Carlhintzeite, Ca$_2$AlF$_7$$\cdot$H$_2$O, from the Gigante granitic pegmatite, Córdoba province, Argentina: description and crystal structure

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ABSTRACT

Carlhintzeite, Ca$_2$AlF$_7$$\cdot$H$_2$O, has been found at the Gigante pegmatite, Punilla Department, Córdoba Province, Argentina. It occurs as colourless prismatic crystals up to 0.8 mm long, ubiquitously twinned on {001}. Electron microprobe analyses provided the empirical formula Ca$_{1.98}$Al$_{1.02}$F$_{6.24}$(OH)$_{0.76}$$\cdot$H$_{1.62}$O. A crystal fragment used for the collection of structure data provided the triclinic, C1 cell: $a$ = 9.4227(4), $b$ = 6.9670(5), $c$ = 9.2671(7) Å, $\alpha$ = 90.974(6), $\beta$ = 104.802(5), $\gamma$ = 90.026(6)$^\circ$, $V$ = 558.08(7) Å$^3$ and $Z$ = 4. The crystal structure, solved by direct methods and refined to $R_1 = 0.0322$ for 723 $F_0 > 4\sigma F$ reflections, is made up of linkages of AlF$_6$ octahedra, CaF$_8$ polyhedra and CaF$_6$(H$_2$O)$_2$ polyhedra. The AlF$_6$ octahedra are isolated from one another, but share polyhedral elements with Ca polyhedra. Most notably, the Al1 octahedron shares trans faces with two CaF$_8$ polyhedra and the Al2 octahedron shares trans edges with two CaF$_6$(H$_2$O)$_2$ polyhedra. The linkage of the Ca polyhedra alone can be described as a framework in which edge-sharing chains along $b$ are cross-linked by edge-sharing. Edge-sharing chains of Ca polyhedra along $b$ in the carlhintzeite structure are similar to those along $c$ in the structures of gearksutite, CaAlF$_4$(OH)·(H$_2$O), and prosopite, CaAl$_2$F$_4$(OH)$_4$.

KEYWORDS: carlhintzeite, gearksutite, prosopite, crystal structure, Córdoba, Argentina.

Introduction

Carlhintzeite is a rare calcium aluminium fluoride hydrate first described by Dunn et al. (1979) from a single museum specimen simply labelled “Hagendorf”. The authors noted the matrix and associated species (rockbridgeite, pyrite, strengite and apatite) to be similar to those from the Hagendorf pegmatites in Bavaria, Germany, but they were unable to determine from which of the pegmatites in this area the specimen may have originated. Since that time, additional specimens containing carlhintzeite have been found at the Hagendorf Süd pegmatite, and this is likely to be the source of the original specimen (Dunn et al., 1979). Carlhintzeite has also been found at the Perda Niedda mine, Sardinia, Italy (Bortolozzi et al., 2007), at Kreuzberg Mount, Bavaria, Germany (Dill et al., 2008) and at the Serra Blanca pegmatite, Paraíba, Brazil (Wegner et al., 1998).

Dunn et al. (1979) were unable to find a carlhintzeite crystal suitable for crystal structure analysis because of ubiquitous twinning by rotation about [010]. During on-going research of the secondary and hydrothermal minerals from the Gigante pegmatite, Córdoba province, Argentina, which has already yielded two new species (gayite and galliskiite: Kampf et al.,...
At the Gigante pegmatite, carlhintzeite occurs as single crystals (Fig. 1) up to 0.8 mm long, and as crystal aggregates up to 5 mm long, growing on drusy bermanite covering dark brown triplite. Microcrystalline crusts of lavender phosphosiderite and pale- to bright-pink strengite are found in the same paragenesis. Carlhintzeite crystals are colourless with vitreous lustre. Crystals are elongated along [010]; the best developed form is {001}, with smaller {100}, {110} and {1¯10} (Fig. 2a). Many crystals are twinned about [010] with {001} as the contact plane; this is evident as grooves in the forms belonging to the {001} zone (Fig. 2b). The streak is white.

