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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.
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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 Kα_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 operat-
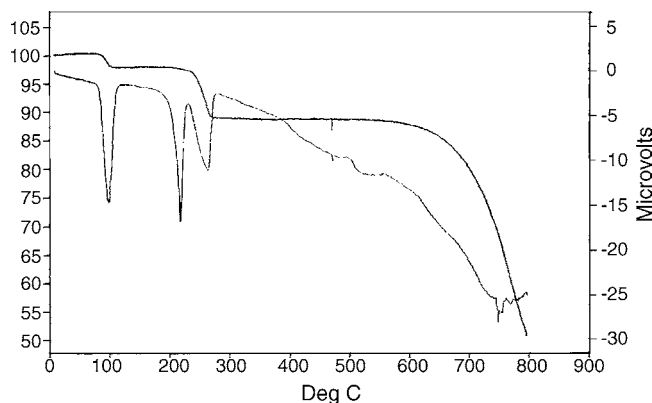

Fig. 1. TG/DTA curve of potassium hexanitronickelate(II) hydrate.

ing at an accelerating voltage of 10 kV. Samples were desorbed from a nitrobenzyl alcohol matrix using 3 keV xenon atoms.

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

3. Results and discussion

3.1. Thermal analysis

The TGA and DTA traces and summary of the thermal decomposition of potassium hexanitronickelate(II) hydrate are shown in Fig. 1 and Table 1, respectively. The curves show the endothermic loss of coordinated water around 100 °C accounting for 3.40% the mass of the sample. The calculated mass loss for one molecule of water from this complex is 3.54% but this discrepancy is not thought to be significant in the light of previous experiments [10–12]. In one study, dehydration of a large number of samples of $K_4[Ni(NO_2)_6]·H_2O$ gave an average mass loss of 2.68% while in other work [10,11] mass loses of 3.3 or 3.9% were obtained. It appears that the actual H_2O content depends somewhat on preparation and drying conditions.

The anhydrous product is stable up to about 200 °C. A second endothermic change, with no mass loss, occurs at around 220 °C. This process probably corresponds to the isomerisation of the remaining nitro groups. At around 270 °C a third endotherm is accompanied by a mass loss of ca. 9.00%. It appears likely that this process corresponds to the loss of NO_2 gas; the calculated mass loss for one NO_2 molecule is 9.04%. Upon further heating the mass of the sample remains constant up to 600 °C.

In an attempt to verify that linkage isomerism does indeed occur at around 220 °C and to characterise the product of the thermal reaction occurring around 270 °C, a sample of $K_4[Ni(NO_2)_6]·H_2O$ was heated in an oven. After heating to temperatures between 200 and 500 °C for several hours in a step by step manner, samples were removed and were analyzed by infrared spectroscopy and powder X-ray diffraction.

3.2. Infrared spectra and powder X-ray diffraction traces of potassium hexanitronickelate(II) hydrate and the decomposition products

The infrared spectrum of the nitrite ion, in particular the symmetric and asymmetric stretching frequencies, has often been used to identify the manner of nitrite coordination in a complex, because the frequencies of the bonds change from the free ion values depending upon the type of nitrite coordination such as nitro, nitrito, chelating (asymmetrically or symmetrically) nitrito and bridging nitrite [14–16]. IR spectra and XRD traces show clearly that there is a distinct, hitherto unreported compound which is formed at around 270 °C from the more well-known linkage isomerism product $K_4[Ni(NO_2)_4(ONO)]·NO_2$ which is produced at lower temperatures. The infrared data are summarised in Table 2.

