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Calcium and Strontium Dichloride Hexahydrates by Neutron Diffraction*

BY P. A. AGRON AND W. R. BUSING

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

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Abstract. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, isotypic, trigonal, $P321$, $Z = 1$, unit cells from X-ray $\text{Cu K}\alpha_1$, $\lambda_x = 1.54051$, $\lambda_N = 1.077 \text{ \AA}$, room temperature. $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $M_r = 219.08$, $a = 7.8759 (2)$, $c = 3.9545 (2) \text{ \AA}$, $V = 212.43 (6) \text{ \AA}^3$, $D_m = 1.71$, $D_x = 1.7126 \text{ g cm}^{-3}$, $\mu = 2.566 \text{ cm}^{-1}$, $F(000) = 14.00 \text{ fm}$, $R(F) = 0.0287$ for 304 unique reflections. $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $M_r = 266.62$, $a = 7.9596 (3)$, $c = 4.1243 (2) \text{ \AA}$, $V = 226.29 \text{ \AA}^3$, $D_m = 1.93$, $D_x = 1.9565 \text{ g cm}^{-3}$, $\mu = 2.430 \text{ cm}^{-1}$, $F(000) = 16.12 \text{ fm}$, $R(F) = 0.0356$ for 325 unique reflections. Nine water molecules are coordinated to each metal ion. Three of these adjoin only one cation and six are shared between two such ions. These water molecules are hydrogen-bonded to the Cl^- ions so that each anion is surrounded by six H atoms in a distorted octahedral arrangement.

Introduction. These single-crystal neutron diffraction studies are part of a program to locate the H atoms precisely and to investigate the role of water in simple salt hydrates.

Experimental. Lattice parameters from least-squares refinement based on X-ray diffractometer Bragg angles for 12 high-angle reflections ($2\theta = 120$ to 130°); $\text{Cu K}\alpha_1$ radiation, $\lambda = 1.54051 \text{ \AA}$. Results agree with reported values (Herrmann, 1930, 1931; Jensen, 1940; Leclaire & Borel, 1977; English & Nassimbeni, 1984).

Crystals for neutron diffraction obtained by slow growth at room temperature in desiccator over concentrated sulfuric acid. Selected crystals mounted on quartz fibers and sealed in thin quartz envelopes (Agron & Busing, 1985). Reported D_m taken from published

values (*CRC Handbook of Chemistry and Physics*, 1984).

Neutron diffraction intensities measured (Busing, Smith, Peterson & Levy, 1964) to $(\sin\theta/\lambda)_{\text{max}} = 0.71 \text{ \AA}^{-1}$, corrected for absorption (Busing & Levy, 1957). No significant variation of standard reflections observed.

Least-squares structure refinement started with reported X-ray structure of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (Jensen, 1940) with H atoms located on expected hydrogen bonds to Cl^- ions (Agron & Busing, 1969). Refinements based on F^2 with weights $w = 1/[\sigma_c^2 + (0.03 F^2)^2]$, where σ_c is the standard error of F^2 based on counting statistics. Variables included scale factors, coordinates, anisotropic temperature-factor coefficients, and extinction parameters. Anisotropic extinction (Coppens & Hamilton, 1970) used for the calcium compound; isotropic extinction (Zachariasen, 1967) sufficed for the strontium salt. Neutron scattering factors: Ca, 4.90; Sr, 7.02; Cl, 9.579; O, 5.805; H, -3.741 fm (Koester & Yelon, 1982). Equivalent reflections, corrected for extinction, combined for final least-squares adjustment. Table 1 summarizes experiments and refinements.†

Computer programs: lattice-parameter refinement (Busing, Ellison, Levy, King & Roseberry, 1968; Busing, 1970); absorption corrections, *ORABS* (Wehe, Busing & Levy, 1962); structure-factor least squares, *XFLS* (Busing, Martin & Levy, 1962); function and error calculation, *ORFFE* (Busing, Martin & Levy, 1964); and crystal-structure illustration, *ORTEP* (Johnson, 1976).

