

THERMAL ANALYSIS OF SOME CYANO COMPOUNDS.

Part IV. * The thermal behaviour of $\text{LnFe}^{3+}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La(III)}, \text{Ce(III)}, \text{Pr(III)}, \text{Nd(III)}$)

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(Received 25 May 1990; in final form 13 August 1990)

ABSTRACT

The thermal behaviour of simple rare earth ferricyanides $\text{LnFe}^{3+}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La(III)}, \text{Ce(III)}, \text{Pr(III)}, \text{Nd(III)}$) has been investigated in static air by thermal analysis and IR spectroscopy.

The investigated compounds decompose in two large steps: in the first step, they lose three HCN moles per mole of initial compound; the remaining product is then completely oxidised to the oxide mixture, $\text{Ln}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ($\text{CeO}_2 + \text{Fe}_2\text{O}_3$ for the cerium compound), with no intermediate formation of cyanate.

In contrast to the alkaline ferricyanides, such as $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{Fe}(\text{CN})_6^{3-}$ in the investigated compounds does not undergo thermally induced intramolecular reduction.

Neither decomplexing nor isomerisation reactions were recorded.

INTRODUCTION

In an oxidising atmosphere, cyano compounds undergo oxidative thermal decomposition within the range 300–500°C, characterised by a strong exothermic band whose shape clearly shows the presence of more overlapping events.

In addition, at lower temperatures one or more endothermic events occur contemporaneously with the emission of gaseous products, see refs. 1–3 and the references therein.

The cations both in the cation and/or in the anion moieties of complex compounds such as ferrocyanides, ferricyanides, cobalticyanides, etc. affect the oxidation mechanism and the nature of the final products.

* Financially supported by MPI.

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For compounds of alkaline ions, such as KCN, and $K_4Fe(CN)_6 \cdot 4H_2O$, the endothermic events between room temperature and 150–200°C are due to the elimination of crystallisation water from the sample. A weight increase is recorded in correspondence to the exothermic peak for the oxidative thermal decomposition of the sample by O_2 from the surrounding atmosphere. The consequent formation of cyanates and carbonates is clear in the IR spectra of the residues of the samples heated at various temperatures [1].

For complex cyanides which, as well as alkaline ions in their cationic moieties, also have multiply charged cations with suitable chemical affinities towards the oxygen atom of the crystallisation water (e.g. rare-earth three-valent cations), the thermal decomposition follows hydrolytic pathways. Instead of H_2O , HCN is preferentially eliminated and hydroxy derivatives are formed [2,4]. In these cases, because of stoichiometric balance, weight increases are not recorded in correspondence to the exo-transitions although the IR spectra of the residues demonstrate the intermediate formation of cyanate, as in the oxidative decomposition of the anionic part of the molecule [2].

Redox as well as bond isomerisation reactions may occur between the cationic and anionic part of the molecule. In $K_2Cu_3Fe^{2+}(CN)_6 \cdot nH_2O$, Cu(II) is reduced to the cyano complex of Cu(I) [4]. In $CrCo(CN)_6$ the CN^- initially bonded to Co(III) via C transfers to Cr(III), transforming the compound to a $Cr(CN)_6^{3-}$ derivative [5].

A further characteristic is the thermally induced reduction of the central ion which is dependent on its nature; this has been observed in $K_3Fe(CN)_6$ and $K_3Co(CN)_6$ [1]. The redox reactions probably occur intramolecularly between the central ion and the coordinated cyanide which is eliminated, probably as cyanogen.

The main aim of this work was to clarify the fairly complex role of the various parameters which determine the mechanism of the thermal decomposition of cyano complexes in an oxidising atmosphere.

EXPERIMENTAL

Preparation of the compounds

The compounds were prepared by following the procedure reported in the literature [6], i.e. by precipitating $Ln(NO)_3$ solution (Ln = lanthanide ion) by addition of a 0.1 M $K_3Fe(CN)_6$ solution. The precipitates were then washed with water and dried at atmospheric pressure over P_2O_5 .

Thermal analysis measurements

The thermal analysis measurements were carried out in static air using a Mettler TA 3000 apparatus. The samples were contained in standard Al_2O_3

crucibles for TG and in standard Al crucibles for DSC measurements, both covered with their respective lids. The lids of the Al crucibles were pierced with three 1 mm holes, 1–2 mm apart from each other at the points of an equilateral triangle. More details concerning the experimental conditions are given in the figure captions.

