

# Energetic co-ordination compounds: synthesis, characterization and thermolysis studies on bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate (BNCP) and its new transition metal (Ni/Cu/Zn) perchlorate analogues

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## Abstract

Bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine[cobalt(III)/nickel(III)] perchlorates (BNCP/BNNP) and mono-(5-nitro-*H*-tetrazolato-*N*)triammine [copper(II)/zinc(II)] perchlorates (MNCuP/MNZnP) have been synthesized during this work. The synthesis was carried out by addition of carbonato tetraammine metal [Co/Ni/Cu/Zn] nitrate [CTCN/CTNN/CTCuN/CTZnN] to the aqueous solution of sodium salt of 5-nitrotetrazole followed by reaction with perchloric acid. The precursors were synthesized by the reaction of aqueous solution of their respective nitrates with ammonium carbonate at 70 °C. The complexes and their precursors were characterized by determining metal and perchlorate content as well as infrared (IR), electron spectra for chemical analysis (ESCA) and X-ray diffraction (XRD) techniques. The TG profiles indicated that BNCP, BNNP and MNCuP are thermally stable up to the temperature of 260–278 °C unlike MNZnP (150 °C). Sudden exothermic decomposition was observed in case of bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate, bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine nickel(III) perchlorate and mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate resulting in the severe damage of the sample cup. Sensitivity data indicated that the Co/Ni/Cu complexes are more friction sensitive (3–4.8 kg) than mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate (14 kg). The impact sensitivity results of the complexes corresponded to *h*<sub>50%</sub> of 30–36 cm.

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**Keywords:** Thermolysis; Synthesis; Characterization; Transition metal analogues of bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate (BNCP); Carbonato tetraammine cobalt(III) nitrate(CTCN); Hazardous materials; Lead-free primary explosives

## 1. Introduction

The conventional primary explosives such as lead azide, despite being excellent detonating agents, suffer from serious drawbacks of hydrolytic instability, high sensitivity towards mechanical stimuli and incompatibility with metals as well as metal alloys commonly used as structure materials in initiating devices. Efforts are in progress in Research and Development laboratories all over the globe to develop

lead-free safe primary explosives based on energetic co-ordination compounds [1–5]. One of the major advantages of energetic co-ordination compounds is the presence of near stoichiometric fuel/oxidizer content. A few studies undertaken on relationship between co-ordinate compound structures and explosive properties, have brought in focus nitrate/perchlorate complexes of transition metal ions with nitro/amino tetrazoles and triazoles as energetic ligands [6–8].

High energy inorganic co-ordination compound; pentaammine (5-cyno-2*H*-tetrazolato-*N*) cobalt(III) perchlorate (CP) has been reported as a detonant for specific applications [9,10]. However, it is no longer manufactured, as one of

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its starting materials; cyanogen falls under the restricted list of Environmental Protection Agency. Tetraammine-cis-bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>) cobalt(III) perchlorate (BNCP) is another interesting compound reported by various researchers [11–15], as a promising lead-free primary explosive for semi-conducting bridge applications. The research programme on BNCP is being actively pursued by Sandia National Laboratories, USA and it is under development at Pacific Scientific-Energetic Materials Co., USA. The finer details on the synthesis of tetraammine-cis-bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>) cobalt(III) perchlorate are not reported in the open literature.

We have recently reported the work on nickel hydrazinium nitrate and cobalt/nickel tris (carbohydrazide) perchlorates as potential lead-free initiators [16–19]. In continuation of our work on energetic co-ordination compounds [16–20], this paper reports the synthesis of one of the most sought after lead-free detonant viz., tetraammine-cis-bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>) cobalt(III) perchlorate based on the lines of the reported method with minor modification (Scheme 1). In addition, new BNCP variants (Ni, Cu and Zn) were also synthesized and characterized during this work (Scheme 2).

## 2. Experimental

### 2.1. Materials

The dicyandiamide (starting material) used for the synthesis was of AR grade, whereas sodium azide, metal nitrates, sodium nitrite, copper sulphate penta-hydrate, perchloric acid, nitric acid, ammonium hydroxide and ammonium carbonate were of SQ grade. They were used as such.