† Lists of anisotropic temperature-factor coefficients and observed and calculated squares of neutron diffraction structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42520 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. Table 2 lists the fractional coordinates and equivalent isotropic thermal parameters. The oxygen positions for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ are in good agreement with the X-ray results of Leclaire & Borel (1977), and the hydrogen positions are roughly the same as those which they obtained from electrostatic calculations (Baur,

1965). These authors correctly deduced that there was a typographical error, later corrected, in our original report (Agron & Busing, 1969). For $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, a comparison with the coordinates from the X-ray study by English & Nassimbeni (1984) shows good agreement for the heavy atoms and fair agreement for hydrogen.

Table 3 gives interatomic distances, bond angles, and dihedral angles between planes defined by three atoms. Fig. 1 is a stereoscopic drawing of the unit cell for $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is essentially the same. The two kinds of water molecules are coordinated differently to the metal ions, with each O(1) adjoining only one cation and each O(2) shared between two metal ions. Thus, these structures are intermediate between that of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Agron & Busing, 1985), where all waters are of the former type, and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Padmanabhan, Busing & Levy, 1978), where all water molecules are shared between two cations. The ninefold coordination polyhedron can be described as a right triangular prism of six O(2) atoms with three O(1) atoms projecting out from its vertical faces. The $M-O(1)$ distances are close to the sums of the ionic packing radii (Pauling, 1960).

Both kinds of H atoms are hydrogen-bonded to Cl^- ions, with three H(1) and three H(2) atoms forming a distorted octahedral coordination shell about the anion. The twist angle of water (1) appears to be determined primarily by the hydrogen bonding, and this in turn tends to pull the Cl^- ion (at the right in Fig. 1) up the threefold axis to a z coordinate larger than 0.5.

Table 1. Summary of experiments and refinements

	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$
All observations		
Number	830	791
$R(F)$	0.0299	0.0405
$R(F^2)$	0.0508	0.0629
$wR(F^2)$	0.0658	0.0768
S	1.635	1.702
Unique observations		
Number	304	325
$R(F)$	0.0287	0.0356
$R(F^2)$	0.0485	0.0488
$wR(F^2)$	0.0635	0.0634
S	1.702	1.408
Δ/σ	0.05	0.003
Index range	$0 \leq h \leq 10$ $0 \leq k \leq 10$ $0 \leq l \leq 5$	$0 \leq h \leq 10$ $0 \leq k \leq 10$ $0 \leq l \leq 6$
Transmission factors		
Maximum	0.465	0.534
Minimum	0.314	0.432
Extinction factor		
Minimum	0.32	0.59
Crystal volume (mm^3)	82.71	34.99
Crystal mass (mg)	139	67.5

Table 2. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters, B_{eq} (\AA^2) for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$

$$B_{eq} = \frac{1}{3} \text{Tr}(\beta g); g_{ij} = a_i \cdot a_j.$$

	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$				$\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$			
	x	y	z	B_{eq}	x	y	z	B_{eq}
Cation	0	0	0	1.41	0	0	0	1.34
Cl	3333	6667	4249 (2)	2.16	3333	6667	4190 (2)	2.44
O(1)	3114 (2)	0	0	2.26	3229 (2)	0	0	2.57
O(2)	-2132 (1)	0	5000	1.94	-2219 (2)	0	5000	1.94
H(1)	4326 (2)	988 (3)	-926 (6)	4.13	4419 (3)	964 (4)	-899 (7)	4.51
H(2)	-2330 (3)	1113 (3)	4835 (5)	3.58	-2415 (4)	1103 (3)	4887 (5)	3.50

