research communications

Crystal structure and electrical resistance property of $Rb_{0.21}(H_2O)_yWS_2$

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$Rb_{0.21}(H_2O)_yWS_2$, rubidium hydrate dithiotungstate, is a new quasi two-dimensional sulfide. Its crystal structure consists of ordered WS_2 layers, separated by disordered Rb^+ ions and water molecules. All atomic sites are located on mirror planes. The WS_2 layers are composed of edge-sharing $[WS_6]$ octahedra and extend parallel to (001). The presence of structural water was revealed by thermogravimetry, but the position and exact amount could not be determined in the present study. The temperature dependence of the electrical resistance indicates that $Rb_{0.21}(H_2O)_yWS_2$ is semiconducting between 80–300 K.

1. Chemical context

Typical two-dimensional structures of MS_2 compounds (M = transition metals of group IVB–VIB) facilitate the intercalation of various atoms, ions or organic molecules (Whittingham et al., 1978). For example, A_xMS_2 (A = alkali metal; M = Nb, Ta, Ti, V) compounds can be prepared in high-temperature solid-state reactions (800–1000 K). These compounds can react with water molecules to form ionic hydrates $A^+_x(H_2O)_y[MS_2]^{x-}$ (Omloo & Jellinek, 1970; Lerf & Schöllhorn, 1977; Lobert et al., 1992) that exhibit ion-exchange and solvent-exchange capacities. Some of the $A^+_x(H_2O)_y[MS_2]^{x-}$ compounds show unusual superconducting properties (Schöllhorn & Weiss, 1974; Sernetz et al., 1974). Recently, by removing alkali ions from intercalated $A^+_x(H_2O)_y[MS_2]^{x-}$ (A = alkali metal) compounds, several metastable MS_2 (M = Mo, W) phases with new crystal structures and novel physical properties were reported (Fang et al., 2018, 2019). In order to identify the formation mechanism of metastable MS_2 from $A^+_x(H_2O)_y[MS_2]^{x-}$, it is necessary to uncover the role of alkali ions intercalated into the interlayers of MS_2.

In this communication, we report the preparation of $Rb_{0.21}(H_2O)_yWS_2$, its crystal structure determination by single crystal X-ray diffraction, its thermal behaviour and its electrical resistance property.

2. Structural commentary

$Rb_{0.21}(H_2O)_yWS_2$ crystallizes in the monoclinic $P2_1/m$ (No. 11) space group. The structure consists of one independent W site, two independent S sites and two independent Rb sites, all of them located on a mirror plane (Wyckoff position 2e). The crystal structure features ordered WS_2 layers separated by

Element	Weight%	Atomic%
S K	26.48	65.22
Rb L	6.48	5.99
W M	67.04	28.79
Totals	100.00	
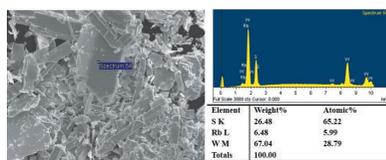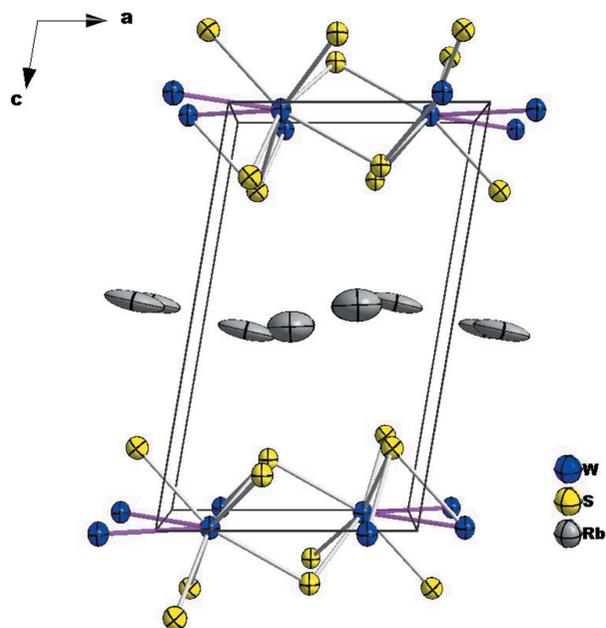
Figure 1
Crystal structure of $Rb_{0.21}(H_2O)_yWS_2$ with displacement ellipsoids drawn at the 30% probability level.

