Cobalt basic salts as inorganic precursors of cobalt oxides and cobalt metal: thermal behaviour dependence on experimental conditions

O. GARCÍA-MARTÍNEZ, P. MILLÁN, R. M. ROJAS
Instituto de Química Inorgánica "Elhúyar", CSIC, Serrano 113, 28006 Madrid, Spain

M. J. TORRALVO
Departamento Química Inorgánica, F. de Químicas, Universidad Complutense, 28040 Madrid, Spain

The influence of heating rates and environment conditions on the thermal behaviour of two cobalt basic salts, β-$Co_2(OH)_3Cl$ and $Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O$, have been studied. The processes were followed using thermogravimetric and differential thermal analysis, X-ray diffraction, and infrared spectroscopy. When decomposition reactions are carried out in a nitrogen atmosphere, Co_3O_4 is always formed in quantities that seem to depend on the heating rates. When decomposition processes are carried out in an X-ray high-temperature diffraction chamber, pure cobalt is obtained at 750° C as the final product. Green cobalt hydroxychloride, the composition of which determined from chemical analysis seems to correspond to the formula $Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O$ or alternatively $4Co(OH)_2 \cdot CoCl_{1.5}(OH)_{0.5} \cdot 2.5H_2O$, has been isolated as a stable compound and the evolution of this material during the ageing process has been followed by X-ray diffraction, electron microscopy and BET surface-area determination.

1. Introduction

Preparative aspects of cobalt metal and cobalt oxides by thermal decomposition of several cobalt compounds, mainly organic and organometallics, under several experimental conditions, have been extensively studied because of their many applications in fields such as ceramics and catalysis.

The formation of a certain oxide, a mixture, or even the obtention of highly dispersed metal particles on the surface of oxide supports, can be achieved depending on both experimental conditions and the nature of the raw materials [1–4].

Having in mind the results already obtained on similar compounds [5, 6], we have undertaken the study of two cobalt basic salts: pink β-$Co_2(OH)_3Cl$ and green $Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O$, in order to determine their possible usefulness as inorganic precursors in the obtention of cobalt oxides or cobalt metal, under certain experimental conditions.

The lavender-coloured β-$Co_2(OH)_3Cl$ is a well-characterized compound [7, 8] and studies on its thermal decomposition have been carried out [9, 10]. Because of the low stability of the green cobalt hydroxychloride, it has only been characterized by the X-ray diffraction technique [11] and up to date no other studies have been made on this compound.

Although a compound of composition $Co(OH)_{1.7}Cl_{0.3}$ has been determined for a freshly precipitated cobalt hydroxychloride, it has been interpreted as a mixture of $Co(OH)_{1.5}Cl_{0.5}$ — or $Co_2(OH)_3Cl$ — and

$Co(OH)_2$ in different proportions [12]; our results seem to indicate that it constitutes a genuine chemical species. We have been able to stabilize this product and some studies on its surface evolution have been attempted.

2. Experimental details

β-$Co_2(OH)_3Cl$ has been prepared by incomplete precipitation of 0.2 M solutions of $CoCl_2 \cdot 6H_2O$ with 0.4 N NaOH; the readily formed green precipitate, which turns pink on standing a few hours at 70° C, was aged at this temperature for 7 days. After filtering the sample was washed with cold water, alcohol and acetone, vacuum dried and kept over P_2O_5.

The evolution of the green precipitate can be avoided if after precipitation it is cooled in the mother liquor at 2° C.

Some other preparations were then carried out, but they were kept at 2° C for periods ranging from 24 h to two months. The precipitates were then filtered off, washed with alcohol and acetone, vacuum dried and kept over P_2O_5.

Nitrogen was bubbled throughout the precipitation vessels and during the precipitation reactions; precipitates were also kept ageing in the mother liquor under a nitrogen atmosphere. The results of chemical analyses are shown in Table I.

The X-ray diffraction diagram of pink cobalt hydroxychloride, β-$Co_2(OH)_3Cl$, is identical to that reported by Wolf [8] and that of green cobalt hydroxy-

TABLE I Analytical results

Sample	Co (%)		Cl (%)		H (%)	
	Calc.	Found	Calc.	Found	Calc.	Found
β-Co$_2$(OH)$_3$Cl	57.68	56.93	17.38	17.34	1.47	1.55
Co$_5$(OH)$_{8.5}$Cl$_{1.5}$ · 2.5H$_2$O*	54.83	53.87	9.89	9.66	2.51	2.49

*Sample aged for 24 h at 2° C.

chloride shows the same lines ascribed by Feicknecht and Fischer [11] to a compound with "ideal formula" Co(OH)Cl · 4Co(OH)$_2$ · 4H$_2$O; the diagram could be indexed within the hexagonal system with the cell parameters proposed by them, $a = 0.315$ nm, $c = 2.44$ nm.

3. Analytical procedures

Differential thermal analysis (DTA) and thermo gravimetry (TG) were carried out on a Stanton STA 781 simultaneous thermal analysis system with about 10 mg samples and Al$_2$O$_3$ as reference material. Thermograms were recorded at 2 and 10° C min^{-1} heating rates in still air and in nitrogen and air flows (50 ml min^{-1}). High-purity nitrogen ($> 99.9992\%$) from S.E.O. (Spanish Society of Oxygen) was used without any further purification. A Dupont 990 thermobalance was occasionally used as well. Chlorine and hydrogen chloride were qualitatively tested for in the way indicated elsewhere [5].

X-ray diffraction diagrams were recorded on a Siemens D-500 diffractometer and monochromatized CuKα radiation was used. The electron micrographs were taken in a Siemens Elmiskop 102 electron microscope operating at 100 kV and fitted with a double-tilting goniometer stage, allowing tilts of ± 45° around both axes. Infrared spectra were scanned in a Pye-Unicam SP3-300S spectrophotometer with samples dispersed in KBr. Surface areas were measured with a volumetric apparatus using N$_2$ adsorption at − 196° C. An Anton PAAR HTK 10 X-ray high-temperature diffraction chamber mounted on a Philips PW 1310 equipment was used, and the experimental disposition and operating procedure have been described elsewhere [5, 6]. Iron-filtered CoKα or monochromatized CuKα radiations were used without distinction.

4. Results

4.1. Stability and surface evolution of green cobalt hydroxychloride Co$_5$(OH)$_{8.5}$Cl$_{1.5}$ · 2.5H$_2$O on ageing

In electron diffraction diagrams obtained on samples aged from 6 days to two months, mixtures of both pink and green cobalt hydroxychloride crystals can be distinguished (Fig. 1b), and X-ray diagrams recorded on samples aged for two months consist of maxima of both basic salts (Fig. 1f). Nevertheless, samples aged for 24 h at 2° C were only cobalt hydroxychloride Co$_5$(OH)$_{8.5}$Cl$_{1.5}$ · 2.5H$_2$O, the electron micrographs showing for this material a plate-like shape and highly porous structure (Fig. 1a). The BET area was 118 m^2 g^{-1} and progressively decreased on ageing (Table II) because of evolution to the more stable β-Co$_2$(OH)$_3$Cl, which has a considerably lower surface area (20 to 10 m^2 g^{-1}). It must be noted that green

cobalt hydroxychloride, after being filtered and dried, remains stable for at least six months.

4.2. Thermal studies
4.2.1. CoCl$_2$ · 6H$_2$O

Because anhydrous cobalt chloride, CoCl$_2$, seems to be an intermediate formed in the thermal decomposition of β-Co$_2$(OH)$_3$Cl, it has been considered worthwhile to study in detail the thermal behaviour of this compound when it is decomposed under the same experimental conditions as for the basic salt. TG and DTA curves recorded in air and nitrogen flows are shown in Fig. 2; the TG curve in air up to 800° C is identical to that reported by Lumme and Vuokila [13]. Anhydrous cobalt chloride is stable in a wide temperature interval (175 to 400° C) and the X-ray diffraction diagram and IR spectrum are shown in Figs 3 and 4a, respectively. They have been recorded on samples heated at 200° C for 30 h; the X-ray diagram shows the (0 0 3) reflexion of CoCl$_2$ as a very sharp and well-defined peak as well as some others poorly-defined maxima that correspond with the low-intensity diffraction lines of anhydrous CoCl$_2$. On standing in the X-ray sample holder, the anhydrous sample rehydrates giving the most stable species CoCl$_2$ · 2H$_2$O [14], changing the initial violet-blue colour into pink and swelling up. Consecutive diffraction diagrams scanned at high scan speed (5° (2θ) min^{-1}) show lines of both anhydrous and dihydrated cobalt chlorides [15, 16] which intensify on consecutive scans. On the other hand, the IR spectrum is identical to that reported by Gamo [17] for CoCl$_2$ · 2H$_2$O, and two strong absorptions at about 3400 and 1610 cm^{-1} are clearly seen.

When anhydrous cobalt chloride decomposes in an air flow Co$_3$O$_4$ is obtained from 670 to 903° C, then it transforms into CoO; the experimental and calculated weight losses agree very well (see Fig. 2a) and the evolution of chlorine is evident over the whole temperature range at which decomposition of cobalt chloride occurs (400 to 667° C). Although the X-ray diagram recorded on the residue before and after it transforms into CoO and reoxidizes to Co$_3$O$_4$ is that of the spinel oxide [18], the IR spectrum (Fig. 4b) differs in some ways from data reported for Co$_3$O$_4$ [19, 20] (compare Figs 4b and 6c below), and it is probably an effect caused by the size of particles of Co$_3$O$_4$ when obtained from different raw materials.

