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Journal of Physics and Chemistry of Solids 65 (2004) 1213-1221

JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS

www.elsevier.com/locate/jpcs

X-ray diffraction, ¹³³Cs and ¹H NMR and thermal studies of CdZrCs_{1.5}(H₃O)_{0.5}(C₂O₄)₄·x H₂O displaying Cs and water dynamic behavior

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Received 18 September 2003; revised 7 January 2004; accepted 21 January 2004;

Available online 4 March 2004

Abstract

A novel mixed cadmium zirconium cesium oxalate with an open architecture has been synthesized from precipitation methods at room pressure. It crystallizes with an hexagonal symmetry, space group $P3_112$ (no. 151), a = 9.105(5) Å, c = 23.656(5) Å, V = 1698(1) Å³ and Z = 3. The structure displays a $[CdZr(C_2O_4)_4]^{2^-}$ helicoidal framework built from CdO₈ and ZrO₈ square-based antiprisms connected through bichelating oxalates, which generates channels along different directions. Cesium cations, hydronium ions and water molecules are located inside the voids of the anionic framework. They exhibit a dynamic disorder which has been further investigated by ¹H and ¹³³Cs solid-state NMR. Moreover a phase transition depending both upon ambient temperature and water vapor pressure was evidenced for the title compound. The thermal decomposition has been studied in situ by temperature-dependent X-ray diffraction and thermogravimetry. The final product is a mixture of cadmium oxide, zirconium oxide and cesium carbonate.

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Keywords: C. X-ray diffraction; D. Crystal structure; D. Nuclear magnetic resonance; D. Phase transitions

1. Introduction

Recent studies on mixed cadmium–zirconium oxalates have revealed the existence of a family of phases with structural arrangements based on MO₈ (M = Cd, Zr) polyhedra connected by bichelating oxalate groups [1–4]. Two open structure frameworks have been pointed out in the family [2,3]. Both of them are built from $[CdZr(C_2O_4)_4]^{2-}$ anionic groups forming two different frameworks with a topology originating from the two frequent configurations in the stereochemistry of eight-fold coordination, i.e. the dodecahedron and the square antiprism [5,6]. With dodecahedra, the structure is built from a net of perpendicular zigzag chains with a (-Cd-oxalate–Zr-oxalate–)_∞ sequence and exhibits tunnels with square cross-sections. Representative examples with counter-cations adopting also an eight-fold coordination are $Cd_2Zr(C_2O_4)_4$ ·6H₂O [1] and $CdZrK_2(C_2O_4)_4$ · 8H₂O [2], in which the anionic framework is counterbalanced by one Cd^{2+} or two K^{+} cations, respectively, located in the voids of the structures. The topology of the anionic framework based on square antiprism polyhedra presents an hexagonal symmetry and is built from interconnected helical chains exhibiting a sequence similar to that found in the zigzag chains. The cations located inside the channels parallel to the *c*-axis counterbalance the anionic framework. This structure has been reported for three compounds with inserted (metallic and organic) cations of different charges, i.e. CdZr(NH₄)₂(C₂O₄)₄·3.9- H_2O [3], $CdZr(C_2N_2H_{10})(C_2O_4)_4 \cdot 4.4H_2O$ [3] and $CdZrNa_2(C_2O_4)_4 \cdot 8.5H_2O$ [4]. For the last material, a dynamic disorder of the cations and water molecules located inside the channels was pointed out from singlecrystal X-ray diffraction and ¹H and ²³Na solid-state NMR. These properties have motivated the investigation of new

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^{0022-3697/\$ -} see front matter @ 2004 Elsevier Ltd. All rights reserved. doi:10.1016/j.jpcs.2004.01.008

phases involving an alkaline element. The present study deals with the new cesium-based compound, its crystal structure determination from X-ray diffraction, its thermal behavior and the use of ¹³³Cs and ¹H solid-state NMR to investigate the dynamic disorder inside the channels of the structure framework.

2. Experimental section

2.1. Synthesis and primary characterization

Crystals of the ternary cadmium zirconium cesium oxalate were obtained through a mild chemistry route. The title compound was synthesized from a mixture of 0.5 g of cadmium nitrate $Cd(NO_3)_2 \cdot 4H_2O$ (Merck), 0.37 g of zirconium hydroxynitrate (Alpha) and 1.12 g cesium nitrate CsNO₃ (Aldrich), dissolved in 50 ml of deionized water. A white precipitate was formed from the titration of this solution by an aqueous solution of oxalic acid (0.1 mol 1^{-1}) in excess. The solution was then heated to ~333 K and ~3 ml of concentrated nitric acid were slowly poured in, under constant stirring, until complete dissolution of the previous precipitate. The evaporation of small transparent bipyramidal crystals. These crystals were subsequently washed with water and ethanol, and dried under air.

