Electronic Supplementary Material (ESI) for Dalton Transactions.


# Inference of Principal Species in Caustic Aluminate Solutions Through Solid-State Spectroscopic Characterization

Mateusz Dembowski[†], Micah P. Prange[†], Maxime Pouvreau[‡], Trent R. Graham[†], Mark E. Bowden[†], Alpha N'Diaye[¤], Gregory K. Schenter[†], Sue B. Clark[†], Aurora E. Clark[‡], Kevin M. Rosso[†] and Carolyn I. Pearce[†]

[†]Pacific Northwest National Laboratory, Richland, Washington, 99352, United States
[‡]Department of Chemistry, Washington State University, Pullman, Washington, 99164, United States
[¤]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, 94720, United States

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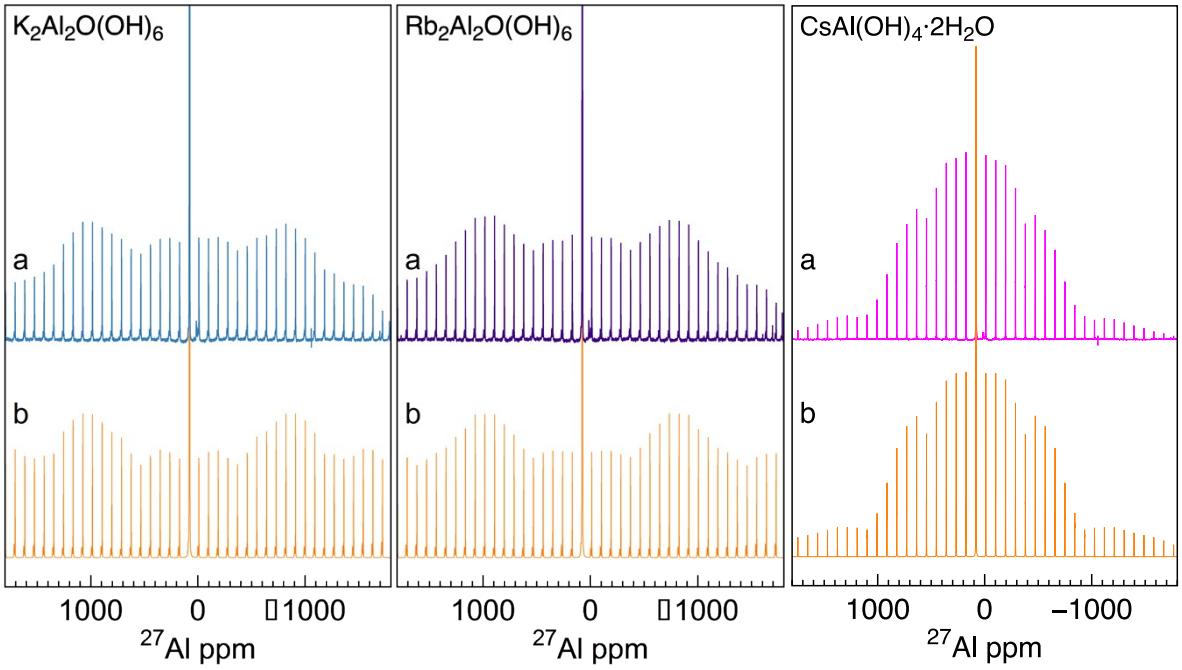


**Figure S1.** Experimental (top) and model fits (bottom) $^{27}$Al MAS-NMR of $K_2Al_2O(OH)_6$ (left), $Rb_2Al_2O(OH)_6$ (center), and $CsAl(OH)_4{\cdot}2H_2O$ collected at 19.975 T and 20 kHz spin rate.

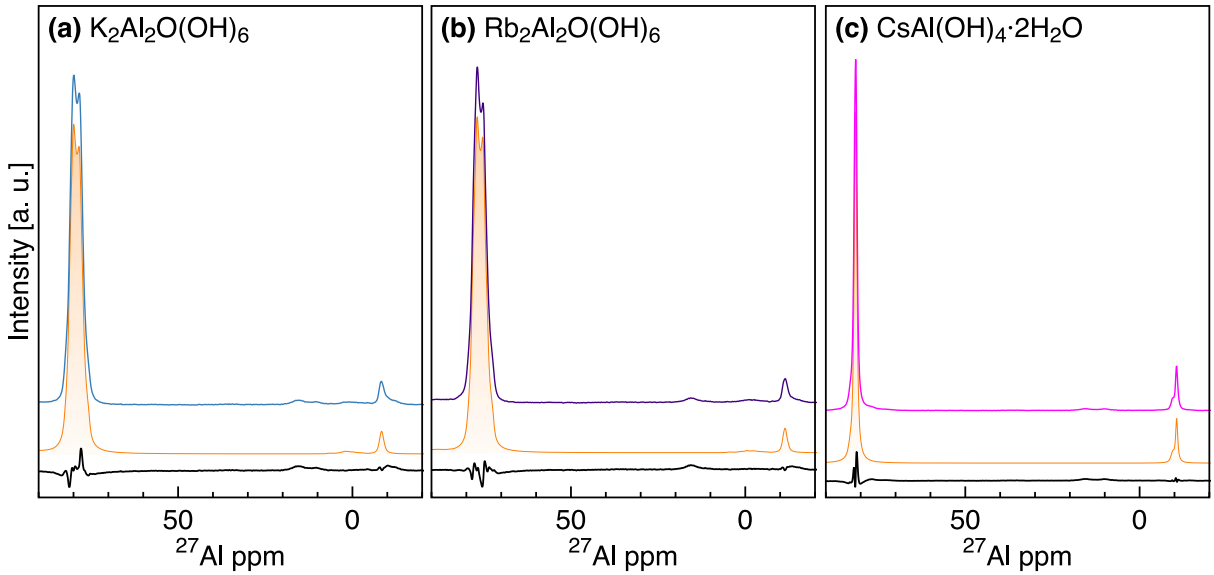


**Figure S2.** Difference (black), experimental (blue, purple, magenta) and model fits (orange) $^{27}$Al MAS-NMR of $K_2Al_2O(OH)_6$ (left), $Rb_2Al_2O(OH)_6$ (center), and $CsAl(OH)_4{\cdot}2H_2O$ collected at 19.975 T and 20 kHz spin rate. Signals at ca. -10 ppm are the spinning side bands. Those at ca. 10-15 ppm correspond to trace octahedral impurities.

