SUPPLEMENTARY MATERIAL

FOR

Phase transitions in $K_2Cr_2O_7$ and structural redeterminations of phase II

T. J. R. Weakley,[a] E. R. Ylvisaker,[b] R. J. Yager,[b] J. E. Stephens,[b] R. D. Wiegel,[b] M. Mengis,[c] M. R. Bauer,[b] P. Wu,[b] P. Photinos[b] & S. C. Abrahams[b*]

[a] Department of Chemistry, University of Oregon, Eugene, OR 97403, USA

[b] Physics Department, Southern Oregon University, Ashland, OR 97520, USA.

[c] North Medford High School, Medford, OR 97504, USA

Abstract

Crystals of phase II $K_2Cr_2O_7$, space group $P\bar{1}$, grown from aqueous solution undergo a first-order transition to phase I, space group reportedly $P2_1/n$, at T_{PT} = 544(2) K on first heating; the corresponding transition on cooling is at 502(2) K. The endotherm on subsequent heatings occurs reproducibly at T_{PT} = 531(2) K. Mass loss between ~531 and 544 K, identified as included water, is rapid and continues more slowly to higher temperatures for a total loss of ~0.20 %. The higher T_{PT} on first heating is associated with the increasing pressure of superheated water occupying inclusion defects. The latent diagonal glide plane in phase II allows the structure of phase I to be inferred. The triclinic structure at 296 K has been independently redetermined. Normal probability analysis shows high consistency between the resulting and previous atomic coordinates but with uncertainties reduced by a factor ~2. The earlier uncertainties are systematically underestimated by a comparable factor. The structure of phase IIb, space group $A2/a$ on

[*] Correspondence email: sca@mind.net

transposing axes, was determined at ~300 K by Krivovichev, Kir'yanova, Filatov & Burns [*Acta Cryst.* (2000), C**56**, 629-630]. The first order transition between phases I and II arises from the ~60º relative rotation of terminal O atoms in each tetrahedron as the *n* glide plane is gained or lost. A transition between phases IIb and I, also of first order, is likely but not between phases II and IIb. An intermediate phase may exist between phases IIb and I.

Supplementary Material Figures Captions

Figure S1. As in Figure 2 but with numbered oxygen atoms.

Figure S2. Normal probability Q_{exp}-Q_{norm} plot for the atomic coordinates determined with Crystal 2 of II-$K_2Cr_2O_7$ *vs.* those reported by Brandon & Brown (1968).

Figure S3. Normal probability Q_{exp}-Q_{norm} plot for the atomic coordinates determined with Crystal 1 of II-$K_2Cr_2O_7$ *vs.* those reported by Brunton (1973).

Figure S4. Normal probability Q_{exp}-Q_{norm} plot for the atomic coordinates determined ith Crystal 2 of II-$K_2Cr_2O_7$ *vs.* those reported by Brunton (1973).

Figure S5. Normal probability Q_{exp}-Q_{norm} plot for the II-$K_2Cr_2O_7$ atomic coordinates determined by Brandon & Brown (1968) *vs.* Brunton (1973).

Supplementary Material Table Captions

Table S1. $K_2Cr_2O_7$ phase II natural triclinic and phase IIb transposed monoclinic atomic coordinates.†

Table S2. Cartesian atomic coordinates for $X||a$, $Z||c^*$ in $K_2Cr_2O_7$ phases II and IIb, with component ($|\Delta\xi|$) and total ($|\Delta(xyz|$) differences between the phases, in Å.

Table S3. Cartesian atomic coordinates for $X||a$, $Z||c^*$ in $K_2Cr_2O_7$ phases I and II, with component ($|\Delta\xi|$) and total ($|\Delta(xyz|$) differences between the phases, in Å.

Table S4. Cartesian atomic coordinates for $X||a$, $Z||c^*$ of $K_2Cr_2O_7$ in phases I and IIb, with component ($|\Delta\xi|$) and total ($|\Delta(xyz|$) differences between the phases, in Å.

