The Crystal Structure of NbO_2I –
A Double-layer Structure with 7-Coordinated Niobium

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Single crystals of NbO_2I were obtained as dark red needles by chemical transport. According to the structure determination (*Pnma*, $a = 20.897(4)$, $b = 3.7654(8)$, $c = 3.9715(8)$ Å, $Z = 4$, 619 reflections, 26 variables, $R_1(F) = 0.0645$, $wR_2(F^2) = 0.1597$) NbO_2I represents a new structure type with 7-coordinated Nb atoms. Pentagonal bipyramids NbO_5I_2 are connected *via* the apical O atoms with alternating short and long Nb–O distances (1.79 / 2.20 Å) to chains and *via* the three equatorial O atoms to double layers. Between the double layers there are only weak van-der-Waals interactions of the I atoms. NbO_2I is the first oxide halide of a transition metal with CN 7. Structurally NbO_2I is closely related to UO_2Br, but with alternating short and long Nb–O distances as a difference.

Key words: Niobium Oxide Halide, Double-layer Structure, 7-Coordination, Single Crystal, Structure Determination

Introduction

Oxide halides of transition metals show a great variety of compositions because several oxidation numbers are possible and the O/X ratio can be different [1]. Usually the metal atoms have octahedral coordination and prefer a linear *M*–O–*M* arrangement. Therefore many structures of compounds MO_nX_m (X = Cl, Br, I) can be classified on the basis of $M(O,X)_6$ octahedra which are connected to chains, double chains or layers. Synthesis and crystal growth of oxide halides is usually done by chemical transport. Although this technique seems to be well established, the number of well characterised crystal structures is limited for two reasons. Firstly the coordination of the transition metal is frequently distorted because of non-symmetric *M*–O distances and/or owing to the formation of metal-metal bonds according to the presence of *d* electrons. Secondly problems arise from the low-dimensional character of the crystal structures. Because there are only weak van-der-Waals interactions between the chains or layers most of the chemically and mechanically very sensitive crystals show strong disorder.

As it is well known from the function of halogens in light bulbs [2] oxide halides of transition metals are important intermediates during the reaction of the binary oxides with elemental halogens. Depending on the reaction conditions (temperature, pressure, stoichiometry *etc.*) they can appear as volatile products. Therefore the usual synthesis and single crystal growth take place by chemical transport reactions. However, frequently oxide halides result as by-products from syntheses with halogens or halides when oxygen or oxides are not excluded from the reaction [3].

Several niobium oxide halides have been described. According to the most common oxidation states the simple compositions $NbOX_2$, $NbOX_3$ and NbO_2X [4] are known. For X = Cl more complex compounds Nb_3O_7Cl [5], $Nb_3O_2Cl_5$ [6] and $Nb_{10}O_7Cl_{16}$ [7] have been reported. Owing to the oxidation state Nb(III) the latter two contain Nb clusters. With the exception of the low-valent Nb(III) compounds the structures show octahedral Nb coordination.

Detailed structural investigations on the basis of single crystal data are complicated by the low-dimensional character of the crystal structures which leads to disorder phenomena. The layer structure of $NbOCl_2$ was investigated by a combination of X-ray methods and atomic force microscopy (AFM) [8].

Recently we presented the crystal structures of $NbOI_3$ and $NbOBr_3$ [9] which represent two different

variants of ordered metal oxide halides MO_nX_m (X = Cl, Br, I) with octahedral coordination and polar double chains in a non-centrosymmetric structure. Now we report on the structure of NbO$_2$I, which was already described by Schäfer *et al.* [10]. On the basis of powder X-ray investigations the compounds MO_2X (M = Nb, Ta; X = Cl, Br, I) were assigned to the UO$_2$Br-type [11], where the metal atoms have a sevenfold coordination MO_5X_2 as a pentagonal bipyramid with 5 nearly equal M–O distances. Our single crystal studies show that NbO$_2$I represents a new structure type which is closely related to the UO$_2$Br-type, but with alternating Nb–O distances.

