# The properties of azole- copper complexes

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For the purpose of improving the reactivity, metal-azole complexes were synthesized and their properties were investigated. 1H-Tetrazole and 1H-1, 2, 4-triazole were used for the ligands which contain nitrogen atoms and can coordinate to metals. Copper was selected as the central metal in anticipation of the catalytic effect. For the counter anion, nitrate was used. The 1H-tetrazole complex was obtained as the salt, $[Cu(CHN_4)_2]H_2O$. The 1H-1, 2, 4-triazole was obtained as $[Cu(C_2H_3N_3)_2](NO_3)_2$.

From the results of the sensitivity tests, the complexes were insensitive to impact and friction. However, they are sensitive to static eletctricity. Compared with pure azoles, the coordination changed the thermal stability and reactivity during the DSC measurement. The complexes generated oxidative gases during the flash pyrolysis/FT-IR measurement while pure azole generated HCN, $NH_3$ and hydrocarbons. From the deflagration test, it was found that these complexes could produce a large amount of gaseous species and the rate of pressure generation was high.

## 1. Introduction

For a long time, energetic materials have been investigated for application as explosives, propellants, and some pyrotechnics such as air bag inflators. A more recent development is to design new energetic material systems which could release non-toxic gases and have higher stability and reactivity as conventional energetic materials.

In the view of achieving high reactivity, the addition of catalysts to the system can be effective. For example, transition metal oxides are added to propellants in order to better conduct heat, promote electron-transfer process, and increase the burning rate[1),2)]. However, the actual mechanism is not yet well understood.

It is well known that the efficient interaction between transition metal catalysts and the fuel becomes stronger when the interaction distance is shorter. The reaction occurs at the interfacial area between the two substances. In order to enhance the catalytic ability of transition metals, short distances between the metal and fuel must be available.

Considering the chemical structure of energetic materials, most of them have electronegative atoms which can easily coordinate to transition metals and form complexes[3)]. Such short distances between the metals and the energetic materials in complexes are expected to have advantages for enhancing the reactivities. However, there have been few studies on energetic metal complexes. Akiyoshi et al. have intensively investigated the properties of carbohydrazide complexes and found that the characteristic behaviors of these complexes depended on the central metal cations[4)]. Moreover, they have recently reported the thermal behavior of an urea complex[5)].

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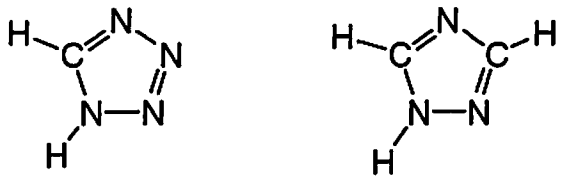


Fig. 1 Chemical structure of 1H-tetrazole and 1H-1, 2, 4-triazole

As components of the complexes, azole compounds could also to be utilized. Especially, tetrazoles and triazoles are excellent energetic materials and contain nitrogen atoms which can coordinate to metals. Previous researchers reported that many azole-complexes can be synthesized, resulting in tetrazole and triazole being bidentate ligands[6),7)] However, these studies focused only on the properties of the central atoms such as their magnetic behavior and no attention was given to energy releasing behavior.

In this report, the 1H-tetrazole-metal complex and 1H-1, 2, 4-triazole-metal complex were evaluated to as energetic metal complexes. 1H-tetrazole (abbreviated 1HT) and 1H-1, 2, 4-triazole (abbreviated 1HTRI) are basic azoles and it is important to obtain some insight into the properties of these complexes (Figure 1).

Many transition metals are able to form complexes with azoles. In this study, copper was used as the central cation because of its catalytic ability[8)]. As a counter anion, nitrate was chosen because it is frequently used as an oxidizer.

## 2. Experimental

### 2. 1 Synthesis

#### 2. 1. 1 1H-Tetrazole and copper complex

The 1H-tetrazole copper complex was first synthesized by Braubaker in 1960[9)]. The sample in this research was prepared following his method.