**Occurrence**

The Gigante pegmatite is 18 km WSW of the town of Tanti, Punilla Department, Córdoba Province, Argentina (31°24′31.0″ S, 64°46′19.6″ W). It is an intragranitic body related to the Devonian Achala batholith, and it is part of the Punilla District (Galliski, 1999). Some of the most relevant features of the pegmatite were summarized by Kampf et al. (2010a).

The rather large F content of the Achala granite (and the related pegmatites) is reflected, among other features, in the ubiquitous presence of triplite and fluorapatite in the pegmatites. Late, F-bearing hydrothermal solutions are presumed to be responsible for the deposition of several unusual minerals in cracks and voids left by altered phosphates and sulphides and, although they are rather widespread, they always occur in extremely small quantities. Some species appear to be restricted to a single pegmatite. In the Gigante pegmatite, some of the F-bearing minerals (in addition to the primary phosphates mentioned above) are morinite, galliskiite, fluellite, lacroixite, and carlhintzeite, whereas fluorite, pachnolite, fluellite and benyacarite are found in the pegmatites of the nearby Cerro Blanco district.

**Chemical composition**

Six analyses were conducted on carlhintzeite (Table 1) at the Centro de Microscopía Electrónica Luis Br (Universidad Complutense de Madrid) using a JEOL JXA 8900M electron microprobe operating in WDS mode. The

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**Fig. 1.** Carlhintzeite crystals up to 0.4 mm long on bermanite.

**Fig. 2.** SEM images of carlhintzeite crystals. (a) Crystals in parallel growth showing the dominant {001} form, with smaller {100}, {110} and {1¯10}. (b) Grooves in the {110} and {110} forms, due to multiple twinning.
CARLHINTZEITE, ARGENTINA

Table 1. EMPA results (wt.%) of carlhintzeite from the Gigante pegmatite.

| Analysis # | 1    | 2    | 3    | 4    | 5    | 6    | Average | Ideal* |
|------------|------|------|------|------|------|------|---------|--------|
| Al₂O₃      | 20.52| 20.69| 20.47| 21.12| 20.31| 20.13| 20.54   | 19.75  |
| CaO        | 43.08| 43.46| 44.69| 43.51| 43.84| 44.34| 43.88   | 43.45  |
| F          | 47.01| 47.40| 46.87| 45.77| 48.46| 46.82| 46.82   | 51.52  |
| −O=F       | 19.79| 19.96| 19.74| 19.27| 20.41| 19.13| 19.71   | 21.69  |
| Total (−O=F)| 90.82| 91.59| 92.29| 91.82| 91.88| 90.77| 91.53   | 93.02  |
| H₂O         | 9.18 | 8.41 | 7.71 | 8.18 | 8.12 | 9.23 | 8.47    | 6.98   |
| a.p.f.u. based on 3 (Al+Ca) Al | 1.03 | 1.03 | 1.01 | 1.03 | 1.02 | 1.00 | 1.02    | 1.00   |
|            | Ca  | 1.97 | 1.97 | 1.99 | 1.97 | 1.98 | 2.00    | 2.00   |
|            | F   | 6.34 | 6.34 | 6.18 | 6.01 | 6.52 | 6.05    | 6.24   |
|            | H   | 2.61 | 2.37 | 2.14 | 2.27 | 2.30 | 2.59    | 2.38   |

* Ideal composition corresponding to Ca₂AlF₇·H₂O
† H₂O calculated by difference

Table 2. Data-collection and structure-refinement details for carlhintzeite.