Even though the structure framework topology of this new cesium phase is analogous to that of previously reported compounds $CdZrA(C_2O_4)_4 \cdot x H_2O$ [A = Na₂, $(NH_4)_2$, $(C_2N_2H_{10})$] [3,4], the title compound possesses interesting features. One of these concerns its nonstoichiometry in cesium which is to be associated with cationic exchange properties. The proposed chemical formula of the compound studied here is CdZrCs_{1.5} $(H_3O)_{0.5}(C_2O_4)_4 \cdot x H_2O$. This formulation was derived from energy dispersive spectroscopy performed using a JSM 6400 spectrometer equipped with an Oxford Link Isis analyzer and atomic absorption spectroscopy analysis with a VARIAN SpetrAA 10 plus. The mean value, found from nine energy dispersive spectroscopy analyses on Cd, Zr and Cs, is 1.5(3) cesium atom per formula unit. This value was confirmed by eight Cd and Cs atomic absorption analyses, which gave a number of 1.4(1) cesium atom per formula unit. The structure solution from single-crystal X-ray diffraction data did not allow to confirm the amount of cesium atoms because of a disorder phenomenon, which is discussed in this study. The number of cesium atoms determined does not counterbalance the anionic charge of the oxalate anions. It is thus necessary to consider that other positive charges are present. As expected from the synthesis, no other heavy atom (Z > 8) was detected by EDS. Consequently, according to the acidic solution used in the preparation, it is reasonable to suggest the presence of H_3O^+ ions. Moreover, the content in hydronium ions, together with Cs⁺, is consistent with weight losses observed

during the thermogravimetric analysis presented in this study.

2.2. Single-crystal data collection

A suitable single crystal was carefully selected. Intensity data were collected on a four-circle Nonius KappaCCD diffractometer equipped with a CCD area detector through the program COLLECT [7]. Lorentz-polarisation factor correction, peak integration and background determination were carried out with the program DENZO [8]. Frame scaling and unit-cell parameters refinement were made with the program SCALEPACK [8]. Numerical absorption correction was performed by modeling the crystal faces using NUMABS [9], included in the WinGX program platform [10]. The resulting set of *hkl* reflections was used for structure refinement. Crystallographic data and details on data collection and refinement are listed in Table 1. Structure drawings were carried out with Diamond 2.1e, supplied by Crystal Impact [11].

2.3. Collection of X-ray powder diffraction data

X-ray powder diffraction data were obtained with a Siemens D500 diffractometer with the parafocusing Bragg– Brentano geometry, using monochromatic Cu K α_1 radiation ($\lambda = 1.5406$ Å) selected with an incident beam curved-crystal germanium monochromator [12]. For pattern

Table 1

Crystallographic data and structure refinement parameters for the anionic framework $[CdZr(C_2O_4)_4]^{2-}$ in the compound $CdZrCs_{1.5}(H_3O)_{0.5}(C_2O_4)_4$. $x H_2O$

Empirical formula	$[CdZr(C_2O_4)_4]^{2-}$
Crystal system	Hexagonal
Space group	<i>P</i> 3 ₁ 12 (No. 151)
Crystal size (mm)	$0.05 \times 0.05 \times 0.05$
a (Å)	9.105(5)
c (Å)	23.656(5)
V (Å ³)	1698(1)
Ζ	3
λ (Μο Κα), Å	0.71073
θ range (°)	2.58-36.72
Index ranges	$-15 \le h \le 15,$
	$-12 \le k \le 12,$
	$-39 \le l \le 39$
Unique data	5451
Observed data $(I > 2\sigma(I))$	2864
$R_1 (I > 2\sigma(I))$	0.048
R_1 (All)	0.091
$\omega R_2 \ (I > 2\sigma(I))$	0.141
ωR_2 (All)	0.157
Refinement method	Full-matrix
	least-squares on $ F^2 $
Goodness of fit	0.973
No. of variables	121
Largest difference map peak and hole (e $Å^{-3}$)	0.709 and -1.648

indexing, the extraction of the peak positions was carried out with the Socabim program PROFILE, which is a part of the DIFFRACT-AT software package supplied by Bruker AXS. Pattern indexing was performed with the program DICVOL91 [13] and full-pattern matching with FULL-PROF [14], available in the software package WinPLOTR [15]. Temperature-dependent X-ray diffraction (TDXD) was performed under dynamic air with a powder diffractometer combining the curved-position-sensitive detector from INEL (CPS 120) and a high-temperature attachment from Rigaku. The detector was used in a semi-focusing arrangement by reflection (Cu K α_1 radiation) as described elsewhere [16].

