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SYNTHESIS, CHARACTERIZATION AND THERMAL ANALYSIS OF $[Fe(N_2H_4)_2(CH_3COO)_2]$

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Abstract

$[Fe(N_2H_4)_2(CH_3COO)_2]$ was synthesised and characterized for the first time by chemical analysis, magnetic measurements, electronic and IR spectral studies. Its thermal reactivity was ascertained by thermogravimetric (TG) and derivative thermogravimetric (DTG) techniques and it has been concluded that unlike some other metal carboxylate hydrazinates, it does not show any autocatalytic behaviour. The decomposition was also subjected to kinetic analysis using the equations of Coats-Redfern and Horowitz-Metzger by the method of weighted least-squares.

Keywords: complexes, $[Fe(N_2H_4)_2(CH_3COO)_2]$, kinetics, TG-DTG

Introduction

Hydrazine, by virtue of its positive heat of formation (ΔH_f^o = 12 kcal·mol^{-1}) is thermodynamically unstable. Practically however, it is quite stable and can be handled safely. The general activity, especially the thermal stability of metal hydrazinates changes dramatically with the anion. Among the hydrazinates of metal carboxylates, those of metal acetates are least studied [1]. There is no report on the synthesis, characterization and thermal studies of Fe(II) acetate hydrazinate. This prompted us to undertake the present investigation.

Experimental

Materials

All chemicals used in the present investigation were of BDH, AnalaR quality. The metal complex was prepared by following methods already reported for

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the preparation of similar complexes with suitable modifications [2]. To a mixture of ethanolic solution of ammonium acetate and hydrazine hydrate, aqueous solution of ammonium ferrous sulphate was added with constant stirring. The reaction proceeded as follows:

$$FeSO_4(NH_4)_2SO_4 \cdot 6H_2O + 2NH_4(CH_3COO) + 2N_2H_4 \cdot H_2O \rightarrow \quad (1)$$
$$\rightarrow [Fe(N_2H_4)_2(CH_3COO)_2] + 8H_2O + 2(NH_4)_2SO_4$$

The complex which precipitated out instantaneously was filtered off, washed with ethanol and dried under reduced pressure over P_4O_{10}.

Methods

The metal and hydrazine present in the complex were estimated by standard methods [3]. The magnetic susceptibility measurement of the complex was done on a Gouy-type magnetic balance employing $Hg[Co(NCS)_4]$ as a calibrant. Diamagnetic correction was made by using Pascal's constants [4]. The electronic spectrum was recorded by reflectance technique on a Hitachi-220 UV/Vis spectrophotometer. The IR spectrum (KBr disc) was recorded on a Perkin-Elmer 397 spectrophotometer.The sample for thermogravimetric (TG) analysis was powdered and the particle size was fixed in the range 150–200 BSS mesh. The TG measurement was performed on a Perkin-Elmer TGA-7 thermobalance with the following operational characteristics: heating rate, 10 deg·min^{-1}; sample size, 14.21 mg; atmosphere, static air; crucible, platinum. The final decomposition product and the stable intermediate in air were examined by independent pyrolysis experiments in which the samples were heated for 2 h in a muffle furnace which was maintained at the required temperature ranges. The numerical analysis of the thermogravimetric data were realized using a program written in microsoft BASIC for an IBM computer using DOS 4.00.

Results and discussion

The data obtained from chemical analysis and physico-chemical measurements can be correlated in a critical manner so as to explain the properties and structure of the complex.

Formulation and general properties

The analytical data of the complex (Fe = 29.45% and hydrazine = 26.75%) correspond to the composition, $[Fe(N_2H_4)_2(CH_3COO)_2]$. It is yellowish brown amorphous powder and is stable in air and insensitive to light. It is found to be

almost insoluble in all solvents, including DMF and DMSO. This is only to be expected as this type of compounds prefer to exist in polymeric structures.