| Diffractometer | Rigaku R-Axis Rapid II |
|----------------|------------------------|
| X-ray radiation / power | Mo-Kα (λ = 0.71075 Å) / 50 kV, 40 mA |
| Temperature | 298(2) K |
| Structural formula | Ca₂AlF₇·H₂O |
| Space group | C1 |
| Unit-cell dimensions | a = 9.4227(4) Å, b = 6.9670(5) Å, c = 9.2671(7) Å, α = 90.974(6)°, β = 104.802(5)°, γ = 90.026(6)° |
| Volume | 558.08(7) Å³ |
| Density (for above formula) | 2.916 g/cm³ |
| Absorption coefficient | 2.179 mm⁻¹ |
| F(000) | 504 |
| Crystal size | 40 μm x 30 μm x 20 μm |
| θ range | 3.69 to 23.24° |
| Index ranges | −10 ≤ h ≤ 10, −7 ≤ k ≤ 7, −10 ≤ l ≤ 10 |
| Reflections collected / unique | 6126 / 841 [Rint = 0.0546] |
| Reflections with Fo > 4σF | 723 |
| Completeness to θ = 27.48° | 99.4% |
| Max. and min. transmission | 0.9577 and 0.9179 |
| Refinement method | Full-matrix least-squares on F² |
| Parameters refined | 109 |
| GoF | 1.056 |
| Final R indices [Fo > 4σF] | R₁ = 0.0322, wR₂ = 0.0782 |
| R indices (all data) | R₁ = 0.0388, wR₂ = 0.0814 |
| Largest diff. peak / hole | +0.565 / −0.354 e/A³ |

Rint = Σ|Fo²−Fc²|/|ΣFo²|, GoF = S = Σ|w(Fo²−Fc²)|/(n−p))¹/², R₁ = Σ|Fo−Fc|/|ΣFo|. wR₂ = Σ|w(Fo²−Fc²)|/|Σw(Fo²)|¹/². w = 1/[σ²(Fo²) + (aP)² + bP] where a is 0.0522, b is 0.5616 and P is [2Fo² + Max(Fo,0)]/3.
analytical conditions were 15 kV, 20 nA and a beam diameter of 5 μm. Counting times were 10 s on peak and 5 s on the background at each side of the peak. The standards were calcite (for Ca), fluorite (for F) and sillimanite (for Al). The H₂O content has been calculated by difference, as the very small amount of available material precluded a direct determination. Other elements sought but not detected (at a 2σ level, in ppm) and their standards were Mg (200, kaersutite), Fe (550, almandine), Mn (420, almandine), Zn (1100, gahnite), Na (210, albite) and P (440, fluorapatite).

The crystals appear to be free of chemical zonation. The average chemical formula, recalculated on the basis of 3 a.p.f.u. (Ca+Al) is Ca₁₀.₉₈Al₁.₀₂F₆.₂₄(OH)₀.₇₆H₁.₆₂O. The only significant difference between the composition of carlhintzeite from the type locality compared to that of the mineral from the Gigante pegmatite is that the latter has a somewhat smaller F content (52.1 vs. 46.8 wt.%). Nevertheless, as noted below, the structure determination provided no evidence to support the assignment of OH to any specific anion sites and the H₂O sites in the structure yield only one H₂O per formula unit.

X-ray crystallography and structure refinement

Dunn et al. (1979) determined carlhintzeite crystals on the type specimen to be twinned ubiquitously by rotation about [010]. Using Weissenberg and precession X-ray diffraction techniques, they correctly concluded that the mineral is triclinic and provided the C-centered pseudomonoclinic cell: \(a = 9.48(5)\) Å, \(b = 6.98(3)\) Å, \(c = 9.30(5)\) Å, \(\alpha = 91.14(10)\)°, \(\beta = 104.85(10)\)° and \(\gamma = 90.0(10)\)°. As described above, carlhintzeite from the Gigante pegmatite is also twinned, but a careful search yielded an untwinned fragment that was subsequently used for structure data collection. To be consistent with the original description, we also used the non-standard C-centred cell in our determination of the carlhintzeite structure. The reduced cell is \(P\bar{1}\), \(a = 5.8581(3)\) Å, \(b = 5.8606(3)\) Å, \(c = 9.2671(7)\) Å, \(\alpha = 78.739(6)\)°, \(\beta = 77.551(7)\)° and \(\gamma = 72.957(5)\)°.