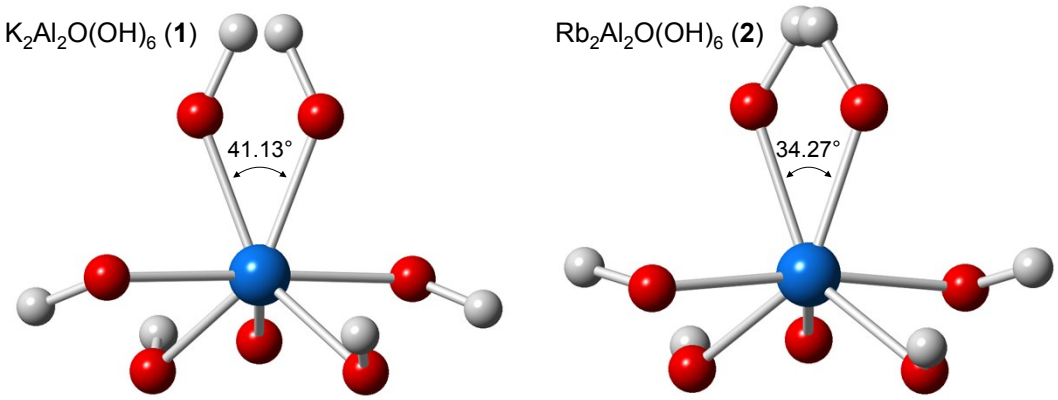


**Figure S3.** Comparison of conformations of the K (left) and Rb (right) salt of the $Al_2O(OH)_6^{2-}$. Blue, red, and white spheres represent aluminum, oxygen, and hydrogen atoms, respectively.

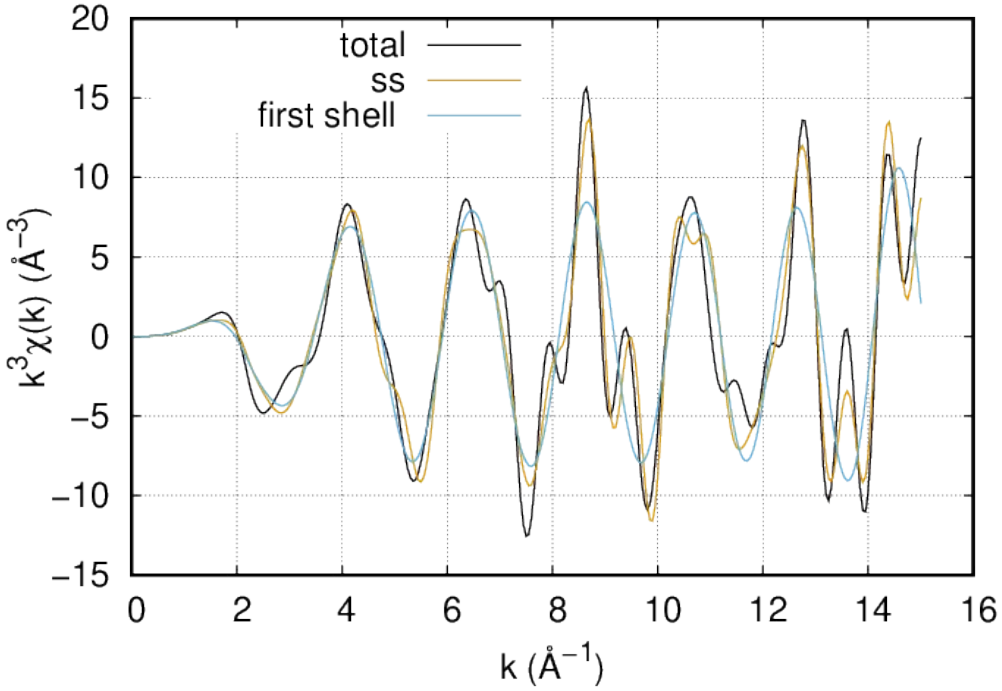


**Figure S4.** AIMD predicted EXAFS in k-space for the full set of paths (black), single-scattering paths (orange), and first-shell single-scattering paths (blue) for a single structure.

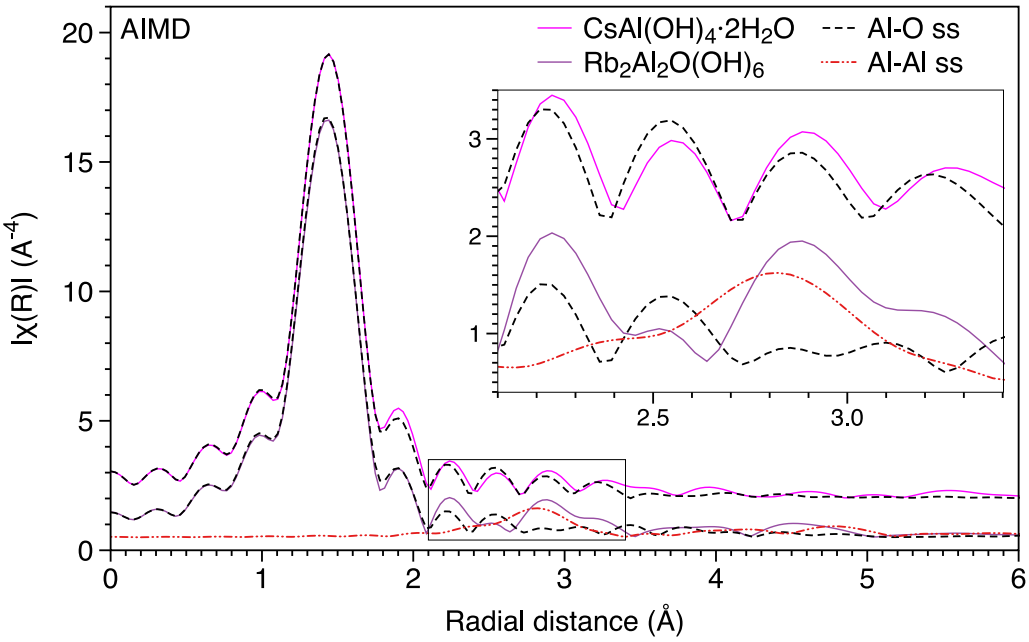


**Figure S5.** R-space EXAFS showing magnitude for **2** and **3**. Forward Fourier transform k-range between 3 and 13 $Å^{-1}$ used.