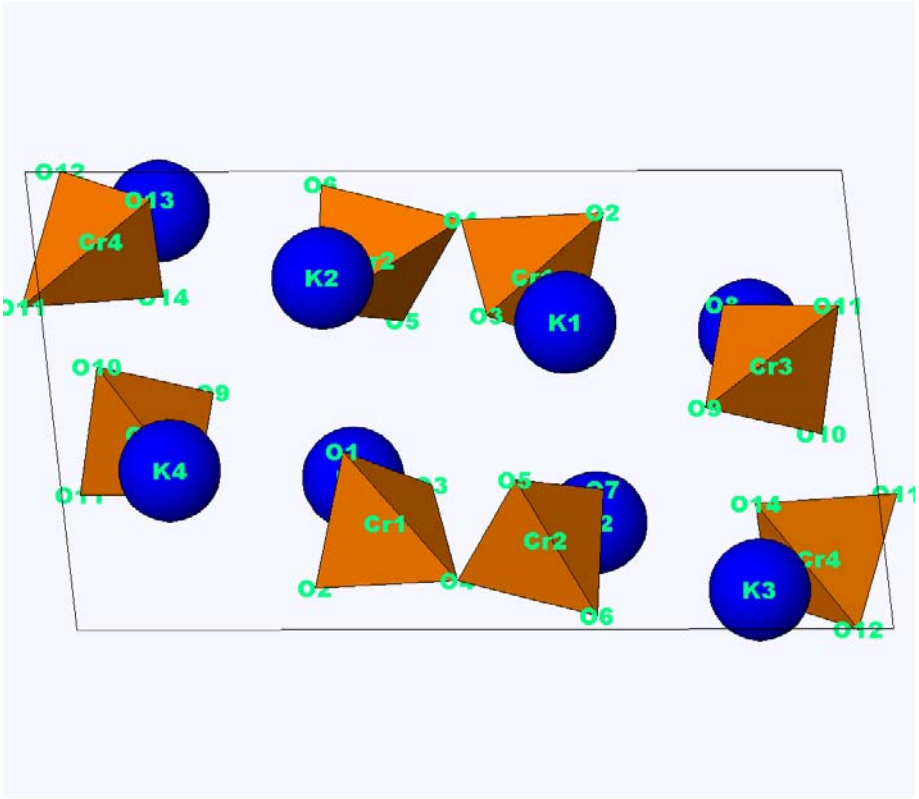

Figure S1

As in Figure 2 but with numbered oxygen atoms.

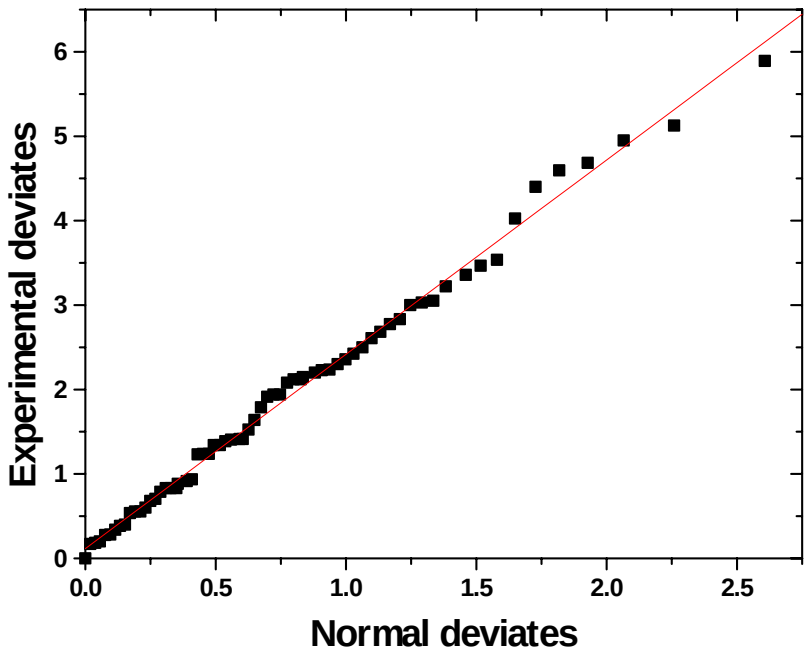

Figure S2.

Normal probability Q_{exp}-Q_{norm} plot for the atomic coordinates determined with Crystal 2 of II-$K_2Cr_2O_7$ *vs.* those reported by Brandon & Brown (1968).

