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$BaCd_2Cl_6 \cdot 5H_2O$, a Pyrochlore with 16(*d*) and 32(*e*) Positions Both Fully Occupied

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The crystal structure of the cubic pyrochlore $BaCd_2Cl_6 \cdot 5H_2O$, space group $Fd3m$, has been investigated by single crystal X-ray diffraction. The result of the final anisotropic refinement corresponds to a R value of 0.022 for 299 reflections with $I > 3\sigma(I)$. Corner-sharing $CdCl_6$ octahedra form the classical three-dimensional pyrochlore framework with tunnels running along the ⟨110⟩ directions. The barium ions and the O(1) oxygens of water molecules are statistically distributed over the 16(*d*) sites on the axis of the tunnels. The 32(*e*) sites are completely occupied by the O(2) oxygens of water molecules forming tetrahedral groups. The structure can be described as the interpenetration of two three-dimensional frameworks: the $CdCl_6$ host lattice and the $[Ba, H_2O][H_2O]_4$ framework formed of chains of face sharing antiprisms $[Ba,O(1)]\,(H_2O)_6$ and tetrahedral groups $[H_2O]_4$. © 1987 Academic Press, Inc.

Introduction

The pyrochlore structure has been the subject of many studies owing to the large deviation from stoichiometry offered by its framework. It was indeed shown that besides the stoichiometric compounds $A_2B_2X_7$, non-stoichiometric pyrochlores $A_{1+x}M_2O_6$ $(0 \leq x \leq 1)$ (*1*) as well as hydrated oxides such as $AM_2O_6 \cdot H_2O$ (*2*) could be isolated. An important point which has not been completely resolved deals with the location of the A ions and of the water molecules in the structure. For instance, it was not possible to determine the accurate position of the H_2O molecules in those hydrated pyrochlores from the X-ray powder diffraction patterns. In the same way, the X-ray powder study of the pyrochlores AM_2X_6 (*3–7*) for A = K, Rb showed that two and even several 32(*e*) sites for the A cations were compatible with the calculations: two R minima were observed corresponding to 32(*e*) sites located between the 8(*b*) and 16(*d*) sites and on the opposite of the 16(*d*) sites, respectively. The single crystal study of the oxyfluoride $TlNb_2O_5F$ (*8*) showed that the Tl^+ ion was located on only one type 32(*e*) site between 8(*b*) and 16(*d*); however, this behavior was considered as being specific of Tl^+ owing to the presence of its lone pair. The comparison of the pyrochlores CsM_2X_6 (*1–8*) with the stoichiometric pyrochlores $A_2B_2X_7$ shows clearly that the seventh anion of the structure can be replaced by a cation such as Cs^+. Consequently, it appears that the different sites of the cavities—8(*b*), 16(*d*), 32(*e*)—could be occupied as well by anions as by cations or neutral molecules such as H_2O. The replacement of oxygen or fluorine by larger anions such as chlorine

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should lead to the formation of larger tunnels and cages and allow one to understand the distribution of ions and molecules in the M_2Cl_6 host lattice. In this respect, barium cadmium hexachloride pentahydrate $BaCd_2Cl_6 \cdot 5H_2O$ studied by Ferrari and Cavalca (*9*) is very attractive since it is the only pyrochlore involving chlorine and a large number of water molecules and barium ions. The authors could determine the positions of the atoms of the Cd_2Cl_6 host lattice and of the barium ions with a rather good accuracy. However, no information could be obtained about the distribution of the water molecules in the cavities of the structure. Thus, the present study deals with the structure determination of a single crystal of $BaCd_2Cl_6 \cdot 5H_2O$ in order to understand the chemical bonding in those compounds.

Experimental

The crystallization of the chloride $BaCd_2Cl_6 \cdot 5H_2O$ has been previously reported (*10*). The crystals used for the morphological study were prepared by evaporation of an aqueous solution containing $CdCl_2$ and $BaCl_2$ in the molar ratio 2 : 1. A rapid growth leads to the formation of octahedra whereas a slow growth leads in addition to the formation of the faces {110} and {113}.