Single-crystal X-ray data were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer utilizing monochromatized Mo-Kα radiation. The Rigaku CrystalClear software package was used for processing the structure data, including the application of an empirical absorption correction. The structure was

| Table 3. Atomic coordinates and displacement parameters \(\AA^2\) for carlhintzeite. |
|---|---|---|---|---|---|---|---|---|---|
|    | \(x\)   | \(y\)   | \(z\)   | \(U_{11}\) | \(U_{22}\) | \(U_{33}\) | \(U_{12}\) | \(U_{13}\) | \(U_{23}\) |
| Ca1 | 0.584(7) | 0.9998(1) | 0.540(8) | 0.340(6) | 0.290(7) | 0.199(6) | 0.193(6) | 0.050(5) | 0.050(5) |
| Ca2 | 0.584(7) | 0.9998(1) | 0.540(8) | 0.340(6) | 0.290(7) | 0.199(6) | 0.193(6) | 0.050(5) | 0.050(5) |
| Al1 | 0.383(3) | 0.029(4) | 0.143(2) | 0.124(2) | 0.114(2) | 0.124(2) | 0.114(2) | 0.050(5) | 0.050(5) |
| Al2 | 0.383(3) | 0.029(4) | 0.143(2) | 0.124(2) | 0.114(2) | 0.124(2) | 0.114(2) | 0.050(5) | 0.050(5) |
| F1  | 0.619(2) | 0.179(3) | 0.114(3) | 0.092(2) | 0.082(3) | 0.072(3) | 0.072(3) | 0.004(2) | 0.004(2) |
| F2  | 0.602(2) | 0.820(3) | 0.124(2) | 0.092(2) | 0.082(3) | 0.072(3) | 0.072(3) | 0.004(2) | 0.004(2) |
| F3  | 0.825(2) | 0.001(4) | 0.369(2) | 0.092(2) | 0.082(3) | 0.072(3) | 0.072(3) | 0.004(2) | 0.004(2) |
| F4  | 0.565(2) | 0.676(3) | 0.387(2) | 0.092(2) | 0.082(3) | 0.072(3) | 0.072(3) | 0.004(2) | 0.004(2) |
| F5  | 0.562(2) | 0.323(3) | 0.382(2) | 0.092(2) | 0.082(3) | 0.072(3) | 0.072(3) | 0.004(2) | 0.004(2) |
| F6  | 0.356(2) | 0.993(3) | 0.396(2) | 0.092(2) | 0.082(3) | 0.072(3) | 0.072(3) | 0.004(2) | 0.004(2) |
| F7  | 0.893(3) | 0.001(4) | 0.104(2) | 0.092(2) | 0.082(3) | 0.072(3) | 0.072(3) | 0.004(2) | 0.004(2) |
| H1  | 0.852(5) | 0.845(6) | 0.001(4) | 0.092(2) | 0.082(3) | 0.072(3) | 0.072(3) | 0.004(2) | 0.004(2) |
| H2  | 0.852(5) | 0.845(6) | 0.001(4) | 0.092(2) | 0.082(3) | 0.072(3) | 0.072(3) | 0.004(2) | 0.004(2) |
Table 4. Selected bond distances (Å) and angles (°) for carlhintzeite.

