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Thermal decomposition of potassium hexanitronickelate(II) hydrate

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Abstract

The thermal decomposition of the complex $K_4[Ni(NO_2)_6]{\cdot}H_2O$ has been investigated over the temperature range 25–600 °C by a combination of infrared spectroscopy, powder X-ray diffraction, FAB-mass spectrometry and elemental analysis. The first stage of reaction is loss of water and isomerisation of one of the coordinated nitro groups to form the complex $K_4[Ni(NO_2)_4(ONO)]{\cdot}NO_2$. At temperatures around 200 °C the remaining nitro groups within the complex isomerise to the chelating nitrite form and this process acts as a precursor to the loss of NO_2 gas at temperatures above 270 °C. The product, which is stable up to 600 °C, is the complex $K_4[Ni(ONO)_4]{\cdot}NO_2$, where the nickel atom is formally in the +1 oxidation state.

Keywords: Thermal analysis; Nickel(II); Nitro; Potassium salt; X-ray diffraction; IR data

1. Introduction

Because of its capability of bonding to metal atoms in a variety of different ways, the nitrite ion in complexes has been of interest for many years and a range of nickel(II) polynitrite complexes of differing composition have been prepared [1–6]. It has been known for 150 years that addition of nickel(II) ions to an aqueous solution of potassium nitrite produces an orange crystalline precipitate [7]. This product was originally formulated as $K_4[Ni(NO_2)_6]$ although it was subsequently shown that the orange compound is in fact a monohydrate. The compound $K_4[Ni(NO_2)_6]{\cdot}H_2O$ contains the $[Ni(NO_2)_6]^{4-}$ ion with 6N bonded nitro ligands. IR and electronic spectra suggest that the water molecule is not directly bonded to the nickel centre [8,9]. The dehydration of $K_4[Ni(NO_2)_6]{\cdot}H_2O$ and the simultaneous linkage isomerisation has been studied using TGA and DSC [10,11] and the kinetics of the isomerisation process has been investigated [12]. While most hydrated compounds can be dehydrated without inducing other changes, it was confirmed that the dehydration of orange $K_4[Ni(NO_2)_6]{\cdot}H_2O$ at 100 °C produces the red complex $K_4[Ni(NO_2)_4(O_2N)]{\cdot}NO_2$ [13]. According to the published data rehydration of the hygroscopic mixture at ≈20 °C causes $K_4[Ni(NO_2)_6]{\cdot}H_2O$ to be reformed [13]. The nickel(II) in $K_4[Ni(NO_2)_4(O_2N)]{\cdot}NO_2$ has a distorted octahedral ligand environment, with four nitrites co-ordinated via nitrogen, and a fifth chelating via the two oxygen atoms [13]. Although dehydration and linkage isomerisation have been studied in detail, a complete thermal decomposition analysis of the complex has never been explored. In the present work the thermal dehydration, isomerisation and decomposition behaviour of potassium hexanitronickelate(II) hydrate ($K_4[Ni(NO_2)_6]{\cdot}H_2O$) over the temperature range 25–800 °C has been investigated. A further decomposition reaction has been discovered in this work, which occurs between 235 and 275 °C and the nature of this reaction is discussed in terms of thermal data, elemental analysis, atomic absorption spectroscopy, infrared spectroscopy, X-ray diffraction and mass spectrometry.

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2. Experimental

2.1. Instrumentation

2.1.1. Thermal analysis unit

A Stanton Redcroft thermal analysis system (TG/DTA-32), with a temperature-programmable thermal balance, and a platinum crucible was used for obtaining TGA and DSC thermograms in air. The rate of heating was fixed at 10 K/min. The sensitivity of the instrument is 0.1 mg.

2.1.2. Infrared spectra

IR spectra of solid complexes in KBr discs were recorded using a Mattson 1000 FT interferometer. A mixture of approximately 5% of the sample with KBr was ground in a pestle and mortar and pressed into a disc. Typically 16 scans were run at 4 cm^{-1} resolution for each spectrum.

