

$(C_7H_6NS)_2[Nb_6Cl_{18}] \cdot 2C_4H_8O$: first niobium cluster with an *N,S*-heterocyclic cation

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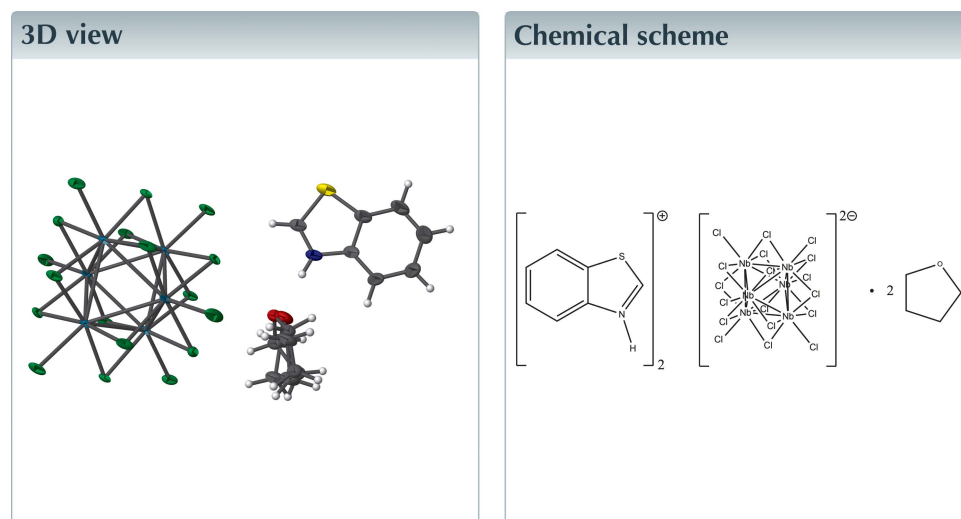
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The title compound bis(benzothiazolium) dodeca- μ -chlorido-hexachlorido-octahedro-hexaniobium(12 *Nb–Nb*) tetrahydrofuran disolvate, $(C_7H_6NS)_2[Nb_6Cl_{18}] \cdot 2C_4H_8O$ or $(HBTh)_2[Nb_6Cl_{18}] \cdot 2THF$, is the first known niobium cluster compound to contain an *N,S*-heterocyclic cation. The synthesis takes place within a few hours as an one-pot reaction at room temperature of the cluster precursor compound $[Nb_6Cl_{14}(H_2O)_4] \cdot 4H_2O$ with $SOCl_2$ in the presence of BTh (benzothiazole) in very high yield. The stabilization of the acidic proton of the cation is achieved by the use of tetrahydrofuran as a co-solvent and by the formation of hydrogen bonds.



Structure description

In 2016, we reported a new synthetic route that allows the generation of niobium cluster compounds of the composition $A_2[Nb_6Cl_{18}]$, where *A* is an organic cation) by the reaction of $[Nb_6Cl_{14}(H_2O)_4] \cdot 4H_2O$ with thionyl chloride (König *et al.*, 2016). The addition of ACl results in the formation of the new compounds. Here, we present a further way to synthesize such compounds. In this case, a neutral heterocyclic compound *L* is used instead of ACl . *L* is protonated and the resulting acidic cation acts as the counter-ion in cluster compounds of the formula $(HL)_2[Nb_6Cl_{18}]$.

The title compound consists of the well known $[Nb_6Cl_{18}]^{2-}$ anion, two benzothiazolium cations $(HBTh)^+$, and two co-crystallized tetrahydrofuran molecules (THF) that bond to the acidic proton of the cation through hydrogen bonds. The disordered THF molecule is present in two different orientations with an occupancy ratio of 0.560 (9):0.440 (9). Only one orientation is shown in Fig. 1 for the sake of clarity. The average *Nb–Nb* distance of the metal cluster unit (Cotton, 1964; Simon, 1988) is 3.0257 Å, which is in the expected range for the doubly negatively charged $[Nb_6Cl_{18}]^{2-}$ anion, and the *Nb–Cl*ⁱ and *Nb–Cl*^o distances with averages of 2.4261 and 2.4863 Å, respectively, are also typical for this anion

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1A···O1A	0.83 (4)	1.86 (4)	2.691 (5)	175 (4)
N1–H1A···O1B	0.83 (4)	1.75 (4)	2.573 (6)	172 (4)

(Koknat & McCarley, 1972; Field *et al.*, 1973; Lin & Williams, 1996; Ströbele & Meyer, 2001; Flemming *et al.*, 2008).

