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Studies on the thermal decomposition of dipotassium *trans*-diaquabis(oxalato-O,O′)nickelate(II) tetrahydrate

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Abstract

The thermal behaviour of the compound $K_2[Ni(C_2O_4)_2(H_2O)_2]\cdot 4H_2O$ has been studied by thermogravimetry and differential thermal analysis. Experiments were carried out in dynamic atmospheres of argon–oxygen and argon, respectively, over the temperature range 20–600°C.

Thermoanalytical data show that the surrounding atmosphere significantly influences the dehydration process as well as the final products. In the oxidative atmosphere, the six water molecules are released during two almost overlapping endothermic steps, whereas in the inert atmosphere, the free water molecules and the coordinated ones are lost in separate stages. In both cases, dipotassium carbonate has been found as the final product, together with NiO in the oxidative environment and metallic nickel in the inert atmosphere.

Keywords: Dicarboxylate ligands; DTA; DTG

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1. Introduction

The coordination chemistry of metal complexes with dicarboxylate ligands has been thoroughly studied for many years because of the analytical, catalytical and biomedical applications of the ligands [1]. Simple metal oxalates and oxalate complexes have been studied for several years using thermal methods [2–7]. Although in the literature there are some works concerning the thermal behaviour of the compound $K_2[Ni(C_2O_4)_2(H_2O)_x]\cdot yH_2O$ ($x + y = 6$) [8–10], some discrepancies have been found concerning the number of free and coordinated water molecules in the crystal structure. In a previous paper [11], we resolved the crystal structure of the title compound. The

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complex anion exhibits an octahedral coordination around the Ni(II) atom, with four oxygen atoms belonging to two bidentate oxalate ligands in the equatorial plane and two coordinated water molecules occupying the axial positions. The other four water molecules are free water. The crystal structure is stabilized by electrostatic interactions and there is an extensive network of hydrogen contacts in which the water molecules and all the oxygen atoms from the oxalate ligands are involved. Fig. 1 shows the structure of the complex anion of the compound *trans*-$K_2[Ni(C_2O_4)_2(H_2O)_2]\cdot 4H_2O$.

In the present paper, we describe the result of the thermal studies on this compound in different dynamic atmospheres in order to reveal the influence of the surrounding atmosphere on its decomposition and to relate its structure to the thermal properties.

2. Experimental

2.1. Sample preparation

trans-$K_2[Ni(C_2O_4)_2(H_2O)_2]\cdot 4H_2O$ (**1**) was prepared at room temperature by slowly mixing aqueous solutions of nickel(II) chloride hexahydrate and potassium oxalate monohydrate [11]. Single crystals were grown by slow evaporation of the resulting green solution (pH 7.5). The chemicals used were purchased from Merck and used without further purification.

2.2. Thermal analysis

Thermal analyses were carried out on a Setaram TAG 24 S 16 simultaneous thermal analyser. Thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) curves were performed at a heating rate of 5°C min^{-1}. All the runs were recorded in dynamic atmospheres of argon–oxygen (4:1 v/v) and argon, respectively, over the temperature range 20–600°C, on samples of finely dispersed powder or crystals. The flow rate was 50 ml min^{-1}. An amount of sample (8–15 mg) was

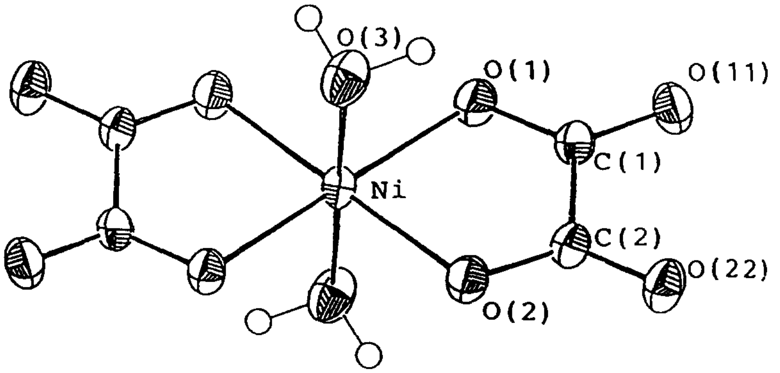


Fig. 1. Ortep view of the complex anion $[Ni(C_2O_4)_2(H_2O)_2]^{2-}$.

weighed exactly in the platinum crucible; the thermally inert reference was 12 mg of α-Al_2O_3 previously calcined at 1300°C for 6 h.

