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# SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF $Fe_4(OH)_{11}NO_3 \cdot 2H_2O$

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A new iron basic salt, $Fe_4(OH)_{11}NO_3 \cdot 2H_2O$, has been prepared by partially hydrolyzing a solution of $Fe(NO_3)_3 \cdot 9H_2O$ with urea.

The X-ray powder diffraction pattern has been indexed within a monoclinic cell $a = 9.99(3)$ Å, $b = 9.48(2)$ Å, $c = 3.074(3)$ Å and $\beta = 90.57(1)°$.

Thermal decomposition reactions in still air and nitrogen flow have been studied by DTA and TG analysis, and the intermediate and final products have been characterized by X-ray diffraction and IR spectroscopy. When this material is thermally decomposed in an X-ray high temperature diffraction chamber, pure iron is formed at 900 °C together with Fe(III) and Fe(II) oxides.

Most of the iron basic salts characterized so far are of a very high technological interest, and they are widely used in many industrial processes [1]; for that reason, some of them, mainly single or double hydroxysulphates have been thoroughly studied [2–6], but very little attention has been paid to iron hydroxynitrates [7], in spite of their importance as oligoelement carriers in nutritional diets [8, 9].

On the other hand, it has been previously shown [10, 11] that some metal oxides or pure metals can be obtained under certain experimental conditions when basic salts are used as inorganic precursors.

Having in mind all indicated above, it has been considered worthwhile to study and characterize a new iron hydroxynitrate.

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## Experimental

Iron hydroxynitrate was obtained by partial hydrolysis with urea, of a 8 N solution of $Fe(NO_3)_3 \cdot 9H_2O$ at 63° under a $N_2$ flow.

The formed precipitate was aged at the same temperature for 15 days, it was then filtered off, washed with water, ethanol and acetone, dried in vacuum and kept over $P_2O_5$.

All reagents were of analytical reagent grade. X-ray powder diagrams have been recorded on a Siemens D-500 diffractometer with monochromatized $CuK_\alpha$ radiation and Ag (99.99% purity) as internal standard.

The IR spectra have been obtained in a Nicolet FTIR 60SX spectrophotometer in KBr discs.

Electron micrographs were made on a Siemens Elmiskop 102 microscope with samples dispersen in *n*-butanol.

The thermal curves have been obtained in a Stanton 781STA System. Approximately 10 mg of the sample were pyrolyzed in platinum/rhodium wells up to 850°, both in air and nitrogen atmospheres, at 2 $deg \cdot min^{-1}$ heating rate, and precalcined alumina was the inert reference.

The X-ray high temperature diffraction studies were performed in an Anton PAAR HTK10 chamber with tantalum strip as the heating element mounted on a Philips PW 1310 equipment and $CuK_\alpha$ radiation. Experimental details have been heated at 450° for $1^1/_2$ hours [13].

Iron was determined by atomic absorption using a Philips Pye-Unicam spectrophotometer.

Nitrates were analyzed by the Kjeldahl method [12].

The analytical results were as follows: Found, % Fe 43.35, % $NO_3$ 12.95. From the observation of the infrared spectrum of this compound, the presence of water and $OH^-$ groups is clearly inferred, and the results of the chemical analysis are in favour of a formulation for this product such as $Fe_4(OH)_{11}NO_3 \cdot 2H_2O$ (Calc. % Fe 43.94, % $NO_3$ 12.20).

## Results and discussion

The X-ray diffraction data of this material are given in Table 1. The X-ray pattern has been indexed within a monoclinic cell and the calculated cell dimensions have been refined by least square calculations. Electron micrographs indicate that this product is a single phase, the crystals are transparent and laminar; Fig. 1 shows a representative micrograph.

**Table 1** X-ray powder diffraction data for iron(III) hydroxynitrate, $Fe_4(NO_3)(OH)_{11} \cdot 2H_2O$

$a$ = 9.99(3) Å $\beta$ = 90.57(1)
$b$ = 9.48(2) Å $V$ = 290.3(8) Å$^3$
$c$ = 3.074(3) Å $Z$ = 1
$D_c$ = 2.90 Mg m$^3$