2.4. NMR measurements

The spectra were recorded at room temperature on a ASX 300 Bruker spectrometer operating at 300 MHz for ¹H (I =1/2) and 39.35 MHz for 133 Cs (I = 7/2) with a 4 mm MAS probe spinning up to 15 kHz. A single pulse sequence was used to acquire the proton signal. The pulse duration was 3 µs and the recycle delay was set to 1 s after having checked that no contribution was favored due to T_1 effect. For ¹³³Cs, the Hahn spin echo sequence was applied for refocusing magnetization lost in the dead time. The first pulse length was chosen equal to 1 µs (2 µs for the second pulse) in order to fulfil the condition $v_{\rm rf} < v_{\rm O}$ that avoids any line distortion due to quadrupolar effects [17]. CsCl dissolved in water was used as reference (0 ppm). The simulations of the experimental spectra were performed using the Dm2000nt version of the Winfit software [18]. The definitions of the measured quadrupolar parameters are the following. V_{XX} , V_{YY} and V_{ZZ} are the principal components of the electric field gradient tensor, with the condition $|V_{ZZ}| \ge |V_{YY}| \ge |V_{XX}|$ and $V_{ZZ} = eq$. The quadrupolar coupling constant is written

$$C_{\rm Q} = \frac{e^2 q Q}{h} = \frac{e Q V_{ZZ}}{h}$$

where *Q* is the quadrupolar moment $(-3 \times 10^{-31} \text{ m}^2 \text{ for}^{133} \text{Cs})$ and the asymmetry parameter is given by $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$. The chemical shift is defined as $\delta_{ii} = \sigma_{\text{ref}} - \sigma_{ii}$, where σ_{ii} (*i* = *x*, *y*, *z*) are the principal components of the shielding tensor. The isotropic chemical shift δ_{iso} , the anisotropy $\delta_{\text{c.s.}}$ and asymmetry $\eta_{\text{c.s.}}$ parameters used for the reconstruction are defined as follows:

$$\delta_{iso} = \frac{1}{3}(\delta_{XX} + \delta_{YY} + \delta_{ZZ}), \ \delta_{c.s.} = \delta_{ZZ} - \delta_{iso} \ \text{and} \ \eta_{c.s.}$$
$$= \frac{\delta_{YY} - \delta_{XX}}{\delta_{iso}}.$$

2.5. Thermal analysis

Thermogravimetric analyses (TG) were carried out with a Rigaku thermoflex instrument for runs under airflow. The powdered samples were spread evenly in large platinum crucibles to avoid mass effects.

3. Results and discussion

3.1. Structure solution

The structure of $CdZrCs_{1.5}(H_3O)_{0.5}(C_2O_4)_4 \cdot x H_2O$ was solved in the hexagonal symmetry, space group P3. The cadmium and zirconium atoms were localized using the direct methods through the program SIR97 [19]. The remaining atoms, constitutive of the anionic framework $[CdZr(C_2O_4)_4]^{2-}$, were localized by successive Fourier difference map analysis with the help of SHELXL97 program [20]. Once all the atoms from the anionic framework were localized, the remaining maximum residual density peaks were weaker than 6.57 e $Å^{-3}$ and could thus not be attributed to a cesium atom. Fourier difference maps, made by including the atoms of the framework, revealed a completely delocalized electronic density inside the channels (Fig. 1a and b). A low temperature X-ray diffraction study was attempted but failed due to the transformation of the single crystal into a polycrystalline pseudomorph under the nitrogen flux.

The refinement of the anionic framework was then performed by ignoring the contribution of the disordered part of the structure. For this, the region containing the disordered electronic density was identified by considering the Van der Waals radii of the atoms constitutive of the ordered part. The contribution of this region to the total structure factor was calculated via a discrete Fourier transformation, and incorporated in a further least-squares refinement. These two procedures were carried out with the program SQUEEZE [21] included in the WinGX platform [10]. It resulted in a significant decrease of the Rvalues and a convergence of the refinement. Moreover, this procedure gives an electron count over the disordered region of 511, which is in agreement with the presence of 1.5 cesium atoms, 0.5 H_3O^+ and about eight water molecules per formula unit (total of 504 electron per unit cell). This hydration content is consistent with that determined for the analogous phase Cd/Zr/Na [4]. The analysis of the symmetry elements of the ordered part of the structure done with ADDSYM [22,23] showed that the structure framework was in agreement with space group $P3_112$. The atomic coordinates of the framework, together with the equivalent isotropic displacement parameters, are given in Table 2 according to the space group $P3_112$. The mean distances are reported in Table 3 according to Hoard and Silverton's formalism [5].



