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Crystal Structure and Temperature-Resolved Powder Diffractometry of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$

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A new cadmium hydroxide nitrate $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ was prepared by an interdiffusion method. It is monoclinic with the cell parameters a = 18.931(3) Å, b = 6.858(2) Å, c = 5.931(1) Å, β = 94.85(2)°; the space group is $C2/m$ with $Z = 2$. The crystal structure has been solved from single-crystal data by means of Patterson and Fourier synthesis (R = 0.043, 2218 hkl). The structure, related to the brucite type, is built up from OH^- ion layers parallel to (100) with $\frac{3}{4}$ of the octahedral holes filled with cadmium atoms. The remaining metal atoms are located above and below the empty octahedral sites; they are sixfold coordinated by three OH^-, one water molecule, and one bidentate nitrate group. The thermal decomposition of this compound was investigated by means of TRXD and TG methods. It proceeds in four or three stages, depending upon the environmental atmosphere. Under vacuum, the hemihydrate $Cd_5(OH)_8(NO_3)_2 \cdot 0.5H_2O$ is obtained during the first stage, whereas a new anhydrous hydroxide nitrate is displayed in the second one. © 1991 Academic Press, Inc.

Introduction

New stoichiometric cadmium hydroxide nitrates have recently been described (*1*). The hydroxide nitrate $Cd_3(OH)_5NO_3$ was observed during the interdiffusion of ammonia in an aqueous solution of cadmium nitrate and α-$Cd(OH)NO_3$ was identified by means of temperature-resolved X-ray diffractometry (TRXD). In the latter case, the technique used, based on a conventional X-ray source, combined with a position-sensitive detector, was clearly a useful tool for tracing structural changes which occur during the thermal decomposition of this kind of solid. Although, from a general point of view, hydroxysalts are frequently considered as disordered nonstoichiometric phases, it is clear that chemically well-defined solids have been reported for cadmium hydroxide nitrates, e.g., $Cd(OH)NO_3 \cdot H_2O$ (2), β-$Cd(OH)NO_3$ (2,3), $Cd_3(OH)_5NO_3$, and α-$Cd(OH)NO_3$ (*1*). Among the crystal structures known for these materials, two have a layered structure related to β-$Cd(OH)_2$; generally, the structures present more interesting features when the amount of substituting anion is low compared with the hydroxyl content, e.g., $Cd_3(OH)_5NO_3$ (*4*). In the course of synthesis of cadmium hydroxide nitrates, rich in hydroxyl anions and water molecules, a new dihydrate compound $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ was prepared. From the indexing of the X-ray diffraction powder pattern (*5*), unit cell parameters comparable to those of the related zinc compound, $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (*6*), were detected. However, it was noted that, in spite of a greater atomic radius for the cadmium atom, an interlayer spacing of 18.856 Å was calcu-

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lated, which is less than the value 19.448 Å observed for the zinc compound. In order to explain this effect the structure of the cadmium compound is needed. The present paper deals with the crystal structure determination of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and its thermal decomposition scheme studied by TRXD and the further thermal analysis methods.

Experimental Considerations

Synthesis

Crystals of cadmium hydroxide nitrate $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ were produced at 5°C by means of an interdiffusion method in aqueous media (*7*). By means of a pipette, a 2 M solution of cadmium nitrate was introduced into a glass container which was three-quarters full of distilled water. The container was connected to a similar one filled with 2 M ammonia. After a few days, powder and some crystals having a platelet shape were deposited on the walls of the first container. Chemical analysis of metal element and TG measurements confirmed the chemical formula.

TG Analysis

TG analysis was carried out with a Rigaku Thermoflex TG-DSC. Powder samples of about 10 mg were spread evenly, in a large platinum sample holder in order to avoid mass effects and to reproduce as much as possible the same conditions as were used in the TRXD study. The samples were heated with a heating rate of $5°C \cdot h^{-1}$.