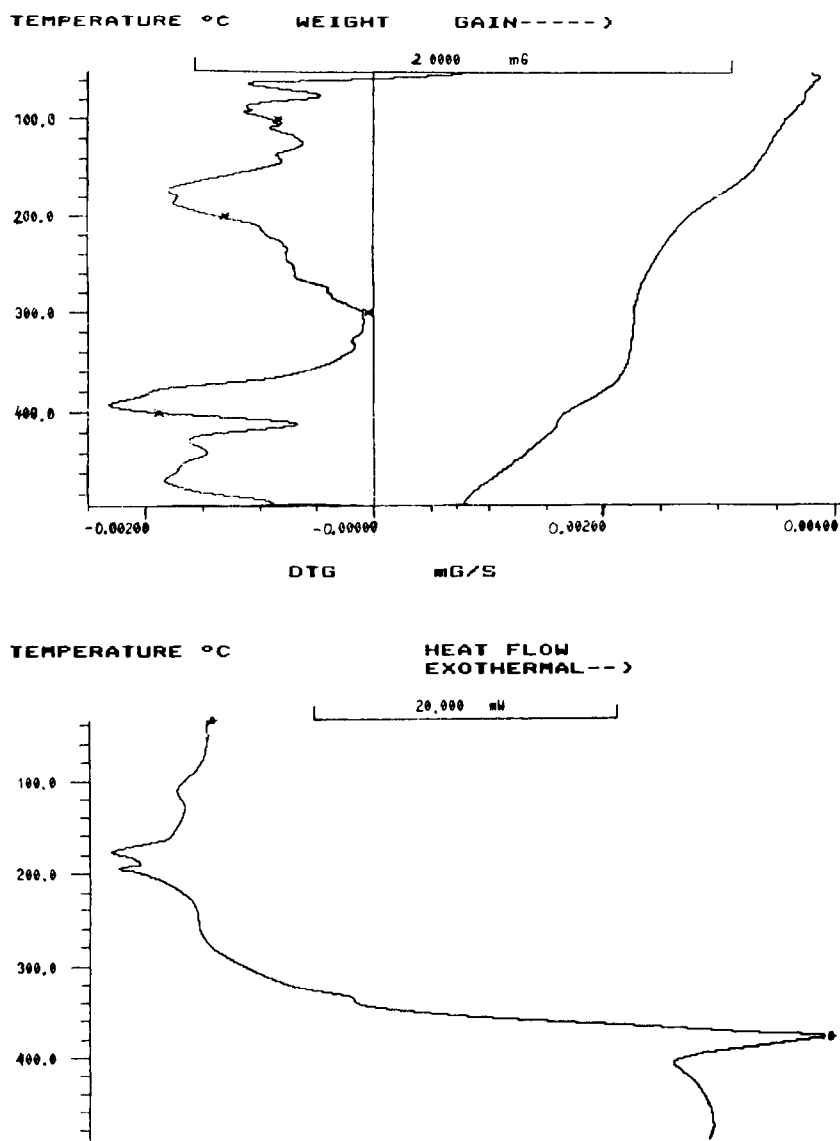


Fig. 1. Thermal analysis curves (TG, DTG and DSC) of $\text{LaFe(CN)}_6 \cdot n\text{H}_2\text{O}$ in static air. Heating rate: $20^{\circ}\text{C min}^{-1}$. Weight of the sample: TG and DTG, 3.083 mg; DSC, 3.06 mg.

IR spectra

IR spectra of the residues at various selected temperatures were recorded in nujol on a Perkin-Elmer IR spectrometer, Mod 783.