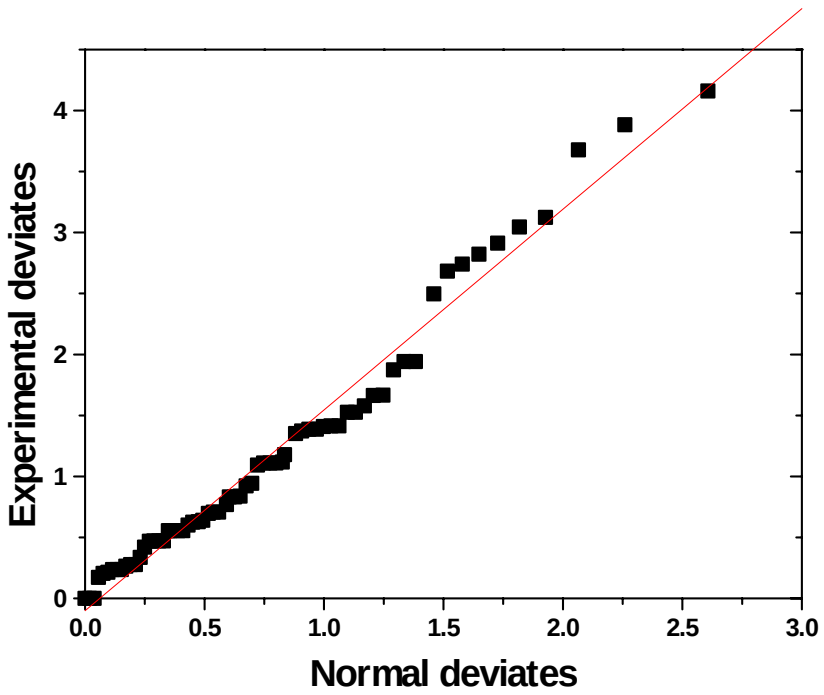

Figure S3.

Normal probability Q_{exp}-Q_{norm} plot for the atomic coordinates determined with Crystal 1 of II-$K_2Cr_2O_7$ *vs.* those reported by Brunton (1973).

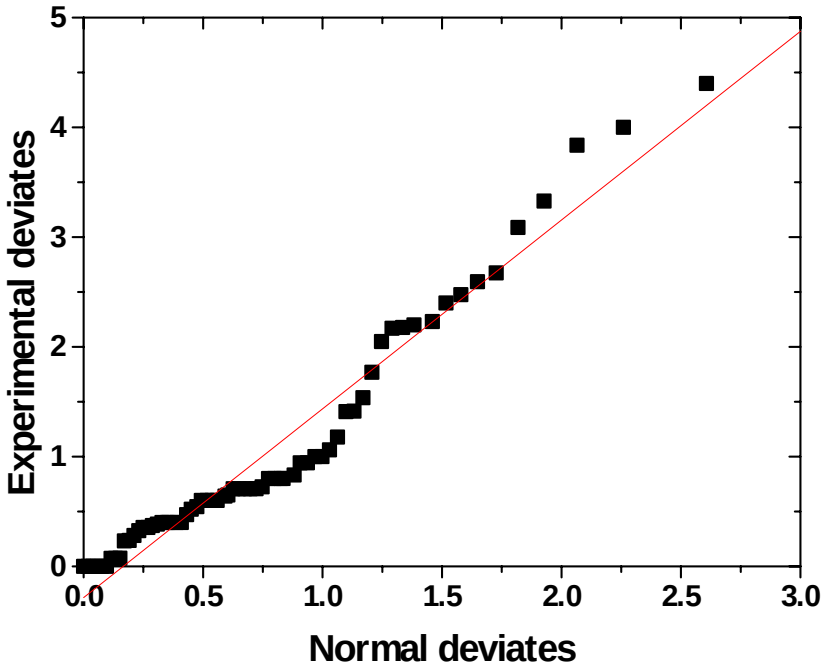

Figure S4.

Normal probability Q_{exp}-Q_{norm} plot for the atomic coordinates determined with Crystal 2 of II-$K_2Cr_2O_7$ *vs.* those reported by Brunton (1973).

