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SHORT COMMUNICATION

Transition Metal Carbohydrazide Nitrates: Burn-rate Modifiers for Propellants

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ABSTRACT

This paper discusses the synthesis and characterisation of cobalt (*Co*), nickel (*Ni*) and copper (*Cu*) carbohydrazide nitrates. In differential scanning calorimetry (DSC), the complexes exhibited exothermic decomposition indicating their energetic nature. The commencement of decomposition was observed at 220 °C for *Ni* complex, and at 160 °C for *Co* complex whereas that of *Cu* complex occurred at 75 °C. In view of the better thermal stability, *Ni* and *Co* complexes were selected for further study. The activation energy of decomposition of *Ni* and *Co* complexes were found to be 47 kcal/mol and 60 kcal/mol respectively. Impact and friction sensitivity test results revealed relatively lower vulnerability of carbohydrazide cobalt nitrate. Its incorporation in an ammonium perchlorate (AP)-based composite propellant led to 9-19 per cent enhancement whereas that of carbohydrazide nickel nitrate resulted in 28-74 per cent enhancement in burning rates in the pressure range 1.9 MPa to 8.8 MPa. Exothermic decomposition of the coordination complexes on propellant surface and involvement of metal at molecular level formed on decomposition of the complexes in combustion environment of composite propellant may be attributed to the catalytic effect of this class of compounds on the lines of reported literature.

Keywords: Burn rate modifier, carbohydrazide complexes, propellants, double-base propellants, thermal stability, composite propellants, ligand fuel

1. INTRODUCTION

Inorganic coordination compounds are of interest as energetic components for explosive and propellant formulations[1]. Sinditskii and Serushkin[2] have reported that coordination compounds can be designed to obtain high energy molecules and suggested that these should possess oxidising species like ClO_4^- and NO_3^- in their molecular structure to exhibit combustion phenomenon. The nitrate and perchlorate- based coordination complexes having ultra high burning rates can be realised by selecting metal as well as the ligand and are envisaged as the potential ballistic modifiers of solid propellants. Metal atom serves as a matrix bonding fuel ligand and oxidiser anion together as well as decides the stability of the compound. Copper (*Cu*), cobalt (*Co*), nickel (*Ni*) and chromium (*Cr*) appear to be the metals of choice. Triazoles, ethylenediamine, and carbohydrazides are considered excellent candidates as the ligand fuel, as these can form complexes with a variety of metals and are relatively stable in the presence of strongly oxidising anions (NO_3^-,ClO_4^-). Carbohydrazide lead nitrate complexes are reported to be used as energetic burning rate catalyst in double-base propellant formulations[3]. In the present study, coordination compounds of general formula of $[M(L)_n]X_2$, where M is metal

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ions of *Co*, *Ni* and *Cu*, *X* is NO_3^- anion, and *L* is carbohydrazide ligand, were considered. The thermal decomposition pattern of the synthesised and characterised complexes was determined by differential scanning calorimetry (DSC) and thermogravimetry (TG) techniques. In view of better thermal stability, cobalt and nickel complexes were evaluated more exhaustively and their potential as burning rate modifiers was assessed in composite propellant formulations.

2. EXPERIMENTAL

2.1 Synthesis

Cobalt(II) nitrate, nickel(II) nitrate, and copper(II) nitrate procured from trade were of LR grade and used directly. Coordination compounds, namely tris-carbohydrazide cobalt(II) nitrate (*CCoN*), tris-carbohydrazide nickel(II) nitrate(*CNiN*) were synthesised by reacting the metal nitrates with carbohydrazide in 1:3 mol ratio in aqueous medium at 60 ± 2 °C for 1 h and precipitating the metal complexes by adding alcohol as per the reported procedure. Under similar conditions, bis-carbohydrazide copper (II) nitrate(*CCuN*) was synthesised by reacting metal nitrate with carbohydrazide in 1:2 mol ratio[4-6]. The yield of the products was > 95 per cent. The compounds were characterised by FTIR (Perkin Elemer spectrophotometer model:1600) in KBr pellet and the metal content was determined as per the standard procedure[7]. Conductivity measurements were carried out using 10-3 M freshly prepared DMSO solutions on digital conductivity meter K612.

2.2 Thermal Analysis

Thermal decomposition patterns of *CoN*, *CNiN*, and *CCuN* were studied by subjecting the sample to DSC (Perkin Elemer make DSC-7) in dynamic mode at 5–25 °C/min (at an increment of 5 °C/min) in nitrogen atmosphere. Activation energy (*Ea*) was computed applying ASTM[8] method based on Kissinger's relation,

$$\ln[\beta/T_m^2] = \ln[ZR/E] - E/RT_m$$

where, β is the heating rate in deg/min, T_m is the maximum peak temperature, and Z is the preexponential factor.