disordered Rb^+ ions, and of water molecules. The latter could not be localized in the current study, hence y in $Rb_{0.21}(H_2O)_yWS_2$ remains undetermined (see *Experimental*, and discussion below). Compared with $[WS_6]^{8-}$ trigonal prisms in 2H-WS_2 (Schutte *et al.*, 1987), the WS_2 layer in $Rb_{0.21}(H_2O)_yWS_2$ is composed of edge-sharing $[WS_6]^{8.21-}$ octahedra. The W—S bond lengths range from 2.403 (4) Å to 2.550 (5) Å, and thus the average W—S distance is larger than that in 2H-WS_2 [2.405 (5) Å; Schutte *et al.*, 1987]. The WS_2 layers extend parallel to (001) (Fig. 1). The shortest W—W bond length of 2.7678 (15) Å is between pairs of W atoms aligned in the [$\bar{1}$10] direction, much shorter than the W···W distance of 3.2524 (18) Å along [010]. Similar metal–metal separations also exist in some metastable MS_2 phases prepared by de-intercalating alkali ions from $A_x(H_2O)_yMS_2$ compounds (Yu *et al.*, 2018; Shang *et al.*, 2018). The Rb^+ cations show a one-sided coordination to the S atoms of the adjacent layer. The Rb—S bonds range from 3.47 (7) Å to 3.64 (5) Å, comparable to the Rb—S bonds [3.344 (7)– 3.561 (1) Å] in $RbCr_5S_8$ (Huster, 1978).

Similar to $K_x(H_2O)_yTaS_2$ and $K_x(H_2O)_yNbS_2$ (Graf *et al.*, 1977), it was impossible to determine the light O atoms of water molecules in the title compound from X-ray diffraction data at room temperature, as a result of diffuse electron density in the interlayer space. However, we could localize the positions of disordered Rb^+ ions with large displacement parameters. Stacking disorder of the layers is common for layered dichalcogenides, which may contribute to the diffuse electron density. Large displacement parameters of exchangeable cations and water molecules were also reported for $A_x(H_2O)_yTaS_2$ and $A_x(H_2O)_yNbS_2$ (A = alkali metal) compounds (Röder *et al.*, 1979; Wein *et al.* 1986; Lobert *et al.*, 1992).
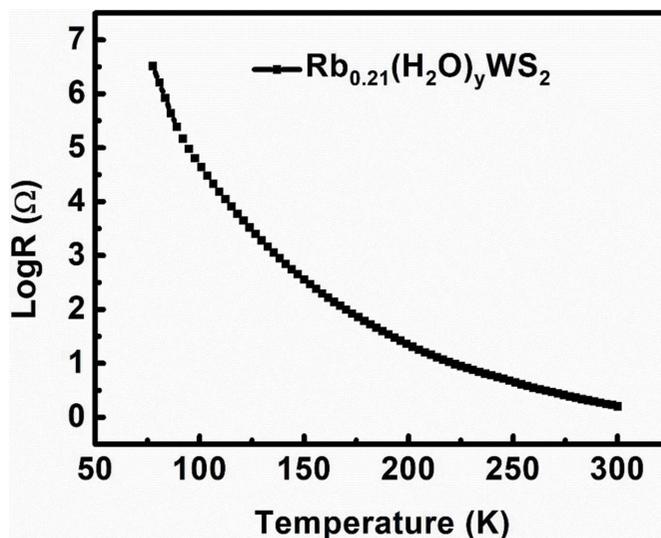
Figure 2
Temperature-dependence of the log(Resistance) for $Rb_{0.21}(H_2O)_yWS_2$.

3. Electrical resistance property

The electrical resistance of $Rb_{0.21}(H_2O)_yWS_2$ increases with the decrease of temperature (80–300 K) (Fig. 2), which is characteristic of a semiconductor.

