Article

A study on the characteristics of azole–metal complexes

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The purpose of this study is to investigate the effect of various metals on the thermal decomposition and sensitivity of azoles –complexes. 1H-tetrazole (1HT) and 1H-1,2,4-triazole (1Htri) were used as ligands which contain nitrogen atoms and can coordinate with metal such as copper, nickel and cobalt. These metals were selected as the central cation for their catalytic ability. Garber synthesized 1HT-Cu complexes in 1967, and Hassnoot synthesized 1Htri-complexes in 1977. Samples in this study were prepared following their methods. An elemental analysis was carried out to determine their composition and the results were compared with the calculated value. 1HT-complexes were obtained as the salt,$[Cu(CN_4H)_2] \cdot 1.5H_2O$, $[Co(CN_4H)_3] \cdot 2H_2O$ and $[Ni(CN_4H)_3] \cdot 3H_2O$. 1Htri-complexes were obtained as $[Cu(C_2H_3N_3)_2(NO_3)_2] \cdot H_2O$, $[Co_2(C_2H_3N_3)_7(NO_3)_4] \cdot 2H_2O$ and $[Ni_3(C_2H_3N_3)_6(H_2O)_6](NO_3)_6 \cdot 2H_2O$.

During Sealed Cell-Differential Scanning Calorimetry (SC-DSC) is measured, pure azoles exhibited an endothermic peak, which corresponded to melting. In the case of complexes, the endothermic peak disappears. This phenomenon might be due to the change of their electronic state. However, the results of the sensitivity test showed that 1Htri- complexes are insensitive to friction and impact. On the other hand, they are sensitive to static electricity, especially in 1Htri-Cu complex. Furthermore, sensitivity is closely related to ligands such as in the case of 1HT, which is more sensitive than 1Htri.

1. Introduction

Energetic materials have been investigated for their application as devices such as airbag inflators. A more recent development is to synthesize new energetic materials, which could exhibit higher stability and reactivity than conventional energetic materials. It is well known that interaction between transition metal catalyst and the fuel is optimum when the interaction distance is short. Therefore, the energetic materials as complexes are expected to have advantages for enhancing the reactivity rather than mixtures.

Azoles are kinds of fuel and its several important properties are brought about by its widespread interest. Because of the position of the donor atoms in the five-member ring, they appear to posses the possibility of linking transition metal ions together. However, its reactivity[1] is low as mixture. Therefore, to improve the reactivity, addition of catalysts to the system can be effective. 1H-tetrazole-copper complexes and 1H-1,2,4 –triazole –copper complexes were synthesized and their properties were investigaced[2] ,though other

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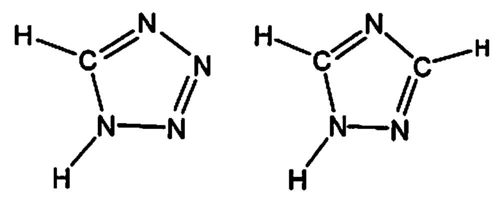

Fig. 1 Chemical structure of 1H-tetrazolle (1HT) and 1H-1,2,4-triazole(1Htri).

Table 1 Chemical analysis data for azole-metal complexes

S.No	Chemical formula	Colour	found (calcd.) (%)		
			C	H	N
1	$[Cu(C_2H_3N_3)_2(NO_3)_2]\cdot H_2O$	dark blue	14.0(14.0)	1.9(2.3)	30.6(32.6)
2	$[Co_2(C_2H_3N_3)_7(NO_3)_4]\cdot 2H_2O$	light orange	19.0(19.0)	2.3(2.8)	39.0(39.6)
3	$[Ni_3(C_2H_3N_3)_6(H_2O)_6](NO_3)_6\cdot 2H_2O$	light violet	13.8(13.0)	2.5(3.1)	31.2(30.4)
4	$[Cu(CN_4H)_2]\cdot 1.5H_2O$	blue	9.7(9.4)	2.0(2.1)	47.6(49.2)
5	$[Co(CN_4H)_3]\cdot 2H_2O$	orange	8.7(8.7)	1.9(1.5)	44.4(44.5)
6	$[Ni(CN_4H)_3]\cdot 3H_2O$	violet	9.3(9.6)	2.3(2.4)	44.2(50.5)

transition metals are able to form complexes with azoles.

