

# Studies on lead-free initiators: synthesis, characterization and performance evaluation of transition metal complexes of carbonylhydrazide

M.B. Talawar\*, A.P. Agrawal, J.S. Chhabra, S.N. Asthana

*High Energy Materials Research Laboratory, Sutarwadi, Pune 411021, India*

Received 8 January 2004; received in revised form 24 June 2004; accepted 8 July 2004

Available online 20 August 2004

## Abstract

Cobalt, nickel and zinc tris(carbonylhydrazide) perchlorates (CoCP, NiCP and ZnCP) as well as copper bis(carbonylhydrazide) perchlorate (CuCP) of desired morphology and bulk density ( $0.85\text{--}0.95\text{ g/cm}^3$ ) have been synthesized during this work. The synthesis was carried out by addition of the aqueous solution of cobalt/nickel/copper/zinc perchlorates to the aqueous solution of carbonylhydrazide. The products were characterized by the metal content analysis and FTIR. The IR spectra and ESCA brought out the coordination of both the end amino groups of carbonylhydrazide with the central metal ion. Differential thermal analysis (DTA) curve indicated that CoCP, NiCP and ZnCP are thermally stable in the temperature range of  $220\text{--}285\text{ }^\circ\text{C}$ , unlike CuCP ( $120\text{ }^\circ\text{C}$ ). The activation energy determined by TG measurements was found to be  $140\text{--}180\text{ kJ/mol}$  for CoCP, NiCP and ZnCP. Sensitivity data revealed their sensitivity to friction stimuli (1 kg). Impact sensitivity test results corresponded to  $h_{50\%}$  of  $50\text{--}60\text{ cm}$  with the exception of CuCP ( $h_{50\%}$ , 11 cm). In order to assess the performance as detonants, the selected compounds were detonated on a lead witness plate of 3 mm thickness using fuse wire as well as evaluated in conjunction with tetryl in detonator No. 27 tube. The results obtained in terms of extent of damage to witness plate were on par with the standard detonator No. 27 containing azide, styphnate and aluminium metal (ASA) composition.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Initiators; Cobalt carbonylhydrazide perchlorate; Nickel carbonylhydrazide perchlorate; Copper carbonylhydrazide perchlorate; Zinc carbonylhydrazide perchlorate; Thermolysis; Hazardous materials; Primary explosives; Carbonylhydrazide

## 1. Introduction

Mercury fulminate (MF) was the initial choice as an initiator. However, MF-based compositions are beset with the tendency to get “dead pressed” at a pressure of 200 MPa. Currently, inorganic azides, namely lead azide (LA) and silver azide (SA), are being widely used as key components of detonant composition. The tubular detonators normally contain a mixture of service lead azide, lead styphnate and aluminium powder (commonly known as ASA composition), pressed above the base charge of high explosive-tetryl/pentaerythritol tetranitrate (PETN). However, lead azide, despite being an

excellent detonating agent, suffers from the drawbacks such as hydrolytic instability, high sensitivity towards mechanical stimuli and incompatibility with metals as well as metal alloys, commonly used for the encapsulation in initiating devices.

These limitations of the conventional initiatory compositions have intensified research efforts towards lead-free safe energetic primary explosives based on coordination compounds [1]. The desirable attribute of this class of energetic coordination compounds is the presence of stoichiometric fuel and oxidizer species. A few studies [2] undertaken on the relationship between structure and explosive properties of coordination compounds have established that coordination compounds offer a wide range of primary explosives for tubular detonators, which remain the key devices

\* Corresponding author. Fax: +91 2025869316.

E-mail address: mbtalawar@yahoo.com (M.B. Talawar).

needed to initiate an explosive train despite the appearance of semi conducting bridge (SCB) devices. In this context, nitrate/perchlorate complexes [3] of transition metal ions have emerged as the preferred choice for specific applications. Energetic heterocyclic compounds based on nitrotetrazoles and triazoles have evinced a great interest as ligands [4]. Carbohydrazide is another interesting azotic ligand with non-bonded lone pair of electrons on the nitrogen of amino group and oxygen of the carbonyl group. It is well reported [5] that carbohydrazide coordinates with many metal ions as bidentate ligand. Chunhua et al. [6] from Beijing Institute of Technology, China, have recently reported the synthesis, molecular structures and explosive properties of  $[M(\text{CHZ})_3](\text{ClO}_4)_2$  ( $M = \text{Cd, Ni, Zn, Mn}$ ;  $\text{CHZ} = \text{Carbohydrazide}$ ). The synthesis and characterization of the transition metal nitrates as well as perchlorates have been reported by Sinditskii et al. [7,8]. Thermodynamics of coordination compounds of Co, Ni, Zn and Cd nitrates and perchlorates with carbohydrazide have been reported by Kon'kov et al. [9]. Zhang et al. [10] studied the molecular structure and physicochemical properties of cadmium carbohydrazide perchlorate (GTG) – a potential primary explosive. We have recently reported [11] the synthesis, characterization and performance evaluation of nickel hydrazinium nitrate (NHN) for its initiator applications. In continuation [11] of our work on energetic coordination compounds as detonants, this paper reports the synthesis, characterization, thermolysis and performance evaluation of tris(carbohydrazide) cobalt/nickel/zinc perchlorates (CoCP, NiCP, ZnCP) [6,7] and bis(carbohydrazide) copper perchlorate (CuCP) [8].