| Bond      | Distance (Å) | Bond      | Distance (Å) | Bond      | Distance (Å) | Bond      | Distance (Å) |
|-----------|--------------|-----------|--------------|-----------|--------------|-----------|--------------|
| Ca1–F4    | 2.235(2)     | Ca2–F7    | 2.232(2)     | Al1–F1    | 1.795(2)     | Al2–F4    | 1.778(2)     |
| Ca1–F7    | 2.236(2)     | Ca2–F2    | 2.367(2)     | Al1–F2    | 1.816(2)     | Al2–F5    | 1.826(2)     |
| Ca1–F6    | 2.278(2)     | Ca2–F3    | 2.376(2)     | Al1–F3    | 1.817(2)     | Al2–F6    | 1.828(2)     |
| Ca1–F7    | 2.281(2)     | Ca2–F1    | 2.417(2)     | 1.809     |              | 1.811     |              |
| Ca1–F5    | 2.297(2)     | Ca2–F5    | 2.427(2)     | 86.96(10) | F5–Al2–F6   | 84.52(9)  |              |
| Ca1–F1    | 2.476(2)     | Ca2–F6    | 2.436(2)     | 87.36(9)  | F4–Al2–F5   | 89.47(10) |              |
| Ca1–F2    | 2.488(2)     | Ca2–OW    | 2.464(3)     | 89.39(10) | F4–Al2–F6   | 90.53(10) |              |
| Ca1–F3    | 2.660(2)     | Ca2–OW    | 2.610(3)     | 90.61(10) | F4–Al2–F5   | 90.61(10) |              |
| <Ca1–F>   | 2.369        | <Ca2–F>   | 2.376        | 91.39(10) | F4–Al2–F5   | 95.48(9)  |              |
|           |              | <Ca2–O>   | 2.537        | 93.04(10) | F5–Al2–F6   | 95.48(9)  |              |
|           |              |           |              |           |              |           |              |

Hydrogen bonds (D = donor, A = acceptor)

| D–H     | d(D–H) | d(H–A) | <DHA | d(D–A) | A    | <HDH |
|---------|--------|--------|------|--------|------|------|
| OW–H1   | 0.88(3) | 2.30(4) | 135(4) | 2.983(4) | F2   |      |
|         |        | 2.62(5) | 96(4)  | 2.851(4) | F4   |      |
|         |        | 2.67(4) | 104(4) | 3.013(4) | F2   |      |
|         |        | 2.38(4) | 135(4) | 3.066(4) | F3   | 111(4) |
| OW–H2   | 0.88(3) | 2.49(3) | 137(4) | 3.185(4) | F1   |      |
|         |        | 2.60(5) | 97(4)  | 2.851(4) | F4   |      |
solved by direct methods using SIR92 (Altomare et al., 1994) and the location of all non-hydrogen atoms was straightforward. SHELXL-97 software (Sheldrick, 2008) was used, with neutral atom scattering factors, for the refinement of the structure. A table of structure factor data has been deposited with the Principal Editor of the journal and is available at http://www.minersoc.org/pages/e_journals/dep_mat_mm.html

With all non-hydrogen atoms refined anisotropically in the centrosymmetric space group C\textbar\textbar, R\textsubscript{1} converged to 3.28\% for 732 reflections with F\textsubscript{o} > 4\sigma F. Bond-valence calculations indicate that one site in the structure (designated OW) is occupied by the O atom of an H\textsubscript{2}O molecule. A difference Fourier analysis revealed likely locations for the H atoms related to this site. The positions of the H atoms were constrained to an H–O distance of 0.90(3) Å and an H–H distance of 1.45(3) Å and their isotropic displacement parameters were held constant at 0.05 Å\textsuperscript{2} in the final refinement, which converged to 3.22\%.

The details of the data collection and structure refinement are provided in Table 2. The final atomic coordinates and displacement parameters are listed in Table 3. Selected interatomic distances are given in Table 4 and a bond-valence analysis in Table 5.

**Description of the structure**

The carlhintzeite structure (Figs 3, 4) is made up of linkages of Al\textsubscript{6} octahedra (Al\textsubscript{1} and Al\textsubscript{2}), Ca\textsubscript{8} polyhedra (Ca\textsubscript{1}) and Ca\textsubscript{6}(H\textsubscript{2}O)\textsubscript{2} polyhedra (Ca\textsubscript{2}). The Al\textsubscript{6} octahedra are isolated from one another, but share polyhedral elements with Ca polyhedra. Most notably, the Al\textsubscript{1} octahedron shares trans faces with two Ca\textsubscript{8} polyhedra and the Al\textsubscript{2} octahedron shares trans edges with two Ca\textsubscript{6}(H\textsubscript{2}O)\textsubscript{2} polyhedra. The linkage of the Ca polyhedra alone can be described as a framework in which edge-sharing chains along \textbf{b} are cross-linked by edge-sharing. All Ca and Al polyhedra are centred at approximately the same height along \textbf{b}. Figure 4 shows one such slice through the structure parallel to \{010\}.