The crystal used for the X-ray diffraction study was a slightly flattened octahedron, with 0.18-mm edges. The intensities of 733 reflections ($h, k, l > 0, h > k$), 299 independent reflections with $I > 3\sigma(I)$, were registered with the CAD4-Nonius diffractometer for K_α-Mo radiation filtered with a graphite monochromator ($\lambda = 0.71069$ Å). The cell parameters were refined from 23 reflections ($7 < \theta < 25°$). The reflections 008, 408, 444 were used as reference and their intensities were measured every 3000 sec ($\Delta I/I < 0.03$).

Lorentz polarization and absorption corrections ($2.31 < A < 2.64$) were performed with the program AGNOSTC (*11, 12*). The space group $Fd\bar{3}m$ was confirmed with the refined parameter $a = 13.797$ (1) Å.

The origin was fixed on a symmetry center $\bar{3}m$ and the initial atomic coordinates of cadmium, chlorine, and barium were those previously given by Ferrari and Cavalca (*9*). The position of the water molecules was determined from the difference Fourier maps. Owing to the random distribution of the 16(d) sites half filled by the barium ions and half by the water molecules represented by O(1) the same thermal factor was assigned to the two atoms O(1) and Ba. It must be pointed out that the oxygen atom O(2) in the 32(e) position is the only atom responsible for the presence of the reflections 424, 824, 10.4.4, 828, and 16.4.10 for which a good agreement between Fo and Fc was observed; it is also worth noting that O(2) contributes with Cl only to the reflections such as $h = 4n$, $k = 4n + 2$, $l = 4n + 2$.

The refinements of the atomic coordinates, anisotropic thermal factors, and secondary extinction coefficients (*13*) were performed on the structure factors. A weighting scheme versus sin θ/λ determined by the program NANOVA (W. C. Hamilton, unpublished) was used. After refinement $R = 0.022$, $wR = 0.019$, $g = 25.9(9)$, $s = 1.2135$. The residual electron density was smaller than 0.25 eÅ^3 and $\Delta p/\sigma p < 0.04$. The hydrogen atoms could not be located. The scattering factors and anomalous dispersion terms of the different atoms were obtained from the "International Tables for X-Ray Crystallography" (*14*). A list of the observed and calculated structure factors is available from the authors.

The final atomic coordinates (Table I) confirm that the Cd^{2+} ions are located in 16(c) positions whereas the Cl^- ions are located in the 48(f) positions with a variable

TABLE I

The Positional and Thermal Parameters[a]

	x	y	z	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{23} \times 10^5$
Ba,O(1)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	243(2)	β_{11}	β_{11}	−19(2)	β_{12}	β_{12}
Cd	0	0	0	162(1)	β_{11}	β_{11}	4(1)	β_{12}	β_{12}
Cl	0.32095(7)	$\frac{1}{8}$	$\frac{1}{8}$	247(4)	205(2)	β_{22}	0	0	66(3)
O(2)	0.70251(20)	x	x	310(8)	β_{11}	β_{11}	−5(9)	β_{12}	β_{12}

[a] The thermal parameters are of the form: $\exp[-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ where $\beta_{11} = \beta_{22} = \beta_{33}$, $\beta_{12} = \beta_{13} = \beta_{23}$ for Ba,O(1), Cd, O(2) and $\beta_{22} = \beta_{33}$, $\beta_{12} = \beta_{13} = 0$ for Cl.

parameter close to the one observed for oxides. The Ba^{2+} ions and H_2O, i.e. O(1), are found to be statistically distributed over the 16(*d*) sites. The interesting feature deals with the H_2O molecules O(2) which are located on the 32(*e*) sites.

Description of the Structure and Discussion

The structure is built up from corner-sharing $CdCl_6$ octahedra which form the classical pyrochlore framework Cd_2X_6. The interatomic distances and angles (Table II) show that the cadmium ion is located at the center of a slightly flattened octahedron along the ternary axis. The Cd–Cl distance is slightly smaller than the one in $BaCdCl_4 \cdot 4H_2O$ (*15*) in which the edge-sharing $CdCl_6$ octahedra form infinite ribbons whose cohesion is ensured by interstitial Ba^{2+} ions.