**Crystallographic Tables**

Crystal data for $K_2Al_2O(OH)_6$ (**1**)

| | |
|---|---|
| K2Al2O7H$_6$ | $D_x$ = 2.169 Mg m$^{-3}$ |
| $M_r$ = 250.21 | Ag *K*a radiation, l = 0.56086 Å |
| Orthorhombic, *Aba*2 | Cell parameters from 2593 reflections |
| *a* = 10.1605 (12) Å | q = 3.1–26.8° |
| *b* = 7.5416 (8) Å | m = 0.75 mm$^{-1}$ |
| *c* = 9.9990 (12) Å | *T* = 110 K |
| *V* = 766.19 (15) Å$^3$ | Blocky, colorless |
| *Z* = 4 | 0.04 × 0.03 × 0.02 mm |
| *F*(000) = 504 | |

*Data collection*

| | |
|---|---|
| Bruker APEX-II CCD diffractometer | 1478 reflections with *I* > 2s(*I*) |
| f and w scans | $R_{int}$ = 0.085 |
| Absorption correction: multi-scan *SADABS* (Krause 2015) | $q_{max}$ = 26.9°, $q_{min}$ = 3.1° |
| $T_{min}$ = 0.663, $T_{max}$ = 0.746 | *h* = -16®16 |
| 9194 measured reflections | *k* = -12®12 |
| 1687 independent reflections | *l* = -16®16 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: difference Fourier map |
| Least-squares matrix: full | All H-atom parameters refined |
| $R[F^2 > 2s(F^2)]$ = 0.037 | $w = 1/[s^2(F_o^2) + (0.0241P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2)$ = 0.068 | $(D/s)_{max} < 0.001$ |
| *S* = 1.12 | $D\rho_{max}$ = 0.46 e Å$^{-3}$ |
| 1687 reflections | $D\rho_{min}$ = -0.53 e Å$^{-3}$ |

| | |
|---|---|
| 63 parameters | Absolute structure: Flack x determined using 623 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| 4 restraints | Absolute structure parameter: 0.00 (6) |

*Special details*

*Geometry*. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for (K2Al2O8H6)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| K1 | 0.30153 (6) | 0.02766 (8) | 0.59783 (6) | 0.00989 (12) |
| Al1 | 0.49154 (8) | 0.20877 (10) | 0.86079 (9) | 0.00461 (16) |
| O1 | 0.6432 (2) | 0.3220 (2) | 0.8575 (3) | 0.0091 (4) |
| H1 | 0.718 (3) | 0.259 (6) | 0.827 (6) | 0.058 (19)* |
| O2 | 0.3787 (2) | 0.3316 (3) | 0.7611 (2) | 0.0078 (4) |
| H2 | 0.380 (6) | 0.446 (3) | 0.799 (5) | 0.054 (18)* |
| O3 | 0.4299 (2) | 0.2183 (3) | 1.0253 (2) | 0.0103 (4) |
| H3 | 0.469 (7) | 0.202 (8) | 1.111 (4) | 0.10 (3)* |
| O4 | 0.500000 | 0.000000 | 0.7927 (3) | 0.0072 (5) |

*Atomic displacement parameters (Å²) for (K2Al2O8H6)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| K1 | 0.0100 (2) | 0.0108 (2) | 0.0089 (2) | 0.0012 (2) | 0.0005 (3) | 0.0011 (3) |
| Al1 | 0.0050 (4) | 0.0042 (3) | 0.0047 (4) | 0.0001 (3) | -0.0006 (4) | -0.0005 (4) |
| O1 | 0.0046 (9) | 0.0080 (8) | 0.0149 (10) | -0.0007 (6) | -0.0013 (10) | -0.0023 (10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2 | 0.0069 (10) | 0.0071 (9) | 0.0094 (10) | 0.0008 (7) | -0.0027 (8) | 0.0005 (7) |
| O3 | 0.0115 (11) | 0.0132 (10) | 0.0062 (9) | 0.0018 (8) | 0.0008 (8) | -0.0011 (8) |
| O4 | 0.0109 (14) | 0.0028 (12) | 0.0078 (12) | 0.0003 (10) | 0.000 | 0.000 |

*Geometric parameters (Å, º) for (K2Al2O8H6)*

| | | | |
|---|---|---|---|
| K1—O1$^{i}$ | 2.716 (3) | K1—Al1 | 3.5365 (11) |
| K1—O3$^{ii}$ | 2.770 (2) | K1—Al1$^{i}$ | 3.7402 (11) |
| K1—O4 | 2.812 (2) | K1—Al1$^{vi}$ | 3.8097 (11) |
| K1—O3$^{iii}$ | 2.850 (2) | K1—Al1$^{ii}$ | 3.8895 (11) |
| K1—O2$^{iv}$ | 2.865 (2) | Al1—O4 | 1.7177 (15) |
| K1—O2 | 2.921 (2) | Al1—O1 | 1.761 (2) |
| K1—O1$^{v}$ | 3.259 (3) | Al1—O3 | 1.762 (3) |
| K1—O3$^{i}$ | 3.412 (2) | Al1—O2 | 1.779 (2) |
| | | | |
| O1$^{i}$—K1—O3$^{ii}$ | 91.30 (7) | O3$^{ii}$—K1—Al1$^{ii}$ | 23.91 (5) |
| O1$^{i}$—K1—O4 | 119.71 (7) | O4—K1—Al1$^{ii}$ | 91.16 (4) |
| O3$^{ii}$—K1—O4 | 77.35 (6) | O3$^{iii}$—K1—Al1$^{ii}$ | 124.50 (5) |
| O1$^{i}$—K1—O3$^{iii}$ | 74.64 (7) | O2$^{iv}$—K1—Al1$^{ii}$ | 110.21 (5) |
| O3$^{ii}$—K1—O3$^{iii}$ | 138.32 (8) | O2—K1—Al1$^{ii}$ | 133.83 (5) |
| O4—K1—O3$^{iii}$ | 143.66 (6) | O1$^{v}$—K1—Al1$^{ii}$ | 161.07 (4) |
| O1$^{i}$—K1—O2$^{iv}$ | 148.45 (7) | O3$^{i}$—K1—Al1$^{ii}$ | 79.68 (4) |
| O3$^{ii}$—K1—O2$^{iv}$ | 90.88 (7) | Al1—K1—Al1$^{ii}$ | 114.89 (3) |
| O4—K1—O2$^{iv}$ | 91.44 (6) | Al1$^{i}$—K1—Al1$^{ii}$ | 70.33 (3) |
| O3$^{iii}$—K1—O2$^{iv}$ | 82.99 (7) | Al1$^{vi}$—K1—Al1$^{ii}$ | 81.793 (14) |
| O1$^{i}$—K1—O2 | 96.40 (7) | O4—Al1—O1 | 113.15 (9) |
| O3$^{ii}$—K1—O2 | 132.91 (7) | O4—Al1—O3 | 115.17 (12) |
| O4—K1—O2 | 58.56 (5) | O1—Al1—O3 | 107.97 (13) |
| O3$^{iii}$—K1—O2 | 88.16 (6) | O4—Al1—O2 | 106.69 (11) |