The position of the acidic proton of the cation was freely refined, resulting in bond lengths [N1–H1A 0.83 (4), O1A···H1A = 1.86 (4), N1–H1B = 0.83 (4), O1B···H1A = 1.75 (4), N1···O1A = 2.691 (5) and N1···O1B = 2.573 (6) Å; Table 1] that agree well with those found in similar bonding situations (Steiner, 2002). The packing is shown in Fig. 2.

Synthesis and crystallization

The preparation of the title compound was carried out via an one-pot reaction. 20 mg (16.70 μmol) of the niobium cluster starting compound [Nb₆Cl₁₄(H₂O)₄].4H₂O and 0.05 ml (0.46 μmol) of benzothiazole (BTh) were dissolved in a mixture of 1 ml (13.79 mmol) thionyl chloride (SOCl₂) and 1 ml (12.50 mmol) tetrahydrofuran (THF). The niobium cluster precursor [Nb₆Cl₁₄(H₂O)₄].4H₂O was dehydrated with thionyl chloride, under evolution of SO₂ and HCl. The remaining chloride ions occupied the vacant ligand positions on the niobium cluster and the neutral ligand was protonated to the benzothiazonium cation. In addition, the niobium

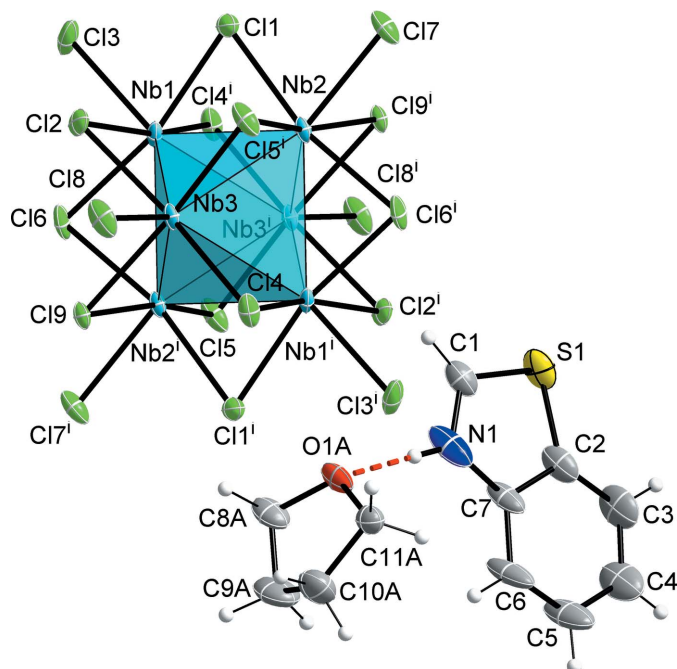


Figure 1

View of the structure of the niobium cluster anion, the benzothiazolium cation and the co-crystallized tetrahydrofuran molecule in crystals of (HBTh)₂[Nb₆Cl₁₈].2THF with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed red line represents a hydrogen bond. The dashed red line represents a hydrogen bond. Symmetry code: (i) $-x, 1 - y, 1 - z$.

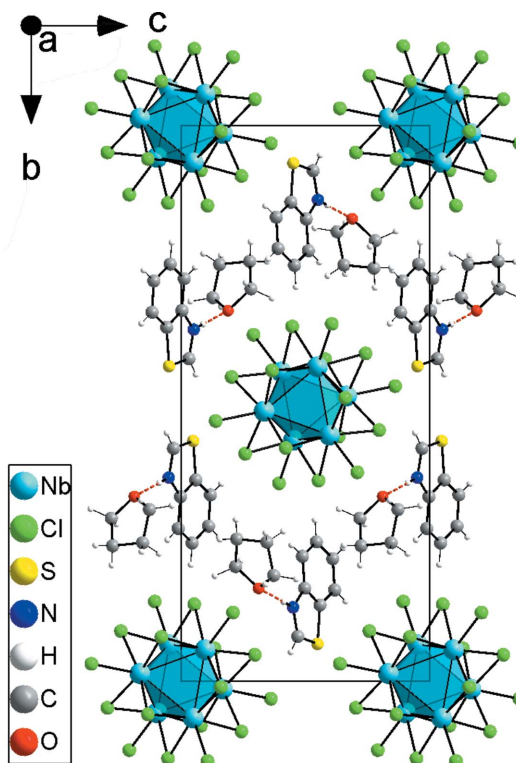


Figure 2

Packing of the cluster anions, cations and THF molecules in the unit cell of (HBTh)₂[Nb₆Cl₁₈].2THF in a view along the *a* axis. The niobium cluster core is shown in a polyhedral representation. Hydrogen bonds are shown as red dashed lines.

