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THERMAL ANALYSIS OF SOME CYANO COMPOUNDS. PART II *. THERMAL BEHAVIOUR OF MIXED $KLnFe(CN)_6 \cdot 4H_2O$ (Ln = La(III), Ce(III), Nd(III))

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ABSTRACT

The thermal behaviour of potassium–rare earth ferrocyanides, $KLnFe(CN)_6 \cdot 4H_2O$ (Ln = La(III), Ce(III), Nd(III)), has been studied in static air by conventional thermal analysis and IR spectroscopy.

The IR inspection of the residues remaining after heating at various temperatures showed that the lanthanide ions induce a hydrolytic mechanism with partial elimination of HCN instead of H_2O.

The combustion of the samples leads to oxide (predominant) and carbonate mixtures with the formation of cyanate and, in the case of $KLaFe(CN)_6 \cdot 4H_2O$, of cyanamide, as intermediates.

The cerium compound decomposes at a lower temperature probably owing to a different mechanism involving the formation of CeO_2.

INTRODUCTION

Researches on the thermal behaviour of various cyano compounds have demonstrated that the metal ions in the cation and anion moieties affect the course of thermally induced reactions [1–14].

Owing to the thermal stability of the oxides and carbonates of some metal ions under normal pressures [15–18], their formation on heating the cyanides of these metal ions in air or in an oxidizing (O_2) atmosphere can easily be foreseen. The existence of a complicated multistage mechanism with intermediate formation of cyanate was demonstrated [1]. Moreover, the recording of only exothermic events (with the exception of those related to the

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dehydration reactions) allowed the exclusion of decomplexing reactions such as eqn. (1)

$$K_nM(CN)_p \rightarrow nKCN + M(CN)_{p-n} \quad (1)$$

where, with M = Fe(II), $n = 4$ and $p = 6$; with M = Fe(III) or Co(III), $n = 3$ and $p = 6$; and with M = Hg(II), $n = 2$ and $p = 4$.

This research concerns the thermal behaviour of potassium–rare earth ferrocyanides $KLnFe(CN)_6 \cdot 4H_2O$ (Ln = La(III), Ce(III), Nd(III)). It was performed using conventional thermal analysis (thermogravimetry (TG) and differential scanning calorimetry (DSC)) in static air and IR spectroscopy of the solid residues at various temperatures.

EXPERIMENTAL

Ferrocyanide ion forms precipitates with many monovalent and/or polyvalent cations in water. In the presence of monovalent cations such as K^+, Rb^+, Cs^+, NH_4^+,..., the chemical composition of the compounds formed varies according to the experimental conditions [19,20]. As far as the ferrocyanides of trivalent lanthanide ions are concerned, previous studies [21,22] showed that in the system $Ln(NO_3)_3$–$K_4Fe(CN)_6$–KNO_3–H_2O (Ln = La(III), Ce(III), Nd(III)) one compound is formed with $Ln{:}Fe(CN)_6 = 1:1$ (formula $KLnFe(CN)_6 \cdot nH_2O$). According to the literature [23,24] $n = 4$ for these compounds.

The mixed La(III), Ce(III) and Nd(III) ferrocyanides were prepared by the same method [21,22] by adding (drop by drop with continuous stirring) the stoichiometric amount of 10^{-1} M $Ln(NO_3)_3$ solution (10 ml) to 100 ml of 10^{-2} M $K_4Fe(CN)_6$ solution. The white precipitates were washed several times with water, collected by centrifugation and then air-dried over P_2O_5 for a week.

Thermal analysis

TG and DSC experiments were performed in static air at a heating rate of 5 °C min^{-1} using a Mettler TA 3000 apparatus.

The samples for DSC measurements were contained in standard aluminium crucibles (No. 27331 [25]). On the lids, three 1 mm holes were made at a distance of about 3 mm apart, in the vertices of an equilateral triangle.

The samples for TG measurements were placed in standard alumina crucibles (No. 24123 [25]) equipped with single-holed lids.

IR spectra

The samples were heated in open porcelain crucibles under isothermal conditions for 5 min. The IR spectra were recorded on a Perkin Elmer model 783 spectrometer in nujol mulls. The heating period of 5 min was selected on the basis of preliminary experiments from which it was found that a longer time (> 15 min) provoked greater chemical transformation than that recorded by thermal analysis and a shorter time did not allow the establishment of thermal equilibrium between sample and environment. The heating temperatures were selected by following the thermal analysis curves. Sampling was carried out over a narrower temperature range in the region of thermal events.

RESULTS

Thermal analysis curves (TG and DSC) for the compounds examined are reported in Figs. 1–3. Notwithstanding their similarity, they show the different behaviours of $KLnFe(CN)_6 \cdot 4H_2O$ (Ln = La(III) and Nd(III)) on the one hand and $KCeFe(CN)_6 \cdot 4H_2O$ on the other.

The thermogravimetric curves of potassium and La(III) or Nd(III) mixed ferrocyanides can be split into two parts: (i) from room temperature to 200 °C and (ii) from 200 °C to the end of the curves.