| $d_{obs.}$, Å | $d_{calc.}$, Å | $I/I_0$ | $hkl$ |
|---|---|---|---|
| 9.48 | 9.485 | 100 | 010 |
| 6.88 | 6.867 | 25 | 110 |
| 4.74 | 4.743 | 2 | 020 |
| 4.40 | 4.407 | 18 | 210 |
| 4.27 | 4.277 | 90 | 120 |
| 3.43 | 3.431 | 7 | 220 |
| 3.13 | 3.132 | 22 | 310 |
| 3.08 | 3.074 | 2 | 001 |
| 3.01 | 3.013 | 4 | 130 |
| 2.924 | 2.9246 | 1 | 011 |
| 2.818 | 2.8181 | 8 | $\bar{1}11$ |
| 2.793 | 2.7941 | 8 | 111 |
| 2.669 | 2.6689 | 23 | 230 |
| 2.636 | 2.6353 | 12 | $\bar{2}01$ |
| 2.595 | 2.5964 | 11 | 201 |
| 2.540 | 2.5391 | 18 | $\bar{2}11$ |
| 2.505 | 2.5058 | 13 | $\bar{1}21$ |
| 2.409 | 2.4072 | 4 | $\bar{4}12$ |
| 2.302 | 2.3036 | 8 | $\bar{2}21$ |
| 2.289 | 2.2891 | 13 | 330 |
| 2.279 | 2.2748 | 12 | 221 |
| 2.205 | 2.2037 | 4 | 420 |
| 2.142 | 2.1409 | 11 | 240 |
| 2.024 | 2.0244 | 8 | $\bar{2}31$ |
| 2.006 | 2.0066 | 4 | 231 |
| 1.955 | 1.9556 | 4 | 430 |
| 1.929 | 1.9293 | 4 | 340 |
| 1.879 | 1.8777 | 2 | 041 |
| 1.864 | 1.8636 | 3 | $\bar{1}50$ |
| 1.849 | 1.8486 | 5 | $\bar{1}41$ |
| 1.826 | 1.8260 | 1 | 331 |

### *Thermal behaviour*

When iron hydroxynitrate decomposes in still air or in a nitrogen flow, the same TG curves are obtained and Fig. 2 presents the thermal curves recorded. A step occurs between 90–145° with a weight loss of $\Delta m_{exp}$ = 7.00%. If it is assumed that the intermediate formed at the latest temperature is $Fe_4(OH)_{11}NO_3$, the calculated weight loss is $\Delta m_{calc.} = 7.08\%$. X-ray diffraction data of this intermediate are given in Table 2. It has been indexed within an orthorhombic cell, and a micrograph of this compound is shown in Fig. 3.

Between 170 and 450° the weight loss is continuous, with two inflexions at 200° and 300°. The intermediates formed at these temperatures could not be identified, since they are highly hygroscopic and amorphous solids.

Iron oxide $\alpha$-$Fe_2O_3$ (JPCDS 13–534) was obtained as the final product at 800°, and Fig. 4 shows the electron micrograph corresponding to this phase, its