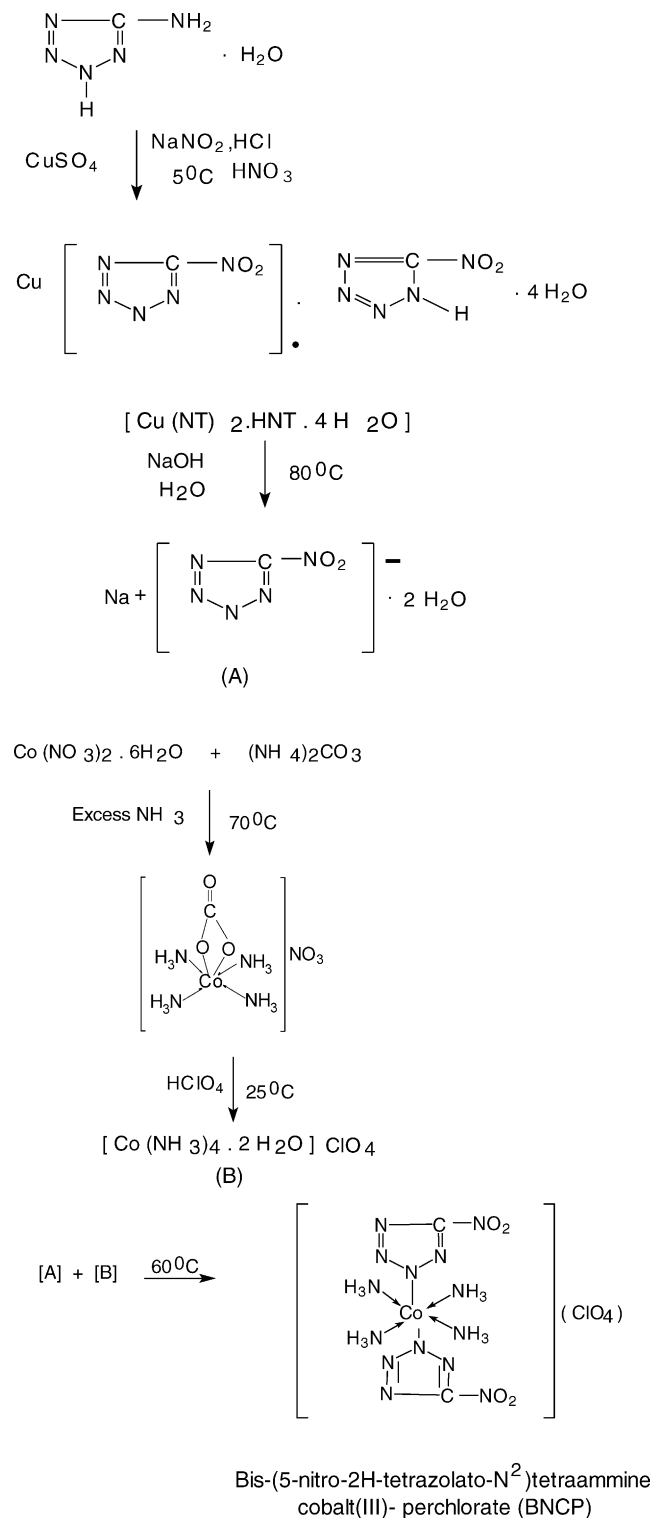
### 2.2. Methodology of synthesis

The sodium salt of nitrotetrazole [21], carbonato tetraammine cobalt(III) nitrate (CTCN) [22] and bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate (BNCP) were synthesized (Schemes 1 and 2) on the lines of the reported methodology [9–11]. The new precursors viz., carbonato tetraammine nickel(III) nitrate (CTNN), carbonato triammine copper(II) nitrate (CTCuN), carbonato triammine zinc(II) nitrate (CTZnN) and metal (Ni, Cu and Zn) analogues of BNCP viz., bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine nickel(III) perchlorate (BNNP), mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II) perchlorate (MNCuP) and mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate (MNZnP) were synthesized on the similar lines (Scheme 1) [9–11].

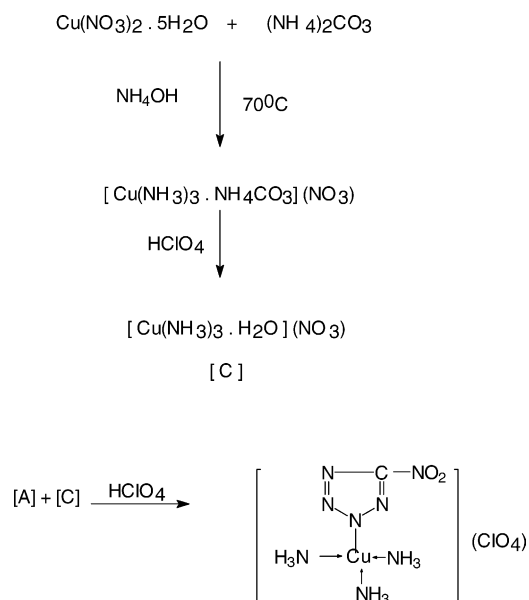
### 2.3. Preparation of sodium salt of 5-nitrotetrazole

The solution of 5-amino tetrazole (42 g, 0.5 mol) and copper sulphate penta-hydrate (2 g, 0.01 mol) in 64 cm<sup>3</sup> of 70%

nitric acid diluted with 700 cm<sup>3</sup> distilled water was added drop wise to the solution of sodium nitrite (~104 g, 1.5 mol), cooled to 5 °C in a 2 l beaker under vigorous stirring over a period of about 90 min. The temperature of the contents was maintained between 15 and 18 °C. After completion of the



Scheme 1. Synthesis of sodium salt of nitrotetrazolate.



Scheme 2. Mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II) perchlorate (MNCuP).

addition, the reaction mixture was digested for 15 min under efficient stirring and then filtered through Whatman filter paper No. 54 under suction. The pale green product obtained was washed with 250 cm<sup>3</sup> of 1.8N nitric acid followed by 3 × 250 cm<sup>3</sup> distilled water. The copper acid salt was transferred to a glass beaker and 600 cm<sup>3</sup> of distilled water was added to obtain a slurry which was alkalinized to pH 9 by adding 50% sodium hydroxide solution. The alkaline mixture was then heated on water bath (80 °C) under stirring. The black precipitate of copper oxide thus obtained was filtered off and the filtrate was cooled down to room temperature. Subsequently, the filtrate was acidified with 13N nitric acid till the pH of the solution reaches ~4. The mother liquor containing sodium salt of nitro tetrazole was used directly for synthesis of title complexes.

