Polar $[NbOCl_3]_{2n}$ and $[NbOX_4^-]_n$ (X = Cl, Br) Chains in the Structures of $NbOCl_3$ and the Thallium-Halogenooxoniobates $Tl[NbOCl_4]$ and $Tl[NbOBr_4]$ − Synthesis, Crystal Structures and Optical Second Harmonic Generation

Johannes Beck* and Jairo Bordinhão

Bonn, Institut für Anorganische Chemie der Universität

Received December 1st, 2004.

Dedicated to Professor Rüdiger Kniep on the Occasion of his 60th Birthday

Abstract. The reactions of thallium(I)halides TlCl and TlBr with Nb_2O_5 and $NbCl_5$, and $NbBr_5$, respectively, under the conditions for chemical vapour transport in closed evacuated ampoules in a temperature gradient from 350 °C to 300 °C give yellow $Tl[NbOCl_4]$ and red $Tl[NbOBr_4]$ in 50 % yield. The crystal structures ($Tl[NbOCl_4]$: orthorhombic, *Pbca*, $a = 1259.9(1)$, $b = 791.9(1)$, $c = 1506.9(1)$ pm; $Tl[NbOBr_4]$: monoclinic, *C*2, $a = 1304.9(3)$, $b = 402.7(3)$, $c = 770.6(3)$ pm, $\beta = 108.150(3)$) are built of linear chains of associated $[NbOX_4^-]_n$ (X = Cl, Br) ions and of Tl^+ ions located between the chains. The individual square-pyramidal $[NbOX_4^-]$ ions are linked by asymmetric O···Nb−O bridges. The Tl^+ ions are coordinated by halogen atoms in form of strongly distorted square antiprisms for X = Cl, and in form of cubes for X = Br. The two structures are not isotypic even though they are made up of analogous building units. The centrosymmetry of the $Tl[NbOCl_4]$ structure causes the polar chains to run in opposite directions. The structure of $Tl[NbOBr_4]$ is acentric and the polar $[NbOBr_4^-]_n$ chains all point into the same direction. An optical second harmonic generation experiment confirmed the recently performed redetermination of the structure of $NbOCl_3$ (Stroebele, Meyer 2002). $NbOCl_3$ crystallizes acentric with analogously polar $[Nb_2O_2Cl_6]_n$ chains.

Keywords: Niobium; Thallium; *catena*-Tetrachlorooxoniobate(V); *catena*-Tetrabromooxoniobate(V); Optical second harmonic generation; SHG effect; Crystal structure.

Introduction

The crystal chemistry of chlorooxo and bromooxo niobates is much less developed than that of the fluorooxo niobates. The underlying compound $NbOCl_3$ belongs to the MOX_3 structure family which is adopted by several trihalogenooxo metalates of elements of groups 5, 6, and 7 such as $NbOBr_3$, $MoOCl_3$, $MoOBr_3$, $WOCl_3$, $WOBr_3$, WOI_3, $TcOBr_3$. The crystal structure of $NbOCl_3$ was initially determined by *Sands*, *Zalkin*, and *Edwards*. The centrosymmetric space group $P4_2/mnm$ was assigned to the needle-shaped colorless crystals with the consequence that the Nb atoms have to be located together with the halogen atoms in a mirror plane leading to planar Nb_2Cl_6 groups which are connected via symmetric −O−Nb−O− bridges to one-dimensional strands $[Nb_2O_2Cl_6]_n$ [1]. The structure determination of the isotypic $MoOBr_3$ by Drew and Tomkins was also performed under the assumption of centrosymmetry but with the need to split the Mo atoms in two closely neighbored positions [2]. In 2002, *Ströbele* and *Meyer* succeeded in the redetermination of the crystal structure of $NbOCl_3$ on an inversion twinned crystal which revealed the non-centrosymmetric space group $P\bar{4}2_1m$ which allows for a polar structure with the Nb atoms shifted out of the plane of the four Cl atoms and strongly asymmetric −O···Nb−O··· bridges [3]. The undistorted, higher symmetric structure type was meanwhile confirmed for WOI_3 [4] and CrF_4 [5].

