Crystal Structure of Calcium Chloride Tetrahydrate

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The crystal structure of calcium chloride tetrahydrate was determined by use of three-dimensional X-ray diffractometer data. Crystals of $CaCl_2.4H_2O$ are triclinic, space group $P\bar{1}$, with $a=6\cdot593$ (2), $b=6\cdot364(5)$, $c=8\cdot557(3)$ Å, $\alpha=97\cdot77(5)$, $\beta=93\cdot52(4)$, and $\gamma=110\cdot56$ (3)°. The structure was refined by least-squares calculations to $R=0\cdot085$. The two chloride ions and four water molecules form a trigonal prismatic coordination polyhedron about the calcium ion.

Introduction

We determined the crystal structure of calcium chloride tetrahydrate as part of an investigation of calcium ion coordination properties. Here we describe the structure, which displays an interesting pattern of calcium coordination.

Experimental

We obtained crystals of calcium chloride as a by-product from an attempt to prepare a geraniol–calcium chloride addition compound. A large volume of ethyl acetate was poured slowly into a test tube that contained a hot slurry of calcium chloride in geraniol. Over a period of several days, clear, well developed, triclinic crystals of $CaCl_2.4H_2O$ grew on the walls of the test tube. It is likely that the water contained in these crystals came from the undried samples of ethyl acetate and calcium chloride. We later checked the purity of the calcium chloride and found that when fused, it released a considerable amount of water. Since the crystals are hygroscopic, they were stored under mineral oil.

A crystal with the approximate dimensions $0\cdot4 \times 0\cdot3 \times 0\cdot2$ mm was transferred, while still heavily coated with mineral oil, into a Lindemann glass capillary, which was then sealed with wax. The crystal was mounted on a Picker FACS-1 diffractometer with its a axis slightly inclined to the φ axis of the diffractometer. Approximate cell parameters for use in collection of intensity data were calculated by a least-squares analysis of the angular settings for nine medium-angle reflexions (Cu $K\alpha$, $\lambda = 1\cdot5418$ Å).

Intensity data were collected with the diffractometer, by use of a scintillation counter, nickel-filtered copper radiation, and a θ–2θ scanning technique. Measurements were made for each of the 1104 independent reflexions with $2\theta < 128°$. Three standard reflexions, which were monitored periodically, showed no decrease in intensity during the collection of data.

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Immediately after data collection, accurate values for the cell parameters were determined by a least-squares analysis of 2θ values for 12 high-angle reflexions (Cu $K\alpha_1$, $\lambda = 1\cdot54051$ Å); these cell parameters were not significantly different from those obtained prior to the collection of intensity data. Crystal data are listed in Table 1.

Table 1. *Crystal data*

Stoichiometry	$CaCl_2.4H_2O$
Z	2
Space group	$P\bar{1}$
$a=6\cdot593$ (2) Å	$\alpha= 97\cdot77$ (5)°
$b=6\cdot364$ (5)	$\beta= 93\cdot52$ (4)
$c=8\cdot557$ (3)	$\gamma=110\cdot56$ (3)
ϱ (calculated) $= 1\cdot837$ g. cm^{-3}	
ϱ (observed) $= 1\cdot85$	
$\mu=148\cdot3$ cm^{-1}	

The reported standard deviations are five times greater than those obtained from the least-squares analysis. The density was measured by flotation in a mixture of benzene and ethylene dibromide.

The intensities were assigned variances, $\sigma^2(I)$, according to the statistics of the scan and background counts plus a correctional term $(0\cdot03S)^2$, S being the scan counts. The intensities and their variances were corrected for Lorentz and polarization factors. Corrections for the crystal absorption were applied by using the program *ORABS* (Wehe, Busing & Levy, 1962), no corrections were made for absorption by the mineral oil and capillary. The data were scaled by means of a Wilson (1942) plot.

Coordinates for the calcium and chloride ions and for the oxygen atoms were readily obtained by direct methods with the use of the computer program *MULTAN* (Germain, Main & Woolfson, 1971). The trial structure was refined by use of a modified version of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). The quantity minimized was $\sum w(F_0^2 - F_c^2/k^2)^2$, where k is a scale factor and the weight w is equal to $1/\sigma^2(F_0^2)$. Scattering factors were from the *International Tables for X-ray Crystallog-*

raphy (1962), and anomalous dispersion correction factors were from Cromer & Liberman (1970). Final cycles of refinement included the positional parameters, anisotropic temperature factors, and Zachariasen's (1963) extinction parameter g [as formulated by Coppens & Hamilton (1970)]. During the final cycle of refinement no parameter shifted more than one fifth of its estimated standard deviation. A final three-dimensional electron-density difference map showed several peaks and troughs of magnitudes ranging up to 1·5 e.Å^{-3}. The final R index $(\sum||F_o|-|F_c||/\sum|F_o|)$ is 0·085 and the final goodness-of-fit is 5·6.