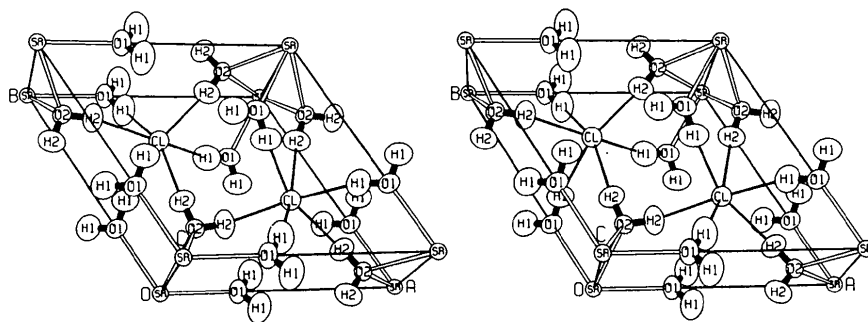


Fig. 1. Stereoscopic drawing of the hexagonal unit cell of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.

Water molecule (2), on the other hand, is oriented in a way which makes the O(2) atom have nearly tetrahedral coordination to its H(2) atoms and the cations. In spite of its hydrogen bonding to the Cl⁻ ion, its twist angle is opposite from what might be expected. Although the Cl⁻ ion at the right in Fig. 1 has a *z* coordinate greater than 0.5, the H(2) atoms bonded to it have *z* coordinates less than 0.5. It is possible that this twist is dictated by the proximity of H(1) atoms at 2.269 and 2.387 Å in CaCl₂·6H₂O and SrCl₂·6H₂O, respectively. The O—H...Cl angles are about 164° for both crystals.

The O—H distances are in the normal range for water molecules. These distances, corrected for thermal motion based on the riding model (Busing & Levy, 1964), are also listed in Table 3. A comparison of the H—O—H angles of the two water molecules shows that

Table 3. *Interatomic distances, bond angles and dihedral angles between planes defined by three atoms*

	CaCl ₂ ·6H ₂ O	SrCl ₂ ·6H ₂ O
Uncorrected for thermal motion, except for O—H corr.		
<i>(a) Distances (Å)</i>		
M—O(1)	2.453 (1)	2.570 (2)
M—O(2)	2.594 (1)	2.715 (1)
O(1)—H(1)	0.953 (2)	0.947 (3)
O(1)—H(1) corr.*	0.986 (2)	0.981 (3)
O(2)—H(2)	0.966 (2)	0.966 (2)
O(2)—H(2) corr.*	0.995 (2)	0.995 (2)
H(1)...Cl	2.266 (2)	2.286 (3)
H(2)...Cl	2.279 (2)	2.265 (2)
O(1)...Cl	3.194 (1)	3.202 (1)
O(2)...Cl	3.218 (1)	3.208 (1)
<i>(b) Angles (°)</i>		
H(1)—O(1)—H(1)	107.2 (3)	107.0 (3)
H(2)—O(2)—H(2)	104.1 (3)	104.0 (3)
O(1)—H(1)...Cl	164.4 (2)	162.6 (2)
O(2)—H(2)...Cl	163.8 (2)	165.0 (2)
H(1)...Cl...H(1)	89.7 (1)	88.4 (1)
H(2)...Cl...H(2)	117.53 (3)	117.23 (4)
<i>(c) Dihedral angles (°)</i>		
M—O(2)—M†		
H(2)—O(2)—H(2)	94.9 (1)	93.5 (2)
M—O(2)—M†		
Cl...O(2)...Cl	82.56 (2)	81.72 (3)
M—O(1)—M†		
H(1)—O(1)—H(1)	61.5 (2)	60.8 (2)
M—O(1)—M†		
Cl...O(1)...Cl	53.53 (2)	53.06 (2)
Cl...Cl...H(1)†		
Cl...Cl...H(2)†	42.4 (1)	46.1 (1)

* Riding-motion correction (Busing & Levy, 1964).

† Planes parallel to the *c* axis.

the shorter M—O distance corresponds to the greater H—O—H angle. This is consistent with bonding effects observed in other hydrates (Agron & Busing, 1985; Chidambaram, 1962; Chidambaram, Sequeira & Sikka, 1964; Hamilton & Ibers, 1968; Datt & Ozerov, 1972).

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