| | | | |
|---|---|---|---|
| O2$^{iv}$—K1—O2 | 104.94 (8) | O1—Al1—O2 | 107.52 (11) |
| O1$^{i}$—K1—O1$^{v}$ | 131.44 (7) | O3—Al1—O2 | 105.83 (11) |
| O3$^{ii}$—K1—O1$^{v}$ | 137.25 (6) | O4—Al1—K1 | 51.57 (7) |
| O4—K1—O1$^{v}$ | 80.09 (6) | O1—Al1—K1 | 130.60 (10) |
| O3$^{iii}$—K1—O1$^{v}$ | 67.65 (6) | O3—Al1—K1 | 121.06 (8) |
| O2$^{iv}$—K1—O1$^{v}$ | 53.83 (5) | O2—Al1—K1 | 55.44 (7) |
| O2—K1—O1$^{v}$ | 54.13 (6) | O4—Al1—K1$^{vii}$ | 135.26 (6) |
| O1$^{i}$—K1—O3$^{i}$ | 53.98 (6) | O1—Al1—K1$^{vii}$ | 42.49 (9) |
| O3$^{ii}$—K1—O3$^{i}$ | 92.34 (7) | O3—Al1—K1$^{vii}$ | 65.57 (8) |
| O4—K1—O3$^{i}$ | 67.38 (5) | O2—Al1—K1$^{vii}$ | 116.14 (8) |
| O3$^{iii}$—K1—O3$^{i}$ | 108.82 (4) | K1—Al1—K1$^{vii}$ | 169.51 (3) |
| O2$^{iv}$—K1—O3$^{i}$ | 157.24 (7) | O4—Al1—K1$^{vi}$ | 43.08 (6) |
| O2—K1—O3$^{i}$ | 57.56 (6) | O1—Al1—K1$^{vi}$ | 74.41 (8) |
| O1$^{v}$—K1—O3$^{i}$ | 111.64 (6) | O3—Al1—K1$^{vi}$ | 149.28 (8) |
| O1$^{i}$—K1—Al1 | 112.55 (5) | O2—Al1—K1$^{vi}$ | 102.29 (8) |
| O3$^{ii}$—K1—Al1 | 105.24 (6) | K1—Al1—K1$^{vi}$ | 66.88 (3) |
| O4—K1—Al1 | 28.59 (2) | K1$^{vii}$—Al1—K1$^{vi}$ | 112.08 (3) |
| O3$^{iii}$—K1—Al1 | 116.41 (5) | O4—Al1—K1$^{viii}$ | 146.44 (6) |
| O2$^{iv}$—K1—Al1 | 97.15 (5) | O1—Al1—K1$^{viii}$ | 98.38 (8) |
| O2—K1—Al1 | 30.10 (5) | O3—Al1—K1$^{viii}$ | 39.60 (7) |
| O1$^{v}$—K1—Al1 | 62.79 (4) | O2—Al1—K1$^{viii}$ | 72.51 (8) |
| O3$^{i}$—K1—Al1 | 60.30 (4) | K1—Al1—K1$^{viii}$ | 114.89 (3) |
| O1$^{i}$—K1—Al1$^{i}$ | 25.98 (5) | K1$^{vii}$—Al1—K1$^{viii}$ | 64.17 (2) |
| O3$^{ii}$—K1—Al1$^{i}$ | 90.98 (5) | K1$^{vi}$—Al1—K1$^{viii}$ | 169.71 (3) |
| O4—K1—Al1$^{i}$ | 94.32 (4) | Al1—O1—K1$^{vii}$ | 111.53 (12) |
| O3$^{iii}$—K1—Al1$^{i}$ | 91.98 (5) | Al1—O1—K1$^{ix}$ | 127.98 (12) |
| O2$^{iv}$—K1—Al1$^{i}$ | 174.21 (5) | K1$^{vii}$—O1—K1$^{ix}$ | 117.22 (7) |
| O2—K1—Al1$^{i}$ | 77.67 (5) | Al1—O2—K1$^{x}$ | 179.30 (13) |
| O1$^{v}$—K1—Al1$^{i}$ | 126.70 (4) | Al1—O2—K1 | 94.46 (9) |

| | | | |
|---|---|---|---|
| O3$^{i}$—K1—Al1$^{i}$ | 28.04 (4) | K1$^{x}$—O2—K1 | 85.12 (6) |
| Al1—K1—Al1$^{i}$ | 87.650 (16) | Al1—O3—K1$^{viii}$ | 116.49 (11) |
| O1$^{i}$—K1—Al1$^{vi}$ | 133.78 (5) | Al1—O3—K1$^{xi}$ | 120.69 (11) |
| O3$^{ii}$—K1—Al1$^{vi}$ | 61.74 (5) | K1$^{viii}$—O3—K1$^{xi}$ | 88.26 (6) |
| O4—K1—Al1$^{vi}$ | 24.664 (17) | Al1—O3—K1$^{vii}$ | 86.39 (9) |
| O3$^{iii}$—K1—Al1$^{vi}$ | 150.12 (5) | K1$^{viii}$—O3—K1$^{vii}$ | 81.25 (6) |
| O2$^{iv}$—K1—Al1$^{vi}$ | 73.60 (5) | K1$^{xi}$—O3—K1$^{vii}$ | 152.75 (9) |
| O2—K1—Al1$^{vi}$ | 80.40 (5) | Al1—O4—Al1$^{vi}$ | 133.26 (19) |
| O1$^{v}$—K1—Al1$^{vi}$ | 83.42 (4) | Al1—O4—K1$^{vi}$ | 112.25 (6) |
| O3$^{i}$—K1—Al1$^{vi}$ | 88.17 (4) | Al1$^{vi}$—O4—K1$^{vi}$ | 99.84 (6) |
| Al1—K1—Al1$^{vi}$ | 50.68 (3) | Al1—O4—K1 | 99.84 (6) |
| Al1$^{i}$—K1—Al1$^{vi}$ | 112.08 (3) | Al1$^{vi}$—O4—K1 | 112.25 (6) |
| O1$^{i}$—K1—Al1$^{ii}$ | 67.44 (5) | K1$^{vi}$—O4—K1 | 92.28 (10) |

Symmetry codes: (i) -*x*+1, -*y*+1/2, *z*-1/2; (ii) *x*, *y*-1/2, *z*-1/2; (iii) -*x*+1/2, *y*, *z*-1/2; (iv) -*x*+1/2, *y*-1/2, *z*; (v) *x*-1/2, -*y*+1/2, *z*; (vi) -*x*+1, -*y*, *z*; (vii) -*x*+1, -*y*+1/2, *z*+1/2; (viii) *x*, *y*+1/2, *z*+1/2; (ix) *x*+1/2, -*y*+1/2, *z*; (x) -*x*+1/2, *y*+1/2, *z*; (xi) -*x*+1/2, *y*, *z*+1/2.