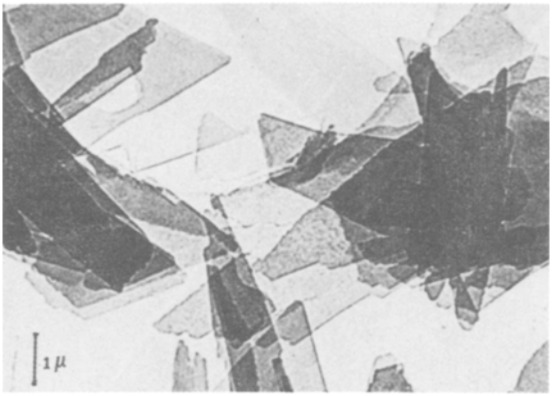

**Fig. 1** Electron micrograph of iron(III) hydroxynitrate. $Fe_4(OH)_{11}NO_3 \cdot 2H_2O$

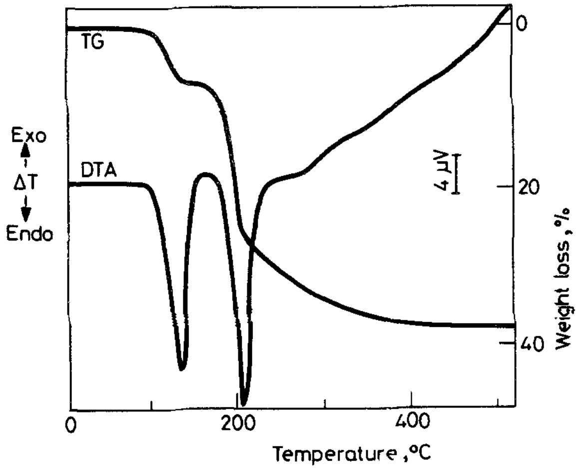

**Fig. 2** DTA and TG curves of iron(III) hydroxynitrate dihydrate. Heating rate 2 deg·min$^{-1}$

**Table 2** X-ray powder diffraction data for $Fe_4(OH)_{11}NO_3$

$a$ = 9.416(5) Å $c$ = 3.631(1) Å
$b$ = 8.952(3) Å $V$ = 306.1(1) Å$^3$

| $d_{obs.}$, Å | $d_{calc.}$, Å | $I/I_0$ | *hkl* |
|---|---|---|---|
| 8.97 | 8.953 | 100 | 010 |
| 6.48 | 6.488 | 35 | 110 |
| 4.71 | 4.708 | 10 | 200 |
| 4.05 | 4.043 | 60 | 120 |
| 2.986 | 2.9842 | 20 | 030 |
| 2.873 | 2.8758 | 25 | 201 |
| 2.842 | 2.8447 | 15 | 130 |
| 2.569 | 2.5700 | 15 | 320 |
| 2.164 | 2.1628 | 10 | 330 |
| 1.622 | 1.6220 | 10 | 440 |
| 1.555 | 1.5550 | 10 | 350 |
| 1.531 | 1.5310 | 10 | 132 |

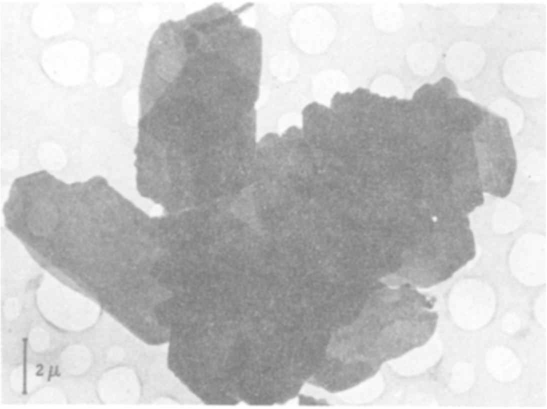

**Fig. 3** Electron micrograph of $Fe_4(OH)_{11}NO_3$

morphology is analogous to that observed for α-$Fe_2O_3$ obtained from α-FeOOH heated at 450° for 1½ hours [13].

The thermal behaviour of $Fe_4(OH)_{11}NO_3 \cdot 2H_2O$ is summarized in Table 3.

### *X-ray high temperature diffraction studies*

When iron hydroxynitrate dihydrate is heated under dynamic vacuum ($10^{-3}$–$10^{-4}$ torr) in an X-ray high temperature diffraction chamber, decomposition occurs at about 70°, and at 100° the X-ray diagram (Fig. 5b) is identical to that recorded for the intermediate, $Fe_4(OH)_{11}NO_3$, isolated at 145° when the starting material is heated in air or $N_2$. As the temperature increases this phase decomposes, and between 200° and 450° the X-ray diagram does not show any diffraction peaks; when the temperature reaches 480° maxima of $\alpha$-$Fe_2O_3$ starts to appear (Fig. 5c); at 600° the recorded diagram consists of lines of both $\alpha$-$Fe_2O_3$ and $\gamma$-$Fe_2O_3$ (Fig. 5d).

As the temperature increases, the intensity of the maxima corresponding to $\alpha$-$Fe_2O_3$ decreases, and those of $\gamma$-$Fe_2O_3$ increases as well, and besides, the most intense diffraction maxima of FeO start to appear. At 700°, both $\gamma$-$Fe_2O_3$ and FeO coexist (Fig. 5e) and when the temperature reaches 800°, FeO is the main compound of the mixture (Fig. 5f) and, when the temperature is held at 900° for 15 minutes, two peaks of low intensity, that correspond to the most intense diffraction lines of the iron metal, are observed (Fig. 5g).*