#### 2.4. Preparation of carbonato tetraammine nickel(III) nitrate

Nickel nitrate (100 g, 0.344 mol) was dissolved in warm distilled water and added to a solution of ammonium carbonate (200 g, 2.08 mol) in ammonium hydroxide (200 cm<sup>3</sup>). The resulting mixture was oxidized by adding 3% hydrogen peroxide (100 cm<sup>3</sup>) drop wise with vigorous mechanical stirring. After completion of addition, the solution was concentrated on a steam bath. The nickel oxide was filtered off and the filtrate was further concentrated. During course of the concentration process, solid ammonium carbonate (50 g) was added in installments. The solution was then cooled in ice and filtered under suction. The product obtained was washed with ethyl alcohol and dried. The carbonato tetraammine cobalt(III) nitrate, carbonato triammine copper(II) nitrate and

carbonato triammine zinc(II) nitrate were synthesized on similar lines.

#### 2.5. Preparation of bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine nickel(III) perchlorate

Three-neck round bottom flask (1 l) fitted with a mechanical stirrer, thermometer and dropping funnel was placed on a steam bath. carbonato tetraammine nickel(III) nitrate (4 g, 0.02 mol) and 30 cm<sup>3</sup> of perchloric acid (60%) were added to distilled water placed in the flask. The resultant mixture was heated to the temperature of 60 ± 10 °C till evolution of carbon dioxide bubbles ceased. Two hundred cubic centimeters of mother liquor containing sodium salt of nitrotetrazole (4.2 g, 6 mol) was added drop wise to the reaction mixture at ~80 °C under vigorous stirring. After completion of the addition, the reaction mixture was digested at elevated temperature for 2 h, then allowed to cool down to room temperature. The BNNP obtained was isolated by filtration under suction and dried at room temperature in an evacuated desiccator. The yield of final product was about 85%. Similarly, bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate, mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II) perchlorate (MNCuP), mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate (MNZnP) were also synthesized. The molar ratio of sodium salt of nitrotetrazole and carbonato triammine copper/zinc nitrate used during the synthesis of MNCuP and MNZnP was 1:2.

### 3. Characterization

#### 3.1. Metal content analysis

The metal and perchlorate contents of synthesized complexes as metal sulphate and salt of nitron respectively were determined by standard gravimetric method [23]. The experimentally obtained cobalt, nickel, copper and zinc content of the complexes were found in close agreement (Table 1) with the theoretical values corresponding to molecular formula: Co<sup>3+</sup>[C<sub>2</sub>H<sub>12</sub>N<sub>14</sub>O<sub>4</sub>]<sup>2-</sup>(ClO<sub>4</sub>)<sup>1-</sup>, Ni<sup>3+</sup>[C<sub>2</sub>H<sub>12</sub>N<sub>14</sub>O<sub>4</sub>]<sup>2-</sup>(ClO<sub>4</sub>)<sup>1-</sup>, Cu<sup>2+</sup>[CH<sub>9</sub>N<sub>8</sub>O<sub>2</sub>]<sup>1-</sup>(ClO<sub>4</sub>)<sup>1-</sup> and Zn<sup>2+</sup>[CH<sub>9</sub>N<sub>8</sub>O<sub>2</sub>]<sup>1-</sup>(ClO<sub>4</sub>)<sup>1-</sup>.

#### 3.2. Infrared (IR) spectral analysis

The bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate and its transition metal analogues were also characterized by Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Model-1605) in KBr matrix.

#### 3.3. Scanning electron microscopy

The morphology of the prepared complexes was investigated by scanning electron microscope (SEM, Philips Icon

Table 1  
Physicochemical and spectroscopic properties of nitrotetrazole complexes

Properties	BNCP	BNNP	MNCuP	MNZnP
Metal content (%)	12.90	12.87	19.40	19.65
Physical form	Needle and plate	Needle shape	Irregular plate	Plate type
BD (g/cm <sup>3</sup> )	0.30–0.60	0.54	0.65	0.85
Decomposition on set temperature (°C)	268	278	260	120
Impact <i>h</i> <sub>50%</sub> (cm)	32	30	30	36
Friction sensitivity (kg)	3	3	4.8	14
IR (cm <sup>-1</sup> )				
NH <sub>3</sub>	3475, 1866	3466, 1870	3488, 1870	3470, 1866
NO <sub>2</sub>	1564	1564	1564	1564
	1326	1326	1326	1334
NT ring	1440, 1230	1442, 1236	1440, 1234	1440, 1232
ClO <sub>4</sub>	1070, 962, 620	1072 & 942, 624	1064 & 938, 618	1088, 625
M–N	478	480	474	472

M = Co, Ni, Cu & Zn; BD: bulk density;  $E_a$ : energy of activation; BNCP: bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate; BNNP: bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine nickel(III) perchlorate; MNCuP: mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II) perchlorate; MNZnP: mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate.

model SEM-XL30) instrument at 10–20 kV. The specimen chamber as well as the microscopic column was maintained at a high vacuum ( $\sim 10^{-5}$  Torr) throughout the study. The surface of all the complexes was coated with conducting material (gold) by the sputtering technique prior to scanning.

#### 3.4. Electron spectroscopy for chemical analysis (ESCA)

The ESCA of all the samples were recorded on an ESCA model 3000, VG Microtech UK instrument, using Mg K $\alpha$  (1253.6 eV) radiation source. The binding energies of all the elements in the complexes were corrected by taking C 1s binding energy = 285.0 eV as an internal standard. The experiments were carried under high vacuum of the order of  $10^{-9}$  Torr. The results obtained were compared with standard binding energies of metal ions reported in literature [24].