Table 2

Experimental details.

Crystal data	
Chemical formula	(C ₇ H ₆ NS) ₂ [Nb ₆ Cl ₁₈].2C ₄ H ₈ O
<i>M_r</i>	1612.14
Crystal system, space group	Monoclinic, <i>P</i> ₂ / <i>c</i>
Temperature (K)	123
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.7110 (3), 24.171 (1), 11.0653 (4)
β (°)	102.598 (1)
<i>V</i> (Å ³)	2273.8 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.61
Crystal size (mm)	0.20 × 0.15 × 0.15
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (SADABS; Bruker, 2017)
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	102833, 5454, 4867
<i>R</i> _{int}	0.045
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.659
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.023, 0.047, 1.05
No. of reflections	5454
No. of parameters	286
No. of restraints	86
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.25, -1.00

Computer programs: APEX3 and SAINT (Bruker, 2017), SHELXT2014 (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg & Putz, 2014).

cluster core was oxidized from $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ to $[\text{Nb}_6\text{Cl}_{12}]^{4+}$. SOCl_2 functionalized as oxidation agent, forming SCl_2 (König *et al.*, 2016). Crystallization was favored by the formation of hydrogen bonds between the proton of the cation and the THF molecules. After one day at room temperature, brown crystals of the title compound $(\text{HBTh})_2[\text{Nb}_6\text{Cl}_{18}] \cdot 2\text{THF}$ formed. The supernatant solution was removed and the crystals were washed three times with diethyl ether. The product was obtained in a yield of 96% (26.60 mg).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The disordered THF molecule was refined with split atom positions over two orientations [occupancy ratio of 0.560 (9):0.440 (9)] with the sum of the occupational factors of each atom being fixed to unity.

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full crystallographic data

IUCrData (2018). 3, x181760 [https://doi.org/10.1107/S2414314618017601]

(C₇H₆NS)₂[Nb₆Cl₁₈]·2C₄H₈O: first niobium cluster with an *N,S*-heterocyclic cation

Eric Sperlich and Martin Köckerling

Bis(benzothiazolium) dodeca- μ -chlorido-hexachlorido-octahedro-hexaniobium(12 Nb–Nb) tetrahydrofuran disolvate

Crystal data

(C₇H₆NS)₂[Nb₆Cl₁₈]·2C₄H₈O

$M_r = 1612.14$

Monoclinic, $P2_1/c$

$a = 8.7110$ (3) Å

$b = 24.171$ (1) Å

$c = 11.0653$ (4) Å

$\beta = 102.598$ (1)°

$V = 2273.8$ (2) Å³

$Z = 2$

$F(000) = 1548$

$D_x = 2.355$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9607 reflections

$\theta = 2.4$ – 27.9 °

$\mu = 2.61$ mm⁻¹

$T = 123$ K

Block, brown

$0.20 \times 0.15 \times 0.15$ mm

Data collection

Bruker APEXII CCD

diffractometer

Radiation source: microfocus sealed tube

φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2017)

5454 independent reflections

4867 reflections with $I > 2\sigma(I)$

$R_{int} = 0.045$

$\theta_{max} = 27.9$ °, $\theta_{min} = 2.4$ °

$h = -11 \rightarrow 11$

$k = -31 \rightarrow 31$

$l = -14 \rightarrow 14$

102833 measured reflections

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.047$

$S = 1.05$

5454 reflections

286 parameters

86 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0133P)^2 + 5.1918P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 1.25$ e Å⁻³