The first part is characterized by a continuous weight loss over the whole temperature range, wherein three negative steps are also sharply evident (for $t < 80$ °C, $t = 140$–160 °C and $t = 180$–200 °C). The curves show a constant weight between 200 °C and 250 °C where a further negative step starts. In this last step, the curves, which in the first step showed a linear decrease with temperature, rapidly slope downwards between 320 and 325 °C. Therefore, the existence of parallel reactions or of accelerating, probably catalytic, thermally induced reaction processes (or both phenomena) can be supposed. The overall percentage losses at 80 °C, 200 °C and 350 °C relative to the initial amounts of the samples are, respectively, 2.8%, 17.9% and 34.7% for $KLaFe(CN)_6 \cdot 4H_2O$ and 3.8%, 20.1% and 38.10% for $KNdFe(CN)_6 \cdot 4H_2O$. The total loss in weight recorded between room temperature and 200 °C (17.9% and 20.1% for $KLaFe(CN)_6 \cdot 4H_2O$ and $KNdFe(CN)_6 \cdot 4H_2O$, respectively) include three steps as is evident in Fig. 1.

In spite of the well-resolved maxima in the first derivative plots (DTG) of the thermogravimetric curves, a well-defined Δw (%) can only be calculated for the first step, at $t < 80$ °C (2.9% and 3.8%). The weight loss between 80 °C and 200 °C must be ascribed to at least two distinct chemical events for which the starting and finishing temperatures cannot be unambiguously identified.

The thermogravimetric curve of $KCeFe(CN)_6 \cdot 4H_2O$ is different from those described above. Firstly, there is no range of thermal stability (the curve is always decreasing); moreover, only two negative steps occur between room temperature and 200 °C ($t = 50$–80 °C and $t = 140$–150 °C. A third negative step occurs between 225 and 260 °C. This temperature is

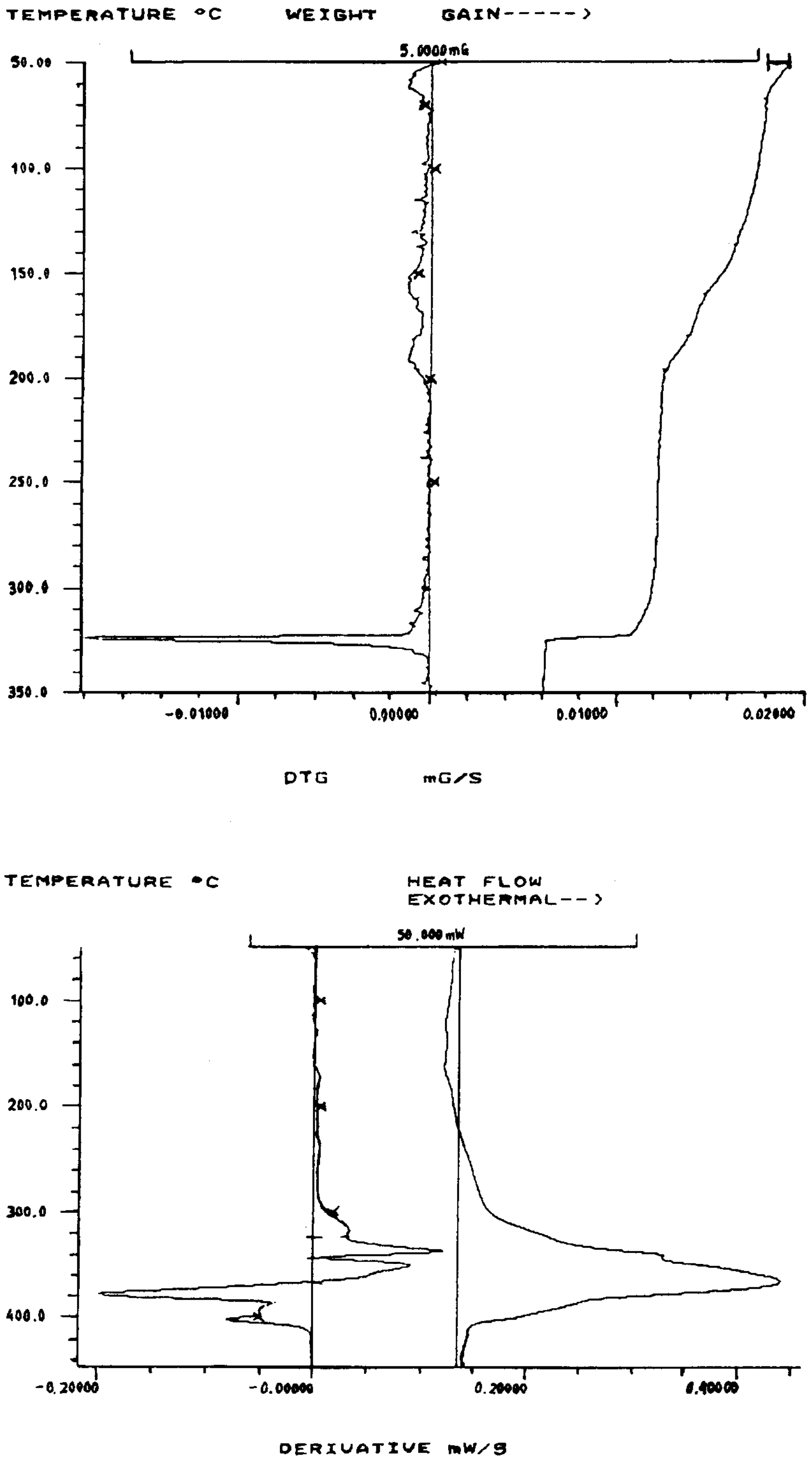

Fig. 1. Thermal analysis curves (TG and DSC; right-hand curves) and their derivatives (left-hand curves) in static air for $KLaFe(CN)_6 \cdot 4H_2O$. Weight of the samples: TG = 5.63 mg, DCS = 5.04 mg; heating rate, 5 ° C min^{-1}.