1H-Tetrazole and $Cu(NO_3)_2 \cdot 3H_2O$ were purchased from Tokyo Kasei Kogyo Co., Ltd., and Wako Pure Chemical Industries, Ltd., respectively. A 247 mg sample of $Cu(NO_3)_2$ in 20 ml of water was slowly added to 140 mg of 1H-tetrazole dissolved in 20 ml of water, pale blue precipitate was immediately generated. The precipitate was subsequently washed with water, methanol, ether and dried under reduced pressure.

An elemental analysis was carried out to determine the weight percent of C, H, N in the complex. Comparing the result of the elemental analysis with the literature values, its molecular formula was determined to be $[Cu(CN_4H)_2]H_2O$ (abbreviated 1HTCu). One proton was liberated from 1H-tetrazole since the parent molecule has a pKa value of $\sim$4. 8, which is similar to that of acetic acid[10)]. The yield was 80 mg (35. 6% based on $Cu(NO_3)_2 \cdot 3H_2O$) (Found: C, 9. 17; H, 1. 71; N, 51. 09%. $CuC_2H_4N_8O$ requires C, 10. 94; H, 1. 84; N, 51. 01%.)

All trials to dissolve the 1HTCu in common solvents failed. Moreover, none of the filtrates were colored during their syntheses in common solvents. 1HTCu had poor solubility which can be explained by the fact that copper tends to form a polymer with bridging atoms[3)].

#### 2. 1. 2 1H-1, 2, 4-Triazole and copper complex

A few complexes of 1H-1, 2, 4-triazole and copper were synthesized in previous studies[11),12)]. However, none of them contained $NO_3^-$ as the counter anion. Therefore, this study would be the first to synthesize a complex from 1H-1, 2, 4-triazole and copper nitrate.

1H-1, 2, 4-Triazole was purchased from the Tokyo Kasei Kogyo Co. A 543 mg sample of $Cu(NO_3)_2$ in 20 ml of methanol was slowly added to 349 mg of 1H-1, 2, 4-Triazole dissolved in 20 ml of water. A purple precipitate was immediately generated. The precipitate was subsequently washed with water, methanol, ether and dried under reduced pressure. From the elemental analysis results, its molecular formula was determined as $[Cu(C_2N_3H_3)_2](NO_3)_2$ (abbreviated 1HTRICu). The yield was 453. 4 mg (55. 6% based on 1HTRI) (Found: C, 16. 65; H, 1. 89; N, 35. 51%. $CuC_4H_6N_8O_6$ requires C, 14. 75; H, 1. 86; N, 34. 41%)

All trials to dissolve 1HTRICu in common solvents also failed. However, colored filtrates were obtained during its synthesis in DMF and water.

### 2. 2 Sensitivity test[13]

The friction sensitivity was measured by the BAM friction test and the 1/6 explosion point was determined.

The mechanical impact sensitivity was measured by the JIS drop hammer test. The sample was tested by an indirect method.

The sensitivity to electric spark was measured by an electrostatic sensitivity test. The apparatus was designed by Mizushima et al.[14]. The sample was sandwiched between two electrodes connected to condensers and the electrical spark applied by discharge. The sensitivity was estimated by the 50% explosion point using an up-and-down method[15].

### 2. 3 Thermal analysis

Sealed Cell-Differential Scanning Calorimetry (SC-DSC) was used for the thermal analysis. The instrument was a DSC20 (Mettler Toledo K.K.) and the operating system was STAR$^e$ System (Mettler Toledo K.K.). The sample weight for the investigation was about 1. 0 mg. The samples were heated in sealed cells made from stainless steel (Nihon Kayaku Co., Ltd.) The heating rate was 10 K/min.