$\Delta\rho_{min} = -1.00$ e Å⁻³

Extinction correction: SHELXL2014 (Sheldrick, 2015b),

$Fc^* = kFc[1 + 0.001x Fc^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00216 (7)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Nb1	0.16489 (2)	0.43379 (2)	0.54806 (2)	0.01537 (6)	
Nb2	-0.17270 (2)	0.44311 (2)	0.40346 (2)	0.01362 (6)	
Nb3	0.08185 (2)	0.51378 (2)	0.33389 (2)	0.01343 (6)	
Cl1	-0.00984 (7)	0.36126 (3)	0.44714 (6)	0.0230 (1)	
Cl2	0.27598 (7)	0.44047 (3)	0.36589 (6)	0.0229 (1)	
Cl3	0.35309 (8)	0.35643 (3)	0.60609 (8)	0.0366 (2)	
Cl4	0.09382 (7)	0.40977 (3)	0.74224 (6)	0.0223 (1)	
Cl5	-0.10366 (8)	0.45219 (3)	0.20332 (5)	0.0257 (2)	
Cl6	-0.38072 (7)	0.51032 (3)	0.34026 (6)	0.0235 (1)	
Cl7	-0.36886 (8)	0.37615 (3)	0.29128 (6)	0.0278 (2)	
Cl8	0.17478 (8)	0.53147 (3)	0.13888 (6)	0.0303 (2)	
Cl9	0.28546 (6)	0.57995 (2)	0.42073 (5)	0.0157 (1)	
S1	0.4979 (1)	0.43271 (4)	-0.04878 (8)	0.0383 (2)	
N1	0.3389 (3)	0.3668 (1)	0.0501 (2)	0.0333 (6)	
H1A	0.273 (5)	0.356 (2)	0.089 (4)	0.05 (1)*	
C1	0.3572 (4)	0.4193 (1)	0.0308 (3)	0.0310 (7)	
H1B	0.2971	0.4474	0.0589	0.037*	
C2	0.5361 (4)	0.3627 (2)	-0.0584 (3)	0.0369 (8)	
C3	0.6409 (5)	0.3356 (2)	-0.1173 (3)	0.050 (1)	
H3	0.7055	0.3557	-0.1609	0.060*	
C4	0.6474 (5)	0.2793 (2)	-0.1103 (4)	0.059 (1)	
H4	0.7164	0.2600	-0.1512	0.071*	
C5	0.5551 (6)	0.2490 (2)	-0.0442 (4)	0.063 (1)	
H5	0.5659	0.2099	-0.0384	0.076*	
C6	0.4500 (5)	0.2751 (2)	0.0121 (4)	0.057 (1)	
H6	0.3864	0.2547	0.0559	0.068*	
C7	0.4395 (4)	0.3324 (1)	0.0030 (3)	0.0378 (8)	
O1A	0.1371 (5)	0.3338 (2)	0.1885 (4)	0.034 (1)	0.560 (9)
C8A	-0.0116 (7)	0.3094 (2)	0.1260 (5)	0.038 (1)	0.560 (9)
H8A	-0.0305	0.3156	0.0355	0.046*	0.560 (9)
H8B	-0.0999	0.3256	0.1572	0.046*	0.560 (9)
C9A	0.0044 (6)	0.2488 (2)	0.1553 (5)	0.040 (1)	0.560 (9)
H9A	-0.0972	0.2332	0.1654	0.048*	0.560 (9)
H9B	0.0393	0.2284	0.0885	0.048*	0.560 (9)
C10A	0.1238 (7)	0.2450 (2)	0.2726 (6)	0.038 (1)	0.560 (9)
H10A	0.1850	0.2103	0.2756	0.046*	0.560 (9)
H10B	0.0732	0.2458	0.3445	0.046*	0.560 (9)
C11A	0.2283 (6)	0.2943 (2)	0.2740 (5)	0.034 (1)	0.560 (9)
H11A	0.2578	0.3103	0.3583	0.041*	0.560 (9)