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Crystal Data for $Rb_2Al_2O(OH)_6$ (**2**)

| | |
|---|---|
| Rb2Al2O7H$_6$ | $D_x$ = 2.795 Mg m$^{-3}$ |
| $M_r$ = 342.95 | Ag *K*a radiation, l = 0.56086 Å |
| Orthorhombic, *Aba*2 | Cell parameters from 5220 reflections |
| *a* = 10.3511 (8) Å | q = 3.0–28.6° |
| *b* = 7.6823 (7) Å | m = 6.58 mm$^{-1}$ |
| *c* = 10.2481 (8) Å | *T* = 110 K |
| *V* = 814.93 (12) Å$^3$ | Blocky, colorless |
| *Z* = 4 | 0.04 × 0.03 × 0.02 mm |
| *F*(000) = 648 | |

*Data collection*

| | |
|---|---|
| Bruker APEX-II CCD diffractometer | 2057 reflections with *I* > 2s(*I*) |
| f and w scans | $R_{int}$ = 0.088 |
| Absorption correction: multi-scan *SADABS* (Krause 2015) | $q_{max}$ = 31.8°, $q_{min}$ = 3.0° |
| $T_{min}$ = 0.639, $T_{max}$ = 0.746 | *h* = -19®18 |
| 17980 measured reflections | *k* = -14®14 |
| 2754 independent reflections | *l* = -19®17 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: difference Fourier map |
| Least-squares matrix: full | All H-atom parameters refined |
| $R[F^2 > 2s(F^2)]$ = 0.043 | $w = 1/[s^2(F_o^2) + (0.0182P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2)$ = 0.062 | $(D/s)_{max} < 0.001$ |
| *S* = 1.07 | $D\rho_{max}$ = 1.14 e Å$^{-3}$ |
| 2754 reflections | $D\rho_{min}$ = -1.49 e Å$^{-3}$ |
| 63 parameters | Absolute structure: Flack x determined using 773 |

| | |
|---|---|
| | quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259). |
| 4 restraints | Absolute structure parameter: 0.004 (10) |

*Special details*

*Geometry*. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$) for (Rb2Al2O8H6)

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Rb1 | 0.20111 (3) | 0.97386 (4) | 0.35079 (4) | 0.00902 (6) |
| Al1 | 0.00211 (11) | 0.79223 (14) | 0.08628 (11) | 0.00433 (19) |
| O1 | 0.1157 (3) | 0.6689 (3) | 0.1785 (3) | 0.0078 (5) |
| O2 | 0.0558 (3) | 0.7775 (4) | -0.0766 (3) | 0.0108 (5) |
| O3 | -0.1470 (3) | 0.6832 (4) | 0.0991 (3) | 0.0094 (5) |
| O4 | 0.000000 | 1.000000 | 0.1489 (4) | 0.0076 (7) |
| H2 | 0.010 (5) | 0.808 (7) | -0.155 (3) | 0.033 (16)* |
| H1 | 0.119 (7) | 0.548 (3) | 0.156 (6) | 0.027 (17)* |
| H3 | -0.213 (7) | 0.765 (10) | 0.079 (13) | 0.11 (4)* |

*Atomic displacement parameters (Å$^2$) for (Rb2Al2O8H6)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Rb1 | 0.00935 (11) | 0.00892 (11) | 0.00880 (11) | 0.00096 (11) | 0.00087 (19) | 0.0012 (2) |
| Al1 | 0.0053 (4) | 0.0021 (4) | 0.0056 (5) | 0.0003 (4) | 0.0002 (4) | -0.0003 (4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O1 | 0.0069 (11) | 0.0050 (11) | 0.0114 (12) | 0.0007 (9) | -0.0030 (10) | 0.0004 (9) |
| O2 | 0.0120 (14) | 0.0138 (14) | 0.0065 (12) | 0.0024 (11) | 0.0008 (10) | -0.0006 (9) |
| O3 | 0.0068 (11) | 0.0062 (12) | 0.0151 (13) | -0.0005 (8) | -0.0001 (11) | -0.0019 (10) |
| O4 | 0.0125 (17) | 0.0026 (17) | 0.0077 (15) | 0.0010 (12) | 0.000 | 0.000 |

*Geometric parameters (Å, º) for (Rb2Al2O8H6)*

| | | | |
|---|---|---|---|
| Rb1—O3$^{i}$ | 2.871 (3) | Rb1—Al1 | 3.6794 (12) |
| Rb1—O2$^{ii}$ | 2.874 (3) | Rb1—Al1$^{i}$ | 3.7985 (13) |
| Rb1—O4 | 2.942 (3) | Rb1—Al1$^{vi}$ | 3.8733 (12) |
| Rb1—O1$^{iii}$ | 2.993 (3) | Rb1—Rb1$^{vii}$ | 3.9722 (4) |
| Rb1—O2$^{iv}$ | 3.027 (3) | Al1—O4 | 1.7203 (18) |
| Rb1—O1 | 3.064 (3) | Al1—O3 | 1.761 (3) |
| Rb1—O3$^{v}$ | 3.253 (3) | Al1—O2 | 1.763 (3) |
| Rb1—O2$^{i}$ | 3.369 (3) | Al1—O1 | 1.781 (3) |
| | | | |
| O3$^{i}$—Rb1—O2$^{ii}$ | 90.56 (8) | O1—Rb1—Rb1$^{vii}$ | 48.25 (5) |
| O3$^{i}$—Rb1—O4 | 120.94 (7) | O3$^{v}$—Rb1—Rb1$^{vii}$ | 61.19 (5) |
| O2$^{ii}$—Rb1—O4 | 75.89 (7) | O2$^{i}$—Rb1—Rb1$^{vii}$ | 69.32 (5) |
| O3$^{i}$—Rb1—O1$^{iii}$ | 148.95 (8) | Al1—Rb1—Rb1$^{vii}$ | 77.051 (18) |
| O2$^{ii}$—Rb1—O1$^{iii}$ | 94.48 (8) | Al1$^{i}$—Rb1—Rb1$^{vii}$ | 67.710 (17) |
| O4—Rb1—O1$^{iii}$ | 89.95 (7) | Al1$^{vi}$—Rb1—Rb1$^{vii}$ | 125.946 (17) |
| O3$^{i}$—Rb1—O2$^{iv}$ | 74.62 (8) | O4—Al1—O3 | 113.71 (11) |
| O2$^{ii}$—Rb1—O2$^{iv}$ | 140.91 (10) | O4—Al1—O2 | 114.61 (16) |
| O4—Rb1—O2$^{iv}$ | 142.67 (7) | O3—Al1—O2 | 108.43 (16) |
| O1$^{iii}$—Rb1—O2$^{iv}$ | 82.40 (8) | O4—Al1—O1 | 107.72 (14) |
| O3$^{i}$—Rb1—O1 | 97.65 (8) | O3—Al1—O1 | 106.63 (14) |
| O2$^{ii}$—Rb1—O1 | 128.23 (8) | O2—Al1—O1 | 105.08 (15) |
| O4—Rb1—O1 | 56.13 (5) | O4—Al1—Rb1 | 51.73 (9) |

