJ)[g]	HP[h]	HN[h]
AgCNO (**1**)		196	5[19]	≤0.1[19]	≤0.28	≤4[19]	det.	det.
$[Ag_2(CNO)_2(4\text{-ATRI})]\cdot H_2O$ (**2**)	64, 89	187	>40	>360	>1000	>200	def.	dec.
$[Ag_4(CNO)_4(BTRI)]$ (**3**)		215	5	10	2.5	55	det.	def.
$[Ag_3(CNO)_3(1,5\text{-DMT})_3]\cdot 3H_2O$ (**4**)	82	138	>40	>360	740	>200	def.	dec.
$[Ag_4(CNO)_4(C_4Tz)_2]$ (**5**)		133	20	84	7.3	>200	det.	def.
$[Ag_3(CNO)_3(1,1\text{-dtm})_3]$ (**6**)		152	6	72	25	28	def.	def.
$[Ag_3(CNO)_3(1,2\text{-dtm})_3]$ (**7**)		144	7	64	203	41	def.	def.
$[Ag_4(CNO)_4(2,2\text{-dtp})]$ (**8**)		177	8	1	0.7	8	det.	det.
LS[19,30]		275−280	2.5−5	0.5−1.5	0.02−1	15	det.	det.

[a]Onset temperature at a heating rate of 5 °C min^{-1} measured by differential thermal analysis. [b]Endothermic peak, which indicates melting or dehydration. [c]Exothermic peak, which indicates decomposition. [d]Impact sensitivity according to the BAM drop hammer (method 1 of 6). [e]Friction sensitivity according to the BAM friction tester (method 1 of 6). [f]Electrostatic discharge sensitivity (OZM Electric Spark XSpark10). [g]Ball drop impact sensitivity determined with the 1 of 6 method in accordance with MIL-STD 1751A (method 1016). [h]dec. = decomposition; def. = deflagration; det. = detonation.

decomposition. However, safety precautions (such as Kevlar gloves, face shields, ear protection, etc.) must be applied when handling pure SF and its complexes. Complexes **2**, **4**, and **6**−**8** can easily be crystallized by dissolving AgCNO in a solution of the appropriate amount of ligand in acetonitrile/water (50:50). Whereas the ECC **5** can be synthesized in the same solvent system using an excess of ligand to prevent the formation of pure SF, the coordination compound **2** can be crystallized by adding some drops of aqueous ammonia to the reaction mixture (Scheme 1).

When SF is added to the dissolved ligands in a relatively small amount of solvent, complexes **2**, **6**, and **8** can also be precipitated from the reaction solution, which has to be stirred for 15 (**6** and **8**) to 45 min (**2**). Interestingly, the ECC **8** can be synthesized in a one-pot reaction, avoiding isolation of the highly sensitive SF. Therefore, elemental silver is reacted with nitric acid, and 1,3-di(tetrazol-2-yl)propane (2,2-dtp) dissolved in ethanol is added, which results in the formation of a colorless precipitate (most probably the corresponding silver nitrate complex). When heated with stirring, the solid dissolves around 70 °C, and the typical formation (gas generation accompanied by the precipitation of an off-white solid) of SF occurs. However, instead of pure AgCNO, the corresponding ECC **8** is formed in a very high yield of 89%. All ECC were investigated by single-crystal XRD experiments. Pure SF occurs in two different polymorphic forms, an orthorhombic one as well as a trigonal one.[23] In both cases, coordination of the fulminate anions can be described as a bridging of the terminal carbon and oxygen atoms (Figure 2, **A**) with shorter Ag−C bond lengths (∼2.2 Å) compared to the Ag−O ones, leading to 3D polymeric structures. Because some of the Ag−O distances are longer than 2.7 Å, the linking of the anion is better represented as being in mode **B** or between that of **A** and **B**. The addition of nitrogen-donor ligands to SF reveals very diverse and worthwhile coordination chemistry. The same two main coordination modes can be observed in the ECC **2**−**8** (Figures 2 and S3−S9 and Tables S1 and S2). While all structures have the bridging behavior of the fulminate carbon atom between two silver cations in common (Ag−C−Ag = 77−91°), in compounds **2**−**4**, **6**, and **7**, no Ag−O interactions are observed at all. The Ag−O distances in the ECC **5** and **8** are in the range of 2.49−3.01 Å, with most of them above 2.6 Å, which indicates rather weak bonding between them. In all structures, the clear presence of Ag−Ag interactions is observable. These argentophilic interactions are defined as sub van der Waals contacts (<3.44 Å) and have gained increasing attention within the last years.[24−27] The closest Ag−Ag distance with 2.7705(5) Å can be found in the ECC **8**, which is very close to the shortest reported argentophilic interaction [2.7599(3) Å].[28] The ECC **4**, **6**, and **7** are the only compounds that form complex monomers that consist of silver trimers. Coordination of the ditetrazolylmethane ligands with only one of their rings in **6** and **7** is a literature-known issue.[22] In complexes **4** and **8**, tetrameric clusters of silver are present, which build up 2D polymeric layers via Ag−Ag and Ag−O bonding. The additional linking of the ligand in **8** is connecting the layers and leads to the formation of a 3D polymeric network. Contrary to **8**, formation of the 3D structure in **3** is caused by 4-fold coordination of the ligand to different silver atoms, preventing the formation of Ag−O bonds. All ECC were analyzed regarding their physicochemical properties, and their sensitivities toward various external stimuli were determined and are summarized in Table 1. Whereas pure SF does not possess no-fire limits for friction and electrostatic discharge sensitivities, in every case, the incorporation of nitrogen-rich ligands leads to stabilization. Considering the friction sensitivity, it becomes clear that it corresponds with the SF to ligand ratio. Therefore, complexes **3** and **8** are the most sensitive ones, with values close to those of lead styphnate (LS). The incorporation of water molecules creates compounds that are completely insensitive and therefore safe to handle. All ECC show lower thermal stabilities compared to pure SF, except compound **3**, which exceeds 200 °C. Interestingly, the incorporation of bridging ligands (**2**, **3**, and **8**) causes higher exothermic decomposition temperatures, whereas monodentate acting ligands (**4**−**7**) lead to lower thermal stabilities.