Slope of plot of $[d\text{-}\ln(\beta/T_m^2)$ against $d(1/T_m)]$ was determined to compute *Ea*. The thermogravimetric analysis (TGA) was undertaken on Mettler Toledo make instrument (model TGA/SDTA 851e) in nitrogen atmosphere. The sample (1-2 mg) was subjected to 10 °C/min during TGA experiments. IR of the gaseous products evolved during TG was determined using FTIR (Equinox 55 of Bruker make) in conjunction with TGA at 8 scans/s in an advanced integrated system supplied by Mettler Toledo.

2.3 Impact & Friction Sensitivity

Impact sensitivity was determined by fall hammer test method (2 kg drop weight), applying standard Bruceton Staircase test procedure. Sample (10 mg) was tested in each experiment and height of 50 per cent explosion probability (h_{50}) was determined by the statistical method. Friction sensitivity was measured on Julius Peters apparatus and reported as minimum weight under which the sample (10 mg) did not ignite/explode in five consecutive experiments.

2.4 Propellant Formulations

Composite propellant selected for the present study comprised 78 per cent AP and 22 per cent binder [pre-polymer-hydroxyl-terminated polybutadiene (HTPB) : 9 per cent, plasticiser–dioctyl adipate (DOA) : 11 per cent, antioxidant-cum crosslinker-pyrogallol : 0.5 per cent, process aid-Lecithin: 0.3 per cent, and curative-toluene diisocyanate (TDI) : 1.2 per cent (*NCO* : *OH* 1:1)]. HTPB (Mn 2200) DOA and pyrogallol were mixed under vacuum (10 torr) for 2 h in a planetary mixer. Monomodal AP (9μ ± 1) was added to the binder and mixing was continued for 30 min. Burning rate catalyst (*CCoN*/*CNiN*) was incorporated in 2 parts by weight over 100 parts of the composition and mixed for 10 min. Subsequently, TDI was added and final mixing of the contents was carried out for 45 min (including 15 min under vacuum). The slurry was cast in a mould evacuated to pressure of < 5 torr and cured at 60 ± 2 °C for 10 days. All the solid ingredients were dried to the moisture level of

< 0.5 per cent before processing the formulations. Particle size of AP was determined on MALVERN particle size analyser (model series 2600C). The size of 80 per cent of particles of the sample corresponds to mean average value (9μ).

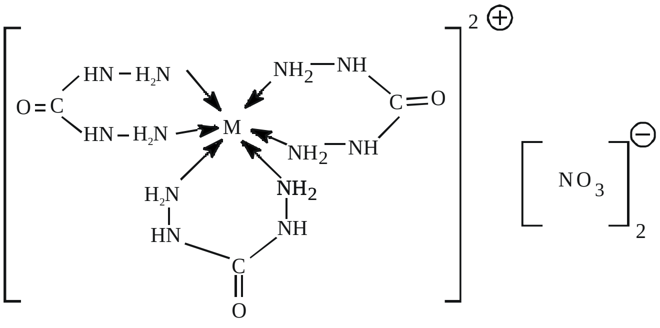
2.5 Burning Rate

Acoustic emission technique[9] was applied to determine the burning rates of the propellants in the pressure range 1.9–8.8 MPa in nitrogen-pressurised closed bomb provided with the piezoelectric transducer of 200 kHz resonance frequency to sense the signals from deflagrating propellant samples transmitted through the water medium. The propellant samples in the form of strand (6 x 6 x 100 mm) were ignited by nichrome wire. The accuracy of the measurement of burning rate was 2-3 per cent. Five experiments were conducted at each pressure for each sample.