Fig. 1. Views of the $[CdZr(C_2O_4)_4]^{2-}$ anionic framework, together with the electronic density contained inside the channels (isosurface at 1.5 e A⁻³), along (a) the *c*-axis and (b) the *a*-axis.

3.2. Structure description

The compound CdZrCs_{1.5}(H₃O)_{0.5}(C₂O₄)₄·x H₂O can be considered as made of a three-dimensional $\left[CdZr(C_2O_4)_4\right]^{2^-}$ anionic framework with inserted disordered counter-cations $(Cs^+ \text{ and } H_3O^+)$. The anionic framework is built up from cadmium and zirconium cations linked through oxalate groups and is isotypic with those already thoroughly described for the compounds $CdZr(NH_4)_2(C_2O_4)_4 \cdot 3.9H_2O_2$, $CdZr(C_2N_2H_{10})(C_2O_4)_4 \cdot 4.4H_2O$ [3] and $CdZrNa_2(C_2O_4)_4 \cdot 4.4H_2O$ 8.5H₂O [4]. Indeed the eight-fold metal atoms arrange themselves in interconnected helical wires which displays tunnels with a circular section along $c (\emptyset \sim 5 \text{ Å})$ (Fig. 1a) and with elliptic ($\sim 5 \times 10$ Å) and square (~ 5 Å) sections along a, b and [110] (Fig. 1b). The parameters of an helix, as defined in Ref. [3], are its period P = c = 23,656 Å and its radius r = a/2 = 4.553 Å. The total volume available for the disordered cesium and hydronium cations is 802 $Å^3$, which corresponds to approximately 47% of the unit-cell volume. By analogy with the related compounds cited above, the counter-cations can be supposed to be inside the circular channels along the 3_1 axis. Water molecules are also present in the different types of channels. The structure study clearly reveals a disorder problem inside the tunnels. To further elucidate this feature, a local probe technique must be used. Solid-state NMR spectroscopy has been employed here to understand this phenomenon. The results are reported below.

The geometry of the ZrO_8 and CdO_8 polyhedra was determined using Haigh's criterion [24], based on the analysis of O–M–O angles. It shows that both polyhedra are square-based antiprisms. The mean planes of the square bases have 0.01 and 0.06° maximum atomic deviations from planarity for CdO₈ and ZrO₈, respectively. Moreover, these bases are nearly parallel with a 0.22 and 0.36° angle between the two mean planes for CdO₈ and ZrO₈. The mean Zr–O distance (2.21(3) Å) is close to the theoretical distance calculated by the bond valence method [25] for an eight-fold coordinated zirconium atom (2.18 Å). The mean Cd–O distance (2.5(1) Å] is also close to the calculated value for an eight-fold coordinated cadmium atom (2.41 Å). It can be noted that half the Cd–O distances are longer than expected, whereas the remaining ones are shorter.

Two oxalate groups, linking the cadmium and zirconium atoms in a bidentate way, are present in the asymmetric unit. The mean distances and angles within these oxalate groups are reported in Table 3. They are close to the values reported by Hahn [26] for oxalate-based compounds, i.e. 1.24 and 1.55 Å, 117 and 125° for the C–O and C–C bonds, and O–C–C and O–C–O angles, respectively. The two oxalate groups are nearly planar with a maximum atomic deviation from mean plane of 0.04 Å.

Table 2

Atomic coordinates and atomic displacement parameters (Å²) for the atoms involved in the framework of CdZrCs_{1.5}(H₃O)_{0.5}(C₂O₄)₄:*x*H₂O, U_{eq.} = $(1/3)\sum_{i}\sum_{j} U_{ij}a_{i}^{*}a_{j}^{*}a_{j}$

Atom	x/a	y/b	z/c	$U_{\rm eq.}$ (Å ²)
Cd	5/6	1/6	1/3	0.0266(1)
Zr	1/3	1/6	1/2	0.0198(1)
01	0.5574(4)	0.3431(4)	0.4475(2)	0.0359(7)
O2	0.7585(5)	0.3652(5)	0.3906(2)	0.049(1)
05	1.0726(4)	0.3250(4)	0.3896(1)	0.0333(7)
C1	0.6334(6)	0.2854(8)	0.4177(2)	0.028(1)
C2	0.5400(5)	0.0853(7)	0.4193(1)	0.0270(9)
O4	0.4184(4)	0.0178(4)	0.4524(1)	0.0309(7)
O3	0.5954(4)	0.0091(5)	0.3891(1)	0.0386(8)
08	0.1110(5)	-0.0103(5)	0.4480(2)	0.0402(8)
07	0.9067(4)	-0.0344(5)	0.3901(2)	0.0432(9)
O6	0.2510(4)	0.3184(4)	0.4527(1)	0.0320(7)
C3	1.1244(5)	0.2475(7)	0.4188(1)	0.0267(9)
C4	0.0304(6)	0.0478(7)	0.4184(1)	0.0277(9)