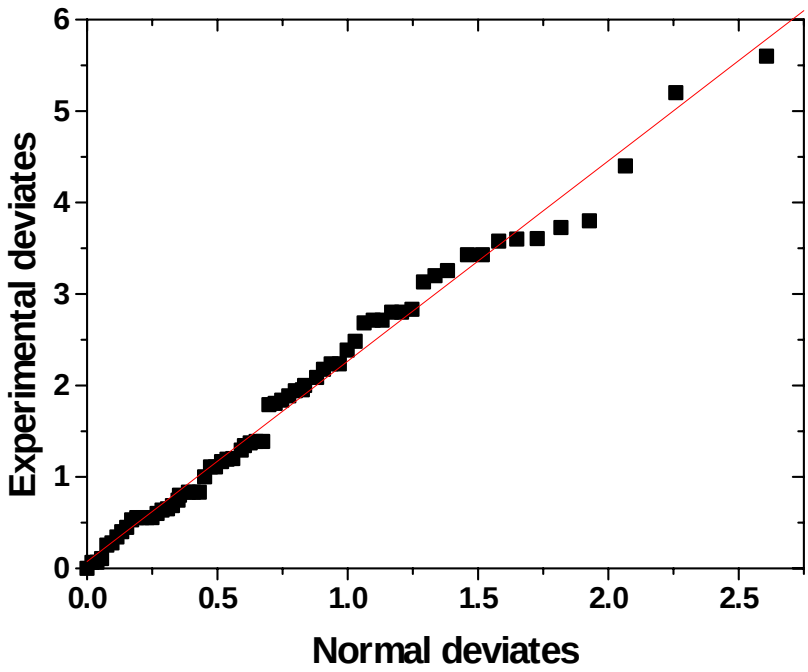

Figure S5.

Normal probability Q_{exp}-Q_{norm} plot for the atomic coordinates determined by Brandon &Brown (1968) *vs.* those reported by Brunton (1973).

Table S1. $K_2Cr_2O_7$ phase II experimental triclinic and phase IIb transposed monoclinic atomic coordinates.[†]

Phase II Crystal II	*x*	*y*	*z*	Phase IIb		*x´*	*y*	*z´*
Cr1	0.59179(4)	0.76891(5)	0.60724(2)	Cr	*d*[‡]	0.63497(5)	0.82571(5)	0.60286(3)
Cr2	0.79289(4)	0.80674(5)	0.41375(2)	Cr	*c*	0.86503(5)	0.82571(5)	0.39714(3)
Cr3	0.81711(4)	0.42584(5)	0.11354(2)	Cr	*g*	0.63497(5)	0.32571(5)	0.10286(3)
Cr4	0.81344(4)	0.15250(4)	-0.08323(2)	Cr	*f*	0.86503(5)	0.32571(5)	-0.10286(3)
K1	1.10341(8)	0.66917(7)	0.64038(4)	K	*b*	1.14438(8)	0.65065(9)	0.64473(8)
K2	0.25001(7)	0.7671(7)	0.34950(4)	K	*e*	0.35562(8)	0.65065(9)	0.35527(8)
K3	0.66252(6)	-0.08518(7)	0.15847(4)	K	*c*	0.64438(8)	-0.15065(9)	0.14473(8)
K4	0.69509(8)	0.6524(7)	-0.13583(4)	K	*d*	0.85562(8)	0.84935(9)	-0.14473(8)
O1	0.7201(3)	0.6124(3)	0.64937(14)	O2	*d*	0.7780(3)	0.7026(3)	0.66247(18)
O2	0.5550(3)	0.9102(3)	0.70198(13)	O4	*d*	0.5494(3)	0.9746(3)	0.67975(19)
O3	0.4024(2)	0.6849(3)	0.54525(14)	O1	*d*	0.4824(3)	0.6929(3)	0.55847(18)
O4	0.7076(2)	0.8937(2)	0.52700(13)	O3	*d*	0.7500	0.9405(4)	0.50000
O5	0.9595(2)	0.6749(2)	0.44295(12)	O1	*c*	1.0176(3)	0.6929(3)	0.44153(18)
O6	0.8687(3)	0.9709(2)	0.36065(13)	O4	*c*	0.9506(3)	0.9746(3)	0.32025(18)
O7	0.6345(2)	0.6952(3)	0.33667(14)	O2	*c*	0.7220(3)	0.7026(3)	0.33753(18)
O8	0.6891(2)	0.2927(2)	0.16402(13)	O4	*e*	1.0494(3)	0.5254(3)	0.17975(19)
O9	0.9757(2)	0.5181(3)	0.19989(12)	O2	*h*	0.7780(3)	0.2026(3)	0.16247(18)
O10	0.6948(3)	0.5751(3)	0.06114(13)	O1	*g*	0.4824(3)	0.1929(3)	0.05847(18)
O11	0.9299(2)	0.2957(2)	0.02274(12)	O3	*g*	0.7500	0.4405(4)	0.00000
O12	0.6919(2)	-0.0006(2)	-0.04330(13)	O1	*b*	0.5176(3)	0.8071(3)	-0.05847(18)
O13	0.9600(2)	1.0608(3)	-0.14886(15)	O4	*a*	1.0494(3)	1.0254(3)	-0.32025(19)
O14	0.6770(2)	0.2738(2)	-0.15168(12)	O2	*f*	0.7220(3)	0.2026(3)	-0.16247(18)

[†] With $abc_{\text{Krivovichev et al. (2000)}}$ in phase Ib transposed to $cb\bar{a}_{\text{transposed cell}}$ and resulting *z´* replaced by 1- *z´* coordinates, see Table 3 for unit cell dimensions.

