

Calcium chloride rhenate(VII) dihydrate

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The crystal structure of calcium chloride rhenate(VII) dihydrate, $\text{CaCl}(\text{ReO}_4)\cdot 2\text{H}_2\text{O}$, investigated at 85 K, consists of calcium cations, chloride anions, rhenate(VII) anions and water molecules. In the nearly tetrahedral rhenate(VII) anion, all constituent atoms lie on special positions of $m2m$ (Re) and m (O) site symmetries. The Cl^- anion and water O atom lie on special positions of $m2m$ and 2 site symmetries, respectively. The Ca^{2+} ion, also on a special position ($m2m$), is eight-coordinated in a distorted square-antiprismatic coordination mode. The crystal has a layered structure stabilized by $\text{Ca}-\text{O}$ coordination bonds and $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonds.

Comment

Currently, all rhenate(VII) salts of the metals of the first and second main groups of the periodic table are known, except for beryllium rhenate(VII) (*e.g.* Krebs & Hasse, 1976; Todorov & Macicek, 1995). Most of these compounds have been investigated as easy-to-prepare crystalline hydrates. The other properties explored include thermal decomposition patterns monitored by thermogravimetric measurements [*e.g.* lithium rhenate(VII) monohydrate; Abakumov *et al.*, 2001]. Calcium chloride rhenate(VII) dihydrate was obtained in an effort to crystallize a new calcium rhenate(VII) hydrate from the reaction between calcium chloride and rhenic(VII) acid in aqueous solution. Previously reported data on calcium rhenate(VII) include three crystal structure determinations of the dihydrate salt (Matveeva *et al.*, 1980; Picard *et al.*, 1988; Baur & Kassner, 1992).

The title crystal structure consists of calcium cations, chloride anions, rhenate(VII) anions and water molecules of crystallization. Atom Re1 lies on a special position of $m2m$ site symmetry and the rhenate(VII) O atoms (O2 and O3) occupy special positions of m site symmetry. The rhenate(VII) anion has a slightly distorted tetrahedral geometry, as shown by the O—Re—O bond angles, which deviate slightly from ideal tetrahedral values (Table 1). The Re—O bond lengths are equal and in good agreement with values observed for similar

compounds [*e.g.* $\text{Sr}(\text{ReO}_4)_2\cdot 2\text{H}_2\text{O}$ (Todorov *et al.*, 1996), $\text{Ba}(\text{ReO}_4)_2\cdot \text{H}_2\text{O}$ (Todorov & Macicek, 1995) and $\text{LiReO}_4\cdot \text{H}_2\text{O}$ (Abakumov *et al.* 2001)].

The chloride anion and water atom O1 lie on special positions of $m2m$ and 2 site symmetries, respectively.

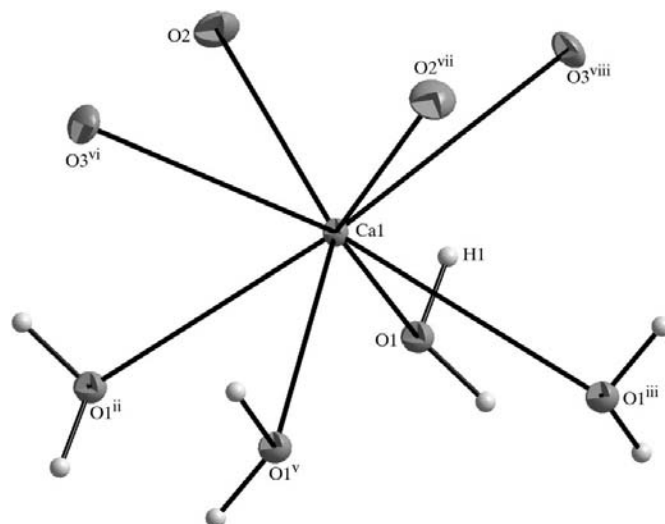


Figure 1

The coordination environment of the calcium ion. [Symmetry codes: (ii) $-x, -y + 1, -z + 1$; (iii) $x, y, -z + \frac{1}{2}$; (v) $-x, -y + 1, z - \frac{1}{2}$; (vi) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (vii) $-x, y, -z + \frac{1}{2}$; (viii) $-x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.]