TRXD Analysis

Temperature-resolved powder diffractometry of powdered cadmium hydroxide nitrate was carried out by means of an INEL (CPS 120) curved position-sensitive detector which allows a simultaneous recording of a powder pattern over a range of 120°. The detector was used in a semifocusing arrangement by reflection. The X-ray generator operated at 40 kV and 44 mA. Monochromatic Cu$K\alpha_1$ radiation (λ = 1.540598 Å) was selected by means of an incident-beam curved-crystal quartz monochromator with asymmetric focusing (short focal distance = 130 mm, long focal distance = 510 mm). The stationary powder sample is located at the center of the goniometer and intercepts the convergent X-ray beam, which is focused on the goniometer circle. The PSD coincides with the goniometer circle. A fixed angle θ_i of 6° between the incident beam and the surface of the sample was selected. In spite of unavoidable defocusing and axial divergence effects, the instrumental resolution was about 0.12°(2θ) at 40°(2θ). The sample was located in a monitored high-temperature X-ray diffractometer attachment (Rigaku) designed to maintain the specimen in a vacuum, inert gas, or ambient atmosphere. To avoid mass effects during the decomposition, the powder was deposited in a thin layer on a nickel grid used as a sample holder. The decomposition was carried out at a heating rate of $5°C \cdot h^{-1}$ in nitrogen, static air, or vacuum. In this latter case, the reaction chamber was connected to the vacuum pump through a liquid nitrogen trap. Owing to the slow heating rate, a counting time of 2000 sec was selected to ensure better counting statistics. The integrated intensities of some lines were obtained by means of a least-squares profile fitting program available in the Siemens DIFFRAC-11 software.

Structure Solution and Refinement

Single-crystal data were measured on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects. Empirical absorption correction was applied using the program DIFABS (*8*). Unit-cell parameters (a = 18.931(3) Å, b = 6.858(2) Å, c = 5.931(1) Å, β = 94.85(2)°) were obtained from a least-squares fitting of the setting angles for 25 well-centered reflections; these were in agreement with the solution derived from the automatic indexing of the powder diffraction pattern (*5*). The space group, determined from Weissenberg photographs, is either *C*2, *Cm* or *C*2/*m*, with systematic *hkl* absences for $h + k = 2n + 1$. On the basis of the centrosymmetric habit of the crystals, the space group *C*2/*m* was adopted and was subsequently found to be correct. A total of 3640 intensities were obtained with the $\omega/2\theta$ scanning mode and with a wide detector opening for $d = 2.50 \pm 0.50\ tg\theta$ (mm). Within this set, 2218 unique reflections were found. No significant variation of the standard reflections was observed during the data collection. The structure was solved by the heavy-atom method, which yielded the positions of the three independent cadmium atoms. The remaining atoms, N and six O, were obtained from normal Fourier methods. The results confirmed the presence of two water molecules in the compound. The final values of R and $R\omega$ ($\omega^{-1} = \sigma^2(F) + (0.04\ |F_0|)^2$), including anisotropic thermal parameters for all atoms, were 0.043 and 0.068, respectively. Atomic scattering factors were taken from "International Tables for X-ray Crystallography" (*9*). All calculations were performed on a PDP 11-60 computer by means of the SDP programs (*10*). The final atomic parameters with equivalent temperature factors are given in Table I and selected bond distances and angles are listed in Table II.

TABLE I

$Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$: POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	*x*	*y*	*z*	B_{eq}(Å^2)
Cd1	0	0	0	1.036(4)
Cd2	0	0.25410(3)	0.5	1.143(3)
Cd3	0.39410(1)	0	0.96930(4)	1.108(3)
OH1	0.0680(1)	0.5	0.3710(4)	1.27(3)
OH2	0.9318(1)	0.2397(3)	0.1539(3)	1.27(3)
OH3	0.0580(1)	0	0.3477(4)	1.16(3)
O1	0.2159(1)	0.3423(4)	0.2122(5)	2.22(4)
O2	0.8129(2)	0	0.3160(9)	2.99(8)
O(H_2O)	0.8072(2)	0.5	0.2748(6)	1.96(5)
N	0.7489(2)	0	0.2497(6)	1.80(5)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}\ \Sigma_i\Sigma_j B_{ij}\ (\mathbf{a}_i \cdot \mathbf{a}_j)$.