H11B	0.3254	0.2839	0.2469	0.041*	0.560 (9)
O1B	0.1404 (9)	0.3237 (3)	0.1642 (7)	0.062 (2)	0.440 (9)
C8B	-0.0152 (9)	0.3084 (3)	0.0947 (7)	0.063 (2)	0.440 (9)
H8C	-0.0089	0.2916	0.0142	0.076*	0.440 (9)
H8D	-0.0848	0.3412	0.0790	0.076*	0.440 (9)
C9B	-0.0757 (8)	0.2673 (3)	0.1745 (7)	0.063 (2)	0.440 (9)
H9C	-0.1426	0.2858	0.2241	0.075*	0.440 (9)
H9D	-0.1384	0.2382	0.1231	0.075*	0.440 (9)
C10B	0.066 (1)	0.2432 (3)	0.2560 (8)	0.062 (2)	0.440 (9)
H10C	0.0982	0.2091	0.2188	0.075*	0.440 (9)
H10D	0.0444	0.2340	0.3380	0.075*	0.440 (9)
C11B	0.1908 (8)	0.2866 (4)	0.2683 (8)	0.061 (2)	0.440 (9)
H11C	0.2014	0.3067	0.3476	0.073*	0.440 (9)
H11D	0.2934	0.2696	0.2656	0.073*	0.440 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nb1	0.0085 (1)	0.0181 (1)	0.0207 (1)	0.00211 (8)	0.00572 (8)	0.00766 (8)
Nb2	0.0103 (1)	0.0202 (1)	0.0109 (1)	-0.00342 (8)	0.00341 (7)	0.00206 (8)
Nb3	0.0105 (1)	0.0203 (1)	0.0106 (1)	-0.00263 (8)	0.00461 (7)	0.00265 (8)
C11	0.0214 (3)	0.0175 (3)	0.0344 (3)	-0.0016 (2)	0.0154 (3)	-0.0019 (2)
C12	0.0189 (3)	0.0219 (3)	0.0337 (3)	0.0011 (2)	0.0184 (3)	0.0020 (3)
C13	0.0192 (3)	0.0299 (4)	0.0647 (5)	0.0131 (3)	0.0181 (3)	0.0254 (4)
C14	0.0140 (3)	0.0303 (3)	0.0215 (3)	-0.0005 (2)	0.0017 (2)	0.0159 (3)
C15	0.0271 (3)	0.0392 (4)	0.0125 (3)	-0.0172 (3)	0.0082 (2)	-0.0039 (3)
C16	0.0082 (3)	0.0335 (4)	0.0265 (3)	-0.0021 (2)	-0.0013 (2)	0.0150 (3)
C17	0.0272 (3)	0.0379 (4)	0.0182 (3)	-0.0185 (3)	0.0051 (2)	-0.0044 (3)
C18	0.0316 (4)	0.0476 (4)	0.0158 (3)	-0.0161 (3)	0.0139 (3)	-0.0001 (3)
C19	0.0112 (2)	0.0224 (3)	0.0147 (3)	-0.0039 (2)	0.0053 (2)	0.0028 (2)
S1	0.0379 (4)	0.0470 (5)	0.0320 (4)	-0.0094 (4)	0.0118 (3)	0.0157 (4)
N1	0.043 (2)	0.042 (2)	0.018 (1)	-0.026 (1)	0.013 (1)	-0.010 (1)
C1	0.032 (2)	0.042 (2)	0.017 (1)	-0.014 (1)	0.003 (1)	0.001 (1)
C2	0.047 (2)	0.046 (2)	0.020 (1)	-0.019 (2)	0.013 (1)	-0.002 (1)
C3	0.060 (2)	0.063 (3)	0.034 (2)	-0.020 (2)	0.029 (2)	-0.003 (2)
C4	0.076 (3)	0.063 (3)	0.049 (2)	-0.022 (2)	0.038 (2)	-0.025 (2)
C5	0.098 (3)	0.042 (2)	0.064 (3)	-0.034 (2)	0.051 (3)	-0.032 (2)
C6	0.089 (3)	0.041 (2)	0.055 (2)	-0.040 (2)	0.047 (2)	-0.031 (2)
C7	0.054 (2)	0.042 (2)	0.022 (1)	-0.028 (2)	0.019 (1)	-0.017 (1)
O1A	0.035 (2)	0.030 (2)	0.043 (2)	-0.010 (1)	0.020 (1)	-0.007 (1)
C8A	0.038 (2)	0.033 (2)	0.047 (2)	-0.011 (1)	0.016 (1)	-0.007 (1)
C9A	0.040 (2)	0.033 (2)	0.049 (2)	-0.010 (1)	0.015 (1)	-0.008 (1)
C10A	0.038 (2)	0.032 (2)	0.048 (2)	-0.010 (1)	0.017 (1)	-0.007 (1)
C11A	0.034 (2)	0.030 (2)	0.044 (2)	-0.010 (1)	0.021 (1)	-0.006 (1)
O1B	0.067 (3)	0.055 (3)	0.078 (4)	-0.021 (2)	0.050 (3)	-0.002 (2)
C8B	0.068 (3)	0.056 (3)	0.080 (4)	-0.022 (2)	0.049 (3)	-0.003 (2)
C9B	0.068 (3)	0.055 (3)	0.080 (4)	-0.022 (2)	0.049 (3)	-0.004 (2)
C10B	0.068 (3)	0.054 (3)	0.079 (4)	-0.021 (2)	0.050 (3)	-0.003 (2)

C11B	0.067 (3)	0.054 (3)	0.078 (4)	-0.021 (2)	0.051 (3)	-0.002 (2)
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Geometric parameters (Å, °)

