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On the thermal decomposition of the zinc(II) hydroxide chlorides $Zn_5(OH)_8Cl_2{\cdot}H_2O$ and β-Zn(OH)Cl

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The thermal decomposition of $Zn_5(OH)_8Cl_2{\cdot}H_2O$ and β-Zn(OH)Cl materials under several experimental conditions has been studied by thermal analysis, X-ray powder diffraction and X-ray high-temperature powder diffraction techniques. Several reaction schemes are proposed to account for thermal decomposition reactions undergone by both zinc hydroxide chlorides.

1. Introduction

Several zinc hydroxide chlorides have been reported in the literature ([1] and references therein). However, to the best of our knowledge, crystal structure determination, thermal and infrared spectroscopic studies have only been carried out on two of them, $Zn_5(OH)_8Cl_2{\cdot}H_2O$ and β-Zn(OH)Cl. Zinc(II) hydroxide chloride, $Zn_5(OH)_8Cl_2{\cdot}H_2O$, crystallizes in the rhombohedral system with $a_h = 0.634 \pm 0.001$ nm, $c_h = 2.364 \pm 0.002$ nm, S.G. R$\bar{3}$m, $Z = 3$ per threefold primitive hexagonal cell [2]. The basic structural unit is a charged layer which may be derived from a hypothetical C6-$Zn(OH)_2$ of the CdI_2 type. A quarter of the octahedrally coordinated Zn atoms are removed and replaced by pairs of tetrahedrally coordinated Zn atoms, one on each side of the layer, giving a layer of composition $[Zn_5(OH)_8]^{2+}$. The fourth bond from the tetrahedrally coordinated Zn is to the Cl^- ion that balance the charge and the water molecules are situated between layers [3]. Crystals of β-Zn(OH)Cl are orthorhombic ($a \simeq 0.586$ nm, $b \simeq 0.658$ nm, $c \simeq 1.133$ nm, S.G. Pcab, $Z = 8$). The structure is built of pseudo-hexagonal zinc layers separated by an ordered layer of oxygen and chlorine atoms, zinc atoms being octahedrally surrounded by three oxygen and three chlorine atoms [4]. A different set of lattice parameters and S.G. Pbca have been also reported [5].

From a general point of view these layered hydroxide halides of Zn(II) look convenient as substrates for grafting and intercalation reactions, and have proved to be excellent precursors for the preparation of ZnO with special morphological characteristics [6]. When such investigations have been carried out, some differences arise in the reported thermal behaviour of these compounds which is specially sensitive to the experimental conditions [7–10]. The present study was undertaken in order to clarify these effects, as well as to establish the mechanisms of the thermal decomposition of both β-Zn(OH)Cl and $Zn_5(OH)_8Cl_2{\cdot}H_2O$.

2. Experimental procedure

$Zn_5(OH)_8Cl_2{\cdot}H_2O$ and β-Zn(OH)Cl were obtained by procedures reported in the literature [8–10]. Partially deuterated $Zn_5(OH)_8Cl_2{\cdot}H_2O$ was obtained by exposing β-Zn(OH)Cl to D_2O vapour.

Differential thermal analysis (DTA) and thermogravimetric (TG) curves were simultaneously obtained on a Stanton STA 781 instrument in the temperature range 25–800 °C. Samples of about 10 mg were used in each run. They were decomposed in still air or flowing air (50 ml min^{-1}) at several heating rates. Calcined Al_2O_3 was used as reference. X-ray powder diffraction patterns were recorded on a Siemens D-501 goniometer with monochromatized CuK_α radiation ($\lambda = 0.154\,178$ nm) in the step-scanning mode with 0.04 °2θ step scan and either 0.25 or 2 s counting time for samples heated to a given temperature.

X-ray high-temperature diffraction studies were carried out using an Anton Paar diffraction chamber mounted on a Philips PW 1310 diffractometer. Infrared spectra were taken on a Nicolet SX 10 spectrometer in the transmission mode on KCl, KBr and polyethylene discs, in the 4000–100 cm^{-1} region.