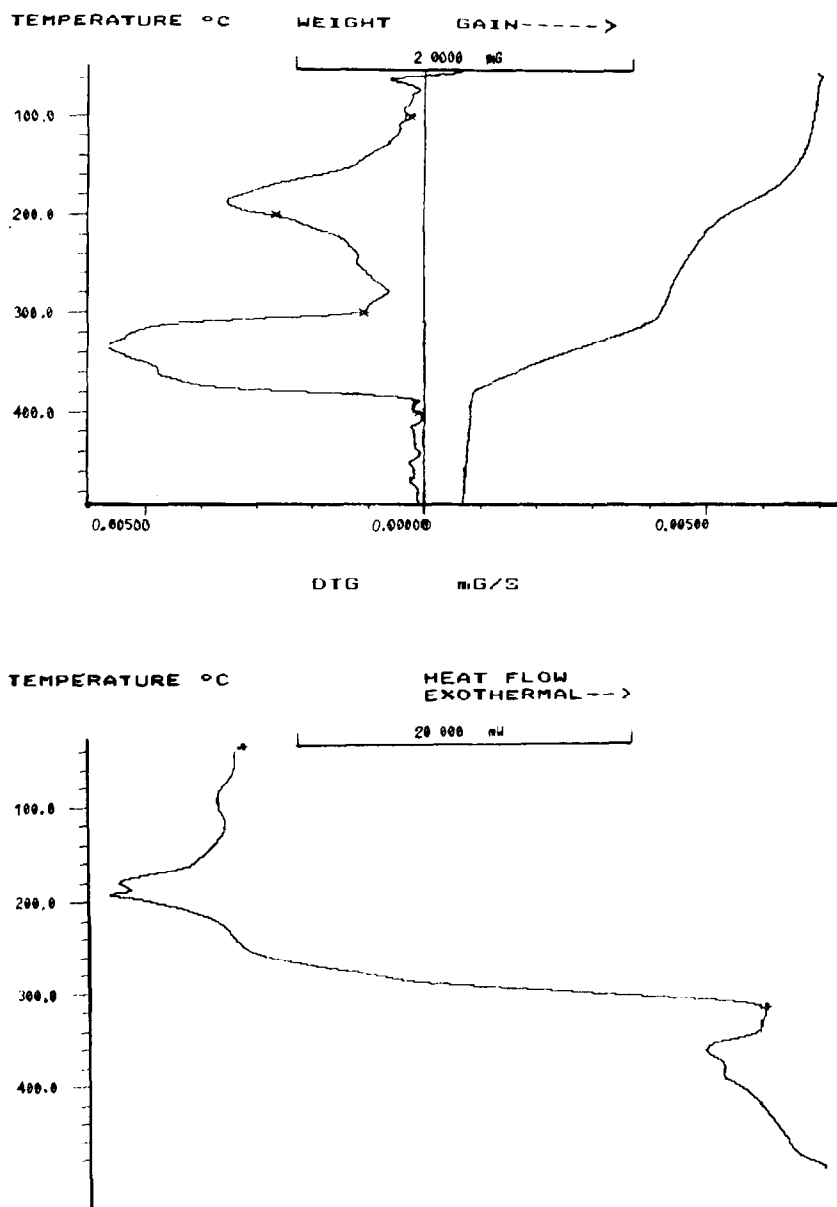


Fig. 2. Thermal analysis curves (TG, DTG and DSC) of $\text{CeFe(CN)}_6 \cdot n\text{H}_2\text{O}$ in static air. Heating rate: $20^\circ\text{C min}^{-1}$. Weight of the sample: TG and DTG, 5.07 mg; DSC, 3.36 mg.

The compounds were heated in an oven in open porcelain crucibles up to selected temperatures, according to the results of the thermal analysis, and were maintained in isothermal conditions for 3–4 minutes. Samples for the IR spectra were removed and the remaining residue was heated up to the next selected temperature. IR spectra were recorded immediately.

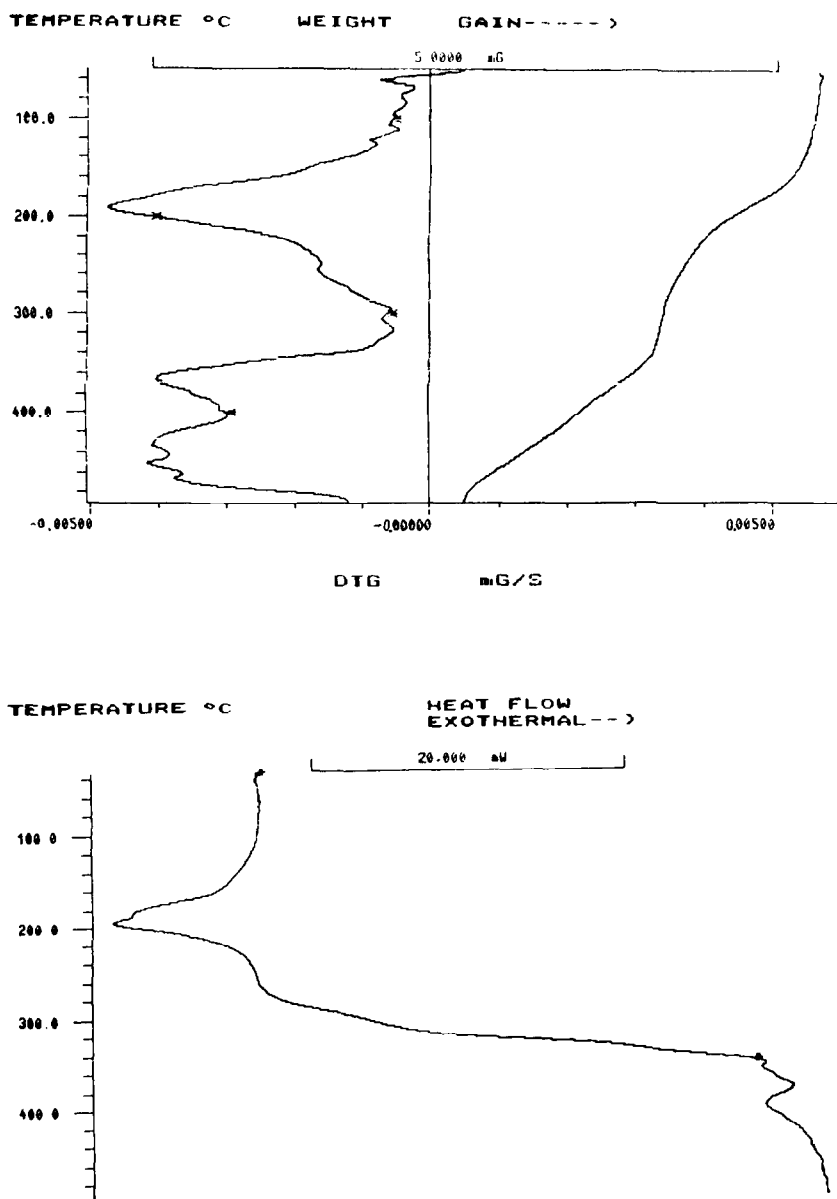


Fig. 3. Thermal analysis curves (TG, DTG and DSC) of $\text{PrFe(CN)}_6 \cdot n\text{H}_2\text{O}$ in static air. Heating rate: $20^{\circ}\text{C min}^{-1}$. Weight of the sample: TG and DTG, 7.07 mg; DSC, 3.79 mg.