Results

Table 2 lists the final atomic parameters and their estimated standard deviations. The average estimated standard deviations in positional coordinates are approximately 0·001 Å for the calcium and chloride ions and 0·004 Å for the oxygen atoms. Table 3 lists the observed and calculated structure factors.

Three crystalline forms of calcium chloride tetrahydrate have been described in the literature (for details see *Gmelins Handbuch der Anorganischen Chemie*, 1957). The modification we obtained appears to correspond with that described as the α form. Apparently the α form is the most stable modification, and, under appropriate conditions, the other crystalline modifications convert to this form.

The two chloride ions and the four water molecules are the six nearest neighbors around the calcium ion. The distorted trigonal prismatic coordination polyhedron defined by these six ligands is shown in Fig. 1, and relevant distances are given in Table 4. In addition

Table 2. *The final atomic parameters and their standard deviations*

The values have been multiplied by 10^4. Temperature factors are in the form

$$T = \exp\left(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl\right).$$

The final value for the isotropic extinction parameter is $g = 0.014$ (5).

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ca	1188 (2)	−140 (2)	2615 (1)	122 (4)	105 (4)	83 (2)	10 (3)	4 (2)	−14 (2)
Cl(1)	2910 (2)	−2777 (2)	504 (2)	148 (5)	128 (5)	66 (2)	27 (3)	16 (2)	−2 (2)
Cl(2)	−2495 (2)	−2393 (2)	4130 (2)	126 (4)	127 (5)	74 (2)	−15 (3)	8 (2)	−10 (2)
O(1)	−1823 (7)	−1871 (7)	434 (6)	141 (12)	134 (12)	109 (7)	8 (9)	10 (7)	−22 (8)
O(2)	−152 (7)	2895 (7)	2715 (6)	181 (13)	128 (12)	91 (7)	43 (10)	−7 (7)	7 (7)
O(3)	4788 (7)	2409 (7)	2663 (5)	171 (13)	165 (13)	79 (7)	−24 (11)	32 (8)	−24 (8)
O(4)	2493 (7)	−2509 (7)	4154 (5)	184 (13)	154 (12)	81 (6)	57 (11)	4 (7)	−9 (7)

Table 3. *Calculated and observed structure factors*

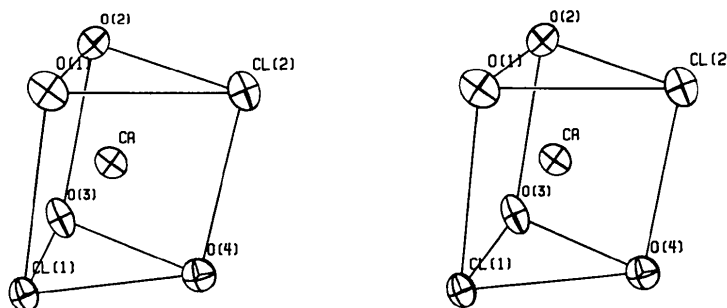From left to right, columns contain values of l, $10F_o$ and $10F_c$.

Fig. 1. Stereoscopic view of the calcium coordination polyhedron. The atoms are represented by ellipsoids, defined by the principal axes of thermal vibration, and scaled to include 50% probability. [This drawing was prepared by use of the computer program *ORTEP* (Johnson, 1965)].

to these nearest neighbors, the calcium ion also forms a close contact (2·936 Å) with a chloride ion of an adjacent polyhedron [Cl(2): $-x$, $-y$, $1-z$]. Of the three geometrical isomers that can be proposed for a trigonal prismatic polyhedron composed of two chloride ions and four oxygen atoms, the one found here has the two chloride ions at maximum separation.

Table 4. *Distances within the coordination polyhedron of the calcium ion*

Ca—Cl(1)	2·853 Å
Ca—Cl(2)	2·842
Ca—O(1)	2·468
Ca—O(2)	2·384
Ca—O(3)	2·352
Ca—O(4)	2·461
Cl(1)–O(1)	3·365
Cl(1)–O(3)	3·323
Cl(1)–O(4)	3·140
Cl(2)–O(1)	3·266
Cl(2)–O(2)	3·585
Cl(2)–O(4)	3·314
O(1)–O(2)	3·165
O(2)–O(3)	3·380
O(3)–O(4)	3·421

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