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SYNTHESIS, TG, DSC AND INFRARED SPECTRAL STUDY OF $NiMn_2(C_4H_4O_4)_3·6N_2H_4$
A precursor for $NiMn_2O_4$ nanoparticles

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Nickel manganese succinato-hydrazinate ($NiMn_2(C_4H_4O_4)_3·6N_2H_4$), has been synthesized for the first time by a novel precursor technique and characterized by IR, AAS and XRD. Thermal decomposition of the compound was studied from room temperature (*rT*) to 800°C by differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis besides isothermal mass loss studies. The compound was found to decompose autocatalytically, once ignited. TG-DSC shows two steps decomposition i.e. dehydrazination followed by decarboxylation. The infrared spectral studies show the N–N stretching frequency at 972 cm^{-1} suggesting a bidentate bridging structure of hydrazine molecule in ($NiMn_2(C_4H_4O_4)_3·6N_2H_4$).

Keywords: *DSC, IR spectra, $NiMn_2(C_4H_4O_4)_3·6N_2H_4$, synthesis, TG*

Introduction

The transition metals and carboxylate solutions containing hydrazine, forms metal carboxylato-hydrazinate complexes [1–3]. The chemistry of hydrazine is interesting not only because it has a potent N–N bond, two free electron pairs and four substitutable hydrogen atoms but also because it forms various complexes with transition metals [4, 5]. Thermal reactivity of metal hydrazine complexes is of interest since the stability of these complexes changes dramatically, depending upon the carboxylate and other anions as well as the metal cations [5, 6]. Secondly, hydrazine being a fuel not only supports combustion but also lowers the decomposition temperature of the metal complexes. These complexes are important as precursors to obtain simple as well as mixed ultrafine metal oxides (nanopartcles), which can have interesting electrical, magnetic, biological and catalytic properties [4, 5]. Nanotechnology has attracted increasing interest in the past 20 years. Therefore, it is not surprising that many authors have studied nanomaterials and their various properties [7–22]. We are reporting here the preparation, infrared spectral studies and thermal reactivity of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$.

Experimental

Preparation of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$

The method of preparation of nickel manganese succinato-hydrazinate is similar to that described for the synthesis of nickel manganese fumarato-hydrazinate [23]. A requisite quantity of sodium succinate in aqueous medium was stirred with hydrazine hydrate, $N_2H_4·H_2O$ (99–100%) in an inert atmosphere for 2 h. To this solution, another solution containing nickel and manganese chloride in stoichiometric amount was added with constant stirring in an inert atmosphere. The precipitate of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$, which was formed immediately was then filtered off, washed with ethanol, dried with ether and stored in a vacuum desiccator for characterisation.

Characterisation of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$

$NiMn_2(C_4H_4O_4)_3·6N_2H_4$ was characterized by infrared analysis using Shimadzu FTIR spectrophotometer, model 8101A. Simultaneous differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis of the complex were carried out on a Netzsch STA 409 (Luxx) analyser from *rT* to 800°C in static air. The heating rate was 10°C min^{-1}. The isothermal and the total mass loss studies of the complex were carried out at various predetermined tempera-

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tures. The isothermal intermediate products were also chemically analysed for the hydrazine content and characterized by infrared spectral measurements. The elemental analysis of the complex has been carried out using an atomic absorption spectrophotometer (model Chemito AAS 201). The hydrazine content of the complex was analysed using KIO_3 as titrant [24].

Results and discussion

Chemical formula fixation and infrared analysis of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$

A chemical formula of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$ has been fixed for nickel manganese succinato- hydrazinate based on the observed percentage of hydrazine (27.08), nickel (8.28) and manganese (15.29), which match closely with the calculated values of 27.09, 8.28 and 15.50 percent for hydrazine, nickel and manganese, respectively (Table 1). Similarly, the observed mass loss of 67.12% when heated in air at 800°C matches well with the calculated one of 67.18% (considering formation of $NiMn_2O_4$), based on the above formula.

Table 1 Observed and calculated chemical compositions and total mass loss of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$

	Ni/ %	Mn/ %	Hydrazine/ %	Total mass loss/%
Obs.	8.28	15.29	27.08	67.12
Calc.	8.28	15.50	27.09	67.18

Infrared spectra of the $NiMn_2(C_4H_4O_4)_3·6N_2H_4$ (Fig. 1) shows three bands in the region 3250–3362 cm^{-1} due to the N–H stretching frequencies. The bands in the range of 1565–1590 cm^{-1} are due to NH_2 deformation while those in the region of 1126–1176 cm^{-1} are due to NH_2 stretching. The N–N stretching frequency at 972 cm^{-1} confirms the bidentate bridging the hydrazine molecule [25]. The asymmetric and symmetric stretching frequencies of the carboxylate ions are seen at 1625 and 1416 cm^{-1}, respectively with the $\Delta\nu(\nu_{asy}–\nu_{sy})$ separation of 209 cm^{-1}, indicating the monodentate linkage of both carboxylate groups in the dianion [26]. The band at 800 cm^{-1} is due to $\delta_{O–C–O}$ frequency.

Thermal analysis of nickel manganese succinato-hydrazinate

Nickel manganese succinato-hydrazinate can be decomposed by normal thermal treatment as well as by autocatalytic decomposition.