TABLE II

PRINCIPAL INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$

Cd1–OH2	(×4)	2.324 (2)	OH2–Cd1–OH3	(×4)	83.33 (6)
Cd1–OH3	(×2)	2.253 (2)		(×4)	96.67 (6)
Cd2–OH1	(×2)	2.291 (1)	OH1–Cd2–OH1		85.27 (8)
Cd2–OH2	(×2)	2.332 (2)	OH2–Cd2–OH2		171.2 (1)
Cd2–OH3	(×2)	2.285 (1)	OH3–Cd2–OH3		80.69 (8)
			OH1–Cd2–OH2	(×2)	91.24 (7)
				(×2)	92.33 (7)
			OH1–Cd2–OH3	(×2)	97.27 (6)
				(×2)	174.20 (7)
			OH2–Cd2–OH3	(×2)	82.42 (7)
				(×2)	93.86 (7)
Cd3–OH1		2.199 (2)	OH1–Cd3–OH2	(×2)	110.03 (5)
Cd3–OH2	(×2)	2.182 (2)	OH1–Cd3–O1	(×2)	85.95 (8)
Cd3–O1	(×2)	2.506 (2)	OH1–Cd3–H_2O		159.0 (1)
Cd3–H_2O		2.548 (4)	OH2–Cd3–OH2		109.81 (1)
			OH2–Cd3–O1		142.45 (8)
					95.00 (8)
			OH2–Cd3–H_2O	(×2)	81.16 (7)
			O1–Cd3–O1		51.1 (1)
			O1–Cd3–H_2O		75.1 (1)
Possible hydrogen bonds					
OH3–O2		3.023 (5)	O1–H_2O–O1		107.0 (2)
H_2O–O1	(×2)	2.919 (3)			
Nitrate group					
N–O1	(×2)	1.267 (3)	O1–N–O1		117.1 (3)
N–O2		1.225 (5)	O1–N–O2	(×2)	121.4 (2)

Description and Discussion of the Structure

This structure consists of three independent cadmium atoms coordinated by six O atoms as shown in Fig. 1. Cd1 and Cd2 (Table II) are bonded to six hydroxyl groups with bond lengths ranging from 2.253 to 2.332 Å. The more distorted octahedral coordination of Cd3 arises from three OH groups (OH1–2), one water molecule, and

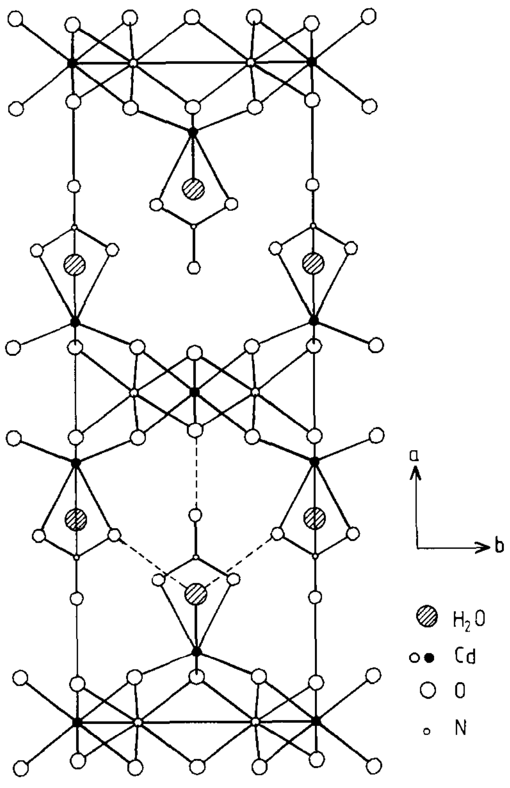

FIG. 1. Projection of the crystal structure along [001], (O, Cd (z = 0.5); ●, Cd (z = 0)).

two oxygen atoms (O1) from the symmetric-bidentate nitrate group. The Cd3–O distances are in the range 2.182 to 2.548 Å. Each OH group is bonded to three cadmium atoms and the water molecule to only one cadmium atom (Cd3). The structure of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ can be described as deriving from the brucite type. It consists of infinite layers of closest-packed hydroxyls parallel to (100). Figure 1 clearly shows the direction of packing. It can be seen that, for each layer, three quarters of octahedral holes are filled with three cadmium atoms (Cd1, Cd2); pairs of cadmium atoms (Cd3) are located out of the layer, on both sides of the empty sites. The water molecule and two oxygen atoms of the nitrate group complete the coordination of these cadmium atoms (Fig. 2a). There are two such layers in the unit cell. The distances O2–OH3 (3.023 Å) and H_2O–O1 (2.919 Å) and the angle O1–H_2O–O1 (107°) are consistent with hydrogen bonds between two adjacent layers, as shown by dotted lines in Fig. 1.