Metal oxidetrichlorides MOX_3 are Lewis acids since they can take up halide ions and can be transformed into square pyramidal $[MOX_4^-]$ anions. An interesting feature of structures containing such ions is the interaction of the anions since one unoccupied position is present in the coordination sphere of the metal atom. Neutral MOX_4 molecules can occur associated to infinite chains as observed for the tungsten oxidehalides WOX_4 (X = Cl [6], Br [7]). These chains exhibit a pronounced polarity since asymmetric −O···W−O··· are present and the W atoms are shifted out of the plane of the surrounding halogen atoms towards one of the O atoms. This structural principle holds for the respective anions, too. The structures of $Te_8[VOCl_4]_2$ [8], $Te_6[WOCl_4]_2$ [9], $Te_7[WOCl_4]Cl$ [10], $Te_7[WOBr_4]Br$ [11], $(Te_{15}X_4)[MOX_4]_2$ (M = Mo, W; X = Cl, Br) [12], $Te_7[NbOX_4]X$ (X = Cl, Br) [13] all contain linear chains of associated $[MOX_4^-]$ anions. Since the majority of the known compounds containing linearly associated $[MOX_4^-]_n$ chains are formed with chalcogen polycationic clusters as cations, we examined the reactions of $NbOX_3$ (X = Cl, Br) with thallium(I) halides.

Experimental

Nb powder (99.95 %, Aldrich), Nb_2O_5 (99.9 %, Merck), TlCl and TlBr (> 99.9 %, Aldrich) were used as obtained. $NbCl_5$ and $NbBr_5$

---

* Prof. Dr. J. Beck
Inst. f. Anorg. Chemie d. Universität
Gerhard-Domagk-Str. 1
D-53121 Bonn
e-mail: j.beck@uni-bonn.de

DOI: 10.1002/zaac.200500041

were prepared from the elements according to described procedures [14]. $NbOCl_3$ was obtained from Nb_2O_5 and $NbCl_5$ in evacuated closed ampoules at 300 °C. The fibrous white volatile material was sublimed twice. $NbCl_5$, $NbBr_5$ and $NbOCl_3$ were stored and handled in an argon-filled glove box. Ampoules were made of borosilicate glass and flame-dried in vacuo before use.

$Tl[NbOCl_4]$. In an argon filled glove box 120 mg TlCl (0.5 mmol), 81 mg $NbCl_5$ (0.3 mmol), and 26 mg Nb_2O_5 (0.1 mmol) were filled in a glass ampoule of 15 cm length and 1.5 cm internal diameter. The ampoule was evacuated, flame-sealed, and placed in a horizontal tube furnace. The furnace was heated to 350 °C and the ampoule placed asymmetrically in order to establish a temperature gradient of 50 °C from the hot, charged end to the empty tip of the ampoule. Within 5 days yellow crystals of $Tl[NbOCl_4]$ formed which were deposited together with white fibrous $NbOCl_3$ in the colder part of the reaction ampoule.

$Tl[NbOBr_4]$. In an argon filled glove box 142 mg TlBr (0.5 mmol), 148 mg $NbBr_5$ (0.3 mmol), and 26 mg Nb_2O_5 (0.1 mmol) were filled in a glass ampoule as described for the synthesis of $Tl[NbOCl_4]$. The applied temperature was 350 °C with a temperature gradient of 50 °C. Within 7 days dark red prismatic crystals of $Tl[NbOBr_4]$ formed which were deposited together with yellow fibrous $NbOBr_3$ and yellow platelike crystals of an unknown phase in the colder part of the reaction ampoule.

Crystal Structure Analyses

Since both compounds are sensitive towards hydrolysis by moist air, opening of the reaction ampoules and selection of crystals were performed in an argon filled glove box. Crystals were filled into glass capillaries which were sealed. The crystals selected had the size $0.26 \cdot 0.12 \cdot 0.04\ mm^3$ for $Tl[NbOCl_4]$ and $0.40 \cdot 0.40 \cdot 0.60\ mm^3$ for $Tl[NbOBr_4]$. Preliminary examinations by precession photographs revealed the orthorhombic crystal system for $Tl[NbOCl_4]$. The systematic extinctions led to the space group *Pbca*. Data were collected at ambient temperature using a STOE IPDS diffractometer equipped with graphite monochromatized Mo-Kα radiation. Due to the high absorption coefficient a numerical absorption correction with the aid of the program HABITUS [15] was applied to the data set. The optimization of the crystal shape was performed by minimalization of the reliability factor of averaging symmetry equivalent reflections. Structure models were obtained by direct methods [16] and refined against F^2 with anisotropic displacement parameters for all atoms [17].