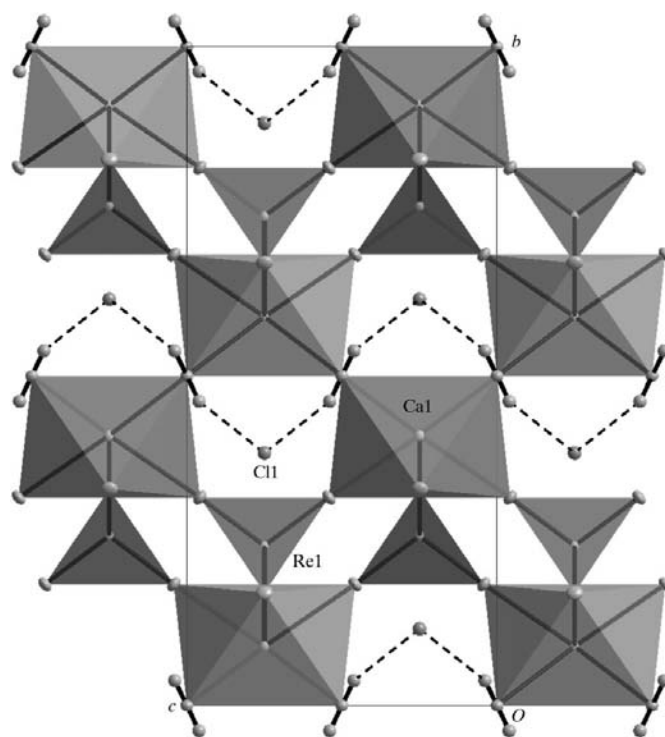


Figure 2

The crystal packing, showing layers of Ca^{2+} cations and Cl^- anions alternating with ReO_4^- anion layers perpendicular to $[010]$. Dashed lines indicate hydrogen bonds.

The calcium ion lies on a special position of $m2m$ symmetry and is eight-coordinated in a distorted square-antiprismatic mode (Fig. 1). The four ligands forming the square basal plane are water molecules [Ca—O = 2.531 (2) Å; Table 1]. The other basal plane is formed by four O atoms from four different rhenate(VII) anions [Ca—O = 2.359 (2) and 2.401 (2) Å; see Fig. 1 for the relevant symmetry operations]. The two basal planes are parallel. The central Ca²⁺ ion deviates by 1.272 (2) and 1.245 (2) Å from the two basal planes formed by the water and rhenate(VII) ligands, respectively. There are no chloride anions within the Ca²⁺ coordination environment. This coordination pattern of the Ca²⁺ ion is comparable to that reported for calcium rhenate(VII) dihydrate (Baur & Kassner, 1992); however, in that crystal structure, the Ca²⁺ ion does not lie on a special position and the distortion of the coordination polyhedron is greater than in the case of the title compound.

The packing (Fig. 2) comprises layers consisting of Ca²⁺ cations and chloride anions alternating with rhenate(VII) anion layers perpendicular to [010]. Neighbouring layers are joined by Ca—O coordination bonds. Within each Ca²⁺ cation—chloride anion layer, cation and anion columns can be distinguished (Fig. 3). Each Cl[−] anion participates in four O—H...Cl hydrogen bonds with four symmetry-related water molecules (Fig. 3). Thus, R₂⁴(8) structural motifs are formed (Etter *et al.*, 1990). Each such motif consists of the following atoms: Cl1, H1, O1, H1($x, -y + 1, -z + 1$), Cl1($-x + 1, -y + 1, z - \frac{1}{2}$), H1($-x + 1, -y + 1, -z + 1$), O1($-x + 1, -y + 1, -z + 1$) and H1($-x + 1, y, z$).

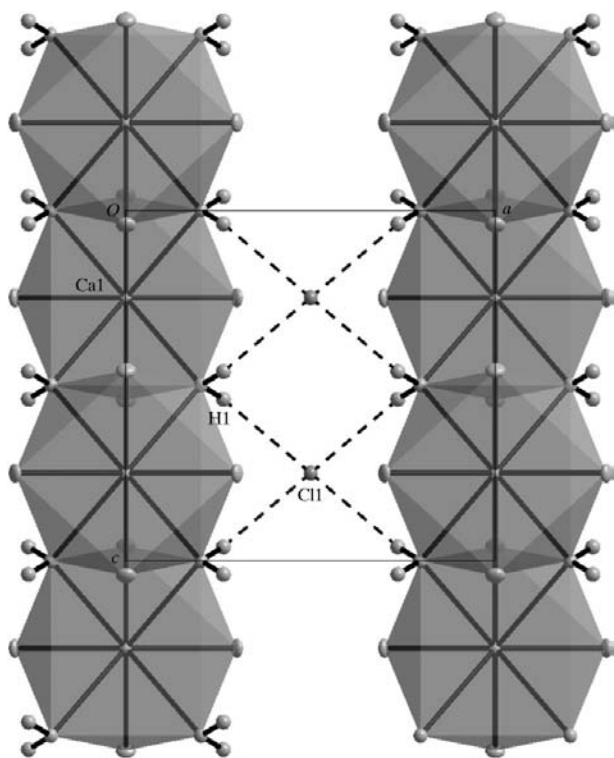


Figure 3
A view of the Ca²⁺ cation and Cl[−] anion layer along [010], showing cation and anion chains extending along [001] and the hydrogen-bonding scheme (dashed lines).