Nb1—C16 ⁱ	2.4234 (7)	C3—C4	1.363 (6)
Nb1—C12	2.4242 (6)	C3—H3	0.9500
Nb1—C11	2.4281 (7)	C4—C5	1.405 (5)
Nb1—C14	2.4326 (6)	C4—H4	0.9500
Nb1—C13	2.4774 (7)	C5—C6	1.368 (6)
Nb1—Nb2 ⁱ	3.0215 (3)	C5—H5	0.9500
Nb1—Nb3	3.0216 (3)	C6—C7	1.392 (5)
Nb1—Nb3 ⁱ	3.0261 (3)	C6—H6	0.9500
Nb1—Nb2	3.0342 (3)	O1A—C11A	1.452 (3)
Nb2—C16	2.4206 (7)	O1A—C8A	1.454 (3)
Nb2—C11	2.4209 (7)	C8A—C9A	1.501 (4)
Nb2—C19 ⁱ	2.4276 (6)	C8A—H8A	0.9900
Nb2—C15	2.4280 (6)	C8A—H8B	0.9900
Nb2—C17	2.4809 (7)	C9A—C10A	1.479 (7)
Nb2—Nb1 ⁱ	3.0215 (3)	C9A—H9A	0.9900
Nb2—Nb3 ⁱ	3.0258 (3)	C9A—H9B	0.9900
Nb2—Nb3	3.0286 (3)	C10A—C11A	1.498 (4)
Nb3—C12	2.4215 (7)	C10A—H10A	0.9900
Nb3—C19	2.4256 (6)	C10A—H10B	0.9900
Nb3—C15	2.4282 (7)	C11A—H11A	0.9900
Nb3—C14 ⁱ	2.4296 (7)	C11A—H11B	0.9900
Nb3—C18	2.5013 (6)	O1B—C11B	1.451 (3)
Nb3—Nb2 ⁱ	3.0258 (3)	O1B—C8B	1.453 (3)
Nb3—Nb1 ⁱ	3.0260 (3)	C8B—C9B	1.500 (4)
C14—Nb3 ⁱ	2.4297 (7)	C8B—H8C	0.9900
C16—Nb1 ⁱ	2.4234 (7)	C8B—H8D	0.9900
C19—Nb2 ⁱ	2.4276 (6)	C9B—C10B	1.477 (7)
S1—C1	1.689 (3)	C9B—H9C	0.9900
S1—C2	1.733 (4)	C9B—H9D	0.9900
N1—C1	1.304 (4)	C10B—C11B	1.497 (4)
N1—C7	1.388 (4)	C10B—H10C	0.9900
N1—H1A	0.83 (4)	C10B—H10D	0.9900
C1—H1B	0.9500	C11B—H11C	0.9900
C2—C3	1.396 (5)	C11B—H11D	0.9900
C2—C7	1.398 (4)		
C16 ⁱ —Nb1—C12	88.91 (2)	C15—Nb3—Nb1 ⁱ	94.04 (2)
C16 ⁱ —Nb1—C11	167.35 (2)	C14 ⁱ —Nb3—Nb1 ⁱ	51.55 (2)
C12—Nb1—C11	89.40 (2)	C18—Nb3—Nb1 ⁱ	134.01 (2)
C16 ⁱ —Nb1—C14	90.07 (2)	Nb1—Nb3—Nb1 ⁱ	90.026 (8)
C12—Nb1—C14	167.17 (2)	Nb2 ⁱ —Nb3—Nb1 ⁱ	60.181 (7)
C11—Nb1—C14	88.80 (2)	C12—Nb3—Nb2	94.40 (2)
C16 ⁱ —Nb1—C13	83.84 (3)	C19—Nb3—Nb2	141.61 (2)
C12—Nb1—C13	84.50 (2)	C15—Nb3—Nb2	51.42 (2)

