

# Investigations on the thermal behaviour of $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$ and $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ using TG–MS and TR-XRD under inert condition

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**Abstract** Thermal behaviour of hexaamminenickel(II) nitrate and tris(ethylenediamine)nickel(II) nitrate have been investigated by means of simultaneous thermogravimetry/DTA coupled online with mass spectral (MS) studies and temperature resolved X-ray diffraction (TR-XRD) techniques under inert atmospheric condition. Both the complexes produce highly exothermic reactions during heating due to the oxidation of the evolved ammonia or ethylenediamine by the decomposition products of  $\text{Ni}(\text{NO}_3)_2$ . Evolved gas analysis by MS studies detected fragments like  $\text{NH}_2$  and  $\text{NH}$  ions with weak intensity. The decomposition of nitrate group generates N,  $\text{N}_2$ , NO,  $\text{O}_2$  and  $\text{N}_2\text{O}$  species. Ethylenediamine ( $m/z$  60) is fragmented to  $\text{H}_2$  ( $m/z$  2), N ( $m/z$  14),  $\text{NH}_3$  ( $m/z$  17) and  $\text{CH}_2=\text{CH}_2/\text{N}_2$  ( $m/z$  28) species. The formation of the intermediates was monitored by in situ TR-XRD. The residue of thermal decomposition for both the complexes was found to be crystalline NiO in the nano range.

**Keywords** Exothermic reactions · NiO · Oxidation · TG–MS · TR-XRD

## Introduction

Thermal decomposition studies of transition metal amine complexes have been a subject of interest for many decades

due to their structural simplicity [1, 2]. Even though, many literature reports are available on the thermal decomposition of transition metal amine complexes, not many studies has been reported to date with regard to the evolved gas analysis (EGA) during thermal decomposition and also in detecting the transient intermediates formed during pyrolysis of the amine complexes [2]. To evolve an unambiguous picture on the decomposition, techniques like thermogravimetry (TG)–mass spectral (MS) and TR-XRD can be of immense use.

Conventional thermoanalytical techniques like TG, DTA and DSC do not tell the nature of the gaseous products. EGA offers a useful tool to identify the fragments which are not detected by other analytical techniques [3–5]. Temperature resolved X-ray diffractometry (TR-XRD) is a powerful tool to study the structural/phase changes occurring during a solid state reaction as well as in identifying the reaction intermediates in situ during pyrolysis. These methods enable the recording of a series of patterns, while the samples are heated continuously, stepwise, or isothermally during the reaction. These series contain information on the lattice of solids and on the structural changes as a function of temperature [6].

In this investigation, we have attempted to exploit these two in situ analytical techniques for a detailed study on the thermal decomposition behaviour of hexaamminenickel(II) nitrate and tris(ethylenediamine)nickel(II) nitrate. Thermal decomposition studies of nitrate containing transition metal amine complexes are of significance because of its exothermic decomposition and can be used in propellants, explosives and pyrotechniques [7–9]. The explosive decomposition of these complexes is attributed to the simultaneous presence of both oxidising (nitrate) and reducing (en or ammonia) groups in the same compound [2]. Among the amine nitrate complexes, bis(ethylenediamine)metal(II) nitrate is being

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employed as a burn rate modifier in the combustion of HTPB-AP based composite solid propellants [9].

## Experimental

The complexes were synthesized as per the procedure reported in the literature [10]. Nickel content in the complexes was determined by means of gravimetry [11]. The complexes were further characterized by spectral and chemical analyses.

### Instrumentations

Thermogravimetry–MS studies were carried out in a thermogravimetric apparatus (TG; Rigaku, TG8120) combined with quadruple mass spectroscopy (Anelva, M-QA200TS) under high-purity He gas flow (99.9999%) at a heating rate of 10 °C min<sup>-1</sup>. The mass spectrometer with high vacuum is connected to furnace with 3 bar He flow by a capillary with 1 m length and the  $m/z$  ranges 1–100.