As expected from the comparison between their unit cell parameters, the structures of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (*6*) appear sensibly different. In the zinc hydroxysalt, the heavy atom located on both sides of the brucite-like sheets is fourfold coordinated by three hydroxyl groups and one water molecule (Fig. 2b); moreover, the nitrate group does not take part in coordination of the cations and can be easily substituted by a chlorine anion to give the corresponding hydroxide chloride (*11*). On the other hand, in the cadmium hydroxysalt the nitrate group is bidentate and completes the sixfold coordination of Cd3 (Fig. 2a); this coordination explains the reduction of the interlayer spacing (18.856 Å for $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ compared with 19.448 Å for $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$). It is interesting to observe the high distortion of the Cd3 octahedron: the OH–Cd–OH angles are close to 109° and the three OH groups could be considered as the base of a tetrahedron; the Cd3–O(H_2O) and Cd3–O(NO_3) distances (2.548 Å and

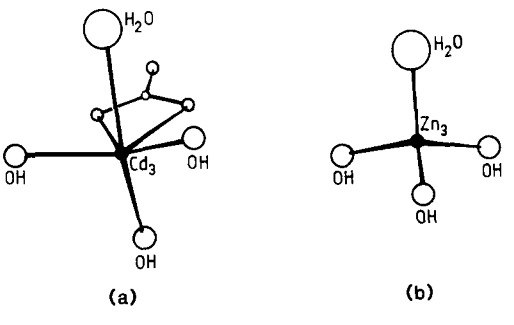

FIG. 2. A perspective view of (a) Cd3 polyhedron in $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ and (b) Zn3 polyhedron in $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$.

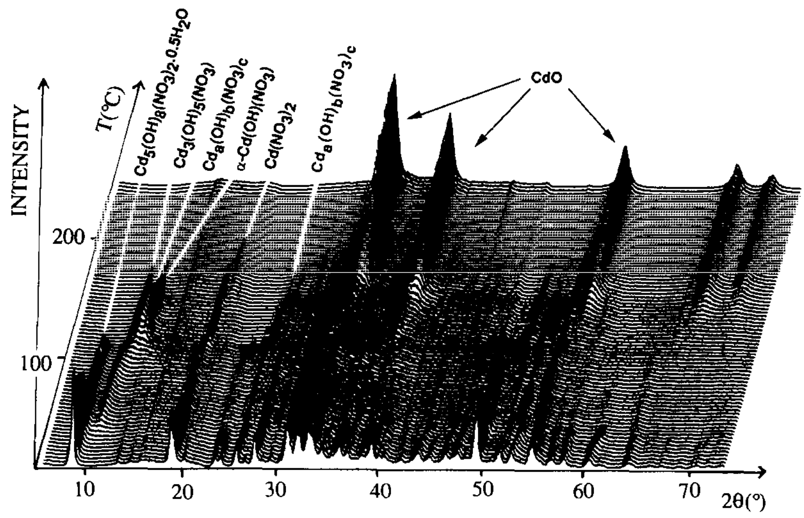

FIG. 3. The TRXD plot of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ in vacuum (heating rate: 5°C · h^{-1}, counting time for each pattern: 2000 sec, pressure: 13.10^{-3} Pa). Intermediate and final phases are indicated by arrows.

2.506 Å, respectively) are significantly longer than the average Cd–OH distance (2.267 Å). The atomic positions are quite identical in the two compounds except for the water molecule and the nitrate group. This latter, lying in the mirror plane of $C2/m$ in the zinc compound, is normal to the mirror and closer to the D_{3h} symmetry in the cadmium compound. Finally, it can be concluded that the cadmium hydroxysalts are characterized by their great variety, in so far as the cadmium atom exhibits five-, six-, and eightfold coordination but rarely fourfold.

Thermal Decomposition: Effects of Environment

Thermal Decomposition in Vacuum

The three-dimensional representation of the evolution of the powder diffraction patterns with temperature (Fig. 3) shows that the decomposition of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ into the final product CdO is rather complex, due to the fact that several phases appear simultaneously and are poorly crystallized. A more detailed picture of the mechanism of these complex transformations can be seen from Fig. 4, which represents the changes of integrated intensities of some X-ray diffraction lines and the TG curve. These figures show that the complete decomposition proceeds through four stages.

