

Possible evidence of the nickel nitrate salt $\text{Ni}(\text{NO}_3)_2 \cdot 5.5 \text{H}_2\text{O}$

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Abstract. In the present work we have focus our care on the controversial intermediate salt : $\text{Ni}(\text{NO}_3)_2 \cdot 5.5 \text{H}_2\text{O}$. To prepare this phase, we have carried out, in the range 60-80°C, a controlled evaporation of a solution of nickel nitrate, hexahydrate resulting from the melting of a 100g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ batch sample in an isothermal pilot reactor. The proof of its existence is given, for the first time, by powder x-ray diffraction data.

1. INTRODUCTION

A $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ molecule might be represented as a lone $3d^8$ ion (Ni^{2+}) surrounded by six water molecules [1-5]. In such a configuration, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is made of hexaaquanickel cation and nitrate anions joined with one another by a network of hydrogen bonds.

B. Morosin and T. Haseda [6] show that $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ has two polymorphs: α and β . They have respectively the monoclinic and triclinic structure. But in both cases, the nitrate ions are in the coordination sphere of the nickel ion which suggest that the nitrate anions are strongly bound.

In the literature, emphasis has been placed to the first internal structural change occurring as $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is degraded [2]. It is claimed that the first step of the thermal decomposition is $\text{Ni}(\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O}$. Unfortunately, the proof of the existence by x-ray diffraction data has not been given despite several works reporting this exotic salt [1-4].

2. EXPERIMENTAL

2.1.Reagents

The raw material used, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was a 2 kg polycrystals lot of high purity grade (>99.9%_w) of Pharmacie Centrale de France S.A. (PCAS group).

2.2.Techniques

Our work was done in an isothermal reactor of about 100cm³ with about 100g for each batch of raw material. The use of a large amount of raw material has let us to carry out five chemical analysis to get an average well-defined composition for the starting material. Determination of nickel content was done by direct titration using murexide ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8$) as indicator [20]. The results were in good agreement with data obtained by means of plasma emission spectroscopy. Ultraviolet spectra were obtained with a Cary 1E double beam spectrometer with 1 cm path length

quartz cells. The calibrated curve was obtained by dilution of nitric acid (1 molL^{-1}), analysis ACS grade product of Merck. When combined the two analysis allow the determination of water molecules in the salt.

Thermogravimetry were carried out by means of a Linseis L81 apparatus. An air flow of $0.2\text{ dm}^3\cdot\text{min}^{-1}$ was used to maintain a permanent excess of oxygen and to exhaust the products out of the thermobalance. All the experiments were carried out at atmospheric pressure: $P(\text{O}_2) \sim 20\text{ kPa}$.

X-ray powder diffraction (XRD) patterns were collected on a Philips PW 1877 diffractometer using the $\text{Cu K}\alpha$ radiation (1.5406 nm) with a scanning speed of 1° min^{-1} . The salt powders were always grinded before exposure to the X ray beam and protected from room moisture by a $25\ \mu\text{m}$ thick film of KaptonTM. For identification purposes, the diffraction patterns (I/I_0 versus d -spacing) were matched with relevant JCPDS standards using a built-in computer search program.

DSC studies were performed using a Mettler Tolédo TA 8000 system working in the temperature range $-170^\circ\text{C}/700^\circ\text{C}$. All experiments were carried out on $\sim 60\text{ mg}$ of polycrystalline material under a flow of dry argon. The sample was previously put into a stainless steel crucible and weighted. In order to avoid the vaporization of water, each crucible was sealed and can resist to an internal pressure up to $4,106\ \text{Pa}$. Calibrations in temperature and enthalpy were performed using the melting of pure metals or organic materials according to the recommendations of the manufacturer. The DSC signal was recorded and stored by means of a Dell computer and the exploitation was subsequently made using a STAR 6.1 Mettler Toledo software. For each specimen, the accurate cycle profile ($25^\circ\text{C}/-50^\circ\text{C}/100^\circ\text{C}/25^\circ\text{C}$ and $5^\circ\text{C}/\text{minute}$) was carried out 3 times in order to test the reproducibility of the experiments.

3. RESULTS AND EXPERIENCE

Accurate analysis of $\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ is not trivial although nickel nitrate hexahydrate composition is often determined on the unique basis of metal content and the salt composition varies with hygrometry conditions since the salt is known to be deliquescent or efflorescent [18,19]. The composition was then determined on both nitrate and nickel experimental content and on the assumption that Ni has a stoichiometry of unity: the starting composition was rather: $\text{Ni}_{0.97-1}(\text{NO}_3)_{2-2.06} \cdot \text{H}_2\text{O}_{5.92-6.10}$ but was reported as $\text{Ni}_1(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the rest of the paper.

DSC study of the thermal degradation of a single crystal salt has been performed with heating rates of $5^\circ\text{C}\cdot\text{min}^{-1}$. The temperature of each endothermic peak observed were: -35°C which has been associated to a solid-solid transition [17,18] and $+54^\circ\text{C}$ which corresponds to the specimen incongruent melting temperature (Fig.5). After 3 runs a similar profile was kept, i.e. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ melts and crystallizes reversibly. A same behavior was observed with a polycrystalline crystal. This is in agreement with the figure 1 where it is suggested that the nitrate anions are joined by hydrogen bonds.