Chemical analysis, thermal analysis and three sensitivity tests were carried out for the synthesized sample. In sensitivity tests, samples that were negative in all three tests were considered relatively insensitive to friction, impact, and electrostatic discharge. Those samples which were positive at the threshold value were further tested and the level at which 50 % of the test were positive was determined. Furthermore, electrostatic discharge sensitivity is an important parameter in the safe handling of energetic materials since electric sparks may develop in handle situations. However, the behavior of other transition metals on the thermal decomposition and sensitivity of azoles complexes are not yet reported in literature. As a part of our research is preparation, characterization and thermolysis of energetic materials, studies on azole metal complexes are also reported. 1H-1,2,4-triazole (1Htri) and 1H-tetrazole(1HT) (see Fig. 1) were used for ligands which contain nitrogen atoms and can coordinate with metals. Copper, nickel and cobalt were selected as the cation for their catalytic ability, and nitrate was used for a counter anion.

2. Experimental

2.1 Synthesis of azole- metal complexes and analytical methods.

The chemicals used in this investigation were reagent grade. An elemental analysis was carried out to determine the presented weight of C, H, and N in the complexes. The results of the elemental analysis were compared with the literature value[1),3)].

1Htri- copper complex

Water solution of 12.5 mmol of 1Htri in 15 ml of water and 2.5 mmol of $Cu(NO_3)_2\cdot 3H_2O$ in 15ml of water were mixed together and the resulting solution was stirred at room temperature. The solution was filtered off. A dark blue precipitate was filtrated and dried under reduced pressure.

1Htri- Co complex

Water solution of 5.0 mmol of 1Htri in 15 ml of water and 2.5 mmol of $Co(NO_3)_2\cdot 6H_2O$ in 15 ml of water were mixed together and the resulting solution was stirred at room temperature. The solution was filtered off. A light orange precipitate was filtrated and dried under reduced pressure.

1Htri- Ni complex

Water solution of 5.0 mmol of 1Htri in 15 ml of water and 2.5 mmol of $Ni(NO_3)_2\cdot 6H_2O$ in 15 ml of water were mixed together and the resulting solution was stirred at room temperature. The solution was filtered off. A light violet precipitate was filtrated and dried under reduced pressure.

1HT- copper complex

Methanol solution of 12.5 mmol of 1HT in 15 ml of mathanol and 2.5 mmol of $Cu(NO_3)_2\cdot 3H_2O$ in 15ml of methanol were mixed together and the resulting solution was stirred at room temperature. The solution was filtered off. A dark blue precipitate was filtrated and dried under reduced pressure.

1HT- Co complex

Methanol solution of 5.0 mmol of 1HT in 15 ml of methanol and 2.5 mmol of $Co(NO_3)_2\cdot 6H_2O$ in 15 ml of methanol were mixed together and the resulting solution was stirred at room temperature. The solution was filtered off. An orange precipitate was filtrated and dried under reduced pressure.

1HT- Ni complex

Methanol solution of 5.0 mmol of 1HT in 15 ml of methanol and 2.5 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ in 15 ml of methanol were mixed together and the resulting solution was stirred at room temperature. The solution was filtered off. A dark violet precipitate was filtrated and dried under reduced pressure.

2.2 Thermal analysis

Sealed Cell – Differential Scanning Calorimetry (SC-DSC) was used for thermal analysis. The instrument was DSC 20 and operating system was STAR^e System (Mettler Toledo K.K.). Samples weight were about 1.0 mg, which was heated in stainless steel sealed cells while the heating rate was 10 K/min.

2.3 Infrared studies

The IR Spectra of the 1Htri metal complexes and 1HT metal complexes were obtained using the KBr disc method.