Experimental

The title compound was obtained by the reaction of calcium chloride with rhenic(VII) acid in aqueous solution. The crystals were obtained in the form of colourless transparent blocks. A crystal suitable for X-ray analysis was cut from a larger crystal.

Crystal data

CaCl(ReO ₄)·2H ₂ O	$V = 660.0 (3) \text{ \AA}^3$
$M_r = 361.76$	$Z = 4$
Orthorhombic, <i>Cmcm</i>	Mo $K\alpha$ radiation
$a = 7.009 (2) \text{ \AA}$	$\mu = 19.5 \text{ mm}^{-1}$
$b = 14.148 (4) \text{ \AA}$	$T = 85 (2) \text{ K}$
$c = 6.656 (2) \text{ \AA}$	$0.09 \times 0.08 \times 0.05 \text{ mm}$

Data collection

Kuma KM-4 CCD diffractometer	8292 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	985 independent reflections
$T_{\min} = 0.265, T_{\max} = 0.423$	935 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.065$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.016$	35 parameters
$wR(F^2) = 0.037$	All H-atom parameters refined
$S = 1.09$	$\Delta\rho_{\max} = 3.32 \text{ e \AA}^{-3}$
985 reflections	$\Delta\rho_{\min} = -2.60 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Re1—O2	1.726 (2)	Ca1—O2	2.359 (2)
Re1—O3	1.723 (2)	Ca1—O3 ⁱ	2.401 (2)
Ca1—O1	2.531 (2)	Ca1—Ca1 ⁱⁱ	4.189 (2)
O2—Re—O2 ^{ix}	106.45 (14)	O3—Re—O3 ^x	108.58 (14)
O3—Re1—O2	110.45 (5)	O1—Ca1—O1 ⁱⁱⁱ	68.33 (9)
O2—Ca1—O2 ⁱⁱⁱ	111.07 (11)	O1—Ca1—O1 ⁱⁱⁱ	82.20 (6)
O3 ⁱ —Ca1—O3 ^{iv}	122.48 (10)	O2—Ca1—O3 ⁱ	74.20 (4)
O1—Ca1—O1 ^v	119.67 (5)		

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x, -y + 1, -z + 1$; (iii) $x, y, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (v) $-x, -y + 1, z - \frac{1}{2}$; (ix) $x, y, -z + \frac{1}{2}$; (x) $-x, y, -z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 ⁱ ...Cl1	0.74 (3)	2.44 (3)	3.135 (2)	159 (4)

The water H atom was located in a difference Fourier map and refined isotropically. The highest peaks in the difference Fourier map are near atom Re1 (a peak of 3.32 e Å^{−3} at a distance of 0.56 Å and a peak of 1.83 e Å^{−3} at 0.61 Å).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3099). Services for accessing these data are described at the back of the journal.

References

- Abakumov, A. M., Rozova, M. G., Shpanchenko, R. V., Mironov, A. V., Antipov, E. V. & Bramnik, K. G. (2001). *Solid State Sci.* **3**, 581–586.
- Baur, W. H. & Kassner, D. (1992). *J. Solid State Chem.* **100**, 166–169.
- Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Version 3. Crystal Impact GbR, Bonn, Germany.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Krebs, B. & Hasse, K. (1976). *Acta Cryst.* **B32**, 1334–1337.
- Matveeva, R. G., Ilyukhin, V. V., Varfolomeev, M. B. & Belov, N. V. (1980). *Dokl. Akad. Nauk SSSR*, **252**, 99–102.
- Oxford Diffraction (2006). *CrysAlis RED* and *CrysAlis CCD*. Versions 1.171. Oxford Diffraction Poland, Wrocław, Poland.
- Picard, J. P., Besse, J. P., Chevalier, R. & Gasperin, M. (1988). *J. Solid State Chem.* **75**, 205–206.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Todorov, T., Angelova, O. & Macicek, J. (1996). *Acta Cryst.* **C52**, 1319–1323.
- Todorov, T. & Macicek, J. (1995). *Acta Cryst.* **C51**, 1034–1038.