## 2. Experimental

### 2.1. Materials and methods

All the reagents of AR grade were used as such. The starting material, carbohydrazide, was synthesized by refluxing diethyl carbonate with hydrazine hydrate and was recrystallised before its use in the synthesis of complexes.

#### 2.1.1. Synthesis of nickel tris(carbohydrazide) perchlorate (NiCP)

A solution containing 3.66 g (0.02 mol) carbohydrazide in 35 cm<sup>3</sup> of water was charged into a stainless steel reactor placed on a water bath. It was kept under mechanical stirring and heated to the temperature of 58–60 °C. 7.32 g (0.07 mol) of nickel perchlorate hexahydrate dissolved in 25–30 cm<sup>3</sup> of double distilled water was added to the carbohydrazide solution over a period of 20 min at 58–60 °C. The addition of the reactant resulted in marginal exothermic reaction leading to an increase in the temperature of the contents. The reaction mixture was allowed to remain at 58–60 °C for about 30 min. Subsequently, the reaction flask was removed from the water bath and digested at room temperature with stirring for an hour. The light blue crystals of NiCP obtained were filtered through a Buchner funnel. The bluish coloured crystals were washed with distilled water (4 × 50 cm<sup>3</sup>), followed by propyl alcohol (50 cm<sup>3</sup>) and dried at 60 °C. The yield obtained was 8.9 g (85%). Similar procedure was adopted for the synthesis of CoCP, CuCP and ZnCP of free-flowing nature. The molar ratio of copper perchlorate and carbohydrazide used during the synthesis of CuCP was 1:2.1.

An attempt was also made to synthesize these complexes at a lower temperature (25 °C) adopting the above procedure. The products obtained at lower temperature were found amorphous in nature with less yield (60–70%) and lower bulk densities (0.65–0.74 g/cm<sup>3</sup>). The intensity of the colour of these complexes obtained at lower temperature was slightly light in comparison to the products obtained at 65 °C. The reaction time required to complete the reaction at 25–30 °C was of the order 1 h. The compounds obtained at 58–60 °C were selected for further studies.

### 2.2. Characterization

Atomic absorption spectrophotometer (Chemito 2001) was used to determine the metal content of the complexes and their structural features were confirmed by FTIR (Perkin-Elmer 1600) in KBr matrix. The metal content results confirmed the molecular formula

Table 1  
Characterization of transition metal perchlorate complexes of carbohydrazide

Property	Carbohydrazide	CoCP	NiCP	CuCP	ZnCP
Molecular formula	CH <sub>6</sub> N <sub>4</sub> O	Co <sup>2+</sup> [C <sub>3</sub> H <sub>18</sub> N <sub>12</sub> O <sub>3</sub> ] [Cl <sub>2</sub> O <sub>8</sub> ] <sup>2-</sup>	Ni <sup>2+</sup> [C <sub>3</sub> H <sub>18</sub> N <sub>12</sub> O <sub>3</sub> ] <sub>3</sub> [Cl <sub>2</sub> O <sub>8</sub> ] <sup>2-</sup>	Cu <sup>2+</sup> [C <sub>2</sub> H <sub>12</sub> N <sub>8</sub> O <sub>2</sub> ] [Cl <sub>2</sub> O <sub>8</sub> ] <sup>2-</sup>	Zn <sup>2+</sup> [C <sub>3</sub> H <sub>18</sub> N <sub>12</sub> O <sub>3</sub> ] [Cl <sub>2</sub> O <sub>8</sub> ] <sup>2-</sup>
Colour	White	Reddish brown	Sky blue	Blue	White
Bulk density (g/cm <sup>3</sup> )		0.90	0.95	0.85	0.90
Metal content (%) (theoretical)		10.96 (11.16)	11.04 (11.12)	14.21 (14.35)	12.13 (12.23)
Impact sensitivity ( <i>h</i> <sub>50%</sub> )		55	11	60	60
Friction sensitivity (kg)		1	1	1	1
IR frequencies (cm <sup>-1</sup> )					
ν C=O	1642	1645	1644	1618	1648
NH <sub>2</sub>	3360, 3204	3262, 3137	3264, 3175	3370, 3169	3268, 3171
C–N	920	969	970	1084	1082

