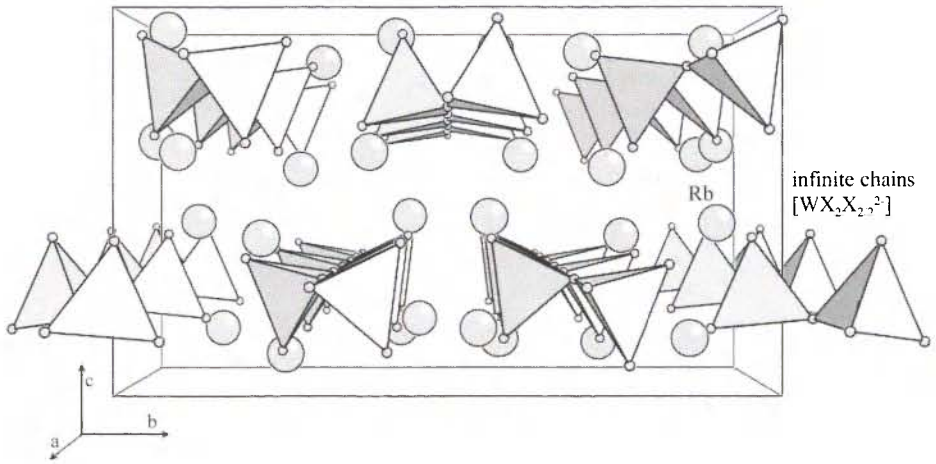
Crystal structure of dirubidium oxodinitridotungstate(VI), $Rb_2[WN_2O]$

R. Niewa*[I,II] and H. Jacobs[II]

[I] Max-Planck Institut für Chemische Physik fester Stoffe, Pirnaer Landstraße 176, D-01257 Dresden, Germany
[II] Universität Dortmund, Lehrstuhl für Anorganische Chemie I, Otto-Hahn-Straße 6, D-44221 Dortmund, Germany

Received September 23, 1999, CSD-No. 409453



Abstract

N_2ORb_2W, orthorhombic, *Ama*2 (No. 40), $a = 6.154(1)$ Å, $b = 20.963(4)$ Å, $c = 12.169(2)$ Å, $V = 1569.9$ Å^3, $Z = 12$, $R_{gt}(F) = 0.041$, $wR(F^2) = 0.095$, $T = 293$ K.

Source of material

Synthesis from exess rubidium amide (made from Rb, Johnson Matthey, 99.5 % and liquid ammonia, Messer Griesheim, 99.999 %) with a stoichiometric mixture of tungsten powder (Johnson Matthey, m5N, grade A1) and tungsten(VI) oxide (Ventron, 99.7 %) in an autoclave designed for salt melts [1] at a temperature of 873 K. By extraction with liquid ammonia long brown needles were isolated from a rubidium matrix, formed from thermal decomposition of the amide.

Discussion

The crystal structure of $Rb_2[WN_2O]$ consists of infinite chains of vertex-sharing tetrahedra $[WX_2X_{2/2}^{2-}]$ (X = $N_{2/3}$, $O_{1/3}$). These are arranged relativ to each other according to the motif of a close rod packing. Bond distances and angles fit well in the ranges of related compounds [2]: d(W—X_{bridge}) = 1.90 Å, d(W—X_{term}) = 1.81 Å. It was not possible to distinguish between oxygen and nitrogen atoms on the non-metal sites. Both species might be disordered. Refinement of the site Rb(5) results in a large value of U_{11}, better described with a split position that can not be resolved by symmetry reduction. Since the refinement of the site occupancies of both split positions resulted in half occupancy they were fixed to 0.5 in the final refinement cyles. Knowing the ratio of N/O from the crystal structure refinement and charge balance the compound was prepared as single phase sample as described in the experimental part.

* Correspondence author (e-mail: niewa@cpfs.mpg.de)

Table 1. Data collection and handling.

Crystal:	brown needle, size 0.025 × 0.025 × 0.3 mm
Wavelength:	Ag K_α radiation (0.56086 Å)
μ:	217.73 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, oscillation, 500 exposures, $\Delta\varphi = 0.4°$, 8 min
$2\theta_{max}$:	47.4°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9743, 2563
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2049
$N(param)_{refined}$:	82
Programs:	SHELXS-86 [3], SHELXL-97 [4], DIAMOND [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
X(1)	4*b*	1/4	0.435(1)	–0.087(2)	0.012(4)
X(2)	4*b*	1/4	0.711(1)	–0.139(2)	0.018(4)
X(3)	4*a*	0	1/2	–0.275(2)	0.022(5)
X(4)	4*b*	1/4	0.764(1)	–0.366(2)	0.020(5)
X(5)	4*b*	1/4	0.377(1)	–0.312(2)	0.016(4)
X(6)	8*c*	–0.001(4)	0.8279(9)	–0.181(2)	0.035(5)
X(7)	4*b*	1/4	0.563(1)	0.410(2)	0.029(5)
X(8)	4*b*	1/4	0.580(2)	0.164(3)	0.053(9)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	4*b*		1/4	0.45144(5)	–0.23562(7)	0.0078(7)	0.0110(4)	0.0143(6)	0	0	–0.0034(4)
W(2)	4*b*		1/4	0.78153(5)	–0.2202(1)	0.0067(6)	0.0114(4)	0.0220(5)	0	0	–0.0011(4)
W(3)	4*b*		1/4	0.61879(5)	0.29903(7)	0.0048(7)	0.0138(4)	0.0137(5)	0	0	0.0027(4)
Rb(1)	4*b*		1/4	0.5810(2)	–0.0583(3)	0.021(2)	0.023(1)	0.030(2)	0	0	–0.009(1)
Rb(2)	4*b*		1/4	0.7526(2)	0.0928(3)	0.025(2)	0.029(1)	0.020(1)	0	0	–0.009(1)
Rb(3)	4*b*		1/4	0.2909(2)	–0.0988(2)	0.015(2)	0.028(1)	0.019(1)	0	0	–0.003(1)
Rb(4)	4*b*		1/4	0.4353(2)	–0.5418(4)	0.024(2)	0.063(2)	0.038(2)	0	0	–0.024(2)
Rb(5A)	4*b*	0.50	1/4	0.9520(4)	–0.3384(5)	0.018(2)	0.035(3)	0.023(2)	0	0	0.015(2)
Rb(5B)	4*b*	0.50	1/4	0.9202(4)	–0.3659(6)	0.018(2)	0.035(3)	0.023(2)	0	0	0.015(2)
Rb(6)	4*b*		1/4	0.6224(2)	–0.3660(3)	0.016(2)	0.023(1)	0.035(2)	0	0	0.007(1)

Acknowledgments. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

1. Brokamp, Th.: Darstellung und Charakterisierung einiger ternärer Tantalnitride mit Lithium, Magnesium oder Calcium. Thesis, Universität Dortmund, Germany 1991.
2. Niewa, R., Jacobs, H.: Group V and VI Alkali Nitridometalates. Chem. Rev. **96** (1996) 2053.
3. Sheldrick, G. M.: SHELXS-86. Program for the Solution of Crystal Structures. Universität Göttingen, Germany 1990.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. Universität Göttingen, Germany 1997.
5. Brandenburg, K.: Diamond Version 2.0f. Crystal Impact GbR, Bonn, Germany 1998.