The elemental analyses were carried out using Vario Elemental III instrument. X-ray powder patterns were recorded on a Bruker D8 Advance diffractometer attached with a programmable temperature device from Anton Paar (TTK 450) up to 300 °C (using Cu K $\alpha$  radiation,  $\lambda = 1.542$  Å). The measurements were performed by placing the sample on a flat sample holder, while the samples were heated by a programmable temperature controller. A series of diffraction patterns were recorded at every 20 °C rise of temperature. Crystallite size was calculated using Scherrer equation:

$$t = 0.9\lambda / \beta \cos\theta,$$

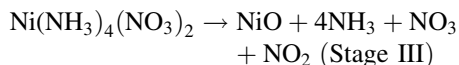
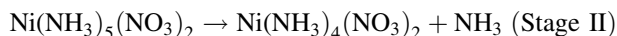
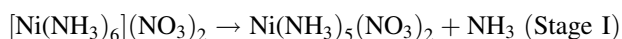
where  $t$  is the thickness of the particle,  $\lambda$  is the wave length,  $\beta$  is full width at half maximum and  $\cos \theta$  is the corresponding angle.

## Results and discussion

### TG–MS studies

#### Hexaamminenickel(II) nitrate

Simultaneous TG/DTA coupled online with MS plot of hexaamminenickel(II) nitrate is shown in Fig. 1a, b. From TG, it can be seen that hexaamminenickel(II) nitrate undergoes a three stage thermal decomposition. The different stages of thermal decomposition are as follows



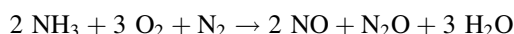
The complex starts to lose mass at 78 °C with the liberation of one molecule of ammonia. The second stage at 116 °C is also a deamination stage in which one molecule of ammonia is liberated to give an intermediate tetraammine complex. Third stage involves (164–300 °C) the simultaneous deamination and decomposition of the tetraammine complex to give NiO as the final residue.

The first two endotherms in the DTA correspond to the liberation of one molecule of ammonia each to form tetraammine complex. The third small endotherm is immediately followed by a sharp exotherm and is due to the initial decomposition of the tetraammine complex.

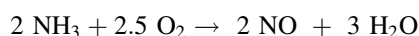
The sharp exothermic peak can be explained on the basis of the decomposition of Ni(NO<sub>3</sub>)<sub>2</sub>, overlapping the deamination reaction. Nickel nitrate on decomposition gives rise to oxides of nitrogen and oxygen as detected by TG–MS (Scheme 1) which in turn would oxidize the liberated ammonia [2]. In TG curve, simultaneous deamination and decomposition appear as a single stage whereas in DTA trace the initial deamination appears as an endotherm.

TG–MS plot reveals the presence of ion peak with mass number 17 in the temperature range 78–164 °C, indicating the evolution of ammonia. Along with the peaks of ammonia, ion peaks with mass numbers 15 and 16 were also observed during this temperature range. This could be due to the presence of NH and NH<sub>2</sub> ion species. The peaks corresponding to  $m/z$  values 14, 16, 28, 30, 32 and 44 indicate the presence of ions like N, O, N<sub>2</sub>, NO, O<sub>2</sub> and N<sub>2</sub>O formed by the fragmentation of NO<sub>3</sub> group. The possible fragmentation pattern for NO<sub>3</sub> is shown below.

The oxidation of ammonia also generates gaseous species like NO and N<sub>2</sub>O. The presence of ion peak with  $m/z$  value 18 can be attributed to the formation of water. The formation and evolution of water has been reported during the thermal decomposition of Co(NH<sub>3</sub>)<sub>6</sub>(NO<sub>3</sub>)<sub>2</sub>, Pd(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> complexes [12, 13]. The formation of water due to the reaction between the evolved gaseous products is shown below [14].



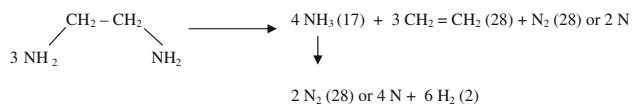
or



#### Tris(ethylenediamine)nickel(II) nitrate

Figure 2 shows the simultaneous TG/DTA coupled online with MS spectra for tris(ethylenediamine)nickel(II) nitrate. The complex decomposes at 220 °C in a single step to give