Crystals of $Tl[NbOBr_4]$ belong to the monoclinic crystal system. Data were collected at ambient temperature using a STOE STADI 4-circle diffractometer. The integral extinction *hkl* only present for $h + k = 2n$ and the absence of further extinctions led to the space groups *C*2/*m*, *Cm*, and *C*2. For $Tl[NbOBr_4]$ the structure was solved assuming the centrosymmetric space group *C*2/*m*. In the initial refinements niobium and bromine atoms had to be positioned in the mirror planes perpendicular to the *b* axis which caused large thermal ellipsoides for the Nb and O atom. In the acentric space group *C*2, however, the refinement converged well and all structural parameters obtained reasonable values. The assumption that the crystal structure of $Tl[NbOBr_4]$ actually is non-centrosymmetric is underlined by a Flack *x* parameter of 0.09(2) [18]. In comparision to $Tl[NbOCl_4]$ the crystals of $Tl[NbOBr_4]$ are of generally lower quality with respect to the X-ray diffraction. The crystal examined showed the presence of an irregular twinning and the reflections of one individuum were recorded only. A numerical absorption correction was not possible under these circumstances, so only an empirical correction based on ψ-scans was applied.

Crystallographic data and details of the structure analyses are given in Tab. 1, positional parameters in Tab. 2, selected bond lengths and angles in Tabs. 3 and 4. Further information on the crystal structure analyses have been deposited with the FIZ Karlsruhe, D-76344 Eggenstein-Leopoldshafen form where they can be obtained by quoting the deposit numbers CSD-415202 for $Tl[NbOCl_4]$ and CSD-415203 for $Tl[NbOBr_4]$.

Table 1 Crystallographic data and details of the structure refinement for $Tl[NbOCl_4]$ and $Tl[NbOBr_4]$. Standard deviations given in brackets refer to the last significant digit.

Formula		$Tl[NbOCl_4]$	$Tl[NbOBr_4]$
Crystal system/space group		orthorhombic / *Pbca*	monoclinic / *C*2
Lattice constants	*a* / pm	1259.9(1)	1304.9(3)
	b / pm	791.9(1)	402.7(3)
	c /pm	1506.9(1)	770.6(3)
	β / °		108.150(3)
Unit cell volume	$V/10^6\ pm^3$	1503.4(3)	384.8(3)
Number of formula units	*Z*	8	2
Density (calculated)	$/\ g \cdot cm^{-3}$	4.021	5.463
Temperature	/ K	293(2)	293(2)
Range of data collection		$3.8° < 2\,\theta < 56.3°$	$4.3° < 2\,\theta < 70.0°$
Number of measured reflections		11343	3382
Number of independent reflections		1749, $R_{int} = 0.054$	1687, $R_{int} = 0.149$
Number of reflections in least squares		1749	1687
Number of refined parameters		65	34
Absorption correction		Numerical, description of the crystal shape by 9 faces, $\mu = 242.5\ cm^{-1}$	Empirical, $\mu = 430.7\ cm^{-1}$
Reliability factors	$R(\|F\|)$ for [number] reflections with $F_o > 4\sigma(F_o)$	0.043 [1351]	0.062 [1179]
	all reflections	0.057	0.086
	$wR(F^2)$	0.095	0.156
Final difference fourier	$/\ e/10^6\ pm^3$	+2.31 / −1.63	+2.82 / −1.35
Flack parameter			0.09(2)

Table 2 Positional coordinates and equivalent isotropic displacement parameter $B_{eq}/10^4\ \mathrm{pm}^2$ for the atoms in the structures for $\mathrm{Tl[NbOCl_4]}$ and $\mathrm{Tl[NbOBr_4]}$. Standard deviations refer to the last significant digit.

Atom	x	y	z	B_{iso}
$\mathrm{Tl[NbOCl_4]}$				
Tl	0.40019(4)	0.49016(5)	0.34274(2)	4.12(2)
Nb	0.24553(5)	0.19236(8)	0.09063(4)	1.47(2)
O1	0.2408(5)	0.4092(7)	0.0912(4)	2.5(1)
Cl1	0.4228(2)	0.1766(3)	0.0368(2)	2.78(4)
Cl2	0.1841(2)	0.1470(3)	−0.0566(2)	2.79(4)
Cl3	0.3148(2)	0.1523(3)	0.2379(2)	3.01(4)
Cl4	0.0713(2)	0.1423(4)	0.1457(2)	3.02(4)
$\mathrm{Tl[NbOBr_4]}$				
Tl	0	0.0008(2)	0	4.48(3)
Nb	0	0.4373(4)	0.5	2.15(3)
Br1	0.14045(8)	0.5123(5)	0.3381(2)	2.80(3)
Br2	−0.14732(8)	0.5105(5)	0.1944(2)	2.87(3)
O	0	0.017(6)	0.5	2.7(3)

Table 3 Selected bond lengths / pm and angles / ° in the structure of $\mathrm{Tl[NbOCl_4]}$.