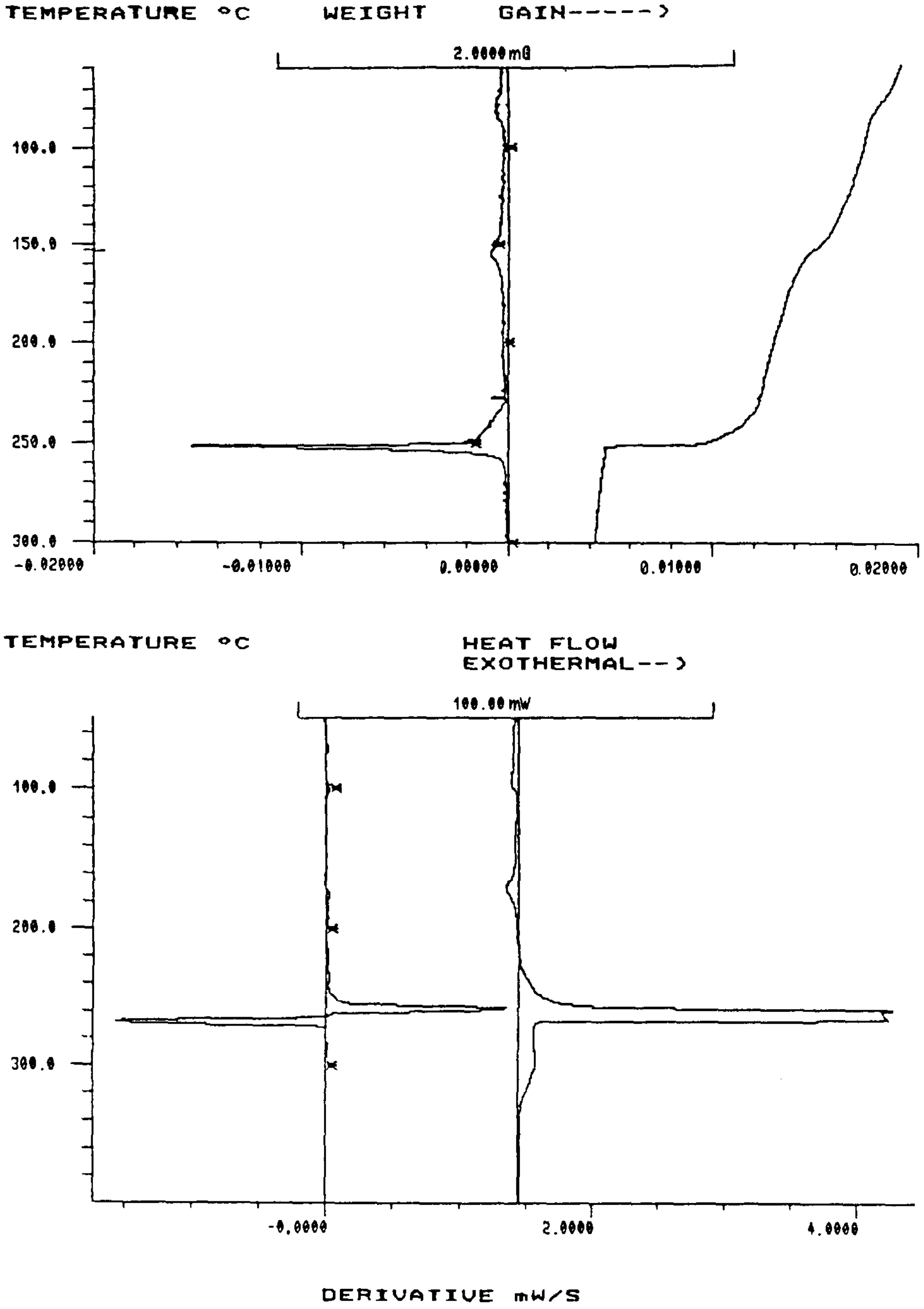

Fig. 2. Thermal analysis curves (TG and DSC; right-hand curves) and their derivatives (left-hand curves) in static air for $KCeFe(CN)_6 \cdot 4H_2O$. Weight of the samples: TG = 3.58 mg, DSC = 4.15 mg; heating rate, 5°C min^{-1}.

