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Dirubidium tetrathiotungstate, $Rb_2[WS_4]$

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$Rb_2[WS_4]$ crystallizes in the orthorhombic space group *Pnma* and is isostructural with $Cs_2[MoS_4]$, $Rb_2[MoS_4]$, $K_2[MoS_4]$ and $(NH_4)_2[WS_4]$. The structure contains discrete tetrahedral $[WS_4]^{2-}$ anions of symmetry *m*, separated by Rb^+ cations. One of the two unique Rb^+ cations is surrounded by nine S atoms and the other by ten S atoms.

Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(W–S) = 0.001 Å
R factor = 0.023
wR factor = 0.061
Data-to-parameter ratio = 27.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The reactive flux method (Sunshine *et al.*, 1987), which is a very effective means of synthesizing metal chalcogenides, has been employed here to afford $Rb_2[WS_4]$. This compound is isostructural with $Cs_2[MoS_4]$ (Raymond *et al.*, 1995), $Rb_2[MoS_4]$ (Ellermeier *et al.*, 1999), $K_2[MoS_4]$ (Emirdag-Eanes & Ibers, 2001) and $(NH_4)_2[WS_4]$ (Sasvári, 1963). The cell constants and space group found for $Rb_2[WS_4]$ are consistent with an earlier determination from X-ray powder data (a = 9.69 Å, b = 7.10 Å, c = 12.45 Å and V = 855.7 Å^3; Müller & Sievert, 1974). A view along [010] of the $Rb_2[WS_4]$ structure is shown in Fig. 1. The structure contains discrete $[WS_4]^{2-}$ anions separated by Rb^+ cations. The W atom is tetrahedrally coordinated by S atoms, with W—S distances ranging from 2.171 (2) to 2.205 (1) Å, comparable to those of 2.165–2.176 Å in $(NH_4)_2[WS_4]$. The compound has two crystallographically unique Rb^+ cations, one (Rb1) surrounded by nine S atoms and the other (Rb2) by ten S atoms. The Rb—S distances range from 3.253 (2) to 3.950 (1) Å.

Experimental

Yellow plates of $Rb_2[WS_4]$ were obtained from a solid-state reaction of Rb_2S_3 (0.5 mmol), W (0.5 mmol, Aldrich, 99%) and S (2.0 mmol, Aldrich, 99.5%). Rb_2S_3 was prepared by the stoichiometric reaction of Rb (Aldrich, 98+%) and S in liquid NH_3. The reactants were loaded into a fused-silica tube under an Ar atmosphere in a glovebox. The tube was sealed under a 10^{-4} torr atmosphere and then placed in a computer-controlled furnace. The sample was heated to 923 K in 15 h, kept at 923 K for 3 d, slowly cooled at 6 K h^{-1} to 373 K, and then cooled to room temperature.

Crystal data

$Rb_2[WS_4]$
M_r = 483.03
Orthorhombic, *Pnma*
a = 9.6254 (6) Å
b = 7.0218 (5) Å
c = 12.3761 (8) Å
V = 836.47 (10) Å^3
Z = 4
D_x = 3.836 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5262 reflections
θ = 2.7–28.9°
μ = 26.27 mm^{-1}
T = 153 (2) K
Plate, yellow
0.25 × 0.12 × 0.03 mm

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Data collection

Bruker 1000 CCD diffractometer	1119 independent reflections
ω scans	1027 reflections with $I > 2\sigma(I)$
Absorption correction: numerical face-indexed (*XPREP* in *SHELXTL*; Sheldrick, 2003)	$R_{int} = 0.035$
	$\theta_{max} = 28.9°$
	$h = -12 \rightarrow 12$
$T_{min} = 0.027$, $T_{max} = 0.438$	$k = -9 \rightarrow 9$
6582 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.061$	$\Delta\rho_{max} = 2.40$ e Å^{-3}
$S = 1.33$	$\Delta\rho_{min} = -3.99$ e Å^{-3}
1119 reflections	Extinction correction: *SHELXTL*
41 parameters	Extinction coefficient: 0.0018 (2)

Table 1
Selected geometric parameters (Å, °).

W—S1	2.1710 (17)	Rb1—S3^{iii}	3.5936 (4)
W—S2^{i}	2.1875 (10)	Rb2—S3^{viii}	3.4982 (15)
W—S2	2.1875 (9)	Rb2—S2	3.5396 (11)
W—S3	2.2053 (14)	Rb2—S2^{i}	3.5396 (11)
Rb1—S1^{ii}	3.2525 (18)	Rb2—S1^{ix}	3.5504 (4)
Rb1—S1	3.3219 (18)	Rb2—S1^{vi}	3.5504 (4)
Rb1—S2^{iii}	3.4202 (11)	Rb2—S2^{vi}	3.5873 (14)
Rb1—S2^{iv}	3.4202 (11)	Rb2—S2^{v}	3.5873 (14)
Rb1—S3^{ii}	3.4496 (17)	Rb2—S3^{x}	3.7483 (17)
Rb1—S2^{v}	3.4663 (12)	Rb2—S2^{xi}	3.9503 (13)
Rb1—S2^{vi}	3.4663 (12)	Rb2—S2^{x}	3.9503 (13)
Rb1—S3^{vii}	3.5936 (4)		
S1—W—S2^{i}	108.92 (4)	S1—W—S3	111.48 (6)
S1—W—S2	108.92 (4)	S2^{i}—W—S3	109.72 (3)
S2^{i}—W—S2	108.01 (6)	S2—W—S3	109.72 (3)

Symmetry codes: (i) $x, \frac{1}{2}-y, z$; (ii) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$; (v) $1-x, \frac{1}{2}+y, 1-z$; (vi) $1-x, -y, 1-z$; (vii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (viii) $1+x, y, z$; (ix) $1-x, 1-y, 1-z$; (x) $\frac{1}{2}+x, y, \frac{3}{2}-z$; (xi) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{3}{2}-z$.

The highest difference peak is located at a distance of 0.07 Å from the W atom, and the deepest hole is 0.69 Å from the same atom.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

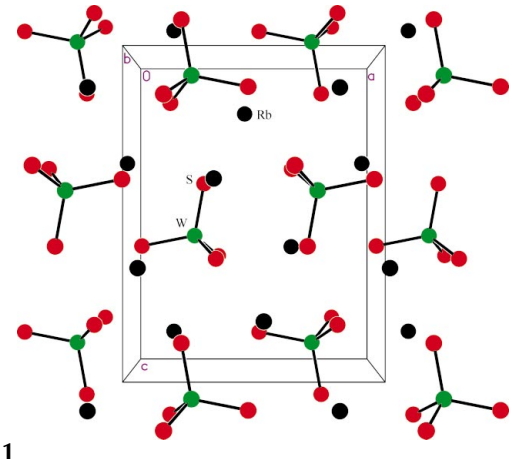

Figure 1
The structure of $Rb_2[WS_4]$, viewed down [010].

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