First stage. This is characterized by a large decrease in the intensity of the *h*00 and *hk*0 lines and the vanishing of the *hkl* lines for the precursor, accompanied by the appearance of one intense line (11.05°(2θ)) at about 40°C. It can be pointed out that structural changes (at 35°C) take place after the removal of part of the water molecules from the precursor, as shown by the TG curve. This observation has been confirmed by complementary experiments performed by the "ramp and hold" method which have revealed that $\Delta m/m_0$ increases to about 2.60% at room temperature after 20 h and remains constant for many hours, whereas the initial diffraction pattern is not significantly modified. The decrease of the initial intensities and the appearance of the new

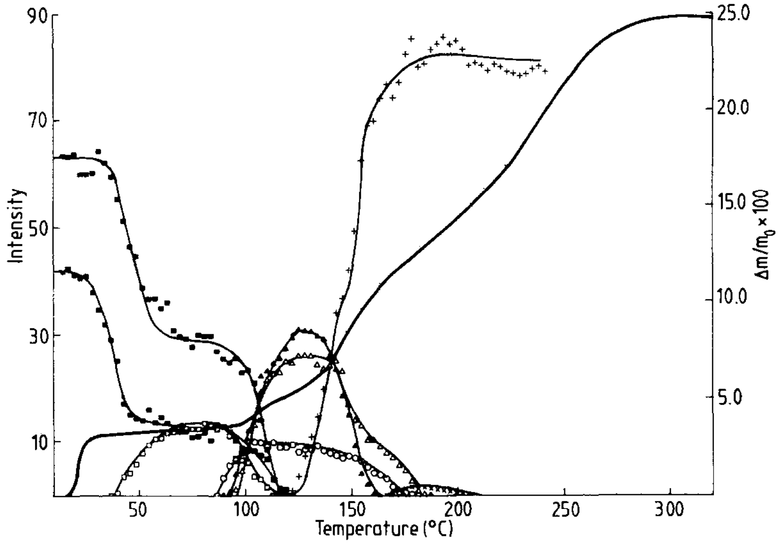

FIG. 4. Integrated intensities of selected diffraction lines vs temperature from the TRXD in vacuum. ■, 200 (9.35°(2θ)) and the cluster of lines (48.00–48.50°(2θ)) of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$; □, line at 11.05°(2$\theta$) of $Cd_5(OH)_8(NO_3)_2 \cdot 0.5H_2O$; △, line at 13.35°(2$\theta$) of α-Cd(OH)($NO_3$); ▲, line at 12.75°(2$\theta$) of $Cd_a(OH)_b(NO_3)_c$; ○, 011 (11.90°(2θ)) $Cd_3(OH)_5(NO_3)$; ×, 111 (26.20°(2θ)) cubic $Cd(NO_3)_2$; +, 220 (55.25°(2θ)) CdO. The full line represents the TG curve.

line (11.05°(2θ)) are only observed near 30°C when $\Delta m/m_0$ reaches 3.20%, no subsequent significant weight loss taking place in the range 30–80°C. This value is in agreement with the loss of 1.5 water molecules (theoretical value: 3.18%).

Figure 5 shows the X-ray diffraction pattern of the initial compound together with the patterns obtained after dehydration at 30 and at 80°C. It can be seen that these latter patterns include the broadened *hkl* lines of the precursor and the new broad line located at 11.05°(2θ). By taking into account the observed weight loss, these could correspond to a hemihydrated salt of formula $Cd_5(OH)_8(NO_3)_2 \cdot 0.5H_2O$. Attempts to index these patterns were unsuccessful, due in part to significant line broadening. Moreover, this broadening is anisotropic as shown by the width of the remaining *h*00, *hk*0 and *hkl* lines from the precursor. For instance, the width of 200 and 400 lines is slightly modified, increasing from 0.09 to 0.15°(2θ) and 0.08 to 0.14°(2θ) respectively, whereas the value for the 310 line ranges from 0.10 to 0.42°(2θ), and, finally, as a consequence of their broadening, all the *hkl* lines merge into the background. These anisotropic changes of the diffraction line broadenings are an indication about the progressive collapsing of the lattice of the precursor. As deduced from the structural study, the planes (*h*00) correspond to the layers, within which the bonds are stronger than the interlayer bonds. So, upon heating, the layers tend to keep their homogeneity, but are progressively disorientated with respect to the others. This could explain the smaller change in the *h*00 line breadths and the increased broadening of the *hkl* lines. Another structural feature concerns the intense line located at 11.05°(2θ), which shifts to 11.35°(2θ) when the sample is heated to 80°C, without significant change in the posi-