Experimental Section

Synthesis and characterisation

Single crystals of NbO$_2$I were first obtained as a by-product. The initial goal was the synthesis of RbNbOI$_4$ [4]. For this target RbI (0.712 mmol), Nb$_2$O$_5$ (0.143 mmol), Nb (0.427 mmol) and I$_2$ (107 mmol) were sealed in an evacuated quartz ampoule (length 10 cm, diameter 1.5 cm) and submitted to the following temperature programme (holding time in parentheses): r. t. 6 K/h 120 °C (6 h) 12 K/h 150 °C (24 h) 12 K/h 700 °C (12 h) 6 K/h 350 °C (16 h) 12 K/h r. t. Dark-red needles were formed in the upper part of the ampoule. Unit cell dimensions were determined by single crystal X-ray investigations (see below). The composition NbO$_2$I was confirmed by the successful structure solution. Once the composition was known the preparation was conducted by chemical transport according to Schäfer [12] using Nb$_2$O$_5$, Nb and I$_2$ (slight excess of I$_2$ according to molar ratios of 2 : 1 : 6.1) in a temperature gradient 500 °C → 475 °C. The powder pattern of the red needles, which were formed in the cooler part after 4 days, could be indexed with an orthorhombic cell. The observed intensities were in a good agreement with the calculated values and the data published by Schäfer [12].

Structure solution and refinement

Single crystals synthesised by chemical transport from Nb$_2$O$_5$, Nb and I$_2$ were not suitable because of strong disorder. The red needles obtained as a by-product from the synthesis of RbNbOI$_4$ showed well defined reflection profiles which allowed a structure determination. Investigations with an Image Plate revealed at first a C-centred orthorhombic unit cell with a = 20.897(4), b = 3.7654(8) and c = 3.9715(8) Å. The additional reflection condition $h0l$ with $l = 2n$ led to the space groups $Cmcm$ and $Cmc2_1$, respectively. According to the value of the E-statistics the structure solution was started in $Cmcm$ by Direct Methods [13] (according to the standard setting of $Cmcm$: a = 3.97, b = 20.90, c = 3.77 Å). A reasonable structure model for NbO$_2$I was derived, but the dis-

Table 1. Crystal structure data for NbO$_2$I.

Formula	NbO$_2$I
M_r	251.81
Temperature, K	293(2)
Crystal shape and colour	red needle
Crystal size, mm^3	$0.04 \times 0.04 \times 0.8$
Crystal system	orthorhombic
Space group	$Pnma$
a, Å	20.897(4)
b, Å	3.7654(8)
c, Å	3.9715(8)
V, Å^3	312.49(2)
Z	4
D_{calcd}, g cm^{-3}	5.35
μ(MoK_α), mm^{-1}	13.5
$F(000)$, e	440
Data collection	Stoe, IPDS I, graphite monochromator
Radiation; λ, Å	MoK_α; 0.71073
ω Range, deg	$0 \leq \omega \leq 180$
ω Increments, deg	$\psi = 0, \Delta\omega = 2$
Measure time, s	540
hkl Range	$\pm31, \pm5, \pm6$
$((sin\theta)/\lambda)_{max}$, Å^{-1}	0.66
Structure solution and refinement	SHELXL-97 [13]
Refl. measured	3079
Refl. unique/with $I \geq 2\sigma(I)$	619/453
Absorption correction	numerical, equivalent method [14]
R_{int}/R_{sigma}	0.156/0.104
Param. refined	26
$R(F)/wR(F^2)$[a]	0.064/0.160
$R(F)$, (all data)	0.090
Weighting scheme[a]	0.075/0.0
GoF (F^2)[a]	1.061
$\Delta\rho_{fin}$ (max / min / σ), e Å^{-3}	+3.29 / −2.60 / 0.60

[a] Definition of R values, Gof, weighting scheme according to SHELXL-97 [13].

placement parameter of the Nb atom was significantly enlarged ($U_{11}/U_{22} \approx 5$) in the direction [100], *i. e.* towards the O atoms. A splitting of the Nb site resulted in a shift from the central position (Nb–Nb: 0.45 Å) and an alternation in the Nb–O distances (1.77/2.21 Å) to the axial O atoms (341 reflections, 13 variables, $R_1(F)$ = 0.069, $wR_2(F^2)$ = 0.164). According to previous experiences with oxide halides of transition metals [8, 9] we expected an ordered crystal structure with unequal Nb–O distances. A careful reinvestigation of the data set revealed weak additional intensities which required a primitive cell with the same dimensions. The measurement of a full Ewald sphere up $2\theta = 66°$ resulted in a data set of 3095 intensities [independent: 619 and 455 with $I \geq 2\sigma(I)$]. For this new data set the reflection conditions led to space groups $Pnma$ and $Pna2_1$, respectively. The structure solution gave a model which turned out to be an ordered variant of the model in $Cmcm$ with unequal Nb–O distances. The subsequent refinement (619 reflections, 26 variables) resulted in satisfactory R values ($R_1(F)$ = 0.0645, $wR_2(F^2)$ =