Table 2  
ESCA analysis results of complexes

Nomenclature	Binding energy (eV)					
	Carbon C <sub>1s</sub>	Carbon C <sub>1s</sub>	Cl <sub>2p</sub>	O <sub>1s</sub>	N <sub>1s</sub>	Metal ion
CoCP	285.0	289.3	208.0	532.7	401.0	779.8 (Co2p <sub>3/2</sub> ), 795.3 (Co2p <sub>1/2</sub> )
NiCP	285.0	289.1	208.4	532.5	400.6	856.4 (Ni2p <sub>3/2</sub> ), 875.0 (Ni2p <sub>1/2</sub> )
CuCP	285.0	288.9	208.6	532.5	400.7	935.5 (Cu2p <sub>3/2</sub> ), 955.5 (Cu2p <sub>1/2</sub> )
ZnCP	285.0	288.9	208.6	532.5	400.7	1021.3 (Zn2p <sub>3/2</sub> ), 1044.2 (Zn2p <sub>1/2</sub> )

assigned to the coordination compounds of carbohydrazide, viz.  $\text{Co}^{2+}[\text{C}_3\text{H}_{18}\text{N}_{12}\text{O}_3][\text{Cl}_2\text{O}_8]^{2-}$ ,  $\text{Ni}^{2+}[\text{C}_3\text{H}_{18}\text{N}_{12}\text{O}_3][\text{Cl}_2\text{O}_8]^{2-}$ ,  $\text{Cu}^{2+}[\text{C}_2\text{H}_{12}\text{N}_8\text{O}_2][\text{Cl}_2\text{O}_8]^{2-}$  and  $\text{Zn}^{2+}[\text{C}_3\text{H}_{18}\text{N}_{12}\text{O}_3][\text{Cl}_2\text{O}_8]^{2-}$ . The experimentally obtained cobalt, nickel, copper and zinc contents (10.96,

11.04, 14.21 and 12.13%, respectively) of the corresponding coordination compounds were closer (99%) to the theoretical values (11.16, 11.12, 14.35 and 12.23%, respectively). The FTIR spectra revealed the stretching frequencies due to  $\text{NH}_2$ ,  $\text{NH}$ ,  $\text{C}=\text{O}$  and metal–amino linkages (Table 1).

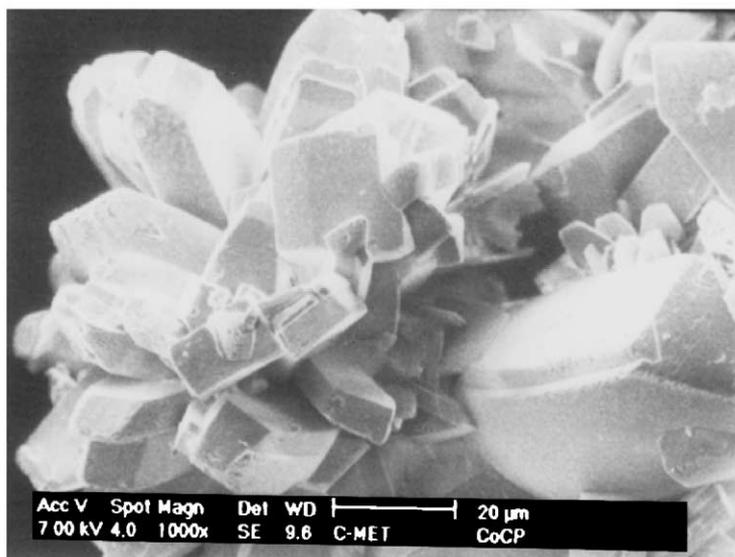
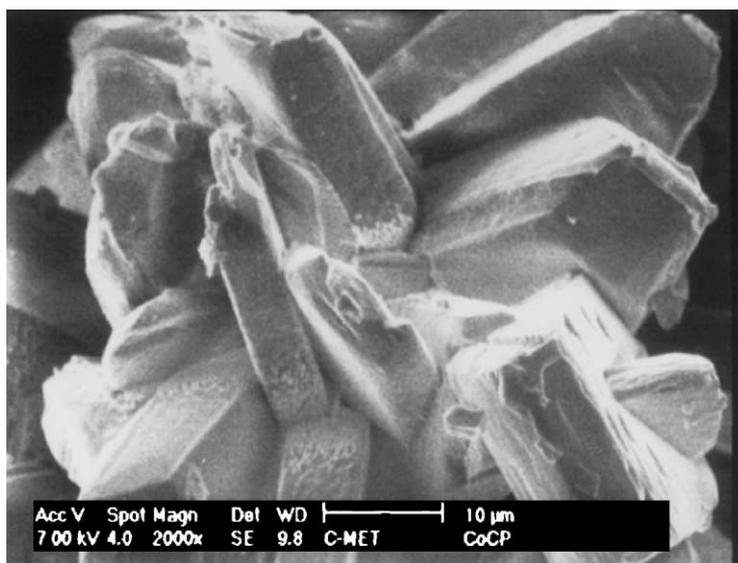


Fig. 1. SEM of CoCP.

### 2.3. Thermal studies

The thermal properties were studied by simultaneous thermogravimetry (TG)/differential thermal analyzer (DTA) of Mettler Toledo (TG/SDTA 8551) subjecting 0.1–1 mg of sample to heating at the rate of 5 °C/min in the nitrogen atmosphere.

### 2.4. TG-FTIR studies

The gaseous product analysis of ZnCP was carried out using FTIR (Bruker Equinox 55) in conjunction with TG.

### 2.5. Electron spectroscopy for chemical analysis (ESCA) studies

The ESCA of the samples was measured on ESCA 3000 (VG Microteck, UK) instrument, using MgK<sub>2</sub> (1253.6 eV) as radiation source. The binding energies of all the elements were corrected by considering C<sub>1s</sub> binding energy =

285.0 eV as internal standard. The analysis of each complex was carried out under high vacuum of the order of 10<sup>-9</sup> Torr.