[‡] Symmetry equivalence in phase IIb: [a] *x*, *y*, *z*; [b] ½-*x*, ½+*y*, ½-*z*; [c] -*x*, -*y*, -*z*; [d] ½+*x*, -*y*, *z*; [e] *x*, ½+*y*, ½+*z*; [f] -*x*, ½-*y*, ½-*z*; [g] ½+*x*, ½-*y*, ½+*z*; [h] ½-*x*, *y*, -*z*.

Table S2. Cartesian atomic coordinates for $X||a$, $Z||c^*$ in $K_2Cr_2O_7$ phases II and IIb, with component ($|\Delta\xi|$) and total ($|\Delta(xyz|$) differences between the phases, in Å. †

Phase II	*x*	*y*	*z*		*x*	*y*	*z*	Δ*x*	Δ*y*	Δ*z*	Δ(*xyz*)
		Phase II				**Phase IIb**					
Cr1	3.137	4.806	8.050	Cr^d	5.005	6.090	7.853	1.87	1.24	0.15	2.26
Cr2	4.980	5.373	5.485	Cr^c	6.633	6.090	5.173	1.66	0.68	0.28	1.81
Cr3	5.768	2.991	1.505	Cr^g	4.786	2.402	1.340	0.98	0.61	0.16	1.16
Cr4	6.144	1.254	-1.103	Cr^f	6.414	2.402	-1.340	0.27	1.14	0.24	1.20
K1	6.864	4.017	8.489	K^b	8.827	4.799	8.399	1.97	0.75	0.04	2.11
K2	1.097	5.174	4.633	K^e	2.811	4.799	4.628	1.72	0.41	0.02	1.76
K3	4.605	-0.866	2.101	K^c	4.875	-1.111	1.885	0.27	0.24	0.20	0.42
K4	5.308	5.041	-1.801	K^d	6.3258	6.264	-1.885	1.02	1.20	0.10	1.58
O1	4.024	3.583	8.609	$O2^d$	6.099	5.182	8.630	2.08	1.57	0.07	2.61
O2	2.670	5.714	9.306	$O4^d$	4.400	7.188	8.855	1.73	1.44	0.39	2.28
O3	1.864	4.275	7.229	$O1^d$	3.846	5.110	7.275	1.98	0.81	0.09	2.14
O4	4.127	5.851	6.986	$O3^d$	5.819	6.936	6.513	1.69	1.05	0.43	2.04
O5	6.171	4.352	5.872	$O1^c$	7.792	5.110	5.752	1.62	0.73	0.09	1.78
O6	5.619	6.669	4.782	$O4^c$	7.238	7.188	4.172	1.62	0.48	0.58	1.79
O7	3.968	4.659	4.463	$O2^c$	5.539	5.182	4.397	1.57	0.49	0.04	1.65
O8	4.7447	1.929	2.174	O1	3.628	1.423	0.762	1.11	0.52	1.40	1.86
O9	6.7659	3.548	2.650	O4	7.915	3.875	2.342	1.15	0.31	0.29	1.23
O10	4.945	4.176	0.810	O2	5.881	1.494	2.116	0.94	2.70	1.31	3.15
O11	6.787	2.160	0.301	$O3^g$	5.600	3.249	0	1.18	1.08	0.30	1.63
O12	5.067	7.478	-0.574	$O1^b$	3.839	5.952	-0.762	1.23	1.57	0.19	2.00
O13	7.237	8.089	-1.974	$O4^a$	7.696	0.187	-4.172	0.34	0.49	2.21	2.29
O14	5.250	2.255	-2.011	$O2^f$	5.320	1.494	-2.116	0.07	0.77	0.12	0.78