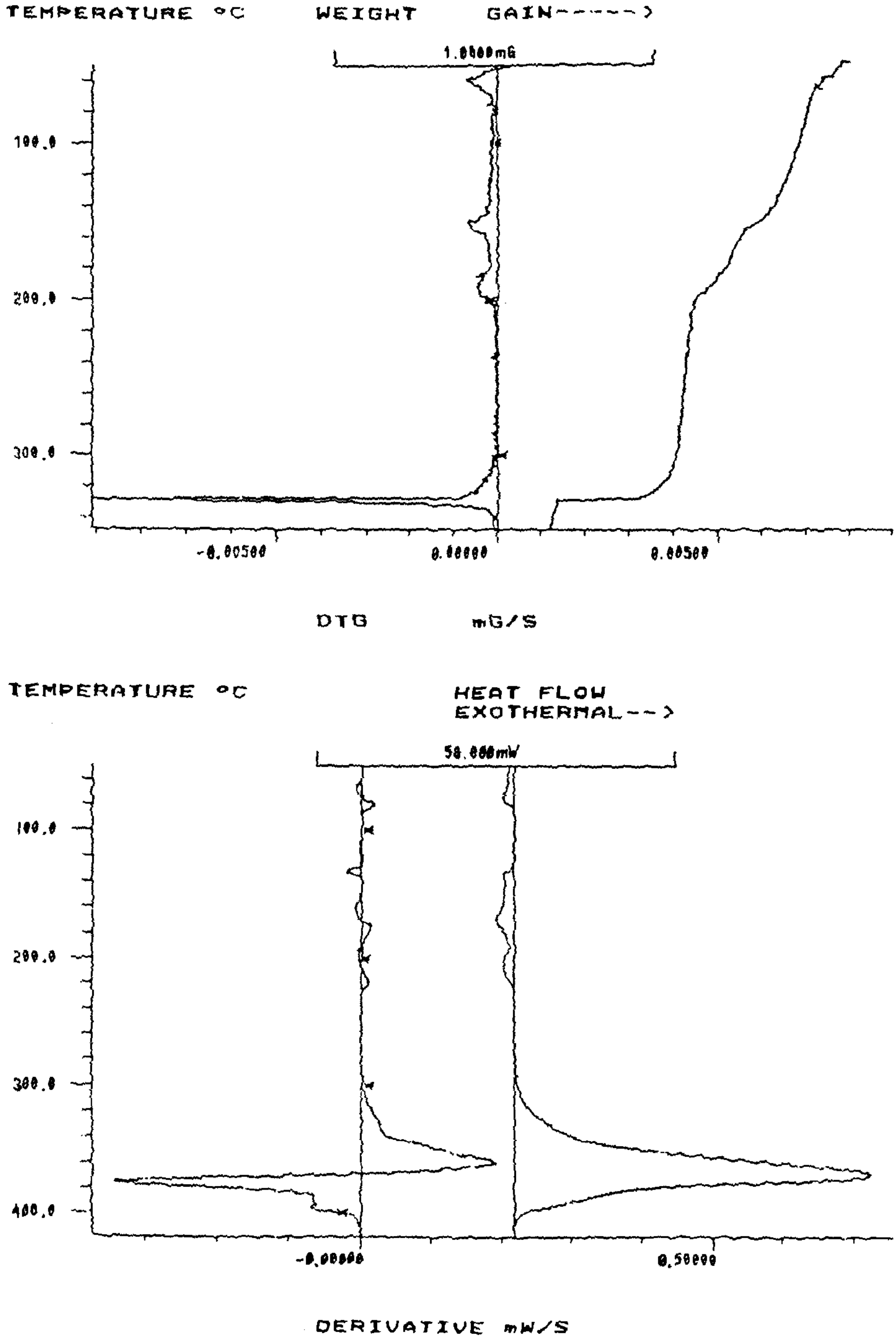

Fig. 3. Thermal analysis curves *(TG and DSC; right-hand* curves) and their derivatives (left-hand curves in static air for $KNdFe(CN)_6 \cdot 4H_2O$. *Weight* of the samples: TG = 2.34 mg, DSC = 3.51 mg; *heating rate,* 5 °C min^{-1}.

much lower than that for the corresponding event in $KLaFe(CN)_6 \cdot 4H_2O$ and $KNdFe(CN)_6 \cdot 4H_2O$. The overall weight losses at $t = 80\,°C$ and $225\,°C$ (where the first part of the DTG curve starts to decrease linearly) and 250 °C are, respectively, 4.0%, 20.3% and 37.4% (relative to the initial amount of sample).

The thermal events recorded in DSC always correspond to TG steps. The most significant is that at the highest temperature and it shows the existence of several reactions whose peaks are not totally resolved. The other events, at lower temperature, involve smaller quantities of heat and are endothermic in nature.

From the DSC curve it can be deduced that the thermogravimetric step at the highest temperature is determined by a series of oxidation reactions which lead to the evolution of gaseous products; the others must be attributed to endothermic decomposition reactions.

Besides the temperature range, the shape of the exothermic peak (broad for the La(III) and Nd(III) compounds and narrow for the Ce(III) compounds) also confirms the different role played by Ce(III) with respect to the other two ions. Moreover, in the range $t = 200\text{–}300\,°C$, where the TG curve of $KLaFe(CN)_6 \cdot 4H_2O$ is horizontal, the corresponding DSC plot for Ce(III) has a positive first step for the exothermic event (events) in progress. This behaviour can be explained either by the appropriate mass balance of the contemporaneous reactions having negative (thermal decomposition reaction) and positive weight changes or, more probably, by the occurrence of a process detectable in DSC (owing to its standard enthalpy change and the sensitivity of the apparatus) but not yet detectable by the TG apparatus used in this work. The phenomenon does not appear in the plots for $KNdFe(CN)_6 \cdot 4H_2O$.

Infrared spectra

The IR spectrum of $K_4Fe(CN)_6 \cdot 3H_2O$ (reported as reference) and selected IR spectra of solid residues of the lanthanide compounds at various temperatures are shown in Figs. 4–7 *. The main bands of $K_4Fe(CN)_6 3H_2O$ (410, 580 nd 2040 cm^{-1}) are shifted in the compounds investigated towards higher wavenumbers. The bending mode $\delta(Fe–C–N)$ ($\nu = 460\ cm^{-1}$) undergoes the highest shift ($\Delta\nu = 50\ cm^{-1}$), while the shift for the other two bands ($\nu(Fe–C) = 595\ cm^{-1}$ and $\nu(C{\equiv}N) = 2060\ cm^{-1}$) is constant ($\Delta\nu = 20\ cm^{-1}$).