Magnetic moment and electronic spectrum

For magnetically dilute octahedral Fe(II) complexes, moments around 5.00 to 5.20 B.M. are expected [4]. However, even a slight deviation from octahedral symmetry may result in drastic reduction of magnetic moments, even upto 3.90 B.M. A magnetic moment value of 5.15 B.M. for $[Fe(N_2H_4)_2(CH_3COO)_2]$ reveals its octahedral geometry. The complex exhibits peak at 1100 nm and an associated weak broad band at 800 nm. These can be assinged to the $^5T_{2g} \rightarrow {}^5E_g$ transition of a spin-free octahedral Fe(II), since this transition usually give rise to a broad absorption split into two components due to the Jahn-Teller effect [5].

Infrared spectrum

The bands above 3000 cm^{-1} can be assigned to νNH of NH_2 groups. The position of these bands at about 50–100 cm^{-1} lower in frequency than in the spectrum of free hydrazine, indicates the participation of the nitrogen atoms in coordination to the metal ion [6]. The wide separation ($\Delta\nu = 190$ cm^{-1}) between $\nu_{asym\ COO^-}$ (at 1610 cm^{-1}) and $\nu_{sym\ COO^-}$ (at 1420 cm^{-1}) of the acetate groups in the spectrum of the complex supports their monodentate nature [7]. The band at 985 cm^{-1} can be attributed to ν_{N-N} of bidentate bridged hydrazine [6]. The bands of medium intensities at 690 and 380 cm^{-1} can be assigned to ν_{M-O} and ν_{M-N} respectively [7].

As the complex was isolated as powder and not as a single crystal, complete structure elucidation by X-ray studies could not be made. However, spectroscopic and magnetic data enable us to predict that CH_3COO^- acts as a unidentate monoanion and N_2H_4 acts as a bidentate bridging neutral ligand and hence the complex will invariably be polymeric with the metal ion in an octahedral environment.

Thermal behaviour

The TG and DTG curves of $[Fe(N_2H_4)_2(CH_3COO)_2]$ are shown in Fig. 1. The thermal decomposition of the complex occurs in two steps. The first step of decomposition starts at 448 K and is marked with a regular loss in mass upto 513 K. This is represented by the DTG peak at 491 K. The initial mass loss for the complex in TG (27.10%) and that obtained in independent pyrolysis (27.25%) agree well with the theoretically expected loss (26.91%) due to the elimination of two hydrazine molecules. The TG remains horizontal to the tem-

perature axis from 513 to 813 K, indicating the stability of dehydrazinated product, $[Fe(CH_3COO)_2]$ in this temperature range.

$$3[Fe(N_2H_4)_2(CH_3COO)_2] \rightarrow 3[Fe(CH_3COO)_2] + 8NH_3 + 2N_2 \quad (2)$$

The second step of decomposition of the complex is between 813 1nd 973 K and is represented by the DTG peak at 917 K. The final decomposition product which is stable beyond 973 K was analysed to be Fe_2O_3.

$$4[Fe(CH_3COO)_2] + 17O_2 \rightarrow 2Fe_2O_3 + 16CO_2 + 12H_2O \quad (3)$$

There is close agreement between the mass loss data from TG (54.62%), independent pyrolysis (54.85%) and theoretical (54.07%) for the above process.

Many hydrazinates of metal carboxylates show autocatalytic behaviour [8], for which the decomposition of hydrazine and metal salt should occur simultaneously. However, as hydrazine is lost exothermically at a lower temperature before the exothermic decomposition of Fe(II) acetate, $[Fe(N_2H_4)_2(CH_3COO)_2]$ does not exhibit any autocatalytic decomposition behaviour.