4. Synthesis and crystallization

A rubidium dithiotungstate Rb_xWS_2 was synthesized in a solid-state reaction. The starting Rb_2S_2 powder was prepared in a reaction of stoichiometric amounts of Rb pieces and S powder in liquid NH_3. The obtained Rb_2S_2 powder, W powder and S powder were mixed in the molar ratio of 1:1:1 in a glove box filled with Ar. The mixture was ground carefully and loaded in a carbon-coated fused-silica tube. The tube was sealed under a 10^{-4} Torr atmosphere and slowly heated to 1123 K at 5 K min^{-1}. After three days, the furnace was cooled down naturally to room temperature. Subsequent removal of the extra flux by washing with distilled water led to the isolation of crystals of $Rb_{0.21}(H_2O)_yWS_2$. The morphology and element composition were investigated by using an EDXS-equipped Hitachi S-4800 scanning electronic microscope. In addition, the Rb/W ratio in the $Rb_x(H_2O)_yWS_2$ crystals was determined by ICP-OES. The SEM image and EDX spectrum of $Rb_{0.21}(H_2O)_yWS_2$ crystals are shown in Fig. 3. The ratio of

Element	Weight%	Atomic%
S K	26.48	65.22
Rb L	6.48	5.99
W M	67.04	28.79
Totals	100.00	
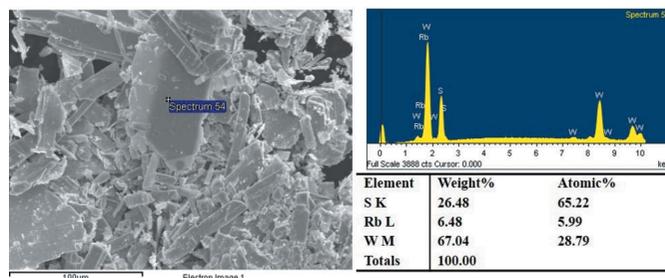
Figure 3
SEM image and EDXS spectrum of $Rb_{0.21}(H_2O)_yWS_2$.

Table 1
Results of ICP–OES measurement of $Rb_{0.21}(H_2O)_yWS_2$.

Element	Weight (%)	atom (%)
W	67.6	36.77
Rb	6.6	7.72

Rb/W from the EDXS analysis is close to 0.21, which is consistent with the the diffraction data and results from ICP–OES measurements (Table 1). The experimental powder X-ray diffraction (PXRD) pattern matches well with the simulated one (Fig. 4) by using the Rietveld refinement method (Rodríguez-Carvajal, 1993; $R_p = 9.9\%$, $R_{wp} = 12.6\%$ and $\chi^2 = 1.3$). In the TG–DTA analyses (Fig. 5), one obvious endothermic effect and concomitant mass loss were observed at 343 K, which is associated with water evaporation. In order to judge whether water molecules are surface-adsorbed water or structural water, the $Rb_{0.21}(H_2O)_yWS_2$ crystals were heated up to 373 K for further PXRD measurement. The sample was prepared in an Ar-protected glove box and sealed with vacuum tape. The (002) reflection clearly moved to higher diffraction angles, indicating the shrinkage of the unit cell due to loss of intercalated water (Fig. 6). However, it was impossible to accurately determine the water content by mass loss alone because of the interference of possible surface-adsorbed water.

5. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. The localization of ordered W and S sites of the WS_2 layers was unproblematic. The highest interlayer difference electron density peak was then treated as a single but partially occupied Rb site. No evidence of superstructure reflections in reciprocal space was found for the ordering of the Rb site. Then, the W, S sites and the underoccupied Rb site were refined with anisotropic displa-

Figure 5
TG–DTA analysis of $Rb_{0.21}(H_2O)_yWS_2$.

cement parameters. Because of very large anisotropic displacement parameters ($U^{11} = 0.59$ Å^2) of the Rb site, splitting of this site was considered, resulting in a residual $R_1 = 0.051$. Modelling the O sites as being part of this disorder, or of remaining electron density peaks in the vicinity of the Rb sites was not successful, and therefore we did not include the apparently disordered water molecules in the final structure model. The remaining maximum and minimum electron densities are located 0.87 and 1.14 Å, respectively, from the W1 site.