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

The morphology of the compounds was investigated by SEM (Philips Icon).

### 2.7. Sensitivity characterization

The impact sensitivity of all complexes was determined on impact machine using drop weight test method (2 kg drop weight) according to Bruceton Staircase approach. The results are reported in terms of height of 50% probability of explosion (*h*<sub>50%</sub>). The friction sensitivity was determined on a Julius Peter's apparatus. The load was increased in increments till there was no explosion/ignition in five consecutive experiments.

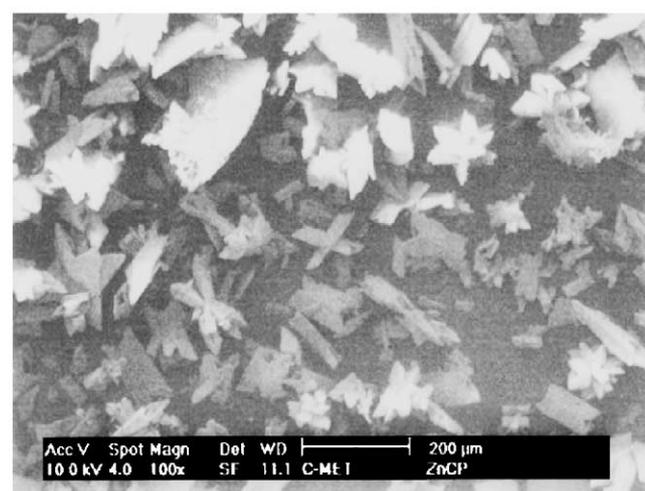
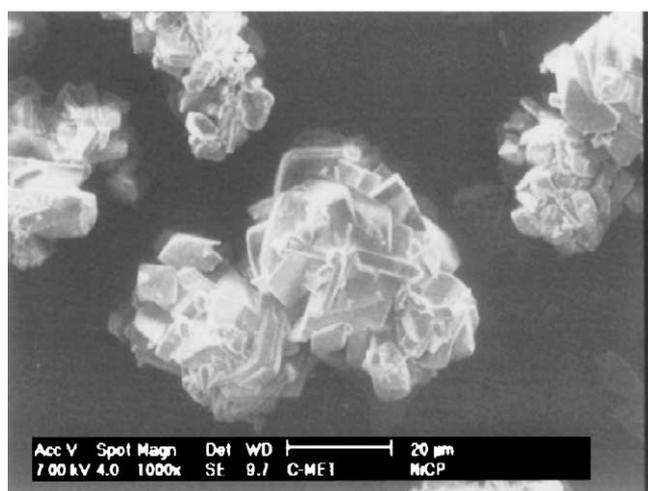
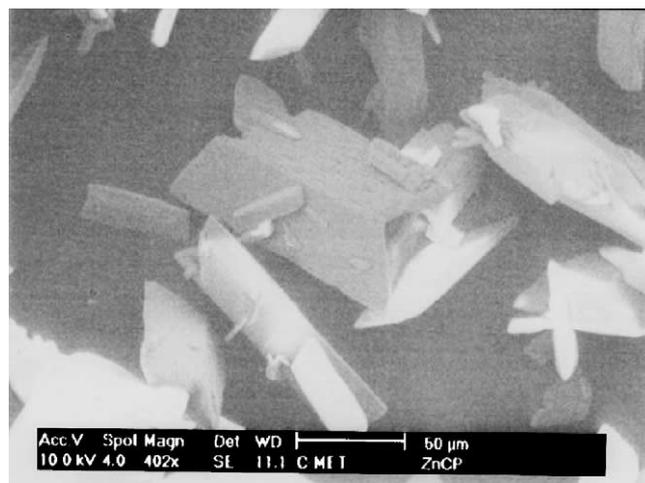
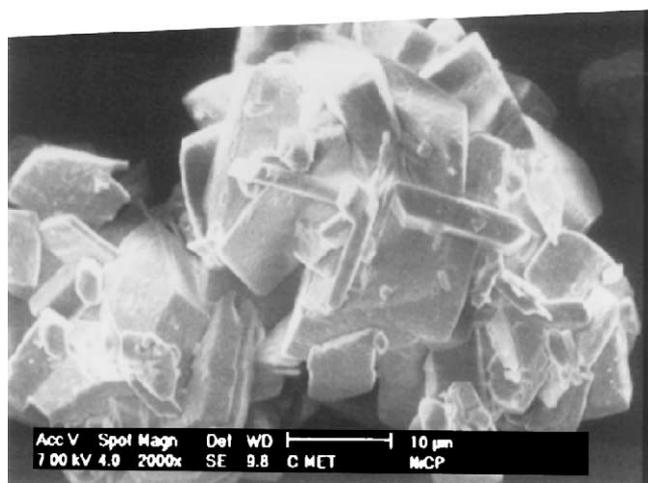


Fig. 2. SEM of NiCP.

Fig. 3. SEM of ZnCP.

