

# Hydrazine complexes of transition metals as perspective explosives

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## 1. Introduction

Research on coordination compounds of transition metals as potential explosives, particularly primary explosives, thrived in the 1950s and 1960s. However, their extremely high sensitivity to mechanical stimuli disrupted this research. A revival has been observed since the 1980s, when new materials appeared, such as NHN/NiHN – nickel hydrazinium nitrate, or HATP – di-(4-amino-3-hydrazino-1,2,3-triazole)-copper(II) perchlorate [1 ÷ 3]. The research is on-going, and the compounds obtained frequently show low sensitivity to mechanical stimuli and high energetic parameters [4, 5] and stimulation by laser radiation, and may therefore be used in the manufacture of laser detonators and primers [6-7]. Modern explosives and blasting agents also include NPED (*Non Primary Explosives Detonator*) type detonators and blasting cups. Complex compounds may constitute excellent material for formulating these.

### 1.1. Hydrazine complexes

One of the ligands present in coordination primary explosives is hydrazine. A research team in China had prepared and studied a compound usually referred to as NHN – nickel hydrazinium nitrate [1].

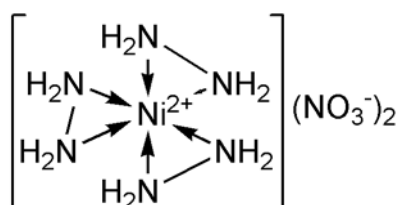


Fig. 1. Structure of nickel hydrazinium nitrate (NHN)

This compound has been examined and described in detail. The following data have been presented: solubility in water, acetone, ethanol, methanol and ether; detonation velocity; sensitivity to friction, impact and electric spark; effect of compacting pressure on density and explosive transformability at given compacting pressure. The study has shown that the compound was practically insoluble in such solvents as water, alcohols, ether; its detonation velocity at maximum density of 1.7 g/cm<sup>3</sup> was 7000 m/s, its impact sensitivity was within 21 ÷ 26 cm as tested by dropping a weight of 400 g. The result of friction sensitivity tests carried out under the pressure of 588.4 kPa, was 12% reaction, whereas the minimum energy of an electric spark that caused firing of NHN was 0.02 J.

The tests have also shown that NHN could be dead-pressed. Above the pressure of 60 MPa the amount of deflagration increased in relation to detonation. The explosivity vs. moisture content characteristics were as follows: 25% water – 80% explosions, 35% water – 20% explosions, 40% water – 0% explosions.

Testing of initiating power showed that the mass of NHN required for detonating pressed PETN was 150 mg when using fuse head and 120 mg when using detonating tube.

Despite lower sensitivity than other primary explosives, such as PbN<sub>6</sub>, tetrazene or diazodinitrophenol (DDNP), it still could hardly be considered a safe or low sensitive primary explosive.

### 1.2. NHN analogues

Another research team in China had synthesized and studied an NHN analogue having an azide group as the anion [8]. This compound, however, was less sensitive to mechanical stimuli and flame – 50 cm in the drop hammer (800g) test, 72% explosions caused by friction under the pressure of 1 kg, and detonation under the action of flame of a black powder pellet.

J. S. Chhabra *et al.* [9] reported on their work on NiHN and its cobalt analogue CoHN. In addition to studies on synthesis, thermal stability and structural analysis, sensitivities to friction and impact were presented along with the characterization of NiHN and CoHN mixtures with KClO<sub>3</sub>, Pb<sub>2</sub>[Fe(CN)<sub>6</sub>], AgN<sub>3</sub> and glass (Tab. I).