Figure 4
Rietveld plot of $Rb_{0.21}(H_2O)_yWS_2$.
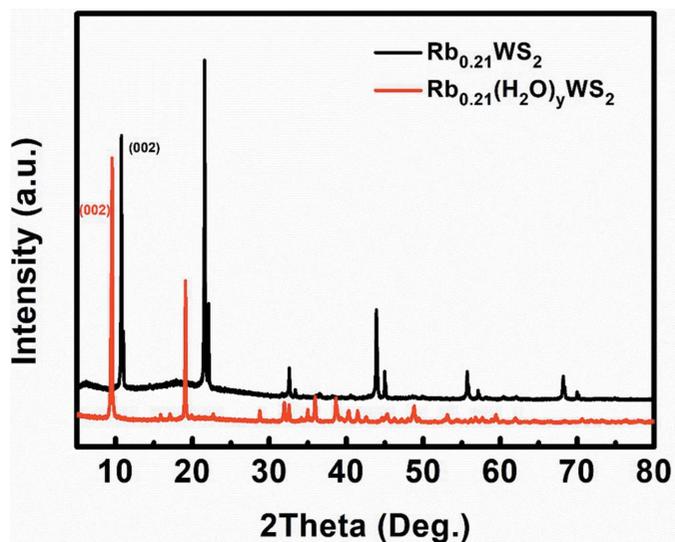
Figure 6
Power X-ray diffraction pattern of $Rb_{0.21}(H_2O)_yWS_2$ and $Rb_{0.21}WS_2$.

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Table 2
Experimental details.

Crystal data	
Chemical formula	$Rb_{0.21}(H_2O)_yWS_2$
M_r	277.23
Crystal system, space group	Monoclinic, $P2_1/m$
Temperature (K)	298
a, b, c (Å)	5.703 (3), 3.2524 (18), 9.423 (5)
β (°)	99.724 (16)
V (Å³)	172.27 (16)
Z	2
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	39.25
Crystal size (mm)	$0.05 \times 0.03 \times 0.01$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.251, 0.674
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1167, 352, 327
R_{int}	0.030
$(\sin \theta/\lambda)_{max}$ (Å⁻¹)	0.593
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.050, 0.124, 1.10
No. of reflections	352
No. of parameters	33
H-atom treatment	H-atom parameters not defined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	2.45, −1.66

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXS* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2004) and *publCIF* (Westrip, 2010).

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Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *publCIF* (Westrip, 2010).

rubidium hydrate dithiotungstate

Crystal data

Rb$_{0.21}$(H$_2$O)yWS$_2$	$F(000) = 237$
$M_r = 277.23$	$D_x = 5.345$ Mg m^{-3}
Monoclinic, $P2_1/m$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 5.703$ (3) Å	Cell parameters from 68 reflections
$b = 3.2524$ (18) Å	$\theta = 3.9$–$23.0°$
$c = 9.423$ (5) Å	$\mu = 39.25$ mm^{-1}
$\beta = 99.724$ (16)°	$T = 298$ K
$V = 172.27$ (16) Å^3	Plate, black
$Z = 2$	$0.05 \times 0.03 \times 0.01$ mm

Data collection

Bruker APEXII CCD diffractometer	352 independent reflections
phi and ω scans	327 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 2015)	$R_{int} = 0.030$
	$\theta_{max} = 24.9°$, $\theta_{min} = 2.2°$
$T_{min} = 0.251$, $T_{max} = 0.674$	$h = -6 \rightarrow 6$
1167 measured reflections	$k = -3 \rightarrow 3$
	$l = -11 \rightarrow 10$

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	H-atom parameters not defined
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.1024P)^2]$
$wR(F^2) = 0.124$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
352 reflections	$\Delta\rho_{max} = 2.45$ e Å^{-3}
33 parameters	$\Delta\rho_{min} = -1.66$ e Å^{-3}

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)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
W1	0.19782 (11)	0.7500	1.00615 (8)	0.0371 (5)	
S2	0.3744 (9)	0.2500	0.8600 (6)	0.0376 (12)	
S3	0.1409 (10)	0.2500	1.1850 (6)	0.0401 (12)	
Rb4	0.21 (4)	−0.2500	0.534 (6)	0.14 (6)	0.14 (7)
Rb5	0.38 (2)	−0.2500	0.525 (8)	0.17 (2)	0.20 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.0319 (7)	0.0374 (7)	0.0423 (7)	0.000	0.0073 (4)	0.000
S2	0.034 (2)	0.038 (3)	0.041 (3)	0.000	0.007 (2)	0.000
S3	0.041 (3)	0.039 (3)	0.041 (3)	0.000	0.008 (2)	0.000
Rb4	0.28 (14)	0.12 (4)	0.04 (2)	0.000	0.06 (4)	0.000
Rb5	0.18 (6)	0.24 (6)	0.08 (3)	0.000	0.01 (3)	0.000