### 2. 4 Thermal decomposition behavior

Flash-pyrolysis was carried out in order to investigate the thermal decomposition behavior. The instrumentation was a Pyroprobe 2000 and Brill cell (CDS Analytical Inc.) combined with a rapid-scan FT-IR spectrometer (MAGNA-IR 850, Nicolet Instrument Corporation). The principle of operation has been described in references[16),17]. The measurement conditions were as follows: The starting and ending temperatures were 30℃ and 1000℃, respectively, with a heating rate of 1000 K/s. The scanning resolution was 4 $cm^{-1}$ and integration of the spectra was 4 times. The measuring time was 1 minute. The measurements were carried out under 1 atm in a $N_2$ buffer gas.

### 2. 5 Deflagration test

Deflagration tests were carried out using a 52 ml type deflagration unit (Kuramochi Kagaku). It was designed in this laboratory to evaluate the gas generation ability. The 52 ml pressure vessel was made of stainless steel.

A nichrome filament was placed in the sample chamber with igniter powder, and 20 pellets of a 100 mg fuel-oxidizer mixture were placed in it. The igniter is activated by applying electricity through the nichrome filament. The pressure generating behavior is monitored with a pressure sensor. In this study, a two-step igniter system was adopted. The first igniter was 100 mg of Ti/$KNO_3$ (45/55 (wt.%)) and the second igniter was 150 mg of B/$KNO_3$ (22/78(wt.%)).

Gas analysis was carried out using a GC-8A gas chromatograph (Shimadzu Co.) and a detector tube (GASTEC Co.). The quantities of HCN, NO, $NO_2$, $NH_3$ were determined by the detector tubes. $N_2$, $O_2$, $CH_4$, CO, $CO_2$ were detected using the gas chromatograph and the quantity was determined using calibration curves.

## 3. Result and discussion

### 3. 1 Sensitivity test

From the friction sensitivity test, the 1/6 explosion point was equal to be 25. 2 kgf for 1HT and 24. 2–25. 2 kgf for 1HTRI. On the other hand, 1HTCu and 1HTRI did not explode at the highest load of 36. 0 kgf. Therefore, they are too insensitive to measure using the BAM friction sensitivity test similar to TNT, HNS, etc. These results are summarized in Table 1.

The drop hammer test was also carried out on 1HT and 1HTRI as a contrasting experiment. Based on the up-and-down method, the 50% explosion height was determined to be 12 cm for 1HT and 3. 4 cm (1HTRI), and the energy at the 50% explosion height ($E_{50}$) was 5. 9J for 1HT and 1. 7J for 1HTRI.

For these two complexes, the test was carried out 6 times with a hammer height setting of 50 cm. Both complexes did not explode in this test and were categorized as grade 8 according to JIS. These results are summarized in Table 2.

The results of the electric spark ignition are shown in Table 3. The test revealed that the complexes were sensitive compared to the pure azoles. The sensitivity of 1HTCu was close to Al/$KClO_4$ ($logE_{50}$ is −0. 76)[18]. Sakata reported that the sodium and potassium salts of 1HT were more insensitive to impact, friction and electric spark than 1HT[19]. The copper complex showed the same trend except for

Table 1 The result of BAM friction sensitivity test

| | Azole | | Complex | |
|---|---|---|---|---|
| Sample | 1HT | 1HTRI | 1HTCu | 1HTRICu |
| $M_{1/6}$[kgf] | 25.2 | 24.2-25.2 | >36.0 | >36.0 |

Table 2 The result of Drop hammer test

| | Azole | | Complex | |
|---|---|---|---|---|
| Sample | 1HT | 1HTRI | 1HTCu | 1HTRICu |
| $\log H_{50}$ | 1.08 | 0.53 | >1.7 | >1.7 |
| $H_{50}$[cm] | 12 | 3.4 | >50 | >50 |
| $E_{50}$[J] | 5.9 | 1.7 | >24.5 | >24.5 |
| $\sigma$ | 0.46 | 0.24 | — | — |