In the FT-IR spectra of the compound before and after heating to 100 °C are in a good agreement with those reported previously [9] for the complexes $K_4[Ni(NO_2)_6]·H_2O$ and $K_4[Ni(NO_2)_4(ONO)]·NO_2$, respectively. The dehydrated complex shows peaks with similar positions and relative intensities to those in the monohydrate, at 810, 826, 1321 and 1346 cm^{-1} and these are assigned to the nitro groups in the $[Ni(NO_2)_4(O_2N)]^{3-}$ complex anion. In addition, a peak of moderate intensity occurs at 1270 cm^{-1} assigned to ν_{asym} of NO_2^- ion which is not coordinated to the nickel centre. The IR spectrum of KNO_2 was obtained for comparison and shows ν_{asym} as an intense broad peak at 1260 cm^{-1}. The remaining peaks seen for the dehydrated product at 866 cm^{-1}, and shoulders at ≈1225 and 1385 cm^{-1} are attributed to the chelating nitrito group in the $[Ni(NO_2)_4(O_2N)]^{3-}$ anion. This assignment is confirmed by examination of an earlier publication [9] which reports the spectrum of pure $K_3[Ni(NO_2)_4(O_2N)]$ prepared by extraction of KNO_2 from the anhydrous residue. Here the peak at 1271 cm^{-1} assigned to NO_2^- almost disappears, and the peaks at 1225 and 1385 cm^{-1} assigned to ν_{asym} and ν_{sym} of the chelating nitrite are much more clearly resolved, demonstrating that overlap did indeed occur in these spectral regions for the mixed sample.

Upon heating to temperatures around 200 °C infrared bands arising from monodentate N-bonded nitro groups decay to extinction while those arising from chelating nitroso groups increase in intensity. At this temperature a second endotherm, with no corresponding loss of mass is

Table 2
Nitrite infrared frequencies (cm^{-1}) for the thermal decomposition products of potassium hexanitronickelate(II) hydrate and some $M(NO_2)_x^{n-}$ anions

Compound	$\nu_s(NO_2)$	$\nu_{as}(NO_2)$	$\nu_s(ONO)$	$\nu_{as}(ONO)$	$\delta(NO_2)$	$\delta(ONO)$
$K_4[Ni(NO_2)_6]·H_2O$	1346 (m)	1319 (s)	–	–	831 (s), 810 (w)	
Heated at 100 °C	1346 (m)	1321 (s)	1385 (sh)	1225 (sh)	826 (s), 810 (w)	866 (s)
Heated at 200–230 °C			1395 (s)	1265 (s)	826 (w), 810 (w)	
Heated at 270–405 °C			1395 (s)	1265 (s)	826 (s), 810 (m)	
Heated at 410–520 °C			1395 (vs)	1265 (vw)	826 (vs), 810 (w)	
KNO_2				1265 (b)	810 (s)	
KNO_2 heated at 270 °C				1265 (b)	810 (s)	
$NO_{2(g)}$[a]	1610	1318			749	
$Cs_2Zn(NO_2)_4$[b]			1381 (s)	1167 (vs)		847 (m)
$K_3[Hg(NO_2)_4]·NO_3$[b]			[c]	1258 (vs, b)		858 (w), 851 (m)
$K_2Cd(NO_2)_4$[b]			[c]	1266 (vs, b)		858 (w), 851 (m)

b: broad; m: medium; s: strong; sp: sharp; sh: shoulder; w: weak; vs: very strong; vw: very weak.

[a] All data were obtained in inert gas matrices.

[b] Taken from Ref. [17].

[c] Band obscured by ν_{as}.

Table 3
Values from mass spectra of thermal decomposition product

Complex	Thermal decomposition product formed at 270 °C
MW	445
Relative intensities of ions and assignments	430 (5) $[M^+ - O]$; 384 (7) $[M^+ - O-(NO_2)]$; 345 (44) $[M^+ - O-(NO_2)-K]$; 276 (17) $[M^+ - O-(NO_2)-2K-NO]$; 230 (45) $[M^+ - O-2(NO_2)-2K-NO]$; 191 (100) $[M^+ - O-2(NO_2)-3K-NO]$; 115 (9) $[M^+ - O-3(NO_2)-3K-2NO]$

For the mass spectral data relative intensities are given in parentheses; probable assignments in square brackets. M^+ refers to the parent molecular ion $\{K_4[Ni(O_2N)_4]\cdot NO_2\}^+$ and the assignments show the loss of specific atoms and groups from this ion.