When decomposition is carried out in a nitrogen flow, hydrogen chloride seems to be the evolved gas

TABLE II Evolution of the BET area of green cobalt hydroxychloride on ageing

Ageing period (h)	24	120	192
BET area (m^2 g^{-1})	118	99	58
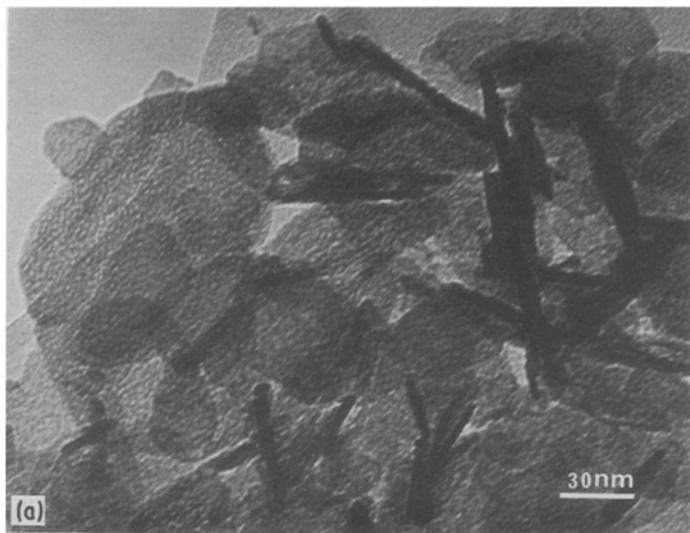
Figure 1 Electron micrographs of green cobalt hydroxychloride, $Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O$, obtained on samples (a) aged at 2°C for 24 h; (b) aged for 15 days; (c, d, e) sample titled to show it is a homogeneous solid. (f) X-ray diagram recorded on sample aged for two months. Indices marked (*) correspond to β-$Co_2(OH)_3Cl$ lines.
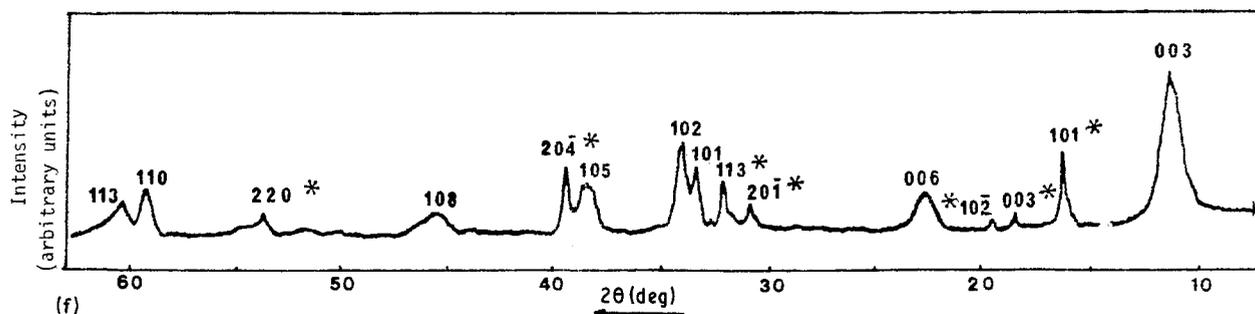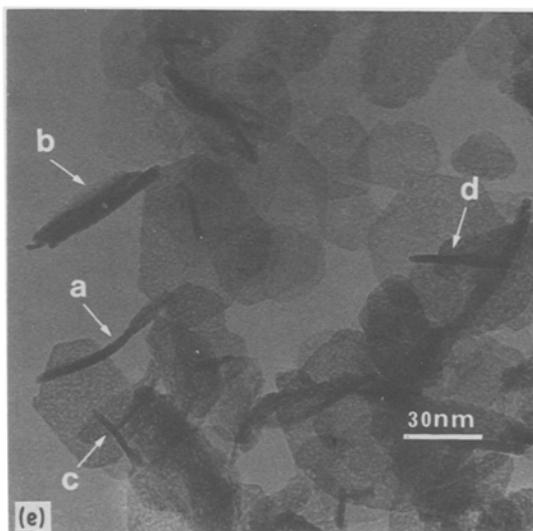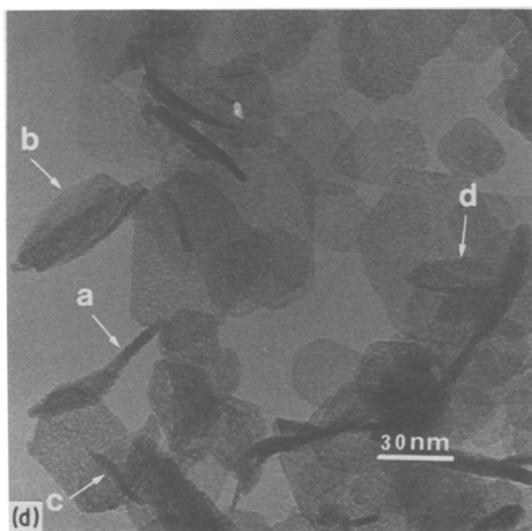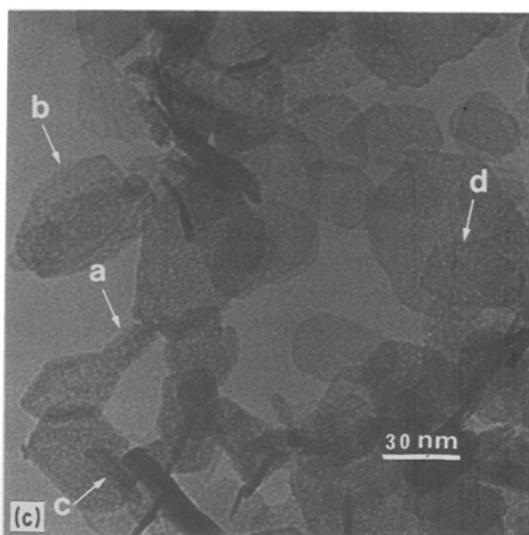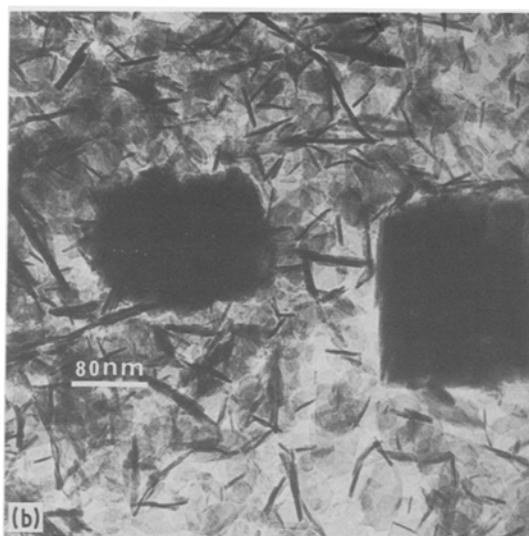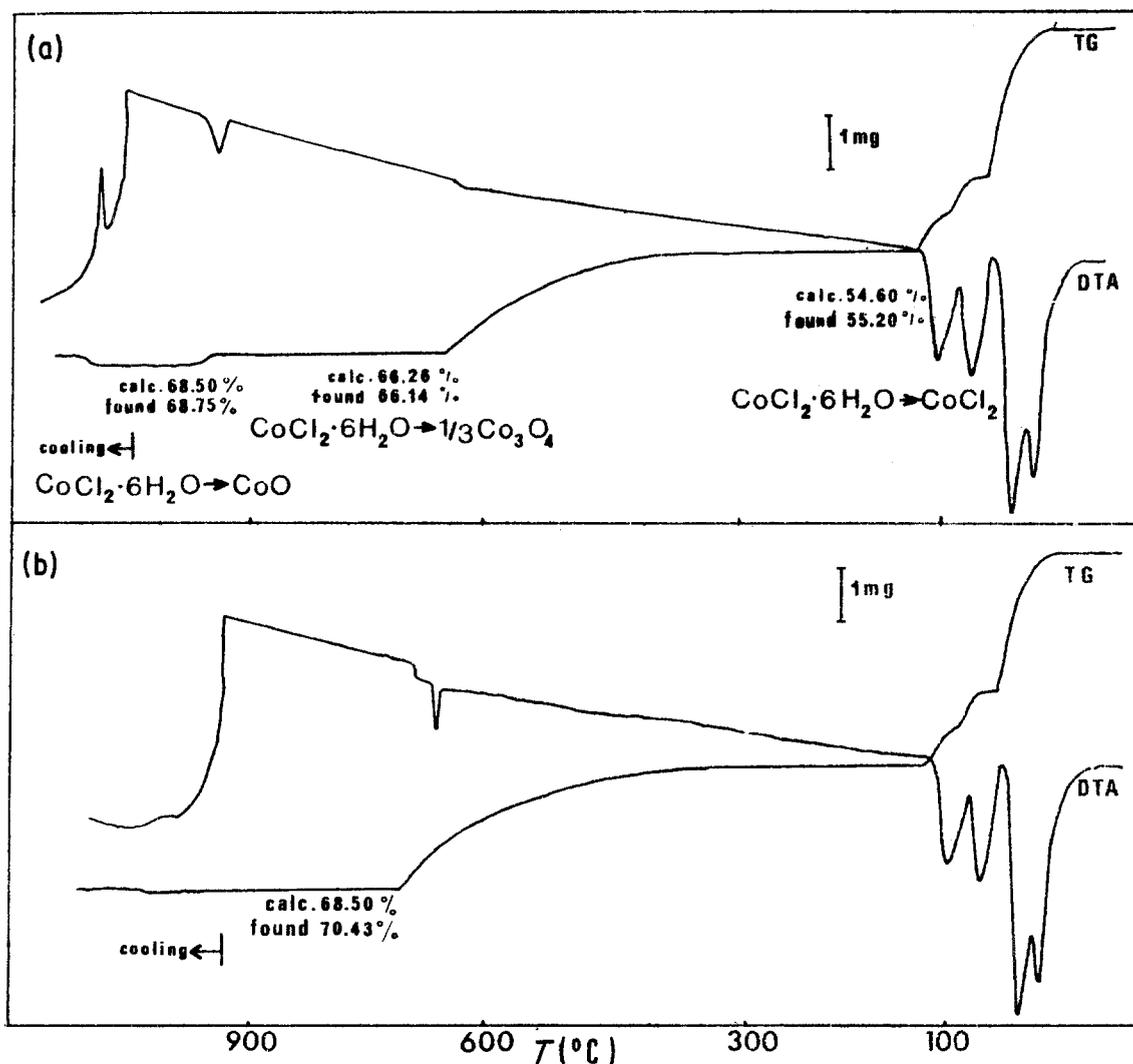
Figure 2 DTA and TG curves of CoCl$_2$ · 6H$_2$O recorded at 10°Cmin^{-1}: (a) in air flow, (b) in nitrogen flow.

since it gives a deep red tinge to universal indicator paper; chlorine was not detected. The evolution of hydrogen chloride can be explained if some cobalt chloride undergoes a hydrolysis reaction yielding cobalt hydroxychloride as intermediate:

$$CoCl_2 + H_2O \rightarrow Co(OH)Cl + HCl\uparrow$$

$$\rightarrow CoO + HCl\uparrow$$
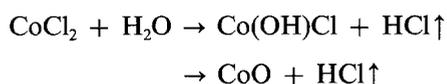
and the remaining non-hydrolysed salt melts at 700° C, causing the small endothermic peak appearing in the temperature range 693 to 705° C (Fig. 2b). The very small amount of water and oxygen carried by the nitrogen, or more probably confined in the thermobalance enclosure, would be enough to hydrolyse anhydrous cobalt chloride and to oxidize to some extent the very reactive CoO formed in the decomposition reaction. If some CoCl$_2$, when liquid, is carried away by the nitrogen flow, it would explain the experimental weight loss being slightly higher than calculated. This result is to some extent in agreement with that obtained by Lumme and Junkkarinen [21], although the volatilization is in our case considerably lower.