$\mathrm{Nb{-}O^{I}}$	224.9(5)	$\mathrm{Tl{-}Cl(1)^{II}}$	322.1(2)
Nb−O	171.8(5)	$\mathrm{Tl{-}Cl(2)^{II}}$	330.1(2)
Nb−Cl(1)	237.9(2)	Tl−Cl(3)	328.8(2)
Nb−Cl(2)	237.7(2)	$\mathrm{Tl{-}Cl(4)^{III}}$	350.2(2)
Nb−Cl(3)	240.6(2)	$\mathrm{Tl{-}Cl(1)^{IV}}$	323.3(2)
Nb−Cl(4)	238.0(2)	$\mathrm{Tl{-}Cl(2)^{V}}$	341.8(2)
		$\mathrm{Tl{-}Cl(3)^{VI}}$	338.8(2)
		$\mathrm{Tl{-}Cl(4)^{VI}}$	322.4(2)
O−Nb−Cl(1)	95.0(3)		
O−Nb−Cl(2)	98.3(2)		
O−Nb−Cl(3)	98.1(2)		
O−Nb−Cl(4)	97.6(3)		
$\mathrm{Nb{-}O{-}Nb^{I}}$	177.6(1)		
$\mathrm{O{-}Nb{-}O^{I}}$	173.6(4)		
Cl(1)−Nb−Cl(2)	88.83(7)		
Cl(4)−Nb−Cl(2)	90.01(8)		
Cl(3)−Nb−Cl(4)	89.47(8)		
Cl(3)−Nb−Cl(1)	88.11(8)		

Symmetry operations
I −x + 1/2, y−1/2 , z
II x , −y + 1/2, z + 1/2
III x + 1/2, y, −z + 1/2
IV −x + 1, y + 1/2, −z + 1/2
V −x + 1/2, −y + 1, z + 1/2
VI −x + 1/2, y + 1/2, z

Results and Discussion

Synthesis

The compounds $\mathrm{Tl[NbOX_4]}$ are formed in reactions of TlX, $\mathrm{Nb_2O_5}$ and $\mathrm{NbX_5}$ (X = Cl, Br). $\mathrm{Nb_2O_5}$ and $\mathrm{NbX_5}$ react at the applied temperatures to $\mathrm{NbOX_3}$ which is then converted with TlX to the quaternary compounds. The reactions can thus be understood as Lewis acid-base reactions between $\mathrm{NbOX_3}$ and $\mathrm{X^-}$. The reactions proceed via the gas phase in closed evacuated ampoules. Since $\mathrm{NbOX_3}$ (X = Cl, Br) and TlX are volatile at sufficiently high temperatures, vapour transport is achieved in a closed system with a temperature gradient from 350 → 300 °C. The deposition of different phases which are deposited in the colder part of the reaction system indicates complex equilibria in the gas phase. Besides the crystals of $\mathrm{Tl[NbOCl_4]}$ and $\mathrm{Tl[NbOBr_4]}$ in all experiments fibrous masses of $\mathrm{NbOCl_3}$ and $\mathrm{NbOBr_3}$ are deposited in the colder tip of the ampoule. The yields of $\mathrm{Tl[NbOCl_4]}$ and $\mathrm{Tl[NbOBr_4]}$ reach to about 50 %. In the reactions of TlBr and $\mathrm{NbOBr_3}$ besides $\mathrm{Tl[NbOBr_4]}$ a further crystalline, yellow compound occurs which could not be definitely identified yet but tentatively is $\mathrm{Tl_2[Nb_3O_5Br_7]}$ crystallizing in the $\mathrm{(NH_4)_2[Nb_3O_5Cl_7]}$ structure type [19].

Table 4 Selected bond lengths / pm and angles / ° in the structure of $\mathrm{Tl[NbOBr_4]}$.