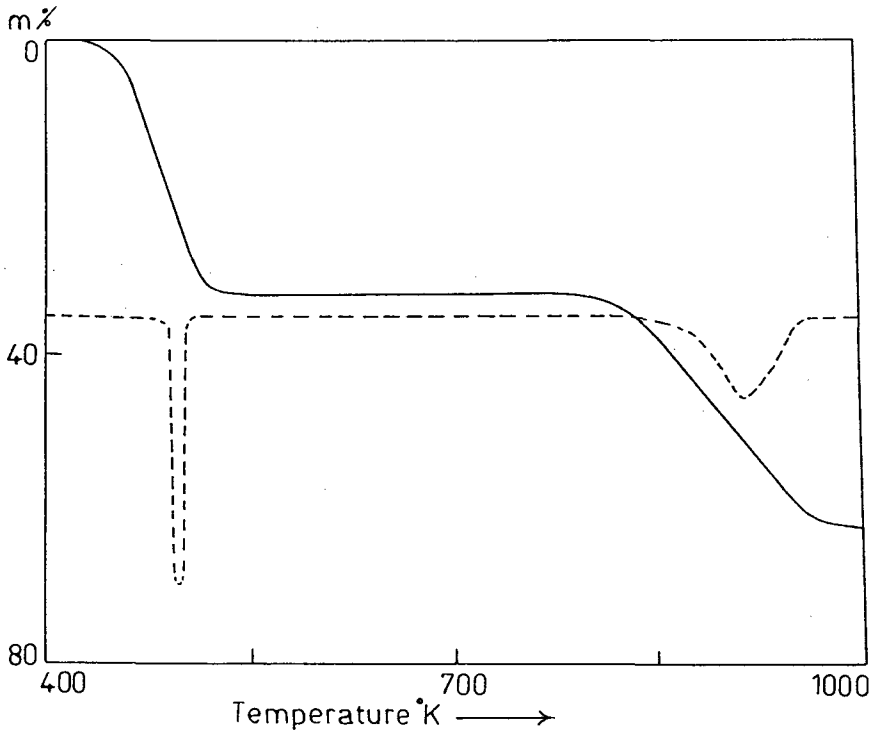

Fig. 1. TG (—) and DTG (-----) traces of $[Fe(N_2H_4)_2(CH_3COO)_2]$

Decomposition kinetics

The instrumental TG trace was redrawn as fraction decomposed (α) against temperature (T) curve to get the primary α–T data for both the stages of decomposition (Fig. 2). The α–T curves begin with acceleratory periods, followed by decay periods. As these curves do not begin with any apparent induction periods, it is clear that the initial stages involve no physical desorption. It also indicates that no surface nucleation or branching occurs before the decomposition starts [9].

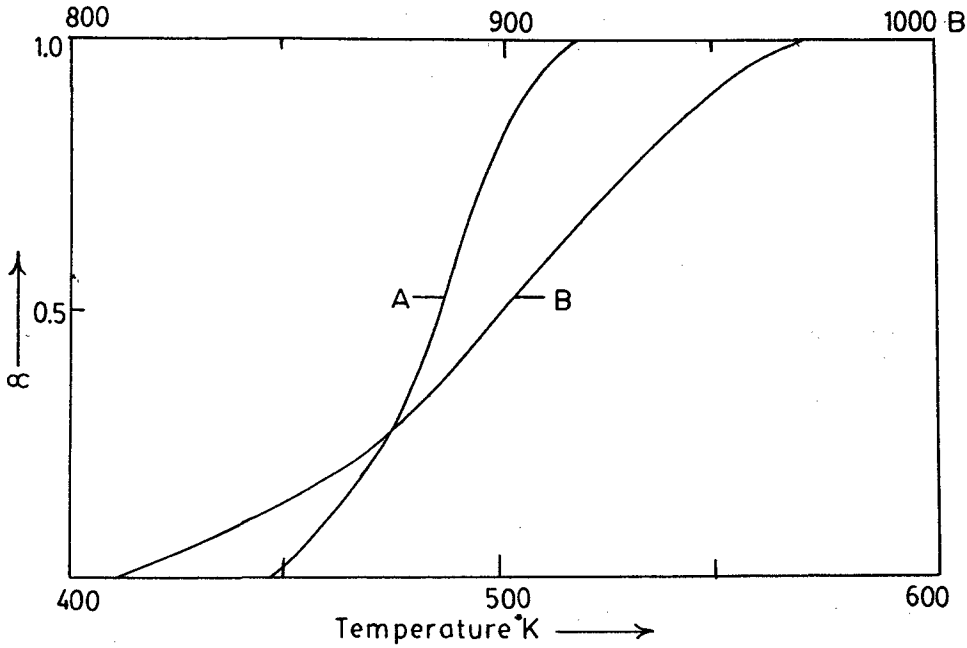

Fig. 2. α–T plots for the decomposition of $[Fe(N_2H_4)_2(CH_3COO)_2]$; (A) first stage and (B) second stage