| | | | |
|---|---|---|---|
| O1$^{iii}$—Rb1—O1 | 103.03 (9) | O3—Al1—Rb1 | 128.04 (11) |
| O2$^{iv}$—Rb1—O1 | 90.03 (8) | O2—Al1—Rb1 | 123.07 (11) |
| O3$^{i}$—Rb1—O3$^{v}$ | 129.87 (9) | O1—Al1—Rb1 | 56.05 (9) |
| O2$^{ii}$—Rb1—O3$^{v}$ | 139.41 (8) | O4—Al1—Rb1$^{viii}$ | 136.81 (8) |
| O4—Rb1—O3$^{v}$ | 79.02 (7) | O3—Al1—Rb1$^{viii}$ | 46.05 (10) |
| O1$^{iii}$—Rb1—O3$^{v}$ | 53.96 (7) | O2—Al1—Rb1$^{viii}$ | 62.50 (11) |
| O2$^{iv}$—Rb1—O3$^{v}$ | 66.94 (7) | O1—Al1—Rb1$^{viii}$ | 114.59 (10) |
| O1—Rb1—O3$^{v}$ | 53.04 (7) | Rb1—Al1—Rb1$^{viii}$ | 169.18 (3) |
| O3$^{i}$—Rb1—O2$^{i}$ | 53.82 (7) | O4—Al1—Rb1$^{vi}$ | 45.71 (8) |
| O2$^{ii}$—Rb1—O2$^{i}$ | 89.71 (8) | O3—Al1—Rb1$^{vi}$ | 72.08 (10) |
| O4—Rb1—O2$^{i}$ | 68.66 (6) | O2—Al1—Rb1$^{vi}$ | 149.71 (11) |
| O1$^{iii}$—Rb1—O2$^{i}$ | 156.50 (7) | O1—Al1—Rb1$^{vi}$ | 103.54 (10) |
| O2$^{iv}$—Rb1—O2$^{i}$ | 108.44 (3) | Rb1—Al1—Rb1$^{vi}$ | 67.20 (2) |
| O1—Rb1—O2$^{i}$ | 57.41 (7) | Rb1$^{viii}$—Al1—Rb1$^{vi}$ | 113.18 (3) |
| O3$^{v}$—Rb1—O2$^{i}$ | 110.11 (7) | O4—Al1—Rb1$^{ix}$ | 142.90 (8) |
| O3$^{i}$—Rb1—Al1 | 112.61 (6) | O3—Al1—Rb1$^{ix}$ | 101.85 (10) |
| O2$^{ii}$—Rb1—Al1 | 101.86 (6) | O2—Al1—Rb1$^{ix}$ | 39.51 (10) |
| O4—Rb1—Al1 | 27.33 (2) | O1—Al1—Rb1$^{ix}$ | 69.83 (10) |
| O1$^{iii}$—Rb1—Al1 | 96.30 (6) | Rb1—Al1—Rb1$^{ix}$ | 112.80 (3) |
| O2$^{iv}$—Rb1—Al1 | 117.23 (6) | Rb1$^{viii}$—Al1—Rb1$^{ix}$ | 64.75 (2) |
| O1—Rb1—Al1 | 28.83 (5) | Rb1$^{vi}$—Al1—Rb1$^{ix}$ | 169.77 (3) |
| O3$^{v}$—Rb1—Al1 | 62.97 (5) | O4—Al1—Rb1$^{x}$ | 85.08 (9) |
| O2$^{i}$—Rb1—Al1 | 60.23 (5) | O3—Al1—Rb1$^{x}$ | 148.48 (11) |
| O3$^{i}$—Rb1—Al1$^{i}$ | 26.21 (6) | O2—Al1—Rb1$^{x}$ | 40.31 (10) |
| O2$^{ii}$—Rb1—Al1$^{i}$ | 88.99 (6) | O1—Al1—Rb1$^{x}$ | 89.93 (10) |
| O4—Rb1—Al1$^{i}$ | 95.26 (5) | Rb1—Al1—Rb1$^{x}$ | 83.48 (2) |
| O1$^{iii}$—Rb1—Al1$^{i}$ | 174.32 (6) | Rb1$^{viii}$—Al1—Rb1$^{x}$ | 102.80 (3) |
| O2$^{iv}$—Rb1—Al1$^{i}$ | 92.07 (6) | Rb1$^{vi}$—Al1—Rb1$^{x}$ | 130.79 (3) |
| O1—Rb1—Al1$^{i}$ | 78.16 (6) | Rb1$^{ix}$—Al1—Rb1$^{x}$ | 58.273 (17) |

| | | | |
|---|---|---|---|
| O3$^{v}$—Rb1—Al1$^{i}$ | 124.88 (5) | Al1—O1—Rb1$^{vii}$ | 175.84 (15) |
| O2$^{i}$—Rb1—Al1$^{i}$ | 27.66 (5) | Al1—O1—Rb1 | 95.12 (11) |
| Al1—Rb1—Al1$^{i}$ | 87.361 (9) | Rb1$^{vii}$—O1—Rb1 | 81.95 (7) |
| O3$^{i}$—Rb1—Al1$^{vi}$ | 135.18 (6) | Al1—O2—Rb1$^{ix}$ | 117.52 (14) |
| O2$^{ii}$—Rb1—Al1$^{vi}$ | 61.33 (6) | Al1—O2—Rb1$^{x}$ | 117.56 (14) |
| O4—Rb1—Al1$^{vi}$ | 24.74 (2) | Rb1$^{ix}$—O2—Rb1$^{x}$ | 84.58 (8) |
| O1$^{iii}$—Rb1—Al1$^{vi}$ | 72.48 (6) | Al1—O2—Rb1$^{viii}$ | 89.84 (12) |
| O2$^{iv}$—Rb1—Al1$^{vi}$ | 148.73 (6) | Rb1$^{ix}$—O2—Rb1$^{viii}$ | 83.73 (7) |
| O1—Rb1—Al1$^{vi}$ | 78.16 (5) | Rb1$^{x}$—O2—Rb1$^{viii}$ | 152.56 (10) |
| O3$^{v}$—Rb1—Al1$^{vi}$ | 83.08 (5) | Al1—O3—Rb1$^{viii}$ | 107.74 (13) |
| O2$^{i}$—Rb1—Al1$^{vi}$ | 89.53 (5) | Al1—O3—Rb1$^{xi}$ | 131.23 (14) |
| Al1—Rb1—Al1$^{vi}$ | 49.93 (3) | Rb1$^{viii}$—O3—Rb1$^{xi}$ | 116.91 (9) |
| Al1$^{i}$—Rb1—Al1$^{vi}$ | 113.17 (3) | Al1—O4—Al1$^{vi}$ | 136.2 (2) |
| O3$^{i}$—Rb1—Rb1$^{vii}$ | 69.10 (6) | Al1—O4—Rb1 | 100.95 (7) |
| O2$^{ii}$—Rb1—Rb1$^{vii}$ | 156.68 (6) | Al1$^{vi}$—O4—Rb1 | 109.55 (8) |
| O4—Rb1—Rb1$^{vii}$ | 104.258 (15) | Al1—O4—Rb1$^{vi}$ | 109.54 (8) |
| O1$^{iii}$—Rb1—Rb1$^{vii}$ | 108.82 (5) | Al1$^{vi}$—O4—Rb1$^{vi}$ | 100.95 (7) |
| O2$^{iv}$—Rb1—Rb1$^{vii}$ | 46.07 (6) | Rb1—O4—Rb1$^{vi}$ | 90.61 (10) |

