

# Synthesis of transition metal picrates

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Received: August 29, 2003 Accepted: December 22, 2003

## Abstract

Picric acid is known to react with metals to form highly unstable metallic picrates, which are known to have been involved in serious explosive accidents. In this study, transition-metal picrates of chromium, manganese, cobalt and nickel salts are synthesized, and the thermodynamic and explosive properties (for example, initiation sensitivity) are examined.

The decomposition of Mn-picrate or Co-picrate determined through differential scanning calorimetry (DSC) begins at a lower temperature than that of picric acid, and the heat of decomposition of transition-metal picrates is found to be lower than that of picric acid. Thermogravimetry and Karl Fischer analysis confirm that transition-metal picrates contain crystal water, and the amount of crystal water in metastable-phase picrates is determined experimentally. Thermogravimetric analysis reveals that crystal water begins to dehydrate in a temperature range extending from slightly above room temperature to approximately 470 K. The activation energies of the decomposition reaction of these transition-metal picrates are 204.1 kJ·mol<sup>-1</sup> for Cr-picrate, 108.1 kJ·mol<sup>-1</sup> for Mn-picrate, 132.3 kJ·mol<sup>-1</sup> for Co-picrate, and 184.3 kJ·mol<sup>-1</sup> for Ni-picrate. Drop-hammer test results show that Cr-picrate has higher strike sensitivity than picric acid, and friction tests reveal that all of the transition metal-picrates examined here have equal or lower friction sensitivity compared to picric acid.

## 1. Introduction

Picric acid was used as a military explosive from World War I until the end of World War II<sup>1)</sup>. At that time, picric acid was known to react with metals to form very unstable metallic picrates. Lea and other authors<sup>2, 3)</sup> attempted to synthesize these picrates. Metallic picrates have been said to be highly sensitive, and have been implicated in accidents attributable to picric acid being brought into contact with metal. Examples of accidents involving metallic picrates were the detonation of metallic picrate after a metal fragment fell into burning picric acid. Another was the picric acid picrate detonation, in which picric acid was splashed onto a metal steam pipe, producing metallic picrate that subsequently exploded when struck<sup>4)</sup>. Metallic picrates, which may form incidentally from picric acid in industrial situations, ought to be examined in order to improve safety, and as a potential component for pyrotechnics. However, only a few studies have employed modern analytical techniques to examine the chemical and pyrotechnic properties of metallic picrates.

In this study, transition-metal picrates (Cr-, Mn-, Co-, Ni-picrate) are synthesized. Then, the chemical and pyrotechnical properties of these synthesized compounds are investigated, focusing on thermal properties, and the results of

analysis are compared with the reported properties of picric acid. The amount of crystal water in metallic picrate is also determined in order to evaluate the effect of formulaic water on explosion sensitivity<sup>4,5)</sup> as a possibly important factor in the consideration of safety.

## 2. Experimental

Transition-metal picrate was synthesized from transition metal compound and picric acid, sodium picrate or barium picrate. Figure 1 shows a typical synthesis reaction, in which a picrate anion bonds to a transition metal cation. Deionized water was used as solvent for synthesis.

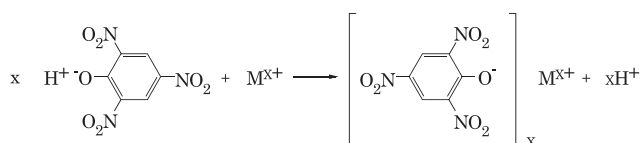


Fig. 1 Synthetic reaction equation of transition-metal picrates (M: transition metal).

## 2.1 Synthesis of chromium picrate (Cr-picrate)

Sodium picrate (Kanto Kagaku, Japan) was prepared by recrystallization from a solution. Chromium nitrate nonahydrate (Kanto Kagaku) was used without modification. Cr-picrate was synthesized from sodium picrate and chromium nitrate.

Chromium nitrate nonahydrate (10 g) was added slowly to 500 ml of sodium picrate solution (4%), and the mixture was stirred for 2 hours at room temperature. Subsequently, the solution was poured into a plastic vessel and dried under draft ventilation, yielding crude crystals. The crude crystals were then dissolved in 300 ml of acetone, causing the precipitation of a white crystal which was identified as a sodium nitrate byproduct. The solution was filtrated, and a green filtrate was obtained. The filtrate was added to dichloromethane (2000 ml) for recrystallization, yielding 11.74 g of the desired product as green crystals.