The two decomposition steps of the complex were subjected to non-isothermal kinetic studies and the parameters, such as the overall order of reaction (n), apparent activation energy (E), the pre-exponential factor (A) and entropy of activation (ΔS) were calculated and are given in Table 1. The weighted least-squares method (weighted LSM) was used to evaluate the kinetic parameters, as detailed in earlier work [10].

The order of the decomposition reaction was determined by computing the correlation coefficient (r), using the weighted LSM, for the equation suggested by Coats and Redfern [11] (with n=0, 1/2, 2/3 and 1) and the maximum value was obtained for the equation with n=1. The method of Horowitz and Metzger

Table 1 Kinetic data of $[Fe(N_2H_4)_2(CH_3COO)_2]$

Equation	Decomp. stage	E / kJ·mol^{-1}	A / s^{-1}	ΔS / J·mol^{-1}·K^{-1}	r
Coats-	first	132.4	$8.19 \cdot 10^{13}$	−171.7	0.9991
Redfern	second	177.0	$3.18 \cdot 10^{9}$	−182.5	0.9980
Horowitz-	first	146.7	$2.95 \cdot 10^{15}$	−168.1	0.9975
Metzger	second	202.9	$1.04 \cdot 10^{11}$	−179.0	0.9949

[12] was also applied and the order was determined by constructing a 'master curve', as reported in earlier work [13]. With this value of n, the kinetic parameters were evaluated separately using the following non-mechanistic equations.

Coats-Redfern equation [11]

$$\ln [- \ln (1 - \alpha)/T^2] = \ln \frac{AR}{qE}\left[1 - \frac{2RT}{E}\right] - \frac{E}{RT} \tag{4}$$

where R is gas constant and q is the constant rate of heating.

Horowitz-Metzger equation [12]

$$\ln [- \ln (1 - \alpha)] = \frac{E\Theta}{RT_s^2} \tag{5}$$

where $\Theta = T - T_s$ and T_s is the DTG peak temperature.

The left-hand side of each of the above equation was plotted, using the weighted LSM, against reciprocal absolute temperature ($1/T$) for Eq. (4) and against Θ for Eq. (5). E and A were calculated from the slope and intercept, respectively for Eq. (4). In the case of Eq. (5) E was calculated from the slope and A was calculated using the equation

$$A = \frac{Eq}{RT_s^2} \exp(E/RT_s) \tag{6}$$

In all cases, ΔS was calculated using the equation

$$\Delta S = R \ln[Ah/kT_s] \tag{7}$$

where h is the Planck constant and k is the Boltzmann constant.

Satisfactory values of $r(r \approx 1)$ in all cases indicate good agreement with the experimental data. The values of kinetic parameters obtained from the two

methods are comparable and in good agreement. The small negative values of the activation entropy indicate that the transition states involved in the decomposition processes have more ordered structures than the reactants and that the reactions are slower than normal [14].

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Zusammenfassung — $[Fe(N_2H_4)_2(CH_3COO)_2]$ wurde erstmalig hergestellt und mittels chemischer Analyse, magnetischen Messungen sowie Elektronen- und IR-Spektraluntersuchungen untersucht. Mit Hilfe von TG- und DTG-Techniken wurde dessen thermische Reaktivität ermittelt und man kam zu der Schlußfolgerung, daß es im Gegensatz zu einigen anderen Metallkarboxylathydrazinaten keinerlei autokatalytisches Verhalten zeigt. Unter Anwendung der Gleichungen von Coats-Redfern und Horowitz-Metzger wurde die Zersetzung auch einer kinetischen Analyse unterzogen.