#### 3.5. X-ray diffraction analysis (XRD)

A Philips automatic X-ray diffractometer (Model PW 1710) using anode operating at 40 kV and 30 mA with the wide angle X-ray diffractometer (WAXRD) was used for the present study on the complexes in powder form [25]. The diffracted X-ray intensities were recorded as a function of  $2\theta$  using Cu-target with nickel filter (Cu K $\alpha$   $\lambda = 1.540$  and  $1.544 \text{ \AA}$ ). The known equation [26] was used for the calculation of  $d$  values for BNCP by using values given in literature for constants  $a$ ,  $b$ ,  $c$ :  $1/d^2 = 1/\sin^2 \beta (h^2/a^2 + K^2 \sin^2 \beta/b^2 + l^2/c^2 - 2hl \cos \beta/ac)$ , where  $h$ ,  $k$ ,  $l$  are Miller indices and  $a$ ,  $b$ ,  $c$  are unit cell parameters.

#### 3.6. Thermal analysis

The thermal properties were studied by conducting simultaneous thermogravimetry (TG)/differential thermal analysis

(DTA) of Mettler Toledo (TG/SDTA 8551) make subjecting 0.3–3.43 mg of sample to heating at the rate of 5 °C/min in the nitrogen atmosphere. The TG of mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate was carried out on DSC-TGA instrument of SDT0500 V5.0 Bold-63 Universal V1-55 TA make.

#### 3.7. Thermo gravimetric Fourier transform infrared (TG-FTIR) studies

The gaseous decomposition products formed during thermo gravimetric analysis of one of the complexes viz., BNCP, were analyzed by FTIR (Brucker Equinox 55) in conjunction with TG (Mettler Toledo TG/SDTA 8551) at scanning rate of 8 scans/s using nitrogen as purging gas.

#### 3.8. Sensitivity

The impact sensitivity of the complexes was determined by the fall hammer method [27] using 2 kg drop weight (Bruceton analytical technique). The results are reported in terms of height for 50% probability of explosion ( $h_{50\%}$ ) and figure of insensitivity was computed with tetryl (composition exploding) as standard. Friction sensitivity was determined on Julius Peter's apparatus, by increasing weight on the lever in the increments of 0.2 kg, till there was no explosion/ignition in five consecutive tests at a given load. The results obtained for impact and friction sensitivity were within the uncertainty limits of  $\pm 2.5$  cm and  $\pm 0.2$  kg respectively.

#### 3.9. Method of disposal

All the complexes could be disintegrated on adding to 10% sodium hydroxide solution and were disposed off after 48 h.



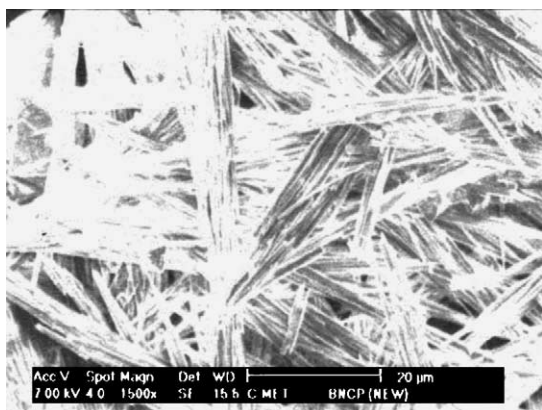


Fig. 1. SEM of BNCP.

## 4. Results and discussion

### 4.1. Infrared spectral studies

The precursors viz., carbonato tetraammine cobalt(III) nitrate, carbonato tetraammine nickel(III) nitrate, carbonato triammine copper(II) nitrate and carbonato triammine zinc(II) nitrate showed infrared absorptions in the range of  $3420\text{--}3440\text{ cm}^{-1}$  for  $\text{--NH}_3$  stretching. The absorption band in the region of  $1260\text{--}1280\text{ cm}^{-1}$  may be assigned to carbonato moiety whereas the bands in the region of  $1360\text{--}1384\text{ cm}^{-1}$  can be attributed to  $\text{NO}_3$ . The absorption in the region of  $470\text{--}510\text{ cm}^{-1}$  can be assigned to M–N stretching frequencies. In final products (BNCP, BNNP, MNCuP and MNZnP), the infrared absorption corresponding to  $\text{--NH}_3$  was observed in the region of  $3466\text{--}3475\text{ cm}^{-1}$  and that assignable to M–N in the region of  $472\text{--}480\text{ cm}^{-1}$ . The absorption in  $1440\text{--}1442\text{ cm}^{-1}$  region for all the complexes is assignable to tetrazole ring, whereas two strong absorptions at  $1564$  and  $1326\text{ cm}^{-1}$  are characteristics of asymmetric and symmetric vibrations due to  $\text{--NO}_2$  group. The absorption bands in the region of  $1064\text{--}1088$  and  $938\text{--}962\text{ cm}^{-1}$  respectively may be attributed to the asymmetric and symmetric stretching of the perchlorate group (Table 1). The bending mode for perchlorate may be resulting

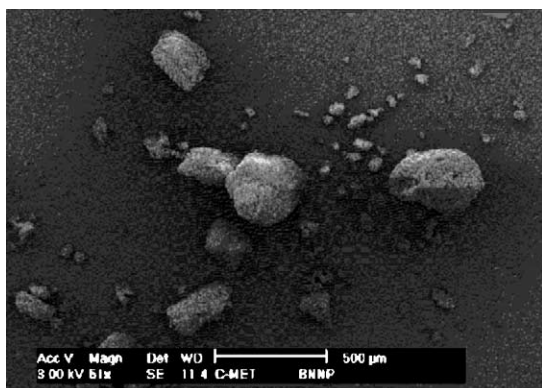


Fig. 2. SEM of BNNP.

