Crystal structure of niobium pentabromide, $NbBr_5$, *a triclinic phase*

Sonja Tragl and Hans-Jürgen Meyer*

Universität Tübingen, Institut für Anorganische Chemie, Abteilung für Festkörperchemie und Theoretische Anorganische Chemie, Ob dem Himmelreich 7, 72074 Tübingen, Germany

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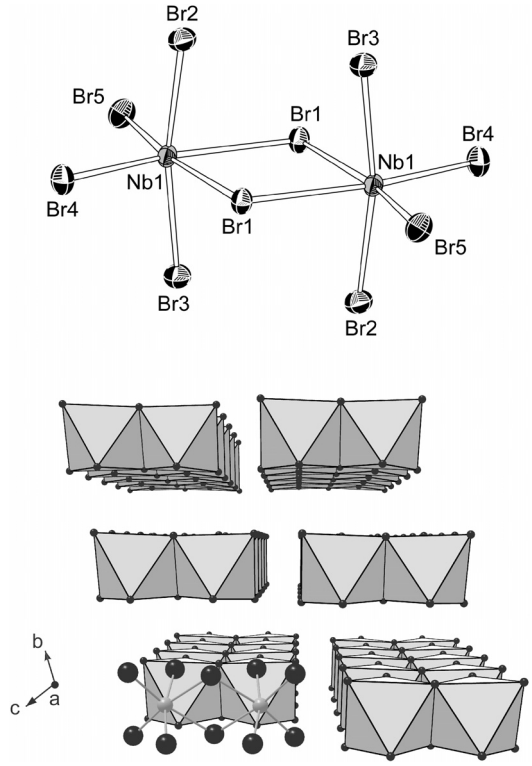

Abstract

Br_5Nb, triclinic, $P\bar{1}$ (no. 2), a = 6.461(1) Å, b = 7.031(1) Å, c = 9.584(2) Å, α = 108.84(2)°, β = 90.89(2)°, γ = 116.16(2)°, V = 363.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.086, T = 215 K.

Source of material

71 mg $NbBr_5$ (0.144 mmol) and 19 mg (0.358 mmol) Li_2CN_2 were ground in an agate mortar and filled into a silica ampule. The ampule was sealed under vacuum, then heated up to 643 K, kept at this temperature for 4 days and was afterwards cooled down to room temperature during 8 h. Black, block-shaped crystals were obtained along with a black powder, containing LiBr, Li_2CN_2 and an unknown compound according to X-ray powder diffraction measurements. The black crystals were characterized by single crystal diffraction at 215 K, showing a triclinic, yet unknown modification of $NbBr_5$. All handling was done in a glove box under argon due to the sensitivity of the materials against air and moisture.

Discussion

Two orthorhombic crystal structures were already reported for $NbBr_5$: α-$NbBr_5$, crystallizing in the space group *Pbma* [1] and β-$NbBr_5$ (space group *Ccmm*) which is showing a one-dimensional stacking disorder [2]. Crystals of α-$NbBr_5$ and β-$NbBr_5$ were obtained at 973 K and 498 K, respectively. Both structures can be described as a hexagonal close packing of Br atoms in which one fifth of the octahedral voids are occupied by Nb.

The triclinic, ordered polymorph of $NbBr_5$ also consists of a slightly distorted hexagonal closest packing of Br atoms. The Nb atoms are situated in 2/5 of the octahedral voids of every second layer, forming dimeric Nb_2Br_{10} units. In α- and β-$NbBr_5$, the Nb_2Br_{10} molecules are stacked perpendicular to the hexagonal layers of bromine atoms, whereas in the triclinic modification, the stacking direction of the Nb_2Br_{10} dimers runs along [100] which is parallel to the hexagonal layers. The intramolecular bond lengths are in good agreement with the atomic distances reported for the α- and β-modification: due to the repulsion between the Nb^{5+} ions, they are not located in the centers of the octahedral voids (d(Nb1—Nb1′) = 4.174(2) Å). Therefore, the bridging Nb1—Br1 bonds (2.712(2) Å and 2.716(1) Å) are significantly longer than the other Nb—Br bonds (2.439(1) Å and 2.456 Å for the axial bonds, 2.405(2) Å and 2.406(1) Å for the equatorial bonds).

Table 1. Data collection and handling.

Crystal:	black block, size 0.12 × 0.26 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	290.22 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS I, φ
$2\theta_{max}$:	51.72°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4301, 1310
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1078
$N(param)_{refined}$:	55
Programs:	SHELXS-97 [3], SHELXS-97 [4], DIAMOND [5]

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb(1)	2*i*	0.8934(1)	0.7775(1)	0.27635(7)	0.0199(4)	0.0164(3)	0.0143(3)	0.0084(3)	0.0022(3)	0.0030(2)
Br(1)	2*i*	0.2479(1)	1.1873(1)	0.45515(8)	0.0198(4)	0.0188(4)	0.0162(3)	0.0060(3)	0.0043(3)	0.0043(3)
Br(2)	2*i*	0.1233(2)	0.6183(1)	0.35255(9)	0.0291(5)	0.0264(4)	0.0277(4)	0.0175(4)	0.0055(4)	0.0097(3)

* Correspondence author (e-mail: juergen.meyer@uni-tuebingen.de)

Table 2. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br(3)	2*i*	0.6926(2)	0.9943(1)	0.25183(9)	0.0280(5)	0.0271(4)	0.0269(4)	0.0166(4)	0.0037(4)	0.0098(3)
Br(4)	2*i*	0.5458(2)	0.4156(1)	0.16637(9)	0.0249(5)	0.0206(4)	0.0266(4)	0.0047(3)	0.0005(3)	0.0043(3)
Br(5)	2*i*	0.0779(2)	0.8151(1)	0.06369(9)	0.0324(5)	0.0291(4)	0.0209(4)	0.0151(4)	0.0107(3)	0.0096(3)

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