RESULTS

The thermal analysis curves in static air are shown in Figs. 1–4. In general, they display the same thermal behaviour: the TG curves drift downwards over all the investigated temperature range but also show

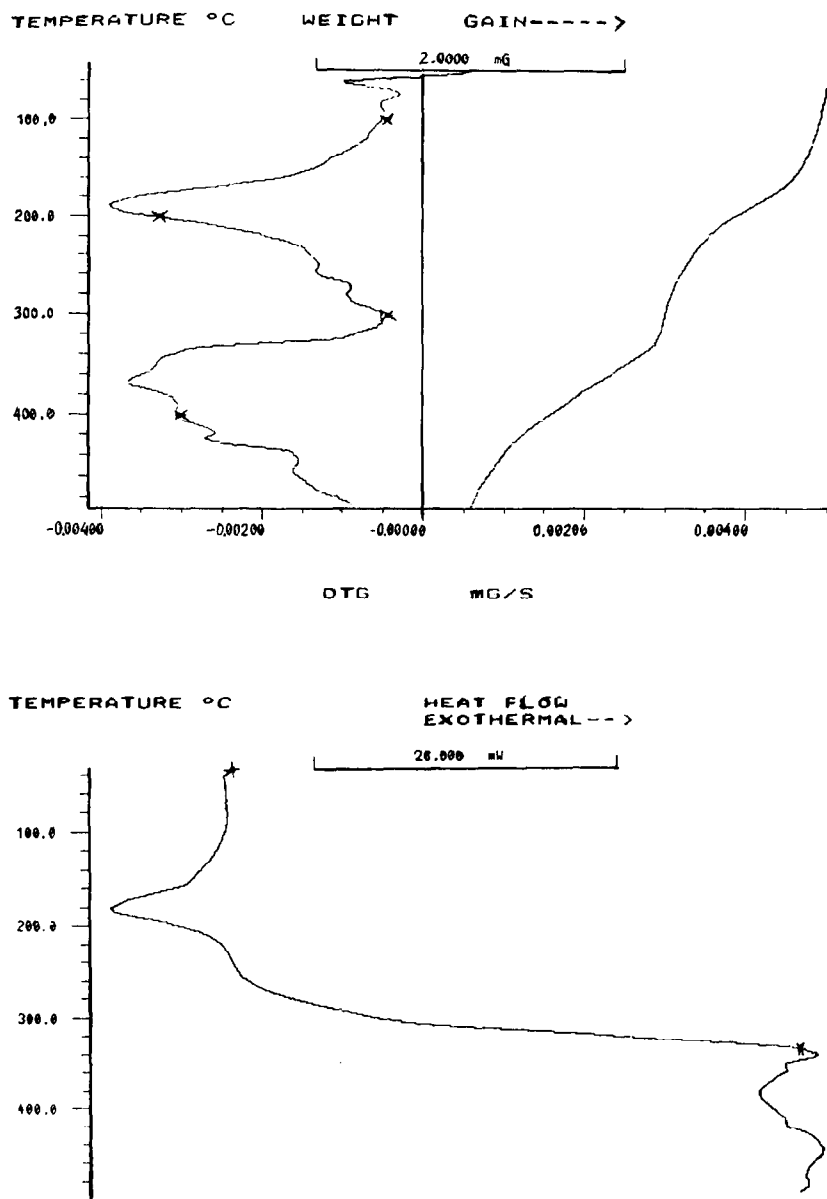


Fig. 4. Thermal analysis curves (TG, DTG and DSC) of $\text{NdFe(CN)}_6 \cdot n\text{H}_2\text{O}$ in static air. Heating rate: $20^{\circ}\text{C min}^{-1}$. Weight of the sample: TG and DTG, 5.81 mg; DSC, 3.19 mg.

TABLE 1

Minimum procedural temperatures in DTG diagrams. The values are in agreement with the DSC peak temperatures

Formula	First step (°C)	Second step (°C)	Third step (°C)
$\text{LaFe}(\text{CN})_6 \cdot n\text{H}_2\text{O}$	55–60	180 (endo)	390 (exo)
$\text{CeFe}(\text{CN})_6 \cdot n\text{H}_2\text{O}$	55–60	180 (endo)	320 (exo)
$\text{PrFe}(\text{CN})_6 \cdot n\text{H}_2\text{O}$	55–60	180 (endo)	360 (exo)
$\text{NdFe}(\text{CN})_6 \cdot n\text{H}_2\text{O}$	55–60	190 (endo)	380 (exo)