The C≡N stretching band loses the fine structure which it has in the $K_4Fe(CN)_6 \cdot 3H_2O$ spectrum, but the characteristic asymmetrical tail to-

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* The IR spectra of the lanthanide compounds differ from that of $K_4Fe(CN)_6 \cdot 3H_2O$, independent of the nature of the lanthanide ion, which does not affect the maxima of the absorption bands of the mixed potassium–lanthanide ferrocyanides.

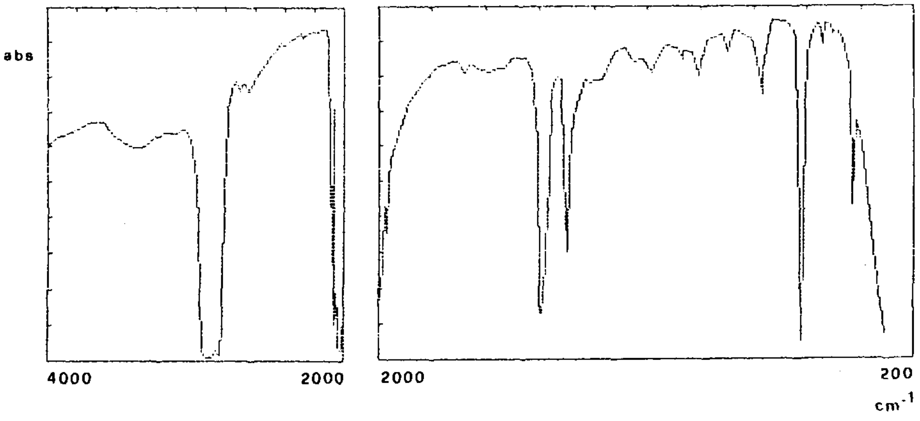

Fig. 4. IR spectrum of $K_4Fe(CN)_6 \cdot 3H_2O$.

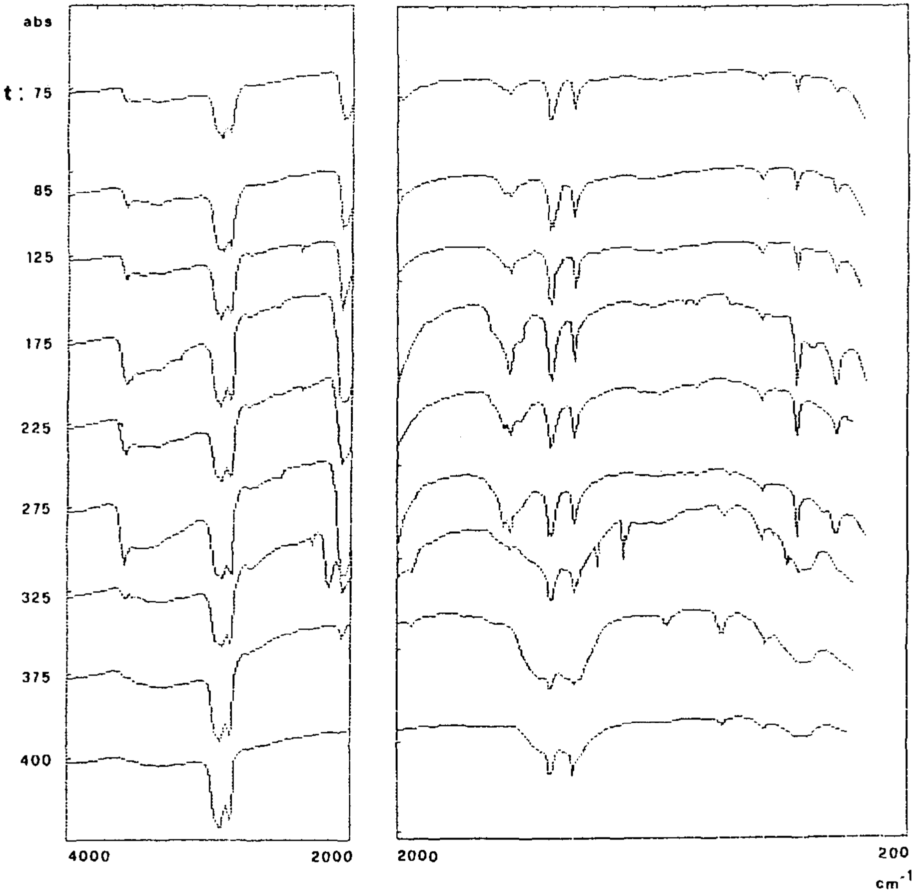

Fig. 5. Selected IR spectra of the residue of $KLaFe(CN)_6 \cdot 4H_2O$ heated to different temperatures (° C).