2.4 Sensitivity test

2.4.1 Electrostatic sensitivity test

The sensitivity to static electricity was measured by an electrostatic sensitivity tester. The apparatus was designed by Mizushima [4]. It is equipped upper and lower electrodes with fixed distance, which were connected to a set of condensers at a predetermined capacitance. The sample was sandwiched between the two electrodes and ignited by discharging of condensers.

2.4.2 Friction sensitivity test

The Julius Peters (BAM) friction tester was used to determine the friction sensitivity of the various metal complexes in this study. The tester operates by rubbing a moving plate against a fixed pin with the material being placed between the plate and pin. The 1/6 explosion point was determined.

2.4.3 Drop hammer test

The sensitivity to mechanical impact was measured by the drop hammer test according to Japanese Industrial Standards (JIS). A drop hammer tester was a set up made by Hosoya

Table 2 T_{DSC} and Q_{DSC}

Sample	T_{DSC}(℃)	Q_{DSC}(J/g)	Q_{DSC}(kJ/mole/1Htri)
1Htri	343	850	587
1Htri-Cu	297	1525	262
1Htri-Co	343	1496	189
1Htri-Ni	379	1418	262

Table 3 T_{DSC} and Q_{DSC}

Sample	T_{DSC}(℃)	Q_{DSC}(J/g)	Q_{DSC}(kJ/mole/1HT)
1HT	209	3484	246
1HT-Cu	262	1840	186
1HT-Co	299	2094	211
1HT-Ni	329	1602	171

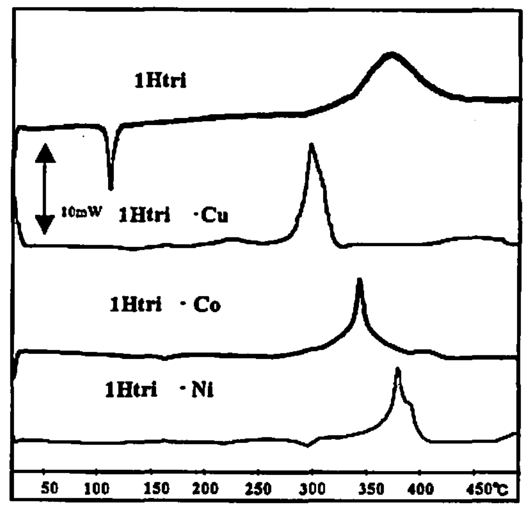

Fig. 2 SC-DSC curves of 1Htri and its metal complexes

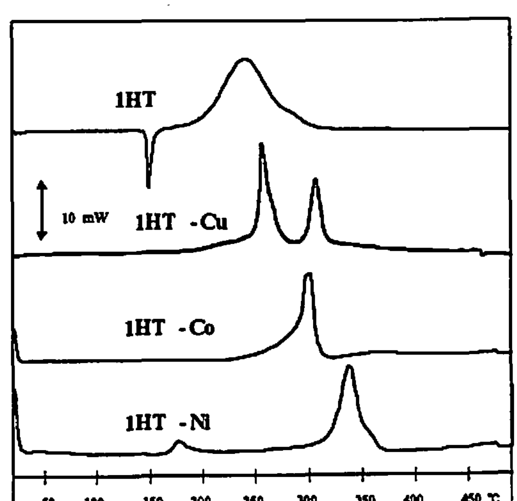

Fig. 3 SC-DSC curves of 1HT and its metal complexes

Firework. Co. Ltd. In operation, a small sample of approximately 0.03 gram of the material is placed in a brass cup. The cup is placed in the device and a weight is dropped from a predetermined height. The test is repeated following up and down method to determine 50 percent ignition energy.

3. Results and discussions

3.1 Thermal analysis

Figure 2 and 3 show SC-DSC curves of azole-metal complexes at a heating rate of 10 K/min. Below decomposition temperatures, azole exhibited an endothermic peak, which corresponded to melting.