## 2.8. Performance evaluation of CoCP, NiCP and ZnCP

### 2.8.1. Detonator filling

Three hundred and fifty milligrams NiCP was placed in the standard detonator No. 27 tube and pressed gently at 7 MPa with dwell time of 45 s. Safety fuse of 20 cm length was inserted into the tubular detonator touching the NiCP layer and crimped softly. The humidity ( $RH < 55\%$ ) was ensured in the process room throughout the filling operation. The NiCP-filled tubular detonator was vertically held on a 3-mm lead plate and the safety fuse was initiated by the safety match. The diameter of the neatly punched hole on the lead plate was measured. Similar set of experiments were carried out using CoCP and ZnCP.

In the second set of experiments, tetryl (500 mg) was filled into tubular detonator and pressed at 1 MPa pressure with dwell time of 45 s. CoCP/NiCP/ZnCP (350 mg) was pressed above the tetryl at 7 MPa under identical conditions. Safety fuse of 20 cm length was inserted into the tubular detonator touching the filled CoCP/NiCP/ZnCP and crimped softly. The filled tubular detonator tube was evaluated as above. Standard detonator No. 27 containing ASA composition pressed above the initially pressed base charge of high explosive (tetryl/pentaerythritol tetranitrate) was evaluated as reference detonator.

### 2.9. Method of disposal

All the synthesized complexes react mildly with 10% sodium hydroxide solution and undergo decomposition. This method may be used for the safe destruction of these materials.

## 3. Results and discussion

### 3.1. Characterization

The bidentate nature of carbohydrazide ligand has been supported by the molecular modeling studies [5]. Carbohydrazide ligand has five possible sites for coordination with the central metal atom. However, the  $\pi$  electrons of the carbonyl group are in resonance with the amide NH group. Therefore, there is least possibility of participation of the amide group for coordination with the metal atom. In view of this, both the end primary amino groups or electron-rich oxygen and one of the primary amino groups may participate in coordination with central metal atom. The IR stretching band corresponding to carbonyl of free carbohydrazide appears at  $1642\text{ cm}^{-1}$  (Table 1) and remains unchanged in the metal perchlorate complexes of carbohydrazide (CoCP and NiCP). This suggests the non-participation of carbonyl oxygen in coordination. The IR bands at  $3360$  and  $3204\text{ cm}^{-1}$  in the carbohydrazide are assigned to asymmetric and symmetric stretching vibrations of  $\text{NH}_2$  group and a band at  $3306\text{ cm}^{-1}$  may be assigned to secondary NH group. It can be deduced



Fig. 4. SEM of CuCP.

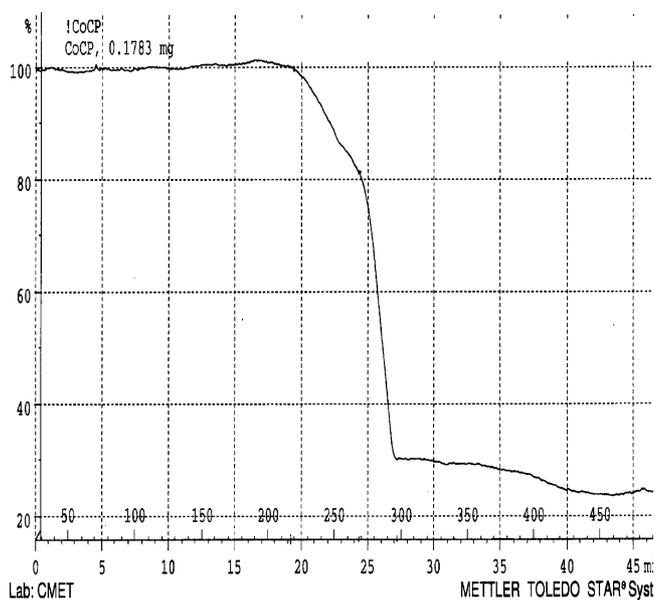


Fig. 5. TG of CoCP.

from the IR data given in Table 1 that the stretching vibrations of the  $\text{NH}_2$  get shifted towards the negative side in the complexes with respect to those in free carbohydrazide. This negative shift of  $\text{NH}_2$  bands suggests the coordination through the end primary amino group of carbohydrazide. ESCA was also undertaken to obtain additional evidences. Intensity versus binding energy (eV) data of different atoms (Co, Ni, Cu, Zn, C, N, O, Cl) of complexes studied during this work is represented in Table 2. The binding energies of all the nitrogen atoms (at N(1), N(2), N(3) and N(4)) were found to be more or less same ( $\sim 400$  eV), indicating their similarity. N(2) and

N(3) were involved in resonance with carbonyl group while the ion pair of electron on N(1) and N(4) was expected to be involved in coordination as indicated by IR. These observations are in agreement with the results reported for similar complexes in literature [5]. However, some of the researchers [6,7] have proposed that carbohydrazide acts as bidentate ligand and by bonding through the carbonyl oxygen atom and terminal N atom of carbohydrazide, forming five-membered rings. This aspect needs further detailed investigations.