3. RESULTS

3.1 Characterisation

In FTIR, starting material–carbohydrazide (ligand) exhibited distinct absorption[6] at 1640 cm^{-1} due to the presence of $> C = O$ moiety, whereas bands at 3360 cm^{-1} and 3202 cm^{-1} can be assigned to asymmetric *NH* vibrations of primary amine (NH_2). The band at 3302 cm^{-1} may be resulting from the vibrations of secondary amine (*NH*). The stretching frequency of $> C = O$ remained almost unaltered in complexes wrt free ligand, indicating non participation of carbonyl group in coordination. IR band corresponding to *NH* also remained unaffected. The shift in absorption corresponding to primary amine (NH_2) group suggests participation of *N*(1) and *N*(4) in the coordination via six-membered ring as proposed by Dutta[6], *et al.* (Table 1). The experimentally determined metal content (*Co*:12.78 %, *Ni* :12.72 %, *Cu* : 17.02 %) of the metal complexes was in close agreement with the theoretical metal content (*Co* : 13.01 %, *Ni* : 12.96 %, *Cu* : 17.28 %) corresponding to the general structure of $[M(CH_6N_4O)_3\ (NO^3)_2]$ for *Co* as well as *Ni* complexes and $[M(CH_6N_4O)_2\ (NO_3)_2]$ for *Cu* complex. The molar conductivity (Λ_m) of *Co* and *Ni* complexes was found > 100 ohm^{-1} cm^2 mol^{-1}, suggesting their electrolytic nature[10].



M = Co & Ni

3.2 Thermal Behaviour

CCoN, *CNiN*, and *CCuN* exhibited exothermic decomposition in DSC. The peak decomposition temperature (T_m) of the exotherm obtained for *CCoN* and *CNiN* at 10 °C/min was 276 °C and 298 °C compared to that of 170 °C for *CCuN*. The onset temperature of the decomposition of *CCuN* was also much lower (75 °C) than those of *Co* and *Ni* complexes (160 °C and 220 °C). The lower

Table 2(a). DSC of tris-carbohydrazide

Heating rate, β (°C)	Peak temp., T_m (K)	$1/T_m \times 10^3$	$\ln(\beta/T_m^2)$	*Ea* (kcal/mol)
10	549	1.821	−10.31	60
15	554	1.805	−9.92	
20	556	1.798	−9.64	
25	558	1.792	−9.42	

Table 1. FTIR of carbohydrazide-based metal complexes

Compound	ν(NH_2) asym	ν(NH_2) sym	ν(NH_2) secondary amine	ν(C=O)
$H_2NHNCONHNH_2$	3360	3202	3302	1640
$Co(H_2NHNCONHNH_2)_3(NO_3)_2$	3266	-	3302	1646
$Ni(H_2NHNCONHNH_2)_3(NO_3)_2$	3264	-	3302	1644
$Cu(H_2NHNCONHNH_2)_2(NO_3)_2$	3248	-	3302	1640

Table 2(b). DSC of tris-carbohydrazide cobalts(II) nitrate

Heating rate, β (°C)	Peak temp, T_m (K)	$1/T_m \times 10^3$	$\ln(\beta/T_m^2)$	*Ea* (kcal/mol)
5	561	1.782	–11.05	47
10	571	1.751	–10.39	
15	576	1.736	–10.00	
20	579	1.727	–9.72	

stability of *Cu* complex exhibited in DSC experiments is in line with reported in literature[3].

In view of overall superior thermal stability, *CCoN* and *CNiN* were selected for further DSC experiments at different scan rates, and the activation energy obtained for their exothermic decomposition was found to be 60 kcal/mol and 47 kcal/mol [Table 2(a) and 2(b)].

TGA of *CCoN* and *CNiN* exhibited more or less similar decomposition pattern as brought out by the single-stage weight loss with maxima at 280 °C and 300 °C in contrast to the two-stage decomposition of carbohydrazide alone (Table 3). The overall weight loss was 78–86 per cent. The residue appears to correspond to metal oxide or the metal itself. The FTIR of gaseous decomposition products of *Co* and *Ni* complexes evolved during TG [Figs 1(a), 1(b), and 1(c)] revealed the presence of additional absorption bands at 1838 cm^{-1} and 2238 cm^{-1}, indicating the presence of oxides of nitrogen along with the decomposition products obtained for carbohydrazide, *ie*, amide/ammonia: 3250 cm^{-1}, 1745 cm^{-1} and their substituted product, as well as a band at 2350 cm^{-1} for nitriles.

3.3 Sensitivity Behaviour of Metal Complexes

The h_{50} for *CCoN* was found to be 75 cm and it was insensitive to friction up to 28.8 kg whereas *CNiN* gave h_{50} of 59 cm and was insensitive to friction stimuli up to 19.2 kg (Table 4). The incorporation of *CCoN* and *CNiN* as additives in propellant formulation did not have adverse effect on sensitivity of the latter. It is not possible to obtain a direct relationship between the sensitivity behaviour of explosive materials and their chemical structure because of a complex interplay of physical and thermochemical characteristics. However, the relative vulnerability of *Cu* and *Ni* complexes appears to be in line with their activation energy, which may be considered as a measure of the probability of formation of hot spots.