Nb−O	169(2)	Tl−O	385.4(2)
$\mathrm{Nb{-}O^{I}}$	233(2)	$\mathrm{Tl{-}O^{VI}}$	385.3(2)
Nb−Br(1)	253.6(1)	Tl−Br(1)	338.1(2)
Nb−Br(2)	255.1(1)	Tl−Br(2)	345.7(2)
$\mathrm{Nb{-}Br(1)^{II}}$	253.6(1)	$\mathrm{Tl{-}Br(1)^{III}}$	332.1(2)
$\mathrm{Nb{-}Br(2)^{II}}$	255.2(1)	$\mathrm{Tl{-}Br(2)^{III}}$	341.0(2)
		$\mathrm{Tl{-}Br(1)^{IV}}$	337.6(2)
		$\mathrm{Tl{-}Br(2)^{IV}}$	345.5(2)
		$\mathrm{Tl{-}Br(1)^{V}}$	332.6(2)
		$\mathrm{Tl{-}Br(2)^{V}}$	341.2(2)
O−Nb−Br(1)	96.78(6)		
O−Nb−Br(2)	96.52(6)		
$\mathrm{O{-}Nb{-}Br(1)^{II}}$	96.84(7)		
$\mathrm{O{-}Nb{-}Br(2)^{II}}$	96.68(6)		
$\mathrm{O{-}Nb{-}O^{I}}$	180		
Br(1)−Nb−Br(2)	89.12(4)		
$\mathrm{Br(1){-}Nb{-}Br(1)^{II}}$	166.4(2)		
$\mathrm{Br(1){-}Nb{-}Br(2)^{II}}$	89.31(5)		
$\mathrm{Br(2){-}Nb{-}Br(2)^{II}}$	166.8 (2)		

Symmetry operations
I x, y + 1, z
II −x, y, −z + 1
III x, y−1, z
IV −x, y, −z
V −x, y−1, −z
VI x, y, z−1

Crystal Structures

Both structures contain chains composed of $[\mathrm{NbOX_4}^-]$ anions. The individual anions are of square pyramidal shape with the oxygen atoms in the apical position and the four halogen atoms forming the basal plane. Asymmetric −O···Nb−O··· bridges connect the $[\mathrm{NbOX_4}^-]$ anions to infinite chains resulting in an octahedral coordination for the Nb atoms. Despite $\mathrm{Tl[NbOCl_4]}$ and $\mathrm{Tl[NbOBr_4]}$ contain analogous building units the two crystal structures are not isotypic.

Figure 1 gives a view of a section of the anionic chain and of the coordination environment of the $\mathrm{Tl^+}$ ion in the structure of $\mathrm{Tl[NbOCl_4]}$, Figure 2 shows the unit cell from two different points of view. The $[\mathrm{NbOCl_4}^-]_n$ chains run along the crystallographic *b* axis and are approximately linear with O−Nb−O angles of 173.6° and Nb−O−Nb angles of 177.6°. The Nb−O bond lengths along the chain differ strongly. The short Nb−O bond of 171.8 pm indicates multiple bond character while in the trans position the long Nb···O bond of 224.9 pm indicates only weak bonding. The Nb atoms are located 29 pm above the plane of the four Cl atoms shifted towards the apical oxygen atoms giving the $[\mathrm{NbOCl_4}^-]_n$ chains a pronounced polarity. The Nb−Cl distances are within the range 237.7 to 240.6 pm and fit well into the region expected for Nb(V)−Cl bonds.

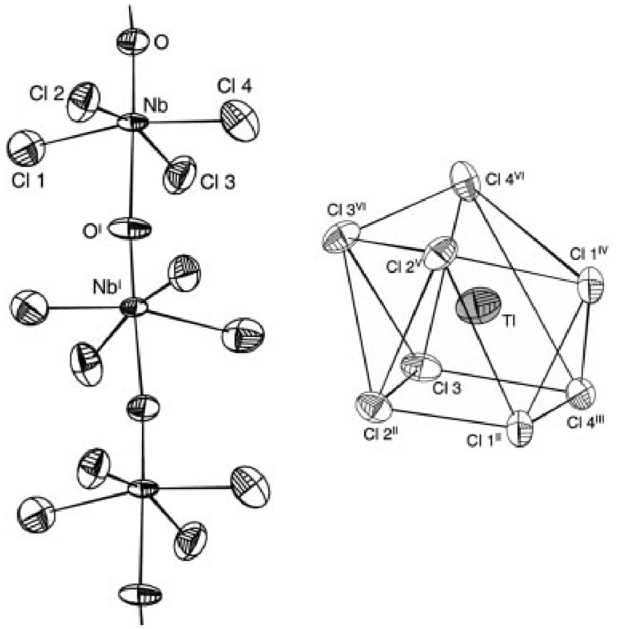

Fig. 1 A section of the chain of associated $[NbOCl_4^-]_n$ ions and the coordination environment of the Tl^+ ion in the structure of $Tl[NbOCl_4]$. Thermal ellipsoides are drawn to include a probability density of 70 %.