TABLE II

Interatomic Distances (Å) and Angles (°)

$CdCl_6$		$[Ba,O(1)]Cl_6(H_2O)_6$	
Cd–Cl^{i}	2.628(1)	Ba,O(1)–Cl^{iv}	3.472(1)
Cl^{i}–Cl^{ii}	3.607(2)[a]	Ba,O(1)–O(2^{v})	2.944(3)
Cl^{i}–Cl^{iii}	3.824(2)	O(2^{v})–Cl^{iv}	3.472(3)
Cl^{i}–Cd–Cl^{ii}	86.66(2)	O(2^{v})–Cl^{vi}	3.381(3)
Cl^{i}–Cd–Cl^{iii}	93.34(2)	O(2^{v})–O(2^{vii})	3.025(4)

Symmetry code

i: $-x + \frac{1}{4}$, y, $-z + \frac{1}{4}$; v: $-x + \frac{5}{4}$, $-y + \frac{5}{4}$, z
ii: $z - \frac{1}{4}$, $x - \frac{1}{4}$, $-y$ vi: $y + \frac{1}{4}$, $z + \frac{1}{4}$, $-x + 1$
iii: $-z + \frac{1}{4}$, $-x + \frac{1}{4}$, y vii: $-x + \frac{5}{4}$, y, $-z + \frac{5}{4}$
iv: x, $y + \frac{1}{2}$, $z + \frac{1}{2}$,

[a] Edge common to $CdCl_6$ and $[Ba,O(1)]Cl_6(H_2O)_6$.

The three-dimensional framework Cd_2Cl_6 forms hexagonal tunnels running along the ⟨110⟩ directions (Fig. 1). These tunnels intersect at the 8(*b*) sites forming very large cages limited by 18 chlorine atoms and noted "Cl_{18}." Each "Cl_{18}" cage is fully occupied by four water molecules noted O(2) located on the 32(*e*) sites at the corners of a regular tetrahedron with an edge of 3.025(4) Å. This is to be compared to the results obtained for the pyrochlore $TlNb_2O_5F$ (*8*) for which 32(*e*) sites were found to be partly and statistically occupied by the thallium ions. However, the two compounds differ by the nature of the 32(*e*) sites: in $TlNb_2O_5F$ the 32(*e*) sites located between the 8(*b*) and 16(*d*) sites are occupied by thallium (see sites I, Fig. 2) whereas in the barium chloride it is clear that H_2O molecules are located on the opposite of the 16(*d*) sites (see sites II, Fig. 2). This behavior is rather similar to the one observed for the hydrated pyrochlore $HTaWO_6 \cdot H_2O$ (*16*) for which the water molecule was found to be located in the 32(*e*) positions with $x \simeq 0.35$.

The barium ions and the "O(1)" water molecules are statistically distributed over the 16(*d*) sites on the axis of the tunnels at the junction between two "Cl_{18}" cages (Fig. 3). Thus each barium ion (or O(1) molecule) is surrounded by six chlorine atoms located at 3.472 (1) Å and six water mole-

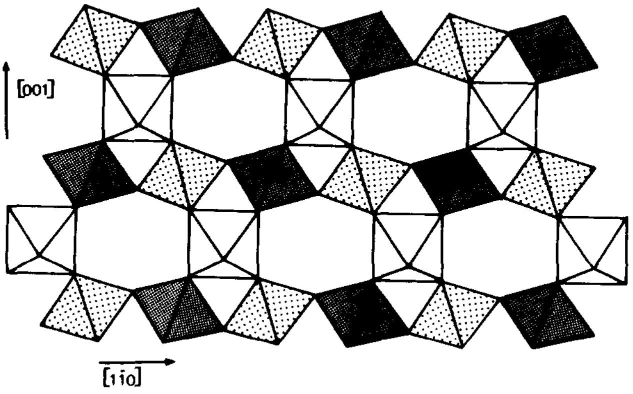

FIG. 1. Projection of the pyrochlore structure along [110] showing the hexagonal tunnels in the $CdCl_6$ framework.