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{13}
Nb	0.43331(7)	1/4	0.9451(3)	0.0151(4)	0.0205(6)	0.0108(2)	0.0140(6)	0.0003(4)
I	0.17545(5)	1/4	0.5008(2)	0.0203(3)	0.0212(5)	0.0148(6)	0.0249(5)	−0.0003(3)
O1	0.4267(5)	1/4	0.498(2)	0.0171(19)	0.015(4)	0.019(6)	0.018(4)	−0.016(3)
O2	0.4673(5)	1/4	0.004(2)	0.0176(19)	0.019(5)	0.010(5)	0.024(5)	−0.008(3)

Table 2. Coordinates and displacement parameters of NbO_2I ($Å^2$) with esd's in units of the last significant figure in parentheses, $U_{12} = U_{23} = 0$.

Nb	–O1	1.781(9)		O1	–Nb	1.781(9) / 2.200(9)	
	···O1	2.200(9)			–O2	2.848(14) – 2.881(14)	4×
	–O2	2.025(3)	2×		–O2	2.974(14) – 2.976(14)	2×
	–O2	2.088(10)			–I	3.462(14) – 3.479(14)	4×
	–I	2.960(1)	2×				
I	–Nb	2.960(1)	2×	O2	–Nb	2.025(3)	2×
	–O2	2.983(14)			–Nb	2.088(10)	
	–O1	3.462(14) – 3.479(14)	4×		–O2	2.327(14)	2×
	–I	3.765(3)	2×		–O1	2.848(14) – 2.881(14)	4×
	–I	3.971(3)	2×		–O1	2.974(14) – 2.976(14)	2×
	–I	4.147(3)	4× between layers		–I	2.983(7)	
O1–Nb–O2	98.1(3)			I–Nb–I	79.01(5)		
O1–Nb–O2	100.0(4)			I–Nb–O1	90.0(3)		
O1–Nb·O1	172.0(6)			I–Nb···O1	83.0(3)		
O2–Nb–O2	68.9(3)			I–Nb–O2	70.7(3)		

Table 3. Selected distances (Å) and angles (deg) in NbO_2I with esd's in parentheses.
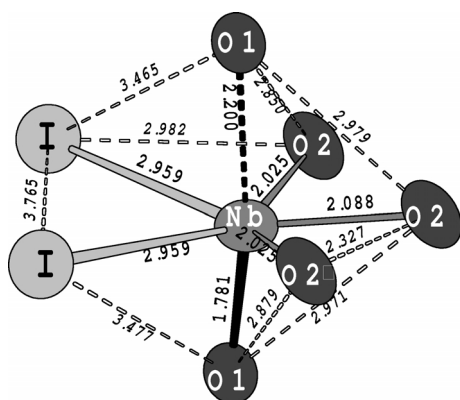

Fig.1. Coordination polyhedron of Nb in NbO_2I; displacement ellipsoids at the 90 % probability level.

0.1597) and reasonable values for all displacement parameters. Further data are listed in Tables 1 – 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anfor derung.html) on quoting the deposition number CSD-418061.

Results and Discussion

The crystal structure of NbO_2I represents a new structure type with a very unusual coordination of the transition metal niobium. As shown in Fig. 1
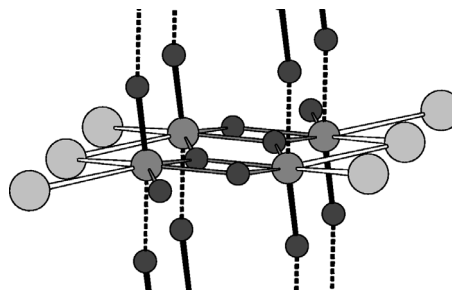

Fig. 2. Connectivity of the polyhedra in NbO_2I.