Table 3 The result of static electricity test

| | Azole | | Complex | |
|---|---|---|---|---|
| Sample | 1HT | 1HTRI | 1HTCu | 1HTRICu |
| $\log E_{50}$ | 0.52 | 0.04 | -0.88 | -0.08 |
| $E_{50}$[mJ] | 3.29 | 1.10 | 0.13 | 0.84 |
| $\sigma$ | 0.08 | 0.05 | 0.20 | 0.16 |

the sensitivity to static electricity. It can be said that the sensitivities depend upon the type of central metals. As for 1HTRICu, the sensitivity was close to B/$KClO_3$ (0.06).

### 3. 2 Thermal analysis

Figures 2 and 3 show the SC-DSC charts of the azoles, azole-metal complexes and tetrazole-metal nitrate mixtures. The heating rate was 10 K/s. Below their decomposition temperatures, the azoles exhibit endothermic behavior which correspond to melting. For the complexes, the endothermic peaks disappeared. This disappearance may be due to a change in their electronic properties. It can be considered that ionic azole molecules link via a Coulombic force in the complex solid while neutral molecules link together via a Van der Waals force in the pure azole crystal. Since the Coulombic force is stronger than the Van der Waals force, an ionic crystal is difficult to melt compared a molecular crystal.

Furthermore, the exothermic peaks of the complex became sharp compared with the pure azole

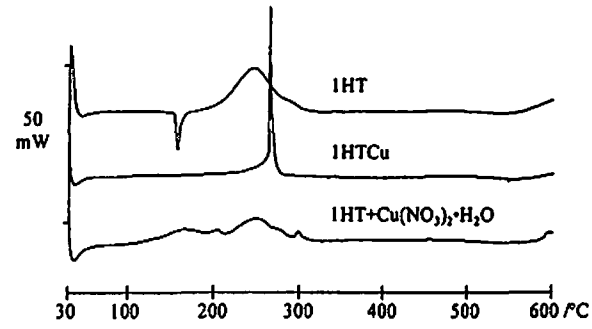



Fig. 2 The DSC charts of tetrazoles, 1HTCu and tetrazole-$Cu(NO_3)_2H_2O$ mixture

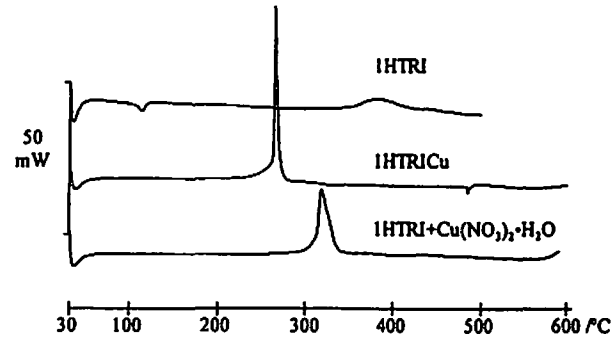



Fig. 3 The DSC charts of triazoles, 1HTCu and triazole-$Cu(NO_3)_2H_2O$ mixture

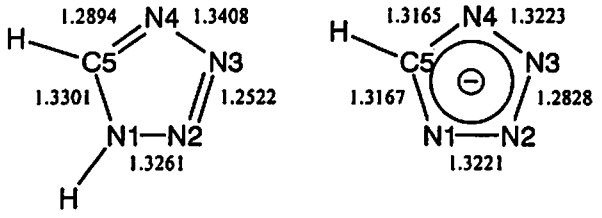
and azole-metal nitrate mixture. These results confirmed that an azole definitely interacts with a metal and coordination to the metal was effective for improving the decomposition velocity.

The values of $T_{DSC}$ and $Q_{DSC}$ are summarized in Table 4. As for 1HTCu, the thermal stability was improved compared to 1HT. Furthermore, the data in the table indicate the tendency that the anionic 1H-tetrazole is more stable than the neutral 1H-tetrazole. Therefore, the negative charge on the tetrazole may stabilize its thermal behavior.