Although thermograms recorded in N$_2$ do not show any thermal effect that would indicate that Co$_3$O$_4$ exits in the residue, the IR spectrum recorded on the product formed at 1000° C and cooled at room tem-

perature in nitrogen flow, clearly shows absorption bands of Co$_3$O$_4$ as well as the strong and broad one of CoO [22] (Fig. 4c).

4.2.2. Thermal decomposition of β-Co$_2$(OH)$_3$Cl in air

The evolution of this basic salt during the heating process in still air as well as in flowing air or nitrogen has been followed by X-ray diffraction and infrared spectroscopy, this technique being a powerful tool that furnishes the most valuable information.

The thermogram recorded at 2° C min^{-1} is shown in Fig. 5a and the temperature ranges at which thermal effects occur are summarized in Table III. No differences are observed between curves recorded in still or flowing air at low heating rates. The basic salt decomposes between 230 and 415° C, yielding Co$_3$O$_4$ which transforms into CoO at 900° C, and it is reoxidized to the former spinel oxide when cooling in air.

The IR spectrum recorded with a batch of sample heated at 360° C (12.6% weight loss) shows features of both β-Co$_2$(OH)$_3$Cl and Co$_3$O$_4$ (Fig. 6b), and two strong absortions at 3400 and 1610 cm^{-1}. The latter could be attributed to the stretching and bending modes of the water molecules attached to the cobalt chloride, formed along the decomposition reaction which, when it is carried out at a low heating rate, takes place as a smooth and continuous process.

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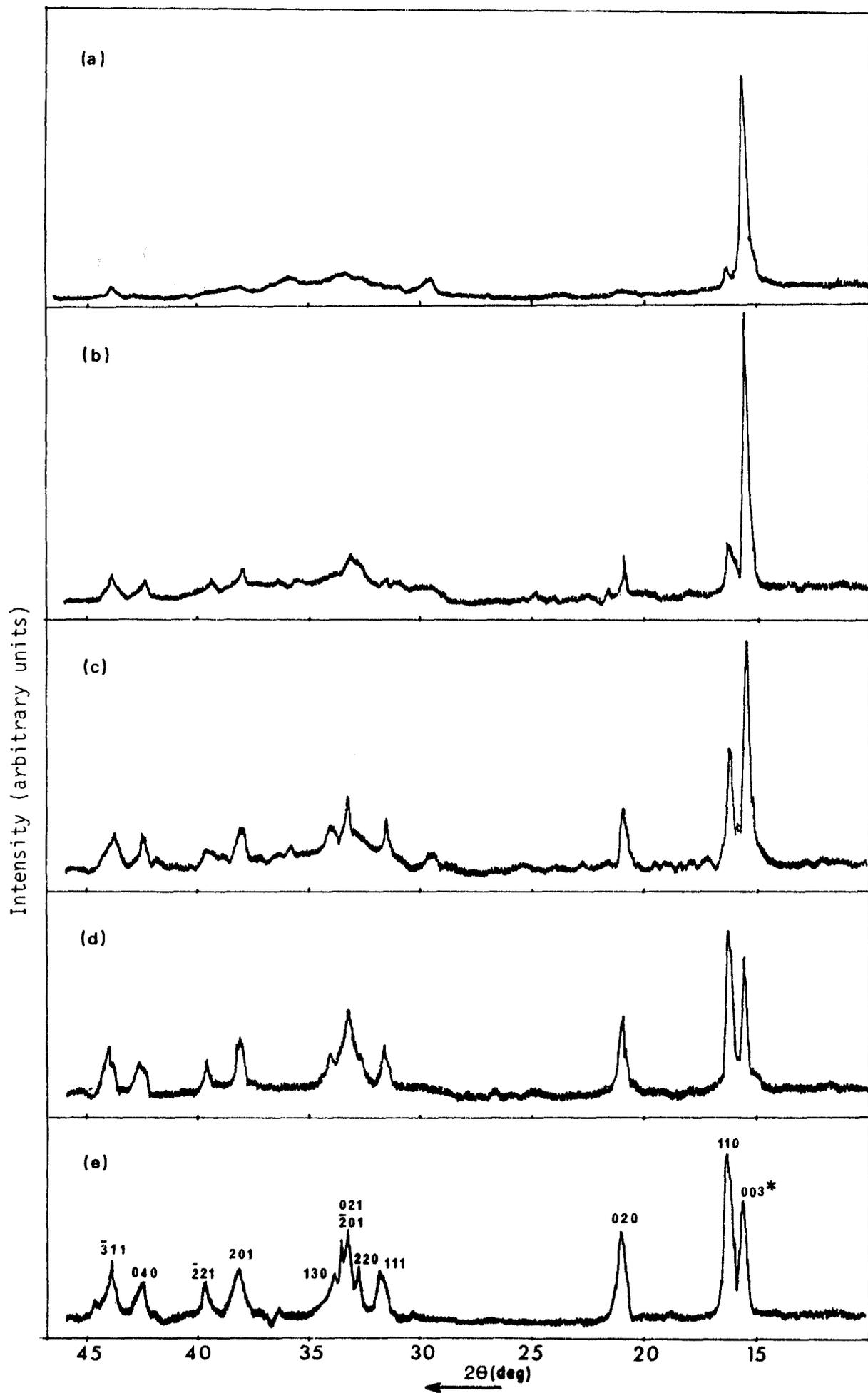
Figure 3 X-ray diffraction diagrams showing the evolution of anhydrous cobalt chloride on standing in the X-ray sample holder. Indices in (e) correspond to $CoCl_2 \cdot 2H_2O$ and the 003^* reflection corresponds to the most intense diffraction line of anhydrous cobalt chloride.

TABLE III Thermal decomposition data of β-$Co_2(OH)_3Cl$ for different atmospheres and heating rates*

Still air

2°C min⁻¹ (I)†				10°C min⁻¹ (II)†					2°C min⁻¹ (III)†				10°C min⁻¹ (IV)†				
$T(°C)$ DTA	TG	Found	Calc.	$T(°C)$ DTA	TG	Found	Calc.	Reaction	$T(°C)$ DTA	TG	Found	Calc.	$T(°C)$ DTA	TG	Found	Calc.	Reaction
T_i 233		21.21	21.45	T_i 258		9.92	9.32	β-$Co_2(OH)_3Cl \to \frac{1}{2}CoCl_2 + \frac{1}{2}Co_3O_4 + \frac{3}{2}H_2O$	T_i 233		21.46	21.45	T_i 251		10.13	9.32	β-$Co_2(OH)_3Cl \to \frac{1}{2}CoCl_2 + \frac{1}{2}Co_3O_4 + \frac{3}{2}H_2O$
T_f 399				T_f 390					T_f 390				T_f 396				
β-$Co_2(OH)_3Cl \to \frac{2}{3}Co_3O_4$				T_i 390		20.92	21.45	β-$Co_2(OH)_3Cl \to \frac{2}{3}Co_3O_4$						T_i 396		21.15	21.45	β-$Co_2(OH)_3Cl \to \frac{2}{3}Co_3O_4$
				T_f 466									T_f 503				β-$Co_2(OH)_3Cl \to \frac{2}{3}Co_3O_4$
T_i 900	900	26.76	26.67	T_i 892	897	25.88	26.66		T_i 900	900	26.70	26.66	T_i 892	892	26.22	26.66	
T_m 908				T_m 915					T_m 903				T_m 915				
T_f 918	908			T_f 950	946				T_f 915	915			T_f 942	931			
β-$Co_2(OH)_3Cl \to 2CoO$				β-$Co_2(OH)_3Cl \to 2CoO$					β-$Co_2(OH)_3Cl \to 2CoO$				β-$Co_2(OH)_3Cl \to 2CoO$				

Air flow (50 ml min⁻¹) (columns III, IV above)

Nitrogen flow (50 ml min⁻¹)

2°C min⁻¹ (V)†					10°C min⁻¹ (VI)†				
$T(°C)$ DTA	TG	Found	Calc.	Reaction	$T(°C)$ DTA	TG	Found	Calc.	Reaction
T_i 257		13.58	13.21	β-$Co_2(OH)_3Cl \to \frac{1}{2}CoCl_2 + \frac{3}{2}CoO + \frac{3}{2}H_2O$	T_i 259		14.94	13.21	β-$Co_2(OH)_3Cl \to \frac{1}{2}CoCl_2 + \frac{3}{2}CoO + \frac{3}{2}H_2O$
T_f 385					T_f 466				
T_i 385		23.05	24.05	β-$Co_2(OH)_3Cl \to \frac{1}{3}Co_3O_4 + CoO$	T_i 466		25.25	25.36	β-$Co_2(OH)_3Cl \to \frac{1}{3}Co_3O_4 + \frac{1}{6}Co_3O_4 + CoO$
T_f 539					T_f 693				
T_i 539		21.73	21.44	β-$Co_2(OH)_3Cl \to \frac{1}{2}Co_3O_4$	T_i 693		24.74	24.05	β-$Co_2(OH)_3Cl \to \frac{1}{3}Co_3O_4 + CoO$
T_f 570					T_f 755				
T_i 755	755	26.84	26.66		T_i 755	772	26.94	26.66	
T_m 800					T_m 804				
T_f 812	808			β-$Co_2(OH)_3Cl \to 2CoO$	T_f 820	828			β-$Co_2(OH)_3Cl \to 2CoO$

*Only DTA temperature peaks corresponding to the reaction $Co_3O_4 \to 3CoO + \frac{1}{2}O_2$ are indicated. Theoretical weight losses have been calculated according to the reaction indicated after each temperature interval.