the coordination of Nb can be described as a distorted pentagonal biypyramide NbO_5I_2. The two iodine atoms are in equatorial positions with a distance of 2.960(1) Å, which is quite long but still comparable to that of other iodides of niobium (2.92 Å for the bridging I atoms in $NbOI_3$ [8], 2.88 Å for the I atoms between Nb_2I_2 units in $NbOI_2$ [15]). The pentagonal basal plane is completed by 2 + 1 O atoms (O2) with distances of 2.025(3) and 2.088(10) Å. Similar Nb–O distances are found in binary oxides like NbO_2 (1.92 – 2.15 Å [16]). The axial sites are occupied by the O atom O1 with very different Nb–O distances of 1.78 and 2.20 Å. This is similar to other oxide halides of Nb like $NbOI_3$ (1.76/2.23 Å [8]), $NbOBr_3$(1.74/2.21 Å [8]) and $NbOCl_3$ (1.76/2.20 Å [17]). Alternatively, the coordination of Nb can also be seen as a NbI_2O_4 octahedron in which the edge formed by O2 atoms is capped by another O2 atom. The pentagonal bipyramids or edge-
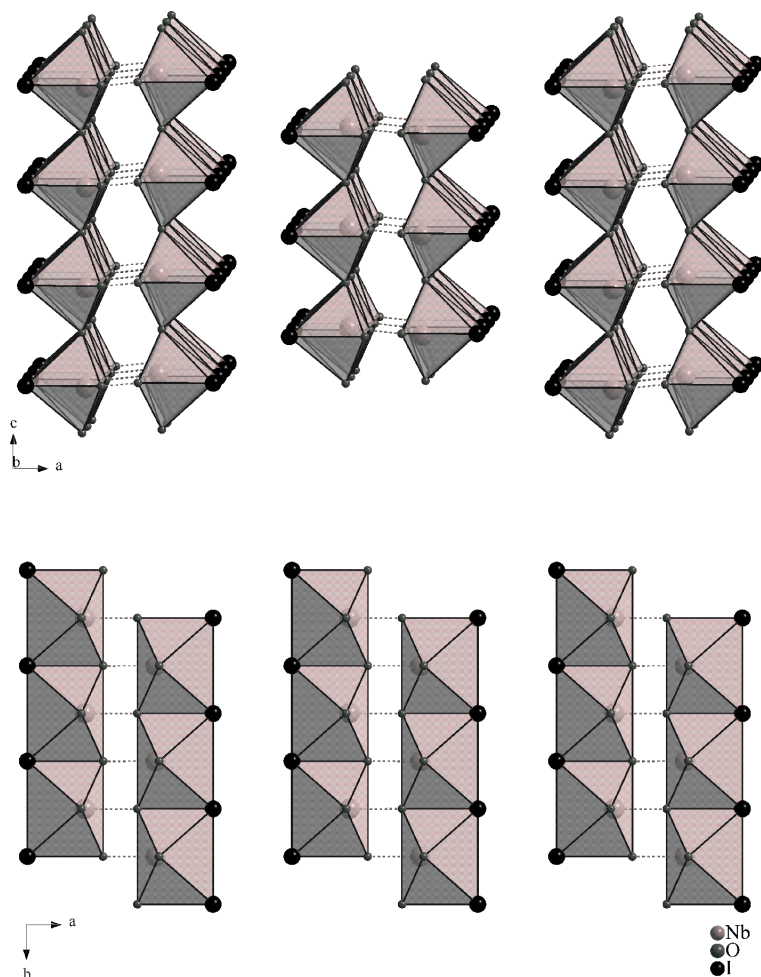
Fig. 3. Arrangement of double layers in NbO$_2$I; view in direction [010] (top) and in direction [001] (bottom).

capped octahedra are linked by a common edge I–O2 to a chain running in [010] direction, and the chains by the apical O1 atoms to layers parallel to (100). Finally two of the layers are connected to double layers *via* the capping O2 atoms (Fig. 2). The double layers are stacked in direction [001] (Fig. 3). Between the double layers there are only weak van-der-Waals interactions of the I atoms at the "outer" side. This explains disorder phenomena. The long *a* axis corresponds to two double layers, while the *b* axis represents the sum of the two Nb–O1 distances and the *c* axis the Nb–Nb distance between the edge-sharing octahedra.