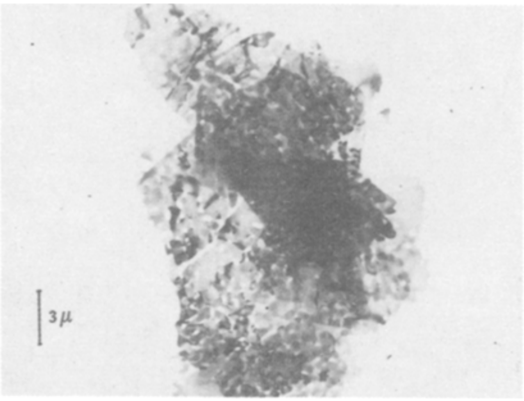

**Fig. 4** Electron micrograph of $\alpha$-$Fe_2O_3$

**TAble 3** Thermal decomposition scheme of iron(III) hydroxynitrate dihydrate

| | $\Delta m$, % | | $T$, °C |
|---|---|---|---|
| | calc. | exp. | |
| $Fe_4(OH)_{11}NO_3 \gamma 2H_2O \rightarrow Fe_4(OH)_{11}NO_3 + 2H_2O\uparrow$ | 7.08 | 7.00 | 90–145 |
| $Fe_4(OH)_{11}NO_3 \rightarrow 2\alpha\text{-}Fe_2O_3 + 1/2N_2O_5\uparrow + 11/2H_2O\uparrow$ | 37.17 | 37.64 | 169–850 |

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* The formation of FeO and iron metal in a "non-reducing" atmosphere can be explained if it is considered that the tantalurm strip not only acts as a heating element, but also plays a non-passive role in the reaction.

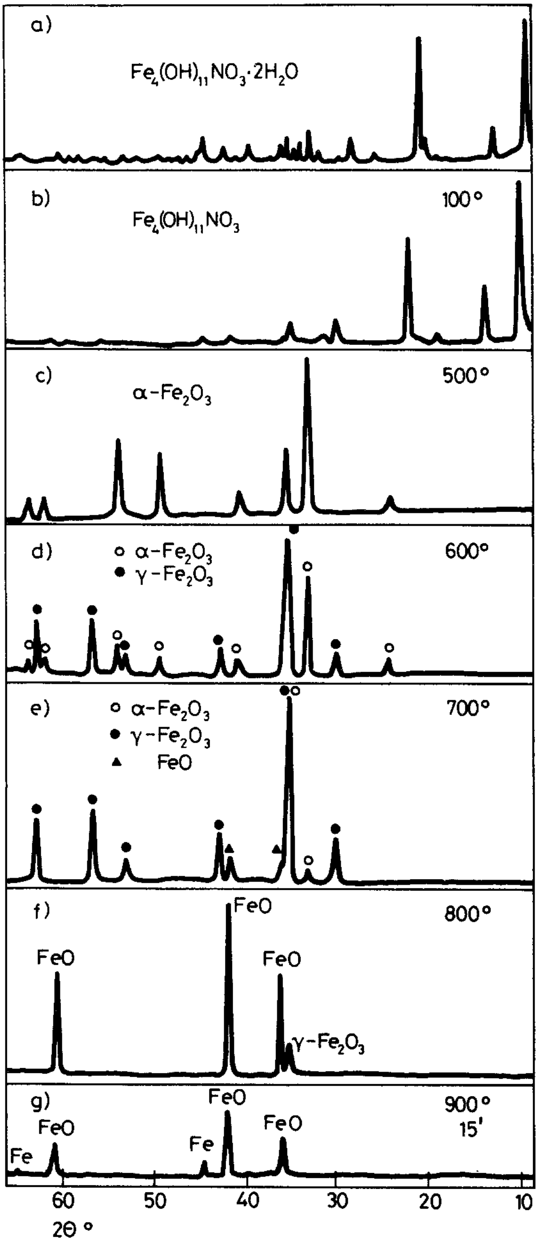

**Fig. 5** Evolution of iron(III) hydroxynitrate when it is decomposed in the X-ray high temperature diffraction chamber

**Table 4** Infrared absorption band frequencies of iron(III) dihydrate hydroxynitrate and products isolated during the thermal decomposition