Symmetry codes: (i) -*x*, -*y*+3/2, *z*+1/2; (ii) *x*, *y*+1/2, *z*+1/2; (iii) -*x*+1/2, *y*+1/2, *z*; (iv) -*x*+1/2, *y*, *z*+1/2; (v) *x*+1/2, -*y*+3/2, *z*; (vi) -*x*, -*y*+2, *z*; (vii) -*x*+1/2, *y*-1/2, *z*; (viii) -*x*, -*y*+3/2, *z*-1/2; (ix) *x*, *y*-1/2, *z*-1/2; (x) -*x*+1/2, *y*, *z*-1/2; (xi) *x*-1/2, -*y*+3/2, *z*.

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## Crystal Data for $CsAl(OH)_4 \cdot 2H_2O$ (**3**)

| | |
|---|---|
| $CsAlO6H_8$ | $F(000) = 228$ |
| $M_r = 245.94$ | $D_x = 2.333$ Mg m$^{-3}$ |

| | |
|---|---|
| Monoclinic, *C*2 | Ag *K*a radiation, l = 0.56086 Å |
| *a* = 10.4124 (15) Å | Cell parameters from 3749 reflections |
| *b* = 6.6986 (10) Å | q = 3.1–21.7° |
| *c* = 6.2156 (10) Å | m = 2.83 $mm^{-1}$ |
| b = 126.129 (4)° | *T* = 110 K |
| *V* = 350.16 (9) $Å^3$ | Acicular, colorless |
| *Z* = 2 | 0.04 × 0.01 × 0.01 mm |

*Data collection*

| | |
|---|---|
| Bruker APEX-II CCD diffractometer | 527 reflections with $I > 2s(I)$ |
| f and w scans | $q_{max}$ = 21.7°, $q_{min}$ = 3.1° |
| Absorption correction: multi-scan *SADABS* (Krause 2015) | *h* = -13®11 |
| $T_{min}$ = 0.625, $T_{max}$ = 0.745 | *k* = 0®8 |
| 527 measured reflections | *l* = 0®8 |
| 527 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters not defined |
| Least-squares matrix: full | $w = 1/[s^2(F_o^2) + (0.0539P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2s(F^2)]$ = 0.027 | $(D/s)_{max} < 0.001$ |
| $wR(F^2)$ = 0.079 | $D\rho_{max}$ = 0.94 e $Å^{-3}$ |
| *S* = 1.21 | $D\rho_{min}$ = -1.02 e $Å^{-3}$ |
| 527 reflections | Absolute structure: No quotients, so Flack parameter determined by classical intensity fit |
| 39 parameters | Absolute structure parameter: -0.03 (12) |
| 1 restraint | |

*Special details*

*Geometry*. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

*Refinement*. Refined as a 2-component twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for (CsAlOH4)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cs1 | 0.500000 | 0.17830 (9) | 0.500000 | 0.0100 (2) |
| Al1 | 0.500000 | 0.662 (3) | 1.000000 | 0.007 (2) |
| O1 | 0.3636 (10) | 0.5095 (12) | 0.7282 (14) | 0.0138 (14) |
| O2 | 0.5884 (10) | 0.8230 (12) | 0.9015 (16) | 0.0133 (15) |
| O1W | 0.2690 (9) | 0.2201 (11) | 0.7680 (13) | 0.017 (2) |

*Atomic displacement parameters (Å²) for (CsAlOH4)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cs1 | 0.0101 (4) | 0.0092 (4) | 0.0118 (3) | 0.000 | 0.0070 (3) | 0.000 |
| Al1 | 0.0081 (14) | 0.008 (6) | 0.0050 (13) | 0.000 | 0.0036 (11) | 0.000 |
| O1 | 0.022 (4) | 0.009 (3) | 0.007 (3) | -0.006 (3) | 0.007 (3) | -0.001 (3) |
| O2 | 0.020 (4) | 0.006 (3) | 0.018 (3) | -0.005 (3) | 0.014 (3) | -0.003 (3) |
| O1W | 0.021 (4) | 0.017 (8) | 0.014 (3) | 0.008 (3) | 0.011 (3) | 0.003 (2) |

*Geometric parameters (Å, º) for (CsAlOH4)*

| | | | |
|---|---|---|---|
| Cs1—O2$^{i}$ | 3.167 (8) | Cs1—O1W$^{vi}$ | 3.696 (6) |
| Cs1—O2$^{ii}$ | 3.167 (8) | Cs1—O1W$^{vii}$ | 3.696 (6) |
| Cs1—O1$^{iii}$ | 3.360 (9) | Cs1—O2$^{viii}$ | 3.788 (8) |
| Cs1—O1$^{iv}$ | 3.360 (9) | Cs1—O2$^{ix}$ | 3.788 (8) |
| Cs1—O1 | 3.366 (9) | Al1—O2 | 1.747 (15) |