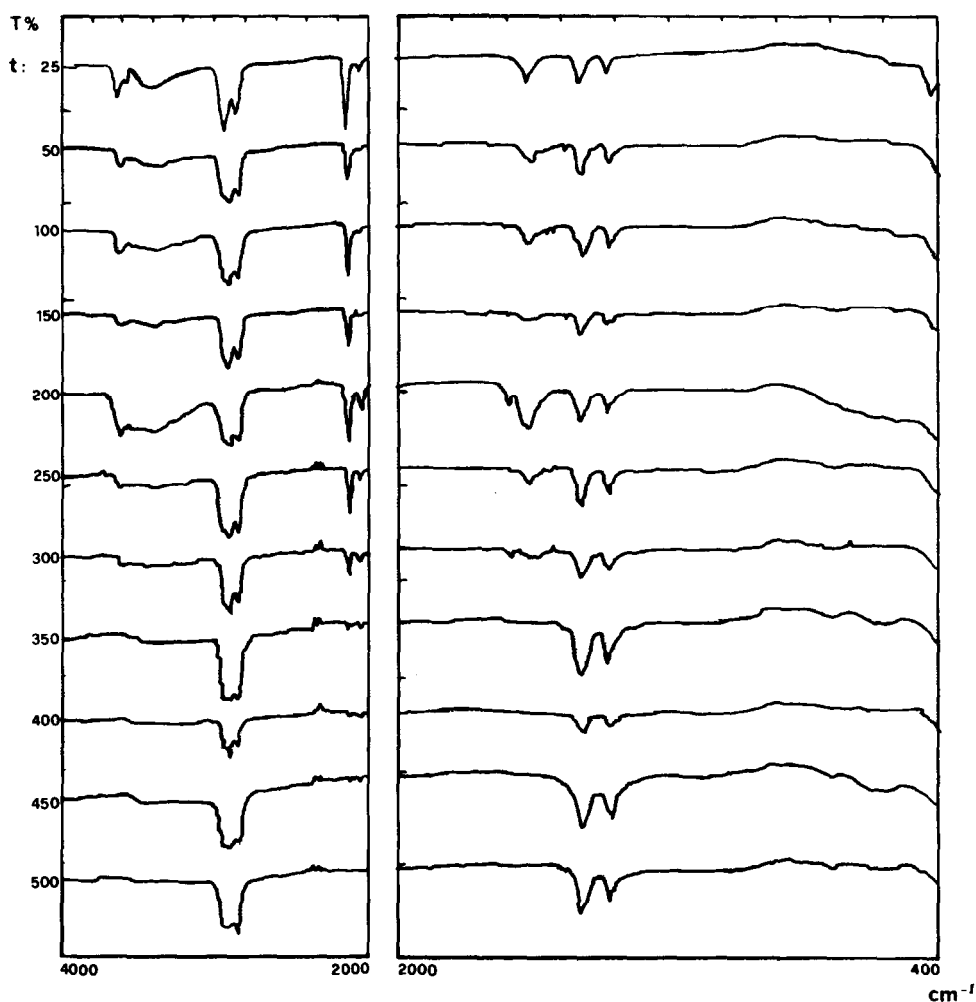


Fig. 5. Selected IR spectra of the residues of $\text{LaFe}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ on heating in air at various temperatures.

negative steps which are easily located by their minimum procedural temperatures in the DTG plots (Table 1). However, the corresponding weight losses cannot be so easily estimated.

The first negative step is a very small one, beginning at room temperature; the DSC plot does not record any corresponding heat flux, probably because only very small, undetectable enthalpy changes are involved. Two large irregular negative steps follow; the weight losses cannot be calculated exactly because of the shape of the thermograms.

From room temperature up to 200–250 °C, the overall enthalpy change for the thermally induced reactions is positive (endothermic event). A very strong exothermic event follows which is different for the various fer-

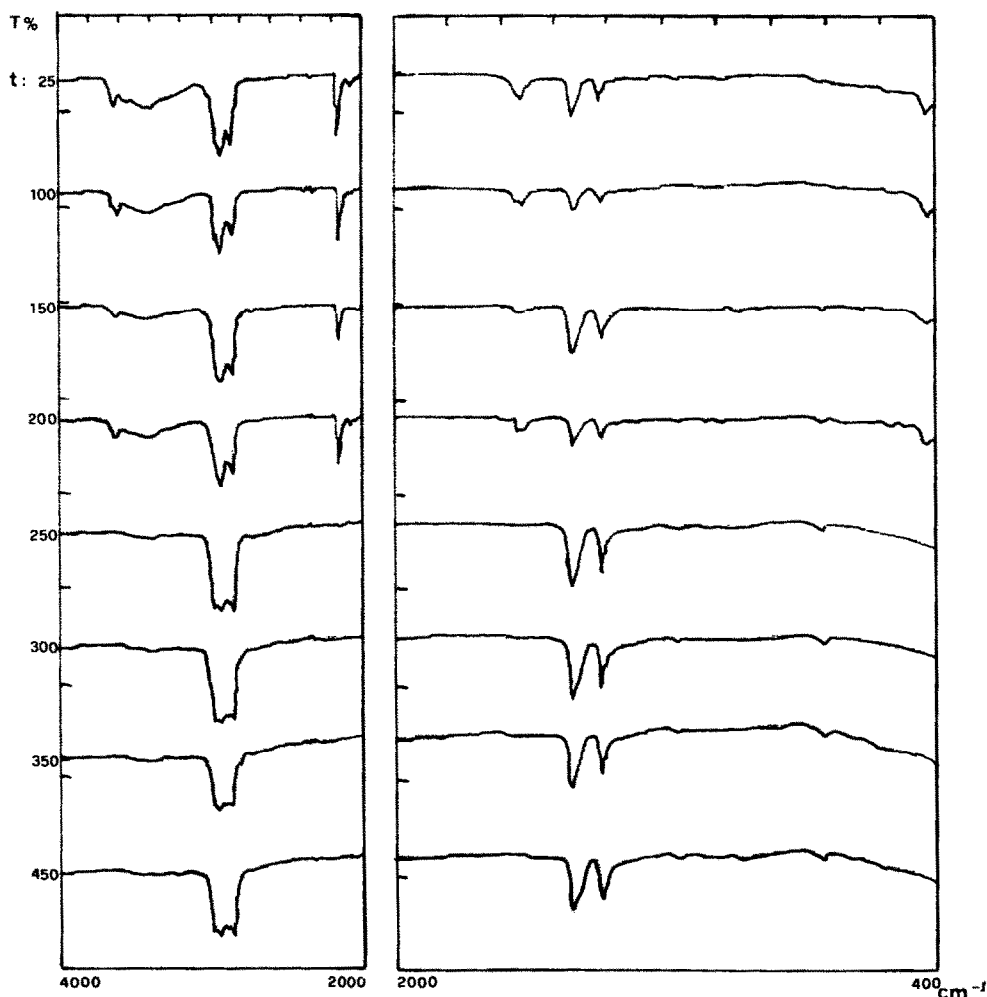


Fig. 6. Selected IR spectra of the residues of $\text{CeFe(CN)}_6 \cdot n\text{H}_2\text{O}$ on heating in air at various temperatures.