The SEM revealed a combination of square and round shaped morphology of CoCP, NiCP and ZnCP (Figs. 1–3),

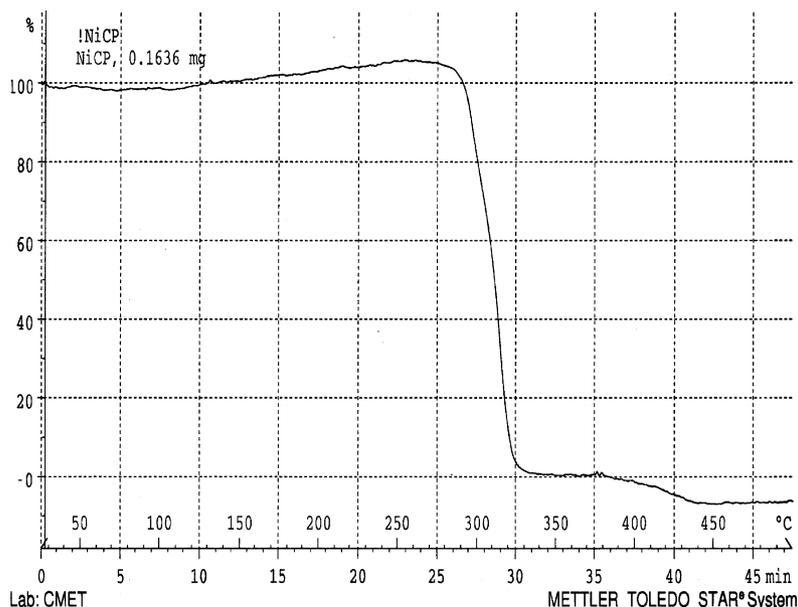


Fig. 6. TG of NiCP.

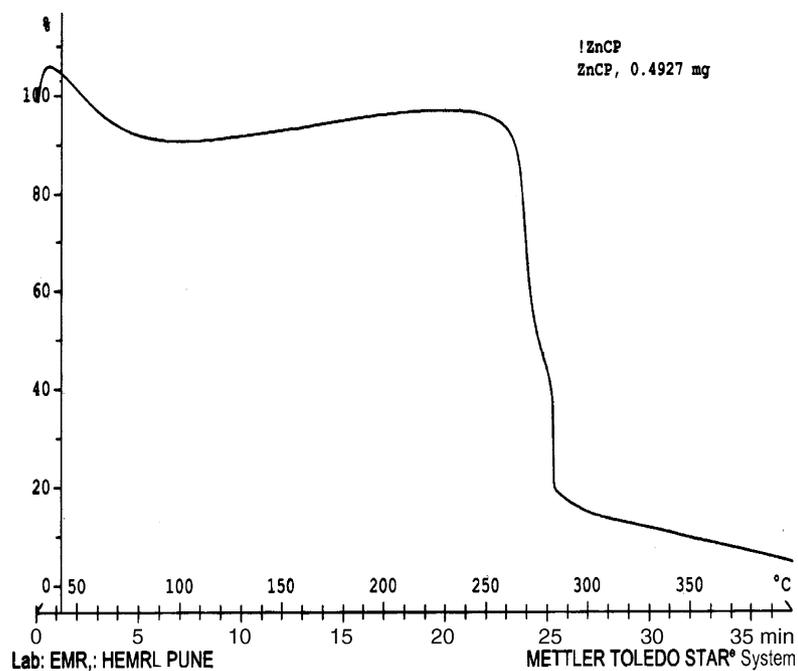


Fig. 7. TG of ZnCP.

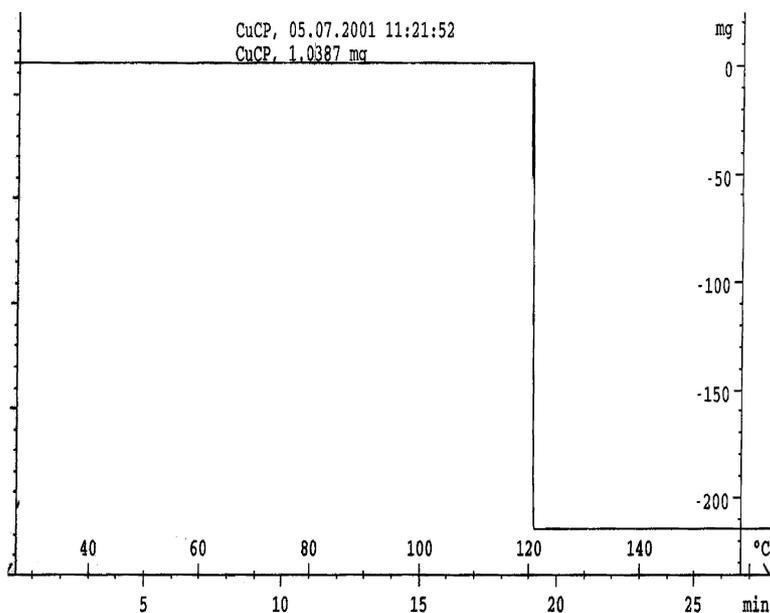


Fig. 8. TG of CuCP.

while a needle-shaped morphology was observed in case of CuCP (Fig. 4).