Ohno concluded that tetrazoles were thermally

Table 4 Thermal properties of azole and complex

| Sample | $T_{DSC}$ [℃] | $Q_{DSC}$ [$Jg^{-1}$] | $Q_{DSC}$ [$kJmol^{-1}$] | $Q_{DSC}$ [$kJazole^{-1}$] |
|---|---|---|---|---|
| 1HT | 204 | 4257 | 298 | |
| 1HTCu | 264 | 2516 | 552 | 276 |
| 1HTNa[19] | 324 | 1700 | 157 | |
| 1HTK[19] | 311 | 1620 | 175 | |
| 1HTRI | 342 | 1506 | 104 | |
| 1HTRICu | 312 | 1987 | 647 | 324 |




neutral 1H-tetrazole

average length 1.3077Å

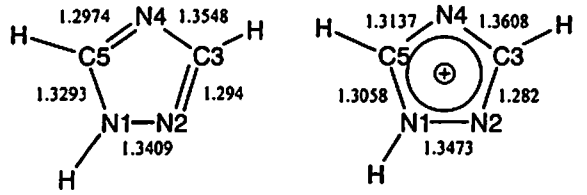
standard deviation 0.0073

anionic 1H-tetrazole

average length 1.3121Å

standard deviation 0.0033

Fig. 4 Optimized structures of neutral and anionic 1H-tetrazole at HF/6-31G* level




neutral 1H-1,2,4-triazole

average length 1.3233Å

standard deviation 0.0029

cationic 1H-1,2,4-triazole

average length 1.3219Å

standard deviation 0.0041

Fig. 5 Optimized structures of neutral and cationic 1H-1, 2, 4-triazole at HF/6-31G* level

stabilized by electron donating substituents[20]. Electron donating substituents make the tetrazole ring slightly anionic. In 1HTCu, the tetrazole valence was -1 and the same effect might occur in the substituted tetrazole. Figure 4 indicates the optimized structures of the anionic and neutral 1H-tetrazoles. The structure was obtained using a molecular orbital calculation at the HF/6-31G* level of theory. In the optimized structures, the uniformity of the bond lengths and an increase in the aromaticity were found in the anionic 1H-tetrazole. Therefore, the anionic character of 1H-tetrazole may influence the thermal stabilities. Furthermore, the N1-C5 and N3-N4 bonds are shorter in the anionic state than in the neutral state. Considering that the decomposition of 1H-tetrazole starts from breaking these bonds under the stated condition[17], it can be said that the anionic state is more stable than the neutral state.

For 1HTRICu, the triazole ring has a slight cationic character due to electron donation. The cationic state of the molecule was optimized and is shown in Figure 5. The standard deviation of the