In case of complexes, the endothermic peak disappeared. Kumazaki[2)] reported that phenomenon might be due to the change of their electronic state. They can be considered that ionic azole molecules link via Coulomb interaction in complex solidity while neutral molecule link together via Van der Waals bond in pure azole crystal. Since the Coulomb's force is stronger than the Van der Waals force, an ionic crystal is difficult to melt compared to a molecular crystal.

Furthermore, exothermic peaks of complexes became sharp comparing with pure azole. These results confirmed that azole interacted with metal and coordination to metal was effective in improvement of thermal stability of pure azole.

Q_{DSC} of 1Htri-metal complexes may be larger than that of 1Htri, because the fragmentation is easily progressed in 1Htri-metal complexes [2)]. William et al. reported that triazole was able to form polymers [5)]. Therefore, a high reactivity causes fragmentation during decomposition and a more exothermic reaction.

3.2 Sensitivity test

Table 5 summarized the result of the each sensitivity test. Within each metal complex the class of friction sensitivity and the 50% explosion energy of impact sensitivity were nearly identical.

From the friction sensitivity test, the1/6 explosion point was equal to 78-157 N for 1Htri .On the other hand, metal complexes did not explode even though at the highest load of 353 N. In the case of 1HT, 1HT-complexes are not different in its friction sensitivity, in which every samples explode at load 157～353 N.

The drop hammer test was carried out based on the up-and -down method. The 50% explosion height (E_{50}) was determined to be 6.76 cm for 1Htri and 26.92 cm for 1HT. Whereas in the case of metal complexes, the test was carried out 6 times at a hammer height setting of 50 cm. Those complexes did not explode in this test. Therefore, they are categorized as grade 8 according to JIS.

From a summarized result of each sensitivity test in table 5, 1Htri and its metal complexes were nearly insensitive than 1HT and its metal complexes. It is well known that both impact and friction sensitivity depend on the chemical structure of the explosive molecule[6)]. Moreover, sensitivity is also related to other measurable quantities such as ionization potential [7)]. While azoles have linkage with metal, 1HT have more electrons in its molecule than 1Htri.Therefore, 1HT metal complexes seem likely having more electron than of 1Htri metal complexes. Consequently, 1Htri metal complexes are

Table 4 The data of azole –metal complexes

Sample	Electrostatic Sensitivity (E_{50}/J)	Drop Hammer ($H_{1/6}$/cm)	Friction Sensitivity ($M_{1/6}$/N)
1Htri	1.26(class 4)	6.76(class 2)	78～157(class 5)
1Htri-Cu	0.19(class 3)	>50(class 8)	>353(class 7)
1Htri-Ni	0.49(class 4)	>50(class 8)	>353(class 7)
1Htri-Co	0.69(class 4)	>50(class 8)	>353(class 7)
1HT	0.14(class 3)	26.92(class 5)	157～353(class 6)
1HT-Cu	0.18(class 3)	>50(class 8)	157～353(class 6)
1HT-Ni	0.22(class 3)	>50(class 8)	157～353(class 6)
1HT-Co	0.21(class 3)	>50(class 8)	157～353(class 6)

approximately considered more insensitive than 1HT metal complexes.

4. Conclusion

Azoles which contain nitrogen atoms can easily coordinate with metal. Complex-formation of ligand azoles with metals was attempted in order to improve the reactivity of 1H-1,2,4-triazole (1Htri) and 1H-tetrazole (1HT).

Some conclusions can be drawn from this study:

- 1Htri's and 1HT's endothermic peaks caused by melting disappeared when these coordinated with metal.
- Q_{DSC} of 1Htri metal complexes were larger than that of 1Htri.
- Interaction and /or coordination of azoles (1Htri and 1HT) with metal (Cu, Ni, Co) were effective in improvement of their thermal reactivity.
- 1Htri metal complexes were less sensitive than 1HT metal complexes.

The results in this paper showed that metals coordinating to azole improved mechanical, impact and friction sensitivities of azoles.

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