### 3.2. Thermal decomposition studies

The DTA profiles reveal a relatively higher onset temperature of  $\sim 260^\circ\text{C}$  for NiCP and ZnCP than that of  $220^\circ\text{C}$  for CoCP. CuCP exhibited much lower onset temperature ( $120^\circ\text{C}$ ). The TG analysis of CoCP exhibited weight loss of 8% ( $220\text{--}268^\circ\text{C}$ ) and 92% ( $268\text{--}295^\circ\text{C}$ ) for the first and second steps, respectively. ZnCP also showed two-step thermal decomposition in TG in the temperature range  $260\text{--}290^\circ\text{C}$  and  $290\text{--}310^\circ\text{C}$ , corresponding to weight loss of 17 and 50%, respectively (Figs. 5–7). NiCP and CuCP exhibited single-step weight loss in the temperature range  $285\text{--}335^\circ\text{C}$  and  $120\text{--}121^\circ\text{C}$ , respectively (Fig. 8). CuCP underwent violent reaction during thermolysis even at 1 mg sample size and caused severe damage to DTA cup. The activation energy obtained from TG data of Co, Ni and Zn complexes was comparable ( $140\text{--}180\text{ kJ/mol}$ ). It could not be obtained for copper complex due to rapid decomposition leading to disturbance of the setup.

The relative stability of NiCP and CoCP can be correlated with the relative acceptor properties of the central ion for the electrons coordinating group as well as the stability constants (Ni: 18.06 and Co: 13.82), as reported [12] in case of [Ni(en)<sub>3</sub>] and [Co(en)<sub>3</sub>]. The stability of coordination complexes is also decided by the size and charge of the central ion as well as their second ionization potential (Ni 18.2 and Co 17.3) [13].

### 3.3. TG-FTIR studies

The FTIR of decomposition products evolved during TG of ZnCP displayed IR stretching frequencies at

$3228\text{--}3854\text{ cm}^{-1}$  (NH and H<sub>2</sub>O) and  $2356\text{--}2359\text{ cm}^{-1}$  (C $\equiv$ N), suggesting evolution of NH<sub>2</sub>CN/NH<sub>3</sub> and HCN as major products (Fig. 9). The presence of peaks at  $3854\text{--}3744$ ,  $3566$  and  $1749\text{ cm}^{-1}$  are indicative of high-temperature oxidation of some of the gases (NH<sub>3</sub> and NH<sub>2</sub>CN) to oxides of nitrogen. Other complexes are also envisaged to undergo similar decomposition reactions.

### 3.4. Sensitivity studies

Sensitivity results bring out that CoCP, NiCP, CuCP and ZnCP are friction insensitive upto 1 kg suggesting their overall safe nature for the detonator applications compared to sensitive lead azide. The impact sensitivity test data revealed  $h_{50\%}$  of the order of 50–60 cm for CoCP, NiCP and ZnCP while CuCP appeared to have relatively lower value (11 cm). The initiation of explosives by the impact and friction stimuli is a complex phenomenon, and depends on the molecular structure, crystal hardness, shape and size as well as on the thermal conductivity.

### 3.5. Performance evaluation studies

The performance evaluation of the filled detonators, brought out that CoCP and NiCP alone (350 mg), could punch 6-mm neat hole on a 3-mm thick lead plate. These complexes also initiated the booster charge (tetryl) filled in detonator tube No. 27, and the extent of damage to the witness plate was of the order of 9 mm (neatly punched hole) which was comparable to the damage caused by standard ASA composition filled detonator No. 27. ZnCP could not be initiated during these experiments. CuCP was not selected for detonator filling due to safety reasons such as its lower

