Crystal structure of trimethylbenzylammonium hexachloroniobate(V), $[(\text{CH}_3)_3\text{C}_7\text{H}_7\text{N}][\text{NbCl}_6]$

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Abstract

$\text{C}_{10}\text{H}_{16}\text{Cl}_6\text{Nb}$, orthorhombic, *Pbcm* (no. 57), $a = 8.246(3)$ Å, $b = 13.104(5)$ Å, $c = 16.142(7)$ Å, $V = 1744.2$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.073$, $wR_{\text{ref}}(F^2) = 0.307$, $T = 293$ K.

Source of material

The title compound was obtained from NbCl_5 , which was previously purified from hydrolysis products by refluxing with SOCl_2 and from trimethylbenzylammonium chloride. Recrystallization by dissolution in hot SOCl_2 followed by subsequent cooling in an ice bath gave bright yellow crystals suitable for X-ray diffraction analysis. To avoid crystal decomposition by air moisture during data collection, the crystal was coated with glue.

Experimental details

The refinement in *Pbc2*₁ (standard *Pca2*₁, no. 29) with and without twin did not converge to significantly more satisfying results: $R_{\text{gt}} = 0.069$ and $wR_{\text{ref}} = 0.261$. These large values probably are the consequence of the poor quality of the crystal, maybe of its degradation.

Discussion

During an attempt to prepare an air-stable hexachloroniobate compound that could be used as a reference material for ^{93}Nb NMR analyses, the title compound was isolated, according to a procedure adapted from [1]. Up to now, the ^{93}Nb NMR chemical shifts were reported in the literature with respect to a CD_3CN solution of a hexachloroniobate complex, $[\text{N}(\text{CH}_3)_4][\text{NbCl}_6]$, with

tetramethylammonium as the counter-ion [2,3]. However, the smaller the counter-ion, the greater the sensitivity of hexachloroniobate complexes toward hydrolysis was reported: while the tetramethylammonium compound is immediately hydrolyzed in air by traces of moisture [1], the trimethylbenzylammonium salt is much more stable under the same conditions and can be handled for short time in air without special care.

In its structure, there are a crystallographic twofold axis passing through Nb, Cl1 and Cl2 as well as a mirror plane passing through C1, C4, C5, N6 and C8 atoms so that the asymmetric unit is only one half complex. The niobium is sixfold coordinated by chloro ligands and the coordination polyhedron is an almost regular octahedron. The Nb—Cl distances vary between 2.321(4) Å and 2.347(4) Å with a mean value of 2.342(4) Å, which is in good agreement with the mean Nb—Cl distances of 2.346 Å reported for $[\text{N}(\text{C}_2\text{H}_5)_4][\text{NbCl}_6]$ [4], 2.342 Å for $[\text{N}(\text{C}_3\text{H}_7)_4][\text{NbCl}_6]$ [5] and 2.339 Å for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{NbCl}_6]$ [6]. The trimethylbenzylammonium cation has a similar geometry as those reported in other crystal structures [7–9].

Table 1. Data collection and handling.

Crystal:	yellow parallelepiped, size $0.30 \times 0.30 \times 0.32$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71069 Å)
μ :	15.92 cm ^{−1}
Diffractometer, scan mode:	MAR345 image plate, 80 images, $\Delta\varphi = 3^\circ$
$2\theta_{\text{max}}$:	49.42°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	17274, 1504
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1278
$N(\text{param})_{\text{refined}}$:	93
Programs:	SHELXS-97 [10], SHELXL-97 [11], PLATON [12]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	8e		−0.0530	0.0603	0.6256	0.12(2)
H(3)	8e		−0.3274	0.0993	0.6281	0.12
H(4)	4d		−0.4593	0.1235	$\frac{3}{4}$	0.12
H(5A)	8e		0.2001	0.0594	0.7985	0.12
H(7A)	8e		0.0054	−0.1255	0.6752	0.12
H(7B)	8e		0.1462	−0.2059	0.6766	0.12
H(7C)	8e		0.1667	−0.1039	0.6268	0.12
H(8A)	4d		0.3913	−0.1697	$\frac{3}{4}$	0.12
H(8B)	8e		0.4112	−0.0669	0.7986	0.12

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Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Nb	4c	0.3039(1)	¼	½	0.038(1)	0.068(1)	0.032(1)	0	0	0.0064(4)
Cl(1)	4c	0.5854(5)	¼	½	0.039(2)	0.211(7)	0.098(4)	0	0	0.059(3)
Cl(2)	4c	0.0195(5)	¼	½	0.037(2)	0.130(4)	0.048(2)	0	0	−0.009(2)
Cl(3)	8e	0.3003(5)	0.0724(3)	0.5183(3)	0.140(3)	0.068(2)	0.093(2)	0.014(2)	0.028(2)	0.012(2)
Cl(4)	8e	0.3028(3)	0.2296(3)	0.3557(2)	0.074(2)	0.119(2)	0.036(2)	0.004(1)	0.010(1)	−0.003(1)
C(1)	4d	−0.026(1)	0.0543(9)	¾	0.040(6)	0.050(6)	0.057(7)	−0.006(5)	0	0
C(2)	8e	−0.107(1)	0.0675(7)	0.6758(6)	0.074(7)	0.055(5)	0.071(6)	0.007(5)	−0.011(5)	0.010(4)
C(3)	8e	−0.271(2)	0.0920(9)	0.6777(9)	0.079(8)	0.069(7)	0.13(1)	0.009(6)	−0.037(7)	0.006(7)
C(4)	4d	−0.350(2)	0.105(1)	¾	0.06(1)	0.049(8)	0.18(2)	0.009(7)	0	0
C(5)	4d	0.151(1)	0.0287(8)	¾	0.047(6)	0.036(5)	0.079(8)	−0.002(5)	0	0
N(6)	4d	0.190(1)	−0.0847(7)	¾	0.040(5)	0.040(5)	0.066(7)	−0.005(4)	0	0
C(7)	8e	0.121(2)	−0.1344(9)	0.6756(8)	0.11(1)	0.067(6)	0.11(1)	0.006(7)	−0.021(8)	−0.040(6)
C(8)	4d	0.366(2)	−0.098(1)	¾	0.054(9)	0.065(9)	0.19(2)	0.009(8)	0	0

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