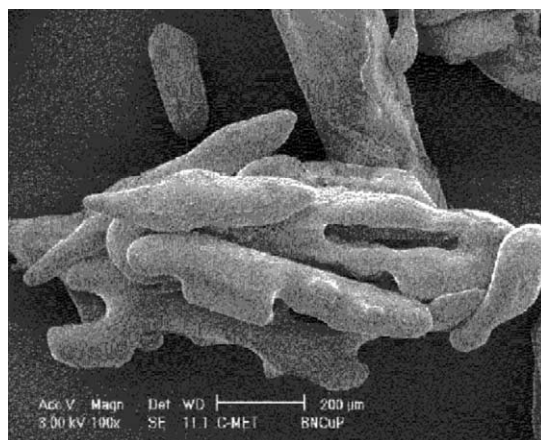


Fig. 3. SEM of MNCuP.

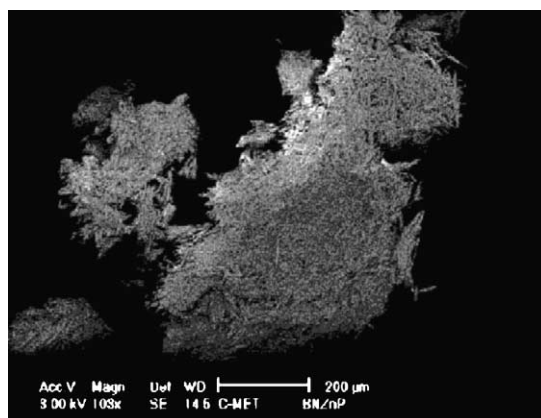


Fig. 4. SEM of MNZnP.

in infrared absorption in the range of  $618\text{--}625\text{ cm}^{-1}$ . The major infrared frequencies obtained for bis-(5-nitro-2*H*-tetrazolato- $N^2$ )tetraammine cobalt(III) perchlorate are in close agreement with the reported data [15].

### 4.2. Scanning electron microscopy (SEM) studies

SEM revealed needle shaped crystals for bis-(5-nitro-2*H*-tetrazolato- $N^2$ )tetraammine cobalt(III) perchlorate, and bis-(5-nitro-2*H*-tetrazolato- $N^2$ )tetraammine nickel(III) perchlorate whereas plate type crystals were observed for

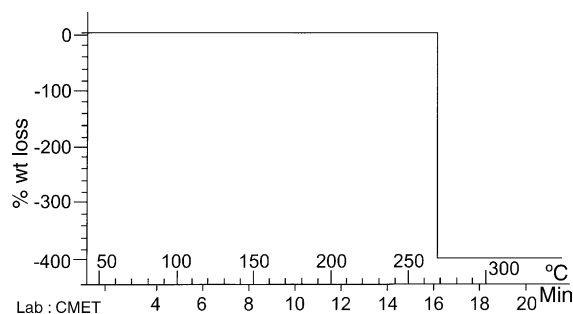


Fig. 5. TG of BNCP.

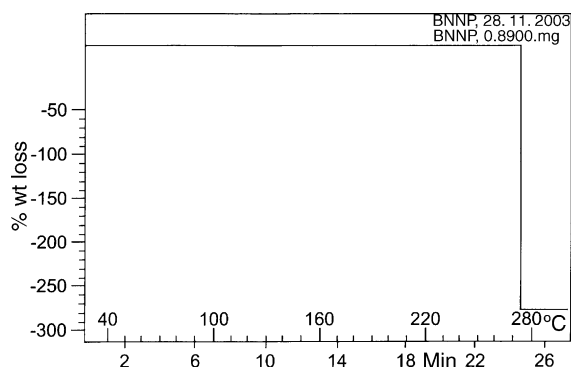


Fig. 6. TG of BNNP.

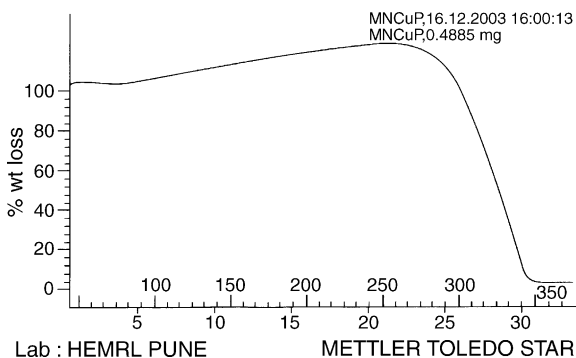


Fig. 7. TG of MNCuP.

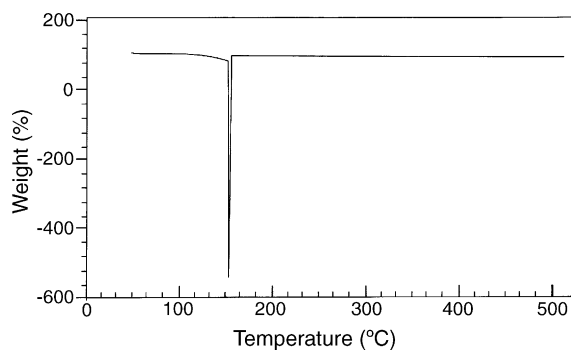


Fig. 8. TG of MNZnP.