**Scheme 2** Fragmentation of ethylenediamine

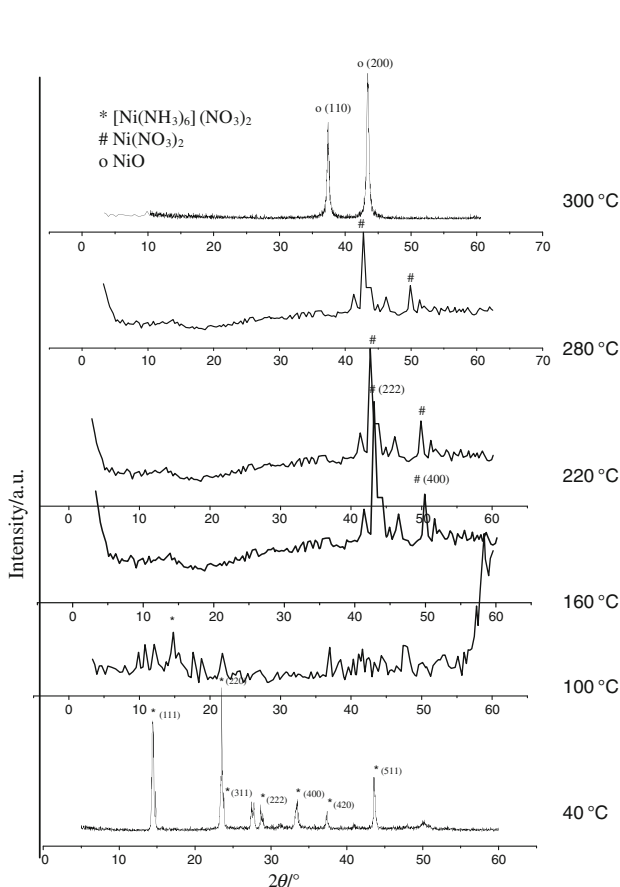
forms part of the lattice plane of the intermediate structures formed due to the deamination. The intermediate complex decomposes to give  $\text{Ni}(\text{NO}_3)_2$  at 160 °C and is stable up to 280 °C and the peaks at 42.68 and 49.92  $2\theta$  are indexed as (222) and (400) planes of  $\text{Ni}(\text{NO}_3)_2$  (JCPDS no. 74-2261). At 300 °C, NiO is formed as the residue by the decomposition of  $\text{Ni}(\text{NO}_3)_2$  and the peaks at 37.39 and 43.44  $2\theta$  correspond to the (110) and (200) planes of NiO (JCPDS no. 78-0429). Average crystallite size of NiO was calculated from the peak broadening value using Sherrer equation and was found to be 25.5 nm.

#### Tris(ethylenediamine)nickel(II) nitrate

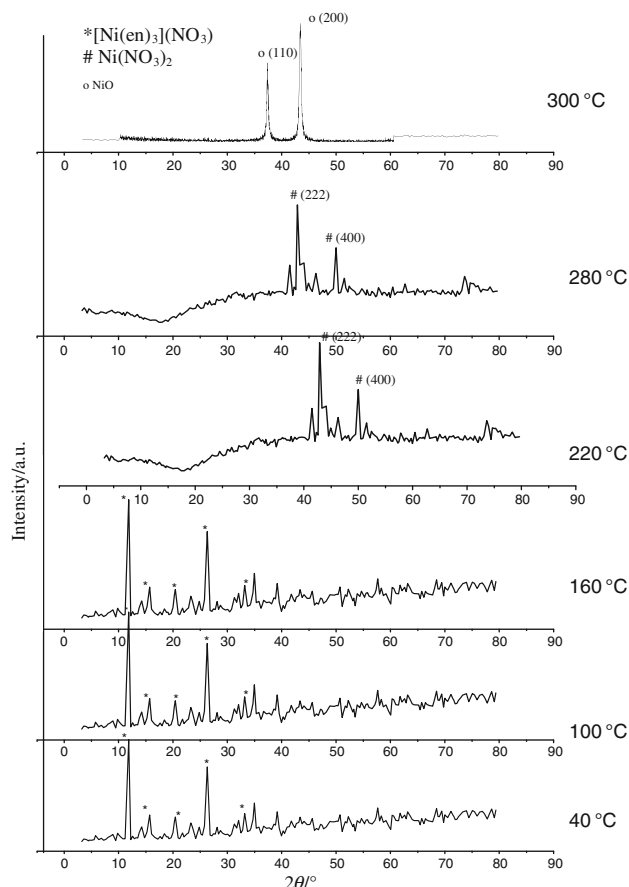
The temperature resolved X-ray diffractograms for the thermal decomposition of  $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$  are shown in Fig. 4. At