3. Results

3.1. Thermal and X-ray powder diffraction studies

3.1.1. $Zn_5(OH)_8Cl_2{\cdot}H_2O$

DTA and TG curves recorded in still air on $Zn_5(OH)_8Cl_2{\cdot}H_2O$ at 10 °C min^{-1} (Fig. 1) differ from those reported in the literature [8–10] in both temperature and shape. The curves show that the decomposition reaction occurs in three well-defined steps. The

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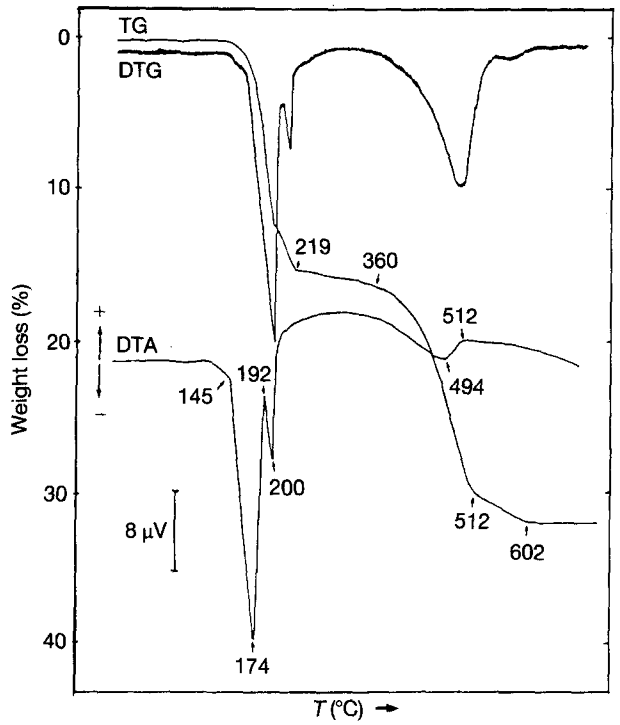

Figure 1 Differential thermal analysis (DTA), thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of $Zn_5(OH)_8Cl_2 \cdot H_2O$. Still air, 10 °C min^{-1} heating rate.

first one takes place between 145 and 192 °C with a weight loss of 12.04%, accompanied by the asymmetric endothermic effect observed in this temperature range (T_{max} = 174 °C). A second endothermic peak and step occurs between 192 and 219 °C (T_{max} = 200 °C), the overall weight loss being 14.65%. The sample continues to lose weight at a slow rate up to about 360 °C, when a new peak and step are recorded in the DTA and TG curves, respectively, between 360 and 512 °C (T_{max} = 494 °C). Finally at 602 °C, TG and DTA curves stabilize yielding a residue of ZnO, with an overall experimental weight loss of 31.94%, that is considerably higher than that calculated (26.27%) for the reaction

$$Zn_5(OH)_8Cl_2 \cdot H_2O \rightarrow 5ZnO \qquad (1)$$

In order to explain this result, as well as to account for the differences reported in the literature, a thermal study of $Zn_5(OH)_8Cl_2 \cdot H_2O$ was also carried out in still air at 1 °C min^{-1} and in flowing air at 5 °C min^{-1} heating rate. Thermograms recorded under both conditions are depicted in Fig. 2a and b. In the former case the shapes of both DTA and TG curves do not greatly differ from those recorded at 10 °C min^{-1}; the experimental overall weight loss obtained from the TG curve (27.94%) agrees fairly well with that calculated for Reaction 1. However, when $Zn_5(OH)_8Cl_2 \cdot H_2O$ is decomposed under the latter conditions, some differences arise: an overlapping of the two first endothermic peaks and steps (see Figs 1 and 2b), and an overall experimental weight loss (34.00%) that is higher than that obtained in still air (31.94%).

X-ray powder patterns recorded on samples heated at 192 and 219 °C are identical, and they only show the $d(002) = 0.565$ nm diffraction peak of β-Zn(OH)Cl and broad diffraction maxima of ZnO, significantly shifted from their typical positions [11].