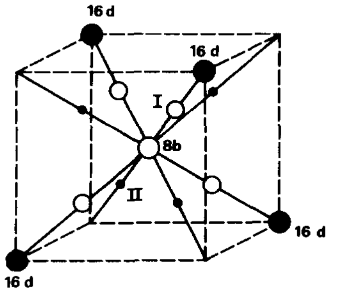

FIG. 2. The two possibilities of location of 32(*e*) sites: sites I between 8(*b*) and 16(*d*) sites; sites II on the opposite of the 16(*d*) sites. Open circles correspond to empty sites (○, 32(*e*) I; ○, 8(*b*)) and full circles correspond to positions occupied by Ba^{2+} and O(1) (●, 16(*d*)) and by O(2) (•, 32(*e*) II), respectively.

cules O(2) located at 2.944(3) Å. The disposition of the chlorine atoms with respect to the barium ion is quite similar to the one observed for oxygen with respect to *A* and H_2O species in the pyrochlores $AB_2O_6 \cdot H_2O$ (*1, 2*): each barium or O(1) molecule is surrounded by six chlorine atoms forming a hexagon with a *trans* conformation. The water molecules O(2) form a trigonal antiprism whose center is statistically occupied by barium ions and O(1) molecules (Fig. 4a). Thus the coordination of barium ions and O(1) molecules can be described by $[Ba,O(1)]\ Cl_6(H_2O)_6$ polyhedra (Fig. 4b) which share their faces $O(^{V}_{2})–O_2^{VII}–Cl^{IV}$ with

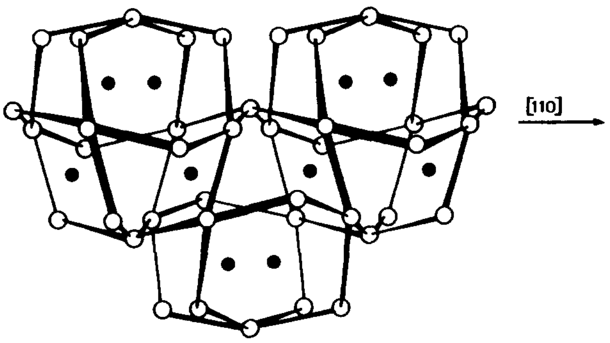

FIG. 3. "Cl_{18}" cages running along [110] with Ba ions or O(1) water molecules at the junction between two cages. ●, Ba^{2+}, O(1); ○, Cl^-.

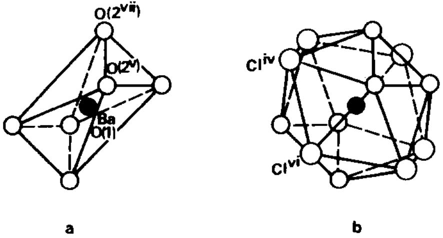

FIG. 4. (a) The trigonal antiprism built up from water molecules O(2) surrounding Ba or O(1). (b) the $Cl_6(H_2O)_6$ icosahedral environment of Ba or O(1). ●, Ba^{2+}, O(1); ○, O(2); ○, Cl^-.

their six equivalent neighbors to form a three-dimensional framework. Such a polyhedron had never been found in the pyrochlore structure up to the present but was observed in the alloy W_3Fe_3C (*17*) where iron atoms are located on the 32(*e*) and 16(*d*) sites whereas tungsten atoms occupy the 48(*f*) positions.

The O(2) water molecules which are located on a ternary axis form tetrahedral groups $(H_2O)_4$ whose barycenters coincide with the 8(*b*) sites. It is worth pointing out that the O(2)–O(2) distances are close to those observed for oxygen close-packings. In addition to its three O(2) neighbors belonging to the $(H_2O)_4$ tetrahedron, each H_2O molecule is surrounded by three barium ions (or O(1) atoms) and six chlorine ions forming an icosahedral environment.