## 2.2 Synthesis of manganese picrate (Mn-picrate)

Manganese picrate was synthesized through barium picrate as an intermediate and manganese sulfate. Manganese sulfate pentahydrate (Kanto Kagaku) was used without modification.

Barium picrate was prepared from saturated picric acid solution and barium carbonate. Barium carbonate was added slowly to picric acid hot solution and the mixture was stirred for two hours. Unreacted barium carbonate was separated by filtration<sup>6</sup>. The solution was then evaporated to obtain dry barium picrate crystals. A 1% barium picrate solution was prepared by dissolving the obtained barium picrate in deionized water. Manganese sulfate (4.27 g) was added slowly to the barium picrate solution (1000 ml) and the mixture solution was stirred for 2 hours. The byproduct barium sulfate was generated as a white precipitate in the solution, and was subsequently filtered out for separation. The filtrate was poured into a plastic vessel and dried under draft ventilation, yielding crude crystals, which were then dissolved in 200 ml of acetone and impurities removed by filtration. The filtrate was concentrated to 100 ml, and the concentrated solution was added to dichloromethane (2000 ml) for recrystallization to yield 8.57 g of the final product as yellow crystals.

## 2.3 Synthesis of cobalt picrate (Co-picrate)

Picric acid (Kanto Kagaku) was prepared by recrystallization from a solution. Cobalt carbonate (Kanto Kagaku) was used without modification. Co-picrate was synthesized from cobalt carbonate and picric acid.

Cobalt carbonate (10 g) was added slowly to 1000 ml of hot picric acid solution (3%). Bubbles were generated in the reacting solution, attributable to carbon dioxide. After reaction, the solution was filtered, and unreacted cobalt carbonate was separated as a residue. The filtrate was poured into a plastic vessel and condensed under draft ventilation to yield crude crystals, which were then dissolved in 300 ml of acetone, affording a clear solution.

The solution was concentrated to 100 ml and then added to dichloromethane (2000 ml) for purification to remove picric acid as a contaminant. Unreacted picric acid was extracted in dichloromethane, yielding refined orange crystals. The synthesis procedure produced 31.75 g of the final product.

## 2.4 Synthesis of nickel picrate (Ni-picrate)

Nickel picrate was synthesized through barium picrate as an intermediate and nickel sulfate. Nickel sulfate hexahydrate (Kanto Kagaku) was used without modification.

Barium picrate was prepared by a method similar to that for manganese picrate. A 1% barium picrate solution was prepared by dissolving the obtained barium picrate in water. Nickel sulfate (4 g) was added slowly to the barium picrate solution (1000 ml) and stirred for 2 hours. A white precipitate was generated in the solution, attributed to barium sulfate as a byproduct. The barium sulfate was filtered and separated. Then, the filtrate was poured into a plastic vessel and dried under draft ventilation to yield crude crystals. The crude crystals were dissolved in 300 ml of acetone, and impurities were removed by filtration. The filtrate was concentrated to 100 ml, and the concentrated solution was added to dichloromethane (2000 ml) for recrystallization to yield 8.80 g of the final product as yellowish green crystals.

## 2.5 Analysis Method

Differential scanning calorimetry (DSC) analysis was employed to characterize the thermodynamic properties of the product. DSC measurements were conducted using a TA Instruments differential scanning calorimeter, model DSC2920. Device parameters, and heat and temperature properties were calibrated with respect to the fusion temperature and endothermic heat of melt for indium. About 0.5mg of sample was sealed in an Au-vapor deposited aluminum crimp cell and loaded into the apparatus under 3 MPa nitrogen gas. Analysis was performed under a heating rate of 10 K·min<sup>-1</sup>. The temperature range was from room temperature (about 298 K) to 823 K. Measurements were also conducted at heating rates of 1, 2, 5, 10, and 20 K·min<sup>-1</sup> in order to evaluate activation energy.

Thermogravimetry (TG) was performed in order to determine the crystal water content of the products. Measurements were conducted using a Rigaku simultaneous thermogravimetry and differential thermal analysis (TG-DTA) instrument, model TG8120, with infrared ramp heater. Device parameters and temperature properties were calibrated with respect to the fusing point of indium. During measurement, the apparatus was flushed with Ar gas flow at atmospheric pressure. The sample weight was approximately 10 mg, and the heating rate was 10 K·min<sup>-1</sup>. A more amount of sample was required for TG-DTA compared to DSC analysis to limit the explosive potential of the sample. The maximum temperature of analysis was also limited to 473 K for this reason, except for a few special cases in which the thermal properties of the sample were unclear beyond this upper limit of 473 K.