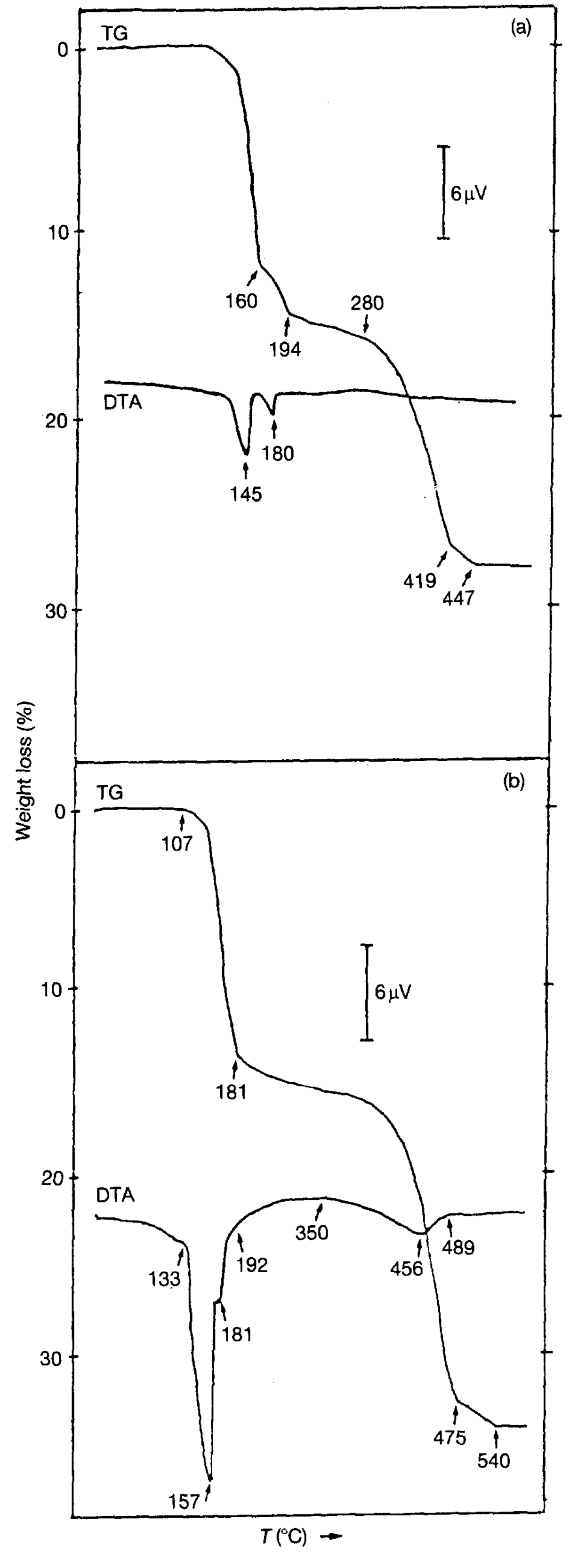

Figure 2 DTA and TG curves of $Zn_5(OH)_8Cl_2 \cdot H_2O$ recorded at (a) 1 °C min^{-1} heating rate, still air; (b) 5 °C min^{-1} heating rate, air flow (50 ml min^{-1}).

On the basis of the presence of endothermic effects at different temperatures, attributed either to the melting [9] or boiling reactions [10], the presence of

$ZnCl_2$ as intermediate has been postulated. However, we have not been able to isolate or identified this compound in the thermolysis residues. Moreover, the endothermic peak at 200 or 180 °C (Figs 1 and 2, respectively) can hardly be attributed to the melting of $ZnCl_2$ (m.p. 275 °C) [12]. Therefore, and in order to verify the formation of this intermediate phase, the following approach was attempted.

A batch of $Zn_5(OH)_8Cl_2 \cdot H_2O$ was heated at several temperatures for different periods. The sample was placed on a glass slide that acted as sample holder and pressed to orientate the crystallographic *c* axis parallel to the sample holder. X-ray diffraction patterns recorded at different temperatures are depicted in Fig. 3. After every thermal treatment the sample was very rapidly put on the goniometer. Patterns obtained after heating at 150 °C for 10 and 30 min are shown in Fig. 3b and c, respectively. The $d(0\,0\,3)$ $Zn_5(OH)_8Cl_2 \cdot H_2O$ diffraction peak disappears on standing 30 min at 150 °C. X-ray diffraction maxima between $2\theta = 30$ and 40 °, corresponding to the ZnO phase, are very broad and shifted about 0.5° to lower angles. Moreover, a new reflection at 15·68° that corresponds to $d(0\,0\,2) = 0.565$ nm for β-Zn(OH)Cl appears. Fig. 3d and e show two consecutives scans run on the sample heated at 180 °C for 15 min. The former only shows broad and shifted diffraction maxima of ZnO, while in the latter (Fig. 3e) the $d(0\,0\,2) = 0.565$ nm of β-Zn(OH)Cl is observed. This shows that although the diffraction maxima of $ZnCl_2$ do not appear, this hygroscopic phase must be present and reacting with water and ZnO to form β-Zn(OH)Cl. On going from 190 to 210 °C (Fig. 3f and g) the ZnO diffraction maxima get sharper and shift to their typical 2θ values.