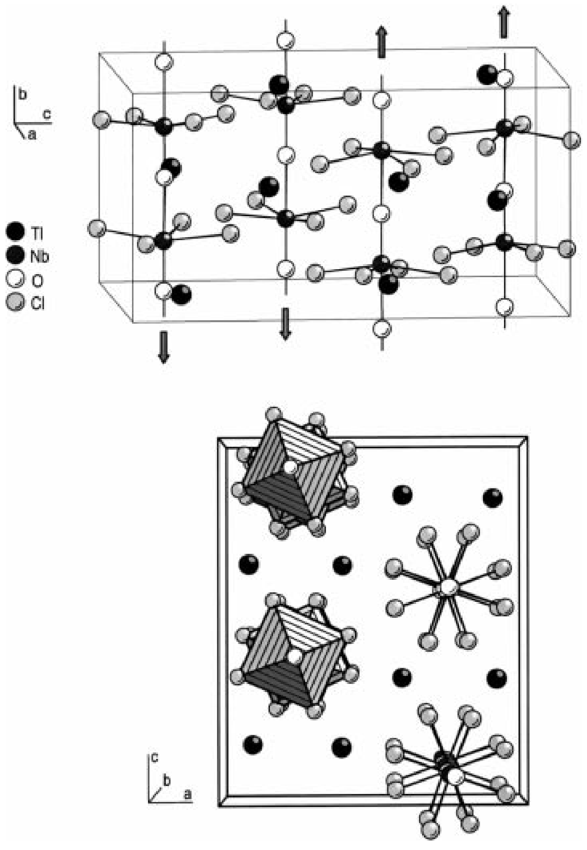

Fig. 2 The unit cell of $Tl[NbOCl_4]$ in two different views, one inclined to the *a* axis (top) and a perspectivic view along the *b* axis parallel to the $[NbOCl_4^-]_n$ chains. The arrows indicate the direction of the polar $[NbOCl_4^-]_n$ chains.

Within the $[NbOCl_4^-]_n$ chain chlorine atoms of neighbored $NbOCl_4$ groups are in a staggered conformation. The dihedral angles $Cl^I-Nb^I-Nb-Cl$ are all between 40° and 50°. The Tl^+ ions are each surrounded by three anionic chains. Eight Tl···Cl distances (Tab. 3) shorter than the sum of the van der Waals radii of 380 pm are present. Comparable distances are found in the structures of $Tl_2[MoCl_6]$ (348.9 pm) [20] and $Tl[AuCl_4]$ (336-358 pm) [21]. The eight Cl atoms form a strongly distorted square-antiprismatic coordination polyhedron around Tl^+.

The structure of $Tl[NbOCl_4]$ is centrosymmetric. The inversion centres are located between the anionic strands. The consequence is that in the crystal half of the chains are directed along the $+b$ axis and the other half along the $-b$ axis. The polarities of the chains are thus compensated and no permanent electrical polarization for the crystal results (Fig. 2).

The anionic chains in the structure ofTl$[NbOBr_4]$ (Fig. 3) differ mainly by their ecliptical conformation from the chains in $Tl[NbOCl_4]$. All $NbOBr_4$ groups along each chain are translationally equivalent. The two Nb−O distances (169 and 233 pm) are distinctly different and of comparable lengths as found in the structure of $Te_7[NbOBr_4]Br$ (174 and 223 pm) [13]. The Nb−Br bond lengths of 253.5 to 255.2 pm are also closely related to those in $Te_7[NbOBr_4]Br$ (253, 254 pm). The Tl^+ ions are surrounded only by two anionic chains. In the first coordination sphere there are eight Br atoms coordinating Tl^+ in form of a slightly distorted cube with Tl···Br distances from 332.1 to 345.7 pm. Comparable distances are found for Tl^+ in an eightfold coordination environment in the structures of Tl_4HgBr_6 (329−369 pm [22]) or Tl_3PbBr_5 (321−372 pm [23]). Two oxygen atoms are located in a distance of 385 pm to Tl^+ over two opposite faces of the coordination cube (Fig. 3).