Table 1 Thermal properties of transition-metal picrates obtained from DSC.

	Cr-picrate	Mn-picrate	Co-picrate	Ni-picrate
$T_0^*$	575.3K	527.3K	505.1K	541.4K
$T_{\text{peak}}^*$	584.8K	581.5K	571.6K	601.8K
Heat of exothermicity	$4758\text{J}\cdot\text{g}^{-1}$	$4364\text{J}\cdot\text{g}^{-1}$	$4368\text{J}\cdot\text{g}^{-1}$	$4155\text{J}\cdot\text{g}^{-1}$

\*  $T_0$ ; Initial temperature of exothermic reaction,  $T_{\text{peak}}$ ; Peak temperature of exothermic reaction.

The crystal water content was investigated by the Karl Fischer method using a Metrohm 758 KFD Titrino apparatus. Riedel-deHaen Hydranal Composite 5 was used as the Karl Fischer reagent, and the machine was calibrated using approximately 30  $\mu\text{L}$  of deionized water.

A Shimadzu wavelength-dispersive x-ray fluorescence spectrometer, model XRF 1500 was employed to determine the metallic elements contained in the products. Analysis was conducted using an LiF crystal with a lattice constant ( $2d$ ) of 4.0267  $\text{\AA}$ . Detection of impurities (e.g., sodium) was performed using a thallium acid phthate (TPA) crystal.

Fourier transform infrared (FT-IR) spectroscopy was carried out by the KBr method using a Shimadzu spectroscope, model FTIR-8200PC. The measurement range was set to 400 to 2000  $\text{cm}^{-1}$  in order to avoid the influence of moisture in the air.

The impact sensitivity was determined by drop hammer test, and friction sensitivity was measured by friction test. Impact sensitivity was performed using 5 kg drop hammer test apparatus, which made by Kuramochi Kagaku Kikai Manufacturing co., ltd, and friction sensitivity was mea-

sured using friction sensitivity test apparatus for explosive test type, which made by Kuramochi Kagaku Kikai Manufacturing co., ltd. Both tests were conducted in accordance to the Japanese standard JIS K 4810<sup>9)</sup>.

### 3. Results and Discussion

#### 3.1 Thermal analysis

Figure 2 and Table 1 show the results of DSC analysis. Mn-picrate and Co-picrate exhibit thermal decomposition peaks at lower temperature than that of picric acid. All transition-metal picrates exhibit bimodal thermal decomposition peaks, except for Cr-picrate. At a heating rate of 10  $\text{K}\cdot\text{min}^{-1}$ , the temperature at which the decomposition of Ni-picrate (541.4 K) starts is nearly equal to that for picric acid (542 K). The heat of decomposition of transition-metal picrates falls approximately in the range 4150 - 4760  $\text{J}\cdot\text{g}^{-1}$ , which is lower than that of picric acid, 5590  $\text{J}\cdot\text{g}^{-1}$ .

Figure 3 shows the TG-DTA analysis results. As the crystal water properties can begin to change immediately after synthesis of the crystals, the as-prepared samples

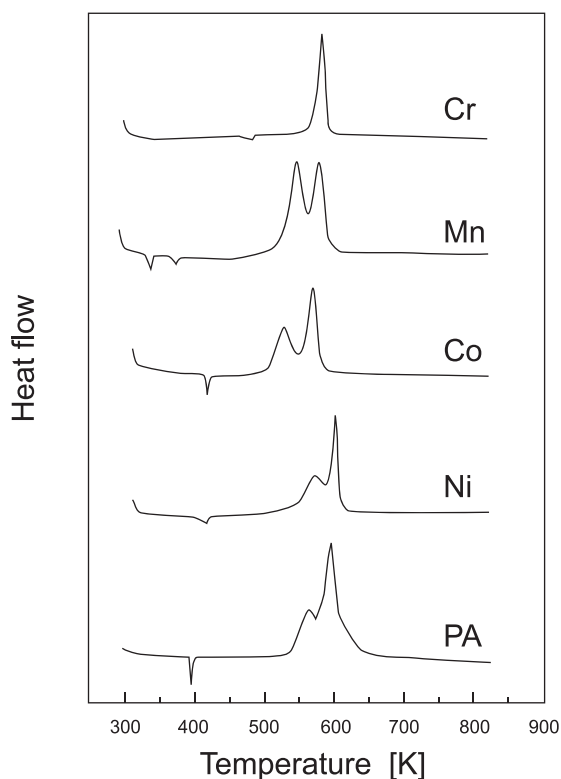


Fig. 2 DSC results for transition-metal picrates and picric acid.