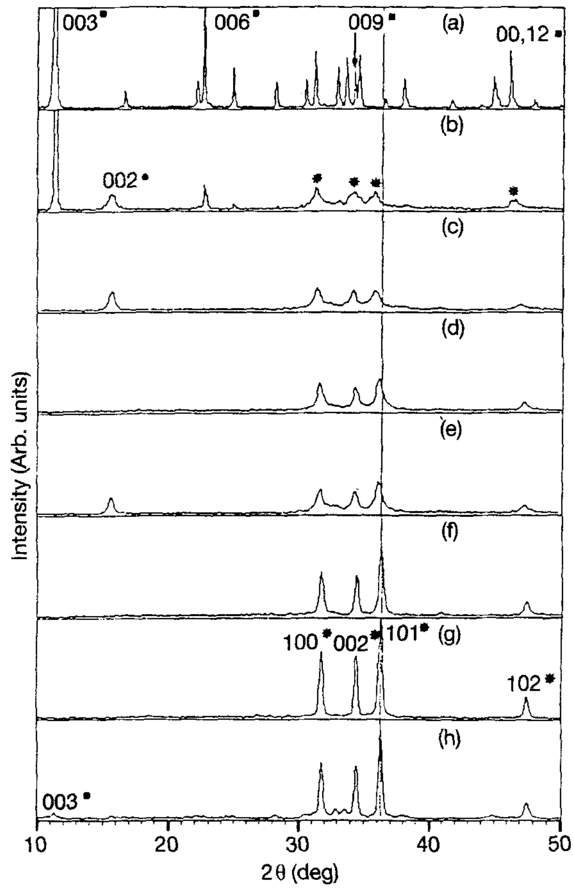

Figure 3 X-ray powder diffraction patterns recorded on $Zn_5(OH)_8Cl_2 \cdot H_2O$ (a) at room temperature, and after standing at (b) 150 °C, 10 min; (c) 150 °C, 30 min; (d) 180 °C, 15 min, first scan; (e) sample (d) second scan; (f) 190 °C, 60 min; (g) 210 °C, 60 min; (h) sample (g) after 24 h exposure to moist air. (■) $Zn_5(OH)_8Cl_2 \cdot H_2O$, (●) β-Zn(OH)Cl, (*) ZnO.

If this sample is scanned after 24 h of exposure to moist air, weak diffraction maxima of the starting zinc(II) hydroxide chloride appear. This reveals that, in spite of thermal treatment, $ZnCl_2$ (or β-Zn(OH)Cl) is not completely removed and some small amount of $Zn_5(OH)_8Cl_2 \cdot H_2O$ is formed through the reversible reactions

$$\begin{tikzcd}
 & \frac{2}{5}Zn_5(OH)_8Cl_2\cdot H_2O + \frac{6}{5}HCl \qquad (4) \\
Zn_5(OH)_8Cl_2\cdot H_2O \arrow[r, "150\,^{\circ}C\ 30\ min"] & 2\beta\text{-}Zn(OH)Cl + 3ZnO + 4H_2O \qquad (2) \arrow[u, "+\frac{8}{5}H_2O\ \text{Room temp.}"'] \arrow[d, shift left=1ex, "180\,^{\circ}C\ \ 1\cdot5\ min"] \\
 & ZnCl_2 + ZnO + H_2O \qquad (3) \arrow[u, shift left=1ex, "\text{Room temp}\ \ 5\ min"]
\end{tikzcd}$$

These processes will take place as long as $ZnCl_2$ is left in the residue.