Table 3 Selected interatomic distances (Å) and bond angles (°) in the structure refinement of $CdZrCs_{1,5}(H_3O)_{0,5}(C_2O_4)_4$: xH_2O

ZrO ₈ antiprism			
M-O			
Zr–O1, O1 ⁽ⁱⁱ⁾	2.236(4)	Zr–O4, O4 ⁽ⁱⁱ⁾	2.180(3)
Zr–O6, O6 ⁽ⁱⁱ⁾	2.182(3)	Zr–O8, O8 ⁽ⁱⁱ⁾	2.226(4)
l		S	
01-01 ⁽ⁱⁱ⁾	2.745(7)	01-04	2.577(5)
O1 ⁽ⁱⁱ⁾ -O4	2.853(4)	04-08	2.682(5)
O4-O6 ⁽ⁱⁱ⁾	2.604(4)	08-06	2.604(5)
O6 ⁽ⁱⁱ⁾ -O8	2.843(4)	06-01	2.687(5)
O8-O8 ⁽ⁱⁱ⁾	2.737(7)	O1 ⁽ⁱⁱ⁾ -O6 ⁽ⁱⁱ⁾	2.687(5)
O8 ⁽ⁱⁱ⁾ -O6	2.843(4)	$O6^{(ii)} - O8^{(ii)}$	2.604(5)
O6-O4 ⁽ⁱⁱ⁾	2.604(4)	$O8^{(ii)} - O4^{(ii)}$	2.682(5)
O4 ⁽ⁱⁱ⁾ -O1	2.853(4)	$O4^{(ii)} - O1^{(ii)}$	2.577(5)
CdO ₈ antiprism			
M-O			
Cd-O2, O2 ⁽ⁱ⁾	2.607(4)	Cd-O3, O3 ⁽ⁱ⁾	2.320(3)
Cd-O5, O5 ⁽ⁱ⁾	2.336(3)	Cd-O7, O7 ⁽ⁱ⁾	2.613(4)
l		S	
O2-O3 ⁽ⁱ⁾	3.316(5)	02-05	3.060(6)
O3 ⁽ⁱ⁾ -O5	2.939(4)	05-07	2.837(5)
O5-O7 ⁽ⁱ⁾	3.314(5)	07-03	3.053(6)
O7 ⁽ⁱ⁾ -O7	2.925(8)	03-02	2.811(6)
O7-O5 ⁽ⁱ⁾	3.314(5)	$O2^{(i)} - O3^{(i)}$	2.811(6)
O5 ⁽ⁱ⁾ -O3	2.939(4)	$O3^{(i)} - O7^{(i)}$	3.053(6)
O3-O2 ⁽ⁱ⁾	3.316(5)	$O7^{(i)} - O5^{(i)}$	2.837(5)
O2 ⁽ⁱ⁾ -O2	2.934(9)	O5 ⁽ⁱ⁾ -O2 ⁽ⁱ⁾	3.060(6)
Oxalate groups			
C1-01	1.271(5)	O1-C1-O2	129.5(3)
C1-O2	1.187(6)	O3-C2-O4	126.0(5)
C2-O3	1.263(5)	C1-C2-O3	119.2(4)
C2-O4	1.241(5)	C1-C2-O4	114.8(4)
C1-C2	1.579(8)	C2-C1-O1	111.9(4)
		C2-C1-O2	121.1(4)
C3-O5	1.237(5)	O5-C3-O6 ⁽ⁱⁱⁱ⁾	124.4(5)
C3-O6 ⁽ⁱⁱⁱ⁾	1.282(5)	07-C4 ⁽ⁱⁱⁱ⁾ -O8 ⁽ⁱⁱⁱ⁾	126.2(6)
$C4^{(iii)}-O7$	1.197(5)	C3-C4 ⁽ⁱⁱⁱ⁾ -O7	121.6(4)
C4 ⁽ⁱⁱⁱ⁾ -O8 ⁽ⁱⁱⁱ⁾	1.303(5)	C3-C4 ⁽ⁱⁱⁱ⁾ -O8 ⁽ⁱⁱⁱ⁾	112.0(4)
C3-C4 ⁽ⁱⁱⁱ⁾	1.576(8)	$C4^{(iii)} - C3 - O5$	120.8(4)
-		C4 ⁽ⁱⁱⁱ⁾ -C3-O6 ⁽ⁱⁱⁱ⁾	114.7(4)

Symmetry codes: (i) 1 - y, 1 - x, 5/6 - z; (ii) x, x - y, 1-z; (iii) 1 + x, y, z.