Geometric parameters (Å, º)

W1—S3[i]	2.403 (4)	Rb4—Rb5	0.99 (10)
W1—S3	2.403 (4)	Rb4—Rb4[x]	2.9 (3)
W1—S3[ii]	2.408 (5)	Rb4—Rb4[xi]	2.9 (3)
W1—S2	2.454 (4)	Rb4—Rb5[xii]	3.0 (3)
W1—S2[i]	2.454 (4)	Rb4—Rb5[xiii]	3.0 (3)
W1—S2[iii]	2.550 (5)	Rb4—Rb4[i]	3.252 (2)
W1—W1[ii]	2.7678 (15)	Rb4—Rb4[v]	3.2524 (19)
W1—W1[iv]	2.7678 (15)	Rb4—Rb5[i]	3.40 (3)
S2—W1[v]	2.454 (4)	Rb4—Rb5[v]	3.40 (3)
S2—W1[iii]	2.550 (5)	Rb4—S2[v]	3.47 (7)
S2—Rb4	3.47 (7)	Rb4—S3[vii]	3.58 (11)
S2—Rb4[i]	3.47 (7)	Rb5—Rb5[xii]	2.23 (19)
S2—Rb5[i]	3.56 (8)	Rb5—Rb5[xiii]	2.23 (19)
S2—Rb5	3.56 (8)	Rb5—Rb4[xii]	3.0 (3)
S3—W1[v]	2.403 (4)	Rb5—Rb4[xiii]	3.0 (3)
S3—W1[ii]	2.408 (5)	Rb5—Rb5[i]	3.2524 (18)
S3—Rb5[vi]	3.53 (6)	Rb5—Rb5[v]	3.2524 (18)
S3—Rb4[vii]	3.58 (11)	Rb5—Rb4[v]	3.40 (3)
S3—Rb4[viii]	3.63 (4)	Rb5—Rb4[i]	3.40 (3)
S3—Rb4[ix]	3.63 (4)	Rb5—S3[vi]	3.53 (6)
S3—Rb5[viii]	3.64 (5)	Rb5—S2[v]	3.56 (8)
S3—Rb5[ix]	3.64 (5)		