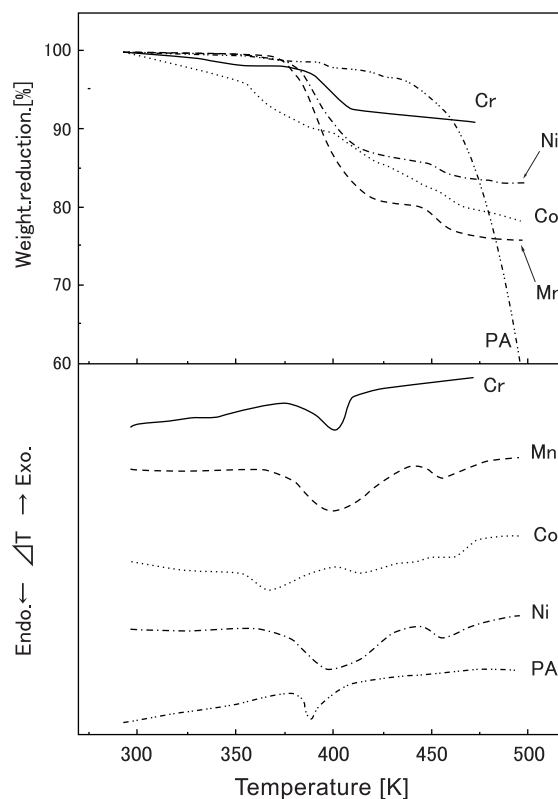


Fig. 3 TG-DTA results for transition-metal picrates and picric acid (upper column: TG, lower column: DTA).

were redissolved in deionized H<sub>2</sub>O, then recrystallized and dried in a vacuum at 298 K for 24 hours prior to TG-TDA. The results of TG-DTA of transition-metal picrates reveal endothermic phenomena attributed to the dehydration of crystal water with an accompanying weight reduction. This occurred in a step-wise manner with increasing temperature. All the transition-metal picrates exhibit different weight-reduction temperatures. It was confirmed that the weight reduction for Cr-picrate and Co-picrate started at nearly room temperature, whereas the weight reduction of Mn-picrate and Ni-picrate began at approximately 370 K. The weight reduction of Mn-picrate, Co-picrate and Ni-picrate ended at approximately 470 K, whereas Cr-picrate ceased weight losing at approximately 420 K.

It is estimated that the endothermic peaks in the DSC analysis of transition-metal picrates represent the reaction of dehydration. However, the endothermic peak occurred at different temperatures in DSC analysis and TG-DTA, attributable to the different sample conditions; in DSC measurement the sample was held in a crimped cell under 3 MPa pressure, whereas in TG-DTA measurement the sample was laid in an open cell at atmospheric pressure. The endothermic phenomenon observed in TG-DTA measurement for picric acid relates to the melting of picric

acid crystal, and weight reduction started at approximately 430 K, which was thought to be due to decomposition and/or evaporation of picric acid<sup>8)</sup>.

### 3.2 Molecular form

The results of x-ray fluorescence analysis for Cr-picrate has reflection patterns which was characteristic of Cr, and signal attributable to Na was not observed. Therefore, the Cr-picrate sample did not contain the intermediate of Na-picrate. Reflection patterns of Mn-picrate and Ni-picrate did not have signal of Ba element. Therefore, the Mn-picrate and Ni-picrate sample did not contain the intermediate of Ba-picrate.

Figure 4 shows the results of FT-IR analysis. The results for all of the transition-metal picrates are similar, and are also similar to the results for iron, copper, zinc and alkaline-earth metal picrates<sup>8-11)</sup>. The adsorption at 1270 cm<sup>-1</sup> in the FT-IR indicates bond stretching between a phenyl group and an oxygen atom, while the absorptions at approximately 1330 cm<sup>-1</sup> and 1560 cm<sup>-1</sup> suggest N-O bond stretching. The FT-IR results for transition-metal picrates are similar to those for picric acid, and this conclude their similar molecular form to picric acid. Similar results have been reported previously for other metal picrates<sup>8-11)</sup>.