3.4 Burning Rates

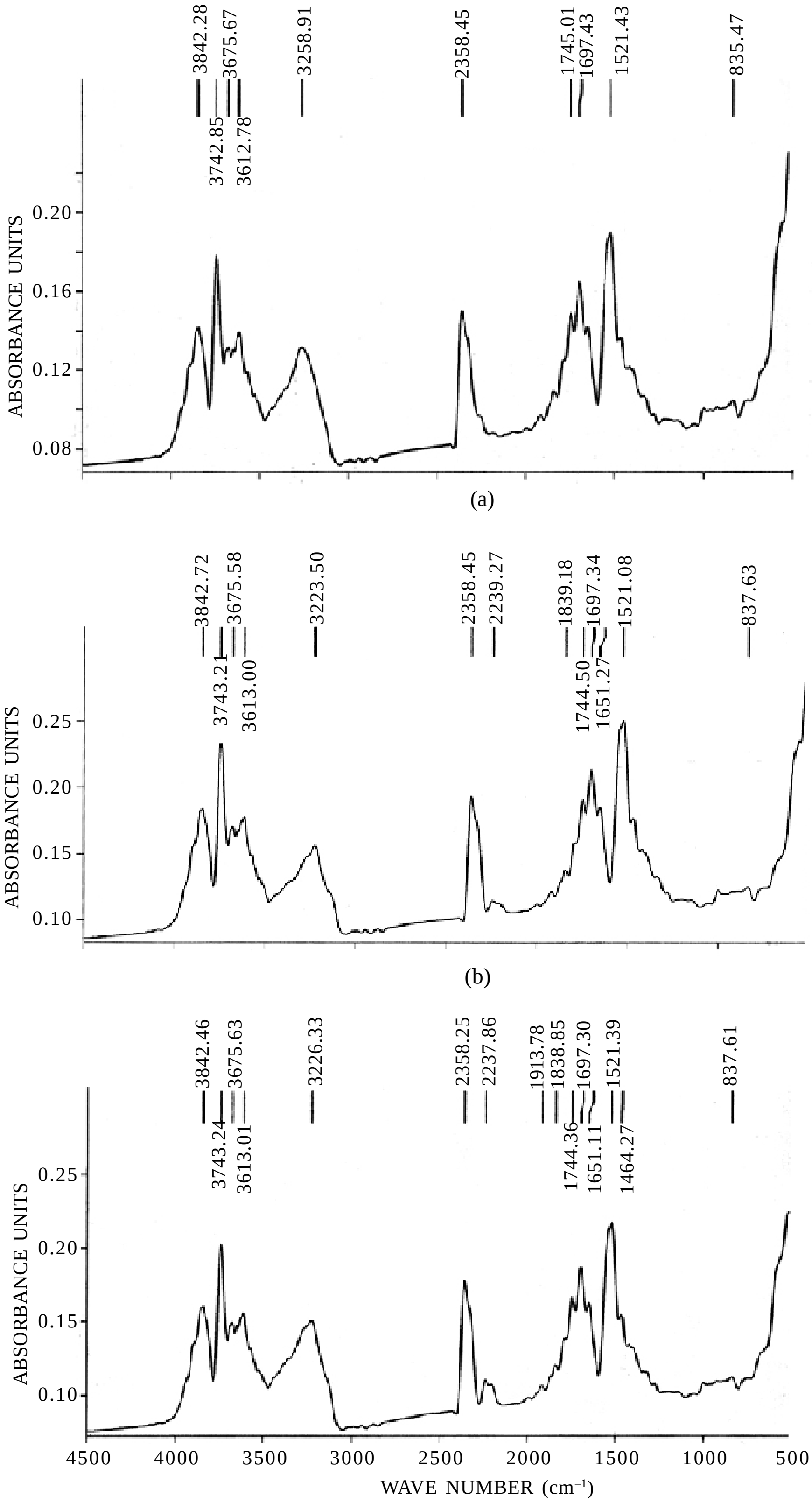
The burning rate results of *CCoN* and *CNiN* incorporated composite propellant formulations are given in Table 5. Control composite propellant gave burning rates of the order of 7.9–12.6 mm/s in the pressure range 1.9–8.8 MPa. Incorporation of *CCoN* resulted in burning rate enhancement of the order 9–19 per cent whereas addition of *CNiN* led to the