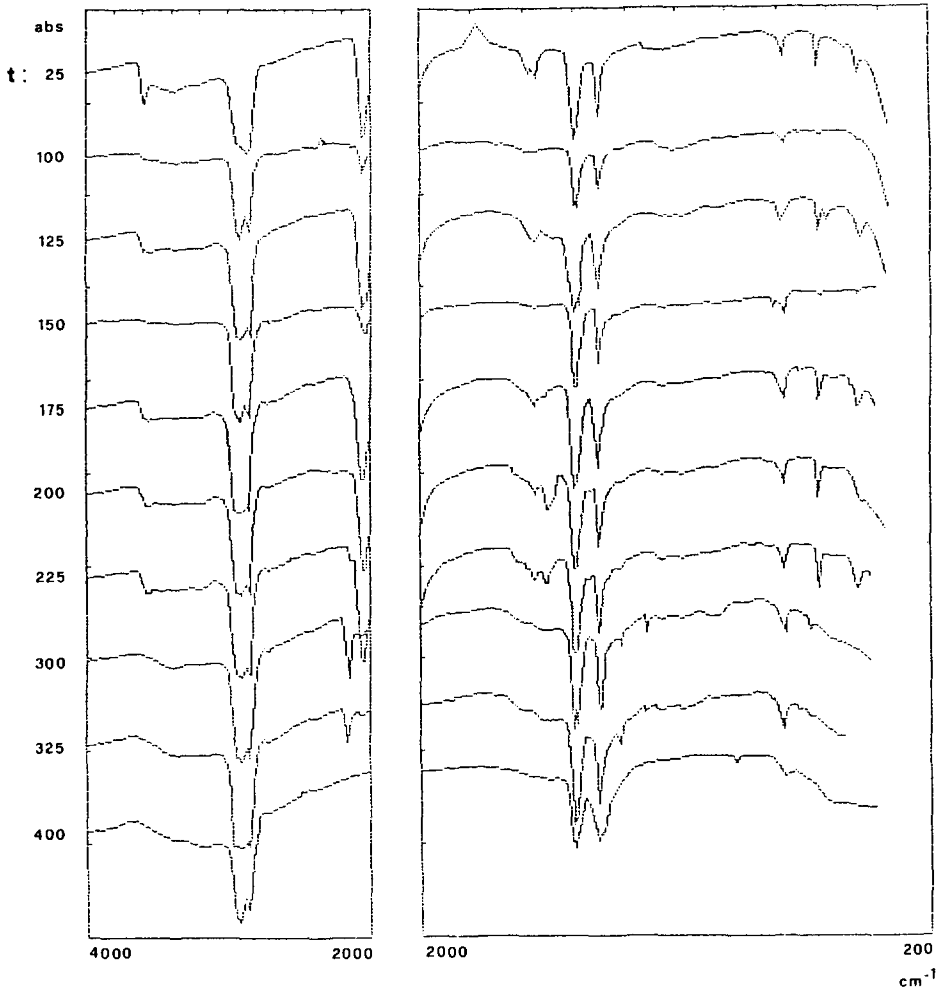

Fig. 6. Selected IR spectra of the residue of $KCeFe(CN)_6 \cdot 4H_2O$ heated to different temperatures (° C).

wards low wavenumbers still persists. The small bands between 1300 and 800 cm^{-1} (Fig. 4) are not present in the rare earth ferrocyanides. In the absorption ranges of H_2O, the potassium ferrocyanide presents only two very broad bands, the first one between 3700 and 3000 cm^{-1} and the second one between 1700 and 1500 cm^{-1}, respectively. The investigated compounds show a further very narrow band centred at 3580 cm^{-1} and, in the bending region, two bands with resolved maxima are evident. The spectra of heated samples remain unaltered up to 125 ° C. At 175 ° C * for $KLaFe(CN)_6 \cdot 4H_2O$ and $KNdFe(CN)_6 \cdot 4H_2O$ and at 150 ° C for $KCeFe(CN)_6 \cdot 4H_2O$ alterations

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* For these temperatures the corresponding thermal analysis curves show negative TG steps with small endothermic events.