3.3. Subtle phase transformation

Powder diffraction data collected without paying attention towards ambient conditions (pressure and temperature) revealed extra diffraction peaks than those expected from a simulated powder pattern calculated from the structure determined by single-crystal X-ray diffraction. These supplementary diffraction peaks were successfully indexed, with the program DICVOL91 [13], with an hexagonal unit-cell characterized by parameters relatively close to those of the phase previously described in this study (a = 9.029(1) Å; c = 23.925(9) Å; M(20) = 21; F(20) =22(0.010, 90)]. It was also noted that diffraction data collections at different times showed a variation of

intensities ratio of the two phases. This feature ruled out the presence of an impurity and suggested the existence of a subtle phase transformation around ambient atmospheric conditions. Taking into account the sensitivity of some other oxalate-based compounds such as YK(C₂O₄)₂·4H₂O [27] or $Cd_2Zr(C_2O_4)_2 \cdot (4 + x)H_2O[1]$ towards water vapor pressure and temperature, it can be thought that the phase transition in the cesium compound could be due to a variation of the water content in the channels. The two phases were successfully isolated and characterized by X-ray powder diffraction at room temperature (295 K) with a humidity of 37% for the low hydrated phase (LH) (Fig. 2a) and 65% for the high hydrated phase (HH) (Fig. 2b). For each of these two phases, the unit-cell parameters were refined using the full-pattern matching option included in the FULLPROF program suite. Observed line profiles were represented by a pseudo-Voigt function. The refinement also included the zero shift, the three FWHM parameters defining the Caglioti function, two variables describing the angular dependence of the profile shape factor and two parameters for peak asymmetry correction in the $10-40^{\circ}(2\theta)$ angular range. The refined unit-cell parameters for the HH phase are a = 9.0168(4) Å, c = 23.882(1) Å, V = 1681.6 Å³ (pattern fitting reliability factor $R_{wp} = 13.6\%$). Those of the LH phase are a = 9.2311(2) Å, c = 22.9296(6) Å, V =1692.2 Å³ (reliability factor $R_{wp} = 8.9\%$). It can be noted that the unit-cell parameters determined from the singlecrystal X-ray diffraction data are close to those of the HH phase (Table 1). Moreover, the analysis of systematic extinctions (00*l*: l = 3n + 1 in agreement with an helicoidal axis along c) shows that the space group probably remains unchanged. The parameter c is the most affected over the phase transition, with a decrease of ~ 1 Å between the HH and LH phases. The *a* parameter varies in the opposite way but with a lower magnitude. It can thus be concluded that the overall crystal structure remains the same over the transformation and that the rise of water content only causes a change in the unit-cell parameters. An interesting feature is, unlike what was observed for $YK(C_2O_4)_2 \cdot 4H_2O$ [27] or $Cd_2Zr(C_2O_4)_2(4 + x)H_2O$ [1], the phase transformation is here sudden. Indeed, in these two phases, the change in the hydration level was followed by a proportional variation of the unit-cell parameters. The LH phase can accommodate up to a certain number of water molecules and when the hydration reaches a critical level, it causes the structure to switch to the HH phase.

The thermal decomposition of $CdZrCs_{1.5}(H_3O)_{0.5}$ (C₂O₄)₄·*x* H₂O was studied by thermogravimetric analysis (Fig. 3) performed under air between 293 and 1173 K. The humidity in air was ~70% during the recording and the starting phase thus corresponds to the most hydrated one (HH). The chemical formula derived for the HH phase is $CdZrCs_{1.5}(H_3O)_{0.5}(C_2O_4)_4$ ·6.8H₂O, which is consistent with the formula derived from X-ray diffraction. Its decomposition can be described by a four-step process. First, an immediate weight loss is observed as soon as the product is



Fig. 2. Full-pattern matching of the X-ray powder diffraction diagrams obtained at 295 K for (a) the LH phase (37% humidity) and (b) the HH phase (65% humidity). $\infty \infty \infty$ experimental pattern, — calculated pattern and ++++ difference curve.

heated. This weight loss ($\sim 4.5\%$) corresponds to the departure of about two water molecules. The TDXD plot showed that this first weight loss corresponds to the transformation of the HH phase into the LH one. A second weight loss ($\sim 14\%$) is seen on the TG curve between ~ 333 and \sim 413 K, which is in agreement with the departure of the remaining water molecules. The loss of these last water molecules leads to an amorphisation of the compound, as shown by the diffraction powder pattern. The third weight loss observed between 443 and 643 K (\sim 43%) is in good agreement with the decomposition of the oxalate moieties and the formation of cadmium oxide, zirconium oxide and cesium carbonate (theoretical weight loss: 41.5%). An X-ray powder diffraction pattern of the compound previously heated at 673 K confirmed the presence of ZrO₂ [PDF2 No. 88-2390], CdO [PDF2 No. 78-0653] and Cs₂CO₃ [PDF2 No. 71-1981] [28]. The final weight loss ($\sim 69\%$) should then correspond to the decomposition of the cesium carbonate (theoretical weight loss: 71.6%). This thermal analysis is in quite good agreement with the chemical formula $CdZrCs_{1.5}(H_3O)_{0.5}(C_2O_4)_4 \cdot x H_2O$ proposed and, furthermore, it allows to estimate the hydration difference between the HH and LH phases, i.e. around two water molecules.