Table I

Friction and impact sensitivities of NiHN and CoHN and mixtures thereof

Mixture (component ratio)	Impact sensitivity $h_{50}$ , cm	Friction sensitivity, N
NiHN	96	10
NiHN + KClO <sub>3</sub>	9:1	10
	7:3	5
NiHN + Pb <sub>2</sub> [Fe(CN) <sub>6</sub> ]	9:1	16
	7:3	64
NiHN + AgN <sub>3</sub>	100:2.5	8
	100:5.0	8
	100:10.0	6
NiHN + glass	100:2.5	10
	100:5.0	10
	100:10.0	8
CoHN	59	60
CoHN + KClO <sub>3</sub>	9:1	16
	7:3	64
CoHN + Pb <sub>2</sub> [Fe(CN) <sub>6</sub> ]	9:1	40
	7:3	64

The tests have also shown that CoHN had no initiating properties like NiHN. NiHN could be used as an explosive alone and in mixtures. CoHN could be used effectively as a propellant or an additive to propellants and powders.

## 2. Experimental

Chemists and process engineers dealing with explosives are interested not only in the use of metal salts already studied, but also in

other metal salts. No direct correlation has so far been found between the core of the complex and its detonation properties. Studies are conducted in such manner as to ensure that the metal introduced into the complex is toxicologically safe, readily available at reasonable price, and above all, that the salt used enables the formation of the adopted complex structure.

## 2.1. Synthesis and structure confirmation

Our plan included the synthesis of hydrazine complexes of copper, mercury, chromium, cobalt, nickel, zinc and cadmium in nitrate and perchlorate analogues (Figs. 2, 3). The high reduction potential of hydrazine precluded the obtaining of copper and mercury complexes. Preliminary tests revealed that nickel hydrazinium nitrate had such high sensitivity to friction that its synthesis on a larger scale enabling the study of its performance was abandoned.

Structural analysis was performed in order to confirm the structure of the complexes obtained. Elemental analysis showed that the compounds contained carbon, nitrogen and hydrogen. X-ray fluorescence spectroscopy confirmed the presence of a metal in the sample, while infrared spectroscopy confirmed the content of individual structural components of the complexes (Tab. 3 ÷ 7).

C, H and N elemental analysis was performed on a Perkin Elmer Series II CHNS/O Analyzer 2400, IR spectra of solids (KBr pellet) were obtained on a BioRad FTIR I 75S spectrometer within the spectral range of  $640 \div 4000 \text{ cm}^{-1}$ , whereas metals were determined on an EDXRF Spectro Xepos analyzer.

### 2.1.1. Nitrate analogues

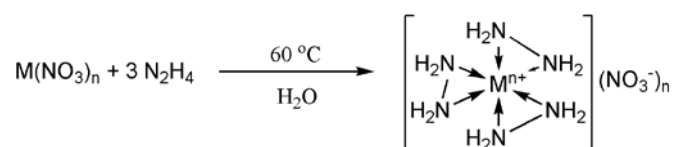


Fig. 2. Preparation route for hydrazine nitrate complexes

Into a 500 cm<sup>3</sup> conical flask placed in a water bath and equipped with a mechanical stirrer, thermometer and dropping funnel, 0.02 mole of appropriate nitrate were introduced, followed by 200 cm<sup>3</sup> water. The dropping funnel was filled with 4.12 cm<sup>3</sup> (3.30 g; 0.066 mole) of 80% solution of hydrazine hydrate. The salt solution was stirred and heated to 60°C. The hydrazine solution was added dropwise over a period of ca. 30 minutes. After all of the hydrazine solution was added the solution was stirred for another 60 minutes, after which it was transferred into a rotary evaporator and evaporated to dryness. The residue obtained was recrystallized from ethanol (Tab. 2).