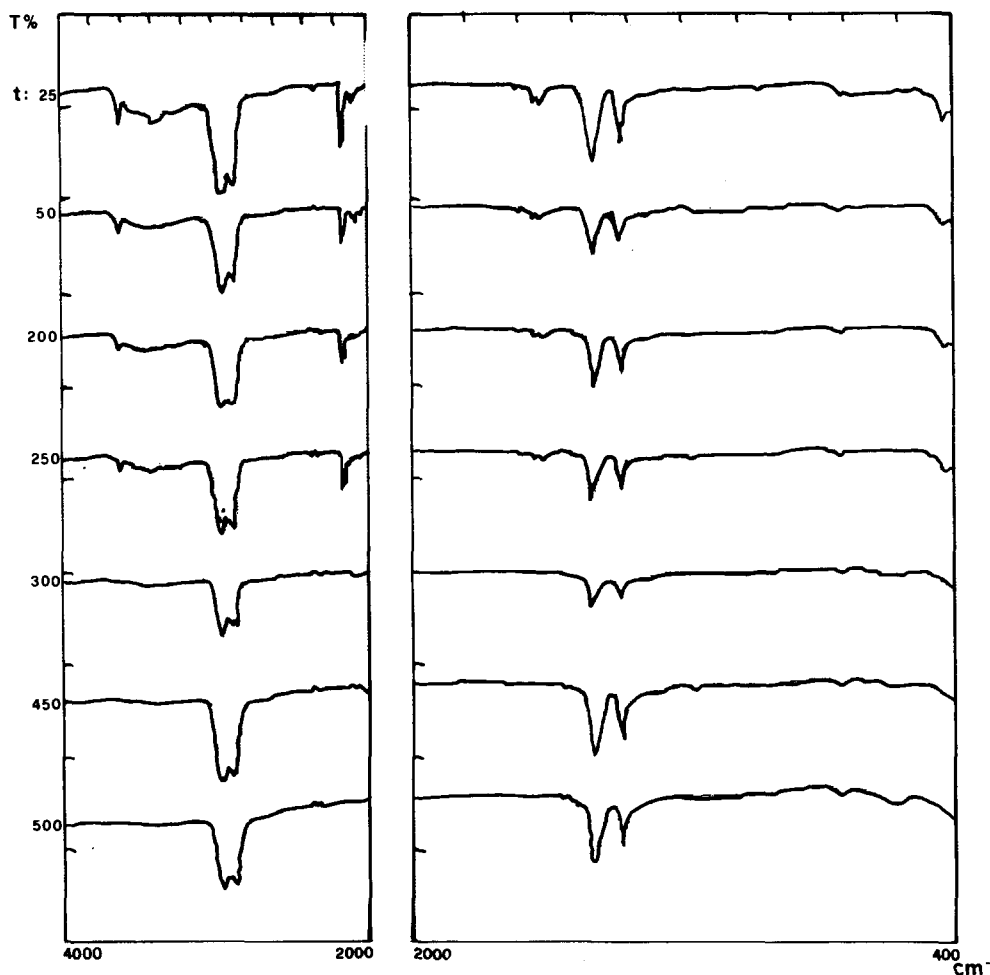


Fig. 7. Selected IR spectra of the residues of $\text{PrFe(CN)}_6 \cdot n\text{H}_2\text{O}$ on heating in air at various temperatures.

ricyanides, which cover the narrow, very sharp, exothermic band between 300 and 400 °C characteristic of the combustion in air of ferro- or ferricyanides [1–3].

Figures 5–8 show the IR spectra of the residues on heating. The original (unheated) sample has four absorption bands in the range 4000–400 cm^{-1} . The first, between 3700 and 3000 cm^{-1} , is due to the crystallisation water, as is the absorption between 1700 and 1500 cm^{-1} . The structure of these well shaped absorption bands (a narrow band centred at 3700 cm^{-1} , and a doublet between 1700 and 1500 cm^{-1}) indicate that the water molecules are strongly and specifically bound in the lattice.