Angle	Value	Angle	Value
S3^{i}—W1—S3	85.18 (18)	Rb5^{xii}—Rb4—Rb5^{i}	40 (3)
S3^{i}—W1—S3^{ii}	109.76 (14)	Rb5^{xiii}—Rb4—Rb5^{i}	106 (4)
S3—W1—S3^{ii}	109.76 (14)	Rb4^{i}—Rb4—Rb5^{i}	16.9 (16)
S3^{i}—W1—S2	163.5 (2)	Rb4^{v}—Rb4—Rb5^{i}	163.1 (16)
S3—W1—S2	93.55 (13)	Rb5—Rb4—Rb5^{v}	73.1 (16)
S3^{ii}—W1—S2	86.20 (17)	Rb4^{x}—Rb4—Rb5^{v}	71 (3)
S3^{i}—W1—S2^{i}	93.55 (13)	Rb4^{xi}—Rb4—Rb5^{v}	140 (7)
S3—W1—S2^{i}	163.5 (2)	Rb5^{xii}—Rb4—Rb5^{v}	106 (4)
S3^{ii}—W1—S2^{i}	86.20 (17)	Rb5^{xiii}—Rb4—Rb5^{v}	40 (3)
S2—W1—S2^{i}	82.99 (18)	Rb4^{i}—Rb4—Rb5^{v}	163.1 (16)
S3^{i}—W1—S2^{iii}	83.36 (18)	Rb4^{v}—Rb4—Rb5^{v}	16.9 (16)
S3—W1—S2^{iii}	83.36 (18)	Rb5^{i}—Rb4—Rb5^{v}	146 (3)
S3^{ii}—W1—S2^{iii}	161.7 (2)	Rb5—Rb4—S2^{v}	87 (10)
S2—W1—S2^{iii}	80.13 (16)	Rb4^{x}—Rb4—S2^{v}	91.3 (12)
S2^{i}—W1—S2^{iii}	80.13 (16)	Rb4^{xi}—Rb4—S2^{v}	124 (4)
S3^{i}—W1—W1^{ii}	102.78 (13)	Rb5^{xii}—Rb4—S2^{v}	108 (5)
S3—W1—W1^{ii}	54.97 (13)	Rb5^{xiii}—Rb4—S2^{v}	79 (2)
S3^{ii}—W1—W1^{ii}	54.79 (10)	Rb4^{i}—Rb4—S2^{v}	118.0 (6)
S2—W1—W1^{ii}	89.78 (11)	Rb4^{v}—Rb4—S2^{v}	62.0 (6)
S2^{i}—W1—W1^{ii}	140.78 (13)	Rb5^{i}—Rb4—S2^{v}	116 (4)
S2^{iii}—W1—W1^{ii}	136.53 (8)	Rb5^{v}—Rb4—S2^{v}	62 (2)
S3^{i}—W1—W1^{iv}	54.97 (13)	Rb5—Rb4—S2	87 (10)
S3—W1—W1^{iv}	102.78 (13)	Rb4^{x}—Rb4—S2	124 (4)
S3^{ii}—W1—W1^{iv}	54.79 (10)	Rb4^{xi}—Rb4—S2	91.3 (12)
S2—W1—W1^{iv}	140.78 (13)	Rb5^{xii}—Rb4—S2	79 (2)
S2^{i}—W1—W1^{iv}	89.78 (11)	Rb5^{xiii}—Rb4—S2	108 (5)
S2^{iii}—W1—W1^{iv}	136.53 (8)	Rb4^{i}—Rb4—S2	62.0 (6)
W1^{ii}—W1—W1^{iv}	71.96 (5)	Rb4^{v}—Rb4—S2	118.0 (6)
W1^{v}—S2—W1	82.99 (18)	Rb5^{i}—Rb4—S2	62 (2)
W1^{v}—S2—W1^{iii}	99.87 (16)	Rb5^{v}—Rb4—S2	116 (4)
W1—S2—W1^{iii}	99.87 (16)	S2^{v}—Rb4—S2	56.0 (12)
W1^{v}—S2—Rb4	96.3 (15)	Rb5—Rb4—S3^{vii}	138 (10)
W1—S2—Rb4	137 (3)	Rb4^{x}—Rb4—S3^{vii}	68 (4)
W1^{iii}—S2—Rb4	122 (3)	Rb4^{xi}—Rb4—S3^{vii}	68 (4)
W1^{v}—S2—Rb4^{i}	137 (3)	Rb5^{xii}—Rb4—S3^{vii}	133.8 (12)
W1—S2—Rb4^{i}	96.3 (15)	Rb5^{xiii}—Rb4—S3^{vii}	133.8 (12)
W1^{iii}—S2—Rb4^{i}	122 (3)	Rb4^{i}—Rb4—S3^{vii}	90.000 (2)
Rb4—S2—Rb4^{i}	56.0 (12)	Rb4^{v}—Rb4—S3^{vii}	90.000 (1)
W1^{v}—S2—Rb5^{i}	150.1 (12)	Rb5^{i}—Rb4—S3^{vii}	102.5 (13)
W1—S2—Rb5^{i}	105.1 (13)	Rb5^{v}—Rb4—S3^{vii}	102.5 (12)
W1^{iii}—S2—Rb5^{i}	106.8 (18)	S2^{v}—Rb4—S3^{vii}	56.3 (7)
Rb4—S2—Rb5^{i}	57.9 (7)	S2—Rb4—S3^{vii}	56.3 (7)
Rb4^{i}—S2—Rb5^{i}	16.1 (18)	Rb4—Rb5—Rb5^{xii}	132 (4)
W1^{v}—S2—Rb5	105.1 (13)	Rb4—Rb5—Rb5^{xiii}	132 (4)
W1—S2—Rb5	150.1 (12)	Rb5^{xii}—Rb5—Rb5^{xiii}	94 (10)
W1^{iii}—S2—Rb5	106.8 (18)	Rb4—Rb5—Rb4^{xii}	146 (2)
Rb4—S2—Rb5	16.1 (18)	Rb5^{xii}—Rb5—Rb4^{xii}	14.3 (18)