### 3.3 Crystal water

The sample crystal was pretreated by drying in a vacuum chamber at 298 K immediately after extraction from solution. Table 2 shows the results of TG analysis, and Table 3 shows the results of the Karl Fischer analysis. The two results confirm that there are no large differences in crystal water content. The results of the two methods differ slightly being attributable to minor changes in atmospheric humidity during the course of measurements. It has been known for some time that the crystal water content in metallic picrates changes with atmospheric temperature<sup>11)</sup>.

### 3.4 Yield

Table 4 shows the synthesis yields of transition-metal picrates calculated using the crystal water content determined by the Karl Fischer method in Table 3. Synthesized sodium picrate was defined as 1.0 hydrate, and barium picrate was as 2.7 hydrate. The yield of Cr-picrate (58.9%) was lower than that for the other picrates. Cr-picrate was synthesized from chromium nitrate, but other picrate were synthesized from sulfate or carbonate. Therefore, it is estimated that a starting material influenced the difference in yield.

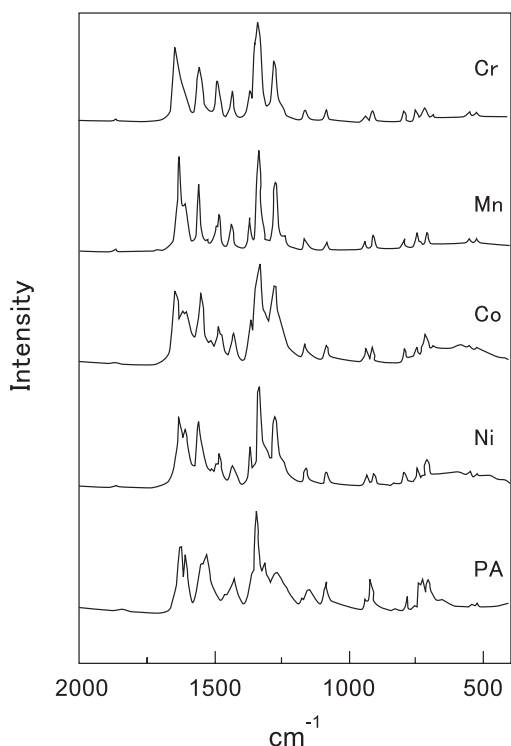


Fig. 4 FT-IR spectra of transition-metal picrates and picric acid.

Table 2 Crystal water of transition-metal picrates obtained from TG.

	Cr-picrate	Mn-picrate	Co-picrate	Ni-picrate
Weight reduction	7.2%	21.6%	20.5%	16.7%
H <sub>2</sub> O molecules*	3.2	7.8	7.4	5.7

\*Numbers of H<sub>2</sub>O molecules per 1 metal-picrate molecule.

**Table 3** Crystal water of transition-metal picrates obtained from Karl Fischer analysis.

	Cr-picrate	Mn-picrate	Co-picrate	Ni-picrate	Picric Acid
H <sub>2</sub> O quantity	8.4%	21.6%	20.6%	17.0%	0.22%
H <sub>2</sub> O molecules*	3.8	7.8	7.4	5.9	–

\*Numbers of H<sub>2</sub>O molecules per 1 metal-picrate molecule.**Table 4** Yield of transition-metal picrates based on crystal water molecules amount.

	Molecule weight as anhydrate	H <sub>2</sub> O molecules*	Yield [%]
Cr-picrate	736.39	3.8	58.9
Mn-picrate	512.23	7.8	84.5
Co-picrate	515.13	7.4	74.8
Ni-picrate	516.01	5.9	91.0

\* Numbers of H<sub>2</sub>O molecules were obtained from Table 3 (Karl Fischer method).**Table 5** Activation energy of the decomposition of transition- metal picrates.

Cr-picrate	Mn-picrate	Co-picrate	Ni-picrate
204.1 kJ·mol <sup>-1</sup>	108.1 kJ·mol <sup>-1</sup>	132.3 kJ·mol <sup>-1</sup>	184.3 kJ·mol <sup>-1</sup>