Table 3. TGA results of carbohydrazide-based metal complexes

Compound	TG Stage	Decomposition peak temp. (°C)	Loss in weight (%)
$H_2NHNCONHNH_2$	I	190	63
	II	310	35
$Co(H_2NHNCONHNH_2)_3(NO_3)_2$	I	285	78
$Ni(H_2NHNCONHNH_2)_3(NO_3)_2$	I	300	86

Table 4. Sensitivity properties of carbohydrazide-based metal complexes

Compound	Impact sensitivity h_{50} (cm)	Friction sensitivity (Insensitive up to kg)
$Co(H_2NHNCONHNH_2)_3(NO_3)_2$	75	28.8
$Ni(H_2NHNCONHNH_2)_3(NO_3)_2$	59	19.2
$Cu(H_2NHNCONHNH_2)_2(NO_3)_2$	32	24



(a)

(b)

(c)

Figure 1. TG-FTIR of gaseous products evolved during TG of : (a) carbohydrazide, (b) tris-carbohydrazide nickel (II) nitrate, and (c) tris-carbohydrazide cobalt (II) nitrate.

Table 5. Burning rates of carbohydrazide metal complexes-based composite propellant formulations

Binder (%)	AP % (9μ)	2 parts of catalyst	Burn rate (mm/s) at pressure (MPa)					*n*	I_{sp}, (Theo.) (s)
			1.9	2.9	4.9	6.9	8.8		
22	78	-	7.9	9.8	10.6	11.9	12.6	0.28	222
22	78	*CCoN*	8.6	10.4	12.6	14.2	15	0.34	223
22	78	*CNiN*	10.1	11.8	13.7	16.2	21.9	0.45	223

Base composition: Binder: 22 % [HTPB: 9.0 %, DOA: 11.0 %, pyrogallol: 0.5 %, lecithin: 0.3 %, TDI: 1.2 %]

burning rate enhancement of the order 27–72 per cent in the pressure range of 1.9–8.8 MPa. An attractive feature of these compounds was that they did not have penalty on I_{sp} of the composition as brought out by the theoretical prediction using REAL program.

4. ~~DIS~~CUSSION

Carbohydrazide complexes contain metal ion, fuel ligand, and oxidiser anion. The combustion of coordination complexes can proceed by various reaction routes. The NO_3^- anion is expected to decompose in subsequent steps to oxidising species ($NO_3^- \rightarrow O^- + NO_2$) as decomposition proposed by Sinditskii and Serushkin[2]. The presence of NO_2 detected in TG-FTIR spectra of gaseous products of *Co* and *Ni* complexes is in line with the proposed course of decomposition.

The combustion of coordination compounds is attributed to the oxidation of ligand via a metal-oxo intermediate formed due to the interaction of metal component with the oxidiser species. Metal ion introduced in this redox system at the molecular level is expected to play a prominent role in the combustion process. Moreover in the presence of ligand, M^{+n}/M^{+m} redox potential is expected to be reduced, facilitating[3] electron transfer-aided reaction occurring during combustion. These factors may be responsible for the catalytic effect of *Ni*/*Co* metal complexes on burning rates of composite propellants considered during this study. At the same time, the role of processes similar to those reported for transition-metal oxides (TMOs) can not be excluded. Most of the TMOs–(Cr_2O_3, *CoO* or Co_2O_3, *NiO*, Fe_2O_3) are well-known catalysts for AP decomposition. Burning rate enhancement effect of Fe_2O_3 and *Cu*-chromite on AP-based composite propellant is widely reported[11].

Kishore,[12] *et al.* have inferred that TMOs promote electron transfer process during AP decomposition, leading to the burning rate enhancement of AP propellant. They have supported their mechanism on the basis of the direct relation between the degree of burning rate enhancement with redox potentials of oxides as well as the heats of reaction associated with the electron transfer process.

5. CONCLUSION

Cobalt, nickel, and copper carbohydrazide nitrates, were synthesised and characterised by FTIR and metal content determination. DSC studies established relatively higher stability of *Co* and *Ni* complexes. TG-FTIR studies revealed that these molecules decompose with the evolution of oxides of nitrogen. Both the compounds catalysed the burning rates of composite propellants, probably due to both exothermic decomposition on the propellant surface and involvement of metal at molecular level in catalysing gas-phase reaction. The mechanism reported for TMOs is also expected to be operative.

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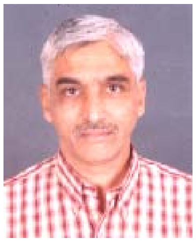

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