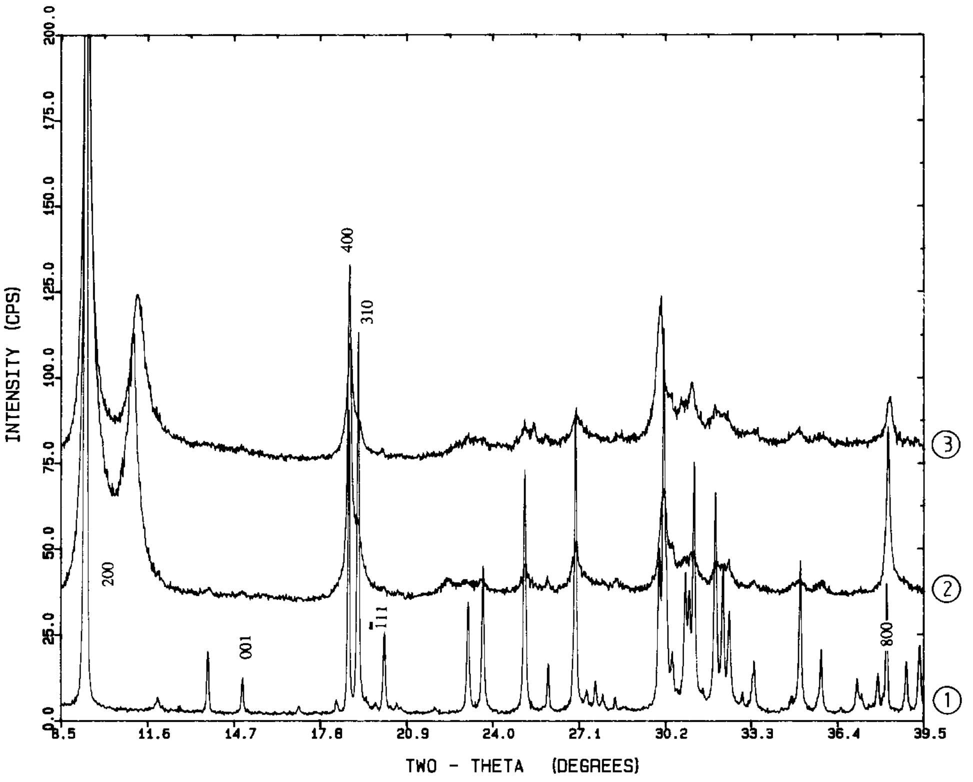

FIG. 5. X-ray powder diffraction patterns of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$: at room temperature (1), heated at 30°C for 20 hr (2) and heated at 80°C (3) (λ = 1.5405981 Å).

tion of the other lines (Figs. 3 and 5). All these pecularities could be related to the slight chemical modification, i.e., loss of part of H_2O molecules, occurring in the solid during the thermal treatment. As described above, the water molecule belongs only to the distorted Cd3 polyhedron (Fig. 2) and has a rather long bond length (2.548 Å). Therefore, it is not inconceivable that this molecule is progressively removed with few structural changes, taking into account that the cadmium atom accepts a smaller coordination.