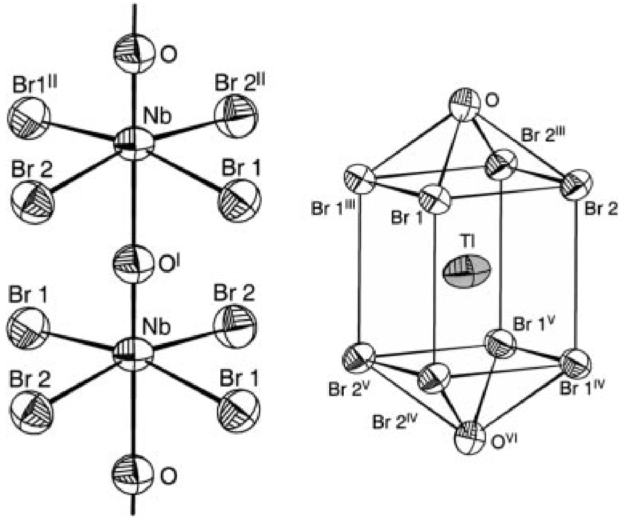

Fig. 3 A section of the chain of associated $[NbOBr_4^-]_n$ ions and the coordination environment of the Tl^+ ion in the structure of $Tl[NbOBr_4]$. Thermal ellipsoides are drawn to include a probability density of 70 %.

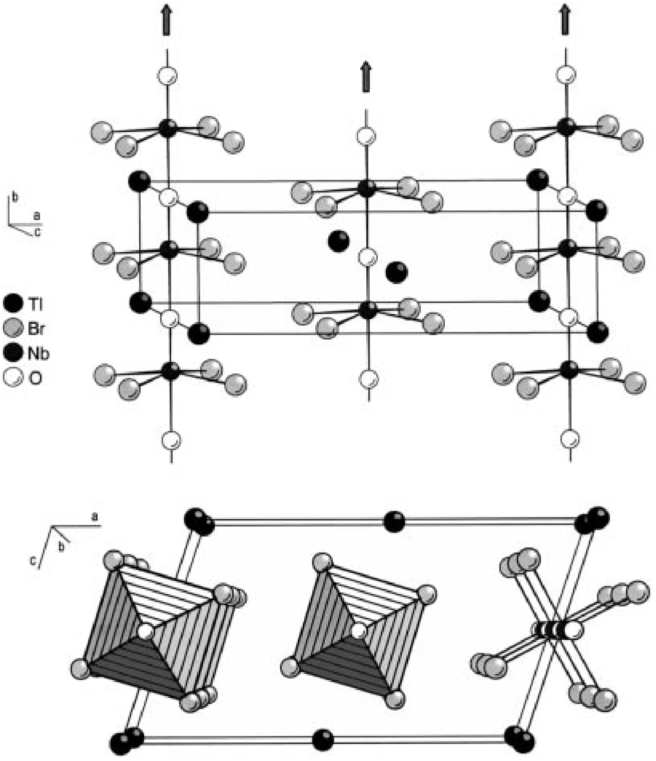

Fig. 4 The unit cell of $Tl[NbOBr_4]$ in two different views, one inclined to the *c* axis (top) and a perspectivic view along the *b* axis parallel to the $[NbOBr_4^-]_n$ chains. The arrows indicate the direction of the polar $[NbOBr_4^-]_n$ chains.

The structure of $Tl[NbOBr_4]$ is non-centrosymmetric. The lack of inversion centres allows for the remarkable structural feature that in the crystal the polar $[NbOBr_4^-]_n$ chains all face into the same direction (Fig. 4). The polarities are not compensated and a permanent electrical polarization of the crystal results.

Optical Second Harmonic Generation by $NbOCl_3$

A clear decision for centrosymmetry or non-centrosymmery of a crystal strucure can be made by a second harmonic generation experiment. If $NbOCl_3$ in fact crystallizes in a non-centrosymmetric space group and contains polar $[Nb_2O_2Cl_6]_n$ chains frequency doubling of emitted light should be observable. Fig. 5 shows the pulse of emitted green light when $NbOCl_3$ is irridiated with pulsed infra-red laser light of a wavelength of 1064 nm. This second harmonic generation experiment shows unequivocally that the recent assignement of a non-centrosymmeric space group was correct and the structure indeed contains polar $[Nb_2O_2Cl_6]_n$ chains with all Nb atoms dislocated from the plane of the four surrounding Cl atoms in the same direction.

Conclusions

The 1:1 adducts of of niobium oxidetrihalides $NbOX_3$ (X = Cl, Br) with thallium(I)halides TlX (X = Cl, Br) are built of one-dimensionally associated $[NbOX_4^-]$ anions. The individual chains are polar. However, crystal structures made up of these chains can be polar in the case of non-centrosymmetry as found for $Tl[NbOBr_4]$. If inversion centres are present the polarities of the chains are compensated as found in the structure of $Tl[NbOCl_4]$. Definite evidence for the acentricity of $NbOCl_3$ was obtained by an optical second harmonic generation experiment.