†Overall reaction schemes:

(I, III) β-$Co_2(OH)_3Cl \xrightarrow[235-390°C]{+\frac{1}{2}O_2} \frac{2}{3}Co_3O_4 + \frac{1}{2}Cl_2\uparrow + \frac{3}{2}H_2O\uparrow \xrightarrow{900-915°C} 2CoO + \frac{3}{9}O_2\uparrow$

(II, IV) β-$Co_2(OH)_3Cl \xrightarrow[250-390°C]{+\frac{1}{4}O_2} \frac{1}{2}CoCl_2 + \frac{1}{2}Co_3O_4 + \frac{3}{2}H_2O\uparrow \xrightarrow[390-500°C]{+\frac{1}{4}O_2} \frac{2}{3}Co_3O_4 + \frac{1}{2}Cl_2\uparrow \xrightarrow{890-930°C} 2CoO + \frac{3}{9}O_2\uparrow$

(V) β-$Co_2(OH)_3Cl \xrightarrow{257-385°C} \frac{1}{2}CoCl_2 + \frac{3}{2}CoO + \frac{3}{2}H_2O\uparrow \xrightarrow[385-539°C]{+\frac{1}{4}H_2O + \frac{1}{4}O_2} \frac{1}{3}Co_3O_4 + CoO + HCl\uparrow \xrightarrow[539-570°C]{+\frac{1}{8}O_2} \frac{2}{3}Co_3O_4 \xrightarrow{755-810°C} 2CoO + \frac{3}{9}O_2\uparrow$

(VI) β-$Co_2(OH)_3Cl \xrightarrow{259-466°C} \frac{1}{2}CoCl_2 + \frac{3}{2}CoO + \frac{3}{2}H_2O\uparrow \xrightarrow[466-693°C]{+\frac{1}{4}H_2O + \frac{1}{4}O_2} \frac{1}{3}Co_3O_4 + \frac{1}{2}CoO + HCl\uparrow \xrightarrow[693-755°C]{+\frac{1}{2}O_2} \frac{2}{3}Co_3O_4 + CoO \xrightarrow{770-825°C} 2CoO + \frac{1}{6}O_2\uparrow$

Figure 4 Infrared spectra of (a) cobalt chloride after heating at 200° C for 30 h; (b) residue of thermal decomposition in air and (c) in nitrogen. Bands arrowed correspond to Co_3O_4.

When a higher heating rate is used ($10° C min^{-1}$) a sort of inflexion is observed in the TG curves recorded in both still and flowing air (Fig. 5b), being more pronounced in the former case, and it occurs at about 396° C and 10.13% weight loss. It can be formally explained if the following reaction occurs:

$$\beta\text{-}Co_2(OH)_3Cl \xrightarrow{+\frac{1}{4}O_2} \tfrac{1}{2}CoCl_2 + \tfrac{1}{2}Co_3O_4 + \tfrac{3}{2}H_2O\uparrow$$

$$\text{(I)}$$
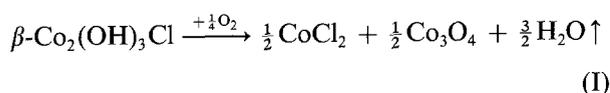
with a calculated weight loss of 9.32%. Nevertheless, in the IR spectra recorded on batches of samples at increasing weight losses (13%, 17.40%) the IR absorptions of $\beta\text{-}Co_2(OH)_3Cl$ appear as strong bands as well as those of Co_3O_4, with two strong features at 3400 and 1610 cm^{-1} (Figs 7a and b). The IR spectrum recorded with a sample that has lost 19% is as shown in Fig. 7c. Bands corresponding to $\beta\text{-}Co_2(OH)_3Cl$ are now very weak; the (O–H) stretching at 3650 cm^{-1} has disappeared and the spectrum is that of the spinel Co_3O_4. Bands at 3400 and 1610 cm^{-1} are still observed. On the other hand, the evolution of chlorine over the whole temperature range in which decomposition takes

place has been qualitatively tested and it is particularly noticeable in the temperature interval 400 to 450° C.

4.2.3. Thermal decomposition of $\beta\text{-}Co_2(OH)_3Cl$ in nitrogen

In order to ensure the nature of the surrounding atmosphere, nitrogen was flowed for at least 1 h before carrying out each experiment.

When thermal decomposition is carried out in a nitrogen flow it leads to slightly different results depending on the heating rate. Thermograms obtained at 10 and 2° C min^{-1} are reproduced in Figs 8a and b, respectively. At low heating rate (Fig. 8b), $\beta\text{-}Co_2(OH)_3Cl$ decomposes into a mixture of Co_3O_4 and CoO (Table III) but this readily oxidizes to Co_3O_4 that remains stable up to 755° C; it transforms into CoO between 755 and 808° C, and even though the residue is cooled in nitrogen, CoO partially oxidizes and the IR spectrum now recorded is as shown in Fig. 9b.

Although an inflexion is observed in the TG curve at 385° C at a weight loss of 13.60%, that can be
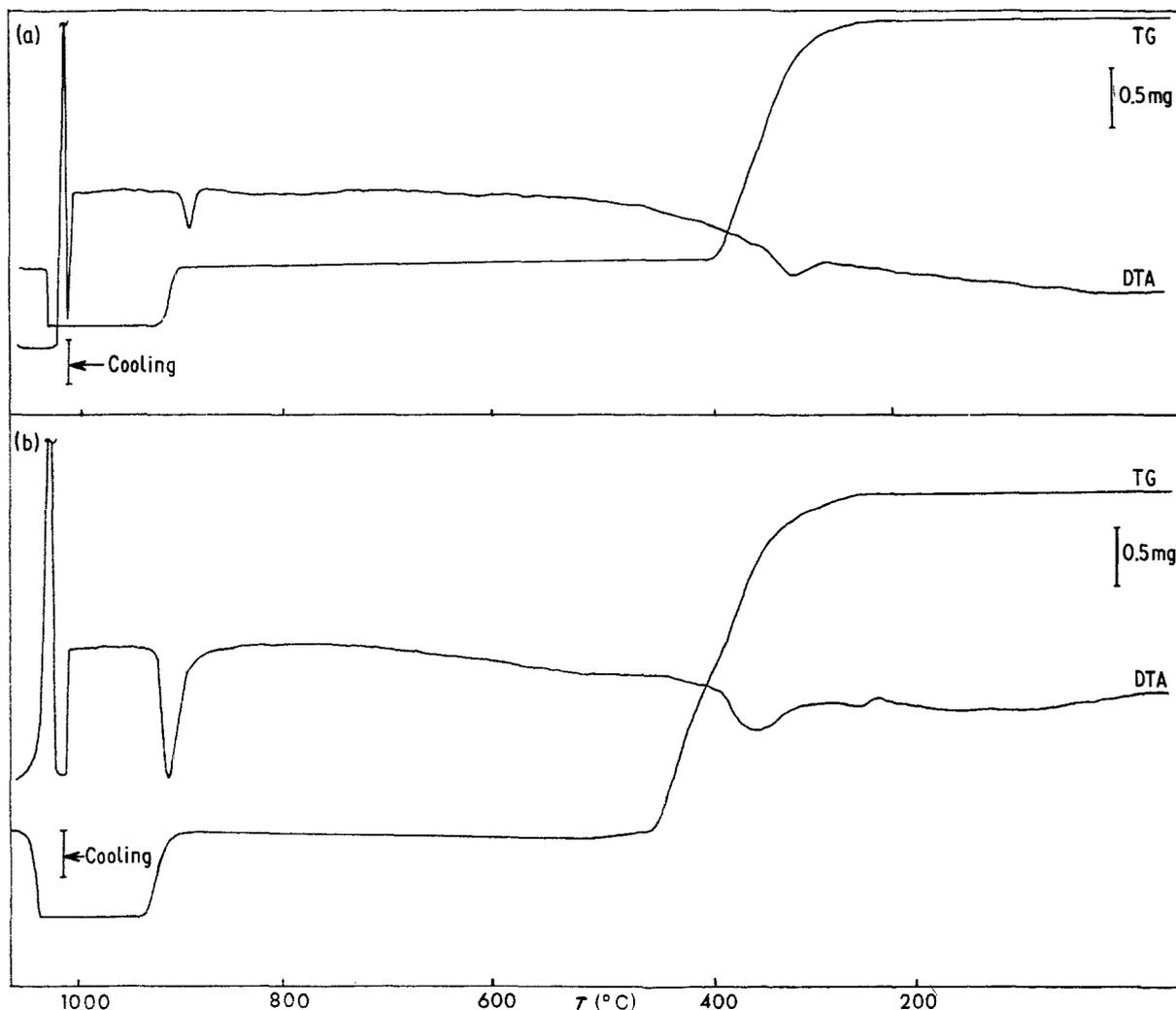
Figure 5 DTA and TG curves of β-Co$_2$(OH)$_3$Cl recorded in air at heating rate (a) $2°\text{C min}^{-1}$, (b) $10°\text{C min}^{-1}$.

formally explained on the basis of an equation such as

$$\beta\text{-Co}_2(\text{OH})_3\text{Cl} \rightarrow \tfrac{1}{2}\text{CoCl}_2 + \tfrac{3}{2}\text{CoO} + \tfrac{3}{2}\text{H}_2\text{O}\uparrow$$

(II)
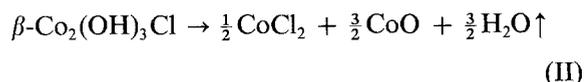
(theoretical weight loss 13.21%), IR spectra recorded on batches of sample heated at 400 and 450° C and cooled at room temperature in nitrogen clearly show IR absorptions of β-Co$_2$(OH)$_3$Cl, Co$_3$O$_4$ and CoO as well as those at 3400 and 1610 cm^{-1} already mentioned and attributed to hydrated cobalt chloride (Fig. 9a).

At a higher heating rate (10° C min^{-1}) (Fig. 8a), an inflexion occurs in the TG curve at about 15% weight loss, as happened at the lower heating rate. In order to isolate the intermediates formed at this temperature (466° C), batches of β-Co$_2$(OH)$_3$Cl were enclosed in aluminium cups, sealed and heated in a nitrogen flow until the same weight loss was attained (Point B, Fig. 10). X-ray diagrams recorded on this intermediate show diffraction lines of CoO and cobalt chloride dihydrate [16]; the IR spectrum shows the broad band of CoO and those at 3400 and 1610 cm^{-1}. If the heating process is stopped at point A (Fig. 10) at about 10% weight loss, diffraction peaks corresponding to β-Co$_2$(OH)$_3$Cl and CoO are clearly seen in the X-ray diffraction diagram and the IR spectrum shows

absorptions of these two compounds, as well as two bands at 3400 and 1610 cm^{-1} but of low intensity. Under these operating conditions the reaction scheme II, indicated above, is probably obeyed.

On the other hand, the IR spectrum recorded on the residue formed at 470° C but when the basic salt is decomposed in an open pan indicates that β-Co$_2$(OH)$_3$Cl exists in the light brown mixture obtained at this temperature, together with CoCl$_2$, Co$_3$O$_4$ and CoO as happened at low heating rate. On continuing the heating process in open conditions, the residue consist of a mixture of CoO and Co$_3$O$_4$ and transformation of the spinel oxide into CoO causes the step and endothermic peak recorded in the temperature interval 755 to 820° C (Fig. 8a).