| Assignment | Frequencies, $cm^{-1}$ | | |
|---|---|---|---|
| | $Fe_4(OH)_{11}NO_3 \cdot 2H_2O$ | $Fe_4(OH)_{11}NO_3$ | $\alpha$-$Fe_2O_3$ |
| $\nu$OH | 3498 vs | 3540 vs | |
| $\nu OH(H_2O)$ | 3342 vs, b | (3400) | |
| $\delta$HOH | 1632 m | — | |
| $\nu_4(—ONO_2)$ | 1435 s | 1500 vs | |
| $\nu_3(—NO_3)$ | 1384 vs | 1384 m | |
| $\nu_1(—ONO_2)$ | 1346 vs | 1350 s<br>1320 sh | |
| $\nu_2(—ONO_2)$<br>$\nu_1(—NO_3)$ | 1048 m | 1035 m | |
| $\delta$(Fe—OH) | 942 w | — | |
| $\varrho(H_2O)$ | 841 m | 875 m | |
| $\nu_6^+(ONO_2)$ | 804 m | 790 s | |
| $\nu_3^+(ONO_2)$ | 735 sh | 750 s | |
| $\nu_5^+(ONO_2)$ | 712 m | 715 m | |
| $\nu$(Fe—O) | 660 s | 685 sh | 645 m |
| | | | 560 sh |
| | | | 520 s |
| | 432 vs | 432 vs | 440 s |
| | 380 m | 360 m | 397 w |
| | 289 m | 300 m | 310 s |
| | 257 m | | 280 sh |

(vs = very strong, s = strong, m = medium, w = weak and sh = shoulder)

## *IR spectroscopy study*

The infrared spectra of the initial compound, the intermediate $Fe_4(OH)_{11}NO_3$, and the final product $\alpha Fe_2O_3$, have been obtained and they have been tentatively assigned on the basis of published data [14–17], Table 4.

The IR spectrum of the hydrated iron hydroxynitrate shows the existence of two types of nitrate groups with a different symmetry $D_3h$ ($\nu_3$ 1384 $cm^{-1}$) and $C_{2v}$ ($\nu_4$ 1435 $cm^{-1}$ and $\nu_1$ 1346 $cm^{-1}$).

It has not been possible to obtain $Fe_4(OH)_{11}NO_3$ IR spectrum free from water because of its high hygroscopicity; in this case, also is observed the existence of nitrate groups of different symmetry together with a band splitting.

The IR spectrum of $\alpha$-$Fe_2O_3$ agrees with that reported by Serna [18] for a laith-shaped phase.

## Conclusions

By partially hydrolyzing a solution of $Fe(NO_3)_3 \cdot 9H_2O$ a new iron basic salt has been obtained. The very hygroscopic intermediate, $Fe_4(OH)_{11}NO_3$, has been isolated.

When this basic salt is decomposed both in air or nitrogen atmospheres, $\alpha$-$Fe_2O_3$ is formed at 800°, while when the thermal decomposition is carried out under vacuum, in an X-ray high temperature diffraction chamber, the formation of $\alpha$-$Fe_2O_3$ takes place at 500°; it transforms to FeO at about 700°, and although some iron metal is detected at about 900°.

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**Zusammenfassung** — Mittels Hydrolyse einer Lösung von $Fe(NO)_3)_3 \cdot 9H_2O$ mit Karbamid wurde das neue basische Eisensalz $Fe_4(OH)_{11}NO_3 \cdot 2H_2O$ dargestellt. Aus einem Röntgenpulververfahren resultieren $a = 9{,}55(3)$ Å, $b = 9{,}48(2)$ Å, $c = 3{,}074(3)$ Å und $\beta = 90{,}57(1)°$ für eine monozyklische Zelle. Mittels DTA- und TG-Untersuchungen wurden die thermischen Zersetzungsreaktionen an Luft und im Stickstofffluß untersucht und die Zwischen- und Endprodukte mit röntgendiffraktionsverfahren und IR-Spectroskopie charakterisiert. Bei einer thermischen Zersetzung dieses Stoffes in einer Hochtemperatur-röntgendiffraktionskammer wird bei 900 °C elementares Eisen zusammen mit Fe(II)- und Fe(III)-oxiden gebildet.

**Резюме** — Частичным гидролизом раствора соли $Fe(NO_3)_3 \cdot 9H_2O$ с мочевиной получена новая основная соль $Fe_4(OH)_{11}NO_3 \cdot 2H_2O$, для которой методом порошкового рентгеноструктурного анализа была установлена моноклинная структура с параметрами ячейки $a = 9,55(3)$ Å, $b = 9,48(2)$ Å, $c = 3,074(3)$ Å и $\beta = 90,57(1)°$. Термическое разложение соли изучено методом ДТА и ТГ в динамической атмосфере воздуха и азота, а образующиеся промежуточные и конечные продукты реакции были охарактеризованы рентгенофазовым анализом и ИК спектроскопией. При термическом разложении соли в высокотемпературной рентгенодиффракционной камере при 900° образуется чистое железо вместе с оксидами двух- и трехвалентного железа.