From the assumption of the formation of a hemihydrated salt, the first stage in the decomposition can be written as follows:

$$Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O_{(cr)} \rightarrow Cd_5(OH)_8(NO_3)_2 \cdot 0.5H_2O + 1.5H_2O_{(g)} \quad (1)$$

Second stage. This takes place between 90 and 125°C and corresponds to the decomposition of the hemihydrated salt into a mixture of $Cd_3(OH)_5(NO_3)$, α-$Cd(OH)(NO_3)$, and a new compound, the amount of which is maximal at about 125°C (Fig. 4). Since CdO does not appear at this stage, it can be assumed that this compound is an anhydrous hydroxide nitrate of formula $Cd_a(OH)_b(NO_3)_c$. In this case, the decomposition reaction can be written as

$$Cd_5(OH)_8(NO_3)_2 \cdot 0.5H_2O_{(cr)} \rightarrow x Cd_3(OH)_5(NO_3)_{(cr)} + y Cd(OH)(NO_3)_{(cr)} + z Cd_a(OH)_b(NO_3)_c + w H_2O_{(g)}. \quad (2)$$

Among the reaction coefficients, only the value of w (0.5) can be estimated from the TG curve. ($\Delta m/m_0$ is close to 4.4% at 120°C, in agreement with the theoretical value, 4.20%, corresponding to the loss of two water molecules.) Unfortunately, no complementary experiments permitted the exact values of *a, b,* and *c* to be determined. However, the chemical formula $Cd_5(OH)_8(NO_3)_2$ can be suggested. Moreover, complementary experiments carried out in air have shown that only $Cd_3(OH)_5(NO_3)$ and α-$Cd(OH)(NO_3)$ resulted from the decomposition of the precursor, with no evidence about the formation of the hemihydrate and the new anhydrous phases. This demonstrates that this anhydrous compound is the result of the decomposition of the hemihydrate only.

Third and fourth stages. Above 135°C (Fig. 4), the decomposition of the three anhydrous hydroxide nitrates occurs almost simultaneously (Eq. (2)). However, the decomposition of $Cd_a(OH)_b(NO_3)_c$ is complete at 160°C, whereas $Cd_3(OH)_5(NO_3)$ and α-$Cd(OH)(NO_3)$ transform into CdO and a small amount of $Cd(NO_3)_2$ at about 180°C. (As previously reported in Ref. (1), $Cd_3(OH)_5(NO_3)$ transforms into CdO and α-$Cd(OH)(NO_3)$, which, in turn, leads to CdO through $Cd(NO_3)_2$.) The last stage corresponds to the disappearance of $Cd(NO_3)_2$ into CdO and is characterized by a great difference between the rate of the structural transformation and the rate of the departure of gases (NO, NO_2, and O_2).

Thermal Decomposition in Nitrogen

Figure 6 shows the change of integrated intensities vs temperature. By comparison with Fig. 4 some differences can be seen. First, the two onset and final temperatures of weight loss correspond well with those of the structural changes. On the other hand, the initial dehydration occurs above 90°C, with the simultaneous formation of $Cd_3(OH)_5(NO_3)$, α-$Cd(OH)(NO_3)$, and the compound with the suggested formula $Cd_5(OH)_8(NO_3)_2$. Moreover, the intense line located at 11.05°(2θ) of $Cd_5(OH)_8(NO_3)_2 \cdot 0.5H_2O$ is not observed during this first part of the process, although the integrated intensity lines for the precursor exhibit a constant value over the short temperature range 105–115°C. In this region, the ratio of the intensities of lines (200 for instance) observed after and before their decrease is close to 0.15. Compared with the value of 0.40 estimated when the decomposition is performed under vacuum, it indicates that the amount of $Cd_5(OH)_8(NO_3)_2 \cdot 0.5H_2O$, formed simultaneously with the other compounds is so small that it could explain the lack of the line at 11.05°(2θ). It could also be argued that this line shifts upon heating and that its position is very close to the line 011 of $Cd_3(OH)_5(NO_3)$, so that it is difficult to locate its position.

The TG curve indicates that the transformation of the precursor into the three hydroxysalts is characterized by a weight loss of 4.5%, which corresponds to the departure of two water molecules. Consequently, the first step of the decomposition can be considered as the superposition of reactions (1) and (2). Upon further heating, CdO is formed and a simultaneous increase of the amount of α-$Cd(OH)(NO_3)$ is observed in the range 150–180°C. This observation allows us to assume that the thermal decomposition of $Cd_5(OH)_8(NO_3)_2$ is similar to that of $Cd_3(OH)_5(NO_3)$, with the simultaneous formation of CdO and α-$Cd(OH)(NO_3)$; this latter being the most thermodynamically stable phase of the cadmium hydroxide nitrates. The two last stages concern the decomposition of α-$Cd(OH)(NO_3)$ and $Cd(NO_3)_2$ as previously described (*1*).