3.4. Solid-state ¹³³Cs NMR

It is often assumed that the quadrupolar interaction effects (QI) are predominant compared to chemical shift anisotropy (CSA). However, it has been shown that in some rare situations, CSA and QI have to be considered simultaneously to take account of NMR spectra. Representative examples are ⁵¹V [29], ¹⁴N [30], ¹⁷O [31] and ¹³³Cs [32]. For ¹³³Cs, the combination of a small quadrupole moment (-3×10^{-31} m²) and a large chemical shift range (400 ppm due to the size of the electronic cloud) makes

the NMR properties of this nucleus more reminiscent of a spin 1/2 than a quadrupolar spin 7/2 [33,34] and, usually, the QI can be neglected.

Fig. 4a and b show the ¹³³Cs static experimental spectra obtained for the HH and LH phases, together with the calculated spectra. The results for both phases are very close to each other. They exhibit an original line shape where the six external transitions, due to the first order QI, are well resolved. In the middle appears the central transition $(1/2 \rightarrow -1/2)$ with a typical line shape due to the CSA. Indeed, it is well known that QI, even with second order effect, cannot give account of such a central line shape. Finally, the whole static spectrum is perfectly reconstructed by only taking into account the QI for the external transition, on one hand, and the CSA for the central line on the other hand. The parameters used for these reconstructions are



Fig. 3. TG curve for $CdZrCs_{1.5}(H_3O)_{0.5}(C_2O_4)_{4}\cdot 6.8H_2O$ under flowing air (heating rate: 5 K h⁻¹ between 293 and 673 K and 10 K h⁻¹ up to 1173 K).



Fig. 4. ¹³³Cs NMR static spectra obtained for (a) HH and (b) LH phases together with their reconstruction.

gathered in Table 4. For each phase, LH or HH, an axial anisotropy has to be considered simultaneously for QI and CSA and the resultant isotropic chemical shifts for central and external transitions are consistent, since they are very close to each other (Table 4). These noteworthy ¹³³Cs static spectra should be put forward, since the CSA and the QI are simultaneously visible and, moreover, independently influence the line shape of central and external transition lines. To our knowledge, it is the first time that such a phenomenon is observed on a NMR spectrum.

The MAS technique simultaneously averages the CSA and the first order QI. The related spectra for the HH phase (Fig. 5) exhibits a unique sharp line keeping the same position whatever the spinning speed, proving that we encounter only one mean type of cesium and confirming the way the static spectrum was treated. For this line, we measured the same isotropic chemical shift value than with the static spectrum reconstruction (-200 ppm). An equivalent result has been obtained for the LH phase. Note that the LH isotropic chemical shift is about 15 ppm higher than the one of the HH phase, whereas the C_Q and $\delta_{c.s.}$ parameters are stronger for the HH phase (Table 4).

At this stage, it is difficult to propose an explanation concerning these values knowing that the sizes of the tunnels containing the Cs^+ ions are almost the same. Nevertheless, the perfect axial symmetry observed for both QI electrical field gradient and CS is in agreement with the motion of the Cs^+ ions into the one dimension channels of the framework. Indeed, the helicoidal geometry of

Reconstruction parameters for the ¹³³Cs NMR spectra of the HH and LH phases

Table 4

	External transition			Central transition		
	$\delta_{\rm iso}~({\rm ppm})$	$C_{\rm Q}~({\rm kHz})$	$\eta_{ m Q}$	$\delta_{\rm iso}~({\rm ppm})$	δ_{σ} (ppm)	η_{σ}
HH phase LH phase	- 202 - 187	153 133	0.02 0	- 199 - 185	18 11	0.03 0

the tunnel along the [001] direction leads to a quick exchange of the X and Y main axis of the QI and CS tensors during the Cs⁺ motion, whereas the Z-axis remains along the [001] direction. Then, the NMR experiments give direct access to the mean values of the chemical shift in the planes perpendicular to [001], i.e. $\delta_{\perp} = (\delta_{XX} + \delta_{YY})/2$, and along the [001] axis, i.e. $\delta_{=} = \delta_{ZZ}$, leading to $\eta_{c.s.} = 0$. As V_{XX} and V_{YY} play an equivalent role, then $\eta_Q = 0$, and V_{ZZ} , which provides the C_Q value, coincides with the [001] axis of the network. It can be noted that, recently, some authors have reported similar effects for ¹²⁹Xe in motion into nanotubes [35,36].