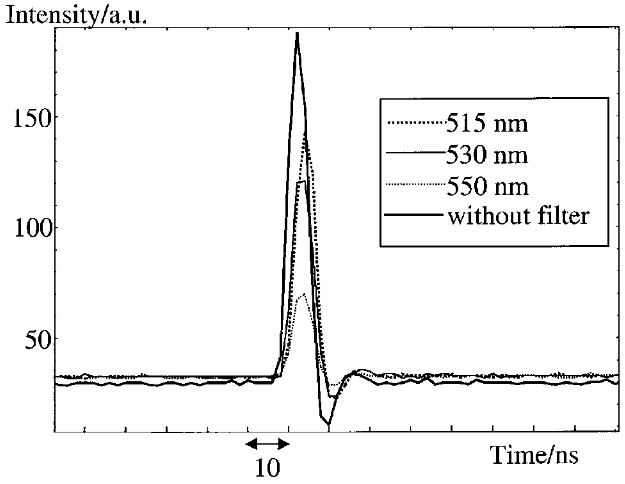

Fig. 5 The emission of green light from powdered samples of $NbOCl_3$, when irradiated with pulsed laser light (λ= 1064 nm). The sample of $NbOCl_3$ was filled in a sealed glass capillary of 2 mm diameter. A superposition of 256 light pulses as the response of the sample to the laser pulses of 10 ns width is shown. The emission was recorded alternatively without and with 515 nm / 530 nm / 550 nm edge filters to suppress all shorter wavelengths, respectively. This experimental technique assures by the strong intensity decrease when going from the 530 nm filter to the 550 nm filter that the emitted light has a wavelength shorter than 550 nm.

Acknowledgement. We thank *Dr. K. Betzler*, Institute of Physics of the University Osnabrück, for the measurement of the SGH effect on $NbOCl_3$ within project A10 of the Collaborative Research Area (SFB 225) of the German Research Council. *J. Bordinhão* thanks the *Deutsche Akademische Austauschdienst DAAD* for a Ph.D. studies grant.

References

[1] D. E. Sands, A. Zalkin, R. E. Elson, *Acta Crystallogr.* **1959**, *12*, 21.
[2] M.G. B. Drew, I. B. Tomkins, *J. Chem. Soc. A*, **1970**, 22.
[3] M. Ströbele, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **2002**, *628*, 488.
[4] B. Krebs, C. J. Brendel, H. Schäfer, *Z. Anorg. Allg. Chem.* **1987**, *553*, 127.
[5] O. Krämer, B. G. Müller, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1969.
[6] H. Hess, H. Hartung, *Z. Anorg. Allg. Chem.* **1966**, *344*, 157.
[7] U. Müller, *Acta Crystallogr.* **1984**, *40C*, 915.

[8] J. Beck, G. Bock, *Angew. Chem.* **1995**, *107*, 2739; *Angew. Chem. Int. Ed.* **1995**, *34*, 2259.

[9] J. Beck, *Chem. Ber.* **1995**, *128*, 23.

[10] J. Beck, *Z. Anorg. Allg. Chem.* **1993**, *619*, 237.

[11] J. Beck, *Angew. Chem.* **1991**, *103*, 1149; *Angew. Chem. Int. Ed.* **1991**, *30*, 1128.

[12] J. Beck, M. Pell, J. Richter, J. A. Ibers, *Z. Anorg. Allg. Chem.* **1996**, *622*, 473.

[13] J. Beck, G. Bock, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1971.

[14] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, F. Enke-Verlag, Stuttgart, **1981**.

[15] W. Herrendorf, H. Bärnighausen, *HABITUS, Program for the Numerical Absorption Correction*, Universities of Karlsruhe and Gießen, Germany, **1993** and **1997**.

[16] G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**.

[17] G. M. Sheldrick, *SHELXL-93, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1993**.

[18] H. D. Flack, G. Bernardinelli, *Acta Crystallogr.* **1999**, *55A*, 908.

[19] U. Reusch, E. Schweda, *Z. Anorg. Allg. Chem.* **1997**, *623*, 805.

[20] J. Beck, M. Hengstmann, *Z. Anorg. Allg. Chem.* **1988**, *624*, 1943.

[21] P. G. Jones, R. Schelbach, E. Schwarzmann, *Acta Crystallogr.* **1987**, *43C*, 1674.

[22] K. Brodersen, G. Thiele, G. Goerz, *Z. Anorg. Allg. Chem.* **1973**, *401*, 217.

[23] H.-L. Keller, *Z. Anorg. Allg. Chem.* **1981**, *482*, 154.