The nature of the chemical bonds which characterize the octahedral framework Cd_2Cl_6, very different from those formed by the barium ions and water molecules, leads us to consider these latter species separately. In this respect, the consideration of the antiprisms [Ba,O(1)] $(H_2O)_6$ and of the tetrahedral groups $[H_2O]_4$ is of interest. Each tetrahedral group $[H_2O]_4$ shares its four faces with an antiprism [Ba,O(1)] $(H_2O)_6$ and reciprocally this latter polyhedron shares its two opposite faces with tetrahedral units. Consequently, these polyhedra form a three-dimensional framework

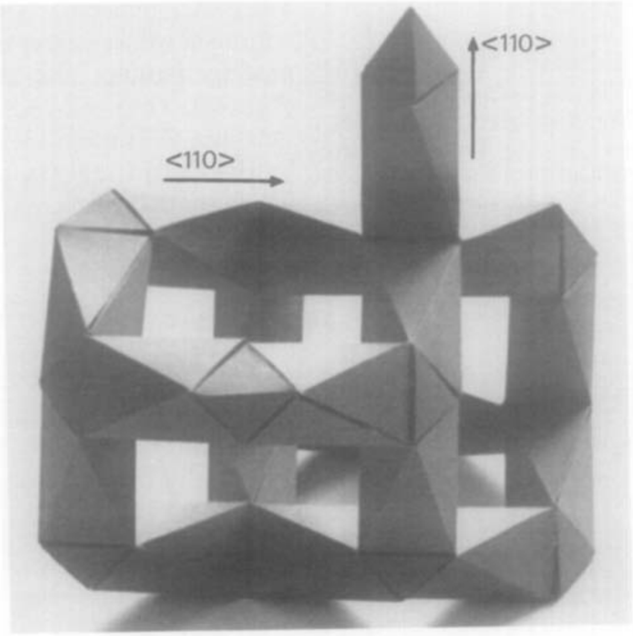

FIG. 5. The three-dimensional framework BaH_2O $(H_2O)_4$ built up of face sharing antiprisms $[Ba,O](H_2O)_6$ and tetrahedral groups $(H_2O)_4$.

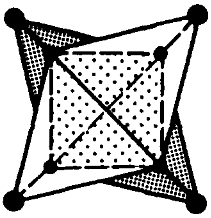

FIG. 6. The superunits built up from five H_2O tetrahedra. O(2) atoms (•) are located on the four corners of the inner tetrahedron; O(1) atoms (●) are located on the external corners of the four tetrahedra built up from three O(2) and one O(1) atom.

$[Ba,H_2O][H_2O]_4$ built up of chains of face sharing antiprisms and tetrahedral groups running along the ⟨110⟩ directions (Fig. 5). This latter framework is somewhat more complex than described above owing to the presence of H_2O (O(1)) molecules in the trigonal antiprism. These latter molecules O(1) which are located at the center of an antiprism form with the molecules O(2) of the tetrahedral groups two additional $(H_2O)_4$ tetrahedra (Fig. 6) so that the presence of "superunits" built up from five $(H_2O)_4$ tetrahedra sharing their corners and faces must be considered. The stability of such a framework results from the presence of Ba–H_2O bonds and may also be due to the formation of hydrogen bonds between H_2O molecules. In the same way the cohesion of the pyrochlore structure is ensured by the existence of hydrogen bonds and ionocovalent bonds between the two frameworks $(Ba, H_2O)(H_2O)_4^{2+}$ and $(CdCl_6)^{2-}$. The values of the angles O–O–O (ranging from 108.35° to 118.17°), O–O–Cl (ranging from 114.75° to 122.19°), and Cl–O–Cl (ranging from 117.36° to 121.32°) as well as the interatomic distances O–O and O–Cl are compatible with the formation of such hydrogen bonds (*18*). A neutron diffraction will be absolutely necessary in order to determine the position of the hydrogen atoms.

The tetrahedral $(H_2O)_4$ groups form an interesting feature of this structure. The thermodifferential and thermogravimetric analyses of this compound confirm their particular role in the structure since four H_2O molecules are lost in a first step without any destruction of the structure, whereas the departure of the fifth water molecule is accompanied by a complete destruction of the structure.

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