Cl1—Nb1—Cl3	83.52 (3)	Cl4 ⁱ —Nb3—Nb2	94.38 (2)
Cl4—Nb1—Cl3	82.67 (2)	Cl8—Nb3—Nb2	135.10 (2)
Cl6 ⁱ —Nb1—Nb2 ⁱ	51.37 (2)	Nb1—Nb3—Nb2	60.198 (7)
Cl2—Nb1—Nb2 ⁱ	94.84 (2)	Nb2 ⁱ —Nb3—Nb2	90.153 (8)
Cl1—Nb1—Nb2 ⁱ	141.28 (2)	Nb1 ⁱ —Nb3—Nb2	59.874 (7)
Cl4—Nb1—Nb2 ⁱ	94.50 (2)	Nb2—Cl1—Nb1	77.47 (2)
Cl3—Nb1—Nb2 ⁱ	135.18 (2)	Nb3—Cl2—Nb1	77.15 (2)
Cl6 ⁱ —Nb1—Nb3	94.00 (2)	Nb3 ⁱ —Cl4—Nb1	76.98 (2)
Cl2—Nb1—Nb3	51.38 (2)	Nb2—Cl5—Nb3	77.17 (2)
Cl1—Nb1—Nb3	94.73 (2)	Nb2—Cl6—Nb1 ⁱ	77.18 (2)
Cl4—Nb1—Nb3	141.44 (2)	Nb3—Cl9—Nb2 ⁱ	77.14 (2)
Cl3—Nb1—Nb3	135.89 (2)	C1—S1—C2	90.9 (2)
Nb2 ⁱ —Nb1—Nb3	60.092 (8)	C1—N1—C7	114.3 (3)
Cl6 ⁱ —Nb1—Nb3 ⁱ	95.25 (2)	C1—N1—H1A	121 (3)
Cl2—Nb1—Nb3 ⁱ	141.35 (2)	C7—N1—H1A	125 (3)
Cl1—Nb1—Nb3 ⁱ	93.89 (2)	N1—C1—S1	113.6 (3)
Cl4—Nb1—Nb3 ⁱ	51.47 (2)	N1—C1—H1B	123.2
Cl3—Nb1—Nb3 ⁱ	134.14 (2)	S1—C1—H1B	123.2
Nb2 ⁱ —Nb1—Nb3 ⁱ	60.105 (7)	C3—C2—C7	120.4 (3)
Nb3—Nb1—Nb3 ⁱ	89.974 (8)	C3—C2—S1	129.9 (3)
Cl6 ⁱ —Nb1—Nb2	141.48 (2)	C7—C2—S1	109.7 (3)
Cl2—Nb1—Nb2	94.21 (2)	C4—C3—C2	117.7 (3)
Cl1—Nb1—Nb2	51.16 (2)	C4—C3—H3	121.1
Cl4—Nb1—Nb2	94.55 (2)	C2—C3—H3	121.1
Cl3—Nb1—Nb2	134.68 (2)	C3—C4—C5	121.9 (4)
Nb2 ⁱ —Nb1—Nb2	90.127 (8)	C3—C4—H4	119.1
Nb3—Nb1—Nb2	60.015 (7)	C5—C4—H4	119.1
Nb3 ⁱ —Nb1—Nb2	59.906 (7)	C6—C5—C4	120.9 (4)
Cl6—Nb2—Cl1	167.24 (2)	C6—C5—H5	119.6
Cl6—Nb2—Cl9 ⁱ	88.70 (2)	C4—C5—H5	119.6
Cl1—Nb2—Cl9 ⁱ	88.53 (2)	C5—C6—C7	117.7 (3)
Cl6—Nb2—Cl5	89.69 (2)	C5—C6—H6	121.1
Cl1—Nb2—Cl5	90.29 (2)	C7—C6—H6	121.1
Cl9 ⁱ —Nb2—Cl5	167.33 (2)	N1—C7—C6	127.3 (3)
Cl6—Nb2—Cl7	84.42 (3)	N1—C7—C2	111.5 (3)
Cl1—Nb2—Cl7	82.90 (3)	C6—C7—C2	121.3 (3)
Cl9 ⁱ —Nb2—Cl7	84.05 (2)	C11A—O1A—C8A	110.3 (3)
Cl5—Nb2—Cl7	83.29 (2)	O1A—C8A—C9A	105.2 (3)
Cl6—Nb2—Nb1 ⁱ	51.45 (2)	O1A—C8A—H8A	110.7
Cl1—Nb2—Nb1 ⁱ	141.24 (2)	C9A—C8A—H8A	110.7
Cl9 ⁱ —Nb2—Nb1 ⁱ	94.66 (2)	O1A—C8A—H8B	110.7
Cl5—Nb2—Nb1 ⁱ	94.15 (2)	C9A—C8A—H8B	110.7
Cl7—Nb2—Nb1 ⁱ	135.86 (2)	H8A—C8A—H8B	108.8
Cl6—Nb2—Nb3 ⁱ	93.95 (2)	C10A—C9A—C8A	105.3 (2)
Cl1—Nb2—Nb3 ⁱ	94.05 (2)	C10A—C9A—H9A	110.7
Cl9 ⁱ —Nb2—Nb3 ⁱ	51.40 (2)	C8A—C9A—H9A	110.7
Cl5—Nb2—Nb3 ⁱ	141.26 (2)	C10A—C9A—H9B	110.7
Cl7—Nb2—Nb3 ⁱ	135.44 (2)	C8A—C9A—H9B	110.7