The surroundings of the anions reflect their function in the double-layer structure. O1 is bonded to two Nb atoms with one short and one quite long distance. Additionally there are 6 contacts to O2 atoms (2.85 – 2.97 Å) and 4 to iodine atoms (3.46 – 3.48 Å). O2

forms 3 nearly equal Nb–O bonds. Furthermore there are two very short O2–O2 contacts (2.327 Å) within the pentagonal bipyramid and 6 longer distances to O1 (2.85 – 2.97 Å). The O2–I distance of 2.98 Å is remarkably short, mainly caused by the geometrical restrictions of a pentagonal bipyramid. To oxygen atoms the iodine atoms have one short (O1: 2.98 Å) and 4 longer (O2: 3.46 – 3.48 Å) contacts. The 4 I–I distances within the double layer amount to 3.765 Å (same chain) and 3.971 Å (neighbouring chain) while the 4 longest I–I distances (4.147 Å) occur between the iodine atoms of different double layers.

The crystal structure of NbO$_2$I is closely related to the UO$_2$Br-type [11]. The only differences are the alternating Nb–O1 distances, while the corresponding U–O distances in UO$_2$Br are of equal length. This relation can easily be described by a group-subgroup re-
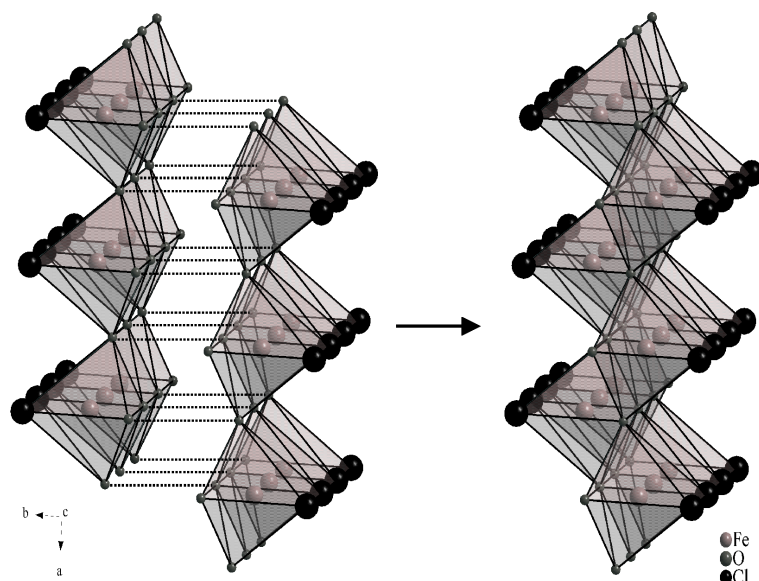
Fig. 4. Double layers in FeOCl; left: single layer of FeCl$_2$O$_4$ octahedra; right: condensed layers with each O atom being a part of four octahedra.

○ Fe
○ O
● Cl

lation [18]. There is a "klassengleiche" transition of index 2 (k2) from *Cmcm* to *Pnma*. The first structure solution for NbO$_2$I (see above) was the UO$_2$Br-type, but with a disorder of Nb.

There are also similarities to the layer structure of the FeOCl-type [1] (Fig. 4). This structure also consists of double layers of FeCl$_2$O$_4$ octahedra, but there are no capping O atoms and the degree of condensation is higher. Each O atom belongs to 4 FeCl$_2$O$_4$ octahedra.

While the coordination number 7 is quite unusual for oxides, halides and oxide halides of transition metals, it is well known for the corresponding compounds of the actinides. Pentagonal bipyramids are not only found for UO$_2$Br (see above) and PaO$_2$Br [19] but also

for U$_3$O$_8$ [20], UOBr$_3$ [21], PaOBr$_3$ [22], UBr$_4$ [23] and PaCl$_5$ [24]. On the other hand it is well known that in the low-temperature modification of ZrO$_2$ [25, 26] the "large" cation Zr^{4+} shows CN 7. Therefore the structure of NbO$_2$I represents a missing link between the oxide halides of the actinides, where the larger size of the cations favours coordination number 7 and of those of the transition metals, which usually have octahedral surroundings, independent of the composition. It should be mentioned that there is no other oxide halide of a transition metal with CN 7. Despite this uncommon coordination the structure of NbO$_2$I verifies again the strong preference for alternating Nb–O distances in oxide halides of Nb.

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