In the whole temperature range in which decomposition occurs, 260 to 700° C, the gas evolved gives a red tinge to universal indicator paper, mainly between 460 and 650° C, and chlorine does not seem to be evolved when thermal decomposition is carried out in nitrogen.

It is interesting to note that when the decomposition reaction is carried out in a nitrogen flow, a mixture of CoO and Co$_3$O$_4$ is always obtained at about 700° C, and this result is perfectly reproduced even if thermograms are recorded in some other equipment (Mettler, Dupont, Perkin-Elmer) as well as in a helium flow of 120 ml min^{-1}.
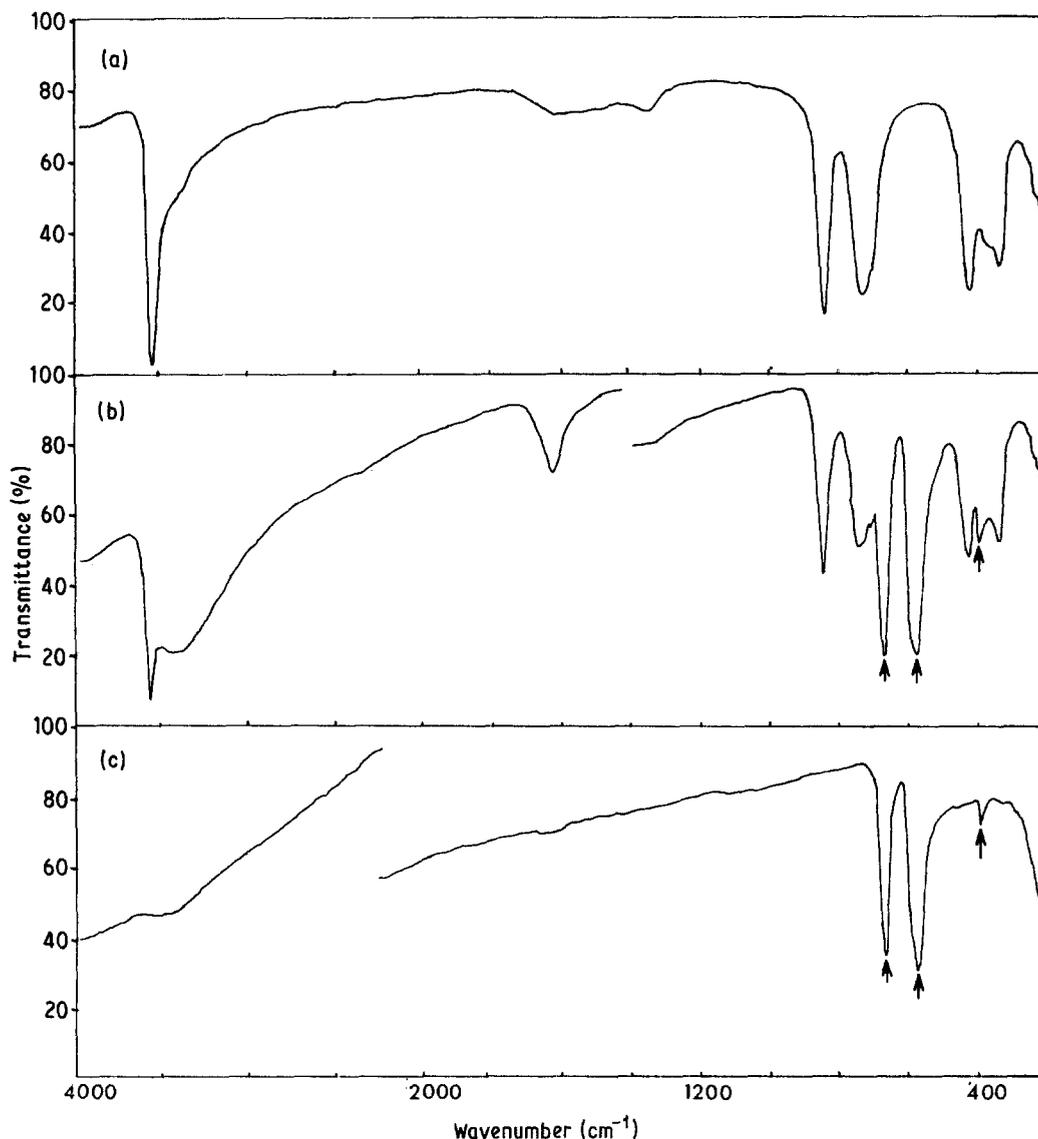
Figure 6 IR spectra of (a) β-Co$_2$(OH)$_3$Cl unheated, (b) heated up to 360° C, (c) heated up to 1000° C and cooled in air (2° C min^{-1} heating rate). Bands arrowed correspond to Co$_3$O$_4$.

4.2.4. Green cobalt hydroxychloride, Co$_5$(OH)$_{8.5}$Cl$_{1.5}$ · 2.5H$_2$O

The green cobalt hydroxychloride (hexagonal lattice $a = 0.315$ nm, $c = 2.44$ nm), the composition of which determined from chemical analysis seems to correspond to the formulation above indicated, when it is decomposed in air or under a nitrogen flow, at 2 or 10° C min^{-1} heating rate, exhibits a rather unusual thermal behaviour (Table IV). Apparently, decomposition patterns are affected neither by the heating rate nor by the surrounding atmosphere. It decomposes between 20 and 500° C in an almost continuous manner, yielding Co$_3$O$_4$; this, when heated in air or nitrogen, transforms into CoO at about 900 or 796° C, respectively. The only differences between the thermograms lies in the fact that in DTA curves recorded in air, three exothermic effects are observed at 165 to 215° C, 215 to 279° C and 337 to 390° C, indicating that excepting dehydration, the decomposition reactions are exothermic processes, probably because of some oxidation or recrystallization occurs simultaneously with decomposition (Fig. 11).

Because of the low crystallinity of the intermediates the evolution of this basic salt when it is decomposed

in air has been followed by IR spectroscopy. A pellet of sample dispersed in KBr was heated at the temperatures shown in Table V, cooled in a dessicator and the spectra were then scanned. At 150° C the strong and broad band at 3460 cm^{-1} observed in the IR spectrum of the initial material (Fig. 12a) splits into two at 3520 and 3440 cm^{-1}, the latter progressively disappears on heating, while anhydrous green cobalt hydroxychloride is transformed continuously into β-Co$_2$(OH)$_3$Cl and Co$_3$O$_4$, as can be deduced from the observation of the spectra shown in Fig. 12. The reaction scheme that could explain the above-indicated behaviour on heating in air would be as follows:

$$Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O \longrightarrow Co_5(OH)_{8.5}Cl_{1.5}$$

$$+ \; 2.5H_2O\uparrow \xrightarrow{+\frac{1}{4}O_2} Co_2(OH)_3Cl + Co_3O_4$$

$$+ \; \tfrac{1}{2}HCl\uparrow + 2.5H_2O\uparrow \xrightarrow{+\frac{1}{6}O_2} \tfrac{5}{3}Co_3O_4$$

$$+ \; HCl\uparrow + H_2O\uparrow \longrightarrow 5\,CoO + \tfrac{5}{6}O_2\uparrow$$
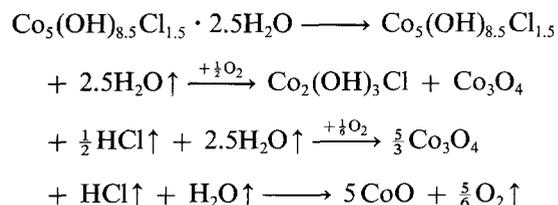
Calculated and experimental weight losses, as well as the temperatures at which intermediate reactions take account, are shown in Table IV. They have been

TABLE IV Thermal decomposition data of $Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O$ for different atmospheres and heating rates*†

| | Still air | | | | | | | | | | Air flow (50 ml min⁻¹) | | | | | | | | | | Nitrogen flow (50 ml min⁻¹) | | | | | | | | | |
| | 2°C min⁻¹ (I)† | | | | | 10°C min⁻¹ (II)† | | | | | 2°C min⁻¹ (III)† | | | | | 10°C min⁻¹ (IV)† | | | | | 2°C min⁻¹ (V)* | | | | | 10°C min⁻¹ (VI)* | | | | |
	T(°C)	DTA	TG	Accumulative weight loss (%) Found	Calc.	T(°C)	DTA	TG	Accumulative weight loss (%) Found	Calc.	T(°C)	DTA	TG	Accumulative weight loss (%) Found	Calc.	T(°C)	DTA	TG	Accumulative weight loss (%) Found	Calc.	T(°C)	DTA	TG	Accumulative weight loss (%) Found	Calc.	T(°C)	DTA	TG	Accumulative weight loss (%) Found	Calc.
	T_i	28		25.25	25.31	T_i	28		25.12	25.31	T_i	35		25.88	25.31	T_i	20		25.78	25.31	T_i	20		25.77	25.31	T_i	35		32.10	–
	T_f		521			T_f		512			T_f		548			T_f		540			T_f		466			T_f		671		
				$Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O \rightarrow \tfrac{5}{3}Co_3O_4$																			$Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O \rightarrow 5CoO$								
	T_i	894	894	30.41	30.47	T_i	900	902	30.15	30.47	T_i	900	900	30.96	30.47	T_i	900	900	31.05	30.47	T_i	763	763	31.05	30.47	T_i	763	763	34.21	–
	T_m	900	915			T_m	915				T_m	908				T_m	905				T_m	796				T_m	807			
	T_f	905	915			T_f	931	923			T_f	918	918			T_f	927	930			T_f	804	804			T_f	820	817		

*Only DTA temperature peaks corresponding to the reaction $Co_3O_4 \rightarrow 3CoO + \tfrac{1}{2}O_2$ are indicated.

† Reaction scheme:

$$Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O \xrightarrow{\quad} Co_5(OH)_{8.5}Cl_{1.5} + 2.5H_2O\uparrow \xrightarrow{+\frac{1}{4}O_2} \beta\text{-}Co_2(OH)_3Cl + Co_3O_4 + \tfrac{1}{2}HCl\uparrow + 2.5H_2O\uparrow \xrightarrow{+\frac{1}{4}O_2} \tfrac{5}{3}Co_3O_4 + HCl\uparrow + H_2O\uparrow \xrightarrow{\quad} 5CoO \cdot \tfrac{5}{6}O_2\uparrow$$

DTA	T_i (°C)	20	164	215	337	900
	T_m (°C)	116	174	258	356	905
	T_f (°C)	152	215	279	390	927
TG	T_i (°C)	20	164	215		900
	T_f (°C)	152	215	540		930
Accumulative weight loss (%)	Calc.	8.37	17.16	25.31		30.47
	Found	7.89	17.40	25.78		31.05

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Figure 7 IR spectra recorded on several batches of β-$Co_2(OH)_3Cl$ at (a) 13%, (b) 17.4%, (c) 19% weight losses ($10°C\,min^{-1}$ heating rate). Bands arrowed correspond to β-$Co_2(OH)_3Cl$ and those with (*) correspond to Co_3O_4.

measured from thermograms recorded in still air at $10°C\,min^{-1}$ heating rate.