In order to confirm this assumption, the 133 Cs spectra of the HH phase have been registered at various low temperatures (Fig. 6). From room temperature to 130 K, the line becomes broader and unresolved, like in amorphous or glassy materials. This behavior is attributed to Cs⁺ ions freezing at random positions into the anionic tunnels, leading thus to a distribution of the quadrupolar and chemical shift parameters. Note that this behavior is



Fig. 5. ¹³³Cs MAS NMR spectra of the HH phase at various spinning speeds.



Fig. 6. ¹³³Cs NMR spectra of the HH phase collected at various temperatures, from room temperature to 130 K.



Fig. 7. 133 Cs NMR spectra of CdZrCs_{1.5}(H₃O)_{0.5}(C₂O₄)₄·*x* H₂O recorded with a random hygrometric degree.

perfectly reversible and in full agreement with the motion of Cs^+ ions in the anionic tunnels. When the sample returns to room temperature, the spectrum recovers its initial specific shape.

Finally, it is interesting to observe the ¹³³Cs spectrum recorded without paying any attention to temperature and hygrometry (Fig. 7). The complex line shape obtained is then the superposition of the two previous spectra attributed to the pure LH and HH phases. The reconstructed line, obtained by summing the components of the pure phases, gives a good account of the experimental spectrum with 33% of HH and 66% of LH as relative intensities. An X-ray diffraction pattern recorded with similar conditions confirmed the presence of these two phases, as already reported above. The MAS spectrum recorded at a spinning rate of 3 kHz enables to confirm that, as expected, two types of ¹³³Cs nucleus are present in the sample, with retrieved isotropic chemical shifts corresponding to those found for the pure phases.

3.5. ¹H spectra

The ¹H spectra of the powdered sample are given in Fig. 8 together with their reconstruction. It is known that the structure contains water molecules, as well as H_3O^+ cations to ensure the electro-neutrality of the material. The coexistence of two chemical species containing ¹H nucleus in the structure is in agreement with the NMR observations. Indeed, to give account of the line shape, two Lorentzian contributions, denoted a and b, are required. They point out that protons have two types of behavior in each crystalline phase. For both phases, the parameters used for the reconstruction are very close to each other (Table 5). Generally, the isotropic chemical shift of protons in water is lower than in hydronium ions [37]. Consequently, the *a* lines at 4 ppm are attributed to water and the b lines at 9–10 ppm are assigned to H_3O^+ . It appears that the *b* lines are much broader than the *a* line, showing that water molecules are in motion in the channel, whereas H_3O^+ ions are more bounded to the framework [37]. Following the same argument, it is clear that water



Fig. 8. ¹H NMR spectra of (a) the HH and (b) the LH phases together with their reconstruction.

Table 5 Reconstruction parameters for the ¹H NMR spectra of the HH and LH phases

		$\delta_{\rm iso}~({\rm ppm})$	Linewidth (kHz)	Intensity (%)
HH phase	a line	4	1.4	82
	b line	10	11.2	18
LH phase	a line	4	2.2	81
-	b line	9	11.1	19

molecules are more mobile in the HH phase than in the LH phase.

4. Conclusion

Compared to the compounds with a related hexagonal structure with isotypic anionic $[CdZr(C_2O_4)]^{2-}$ frameworks containing ammonium, amine or sodium, the cesium compound reveals some peculiar features. Single-crystal X-ray diffraction data together with ¹H and ¹³³Cs solid-state NMR spectroscopy have shown that the cesium cations and water molecules exhibits a dynamic disorder along the *c*-axis of the hexagonal cell. Moreover, the cesium motion into the channels with a hexagonal cross-section gives rise to a noteworthy ¹³³Cs NMR spectra, in which axial CSA and QI, simultaneously and independently, influence the shapes of the central and external transitions. Additionally, the diffraction and NMR studies have clearly shown that the Cs compound exhibits a phase transformation around ambient temperature, which depends both on temperature and water vapor pressure. It should be noted that the existence of a dynamic disorder inside the channels is likely to be correlated with the ability of the compound to exchange cations, from which the nonstoichiometry of the material must originate.

Acknowledgements

The authors are indebted to Mr J.C. Ameline (GMCM, University of Rennes), Dr T. Roisnel (CDIFX, University of Rennes) and Mr G. Marsolier for their technical assistance.

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