40 °C, the pattern corresponds to the trisethylenediamine complex and the peaks at 11.74, 15.76, 20.39 and 26.24  $2\theta$  indicate the different planes. In the temperature range 60–200 °C, the complex undergoes decomposition and consequent to that the intensity of the peaks decreases. At 220 °C, the deamination (release of three ethylenediamine molecules) process was completed resulting in the formation of  $\text{Ni}(\text{NO}_3)_2$  as intermediate in the temperature range 240–280 °C. The peaks at 42.91 and 49.97  $2\theta$  correspond to (222) and (400) planes of  $\text{Ni}(\text{NO}_3)_2$  (JCPDS no. 74-2261). It is to be noted that the detection of  $\text{Ni}(\text{NO}_3)_2$  phase in the TR-XRD in this temperature range (240–280 °C) as an intermediate during the thermal decomposition was not detected in the TG, DTA or DSC (Fig. 3) and TG result shows that this trisethylenediamine complex decomposes in a single step to give nickel oxide as the final product. This shows the advantage of temperature resolved X-ray measurements over DTA/DSC and TG in detecting intermediate phases during thermal decomposition.

Till 280 °C, the intermediate  $\text{Ni}(\text{NO}_3)_2$  phase is stable and on further heating decomposes to NiO as the final residue. The peaks at 37.29 and 43.43  $2\theta$  correspond to the

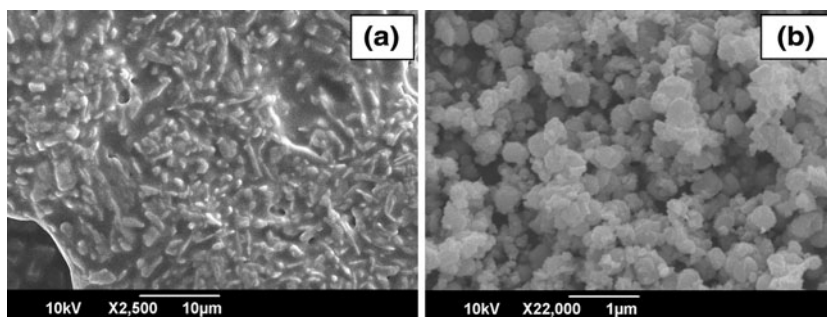


**Fig. 3** TR-XRD patterns for the thermal decomposition of hexaaminenickel(II) nitrate

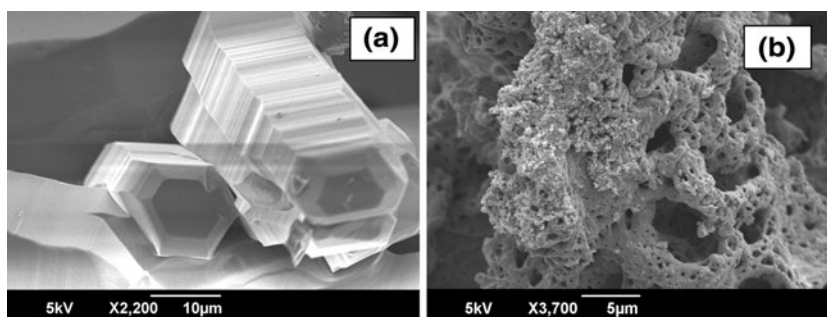


**Fig. 4** TR-XRD patterns for the thermal decomposition of tris(ethylenediamine)nickel(II) nitrate

**Fig. 5** SEM images of **a** hexaamminenickel(II) nitrate and **b** NiO



**Fig. 6** SEM images of **a** tris(ethylenediamine)nickel(II) nitrate and **b** NiO



(111) and (200) planes of NiO. MS spectra complement the observed TR-XRD results and the spectra show the evolution of NO,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , N and O at the temperature range 260–290 °C as the decomposition products of  $(\text{NO}_3)_2^-$  group. Average crystallite size of NiO was calculated from the peak broadening value using Sherrer equation and was found to be 23 nm.

### SEM analysis

The SEM images of hexaamminenickel(II) nitrate and the residue are shown in Figs. 5a, b. NiO formed from hexaamminenickel(II) nitrate is porous in nature. From the XRD measurement it is found that NiO formed is in the nano range.