3.1.2. β-Zn(OH)Cl

DTA, TG and DTG curves recorded on β-Zn(OH)Cl in still air at 5 °C min^{-1} heating rate are depicted in Fig. 4. It remains stable up to 217 °C and then dehydroxylates, yielding zinc chloride and oxide. The dehydroxylation reaction causes the endothermic effect and the step recorded between 217 and 260 °C ($T_{max} = 243$ °C) (calculated weight loss 7.63%, found 6.41%). The small and sharp endothermic peak observed in the DTA curve between 279 and 292 °C ($T_{max} = 290$ °C) is caused by the melting of $ZnCl_2$ (m.p = 275 °C [12]). The sample undergoes a rather smooth and continuous weight loss from 260 to 350 °C, and from this temperature up to 730 °C a pronounced step is recorded in the TG curve (overall weight loss 49.70%) that corresponds to the highly

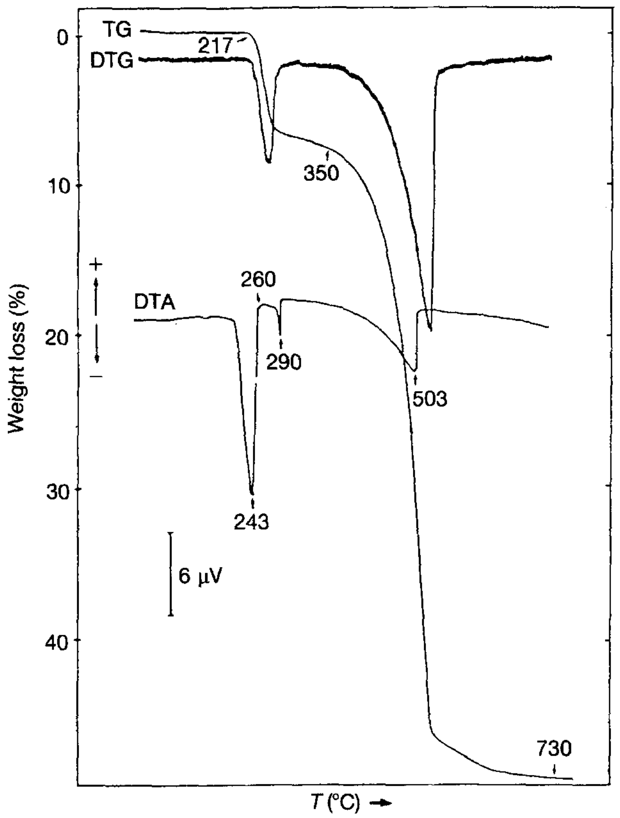

Figure 4 DTA, TG and DTG curves of β-Zn(OH)Cl recorded in still air at 5 °C min^{-1} heating rate.

asymmetric endothermic effect with onset temperature 350 °C and $T_{max} = 503$ °C. The experimental weight loss (49.70%) is considerably lower than that calculated for the complete removal of 1 mol of $ZnCl_2$ (65.48%).

In this case, X-ray high-temperature powder diffraction studies carried out on β-Zn(OH)Cl show the formation of $ZnCl_2$ as an intermediate. The highly oriented hydroxide chloride phase remains stable up to 200 °C (Fig. 5a). However, at 250 °C the pattern is quite different (Fig. 5b). In addition to diffraction maxima of the ZnO phase that now are situated at their characteristic positions, some other sharp maxima are also present. These latter agree reasonably well with those reported for β-$ZnCl_2$ [13], which was formed because of the experimental vacuum conditions. Finally, at 330 °C (Fig. 5c) well-crystallized ZnO is formed as the only phase.

It has been pointed out that hygroscopic β-Zn(OH)Cl, after prolonged exposure to moist air, hydrolyses to the more basic $Zn_5(OH)_8Cl_2\cdot H_2O$ [10]. Moreover, if the zinc(II) hydroxide chloride formed as hydrolysis product is heated to a temperature below the decomposition temperature of β-Zn(OH)Cl, the transformation of β-Zn(OH)Cl into $Zn_5(OH)_8Cl_2\cdot H_2O$ and vice versa is a reversible process, as shown by the X-ray patterns depicted in Fig. 6. Fig. 6b shows the diagram recorded from β-Zn(OH)Cl after overnight exposure to moist air; it is identical to the one shown in Fig. 3a and corresponds to $Zn_5(OH)_8Cl_2\cdot H_2O$. When this "fresh" zinc(II) hydroxide chloride is heated at 180 °C for 30 min (Fig. 6c), β-Zn(OH)Cl is obtained. It is worth noting that the preferred orientation of β-Zn(OH)Cl has now been partially destroyed; the intensities of $d(0\,0\,4)$ and $d(0\,0\,6)$ reflections have considerably diminished. Moreover, between $2\theta = 30$ and 40°, ZnO diffraction maxima can hardly be observed. Nonetheless, if β-Zn(OH)Cl is again left overnight in moist air it transforms again to $Zn_5(OH)_8Cl_2\cdot H_2O$ (Fig. 6d), the intensities of the diffraction maxima being almost identical to those in Fig. 6b. These observations can be explained by the following reaction scheme:

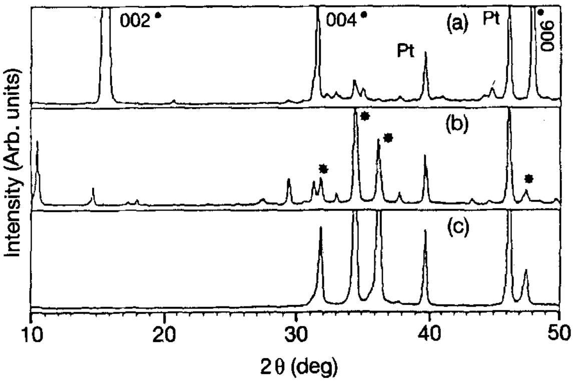

Figure 5 X-ray high-temperature powder diffraction patterns recorded on β-Zn(OH)Cl at (a) 200 °C, (b) 250 °C, (c) 330 °C. (●) β-Zn(OH)Cl, (∗) ZnO.

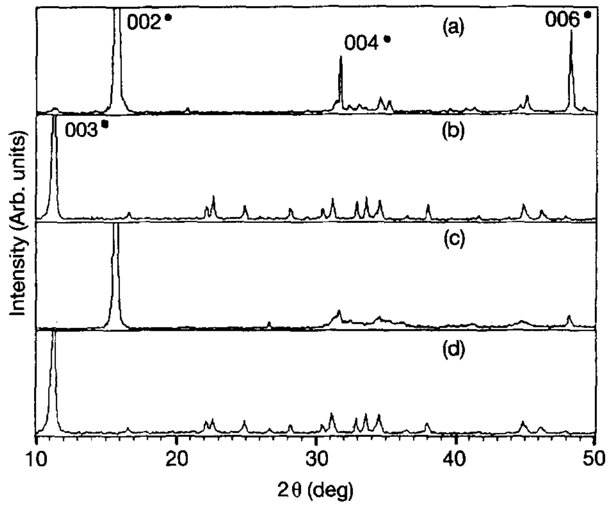

Figure 6 X-ray powder diffraction patterns of a batch of β-Zn(OH)Cl recorded at (a) room temperature, (b) after overnight exposure to moist air, (c) after heating at 180 °C for 30 min, (d) after overnight exposure to moist air. (●) β-Zn(OH)Cl, (■) $Zn_5(OH)_8Cl_2{\cdot}H_2O$.

$$5\beta\text{-Zn(OH)Cl} + 3H_2O \xrightarrow{\text{Room temp. 12 h}} Zn_5(OH)_8Cl_2\cdot H_2O + 3HCl \qquad (5)$$

$$\Big\updownarrow \begin{array}{l}180\ {}^\circ C\\ 20\ \text{min}\end{array}$$

$$3HCl + 3ZnO \rightarrow \begin{cases} 2\beta\text{-Zn(OH)Cl} + 3ZnO + 3H_2O & (6)\\ 3\beta\text{-Zn(OH)Cl} & (7)\end{cases}$$

HCl formed in Reaction 5 remains somehow retained by the basic hydroxide chloride; it reacts with the ZnO formed in Reaction 6, yielding β-Zn(OH)Cl that transforms to the more basic 4:1 hydroxide chloride with atmospheric moisture. These processes can be indefinitely repeated as long as HCl is not completely removed during the heating–cooling cycles.

On the other hand, when β-Zn(OH)Cl is left standing in D_2O vapour, deuterated zinc(II) hydroxide chloride is obtained; the i.r. spectrum is shown in Fig. 7b. Bands at 3500, 1035, 900 and 720 cm^{-1} in the spectrum of $Zn_5(OH)_8Cl_2 \cdot H_2O$ (Fig. 7a) shift to lower frequencies on deuteration, with a ν_H/ν_D ratio falling within the 1.30–1.35 range. The absorption at 460 cm^{-1} is only partially affected on deuteration. The intensity of this band is smaller in the deuterated compound, and it could correspond to the broad one centred at 340 cm^{-1}. Bands appearing at 275 and 195 cm^{-1} do not shift, confirming the assignment of the former one to ν(Zn–Cl) [14].