On the other hand, when green cobalt hydroxy-chloride is decomposed at up to 1000° C in a nitrogen flow at $10°C\,min^{-1}$ heating rate, an abnormally high weight loss is always obtained (34.21%) and up to the moment we are not able to explain the discrepancy between this value and the calculated weight loss (30.47%).

4.3. X-ray high-temperature diffraction studies

4.3.1. β-$Co_2(OH)_3Cl$

When the above-indicated material is decomposed in an X-ray high-temperature diffraction chamber that has a tantalum strip as heating element, cobaltous oxide starts to appear at about 300° C. From this temperature up to about 400° C the diffraction patterns of both the cobaltous oxide and β-$Co_2(OH)_3Cl$ are clearly shown. From 480 up to 700° C, CoO is the only compound. If the temperature is held at 740° C for about 10 min, diffraction lines of cobalt metal are already observed and it is obtained as the sole material at 750° C (Fig. 13).

4.3.2. Green cobalt hydroxychloride, $Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O$

Between room temperature and 115° C the X-ray diffraction pattern of the original sample does not alter, but from this temperature onwards the diffraction maxima become poorly defined, and at 180° C the diagram is that of the background, remaining so up to 300° C. At this temperature, some broad maxima appear in the 2θ interval where the most intense diffraction lines of CoO would be observed. On increasing the temperature up to 600° C, the crystallinity of the oxide seems to increase as well, and the X-ray diagram recorded at this temperature is shown in Fig. 14b; cobalt metal is already formed and a mixture of both cobalt and cobalt(II) oxide is present until the temperature reaches 750° C. If this temperature is held for at least 60 min (Fig. 14d) the sample consists of only cobalt metal (cubic form).

5. Conclusions

The reaction schemes proposed in Tables III and IV would be a reasonable approach to explain the weight variations recorded in TG curves. Nevertheless, thermal decomposition of β-$Co_2(OH)_3Cl$ seems to be a
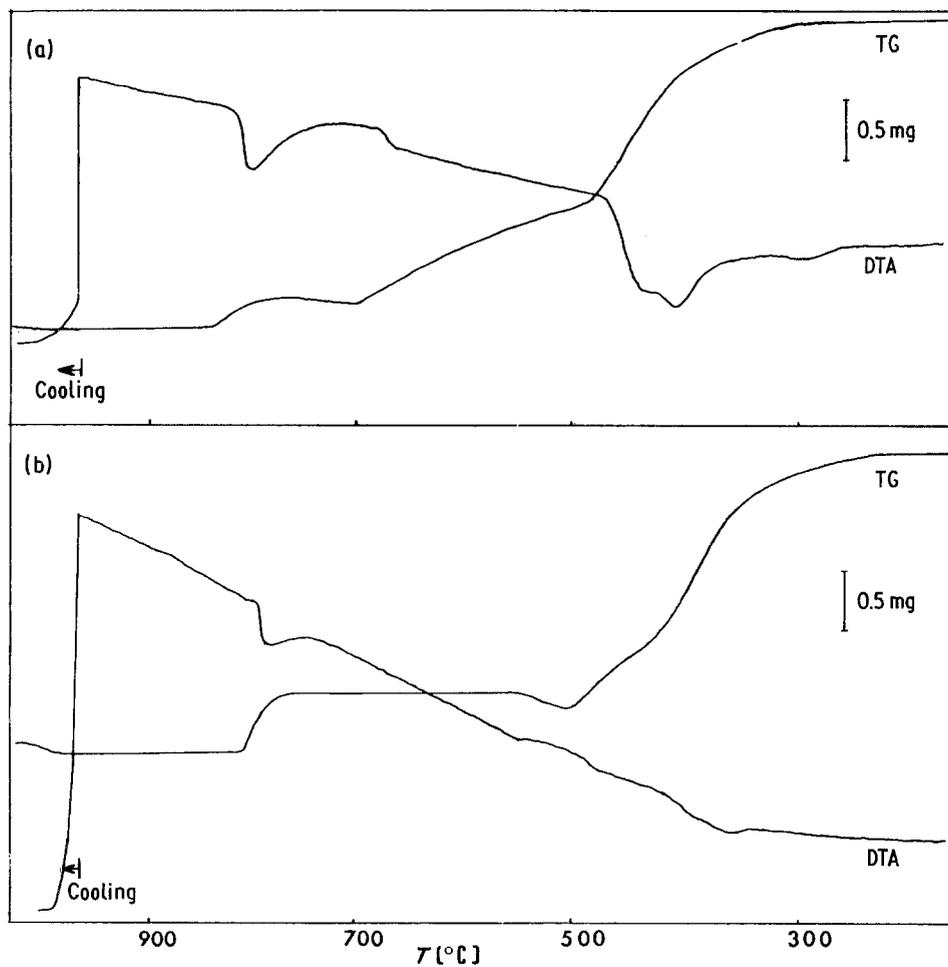
Figure 8 DTA and TG curves of β-$Co_2(OH)_3Cl$ recorded in nitrogen flow at (a) $10°C\,min^{-1}$, (b) $2°C\,min^{-1}$ heating rates.
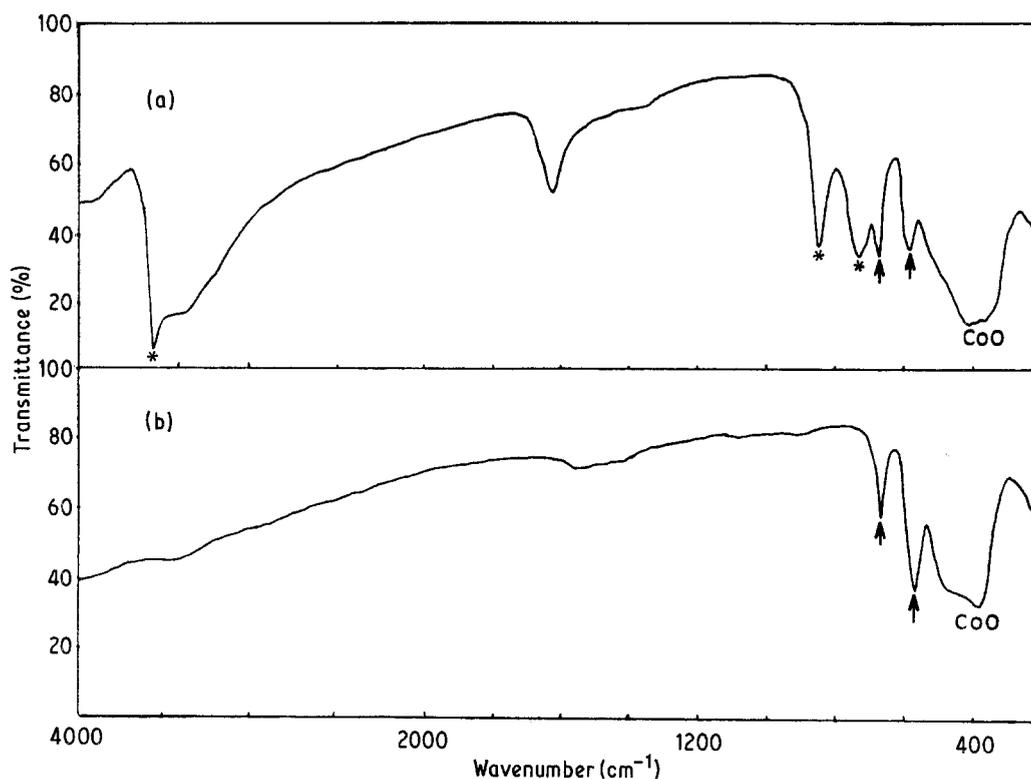
Figure 9 (a) IR spectrum of β-$Co_2(OH)_3Cl$ after heating at $450°C$ and cooled in nitrogen flow ($2°C\,min^{-1}$ heating rate). Bands arrowed correspond to Co_3O_4 and bands with (*) correspond to β-$Co_2(OH)_3Cl$. (b) IR spectrum of the residue of thermogram shown in Fig. 8b.