Hot plate and hot needle tests reveal the energetic character of the complexes, which all show deflagrations or even detonations (Figures 2 and S13−S20). Whereas none of the ECCs can detonate nitropenta in classical initiation tests, the energetic performances of complexes **3** and **8** are similar to that of LS, making them potential lead-free replacements. Scanning electron microscopy (SEM) was performed to examine the morphology of some of the compounds and compare it with that of pure SF (Figures 2 and S21−S24). Interestingly, SF is the first primary explosive in our research group that is too sensitive to be investigated using SEM. During the sample preparation, the substances have to be sputtered using a high-voltage pulse. Most likely, it is the high electrostatic discharge sensitivity of **1** that causes decomposition during the process. In contrast, the ECC show different crystal morphologies with differing crystal sizes, demonstrating their improved stability.

In conclusion, we successfully synthesized seven new SF complexes based on different neutral nitrogen-rich azole ligands. All ECC show fascinating coordination behavior with cluster formation and argentophilic interactions close to the shortest reported Ag−Ag distances. The resulting compounds possess manageable sensitivities, and ligands with bridging character increased the thermal stability up to 215 °C. The possible synthesis of complex **8** in a one-pot reaction from elemental silver, ethanol, nitric acid, and ligand in high yields avoids the isolation of pure SF and opens the field to a safe synthesis of SF complexes, which could be used as a potential replacement for LS.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03027.

Experimental part and general methods, IR spectroscopy, XRD, differential thermal analysis and thermogravometric analysis plots, hot plate and hot needle tests, and SEM (PDF)

Accession Codes

CCDC 2021064−2021070 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(29) Selected X-ray data: **3**, *Ccca*, a = 11.8399(9) Å, b = 20.8348(16) Å, c = 5.8163(3) Å, V = 1434.78(17) Å^3, Z = 8, ρ = 3.406 g cm^{-3}; **4**, $P6^3/m$, a = 15.0648(5) Å, c = 6.1186(4) Å, V = 1202.57(13) Å^3, Z = 2, ρ = 2.204 g cm^{-3}; **5**, $C2/c$, a = 32.653(3) Å, b = 5.4602(5) Å, c = 12.9896(11) Å, β = 97.805(3)°, V = 2294.5(4) Å^3, Z = 8, ρ = 2.454 g cm^{-3}; **8**, $P2/c$, a = 12.5173(11) Å, b = 5.6400(4) Å, c = 12.8877(10) Å, β = 100.146(8)°, V = 895.61(12) Å^3, Z = 2, ρ = 2.891 g cm^{-3}.

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