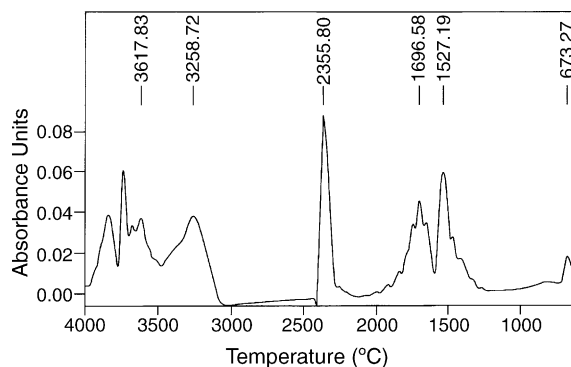


Fig. 9. TG-FTIR of BNCP.

mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II) perchlorate, mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate (Figs. 1–4).

#### 4.3. Thermal decompositions studies

In thermogravimetry analysis sudden weight loss was observed at 264, 278 and 150 °C for bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate (BNCP) (Fig. 5), bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine nickel(III) perchlorate (BNNP) (Fig. 6) and mono-(5-nitro-

*H*-tetrazolato-*N*)triammine zinc(II) perchlorate (MNZnP) (Fig. 7) respectively, whereas mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II) perchlorate (MNCuP) showed single stage decomposition (Fig. 8) in the temperature range of 260–338 °C accompanied with 95% weight loss. The relative thermal stability of BNCP and BNNP can be co-related with the relative acceptor properties of the central ion for the electrons co-ordinating group as well as stability constants (Ni: 18.06 and Co: 13.82) as reported [28] in case of (Nien<sub>3</sub>) and (Coen<sub>3</sub>) where en = ethylenediamine. The stability of co-ordination complexes is also decided by the size and charge of the metal ion as well as the second ionization potential

Table 2

Characterization of bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate and its metal analogues by electron spectrometer for chemical analysis (ESCA)

Sample name	Binding energy (eV)							
	C 1s	C 1s	Cl 2p	O 1s	N 1s	N 1s	2p <sub>3/2</sub>	2p <sub>1/2</sub>
CTCN	285.0	288.1	–	536.3	403.7	410.5	785.8 (Co)	802 (Co)
CTNN	285.0	289.4	–	532.0	407.6	409	856.8 (Co)	875 (Ni)
CTCuN	285.0	290.1	–	538.2	402.7	405.7	940.70 (Cu)	960 (Cu)
CTZnN	285.0	291.0	–	539.7	408.7	415.7	1030.2 (Zn)	1040 (Zn)
BNCP	285.0	287.3	207.9	532.5	401.1	406.5	783.0 (Co)	798.5 (Co)
BNNP	285.0	287.2	208.0	532.4	402.5	403.8	788.5 (Ni)	805.6 (Ni)
MNCuP	285.0	287.0	208.4	532.0	400.8	407.4	845.7 (Cu)	867.8 (Cu)
MNZnP	285.0	286.8	208.7	532.5	400.8	407.2	936.5 (Zn)	980.5 (Zn)

CTCN: carbonato tetraammine cobalt(III) nitrate; CTNN: carbonato tetraammine nickel(III) nitrate; CTCuN: carbonato triammine copper(II) nitrate; CTZnN: carbonato triammine zinc(II) nitrate; BNCP: bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate; BNNP: bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine nickel(III) perchlorate; MNCuP: mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II) perchlorate; MNZnP: mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate.

Table 3  
X-ray diffraction data of bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate (BNCP)

<i>d</i> -Value (Å)	Relative intensity (%)
7.1784	3.5
6.5390	12.2
5.9111	14.1
5.5571	31.2
5.4685	14.1
5.3449	12.8
4.8126	6.0
4.4825	83.3
4.3225	71.0
4.0252	36.3
3.8895	69.6
3.8275	100.0
3.7441	46.2
3.5554	13.1
3.5003	13.5
3.4036	12.2
3.2752	6.4
3.2065	16.5
3.0441	40.1
2.9388	2.5
2.8009	9.6
2.7270	6.2
2.6817	14.8
2.6448	8.3
2.5422	5.6
2.4649	8.1
2.4090	5.2
2.3259	6.2
2.2565	3.2
2.2197	6.6
2.1964	5.8
2.1036	10.4
2.0265	14.8
1.9962	4.0
1.9464	4.6
1.9162	5.8
1.8762	4.6
1.8093	4.4
1.7850	3.7
1.7562	3.2
1.7148	3.4
1.6453	1.5
1.5157	1.4

Table 4  
X-ray diffraction data of bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine nickel(III) perchlorate (BNNP)

<i>d</i> -Value (Å)	Relative intensity (%)
9.4257	100.0
5.8702	19.0
5.4668	29.1
4.7324	21.8
4.4184	37.8
4.0099	11.7
3.7581	14.1
3.5850	66.7
3.5044	23.0
3.4909	25.2
3.2373	45.6
3.1047	11.8
3.0953	11.3
2.9150	89.5
2.7465	1.9
2.6395	56.9
2.6308	62.0
2.5932	23.2
2.4850	6.0
2.4219	16.7
2.2823	2.4
2.2153	8.0
2.1558	22.0
2.0725	7.0
2.0560	4.5
2.0071	11.0
1.9627	1.4
1.8848	11.3
1.8420	8.0
1.8279	6.5
1.7950	2.1
1.7795	2.5
1.7475	5.0
1.7063	5.7
1.6640	11.8
1.6183	4.0
1.5988	0.9
1.5525	2.5
1.5211	7.3
1.4603	2.4
1.4457	1.6
1.4232	2.3
1.411	2.2
1.3925	3.1
1.3578	1.2