The SEM images of tris(ethylenediamine)nickel(II) nitrate and the residue NiO are given in Figs. 6a, b. The SEM image shows that nano NiO formed is highly porous in nature. The porosity of the residues may be due to the escape of gaseous product during pyrolysis.

### Conclusions

Investigations on the thermal behaviour of hexaamminenickel(II) nitrate and tris(ethylenediamine)nickel(II) nitrate have been carried out by means of simultaneous TG/DTA coupled online with MS and TR-XRD techniques. Decomposition reactions involve highly exothermic oxidation reactions. EGA by MS detected  $\text{NH}_2$  and  $\text{NH}$  ions along with ammonia. The decomposition of nickel nitrate

generates ions like N,  $\text{N}_2$ , NO,  $\text{O}_2$  and  $\text{N}_2\text{O}$ . Oxidation of  $\text{NH}_3$  generates  $\text{N}_2\text{O}$ , NO and water and these species are evolved during pyrolysis. Ethylenediamine produces various ions like  $\text{NH}_3$ ,  $\text{CH}_2=\text{CH}_2$ ,  $\text{N}_2$ , N and  $\text{H}_2$ . The formation of the intermediates was monitored by in situ TR-XRD. The final residue of the decomposition is highly crystalline NiO nanoparticles for both complexes.

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### References

- George TD, Wendlandt WW. The thermal decomposition of metal complexes—II. Some ammine and ethylenediamine complexes of nickel (II). *J Inorg Nucl Chem.* 1963;25:395–405.
- Mathew S, Nair CGR, Ninan KN. Thermal decomposition studies on amine complexes of copper(II) nitrate in solid state. *Bull Chem Soc Jpn.* 1991;64:3207–9.
- Kooli F. Thermal stability investigation of organo-acid-activated clays by TG–MS and in situ XRD techniques. *Thermochim Acta.* 2009;486:71–6.
- Madara'sz J. Evolved gas analyses on a mixed valence copper(I, II) complex salt with thiosulfate and ammonia by insitu TG-EGA-FTIR and TG/DTA-EGA-MS. *J Therm Anal Calorim.* 2009;97:111–6.
- Sanders JP, Gallagher PK. Kinetic analysis of complex decomposition reactions using evolved gas analysis. *J Therm Anal Calorim.* 2009;96:805–11.
- Mathew S, Eisenreich N, Engel W. Thermal analysis using X-ray diffractometry for the investigations of the solid state reaction of ammonium nitrate and copper oxide. *Thermochim Acta.* 1995; 269/270:475–89.

7. Singh G, Pandey DK. Studies on energetic compounds: kinetics of thermal decomposition of nitrate complexes of some transition metals with propylenediamine. *Combust Flame*. 2003;135:135–43.
8. Kapoor IPS, Kapoor M, Singh G, Singh UP, Goel N. *J Hazard Mater*. 2010;173:173–80.
9. Singh G, Pandey DK. Studies on energetic compounds: kinetics and mechanism of thermolysis of bis(ethylenediamine)metal nitrate and their role in the burning rate of solid propellants. *Propellants Explos Pyrotech*. 2003;28:231–9.
10. Brauer G. *Hand book of preparative inorganic chemistry*. 2nd ed. New York: Academic press; 1965.
11. Vogel AG. *Text book of quantitative inorganic analysis*. 4th ed. Harlow: Longmann; 1978.
12. Skoczylas ML, Mikuli E, Szklarzewicz J, Hetmanczyk J. *Thermochim Acta*. 2009;496:38–44.
13. Madarasz J, Bombicz P, Matyas C, Reti F, Kiss G, Pokol G. Comparative evolved gas analytical and structural study on *trans*-diammine-bis(nitrito)-palladium(II) and platinum(II) by TG/DTA-MS, TG-FTIR and single crystal X-ray diffraction. *Thermochim Acta*. 2009;490:51–9.
14. Mikuli AM, Hetmanczyk J, Mikuli E, Hetmanczyk L. Thermal behaviour of polycrystalline  $[\text{Ba}(\text{H}_2\text{O})_3](\text{ClO}_4)_2$  and  $[\text{Ba}(\text{NH}_3)_4](\text{ClO}_4)_2$ . *Thermochim Acta*. 2009;487:43–8.