Table 4
Elemental analysis results (%)

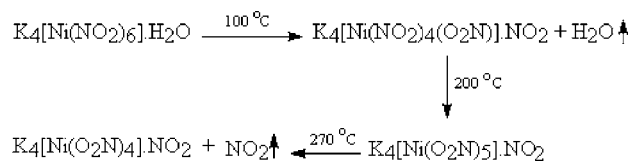| Complex	Found (calculated) (%)			
	K	Ni	N	H
$K_4[Ni(NO_2)_6]\cdot H_2O$	30.53 (30.65)	11.45 (11.59)	16.44(16.50)	0.36 (0.39)
Thermal decomposition product at 270 °C	34.93 (35.06)	13.11 (13.26)	15.62 (15.73)	–

seen. These findings indicate that isomerisation of the remaining nitro groups within the complex occurs, forming $K_4[Ni(O_2N)_5]\cdot NO_2$ which contains the $[Ni(O_2N)_5]^{3-}$ ion. There are precedents for a formulation of a complex ion where all of the NO_2 groups adopt a chelating bidentate structure, e.g. in the mercury(II) complex $K_3[Hg(O_2N)_4]\cdot NO_3$ and the zinc(II) complex $Cs_2[Zn(O_2N)_4]$ [17].

Upon heating to temperatures above 270 °C, the IR features assigned to the complex $K_4[Ni(O_2N)_5]\cdot NO_2$ decay. A gaseous product is also formed which was studied by IR spectroscopy. The spectrum of this gas shows peaks at around 1600 and 1300 cm^{-1}. These identify the product as NO_2 [14].

The next stage of the investigation was to attempt to identity the solid product formed by loss of NO_2 gas. Infrared spectra of the solid product show the presence of chelating ONO groups, as evidenced by bands at 1395 cm^{-1} (ν_s(ONO)), 1265 cm^{-1} (ν_{as}(ONO)) and 826 and 810 cm^{-1} (δ(ONO)) [14–17]. There is no evidence for any monodentate nitro (NO_2) groups. It therefore seems likely that all of the NO_2 groups in this product adopt a chelating nitro coordination. The product shows the following features in the powder X-ray diffraction pattern (d-spacings measured in Å with relative intensities in parentheses): 4.922 (76), 4.035 (100), 3.183 (32), 2.975 (57), 2.711 (35), 2.562 (30), 2.365 (33), 2.307 (62), 2.251 (21), 2.101 (32), 2.012 (14), 1.822 (9), 1.495 (7), 1.237 (6) and 1.198 (14). This pattern does not correspond to that of the high-temperature cubic form of KNO_2 [18a] nor to that of any other known form of KNO_2 [18b–d]. Thus it is shown that the product is not a mixture containing KNO_2, but rather a single phase best formulated as $K_4[Ni(O_2N)_4]\cdot NO_2$. This observation is in keeping with the FAB-mass spectrum of the product (Table 3) which shows fragmentation of the parent molecular ion $\{K_4[Ni(O_2N)_4]\cdot NO_2\}^+$ and with the results of elemental analysis (Table 4). This means that the nickel atom is in the unusual but not unknown (e.g. $[Ni(PMe_3)_4][BPh_4]$ [19]) oxidation state of +1. The disproportionation reaction in which the nickel centre is reduced from the +2 to the +1 oxidation state is driven by the production of NO_2 gas.

4. Conclusion

On the basis of the studies reported here it is possible to propose a mechanism for the thermal decomposition of $K_4[Ni(NO_2)_6]\cdot H_2O$ over the temperature range 25–600 °C. Around 100 °C dehydration occurs to give rise to the complex $K_4[Ni(NO_2)_4(O_2N)]\cdot NO_2$. Above 200 °C a further isomerisation takes place such that all of the groups adopt a chelating bidentate structure. This step appears to be a crucial precursor to the subsequent loss of NO_2 gas above 270 °C and the concomitant reduction of the nickel(II) centre to nickel(I).

$$K_4[Ni(NO_2)_6]\cdot H_2O \xrightarrow{100\,°C} K_4[Ni(NO_2)_4(O_2N)]\cdot NO_2 + H_2O\uparrow$$

$$\downarrow 200\,°C$$

$$K_4[Ni(O_2N)_4]\cdot NO_2 + NO_2\uparrow \xleftarrow{270\,°C} K_4[Ni(O_2N)_5]\cdot NO_2$$

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