Table 2

Summary of synthesis of hydrazine nitrate complexes

#	Nitrate used	Nitrate amount, g	Compound obtained	Compound amount, g	Reaction yield, %
1	Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	5.82	[Co(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	3.13	47.0
2	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	6.82	[Ni(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	6.06	91.1
3	Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	5.95	[Zn(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	6.16	90.8
4	Cd(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	6.17	[Cd(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	7.24	93.7
5	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	8.00	[Cr(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	7.23	93.4

Table 3

Results of instrumental and XRF analysis of hydrazine nitrate complexes

#	Compound	Elemental analysis, %						XRF analysis, %	
		Calculated			Determined			M <sub>cal.</sub>	M <sub>det.</sub>
		C	H	N	C	H	N		
1	[Co(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	0.00	2.61	31.73	0.00	2.66	31.79	19.07	19.02
2	[Ni(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	0.00	4.34	40.19	0.00	4.26	40.26	21.05	21.01
3	[Zn(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	0.00	4.24	39.24	0.00	4.20	39.29	22.91	22.87
4	Cd(Hz) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub>	0.00	3.64	33.69	0.00	3.72	33.63	33.60	33.68
5	[Cr(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	0.00	3.62	37.73	0.00	3.73	37.87	15.56	15.68

Table 4

Results of IR spectrophotometry of hydrazine nitrate complexes

#	Compound	IR spectroscopy (KBr), cm <sup>-1</sup>	
		NO <sub>3</sub>	NH <sub>2</sub>
1	[Co(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	1381	1624, 3265
2	[Ni(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	1385	1628, 3241
3	[Zn(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	1381	1624, 3261
4	Cd(Hz) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub>	1354	1597, 3265
5	[Cr(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	1362	1620, 3234

### 2.1.2. Perchlorate analogues

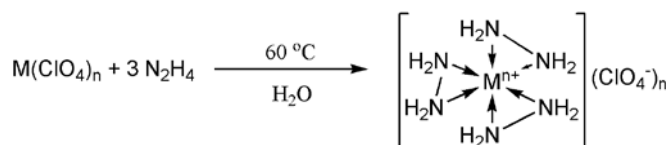


Fig. 3. Preparation route for hydrazine perchlorate complexes

In a 500 cm<sup>3</sup> conical flask placed in a water bath and equipped with a mechanical stirrer, thermometer and dropping funnel, 0.02 mole of respective perchlorate were introduced, followed by 200 cm<sup>3</sup> water. The dropping funnel was filled with 4.12 cm<sup>3</sup> (3.30 g; 0.066 mole) of 80% solution of hydrazine hydrate. The salt solution was stirred and heated to 60°C. The hydrazine solution was added dropwise over a period of ca. 30 minutes. After all of the hydrazine solution was added the solution was stirred for another 60 minutes, after which it was transferred into a rotary evaporator and evaporated to dryness. The residue obtained was recrystallized from ethanol (Tab.5).

Table 5

Summary of synthesis of hydrazine perchlorate complexes

#	Perchlorate used	Perchlorate amount, g	Compound obtained	Compound amount, g	Reaction yield, %
1	Co(ClO <sub>4</sub> ) <sub>2</sub>	5.16	[Co(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	3.76	46.1
2	Ni(ClO <sub>4</sub> ) <sub>2</sub>	5.15	[Ni(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1.80	22.1
3	Zn(ClO <sub>4</sub> ) <sub>2</sub>	5.28	[Zn(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	7.96	96.1
4	Cd(ClO <sub>4</sub> ) <sub>2</sub>	6.23	[Cd(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	8.60	93.2
5	Cr(ClO <sub>4</sub> ) <sub>3</sub>	7.01	[Cr(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	9.11	91.0

Table 6

## Results of instrumental and XRF analysis of hydrazine perchlorate complexes

#	Compound	Elemental analysis, %						XRF analysis, %	
		Calculated			Determined			M <sub>cal.</sub>	M <sub>det.</sub>
		C	H	N	C	H	N		
1	[Co(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	0.00	2.67	18.53	0.00	2.49	18.50	13.00	13.15
2	[Zn(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	0.00	3.36	23.32	0.00	3.49	23.39	18.15	18.29
3	[Cd(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	0.00	2.97	20.63	0.00	3.02	20.77	27.59	29.68
4	[Cr(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	0.00	2.71	18.82	0.00	2.70	18.78	11.65	11.76