Conclusion

A new cadmium hydroxide nitrate $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$, characterized by a low nitrate content was prepared by means of an interdiffusion method. Its structure is related to the brucite-type and has been compared with those of the similar com-

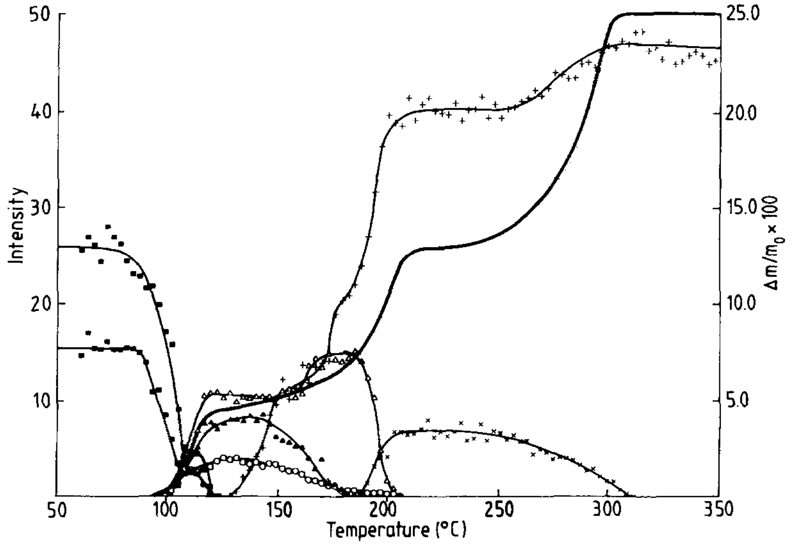

FIG. 6. Integrated intensities of selected diffraction lines vs temperature from the TRXD in nitrogen atmosphere. ■, 200 (9.35°(2θ)) and the cluster of lines (48.00–48.50°(2θ)) of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$; △, line at 13.35°(2$\theta$) of α-$Cd(OH)(NO_3)$; ▲, line at 12.75°(2θ) of $Cd_a(OH)_b(NO_3)_c$; ○, 011 $Cd_3(OH)_5(NO_3)$; ×, 111 cubic $Cd(NO_3)_2$; +, 220 CdO. The full line represents the TG curve.

pound $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, which belongs to the structural type IIb of the structural classification of hydroxide nitrates with bivalent metal (*13*). The two structures differ by the role played by the nitrate group. It is bidentate and directly involved in the sixfold coordination of the metal atom located on either side of the octahedral sheet in the cadmium hydroxysalt, while it is intercalated between the layers in the zinc compound and there is tetrahedral coordination of the zinc atom on the outer surfaces of the layers. The thermal behavior of the new compound has been analyzed and the various stages which occur during the decomposition process have been clearly displayed by means of the TRXD technique. From this detailed study, the TRXD analysis confirms its particular strength for observing *in situ* dynamical processes and for making conspicuous new compounds, often unstable at room temperature. It greatly contributes to the understanding of chemical transformations and it appears as a necessary complement to other conventional thermal analysis methods, particularly when several compounds are formed simultaneously. From both TRXD and TG results, the existence of a new compound $Cd_5(OH)_8(NO_3)_2 \cdot 0.5H_2O$ is noted. Moreover, the second stage of the decomposition shows the simultaneous formation of α-$Cd(OH)(NO_3)$, $Cd_3(OH)_5(NO_3)$, and another anhydrous hydroxysalt with the suggested formula $Cd_5(OH)_8(NO_3)_2$. By acting on the reactional environment, it has been concluded that this latter hydroxysalt derives directly from the hemihydrated salt. Another peculiar feature concerns the discrepancy between the rate of the structural changes and that of weight loss recorded. For instance, when the decomposition is performed under vacuum, TRXD analysis has clearly shown that the structural transformation proceeds after the dehydration, whereas in the last stage it occurs before the removal of gases which remain adsorbed on the microcrystalline cadmium oxide. Finally, it can be concluded that the thermal decomposition scheme of $Cd_5(OH)_8(NO_3)_2 \cdot 2H_2O$ is totally different to that observed for $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (*14*), since this latter decomposes in the corresponding anhydrous compound, stable between 110 and 125°C. The differences reported for the crystal structure of both solids explain these properties.

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