A second absorption due to the $\nu(\text{CN})$ in $\text{Fe}^{3+}(\text{CN})_6$, occurs between 2150 and 2000 cm^{-1} . It is asymmetrical in the direction of the lower

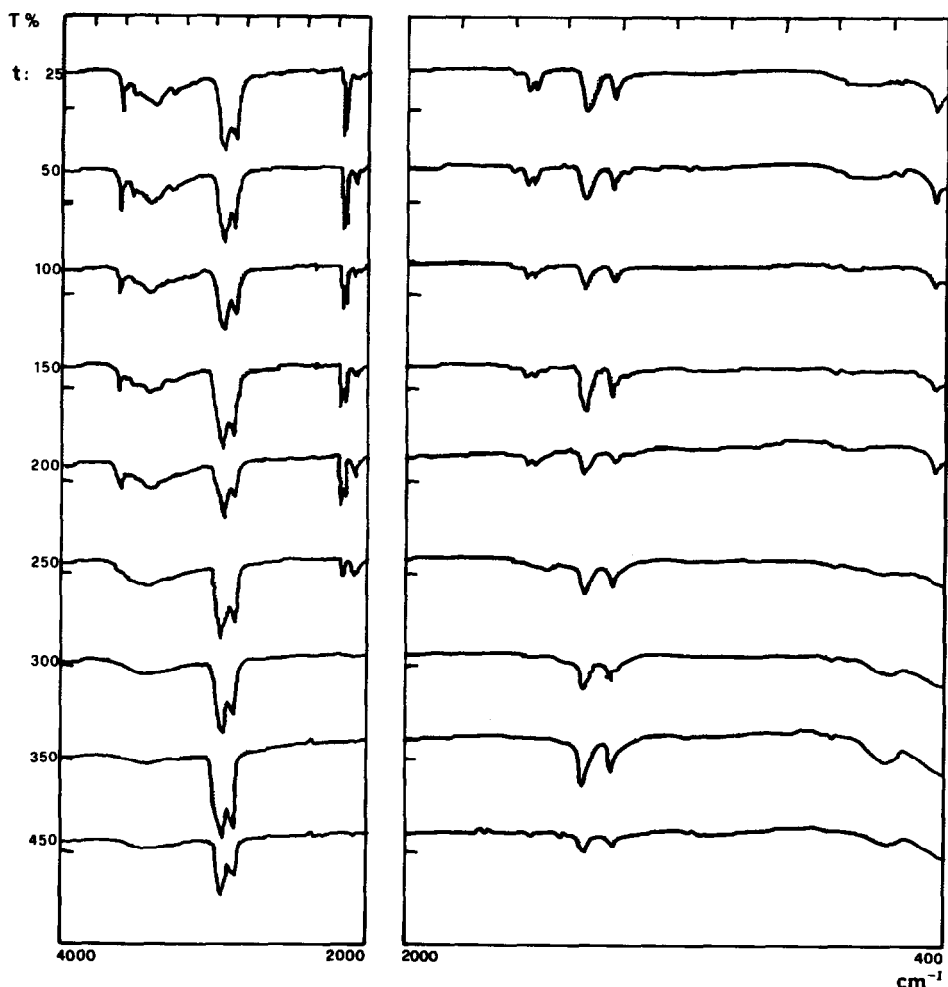


Fig. 8. Selected IR spectra of the residues of $\text{NdFe(CN)}_6 \cdot n\text{H}_2\text{O}$ on heating in air at various temperatures.

wavenumbers and consists of a doublet of strong narrow bands (2140 and 2125 cm^{-1}) and a smaller band at 2060 cm^{-1} .

At least one other band, ascribed to the $\nu(\text{Fe}^{3+}-(\text{CN}))$ stretching [7,8], is recorded at 420 cm^{-1} .

In comparison with $\text{K}_3\text{Fe(CN)}_6$, the recorded absorption maxima are shifted towards higher wavenumbers as a consequence of the interaction between the CN^- of the coordination sphere of Fe(III) and the lanthanide cation in the cationic part of the lattice. The shift is independent of the nature of the lanthanide cation.

The IR spectra of the residues on heating show a basic similarity for all the investigated compounds. The bands related to the presence of crystallisation water are recorded up to 200°C , but the intensity ratios between the

$\nu(\text{CN})$ stretching bands modify in favour of the band at 2060 cm^{-1} , though they all remain centred on the same wavenumbers.

Corresponding to the exothermic flux seen in the DSC plot, the bands related to cyanide ion (both CN and $\text{Fe}^{3+}\text{-CN}$) disappear, and bands characteristic of oxides and carbonates are recorded. The band at 720 cm^{-1} for cerium compounds indicates the formation of CeO_2 [9], in accordance with the behaviour of this element [6,10].

DISCUSSION AND CONCLUSIONS

The simple rare earth ferricyanides investigated in this work have, in general, lower thermal stabilities than the mixed potassium–lanthanon ferrocyanides, $\text{KLnFe}^{2+}(\text{CN})_6 \cdot n\text{H}_2\text{O}$. The steady drifts downwards in the TG plots and the endothermic fluxes in the first part of the DSC diagrams (Figs. 1–4) indicate continuous thermal decompositions starting from room temperature and extending over all the investigated range; whereas for $\text{KLnFe}^{2+}(\text{CN})_6 \cdot n\text{H}_2\text{O}$, there are ranges within which the samples have constant weight and no heat flux is recorded in the thermal analysis diagrams. Despite this, the two classes of compounds have unquestionable analogies such as the two large TG steps with corresponding DSC heat fluxes in the same directions, the first endothermic and the second exothermic. These analogies are surely not just restricted to the shapes of the curves but must also reflect indentifiable chemical events which occur in common.