| | | | |
|---|---|---|---|
| Cs1—O1$^{v}$ | 3.366 (9) | Al1—O2$^{vi}$ | 1.747 (15) |
| Cs1—O1W$^{v}$ | 3.656 (7) | Al1—O1 | 1.756 (14) |
| Cs1—O1W | 3.656 (7) | Al1—O1$^{vi}$ | 1.756 (14) |
| | | | |
| O2$^{i}$—Cs1—O2$^{ii}$ | 82.6 (3) | O1W$^{vi}$—Cs1—O1W$^{vii}$ | 171.3 (2) |
| O2$^{i}$—Cs1—O1$^{iii}$ | 71.52 (19) | O2$^{i}$—Cs1—O2$^{viii}$ | 126.9 (2) |
| O2$^{ii}$—Cs1—O1$^{iii}$ | 79.13 (19) | O2$^{ii}$—Cs1—O2$^{viii}$ | 77.50 (14) |
| O2$^{i}$—Cs1—O1$^{iv}$ | 79.13 (19) | O1$^{iii}$—Cs1—O2$^{viii}$ | 147.30 (16) |
| O2$^{ii}$—Cs1—O1$^{iv}$ | 71.52 (19) | O1$^{iv}$—Cs1—O2$^{viii}$ | 47.98 (17) |
| O1$^{iii}$—Cs1—O1$^{iv}$ | 140.7 (3) | O1—Cs1—O2$^{viii}$ | 86.08 (18) |
| O2$^{i}$—Cs1—O1 | 146.0 (2) | O1$^{v}$—Cs1—O2$^{viii}$ | 74.39 (18) |
| O2$^{ii}$—Cs1—O1 | 99.33 (18) | O1W$^{v}$—Cs1—O2$^{viii}$ | 76.14 (16) |
| O1$^{iii}$—Cs1—O1 | 75.48 (12) | O1W—Cs1—O2$^{viii}$ | 101.56 (16) |
| O1$^{iv}$—Cs1—O1 | 134.0 (2) | O1W$^{vi}$—Cs1—O2$^{viii}$ | 39.94 (16) |
| O2$^{i}$—Cs1—O1$^{v}$ | 99.33 (18) | O1W$^{vii}$—Cs1—O2$^{viii}$ | 136.71 (17) |
| O2$^{ii}$—Cs1—O1$^{v}$ | 146.0 (2) | O2$^{i}$—Cs1—O2$^{ix}$ | 77.50 (14) |
| O1$^{iii}$—Cs1—O1$^{v}$ | 134.0 (2) | O2$^{ii}$—Cs1—O2$^{ix}$ | 126.9 (2) |
| O1$^{iv}$—Cs1—O1$^{v}$ | 75.48 (12) | O1$^{iii}$—Cs1—O2$^{ix}$ | 47.98 (17) |
| O1—Cs1—O1$^{v}$ | 97.5 (2) | O1$^{iv}$—Cs1—O2$^{ix}$ | 147.30 (16) |
| O2$^{i}$—Cs1—O1W$^{v}$ | 70.25 (18) | O1—Cs1—O2$^{ix}$ | 74.39 (18) |
| O2$^{ii}$—Cs1—O1W$^{v}$ | 116.94 (18) | O1$^{v}$—Cs1—O2$^{ix}$ | 86.09 (18) |
| O1$^{iii}$—Cs1—O1W$^{v}$ | 135.53 (16) | O1W$^{v}$—Cs1—O2$^{ix}$ | 101.56 (16) |
| O1$^{iv}$—Cs1—O1W$^{v}$ | 48.54 (17) | O1W—Cs1—O2$^{ix}$ | 76.14 (16) |
| O1—Cs1—O1W$^{v}$ | 134.11 (17) | O1W$^{vi}$—Cs1—O2$^{ix}$ | 136.71 (17) |
| O1$^{v}$—Cs1—O1W$^{v}$ | 37.14 (18) | O1W$^{vii}$—Cs1—O2$^{ix}$ | 39.94 (16) |
| O2$^{i}$—Cs1—O1W | 116.94 (18) | O2$^{viii}$—Cs1—O2$^{ix}$ | 150.3 (2) |
| O2$^{ii}$—Cs1—O1W | 70.25 (18) | O2—Al1—O2$^{vi}$ | 103.6 (12) |
| O1$^{iii}$—Cs1—O1W | 48.54 (17) | O2—Al1—O1 | 108.4 (3) |
| O1$^{iv}$—Cs1—O1W | 135.54 (16) | O2$^{vi}$—Al1—O1 | 113.7 (4) |

| | | | |
|---|---|---|---|
| O1—Cs1—O1W | 37.14 (18) | O2—Al1—O1$^{vi}$ | 113.7 (4) |
| O1$^{v}$—Cs1—O1W | 134.11 (17) | O2$^{vi}$—Al1—O1$^{vi}$ | 108.4 (3) |
| O1W$^{v}$—Cs1—O1W | 171.2 (2) | O1—Al1—O1$^{vi}$ | 109.0 (12) |
| O2$^{i}$—Cs1—O1W$^{vi}$ | 134.65 (18) | O2—Al1—Cs1$^{x}$ | 64.2 (3) |
| O2$^{ii}$—Cs1—O1W$^{vi}$ | 53.93 (19) | O2$^{vi}$—Al1—Cs1$^{x}$ | 113.8 (5) |
| O1$^{iii}$—Cs1—O1W$^{vi}$ | 107.38 (17) | O1—Al1—Cs1$^{x}$ | 132.3 (6) |
| O1$^{iv}$—Cs1—O1W$^{vi}$ | 75.66 (17) | O1$^{vi}$—Al1—Cs1$^{x}$ | 50.0 (3) |
| O1—Cs1—O1W$^{vi}$ | 63.97 (17) | O2—Al1—Cs1$^{xi}$ | 113.8 (5) |
| O1$^{v}$—Cs1—O1W$^{vi}$ | 109.80 (17) | O2$^{vi}$—Al1—Cs1$^{xi}$ | 64.2 (3) |
| O1W$^{v}$—Cs1—O1W$^{vi}$ | 115.4 (2) | O1—Al1—Cs1$^{xi}$ | 50.0 (3) |
| O1W—Cs1—O1W$^{vi}$ | 63.8 (2) | O1$^{vi}$—Al1—Cs1$^{xi}$ | 132.3 (6) |
| O2$^{i}$—Cs1—O1W$^{vii}$ | 53.93 (19) | Cs1$^{x}$—Al1—Cs1$^{xi}$ | 177.0 (5) |
| O2$^{ii}$—Cs1—O1W$^{vii}$ | 134.65 (18) | Al1—O1—Cs1$^{xi}$ | 106.4 (5) |
| O1$^{iii}$—Cs1—O1W$^{vii}$ | 75.66 (17) | Al1—O1—Cs1 | 119.0 (5) |
| O1$^{iv}$—Cs1—O1W$^{vii}$ | 107.38 (16) | Cs1$^{xi}$—O1—Cs1 | 134.0 (2) |
| O1—Cs1—O1W$^{vii}$ | 109.80 (17) | Al1—O2—Cs1$^{xii}$ | 140.6 (5) |
| O1$^{v}$—Cs1—O1W$^{vii}$ | 63.97 (17) | Al1—O2—Cs1$^{x}$ | 91.3 (4) |
| O1W$^{v}$—Cs1—O1W$^{vii}$ | 63.8 (2) | Cs1$^{xii}$—O2—Cs1$^{x}$ | 126.9 (2) |
| O1W—Cs1—O1W$^{vii}$ | 115.4 (2) | Cs1—O1W—Cs1$^{xiii}$ | 115.4 (2) |

Symmetry codes: (i) -*x*+1, *y*-1, -*z*+1; (ii) *x*, *y*-1, *z*; (iii) -*x*+1/2, *y*-1/2, -*z*+1; (iv) *x*+1/2, *y*-1/2, *z*; (v) -*x*+1, *y*, -*z*+1; (vi) -*x*+1, *y*, -*z*+2; (vii) *x*, *y*, *z*-1; (viii) -*x*+3/2, *y*-1/2, -*z*+2; (ix) *x*-1/2, *y*-1/2, *z*-1; (x) *x*+1/2, *y*+1/2, *z*+1; (xi) *x*-1/2, *y*+1/2, *z*; (xii) *x*, *y*+1, *z*; (xiii) *x*, *y*, *z*+1.

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