The Ca polyhedra

As noted by Marchetti and Perchiazzi (2000) for gearskitite, the eightfold coordination geometry of Ca\textsuperscript{2+} in carlhintzeite cannot be easily described in terms of an idealized polyhedron. In carlhintzeite, the geometries of the Ca coordination polyhedra (Fig. 5) and, in particular, the lengths of their F–F edges can be readily correlated with their linkages to Al\textsubscript{6} octahedra and to other Ca polyhedra. In general, the shortest polyhedral edges in both of the Ca polyhedra (Ca\textsubscript{1} and Ca\textsubscript{2}), ranging from 2.458 to 2.523 Å, correspond to edges and faces shared with Al\textsubscript{6} octahedra, while somewhat longer F–F edges, ranging from 2.613 to 2.891 Å, correspond to edges shared with other Ca polyhedra. The longest F–F edges and the edges that include O atoms are not shared with any other polyhedra.

The Ca\textsubscript{6} polyhedron (Ca\textsubscript{1}) shares a face (F1–F2–F3) with an Al\textsubscript{6} octahedron (Al\textsubscript{1}), one edge (F7–F7) with another Ca\textsubscript{1} polyhedron, and three edges (F1–F7, F2–F6 and F3–F5) with

### Table 5. Bond-valence analysis for carlhintzeite. Values are expressed in valence units.

|       | Ca1  | Ca2  | Al1     | Al2     | H1     | H2     | Sum   |
|-------|------|------|---------|---------|--------|--------|-------|
| F1    | 0.180| 0.211| 0.509 × 2| 0.059 × 2| 0.065 | 0.030 | 0.945 |
| F2    | 0.110| 0.242| 0.481 × 2| 0.318 × 2| 0.065 | 0.030 | 0.928 |
| F3    | 0.174| 0.236| 0.479 × 2| 0.318 × 2| 0.065 | 0.030 | 0.944 |
| F4    | 0.346|      | 0.533 × 2| 0.065 | 0.035 | 0.949 |
| F5    | 0.292| 0.206| 0.468 × 2| 0.318 × 2| 0.065 | 0.030 | 0.966 |
| F6    | 0.308| 0.201| 0.465 × 2| 0.318 × 2| 0.065 | 0.030 | 0.974 |
| F7    | 0.345,0.305| 0.349|      |        | 0.999|
| OW    | 0.261,0.176|      | 0.870 | 0.865 | 2.172 |
| Sum   | 2.060| 1.882| 2.938 | 2.932 | 1.00  | 1.00  |       |

Al\textsuperscript{3+}–F, Ca\textsuperscript{2+}–F and Ca\textsuperscript{2+}–O bond strengths from Brown and Altermatt (1985); hydrogen-bond strengths based on H...F bond lengths, also from Brown and Altermatt (1985).
Fig. 3. Crystal structure of carlhintzeite along [100].

Fig. 4. Crystal structure of carlhintzeite along [010]. Note that only one layer parallel to (010) is shown. H bonds are shown as dotted lines.
Fig. 5. Ca coordinations in carlhintzeite. Bold numbers correspond to bond distances; non-bold to lengths of polyhedral edges; both are in Å.

Fig. 6. Face-sharing Ca1–Al1–Ca1 trimer (left) and edge-sharing Ca2–Al2–Ca2 trimer (right) in carlhintzeite. Upper Ca1 and Ca2 polyhedra are in the same orientation as in Fig. 4.
CaF$_6$(H$_2$O)$_2$ polyhedra (Ca2). The CaF$_6$(H$_2$O)$_2$ polyhedron (Ca2) shares an edge (F5–F6) with an AlF$_6$ octahedron (Al2) and three edges (F1–F7, F2–F6 and F3–F5) with Ca1 polyhedra.