In the autocatalytic decomposition the dried complex is first spread over a ceramic tile and a burning splinter is brought near to it. A small portion of the complex, which is close to the burning splinter catches fire and a red glow that forms spreads slowly over the entire bulk completing the total decomposition of the complex in an ordinary atmosphere to form $NiMn_2O_4$. This autocatalytic decomposition is possible due to the fact that hydrazine present in the complex reacts with the atmospheric oxygen, once ignited, to liberate enormous energy in the form of heat that is sufficient to ox-

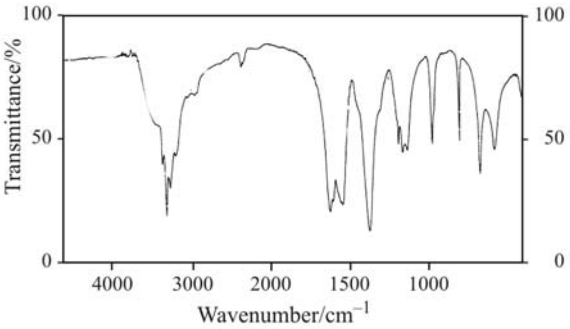

Fig. 1 Infrared spectra of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$

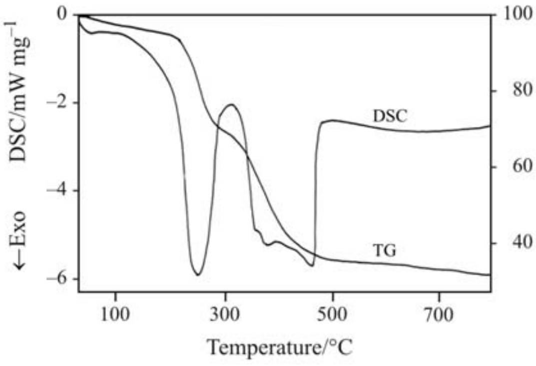

Fig. 2 TG-DSC curves of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$

Table 2 Thermo-analytical data of $NiMn_2(C_4H_4O_4)_3·6N_2H_4$

Compound	TG		DSC
	Temp. range/°C	Mass loss/%	Exo/endo peaks/°C
$NiMn_2(C_4H_4O_4)_3·6N_2H_4$	*rT*–200	4.83	weak exo/80
	200–290	24.83	intensive exo/249
	290–469	34.52	broad exo/464
	469–800	4.46	weak exo/600

idatively decompose the dehydrazinated complex into metal oxide. It is known that oxidation of hydrazine produces nitrogen and water along with the liberation of 621 kJ mol^{-1} of energy [27].

The TG trace of $NiMn_2(C_4H_4O_4)_3 \cdot 6N_2H_4$ (Fig. 2) from *rT* to 800°C shows four mass loss regions with two major ones. The mass losses of 4.83 and 24.83% from *rT* to 200°C and from 200 to 290°C (Table 2) were due to the decomposition of one and five N_2H_4 molecules, respectively. DSC curve of the complex (Fig. 2) shows a sharp exothermic peak at 249°C due to the dehydrazination. The major mass loss of 34.52% on TG curve from 290 to 469°C can be attributed to the decarboxylation of dehydrazinated succinate precursor. DSC curve also shows a broad exothermic peak between 290 to 469 °C with maximum peak temperature at 464 °C due to oxidative decarboxylation. A minor mass loss of 4.46%, which has been observed in TG curve from 469°C onwards may be due to two simultaneous processes namely, oxidation of small parts of unburnt carbon (left over after decarboxylation) using oxygen from nickel oxide thereby reducing it to nickel and thus amounting to further mass loss on TG curve.

Isothermal mass loss studies of the complex in air along with the constant monitoring of hydrazine percentage in it, shows that total dehydrazination takes place around 200°C while total mass loss of 67.13% takes place at 400°C. The infrared spectra of the intermediate product and final product taken at 200 and 400°C, respectively confirms the results obtained in the isothermal mass loss studies.

Conclusions

- Nickel manganese succinato-hydrazinate can be synthesized easily from sodium succinate, nickel chloride, manganese chloride and hydrazine hydrate in an inert atmosphere at room temperature.
- Chemical analysis, total mass loss and infrared studies of the complex confirms the formation of the complex with formula $NiMn_2(C_4H_4O_4)_3 \cdot 6N_2H_4$.
- The N–N stretching frequency in IR spectra at 972 cm^{-1} confirms the presence of the bidentate bridging hydrazine molecule while $\Delta\nu_{coo}(\nu_{asy}-\nu_{sy})$ separation of 209 cm^{-1}, indicate the monodentate linkage of both carboxylate groups in the dianion.
- TG-DSC studies of the complex show two steps for dehydrazination followed by decarboxylation.
- The complex decomposes autocatalytically once ignited to form $NiMn_2O_4$ at 400°C.

This method thus gives an efficient way of preparing $NiMn_2O_4$ nanoparticles at lower temperature. Preliminary studies have proved that the $NiMn_2O_4$ has a nanoparticle structure. Semiconductive magnetic nanoparticles have numerous biological and many other applications including the drug delivery, tumour detection, contaminated land cleaning and polluted water purification. The details of $NiMn_2O_4$ nanoparticles synthesis together with their magnetic and semiconductor properties as well as TEM, XRD, FTIR spectral analysis will be published in a future article.

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