4. Discussion

From the results indicated above it follows that, during the decomposition reaction of $Zn_5(OH)_8Cl_2 \cdot H_2O$, β-Zn(OH)Cl and $ZnCl_2$ are formed as intermediate products. Depending on experimental conditions, the hydrolysis of the latter compound is more or less favoured and, according to this, two different mechanisms can be proposed (square brackets indicate non-isolated or proposed intermediates):

(a) Still atmosphere, high heating rate (10 °C min^{-1}):

$$Zn_5(OH)_8Cl_2 \cdot H_2O \xrightarrow{145-192\,^{\circ}C}$$

$$2\beta\text{-}Zn(OH)Cl + 3ZnO + 4H_2O\uparrow \xrightarrow{192-219\,^{\circ}C}$$

$$[ZnCl_2 + \tfrac{1}{2}H_2O] + 4ZnO + \tfrac{1}{2}H_2O\uparrow \xrightarrow{219-602\,^{\circ}C}$$

$$[\tfrac{1}{2}ZnCl_2\uparrow + HCl\uparrow] + \tfrac{1}{2}ZnO + 4ZnO \equiv 4.5ZnO$$

A similar scheme accounts for the thermal behaviour of $Zn_5(OH)_8Cl_2 \cdot H_2O$ when it is decomposed in air flow at 5 °C min^{-1}. However, under these conditions slightly larger amounts of both $ZnCl_2$ and water are removed and accordingly a smaller fraction of $ZnCl_2$ is hydrolysed to ZnO. In the former case (still air and 10 °C min^{-1}) the experimental weight loss corresponds to the formation of 4.6 mol of ZnO, whereas in air flow and 5 °C min^{-1} heating rate the experimental weight loss corresponds to the formation of 4.47 mol ZnO.

(b) Still atmosphere, low heating rate (1 °C min^{-1}):

$$Zn_5(OH)_8Cl_2 \cdot H_2O \xrightarrow{100-160\,^{\circ}C}$$

$$2\beta\text{-}Zn(OH)Cl + 3ZnO + 4H_2O\uparrow \xrightarrow{160-194\,^{\circ}C}$$

$$\rightarrow [ZnCl_2 + H_2O] + 4ZnO \xrightarrow{194-447\,^{\circ}C}$$

$$5ZnO + 2HCl\uparrow \equiv 5ZnO$$

In these conditions, $ZnCl_2$ is fully hydrolysed to ZnO at 447 °C. A similar reaction scheme can account for the thermal behaviour of β-Zn(OH)Cl in still air. Melted $ZnCl_2$ is partially hydrolysed to ZnO according to the reaction

$$2\beta\text{-}Zn(OH)Cl \xrightarrow{217-260\,^{\circ}C} [\tfrac{1}{2}ZnCl_2 + \tfrac{1}{2}H_2O]$$

$$+ \tfrac{1}{2}ZnCl_2\uparrow + ZnO + \tfrac{1}{2}H_2O\uparrow$$

$$\xrightarrow{350-730\,^{\circ}C} \tfrac{1}{2}ZnO + HCl\uparrow + ZnO \equiv 1.5ZnO$$