Rb4^{i}—S2—Rb5	57.9 (7)	Rb5^{xiii}—Rb5—Rb4^{xii}	80 (8)
Rb5^{i}—S2—Rb5	54.4 (14)	Rb4—Rb5—Rb4^{xiii}	146 (2)
W1^{v}—S3—W1	85.18 (18)	Rb5^{xii}—Rb5—Rb4^{xiii}	80 (8)
W1^{v}—S3—W1^{ii}	70.24 (14)	Rb5^{xiii}—Rb5—Rb4^{xiii}	14.3 (18)
W1—S3—W1^{ii}	70.24 (14)	Rb4^{xii}—Rb5—Rb4^{xiii}	66 (7)
W1^{v}—S3—Rb5^{vi}	111.4 (15)	Rb4—Rb5—Rb5^{i}	90.00 (5)
W1—S3—Rb5^{vi}	111.4 (16)	Rb5^{xii}—Rb5—Rb5^{i}	43 (5)
W1^{ii}—S3—Rb5^{vi}	178 (2)	Rb5^{xiii}—Rb5—Rb5^{i}	137 (5)
W1^{v}—S3—Rb4^{vii}	132.7 (12)	Rb4^{xii}—Rb5—Rb5^{i}	57 (3)
W1—S3—Rb4^{vii}	132.7 (11)	Rb4^{xiii}—Rb5—Rb5^{i}	123 (3)
W1^{ii}—S3—Rb4^{vii}	94 (3)	Rb4—Rb5—Rb5^{v}	90.00 (10)
Rb5^{vi}—S3—Rb4^{vii}	83.2 (13)	Rb5^{xii}—Rb5—Rb5^{v}	137 (5)
W1^{v}—S3—Rb4^{viii}	159 (2)	Rb5^{xiii}—Rb5—Rb5^{v}	43 (5)
W1—S3—Rb4^{viii}	109.0 (6)	Rb4^{xii}—Rb5—Rb5^{v}	123 (3)
W1^{ii}—S3—Rb4^{viii}	129 (3)	Rb4^{xiii}—Rb5—Rb5^{v}	57 (3)
Rb5^{vi}—S3—Rb4^{viii}	49 (5)	Rb5^{i}—Rb5—Rb5^{v}	180.00 (7)
Rb4^{vii}—S3—Rb4^{viii}	47 (5)	Rb4—Rb5—Rb4^{v}	73.1 (17)
W1^{v}—S3—Rb4^{ix}	109.0 (6)	Rb5^{xii}—Rb5—Rb4^{v}	153 (5)
W1—S3—Rb4^{ix}	159 (2)	Rb5^{xiii}—Rb5—Rb4^{v}	60 (6)
W1^{ii}—S3—Rb4^{ix}	129 (3)	Rb4^{xii}—Rb5—Rb4^{v}	140 (3)
Rb5^{vi}—S3—Rb4^{ix}	49 (5)	Rb4^{xiii}—Rb5—Rb4^{v}	74 (4)
Rb4^{vii}—S3—Rb4^{ix}	47 (5)	Rb5^{i}—Rb5—Rb4^{v}	163.1 (16)
Rb4^{viii}—S3—Rb4^{ix}	53.3 (7)	Rb5^{v}—Rb5—Rb4^{v}	16.9 (16)
W1^{v}—S3—Rb5^{viii}	147.5 (16)	Rb4—Rb5—Rb4^{i}	73.1 (16)
W1—S3—Rb5^{viii}	103.9 (12)	Rb5^{xii}—Rb5—Rb4^{i}	60 (6)
W1^{ii}—S3—Rb5^{viii}	142.2 (16)	Rb5^{xiii}—Rb5—Rb4^{i}	153 (5)
Rb5^{vi}—S3—Rb5^{viii}	36 (3)	Rb4^{xii}—Rb5—Rb4^{i}	74 (4)
Rb4^{vii}—S3—Rb5^{viii}	61 (4)	Rb4^{xiii}—Rb5—Rb4^{i}	140 (3)
Rb4^{viii}—S3—Rb5^{viii}	15.7 (16)	Rb5^{i}—Rb5—Rb4^{i}	16.9 (16)
Rb4^{ix}—S3—Rb5^{viii}	55.8 (6)	Rb5^{v}—Rb5—Rb4^{i}	163.1 (16)
W1^{v}—S3—Rb5^{ix}	103.9 (12)	Rb4^{v}—Rb5—Rb4^{i}	146 (3)
W1—S3—Rb5^{ix}	147.5 (16)	Rb4—Rb5—S3^{vi}	125 (9)
W1^{ii}—S3—Rb5^{ix}	142.2 (16)	Rb5^{xii}—Rb5—S3^{vi}	75 (3)
Rb5^{vi}—S3—Rb5^{ix}	36 (3)	Rb5^{xiii}—Rb5—S3^{vi}	75 (3)
Rb4^{vii}—S3—Rb5^{ix}	61 (4)	Rb4^{xii}—Rb5—S3^{vi}	67 (4)
Rb4^{viii}—S3—Rb5^{ix}	55.8 (6)	Rb4^{xiii}—Rb5—S3^{vi}	67 (4)
Rb4^{ix}—S3—Rb5^{ix}	15.7 (16)	Rb5^{i}—Rb5—S3^{vi}	90.000 (5)
Rb5^{viii}—S3—Rb5^{ix}	53.0 (8)	Rb5^{v}—Rb5—S3^{vi}	90.000 (2)
Rb5—Rb4—Rb4^{x}	141 (2)	Rb4^{v}—Rb5—S3^{vi}	100 (3)
Rb5—Rb4—Rb4^{xi}	141 (2)	Rb4^{i}—Rb5—S3^{vi}	100 (3)
Rb4^{x}—Rb4—Rb4^{xi}	69 (9)	Rb4—Rb5—S2^{v}	77 (8)
Rb5—Rb4—Rb5^{xii}	34 (2)	Rb5^{xii}—Rb5—S2^{v}	128 (3)
Rb4^{x}—Rb4—Rb5^{xii}	157 (2)	Rb5^{xiii}—Rb5—S2^{v}	87 (3)
Rb4^{xi}—Rb4—Rb5^{xii}	107.5 (14)	Rb4^{xii}—Rb5—S2^{v}	123 (3)
Rb5—Rb4—Rb5^{xiii}	34 (2)	Rb4^{xiii}—Rb5—S2^{v}	92.3 (10)
Rb4^{x}—Rb4—Rb5^{xiii}	107.5 (13)	Rb5^{i}—Rb5—S2^{v}	117.2 (7)
Rb4^{xi}—Rb4—Rb5^{xiii}	157 (2)	Rb5^{v}—Rb5—S2^{v}	62.8 (7)
Rb5^{xii}—Rb4—Rb5^{xiii}	66 (7)	Rb4^{v}—Rb5—S2^{v}	59.7 (19)