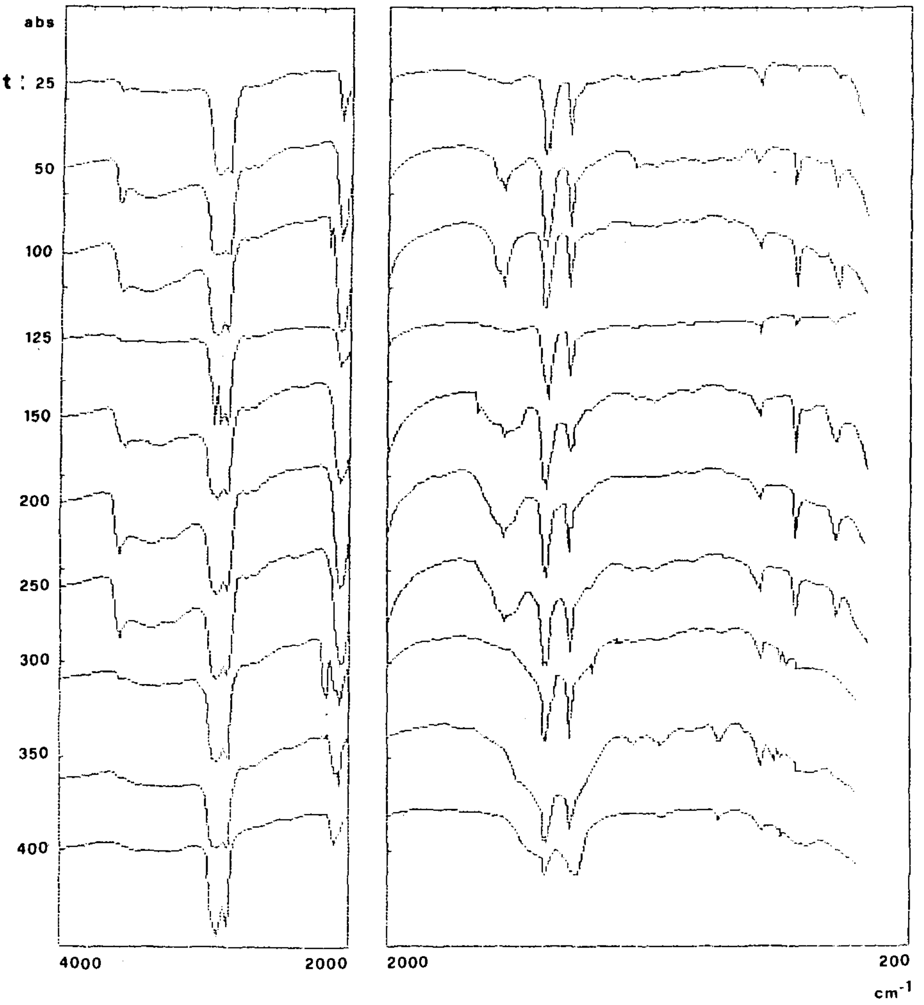

Fig. 7. Selected IR spectra of the residue of $KNdFe(CN)_6 \cdot 4H_2O$ heated to different temperatures (°C).

of the respective IR plots are noticed (see the strong absorption in the region around 1600 cm^{-1} and the small bands between 1300 cm^{-1} and 400 cm^{-1}). A further mark of chemical changes in progress is the colour of the samples which, on heating up to the above temperatures, changes from white (unheated samples) to pale blue. The main absorption bands of the $Fe(CN)_6^{4-}$ complex are still present. So, also, are the bands of the water molecules, where, however, some alteration of the band structure is observed (see IR spectrum of the residue at 175°C of $KLaFe(CN)_6 \cdot 4H_2O$ (Fig. 5). This status persists up to 275°C for $KLaFe(CN)_6 \cdot 4H_2O$, up to 250°C for $KNdFe(CN)_6 \cdot 4H_2O$ and up to 225°C for $KCeFe(CN)_6 \cdot 4H_2O$. The colour of the residue of $KLaFe(CN)_6 \cdot 4H_2O$ (rust coloured on the surface but pale blue in colour when mulled with nujol) indicate the beginning of chemical transformations at the surface which involve the iron atom of the cyano complex. At these temperatures the bands due to the presence of water are still evident. At 300 ° C the residues of all three compounds are brown in colour (that of $KCeFe(CN)_6 \cdot 4H_2O$ was already brown in colour at 250 ° C) and the IR spectra denote significant changes in the samples.

As far as the water absorption is concerned, at this temperature a sharp increase in transmittance is recorded.

For all three compounds the bending δ(Fe–C–N) bands and the ν(Fe–C) stretching mode bands (at 455 and 597 cm^{-1} respectively) disappear, or the latter appears noticeably deformed (see the IR spectrum of the residue of $KLaFe(CN)_6 \cdot 4H_2O$ at 300 ° C, Fig 5). The following features are recorded in the spectra at 300 ° C: (a) a remarkable absorption in the range 1200–1700 cm^{-1}; (b) a couple of bands at 1200 and 1300 cm^{-1}; (c) a strong band at 2160 cm^{-1}; (d) small bands between 600 cm^{-1} and 700 cm^{-1}; and (e) a large alteration of the band at 2060 cm^{-1}. The wavenumber of the maximum absorption remains unaltered, while the band height decreases. Moreover, in the spectrum of the residue of $KLaFe(CN)_6 \cdot 4H_2O$ (Fig. 5) a further absorption with the maximum at 1950 cm^{-1} can be seen.

A further temperature increase ($t = 375$ ° C for $KLaFe(CN)_6 \cdot H_2O$ and $t = 350$ ° C for $KNdFe(CN)_6 \cdot 4H_2O$) provokes: (a) a progressive broadening of the band between 1700 and 1200 cm^{-1}; (b) the appearance of a set of bands between 1100 and 500 cm^{-1} and both for the La(III) and Ce(III) compounds; (c) the decrease of the intensity of the C≡N stretching band; (d) the persistence in the spectrum of $KLaFe(CN)_6 \cdot 4H_2O$ of the band at 1950 cm^{-1}; and (e) the complete disappearance of the O–H stretching band at 3600 cm^{-1}.

At 400 ° C the spectra of the residues essentially consist of a very broad central band. The residues are brown in colour, but clearly show the presence of a white coloured substance (substances).

DISCUSSION

The experimental results show the different behaviour of the rare earth ferrocyanides investigated with respect to $K_4Fe(CN)_6 \cdot 3H_2O$.

Potassium ferrocyanide easily loses its water of crystallization [1] which can be classified as lattice water (weakly bonded in the crystal lattice) [26,27]. Moreover, for $t > 300$ ° C, it shows a positive thermogravimetric step (like NaCN and $K_3Fe(CN)_6$) resulting from the formation of carbonate by a complicated mechanism (where it was possible to demonstrate the presence of cyanate [1]).