For both the ferrocyanides, $\text{KLnFe}^{2+}(\text{CN})_6 \cdot n\text{H}_2\text{O}$, and ferricyanides, $\text{LnFe}^{3+}(\text{CN})_6 \cdot n\text{H}_2\text{O}$, the IR spectra of the residues on heating show the presence of crystallisation water up to 200°C in spite of the first large thermal event. Simultaneously, the $\nu(\text{CN})$ stretching bands at 2140 and 2125 cm^{-1} decrease in intensity. These bands, in analogy to other solid cyanide complexes [11], can be ascribed to those CN groups which interact more with the cationic part of the molecule in the crystal lattice. Therefore the recorded changes in the TA curves can be ascribed to the prevalent, but not exclusive elimination of CN groups as gaseous products, and not to the loss of water. The elimination can occur in two possible ways:

- (i) By means of redox reaction(s) with formation of cyanide-related gaseous products (e.g. cyanogen)
- (ii) By means of HCN elimination in the case of interaction between the coordinated cyanide and the hydrogen atoms of coordinated-to-cation water molecules.

The redox hypothesis, (i), is unlikely for the following reasons. The species that can be reduced by oxidising the cyanide are (a) the lanthanide ion, (b) the Fe(III) of the complex or (c) the oxygen of the surrounding atmosphere.

The first eventuality conflicts with the redox behaviour of the lanthanons in air [6,10].

The reduction of Fe(III) leads, as in other cases [1], to the formation of Fe(II) cyanide complexes and, consequently, to pronounced changes in the IR spectra of the residues.

The third eventuality leads to solid, not gaseous, oxygenated compounds (e.g. cyanate [1,2]) which would be indicated on the IR spectra. Moreover, in such a case, the TG plots would show increasing weight and the DSC peak would become exothermal, in contrast to the experimental findings.

Therefore, gaseous elimination of HCN seems to be the likely hypothesis. This is confirmed by the fact that HCN elimination has also been demonstrated in the thermal behaviour of $\text{KLnFe}^{2+}(\text{CN})_6 \cdot n\text{H}_2\text{O}$ [2,4].

In the preceding description of the experimental results, it has been said that the TG steps cannot be readily characterised by their respective weight losses. As a consequence, only estimates can be made.

In the TG curves from room temperature to the temperature corresponding to the maximum in the DTG curves which follows the first large TG step, the overall weight losses are -22% , -17.7% , -18.2% and -18.5% for the lanthanum, cerium, praseodymium and neodymium compounds $\text{LnFe}^{3+}\text{Fe}(\text{CN})_6 \cdot n\text{H}_2\text{O}$, respectively. In the first part of the diagram (the first step in the TG curve; $t = 55\text{--}60^\circ\text{C}$ in Table 1) the weight losses are due to the elimination of absorbed water. From the shapes of the curves, it can be seen that the moisture level is fairly low for the cerium, praseodymium and neodymium compounds, and is a little higher in the lanthanum compound. It follows that the above ΔW values reflect only a small loss of moisture, most of the weight loss being due to the elimination of HCN. From stoichiometric estimates of the theoretical ΔW values for the evolution of 3 HCN moles per mole of initial hydrated compound ($\text{LaFe}(\text{CN})_6 \cdot 4.5\text{H}_2\text{O}$, $\text{CeFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, $\text{PrFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$ and $\text{NdFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, according to the literature [6]), $\Delta W_{\text{theor.}} = -18.75\%$, -19.1% , -19.05% and -18.92% , respectively. Therefore, thermogravimetric quantitative data are in agreement with the loss of 3 moles of HCN per mole of initial hydrated compound.

The elimination of three moles of HCN can occur in different ways: three HCN groups can be eliminated for each $\text{Fe}^{3+}(\text{CN})_6$ group present; or six HCN molecules can be lost from a single $\text{Fe}^{3+}(\text{CN})_6$ group for every two $\text{Fe}^{3+}(\text{CN})_6$ groups.

The first hypothesis requires the perfect equivalence of all the $\text{Fe}^{3+}(\text{CN})_6$ groups in the crystal lattice and would produce significant changes in the IR spectrum because $\text{Fe}^{3+}(\text{CN})_3$ is formed from $\text{Fe}^{3+}(\text{CN})_6$. The second hypothesis implies that two distinct $\text{Fe}^{3+}(\text{CN})_6$ groups are present in equal amounts in the lattice. The elimination of HCN would occur from those groups most closely sited to the cationic part of the molecule. This second hypothesis also requires that part of the IR spectrum remains unaltered or

almost unaltered. The loss in intensity of the bands at 2140 and 2125 cm^{-1} with respect to the band at 2060 cm^{-1} strengthens this hypothesis.

Final thermogravimetric quantitative data for the cerium, praseodymium and neodymium compounds ($\Delta W = -41\%$, -42% and -40.3% : for the lanthanum compound the TG plot is too steep for even an approximate estimate) indicate the formation of oxides as final products ($\Delta W_{\text{Theor.}} = -40.52\%$, -42.39% and -42.06%). The formation of ferrites must be excluded because of the high temperatures at which these compounds are usually prepared.

The cerium compound decomposes at lower temperatures compared with the other compounds. Because this also occurs for other cerium compounds, iron-cyanide-related or not [2,12], such behaviour can be ascribed to the redox properties of $\text{CeO}_2/\text{Ce}_2\text{O}_3$ which favour the oxidation of the remaining part of the molecule.

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