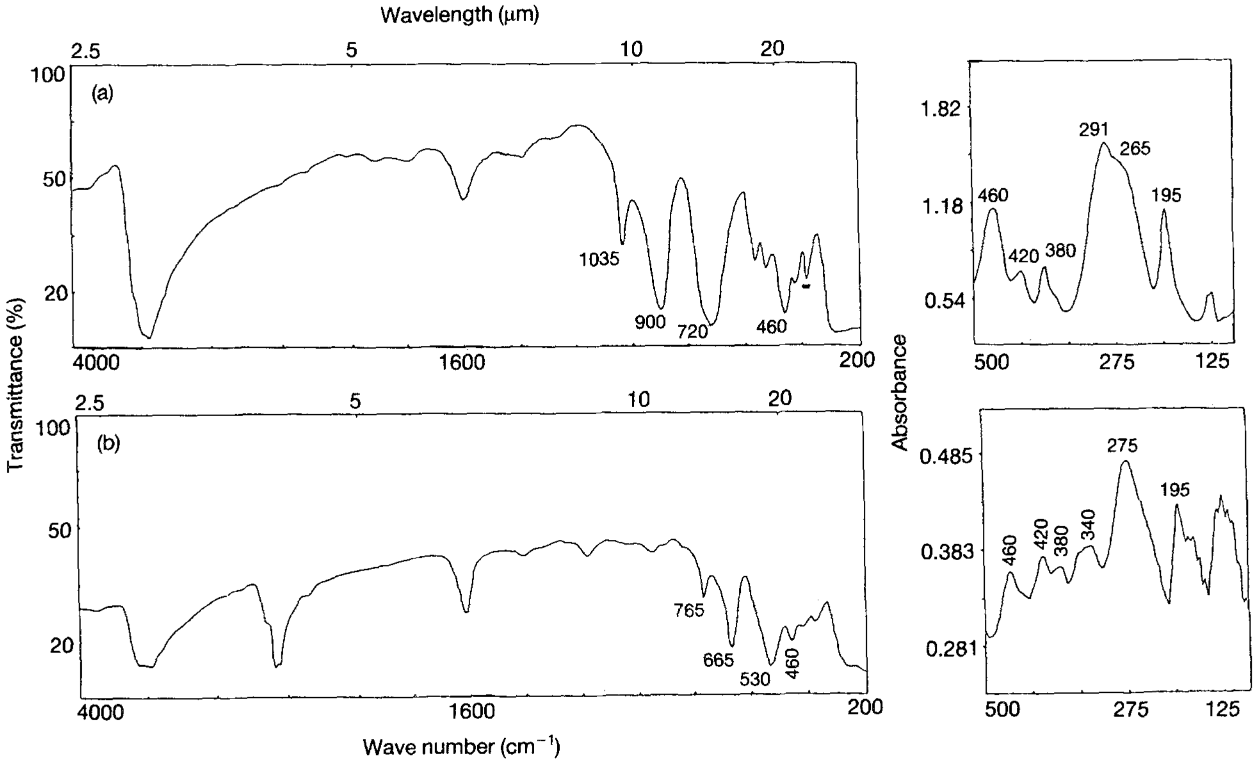

Figure 7 Infrared spectra of (a) $Zn_5(OH)_8Cl_2 \cdot H_2O$, (b) partially deuterated $Zn_5(OH)_8Cl_2 \cdot H_2O$.

The endothermic effect at 290 °C that corresponds to the melting of $ZnCl_2$, is only observable in the β-Zn(OH)Cl DTA curve, whereas the endothermic effect recorded at 200 °C in the DTA curve of $Zn_5(OH)_8Cl_2 \cdot H_2O$ has to be attributed to the decomposition reaction of β-Zn(OH)Cl. In the former case, the relatively higher amount of $ZnCl_2$ allows the observation of the melting process.

5. Conclusions

Several reaction schemes are proposed to give account for thermal decomposition reactions undergone by $Zn_5(OH)_8Cl_2 \cdot H_2O$ and β-Zn(OH)Cl under different experimental conditions.

From thermal analysis and X-ray powder diffraction studies we can infer a decisive role for $ZnCl_2$, which can undergo two different reactions: it can either hydrolyse to ZnO or react with ZnO to yield β-Zn(OH)Cl. The former reaction seems to be the overriding factor at high temperature and accounts for the thermal behaviour of both basic hydroxide chlorides studied here, as well as for the differences observed among the experimental weight losses. The latter reaction takes place at room temperature; highly hygroscopic $ZnCl_2$ hydrates on cooling and reacts with ZnO leading to the formation of β-Zn(OH)Cl. This reaction can explain the reversibility of 4:1 to 1:1 basic hydroxide chloride transformations.

It is worth mentioning that X-ray patterns recorded from $Zn_5(OH)_8Cl_2 \cdot H_2O$ at temperatures below 190 °C always show the ZnO diffraction maxima non-systematically shifted from their typical positions. This result cannot be explained in terms of the small particle size of ZnO.

From observation of the i.r. spectra it can be pointed out that (–OD) groups enter the β-Zn(OH)Cl structure, which transforms to $Zn_5(OH)_8Cl_2 \cdot D_2O, H_2O$.

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