2.3. X-ray diffraction analysis

The final products of the decomposition were analysed by X-ray powder diffraction techniques using a Philips PW 1710 instrument with Cu $K\alpha$ radiation. Diffraction patterns were compared with those reported in the ASTM powder diffraction files of the Joint Committee on Powder Diffraction Standards [12].

3. Results and discussion

Table 1 lists the thermal data for the decomposition of 1 in argon–oxygen and argon atmosphere. The thermal behaviour in the oxidative atmosphere is quite different from that in the inert atmosphere.

In argon–oxygen atmosphere, thermal decomposition (Fig. 2(a)) starts with the loss of the water molecules, which occurs as a two-stage endothermic process (Fig. 2(b)) in the range 40–112°C. The four lattice water molecules are lost in the first dehydration step, whereas the coordinated water molecules are released at slightly higher temperatures. These two dehydration stages are almost overlapped but are well-defined in the DTA and DTG curves.

The amount of lost water fits rather well with the composition established by structural work and chemical analysis.

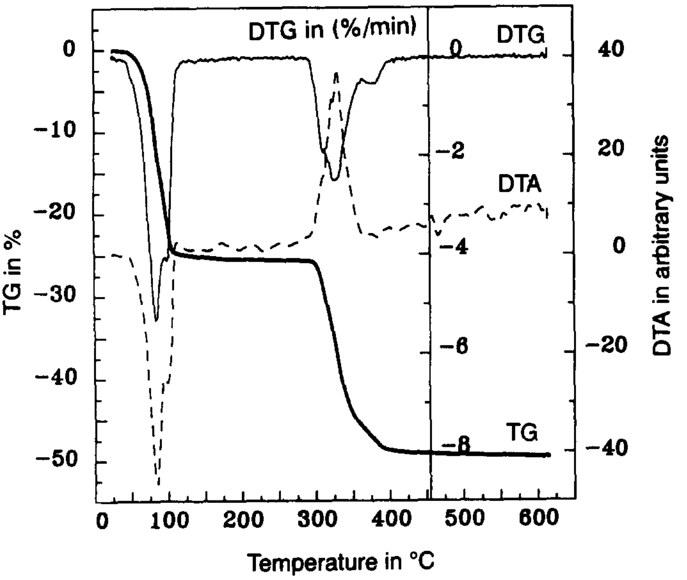
Although the temperature range of the dehydration of the coordinated water molecules is at the lower end of those observed for this type of water in metallic

Table 1
Thermoanalytical data for the thermal decomposition of compound 1 in argon–oxygen and argon atmospheres

Step	T_i/°C	T_f/°C	T_m/°C	ΔH	Δm %	Atrib.	Δm_{theor} %
Argon–oxygen							
1	40	93	80	Endo	17.05	$-4H_2O$	17.12
2	93	112	97	Endo	8.55	$-2H_2O$	8.56
3	290	365	325	Exo	20.88	$-[C_2O_4]^{2-}$	20.91
4[a]	365	410			2.91	$-$ C	2.85
	Total				49.39		49.44
Argon							
1	45	110	75	Endo	12.93	$-3H_2O$	12.84
2	130	185	155	Endo	4.25	$-H_2O$	4.28
3	300	316	314	Endo	8.56	$-2H_2O$	8.55
4	316	350	332	Endo	14.29	$-CO_3^{2-}$	14.25
5	350	460			13.29	$-2CO$	13.30
	Total				53.32		53.22

[a] Progressive mass loss without clear peaks in the DTA curve.