Table 7

## Results of IR spectrophotometry of hydrazine perchlorate complexes

#	Compound	IR spectroscopy (KBr), cm <sup>-1</sup>	
		ClO <sub>4</sub>	NH <sub>2</sub>
1	[Co(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	1142	1628, 3241
2	[Zn(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1084	1609, 3241
3	[Cd(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1084	1605, 3245
4	[Cr(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	1092	1628, 3245

## 2.2. Safety of use testing

## 2.2.1. Friction sensitivity

The obtained explosives were tested for friction sensitivity in accordance with the PN-EN 13631-3:2006 standard. The tests were performed until two sensitivity limits were determined: upper insensitivity limit (UIL), that is the highest load at which no reaction was obtained in the material tested in six subsequent trials, and lower sensitivity limit (LSL), that is the lowest load at which a reaction was obtained in the material tested in at least one out of six trials (Tab. 8).

Table 8

## Friction sensitivity values of nitrate and perchlorate complexes containing hydrazine as the ligand

Compound	Friction sensitivity, N		Compound	Friction sensitivity, N	
	UIL	LSL		UIL	LSL
[Co(Hz) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	54	60	[Co(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	28	36
[Ni(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	20	24	[Ni(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	< 1	---
[Zn(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	360	> 360	[Zn(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	180	192
[Cd(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	192	216	[Cd(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	1.5	2
[Cr(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	60	64	[Cr(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	84	96

## 2.2.2. Impact sensitivity

The obtained explosives were tested for impact sensitivity in accordance with the PN-EN 13631-4:2006 standard.

The tests were performed until two impact sensitivity limits were determined: upper insensitivity limit (UIL), that is the highest impact energy at which no reaction was obtained in the material tested in six subsequent trials, and lower sensitivity limit (LSL), that is the lowest impact energy at which a reaction was obtained in the material tested in at least one out of six trials (Tab.9).

Table 9

## Impact sensitivity values of nitrate and perchlorate complexes containing hydrazine as the ligand

Compound	Impact sensitivity, Nm		Compound	Impact sensitivity, Nm	
	UIL	LSL		UIL	LSL
[Co(Hz) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	---	> 25	[Co(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	---	> 25
[Ni(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	9	10	[Ni(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	---	---
[Zn(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	---	> 25	[Zn(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	---	> 25
[Cd(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	---	> 25	[Cd(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	5	6
[Cr(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	---	> 25	[Cr(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	1	2

## 2.2.3. Sensitivity to static electricity

There are no standards concerning testing of explosives with regard to their sensitivity to static electricity. In our tests we have applied a method and apparatus developed by the Institute of Industrial Organic Chemistry in Warsaw (IPO), Krupski Młyn Branch, for determining sensitivity to static electricity.

The basic component of the apparatus was a spark generator comprising a high voltage power supply and a battery of capacitors. The power supply charges the battery of capacitors of defined capacity, at set voltage, after which the battery of capacitors is discharged in the form of a spark through the compound tested placed between two electrodes.

Table 10

## Static electricity sensitivity values of nitrate and perchlorate complexes containing hydrazine as the ligand

Compound	Spark energy, J		Compound	Spark energy, J	
	UIL	LSL		UIL	LSL
[Co(Hz) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	2.000	2.250	[Co(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	0.720	0.840
[Ni(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	0.023	0.027	[Ni(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	---	---
[Zn(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	0.600	0.720	[Zn(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	7.500	9.000
[Cd(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	0.070	0.080	[Cd(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	0.007	0.010
[Cr(Hz) <sub>3</sub> ](NO <sub>3</sub> ) <sub>3</sub>	1.000	1.167	[Cr(Hz) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	1.500	1.750

A standard sample of the tested compound was placed in the pocket of the electrode socket; it was covered with a foil disk with a central hole and secured with a cap. The top and bottom electrodes were brought closer together and the spark generator was actuated.