Table S3. Cartesian atomic coordinates for $X||a$, $Z||c^*$ in $K_2Cr_2O_7$ phases I and II, with component ($|\Delta\xi|$) and total ($|\Delta(xyz|$) differences between the phases, in Å.[†]

	phase II			phase I			phases II - I			
	x	y	z	x	y	z	Δx	Δy	Δz	$\Delta(xyz)$
Cr1	3.135	4.837	8.001	4.591	5.345	7.843	1.46	0.51	0.16	1.55
Cr2	4.978	5.405	5.452	5.413	6.515	5.272	0.44	1.11	0.18	1.21
Cr3	5.766	3.008	1.496	5.715	2.755	1.316	0.05	0.25	0.18	0.32
Cr4	6.141	1.260	-1.097	6.537	1.584	-1.254	0.40	0.32	0.16	0.54
K1	6.862	4.045	8.438	8.298	4.716	8.557	1.44	0.67	0.12	1.59
K2	1.096	5.205	4.605	1.540	6.071	4.703	0.44	0.87	0.10	0.98
K3	4.603	-0.869	2.088	4.720	-0.957	1.969	0.12	0.09	0.12	0.19
K4	5.305	5.067	-1.790	5.512	5.208	-1.886	0.21	0.14	0.10	0.27
O1	4.022	3.608	8.557	5.534	4.180	7.857	1.51	0.57	0.70	1.76
O2	2.669	5.751	9.250	4.135	6.332	8.918	1.47	0.58	0.33	1.61
O3	1.864	4.302	7.185	3.322	4.684	7.868	1.46	0.38	0.68	1.65
O4	4.125	5.887	6.944	4.625	6.352	6.616	0.50	0.47	0.33	0.76
O5	6.169	4.379	5.837	6.530	5.518	5.132	0.36	1.14	0.71	1.39
O6	5.616	6.708	4.753	6.161	7.693	5.268	0.54	0.98	0.52	1.24
O7	3.967	4.687	4.437	4.249	6.442	4.195	0.28	1.75	0.24	1.79
O8	4.743	1.941	2.161	4.598	1.758	1.456	0.15	0.18	0.70	0.74
O9	6.763	3.569	2.634	6.879	2.682	2.393	0.12	0.89	0.24	0.93
O10	4.943	4.199	0.805	4.966	3.933	1.320	0.02	0.27	0.52	0.58
O11	6.784	2.172	0.299	6.502	2.592	-0.028	0.28	0.42	0.33	0.60
O12	5.065	7.518	-0.571	5.594	7.940	-1.269	0.53	0.42	0.70	0.97
O13	7.357	0.674	-1.962	7.806	0.924	-1.279	0.45	0.25	0.68	0.85
O14	5.247	2.266	-1.999	6.193	2.572	-2.330	0.95	0.31	0.33	1.05

[†] See Table 1 for unit cell dimensions.

Table S4. Cartesian atomic coordinates for $X||a$, $Z||c^*$ of $K_2Cr_2O_7$ in phases I and IIb, with component ($|\Delta\xi|$) and total ($|\Delta(xyz|$) differences between the phases, in Å. †

	Phase I				Phase IIb						
I	*x*	*y*	*z*	IIb	*x*	*y*	*z*	Δ(*x*)	Δ(*y*)	Δ (*z*)	Δ(*xyz*)
Cr1	4.591	5.344	7.843	Cr [d]	5.005	6.090	7.853	0.41	0.75	0.01	0.85
Cr2	5.413	6.515	5.2712	Cr [c]	6.633	6.090	5.173	1.22	-0.42	-0.10	1.30
K1	8.298	4.716	8.557	K [b]	8.827	4.799	8.399	0.53	0.08	-0.16	0.56
K2	1.540	6.0713	4.703	K [e]	2.811	4.799	4.628	1.27	-1.27	-0.07	1.80
O1	5.512	5.208	-1.886	O4 [d]	6.099	5.182	8.630	0.57	1.00	0.77	1.39
O2	5.534	4.180	7.857	O2 [d]	4.400	7.188	8.855	-0.54	0.86	-0.06	1.01
O3	4.9351	6.332	8.918	O1 [d]	3.846	5.110	7.275	0.52	0.43	-0.59	0.90
O4	3.3221	4.684	7.868	O3 [d]	5.819	6.936	6.513	1.19	0.58	-0.10	1.33
O5	4.625	6.352	6.616	O1 [c]	7.792	5.110	5.752	1.26	-0.41	0.62	1.46
O6	6.530	5.518	5.132	O2 [c]	7.238	7.188	4.172	1.08	-0.51	-1.10	1.62
O7	6.161	7.693	5.268	O4 [h]	5.539	5.182	4.397	1.30	-1.26	0.20	1.81

† See Table 1 for unit cell dimensions.