Nb1 ⁱ —Nb2—Nb3 ⁱ	59.955 (7)	H9A—C9A—H9B	108.8
Cl6—Nb2—Nb3	95.25 (2)	C9A—C10A—C11A	105.6 (2)
Cl1—Nb2—Nb3	94.71 (2)	C9A—C10A—H10A	110.6
Cl9 ⁱ —Nb2—Nb3	141.25 (2)	C11A—C10A—H10A	110.6
Cl5—Nb2—Nb3	51.42 (2)	C9A—C10A—H10B	110.6
Cl7—Nb2—Nb3	134.70 (2)	C11A—C10A—H10B	110.6
Nb1 ⁱ —Nb2—Nb3	60.022 (7)	H10A—C10A—H10B	108.7
Nb3 ⁱ —Nb2—Nb3	89.847 (8)	O1A—C11A—C10A	105.8 (3)
Cl6—Nb2—Nb1	141.31 (2)	O1A—C11A—H11A	110.6
Cl1—Nb2—Nb1	51.37 (2)	C10A—C11A—H11A	110.6
Cl9 ⁱ —Nb2—Nb1	94.32 (2)	O1A—C11A—H11B	110.6
Cl5—Nb2—Nb1	94.78 (2)	C10A—C11A—H11B	110.6
Cl7—Nb2—Nb1	134.27 (2)	H11A—C11A—H11B	108.7
Nb1 ⁱ —Nb2—Nb1	89.874 (8)	C11B—O1B—C8B	110.4 (3)
Nb3 ⁱ —Nb2—Nb1	59.915 (7)	O1B—C8B—C9B	105.3 (3)
Nb3—Nb2—Nb1	59.787 (7)	O1B—C8B—H8C	110.7
Cl2—Nb3—Cl9	89.86 (2)	C9B—C8B—H8C	110.7
Cl2—Nb3—Cl5	89.50 (3)	O1B—C8B—H8D	110.7
Cl9—Nb3—Cl5	166.95 (2)	C9B—C8B—H8D	110.7
Cl2—Nb3—Cl4 ⁱ	166.95 (2)	H8C—C8B—H8D	108.8
Cl9—Nb3—Cl4 ⁱ	89.24 (2)	C10B—C9B—C8B	105.5 (2)
Cl5—Nb3—Cl4 ⁱ	88.45 (3)	C10B—C9B—H9C	110.6
Cl2—Nb3—Cl8	84.50 (2)	C8B—C9B—H9C	110.6
Cl9—Nb3—Cl8	83.27 (2)	C10B—C9B—H9D	110.6
Cl5—Nb3—Cl8	83.69 (2)	C8B—C9B—H9D	110.6
Cl4 ⁱ —Nb3—Cl8	82.46 (2)	H9C—C9B—H9D	108.8
Cl2—Nb3—Nb1	51.46 (2)	C9B—C10B—C11B	105.9 (2)
Cl9—Nb3—Nb1	94.70 (2)	C9B—C10B—H10C	110.6
Cl5—Nb3—Nb1	95.09 (2)	C11B—C10B—H10C	110.6
Cl4 ⁱ —Nb3—Nb1	141.58 (2)	C9B—C10B—H10D	110.6
Cl8—Nb3—Nb1	135.96 (2)	C11B—C10B—H10D	110.6
Cl2—Nb3—Nb2 ⁱ	94.79 (2)	H10C—C10B—H10D	108.7
Cl9—Nb3—Nb2 ⁱ	51.46 (1)	O1B—C11B—C10B	105.8 (3)
Cl5—Nb3—Nb2 ⁱ	141.56 (2)	O1B—C11B—H11C	110.6
Cl4 ⁱ —Nb3—Nb2 ⁱ	94.82 (2)	C10B—C11B—H11C	110.6
Cl8—Nb3—Nb2 ⁱ	134.73 (2)	O1B—C11B—H11D	110.6
Nb1—Nb3—Nb2 ⁱ	59.953 (8)	C10B—C11B—H11D	110.6
Cl2—Nb3—Nb1 ⁱ	141.48 (2)	H11C—C11B—H11D	108.7
Cl9—Nb3—Nb1 ⁱ	94.57 (2)		

Symmetry code: (i) $-x, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A \cdots O1A	0.83 (4)	1.86 (4)	2.691 (5)	175 (4)
N1—H1A \cdots O1B	0.83 (4)	1.75 (4)	2.573 (6)	172 (4)