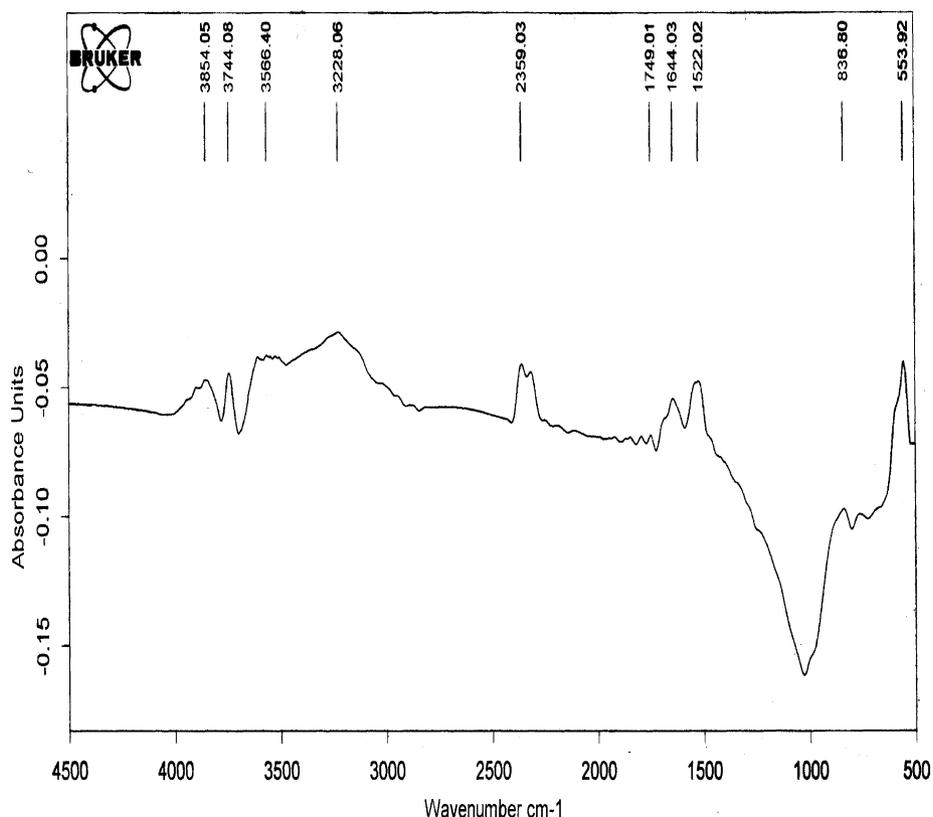


Fig. 9. TG-FTIR of ZnCP.

thermal stability and higher sensitivity towards impact and friction.

#### 4. Conclusion

The preparation of the energetic coordination compounds, viz. CoCP, CuCP and ZnCP of the desired morphology has been accomplished from the respective metal perchlorates and carbonylhydrazide. Thermal studies indicated that NiCP, CoCP and ZnCP are stable up to higher temperature than CuCP. The activation energy data brought out that the energy barrier for decomposition of Co, Ni and Zn complexes is nearly same. The thermal as well as sensitivity characteristics and limited performance evaluation of these metal complexes bring out the potential of CoCP and NiCP as energy-providing component of lead-free detonators for futuristic programmes. These investigations also reveal that NiCP and CoCP are superior detonants as compared to mercuric fulminate and service lead azide in terms of low vulnerability to initiation by mechanical and thermal stimuli. It warrants further in-depth trials for their adoption in detonators as eco-friendly and chemically compatible primary explosive. Practical data on the effect of ageing on shelf life and performance change (useful life) of NiCP and CoCP need to be generated in future.

#### Acknowledgements

Authors are grateful to Shri S. Jayaraman, Associate Director, HEMRL and Ghatak for extending necessary facilities for carrying out performance evaluation trials. Authors also thank Dr. R. Sivabalan for his assistance in preparing this manuscript.

#### References

- [1] M.L. Lieberman, J.W. Fronabarger, Status of the development of 2-(5-cyanatotetrazolato) pentaamine cobalt (iii) perchlorate for DDT devices, in: Proceedings of 7th International Pyrotechnic Seminar, Colorado, USA, 1980, p. 322.
- [2] S.V. Sinditskii, V.V. Serushkin, Defence Sci. J. 46 (1996) 371.
- [3] B. Hariharanath, A.G. Rajendran, K.S. Chandrabhanu, M. Ravindran, C.B. Kartha, Characterization of nickel hydrazinium nitrate as a new charge for initiator applications, in: Proceedings of 3rd International High Energy Materials Conference and Exhibit, Thiruvananthapuram, India, 2000, p. 469.
- [4] J.W. Fronabarger, M.L. Lieberman, Performance of chemical analogs of explosive cp, in: Proceedings of 11th Symposium on Explosives and Pyrotechnics, Philadelphia, USA, 1981, p. 38 (1).
- [5] R.L. Dutta, A.K. Sarkar, J. Inorg. Nuc. Chem. 43 (1981) 2557.
- [6] Lu Chunhua, Zhong Tonglai, Cai Ruijiao, Synthesis, molecular structures and explosive properties of  $[M(CHZ)_3](ClO_4)_2$  ( $M = Cd, Ni, Mn$ ), in: Proceedings of 3rd International Autumn Seminar on Propellants, Explosives and Pyrotechnics, Beijing, Republic of China, 1999, p. 33.

- [7] V.P. Sinditskii, A.E. Fogel'zang, M.D. Dutov, V.I. Sokol, V.V. Serushkin, B.S. Porai, M.A. Koshits, *Zh. Neorg. Khim.* 31 (7) (1986) 1759.
- [8] V.P. Sinditskii, A.E. Fogel'zang, M.D. Dutov, V.I. Sokol, V.V. Serushkin, B.S. Porai, M.A. Koshits, *Zh. Neorg. Khim.* 32 (8) (1987) 1944.
- [9] T.S. Kon'kov, T.S. Matyushin, N. Yu, V.P. Sinditskii, A.E. Fogelzang, *Khim. Fiz.* 14 (6) (1995) 109.
- [10] T. Zhang, Z. Wei, C. Lu, J. Zhang, *Baopo Qicai.* 28 (3) (1999) 16.
- [11] J.S. Chhabra, M.B. Talawar, P.S. Makashir, S.N. Asthana, H. Singh, *J. Haz. Mat.* A99 (2003) 225.
- [12] E. Cartmell, G.W.A. Fowles, *Valency and Molecular Structure—The Stability of Complex Compounds*, ELBS and Butler Worths and Co Ltd., 1970, p. 231.
- [13] E.S. Gilreath, *Fundamental Concepts of Inorganic Chemistry, Complex Ions and Co-ordination Compounds*, McGraw Hill Company Inc., 1958, p. 224 (Chapter 5).