of metal atoms (Ni: 18.2 and Co: 17.3) [29]. The activation energy ( $E_a$ ) obtained from thermo gravimetric experiments revealed that relatively smaller energy barrier (124 kJ/mol) is encountered for the decomposition MNCuP as in case of well known initiators such as lead styphnate, lead azide and mercuric fulminate [30]. The activation energy of decomposition of bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate, bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine nickel(III) perchlorate, mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate could not be determined as they underwent violent reaction during thermolysis even at 1 mg sample size and caused severe damage to sample holder. The thermo gravimetric analysis of mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate showed

some progressive slow mass loss before it underwent violent reaction. The violent reaction may be due to detonation to deflagration transition of these materials.

The FTIR spectrum of decomposition products (Fig. 9) evolved during thermo gravimetric analysis of bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate revealed the absorptions assignable to  $-\text{NH}$  ( $\sim 3259 \text{ cm}^{-1}$ ) and  $\text{C}\equiv\text{N}$  ( $2095 \text{ cm}^{-1}$ ) containing species as well as  $\text{CO}_2$  ( $\sim 2357 \text{ cm}^{-1}$ ). The bands at 3843, 3742, 2161 and  $1697 \text{ cm}^{-1}$  may be due to the species formed during oxidative/reductive reactions of the decomposed products. The response at  $600\text{--}700 \text{ cm}^{-1}$  may be due to Cl–Cl bending

Table 5

X-ray diffraction data of mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II) perchlorate (MNCuP)

<i>d</i> -Value (Å)	Relative intensity (%)
9.3462	20.2
5.9229	0.4
5.7453	9.0
5.4302	4.5
4.7125	5.1
4.4282	1.3
4.0207	0.6
3.8811	0.3
3.6950	10.0
3.5673	10.1
3.2241	2.2
3.1074	0.5
2.9112	6.1
2.7363	0.4
2.8234	10.4
2.4843	0.5
2.4311	0.4
2.2608	0.1
2.2420	0.9
2.1637	0.9
2.0667	1.2
2.0107	0.5
1.8870	0.6
1.8476	0.9
1.8232	1.0
1.7899	0.4
1.7476	0.3
1.7081	0.8
1.5572	0.2
1.5189	1.0
1.4631	0.2
1.4517	0.2
1.3976	0.4
1.3555	0.4

Table 6

X-ray diffraction data of mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate (MNZnP)

<i>d</i> -Value (Å)	Relative intensity (%)
5.9804	18.00
5.5004	63.64
4.7400	64.00
4.4576	36.36
4.0371	13.64
3.5205	94.00
3.5318	16.00
3.2639	63.64
3.1400	14.00
2.9764	9.00
2.9378	95.46
2.7609	5.00
2.6497	100.0
2.6200	9.1
2.5050	11.40
2.4469	12.00
2.2359	9.00
2.1741	27.27
2.0830	18.18
2.0212	14.00
1.9005	18.18
1.8539	5.00
1.8362	9.00
1.8023	6.00
1.7570	4.00
1.7144	14.00
1.6851	6.00
1.6326	4.00
1.5666	2.00
1.5308	15.46
1.4553	5.00
1.4244	6.00
1.4067	6.00
1.3633	9.00
1.3265	5.00

mode. The bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate variants (Ni, Cu and Zn) are also expected to undergo similar decomposition process.

#### 4.4. Electron spectroscopy for chemical analysis (ESCA) and X-ray diffraction studies (XRD)

The intensity versus binding energy (eV) obtained for different elements (C, N, Cl, O, Co and Ni) in ESCA of synthesized complexes are given in Table 2. The presence of nitrogen in ammonia and nitrotetrazole moiety was indicated by the presence of two sharp peaks corresponding to the binding energy of 401–412 eV. The peak with binding energy in the range of 401–406 eV may be assigned to nitrogen of –NH<sub>3</sub> group where as the peak with binding energy of 403–412 eV may be attributed to the nitrogens of nitrotetrazole ring. The prominent peak corresponding to the binding energy of 783 and 788 eV appear to be corresponding to central metal atom viz., Co and Ni respectively in (III) oxidation state (Table 2) as per literature reported for similar compounds. Similarly, in case of mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II)

perchlorate and mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate the peaks observed at 945 and 1028 eV may be attributed to Cu and Zn in II oxidation state [24]. The data on precursors also suggests similar trends (Table 2).

The *d*-spacing calculated from X-ray diffraction data for complexes and their precursors in powder form are given in Tables 3–9. The nature of diffractograms, *d*-spacing and relative intensity gave an indication of crystalline nature of all the complexes synthesized in the present study. The difference in the *d*-spacing of (nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine nickel(III) perchlorate, mono-(5-nitro-*H*-tetrazolato-*N*)triammine copper(II) perchlorate and mono-(5-nitro-*H*-tetrazolato-*N*)triammine zinc(II) perchlorate in comparison to bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate, suggest that they have different crystal structure than that of latter. An in-depth study applying single crystal X-ray diffractometer could not be undertaken during this work in view of inherent hazards of the compounds. Morrison et al. [31] confirmed the monoclinic nature of BNCP with *cis* relationship of the two nitrotetrazolato ligands. The