(a)



(b)

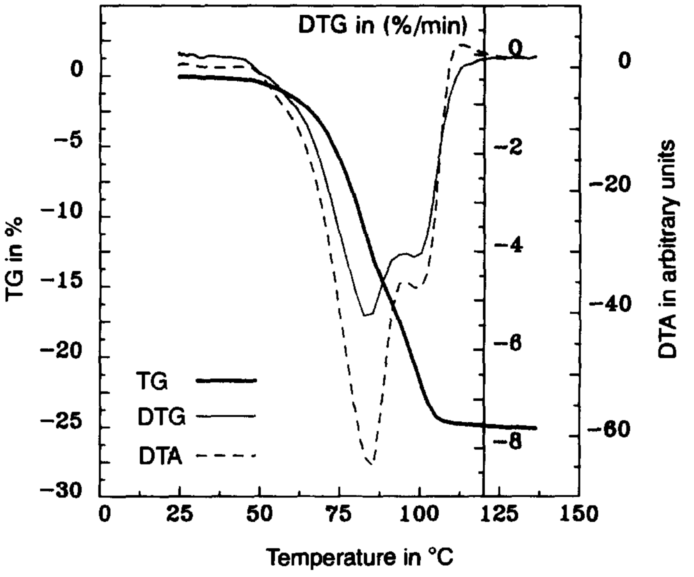


Fig. 2. Thermal decomposition of compound 1 in argon–oxygen atmosphere: (a) TG, DTG and DTA curves for the total decomposition process; and (b) dehydration process.

complexes, it is similar to those found for analogous oxalato complexes [13]. Thus, the dehydration process can be expressed by the reactions

$$K_2[Ni(C_2O_4)_2(H_2O)_2]\cdot 4H_2O \xrightarrow{[Ar+O_2]} K_2[Ni(C_2O_4)_2(H_2O)_2] + 4H_2O\uparrow \quad (1)$$

$$K_2[Ni(C_2O_4)_2(H_2O)_2] \xrightarrow{[Ar+O_2]} K_2[Ni(C_2O_4)_2] + 2H_2O\uparrow \quad (2)$$

These results are in good agreement with the structural crystallographic work which shows the existence of two types of water molecules, but are not in accordance with the results of Diefallah et al. [10], who found a broad endothermic peak in the range 40–110°C and concluded that all six H_2O molecules are lattice water.

In this atmosphere, the dehydration and decomposition processes are separate stages, and the anhydrous compound is stable up to 290°C. Some authors suggest that the dehydration process does not imply a lowering in the coordination number of the metal, because some of the oxalate groups probably function as bisbidentate bridge ligands in order to maintain the coordination number of six [13–15].

The decomposition of the anhydrous compound involves two exothermic steps which correspond to the rupture of the oxalate groups and the reordering of the solid inorganic residues. Above 410°C, a mixture of dipotassium carbonate (ASTM 16-820) and nickel(II) oxide (ASTM 4-0835) in a ratio of 1:1 was identified as the final product.

According to the mass losses, the decomposition process can be described by the reactions

$$K_2[Ni(C_2O_4)_2] \xrightarrow{[Ar+O_2]} K_2C_2O_4 + NiO + 2CO_2\uparrow \quad (3)$$

$$K_2C_2O_4 + NiO \xrightarrow{[Ar+O_2]} K_2CO_3 + NiO + CO_2\uparrow \quad (4)$$

In the argon atmosphere, the water molecules are lost during three endothermic processes, which are clearly separated (Fig. 3).

The first weight loss ($\Delta m_{exp} = 12.93$) takes place between 45 and 110°C and is attributable to the release of three free water molecules ($\Delta m_{theor} = 12.84$). The fourth molecule of water of crystallization is removed between 130 and 185°C. This behaviour is not in agreement with the crystal structure, which shows that there are only two crystallographically independent types of free water molecules, so that they should be removed in a relation of 2:2. Therefore, it is possible that the loss of the first free water molecules produces some modification in the crystal-packing network. The dehydrated compound is stable up to 300°C, beyond which coordinated water molecules are lost during a process which is almost overlapped with the breakdown of the complex. DTA and DTG curves show separate stages for the two processes not observable in the TG curve. The loss of all water molecules is complete at 316°C. Thus, in the inert atmosphere the water molecules are lost according to the equations

$$K_2[Ni(C_2O_4)_2(H_2O)_2]\cdot 4H_2O \xrightarrow{[Ar]} K_2[Ni(C_2O_4)_2(H_2O)_2]\cdot H_2O + 3H_2O\uparrow \quad (5)$$