After the capacitors were charged to the required voltage, a spark was triggered. If a reaction was observed in the material tested, i.e. when a sound of a crack or a flash occurred, or the material had burnt or charred, then the test was repeated with a new sample using lower spark energy. The sample was also observed by a photo detector, which transmitted an impulse to an oscilloscope when a flame occurred.

The tests were performed until two sensitivity limits were determined: upper insensitivity limit (UIL), that is the highest spark energy, at which no reaction was obtained in the material tested in six subsequent trials, and lower sensitivity limit (LSL), that is the lowest spark energy at which a reaction was obtained in the material tested in at least one out of six trials.

### 3. Summary

Synthesis of nitrate and perchlorate hydrazine complexes of cobalt, zinc, cadmium, nickel and chrome can be carried out in a controlled and safe manner with satisfactory yields under laboratory conditions without the need to use expensive inaqueous solvents. Elemental, IR and XRF analyses have confirmed the structure of the complexes obtained and purity thereof after single crystallization.

The lowest sensitivity to fracture was shown by compounds of chromium, zinc and cadmium, except for  $[\text{Cd}(\text{Hz})_3](\text{ClO}_4)_2$ , which showed sensitivity equal to that of typical primary explosives. Sufficiently safe in use and processing proved to be the compounds of cobalt and nickel, in the case of which the load that triggered a reaction of the material reached tens or even hundreds of N. One exception was  $[\text{Ni}(\text{Hz})_3](\text{NO}_3)_2$ , the sensitivity of which at a level of 20 N was reported in the literature [1]. Its perchlorate analogue showed such high sensitivity to friction that after synthesizing 2 g of this compound further studies on it were halted, and its precise friction sensitivity has not been determined during the tests.

Friction sensitivities of some traditional explosives (lead azide – 0.1 N; lead trinitroresorcinate – 1.5 N; mercury fulminate (white) – 5.0 N; tetrazene – 8.0 N; PETN – 60 N; hexogen – 120 N; octogen – 120 N [10], show that the explosives obtained are not very sensitive, and are thereby not exceedingly hazardous in handling.

The compounds tested showed high resistance to impact stimulus. Most of them were not initiated by a drop hammer impact of 25 Nm, which was adopted as the set upper limit. One exception was  $[\text{Cr}(\text{Hz})_3](\text{ClO}_4)_3$ , in the case of which the limits of 1 and 2 Nm indicated high sensitivity to this type of stimulus. The other compounds, the sensitivities of which were determined at the level of 6 to 9 Nm, should not be deemed exceedingly sensitive if one takes into account the fact that the corresponding values for such traditional explosives as PETN or lead azide are much lower (lead azide – 7.5 Nm; lead trinitroresorcinate – 15 Nm; mercury fulminate (white) – 2 Nm; tetrazene – 2 Nm; PETN – 3 Nm; hexogen – 7.5 Nm; octogen – 7.4 Nm; tetryl – 3 Nm) [11].

Sensitivity to static electricity is not part of usual testing of the reaction of explosives to simple stimuli. Such test, however, is important as the probability of producing an electrostatic spark during transportation and handling of explosives is high.

The compounds studied demonstrated diverse sensitivities to this type of stimulus.  $[\text{Cd}(\text{Hz})_3](\text{ClO}_4)_2$  proved to be the most sensitive, and it also showed the highest sensitivity in friction and impact tests. This compound has the properties of a primary explosive [12] and the sensitivities it shows are characteristic of this group of materials. In relation to the sensitivities to electrostatic stimulus reported in the literature (lead azide – 0.037 - 0.113  $\mu\text{J}$ ; lead trinitroresorcinate – 0.40 - 0.72  $\mu\text{J}$ ; tetrazene – 2.0 - 7.6 mJ; PETN – 300 - 436 mJ;  $\mu$ -tris(4-amino-1,2,4-triazole)-copper(II) chlorate – 120 - 198 mJ) [13], the compounds studied showed moderate sensitivity values.

The compounds obtained constitute prospective explosives that could be used both in blasting agents, as well as form explosives on their own or be included as ingredients of detonating or priming materials.

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