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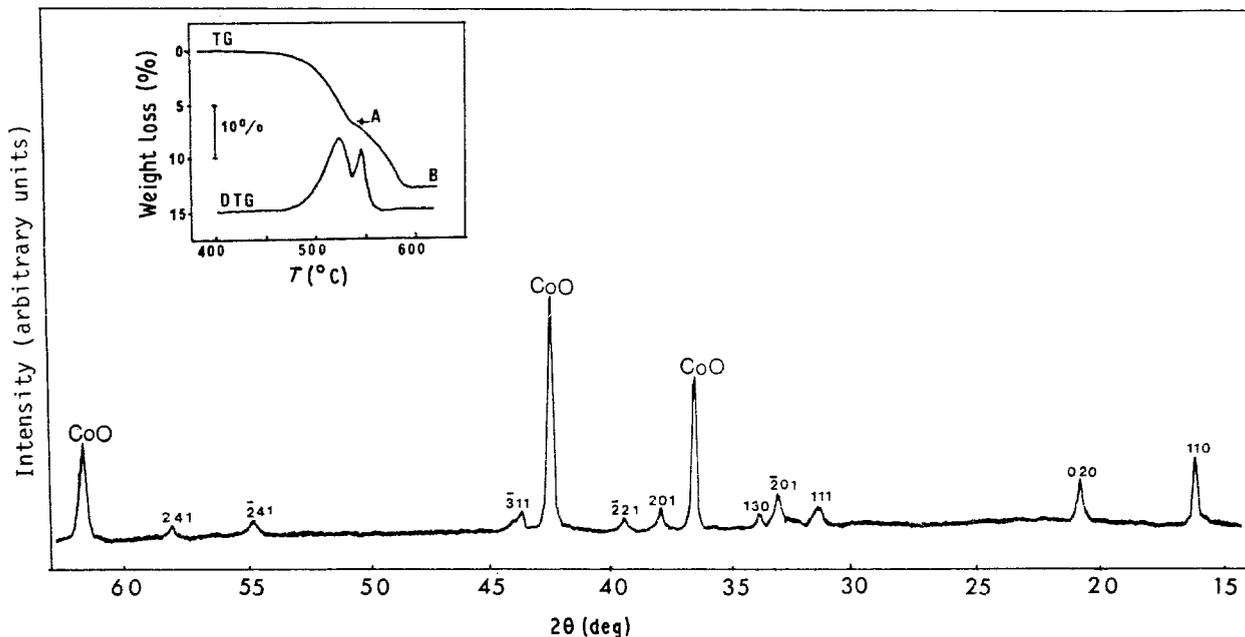
Figure 10 X-ray diffraction diagram of residue obtained at B in the inset: this shows thermogravimetric (TG) and differential thermogravimetric (DTG) curves recorded on β-Co$_2$(OH)$_3$Cl enclosed in a sealed cup in nitrogen flow ($10°$C min^{-1} heating rate). For CoCl$_2$ · 2H$_2$O $a = 0.7280$ nm, $b = 0.8552$ nm, $c = 0.3573$ nm, $\beta = 97.55°$.
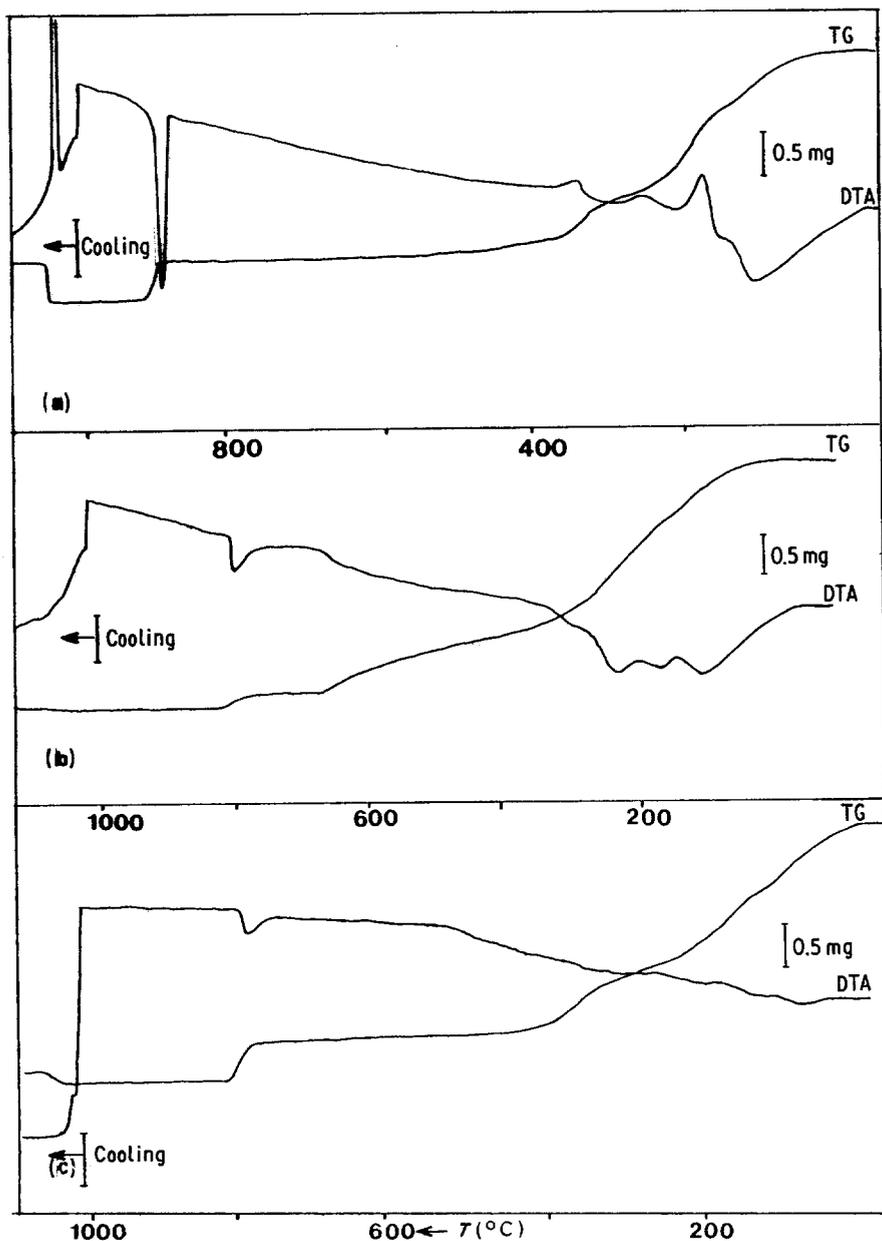
Figure 11 DTA and TG curves of Co$_5$(OH)$_{8.5}$ Cl$_{1.5}$ · 2.5H$_2$O recorded at (a) $10°$C min^{-1} heating rate, in air; (b) nitrogen flow, $10°$C min^{-1} heating rate; (c) nitrogen flow, $2°$C min^{-1} heating rate.
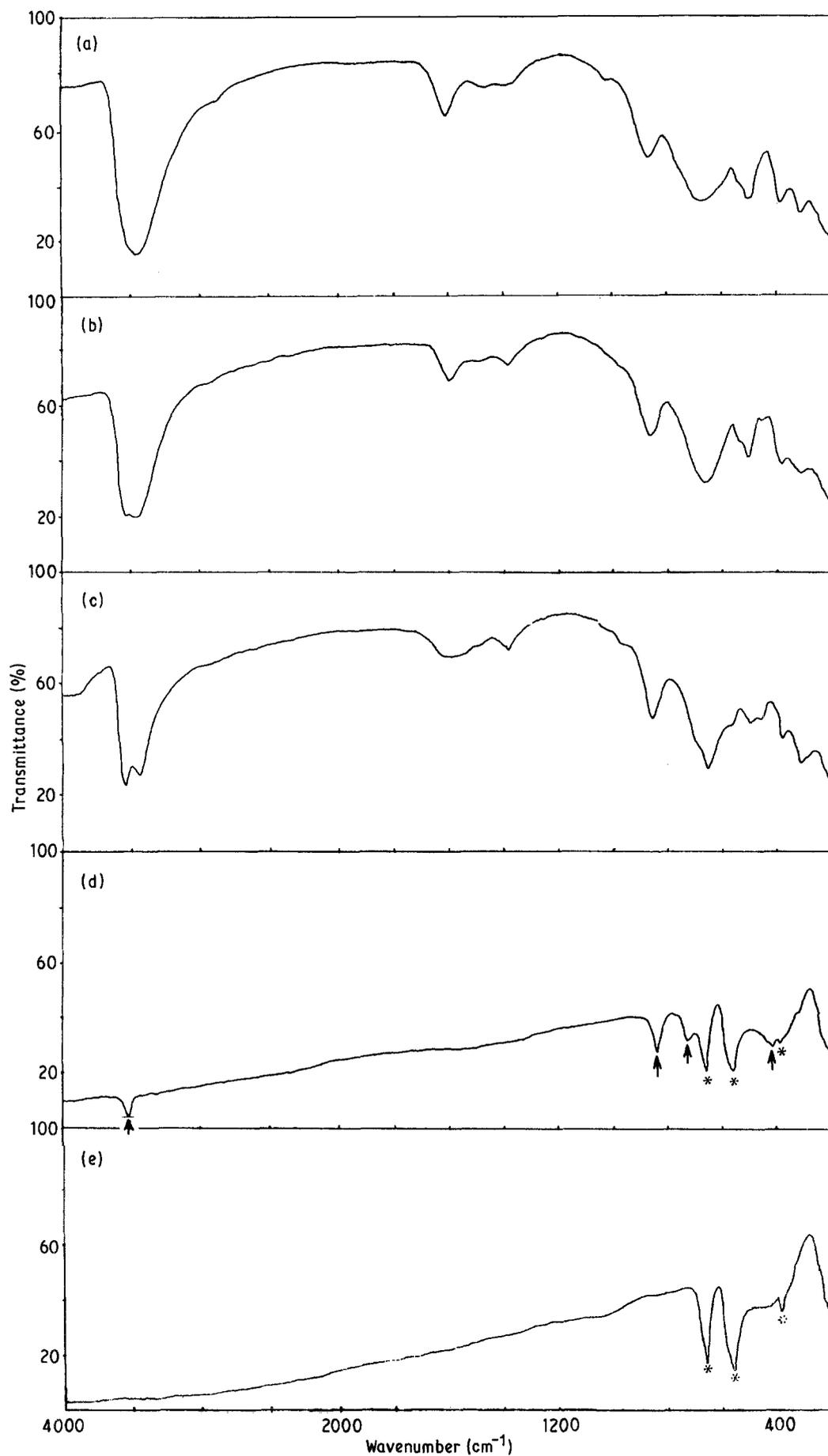
Figure 12 Infrared spectra of $Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O$. (a) Unheated; (b) 150°C for 5 min; (c) 200°C for 30 min; (d) 270°C for 15 min; (e) 400°C for 15 min. Bands arrowed correspond to β-$Co_2(OH)_3Cl$ and bands with (*) correspond to Co_3O_4.