Rb5—Rb4—Rb4ⁱ	90.00 (5)	Rb4ⁱ—Rb5—S2^v	112 (3)
Rb4^x—Rb4—Rb4ⁱ	125 (5)	S3^{vi}—Rb5—S2^v	55.4 (8)
Rb4^{xi}—Rb4—Rb4ⁱ	55 (5)	Rb4—Rb5—S2	77 (8)
Rb5^{xii}—Rb4—Rb4ⁱ	57 (3)	Rb5^{xii}—Rb5—S2	87 (3)
Rb5^{xiii}—Rb4—Rb4ⁱ	123 (3)	Rb5^{xiii}—Rb5—S2	128 (3)
Rb5—Rb4—Rb4^v	90.000 (19)	Rb4^{xii}—Rb5—S2	92.3 (10)
Rb4^x—Rb4—Rb4^v	55 (5)	Rb4^{xiii}—Rb5—S2	123 (3)
Rb4^{xi}—Rb4—Rb4^v	125 (5)	Rb5ⁱ—Rb5—S2	62.8 (7)
Rb5^{xii}—Rb4—Rb4^v	123 (3)	Rb5^v—Rb5—S2	117.2 (7)
Rb5^{xiii}—Rb4—Rb4^v	57 (3)	Rb4^v—Rb5—S2	112 (3)
Rb4ⁱ—Rb4—Rb4^v	180.00 (10)	Rb4ⁱ—Rb5—S2	59.7 (19)
Rb5—Rb4—Rb5ⁱ	73.1 (16)	S3^{vi}—Rb5—S2	55.4 (8)
Rb4^x—Rb4—Rb5ⁱ	140 (7)	S2^v—Rb5—S2	54.4 (14)
Rb4^{xi}—Rb4—Rb5ⁱ	71 (3)		

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