Table 7  
X-ray diffraction data of carbonato tetraammine cobalt(III) nitrate (CTCN)

<i>d</i> -Value (Å)	Relative intensity (%)
8.9788	81.2
5.0521	17.3
4.5084	100.0
3.9640	3.4
3.6289	53.7
3.3979	1.0
3.0487	7.7
2.9795	29.7
2.8910	3.9
2.7010	31.3
2.6082	34.7
2.5304	50.8
2.5058	22.1
2.3973	6.1
2.3193	5.2
2.2770	33.0
2.2589	9.1
2.1477	3.0
2.0721	8.2
2.0297	12.0
1.9840	54.7
1.9389	14.9
1.8745	2.7
1.8172	32.4
1.7496	6.1
1.7081	19.4
1.7034	8.0
1.8574	3.9
1.6228	2.2
1.5814	4.1
1.5690	9.1
1.5052	5.4
1.491	9.4
1.4672	5.9
1.4486	12.0
1.4339	3.4
1.3950	1.3
1.3633	2.4

*a*, *b*, *c* values reported by Morrison et al. [31] were used as input parameters in the equation [26] of monoclinic crystal to obtain *d*-values. The computed *d*-values were comparable with the *d*-values obtained in the powder X-ray diffraction of bis-(5-nitro-2*H*-tetrazolato-*N*<sup>2</sup>)tetraammine cobalt(III) perchlorate during this work.

Table 8  
X-ray diffraction data of carbonato tetraammine nickel(III) nitrate (CTNN)

<i>d</i> -Value (Å)	Relative intensity (%)
7.7048	44.1
4.3039	1.8
2.3297	100.0
1.7560	35.1
1.5633	22.9
1.4793	9.9
1.3310	12.9
1.2960	8.2

Table 9  
X-ray diffraction data of carbonato triammine copper(II) nitrate (CTCuN) and zinc(II) nitrate (CTZnN)

<i>d</i> -Value (Å)	Relative intensity (%)
Carbonato-triammine copper(II) nitrate (CTCuN)	
17.128	0.2
6.827	1.8
5.769	100.0
5.178	4.4
4.131	8.4
3.974	7.3
3.434	65.1
3.186	8.8
3.069	3.4
3.028	0.3
2.898	14.6
2.864	19.3
2.807	4.7
2.697	0.5
2.604	5.2
2.473	3.4
2.352	0.8
2.293	0.6
2.246	2.6
2.202	0.3
2.168	0.6
2.126	3.5
2.099	3.8
2.072	1.8
2.030	1.0
2.000	2.7
1.936	4.6
1.842	2.5
1.789	1.3
1.723	9.4
1.718	4.2
1.656	0.8
1.631	1.3
1.597	0.7
1.583	1.7
1.544	0.7
1.505	0.6
1.481	0.3
1.454	0.8
1.436	0.6
1.413	0.8
1.369	1.0
Carbonato-triammine zinc(II) nitrate (CTZnN)	
10.0746	22.9
6.7171	61.8
5.3153	7.0
5.1700	7.50
4.8796	3.9
4.0126	26.3
3.6957	11.7
3.5736	9.50
3.4178	12.9
3.1520	51.50
2.8590	38.90
2.7145	100.0
2.6677	100.0
2.5644	68.70
2.4787	47.90
2.3181	14.10

Table 9 (Continued)

<i>d</i> -Value (Å)	Relative intensity (%)
2.1903	10.0
2.0789	12.90
1.9120	13.50
1.7077	7.50
1.5808	17.50
1.5577	28.1
1.4721	1.56

#### 4.5. Sensitivity studies

The friction sensitivity test results of Co, Ni and Cu complexes indicated their higher vulnerability towards friction stimuli of (3–4.8 kg) compared to the zinc complex (14 kg), whereas impact sensitivity test revealed their moderate vulnerability in terms of  $h_{50\%}$  (30–36 cm) (Table 1). These trends are indicative of relatively safe nature of the synthesized compounds for detonator applications compared to conventional initiators such as lead azide and silver azide.

#### 5. Conclusion

The lab scale method of synthesis of free flowing bis-(5-nitro-2*H*-tetrazolato- $N^2$ )tetraammine cobalt(III) perchlorate (BNCP), bis-(5-nitro-2*H*-tetrazolato- $N^2$ )tetraammine nickel(III) perchlorate (BNNP), mono-(5-nitro-*H*-tetrazolato- $N$ )triammine copper(II) perchlorate (MNCuP) and mono-(5-nitro-*H*-tetrazolato- $N$ )triammine zinc(II) perchlorate (MNZnP) having bulk density 0.6–0.89 g/cm<sup>3</sup> has been established at multigram level. The thermal studies of the complexes revealed that BNCP, BNNP and MNCuP are relatively thermally stable when compared with MNZnP. The hyphenated TG-FTIR studies on BNCP indicated the evolution of NH containing species and CO<sub>2</sub> as major products of decomposition. Sensitivity test results suggest their response to mechanical stimuli albeit to a lesser extent than conventional primary explosives. Thermal and physicochemical characteristics bring out the possibility of utilizing BNNP/BNCP as deflagration to detonation transition (DDT) material in various futuristic detonating devices. Practical data on the effect of ageing on shelf life and performance change (useful life) of bis-(5-nitro-2*H*-tetrazolato- $N^2$ )tetraammine cobalt(III) perchlorate and bis-(5-nitro-2*H*-tetrazolato- $N^2$ )tetraammine nickel(III) perchlorate need to be generated in future for their application in systems.

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