TABLE V Evolution of infrared spectra of the green cobalt hydroxychloride, $Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O$, on heating*

Room temperature	150°C/5 min	175°C/150 min	200°C/30 min	270°C/15 min	285°C/15 min	400°C/10 min
3460 vs, bd	3525 vs	3520 vs	3520 vs	3520[†] s	3520[†] s	
	3450 vs	3440 vs	3440 s			
1610 m	1600 m	1600 m	1600 m			
1470 w	1470 w	1490 w	1490 w			
1380 w	1380 w	1385 w	1380 w			
870 s	860 s	855 s	855 s	840[†] s	840[†] s	
				730[†] s	730[†] m	
680 s, bd	660 s, bd	652 s	652 s	658[‡] vs	658[‡] vs	658[‡] vs
		560 sh	560[‡] sh	560[‡] vs	560[‡] vs	560[‡] vs
535 sh	538 sh					
500 m	500 m	500 m	500 m			
		455 w	455 w	425[†] w	420[†] w	
385 m	385 m	380 m	380 m	385[‡] m	385[‡] m	385[‡] m
310 m	310 m	310 m	310 m	310 vw	315 vw	

*Frequencies in cm^{-1}. Bands marked ([†]) correspond to β-$Co_2(OH)_3Cl$, bands marked ([‡]) correspond to Co_3O_4; vs = very strong, v = strong, m = medium, w = weak, bd = broad, sh = shoulder.
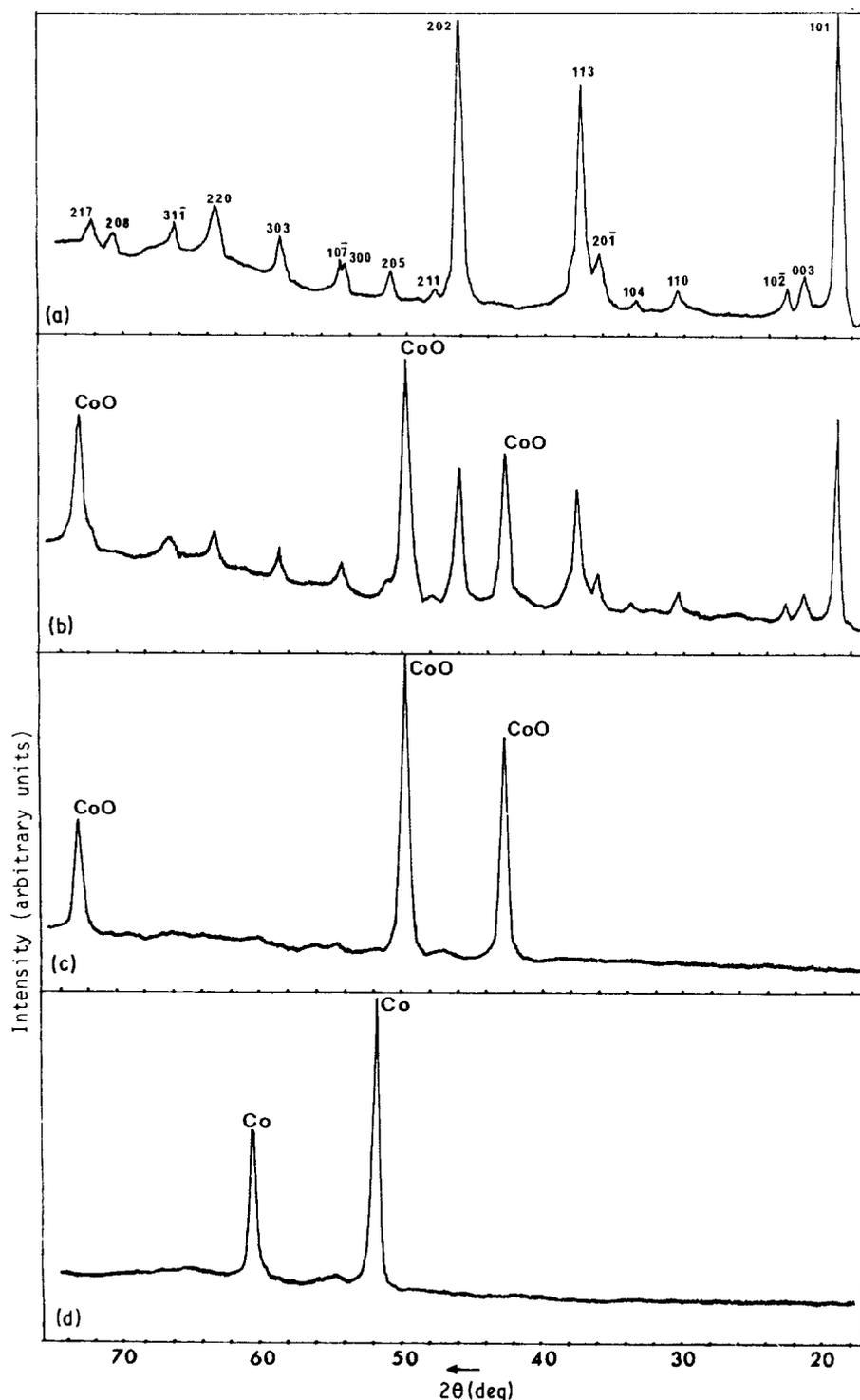
Figure 13 Evolution of β-Co_2 $(OH)_3Cl$ when it is decomposed in the X-ray high-temperature diffraction chamber: (a) unheated, (b) 370°C, (c) 590°C, (d) 750°C. Diagrams recorded with Co$K\alpha$ radiation. a_{hex} = 0.684 nm, c_{hex} = 1.450 nm.
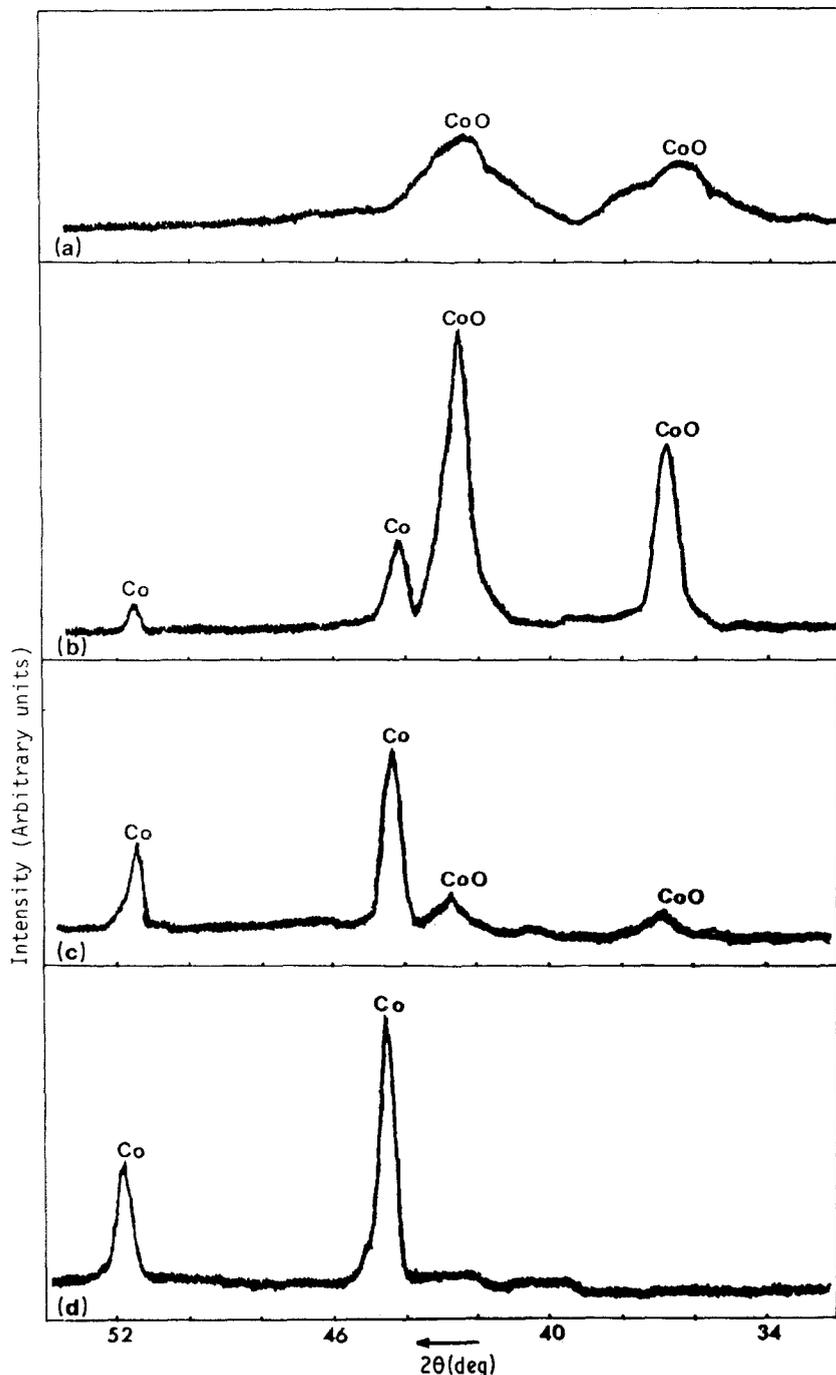
Figure 14 Evolution of $Co_5(OH)_{8.5}Cl_{1.5} \cdot 2.5H_2O$ when decomposed in the X-ray high-temperature diffraction chamber ($CuK\alpha$ radiation): (a) 300°C, (b) 600°C, (c) 700°C, (d) 750°C (60 min).

continuous process and although some inflexions are observed in the TG curves and some more or less well-defined peaks appear in the DTA curves, cobalt oxides and cobalt chloride as well as β-$Co_2(OH)_3Cl$ coexist during the whole decomposition reaction, as is clearly shown in the IR spectra recorded on intermediates formed at different temperatures, both in air and nitrogen atmospheres. Otherwise, even though decomposition is carried out in a nitrogen flow, the formation of Co_3O_4 cannot be avoided unless the sample is enclosed in sealed cups where, because of the nature of the inner atmosphere, oxidation of Co^{2+} is unfavourable. On the other hand it is only in this situation that the formation of $CoCl_2$ is clearly evident, as indicated by the X-ray diagram recorded on the residue formed at 466° C (Fig. 10), since the strong IR absorptions appearing at 3400 and 1610 cm^{-1} cannot be considered as conclusive proof of the presence of this salt among the decomposition products.

Anhydrous cobalt chloride, once it is formed, oxi-

dizes to Co_3O_4 when working in air and when thermal decomposition is carried out in nitrogen it probably hydrolyses, as has been seen to occur when this pure salt is decomposed in nitrogen; it transforms into a highly reactive CoO that is more or less readily oxidized to Co_3O_4, depending mainly on the programmed heating rate.

As a general conclusion and according to the results indicated above, it is of the greatest importance to control very carefully the atmosphere when performing thermal analysis, and specially if the experiments are carried out at low heating rates.

On the other hand, Co_3O_4 obtained as a residue transforms into cobaltous oxide, CoO, at a considerably lower temperature when the reaction takes account under a nitrogen flow (750 to 800° C), 150° C below the reported temperature for this transformation in air (900 to 950° C), but the temperature at which transformation occurs is not affected by the heating rate.

No other intermediate but CoO seems to be formed when these two basic salts are decomposed in the X-ray high-temperature diffraction chamber, and the formation of cobalt as the only material is achieved in both cases in the temperature range 700 to 750° C.

The formation of cobalt metal (cubic form) together with CoO, attained at a significantly low temperature (600° C), could be favoured by the small particle size and low crystallinity of green cobalt hydroxychloride. The very broad bandwidth observed in the X-ray diffraction diagrams of both CoO and cobalt metal permit us to suppose for these two material some physico-chemical characteristics, such as surface area of crystallite size, that could involve some particular properties closely related to their reactivity.

If the vacuum conditions could be improved, it is most probable that the temperature of formation of pure cobalt could be lowered, as it would be if the period of treatment at certain temperatures was lengthened, and studies in this direction are now being attempted.

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