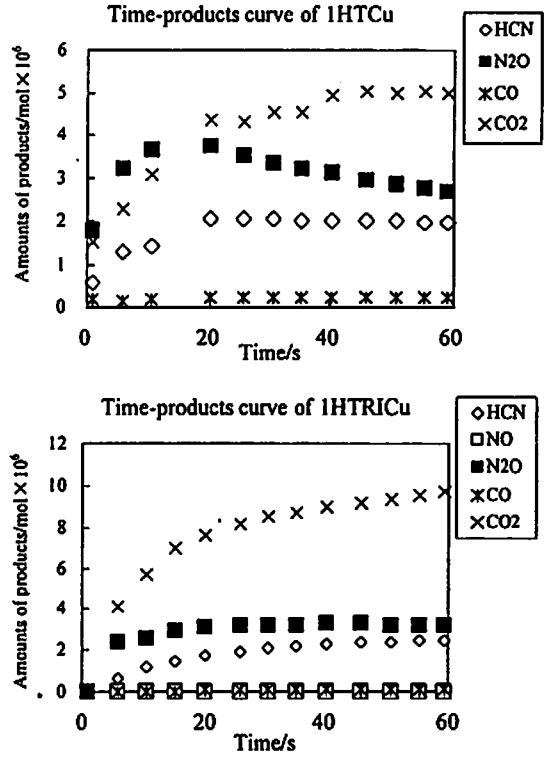



Fig. 6 Time-product curves of flash thermolysis/FT-IR of 1HTCu and 1HTRICu

average bond length became greater in the cationic state than in the neutral state. This might indicate a decrease in aromaticity.

$Q_{DSC}$ is the heat of reaction per unit mass. Since there are azole molecules and copper atoms (and nitrate anion for 1HTRICu) in the complex, the $Q_{DSC}$ of the complexes should decrease. As for 1HTCu, the heat of reaction per unit mass was smaller than 1HT. However, the heat of reaction per azole molecule is almost the same as 1HT, but larger than the potassium and sodium salts.

Meanwhile, $Q_{DSC}$ of 1HTRICu was larger than that of the 1H-1, 2, 4-triazole. This may be because fragmentation easily progresses in 1HTRICu. Williams et al. reported that triazoles are able to form polymers[21]. In this case, a high reactivity causes fragmentation during decomposition and a more exothermic reaction.

### 3. 3 Thermal decomposition behavior

The temporal profiles of the gas products are shown in Figure 6. The products from the complexes were HCN and oxidized gases. Under the same conditions, the 1H-tetrazole releases HCN, $CH_4$, $C_2H_2$, $NH_3$, and 1H-1, 2, 4-triazole releases HCN and $CH_4$.

It is uncertain whether the difference depends on the change in the initial decomposition process or the existence of Cu, $NO_3$, and $H_2O$.

### 3. 4 Deflagration test

The time-pressure curves are shown in Figure 7 and a summary of the characteristic values is shown in Table 5. $Sr(NO_3)_2$ was used as the oxidizer for 1HTRICu. As for 1HTCu, 1HTCu and $Sr(NO_3)_2$ generate heat and smoke during mixing in a mortar. Consequently, $NH_4NO_3$ was used for 1HTCu.

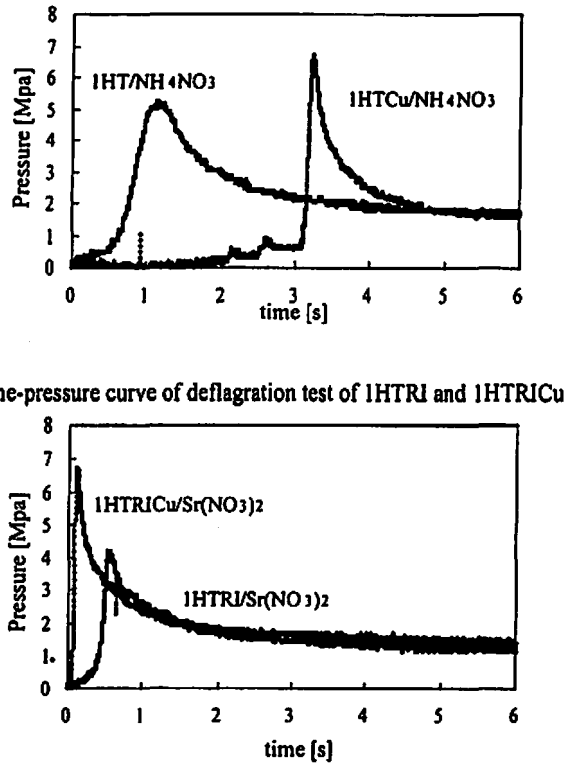



Fig. 7 Time-pressure curve of deflagration test of azoles and complexes

Table 5 The characteristic value of the deflagration test of complexes and azoles

| | Sample | Pmax [MPa] | (dP/dt)max [MPa/s] |
|---|---|---|---|
| 1HT | 1HT/$NH_4NO_3$ | 5.3 | 46 |
| | 1HTCu/$NH_4NO_3$ | 6.8 | 169 |
| 1HTRI | 1HTRI/$Sr(NO_3)_2$ | 4.4 | 187 |
| | 1HTRICu/$Sr(NO_3)_2$ | 6.6 | 218 |
| | 1HTRICu/$NH_4NO_3$ | No ignition | No ignition |