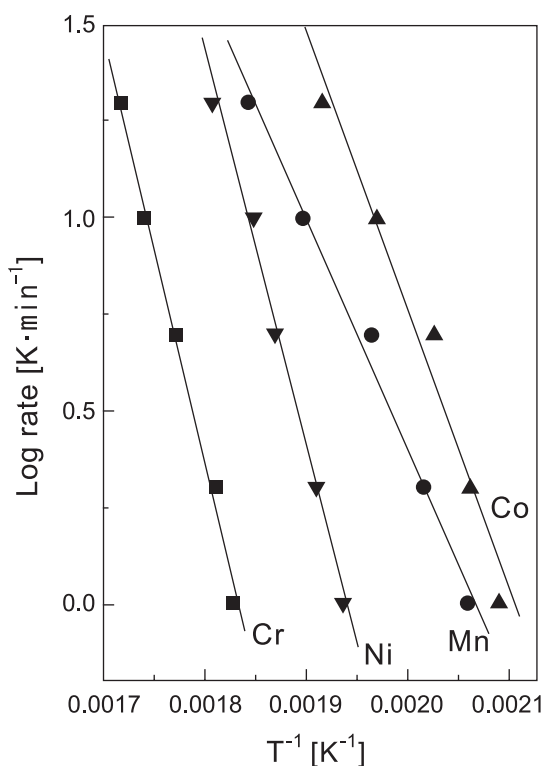
### 3.5 Activation energy of exothermal decomposition

The activation energies of the transition metal picrates were obtained by the method of Ozawa<sup>12)</sup>. The results are listed in Table 5. The DSC were measured at 1, 2, 5, 10, and 20 K·min<sup>-1</sup>, and the decomposition start temperatures (T<sub>0</sub>) obtained from the exothermic curve of decomposition were extrapolated to determine the baseline. T<sub>0</sub> was plotted at each heating rate (Fig. 5), and the activation energy was determined by Ozawa's equation.

Mn-picrate and Co-picrate were found to have lower activation energies than the other picrates and picric acid (144 kJ·mol<sup>-1</sup>), the activation energy of Cr-picrate was higher than 200 kJ·mol<sup>-1</sup>, much higher than the other picrates. The value was in the order of Cr-picrate > Ni-picrate (> picric acid) > Co-picrate > Mn-picrate.

### 3.6 Sensitivity test

Table 6 shows the results of drop hammer and friction sensitivity tests for samples pretreated in a vacuum at 298 K. In the drop hammer tests, Cr-picrate was found to be the most sensitive to impact, but the samples were confirmed to have undergone decomposition rather than explosion. Extremely sensitive materials commonly explode upon impact in drop hammer tests even when the hammer is dropped from low heights. However, in this case, even at the highest drop height (50 cm), the Cr-picrate could only induce decomposition. Therefore, Cr-picrate undergoes decomposition with only a slight impact,

**Fig. 5** Ozawa's plots for the decomposition of transition metal picrates.

**Table 6** Sensitivities of drop hammer and friction tests for transition-metal picrates.

	Cr-picrate	Mn-picrate	Co-picrate	Ni-picrate	Picric Acid
Drop hammer test (1/6 Explosion point)	5–10cm	More than 50cm	15–20cm	40–50cm	15–20cm
	Class 2	Class 8	Class 4	Class 7	Class 4
Friction sensitivity test (1/6 Explosion point)	16–36 kgf	over 36 kgf	over 36 kgf	16–36 kgf	16–36 kgf
	Class 6	Class 7	Class 7	Class 6	Class 6

but does not explode.

The results of the friction sensitivity test revealed that all of the transition-metal picrates are less than or equally sensitive to friction compared to picric acid.

### Conclusions

It was confirmed that pure forms of the intended transition metal picrates were successfully synthesized, and that the products have a molecular structure similar to that of picric acid. The decomposition reactions of Mn-picrate and Co-picrate occur at lower temperature than that of picric acid, indicating that the heat of decomposition for these transition-metal picrates is also lower than that of picric acid. Crystal water dehydrates from these picrates at the temperature between just above room temperature and approximately 470 K. With additional analysis by the Karl Fischer method, it was shown that these picrates hold an appreciable amount of crystal water even after vacuum drying at 298 K. The activation energies of the decomposition reaction of these transition-metal picrates were 204.1 kJ·mol<sup>-1</sup> for Cr-picrate, 108.1 kJ·mol<sup>-1</sup> for Mn-picrate, 132.3 kJ·mol<sup>-1</sup> for Co-picrate, and 184.3 kJ·mol<sup>-1</sup> for Ni-picrate, respectively. Drop hammer and friction tests revealed that Cr-picrate has higher impact sensitivity than picric acid, but that all of the transition-metal picrates have low friction sensitivity.

### Acknowledgments

This study was conducted under the auspices of the ACW office of the Cabinet Office and the Japan Institute of International affairs.

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