**Ca-Al-Ca polyhedral trimers**

The AlF$_6$ octahedron (Al1) shares trans F1–F2–F3 faces with two CaF$_8$ polyhedra (Ca1) forming an unusual face-sharing Ca1–Al1–Ca1 trimer (Fig. 6). In apparent response to cation-cation repulsion, the Ca bonds to each of the F atoms in the shared face are appreciably longer than the other Ca–F bonds in the CaF$_8$ polyhedra and the Al1 octahedron exhibits significant elongation in the direction of the normal to the shared faces, as shown by the smaller F–Al1–F angles (from 86.96 to 88.61°; Table 4) corresponding to the F atoms in the shared faces.

The AlF$_6$ octahedron (Al2) shares trans F5–F6 edges with two CaF$_6$(H$_2$O)$_2$ polyhedra (Ca2) forming an edge-sharing Ca2–Al2–Ca2 trimer (Fig. 6). Again, in apparent response to cation-cation repulsion, the Ca bonds to the F atoms in the shared edges are the longest Ca–F bonds in the CaF$_6$(H$_2$O)$_2$ polyhedron and the Al2 octahedron exhibits significant elongation in the direction of the normal to the shared edges, as is shown by the much smaller F–Al2–F angles corresponding to the F atoms in the shared faces (84.52°; Table 4).

**Hydrogen bonding**

The H atoms (H1 and H2) of the H$_2$O molecule (OW) project into open space in the framework and are surrounded by F atoms. Without considering hydrogen bonds, all F atoms except F7 are undersaturated (Table 5) and, in fact, the only F atom that is not positioned to participate in at least weak hydrogen bonding is F7. We have assigned three hydrogen bonds to each H atom (Table 4, Fig. 7); however, F1 to F6 remain somewhat undersaturated and the O atom of the H$_2$O molecule remains oversaturated. It appears likely, therefore, that H1 and H2 participate in additional longer hydrogen bonds to surrounding F atoms.

**Comparison with the structures of gearksutite and prosopite**

Three other minerals with similar chemical constituents are known: gearksutite, CaAlF$_4$(OH)·(H$_2$O), prosopite, CaAl$_2$F$_4$(OH)$_4$, and yaroslavite, Ca$_3$Al$_2$F$_{10}$(OH)$_2$·(H$_2$O). The structure of yaroslavite is not known (Novikova et al., 1966); however, the structures of both gearksutite (Marchetti and Perchiazi 2000) and prosopite (Pudovkina et al., 1973) exhibit similarities with that of carlhintzeite. All three structures contain Al(F,OH)$_6$ octahedra and Ca in similar eightfold coordinations to F and O atoms. All three structures also contain very similar edge-sharing chains of Ca polyhedra. The chains in gearksutite and prosopite are parallel to c and correspond to the cell parameters 6.978 and 7.32 Å, respectively. These match closely with the b cell parameter of 6.9670 Å for carlhintzeite, which corresponds to its chain direction.

The Ca:Al ratios in carlhintzeite, gearksutite and prosopite are 2:1, 1:1 and 1:2, respectively, and these are reflected in quite different polymerizations of Al and Ca polyhedra. The Al octahedra are isolated from one another in
carlhintzeite, form edge-sharing dimers in gearksutite and edge-sharing chains in prosopite. The Ca polyhedra, on the other hand, decrease in polymerization from an edge-sharing framework in carlhintzeite, to an edge-sharing sheet in gearksutite, to an edge-sharing chain in prosopite. When the edge-sharing linkages of both Al octahedra and Ca polyhedra are considered, prosopite is seen to be a framework, while gearksutite is a sheet. Finally, it is noteworthy that face-sharing between Al octahedra and Ca polyhedra only occurs in the carlhintzeite structure.

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