$P_{max}$ is the peak value of the pressure profile which indicates the gas generation quantity. $[dP/dt]_{max}$ is the slope of the time-pressure profile registering the gas generation velocity. The result showed that coordination to a metal was effective for improving the maximum pressure and the velocity of the pressure generation.

Furthermore, it was revealed that 1HTCu-$NH_4NO_3$ had a potential for practical use. Although the rate of gasification is 100% and no residue is left after the decomposition, $NH_4NO_3$ has not been utilized due to the slow decomposition velocity. The 1HTCu-$NH_4NO_3$ system bears comparison with common oxidizer-fuel systems.

The compositions of the product gas are shown in Table 6. Nitrogen was detected as the main component by gas chromatography. The amount of NOx was beyond the limit of the indicator tube (200 ppm) and generation of NOx could not be neglected. However, the igniter is also a NOx source. By using other igniters, it may be possible to build a new system having a reduced NOx release.

## 4. Conclusion

Although metal oxides have been utilized in energetic material systems, there has been little interest in organic energetic molecules-metal complexes. The reasons may be to avoid reducing the energy release per weight and increasing the sensitivity.

From this study, azole-copper complexes exhibited

Table 6 The composition of product gases from the deflagration test of 1HTCu and 1HTRICu

| Sample | | 1HTCu/$NH_4NO_3$ | 1HTRI/$Sr(NO_3)_2$ |
|---|---|---|---|
| $N_2$ | [vol%] | 83.7 | 64.7 |
| $O_2$ | | 0.1 | 5.1 |
| $CO_2$ | | 12.1 | 17.9 |
| CO | | trace | 11.4 |
| $CH_4$ | | 4.1 | trace |
| NO | [ppm] | >200 | >200 |
| $NO_2$ | | >200 | >200 |
| HCN | | 60 | 40 |
| $NH_3$ | | — | — |

useful properties and they have been superior to pure azoles in its some respects. 1HTCu showed improvement in sensitivity to mechanical impact, friction and heat. As for 1HTRICu, the sensitivity to mechanical impact and friction was also improved and the heat of reaction ability increased. Furthermore, the complexes showed improved performance in gas generation based on the deflagration test. Although the heavy gas generators are avoided in view of cost and efficiency, an improvement in reactivity may make it possible so that energetic complexes are utilized in spite of the weight.


## 5. Acknowledgement

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# アゾール類銅錯体の特性

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反応性の向上を目的として金属－アゾール類錯体を合成し，その性質を調べた。配位子として，金属に配位可能な窒素原子を含む1H-テトラゾールと1H-1,2,4-テトラゾールを用いた。中心金属には，触媒効果が期待される銅を選んだ。また，対イオンには硝酸イオンを用いた。1H-テトラゾールは合成の結果塩である$[Cu(CHN_4)_2]H_2O$が得られた。また，1H-1,2,4-テトラゾールからは$[Cu(C_2H_3N_3)_2](NO_3)_2$が得られた。

感度試験の結果，錯体は打撃感度，摩擦感度は鈍感であったが，静電気感度は鋭感であった。また，アゾール類と比較してDSC測定では錯体化によって熱安定性と反応性が変化することがわかった。高速熱分解/FT-IR測定では，錯体が酸化されたガスを放出することがわかった。爆燃性試験からはこれらの錯体によって高い圧力と圧力発生速度が発生することがわかった。

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