In contrast, potassium–rare earth mixed ferrocyanides decompose on thermal treatment in air by a hydrolytic mechanism. In fact, the IR spectra of the unheated samples show the presence of strongly coordinated water (band at 3580 cm^{-1} in Figs. 5–7) in the coordination sphere of a metal ion [26], obviously the lanthanide trivalent ion. This band persists in the IR spectra of the residues at $t > 200°C$. It can be deduced that, whilst the TG step between room temperature and $t = 80°C$ must be ascribed, without any doubt, to the loss of imbibition water, the negative TG steps recorded between 100°C and 200°C (to which small endothermic heat fluxes correspond) do not originate from losses of water of crystallization. The colour change (from white to pale blue), clearly seen when these compounds are heated up to $t < 200°C$, indicates the formation of small quantities of Fe(III) which produces blue-coloured prussiates by reacting with the $Fe(CN)_6^{4-}$ ion.

By taking these points into account we can conclude that the above two steps are due to an iron decomplexing process allowing the oxidation to Fe(III). The acceptable hypothesis is that HCN elimination occurs between the CN^- (in the anion moiety) and the hydrogen atom of the water bound to the trivalent ion. On the basis of the formula $KLnFe(CN)_6 \cdot 4H_2O$ (Ln = La(III), Ce(III), Nd(III)) and by supposing that the recorded negative weight changes are due exclusively to HCN elimination, the loss of 2.5–2.9 moles of HCN per $KLnFe(CN)_6 \cdot 4H_2O$ is calculated, in two stages for both the lanthanum and neodymium ferrocyanides, and in a single stage for the potassium–cerium ferrocyanide.

A further discriminating factor between $K_4Fe(CN)_6 \cdot 3H_2O$ and the ferrocyanides investigated is the mass balance corresponding to the exothermic transition (positive in the first case and for NaCN and the alkaline ferrocyanide and ferricyanide [1] and negative in the cases considered in the present contribution). The IR spectra show the formation of oxides (see bands between 1100 and 400 cm^{-1}. The Fe(II) is oxidized to Fe(III)) and carbonates (band between 1700 and 1200 cm^{-1} [26–29]). The two bands recorded at 1200 and 1300 cm^{-1} demonstrate the existence of an intermediate stage with the formation of cyanate (for $KLaFe(CN)_6 \cdot 4H_2O$ the bands at 2160, 1950, 630 and 650 cm^{-1} indicate also, the presence of cyanamide [27,29]). It follows that the oxidative mechanism of the anion moiety is fundamentally similar in both cases, notwithstanding the different shapes of the TG curves which originate from the different stoichiometric balance consistent with the thermal stability of the products. In the oxidation of $K_4Fe(CN)_6$(NaCN) four (one) positive charges in addition to those of the iron ion must be counterbalanced. For $KLnFe(CN)_6 \cdot H_2O$, the positive charges of the molecule are neutralized as a consequence of the thermal elimination of H^+ as HCN.

CONCLUSIONS

In the mixed rare earth ferrocyanides $KLnFe(CN)_6 \cdot 4H_2O$ the presence of a trivalent lanthanide cation (La(III), Ce(III), Nd(III)) induces a hydro-

TABLE 1

Calculated and experimental percentage weight losses for the thermal decomposition of potassium–rare earth mixed ferrocyanides

Initial compound	Final product	Calculated (%)	Experimental (%)	(%) [a]
$KLaFe(CN)_6 \cdot 4H_2O$	$K_2O + La_2O_3 + Fe_2O_3$	−37.3	−36	−32.5
$KCeFe(CN)_6 \cdot 4H_2O$	$K_2O + CeO_2 + Fe_2O_3$	−34.45	−34.4	−30.7
$KNdFe(CN)_6 \cdot 4H_2O$	$K_2O + Nd_2O_3 + Fe_2O_3$	−36.6	−35	−31.8

[a] The values in this column are calculated by supposing the substitution of one oxygen equivalent with one carbonate equivalent.

lytic mechanism of thermal decomposition with the elimination of HCN in preference to H_2O.

The reasons for this behaviour are : (a) the high polarization of the hydrogen atoms of the water molecule (molecules) bound to the trivalent ion and (b) the existence of notable interaction in the crystal phase between the water bound to the lanthanide ion and the CN^- bound to the anion part of the molecule.

The points (a) and (b) make the hydrogen atom easily detachable from H_2O and favour the elimination of HCN.

$KCeFe(CN)_6 \cdot 4H_2O$ has a lower oxidation temperature than those of the other two compounds. This behaviour, considered with respect to the other rare earth compounds, conforms with that of some Ce(III) salts [15,23] which produce CeO_2.

It can be supposed that the oxidation of the anion is catalyzed by Ce(III) which is first oxidized to CeO_2. It then oxidizes $Fe(CN)_6^{4-}$ (it must be noted that the shape of the DSC curve for the cerium compound differs significantly from the others).

The calculated values of the percentage weight losses for the reactions of potassium rare earth ferrocyanides to oxides are reported in Table 1 together with the experimental values evaluated with respect to the dry sample on the basis of the reported results. The theoretical values are systematically greater than the experimental ones. A comparison of the experimental values with those reported in the third column (calculated by supposing that one oxygen equivalent is substituted by one carbonate equivalent) shows an opposite relationship. Therefore, the data allow us to conclude that the final product after heating to the highest temperature in Figs. 1–3 is an oxide mixture formed by a multistage hydrolytic mechanism in which cyanate, carbonate and cyanamide (in the case of $KLaFe(CN)_6 \cdot 4H_2O$) are intermediates.

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