The dehydration mechanism is carried out in a double walled cylindrical reactor at 75°C by thermostatic fluid circulation. The equilibrium liquid was evaporated off using an argon flow at the top of the vessel. The salt was continuously under agitation. After about 3 hours, a solid phase appears in the vessel. The agitation is stopped and the solid is decanted at the bottom of the vessel after 1 hour. The liquid is then pumped out of the vessel, filtered, cooled and crystallized under an

argon top. Three chemical analysis show that the solidified liquid composition corresponds to: $\text{Ni}(\text{NO}_3)_2 \cdot 5.4\text{-}5.6 \text{ H}_2\text{O}$, determined on the basis of both nitrates and metal content. (It is worth noticing that we have checked the nature of the vapor species emitted by the hexahydrate salt in the range 60°C-80°C storing first the sample in a sealed vessel under a 0.1 Pa vacuum and then analyzing the resulting condensed vapor. In the studied temperature range, we did not find any evidence of denitration. We have then assumed that only H_2O molecules were expelled from the salt and therefore that under our experimental conditions, the thermal degradation is indeed a dehydration process: there is no overlapping between the process of water departure and that of gaseous decomposition products of nitrogen oxides.) The process has been repeated several times with the same result in the range 60°C to 80°C.

A x-ray powder diffraction pattern has been collected. All the lines obtained can be attributed to a triclinic structure with the parameters calculated by least squares unit cell refinement: $a = 0.757$ (4) nm, $b = 1.216$ (7) nm, $c = 0.614$ (3) nm, $\alpha = 100.2$ (7), $\beta = 112.3$ (4) and $\gamma = 98.2$ (7) (Table 1). Moreover, after standing in the room atmosphere for a few hours, XRD shows that the compound reverts to $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ according to the reaction: $\text{Ni}(\text{NO}_3)_2 \cdot 5.5 \text{ H}_2\text{O} + 0.5 \text{ H}_2\text{O} \rightarrow \text{Ni}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$.

Table 1. X ray diffraction lines characteristic of the liquid phase after cooling and crystallization at room atmosphere under argon (d_{obs} and d_{calc} in nm)

h	k	l	d_{obs}	d_{calc}	I/I_0						
-1	1	0	0,6602	0,6583	6	2	1	-1	0,3411	0,3412	4
0	2	0	0,5862	0,5825	42	2	-2	0	0,3282	0,3292	60
-1	0	1	0,5552	0,5549	25	-1	-3	1	0,3282	0,3288	60
0	-1	1	0,5552	0,5538	25	1	-3	1	0,3151	0,3130	39
0	0	1	0,5552	0,5495	25	2	1	0	0,3085	0,3087	4
1	1	0	0,5401	0,5372	11	1	1	-2	0,3058	0,3056	4
-1	1	1	0,4924	0,4883	8	1	0	-2	0,3035	0,3019	4
0	-2	1	0,4595	0,4621	100	2	-3	0	0,2919	0,2917	26
0	1	1	0,4458	0,4547	4	-1	1	2	0,2812	0,2806	5
1	2	-1	0,4149	0,4161	5	-2	0	2	0,2767	0,2774	9
1	2	0	0,3966	0,3999	4	0	-2	2	0,2767	0,2769	9
1	-2	-1	0,3864	0,3889	21	-2	-2	0	0,2696	0,2686	9
0	3	0	0,3864	0,3884	21	2	-1	-2	0,2662	0,2659	10
1	-3	0	0,3778	0,3768	8	-1	-3	2	0,2616	0,2616	4
1	-1	1	0,3735	0,3767	16	2	3	-1	0,2569	0,2563	4
-2	1	1	0,3559	0,3569	4	-2	-2	2	0,2569	0,2573	4
1	-2	1	0,3559	0,3561	4	-2	1	-1	0,2569	0,2571	4
2	-1	0	0,3504	0,3497	14	0	3	-2	0,2569	0,2569	4
2	0	0	0,3411	0,3410	4						

A DSC analysis carried out on $\text{Ni}(\text{NO}_3)_2 \cdot 5.5 \text{ H}_2\text{O}$ polycrystals shows 3 endothermic peaks: -30°C, -10°C and +42°C (Fig.1). The asymmetrical peak of fusion of the specimen suggests that the sample is not pure or the liquefaction of the sample is accompanied by a decomposition of

the molecules. However after complete liquefaction of the hydrate, the sample crystallizes (Fig.1 – Peak 4) and similar DSC profile is recovered at each new run. The profile is very similar with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as far as the peaks 3 and 4 were of concern.

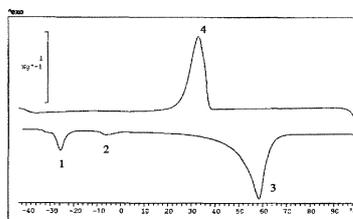


Figure 1. DSC relative to the liquid phase after cooling and crystallization at room atmosphere under argon. On heating, peak 1: solid-solid transition (-15.6Jg^{-1}); Peak 2: solid-solid transition (-3.4Jg^{-1}); Peak 3: melting transition (-126.8Jg^{-1}) and Peak 4:recrystallization (-125.2Jg^{-1}) on cooling .

This suggests that nitrate anions are joined by hydrogen bonds in the $\text{Ni}(\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O}$ molecule (as in $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ molecule) allowing re-crystallization. In the case of $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ salt samples a vitreous transition occurs in the range $-25^\circ\text{C}/-40^\circ\text{C}$ and impedes any re-crystallization on heating. The direct bonding of nitrate anions to nickel (Ni-O-N=O) in the molecule are not easily reconstituted.

4. CONCLUSION

In this work emphasis has been placed on the study of the first internal structural change occurring when hexahydrate is evaporated off at 75°C . $\text{Ni}(\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O}$ hydrate has been prepared for the first time and has been characterized by x-ray analysis and DSC. The salt is unstable and reverts to hexahydrate: $\text{Ni}(\text{NO}_3)_2 \cdot 5.5\text{H}_2\text{O} + 0.5\text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

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