2.1.3. X-ray diffraction data

X-ray powder diffraction (XRD) patterns were recorded at the Cu $K\alpha_1$ wavelength of 1.540598 Å on a spectrolab CPS 120 Series 3000 X-ray diffractometer attached to a microprocessor equipped with an Inel Multichannel position-sensitive detector. Samples were ground into a very fine powder before analysis.

2.1.4. Elemental analysis

CHN analyses were performed at The Technical and Scientific Research Council of Turkey, TUBITAK by burning the sample at high temperature (1000–1100 °C) and measuring CO_2, H_2O and N_2 concentrations on a LECOCHNS-0-9320 instrument. Potassium and nickel concentration were measured at The University of Reading using a Sherwood Model 410 Flame Photometer and a Perkin-Elmer Model 1100B Atomic Absorption Spectrophotometer, respectively.

2.1.5. FAB-mass spectra

Fast atom bombardment (FAB) mass spectrometry is a technique in which samples are ionised by bombardment with a beam of highly energetic atoms of (for example) xenon or argon. Samples are typically dissolved in a non-volatile solvent in order to reduce the lattice enthalpy that must be overcome if the ions are to be liberated from a sample. FAB-ionisation techniques are particularly suitable for analysing higher molecular weight samples. In the current work positive-ion FAB-mass spectra were recorded at TUBITAK on a JEOL SX102 mass spectrometer operating at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol matrix using 3 keV xenon atoms.

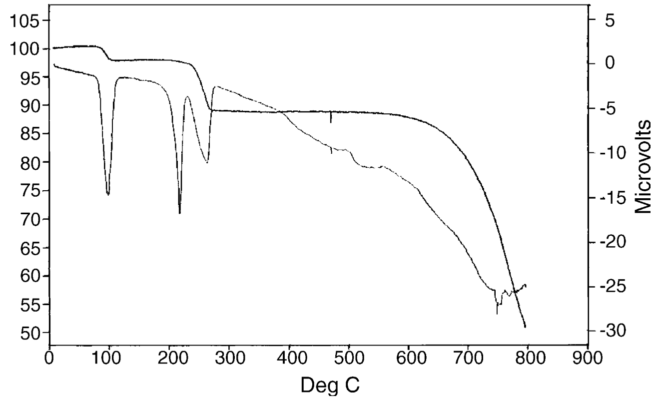

Fig. 1. TG/DTA curve of potassium hexanitronickelate(II) hydrate.

2.1.6. The apparatus for the collection of gaseous products on the vacuum line

A glass vacuum line fitted with Young's taps was used for the thermal decomposition experiment, in order to sample gaseous products. In this apparatus a speedivac mercury diffusion pump, backed by a high vacuum rotary pump, enabled a pressure of ca. 1×10^{-5} Torr to be attained. A 0.27 g sample of $K_4[Ni(NO_2)_6]\cdot H_2O$ was placed in an evacuated reactor (volume 200 cm^3) fitted with a break seal. The reactor was removed from the vacuum line after sealing and was left in an oven at 280 °C overnight. After this time the reactor was left to cool before being fitted with a tap, joint and side arm containing a ball bearing to open the break seal. This apparatus was transferred back onto the vacuum line and the connector was evacuated before the seal was broken. The gaseous products were transferred to a gas cell fitted with KBr windows for IR spectroscopic analysis.

2.2. Preparation and analysis

The $K_4[Ni(NO_2)_4]\cdot H_2O$ complex salt was prepared by adopting the method of Goodgame and Hitchman [9]. A concentrated aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$ was added to a saturated solution of KNO_2. The latter compound was in excess. The solid product was separated by filtration and was dried for several days in a desiccator.

Table 1
Summary of the thermal decomposition of the potassium hexanitronickelate(II) hydrate

Compound	ΔT_{min} (°C)	Step number	Temperature (°C)		Loss in weight (%)	
			Starting	Ending	Observed	Calculated
$K_4[Ni(NO_2)_6]\cdot H_2O$	100	1	95.2	103.0	3.40	3.54
	220					
	270	2	235.7	273.4	9.00	9.04