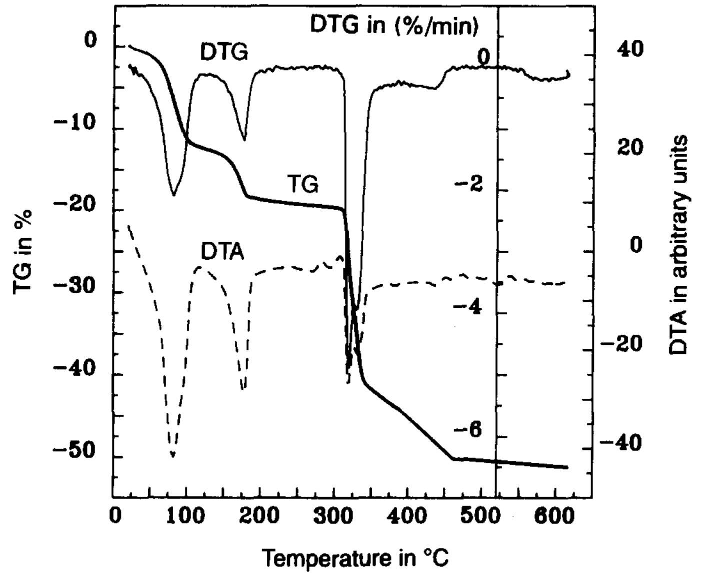


Fig. 3. TG, DTG and DTA curves for the thermal decomposition process of compound 1 in argon atmosphere.

$$K_2[Ni(C_2O_4)_2(H_2O)_2]\cdot H_2O \xrightarrow{[Ar]} K_2[Ni(C_2O_4)_2(H_2O)_2] + H_2O\uparrow \tag{6}$$

$$K_2[Ni(C_2O_4)_2(H_2O)_2] \xrightarrow{[Ar]} K_2[Ni(C_2O_4)_2] + 2H_2O\uparrow \tag{7}$$

In the range 316–350°C, the mass loss corresponds closely to that expected for a carbonate group (Eq. (8)). The next step occurs between 350–460°C with a mass loss attributable to two CO groups (Eq. (9))

$$K_2[Ni(C_2O_4)_2] \xrightarrow{[Ar]} K_2C_2O_4 + NiOC + CO\uparrow + O_2\uparrow \tag{8}$$

$$K_2C_2O_4 + NiOC \xrightarrow{[Ar]} K_2CO_3 + Ni + 2CO\uparrow \tag{9}$$

From the respective weight losses and powder diffraction analysis of the residue, the decomposition was confirmed to lead to dipotassium carbonate (ASTM 16-820) and metallic nickel (ASTM 4-0850) as final products in a ratio of 1:1.

4. Concluding remarks

The thermoanalytical results indicate that the thermal decomposition of the compound as well as the final products are strongly influenced by the atmosphere involved.

The main feature of the thermal dehydration of **1** in an argon–oxygen atmosphere is that water molecules are removed in two steps. This is in accordance with the X-ray structural studies which show that there are four free water molecules and two coordinated ones in the crystal lattice. The anhydrous complex is stable up to 290°C. Its thermal decomposition occurs in two exothermic stages (40–112°C) and yields a mixture of dipotassium carbonate and nickel(II) oxide as final products. A comparison of the dehydration step in argon atmosphere with that in oxidative atmosphere shows important differences. The total dehydration process in the inert atmosphere takes place over a wider temperature range (45–316°C). The free water molecules are removed in two steps and the coordinated ones are lost in a clearly separate stage by 115°C. The anhydrous compound is not stable and the decomposition follows immediately after the dehydration step. The residue consists of a mixture of dipotassium carbonate and metallic nickel.

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