IUCrData

ISSN 2414-3146

Hexaaquadodeca-μ_2-chlorido-*octahedro*-hexaniobium diiodide

Florian Schröder and Martin Köckerling*

Universität Rostock, Institut für Chemie, Anorganische Festkörperchemie, Albert-Einstein-Str. 3a, D-18059 Rostock, Germany. *Correspondence e-mail: Martin.Koeckerling@uni-rostock.de

Received 1 June 2021
Accepted 6 July 2021

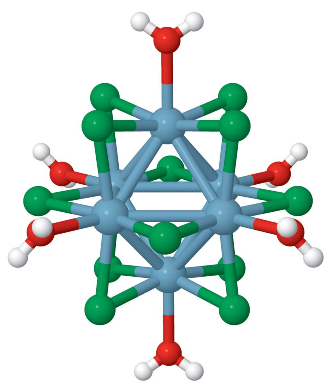
Edited by M. Bolte, Goethe-Universität Frankfurt, Germany

Keywords: crystal structure; cluster; niobium; iodide.

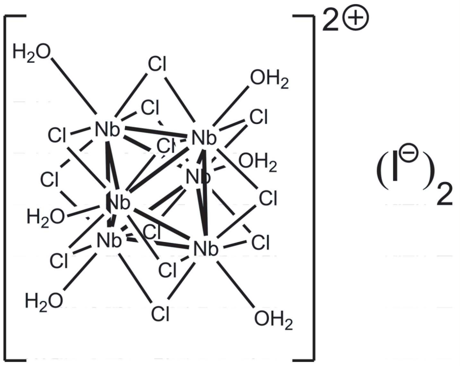
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $[Nb_6Cl_{12}(H_2O)_6]I_2$, consists of the niobium cluster cation $[Nb_6Cl_{12}(H_2O)_6]^{2+}$ and two non-coordinating, charge-balancing iodide ions. The edges of the Nb_6 octahedron are bridged by chlorido ligands. Each Nb atom is further coordinated by a water ligand. The cluster cation has a charge of +2, which is balanced by that of two iodide anions.

3D view



Chemical scheme



Structure description

Cluster complexes of transition metals have been an interesting research area for many years (Cotton, 1964; Simon, 1988). Ligand-exchange reactions in solvents have opened up a wide field of new cluster compounds (Lemoine *et al.*, 2019), of which so far iodides have been investigated much less than chlorides.

The title compound crystallizes in the trigonal space group $P\bar{3}1m$. The asymmetric unit consists of an $[NbCl_2(H_2O)]_{0.5}$ unit, which is located close to the Wyckoff site 1*a* with $\bar{3}m$ symmetry, and one-sixth of an iodide ion. The Nb_6 unit is a metal atom octahedron with an Nb—Nb bond length of 2.8960 (4) Å. The twelve μ_2 bridging positions of the inner ligand sphere are occupied by chlorido ligands. An average Nb—Cl bonding length of 2.456 Å and an average Nb—Cl—Nb angle of 72.31° are present. The six positions of the outer ligand sphere are occupied by water ligands, reaching Nb—O bond lengths of 2.250 (2) Å. The structure of the cluster cation and the packing are shown in Figs. 1 and 2. The charge of the two iodide anions are counter-balanced by that of the doubly positive charged cluster cation $[Nb_6Cl_{12}(H_2O)_6]^{2+}$. Based on the ion ratio and Nb—Nb bond lengths of comparable structures, 16 cluster-based electrons (CBE) are present. Even though six water molecules are present per formula unit, hydrogen bonding is essentially not present in crystals of the title compound, because the large iodide anions separate the cluster units such that the shortest O···O distance is 4.432 (2) Å. The only weak

https://doi.org/10.1107/S2414314621006969

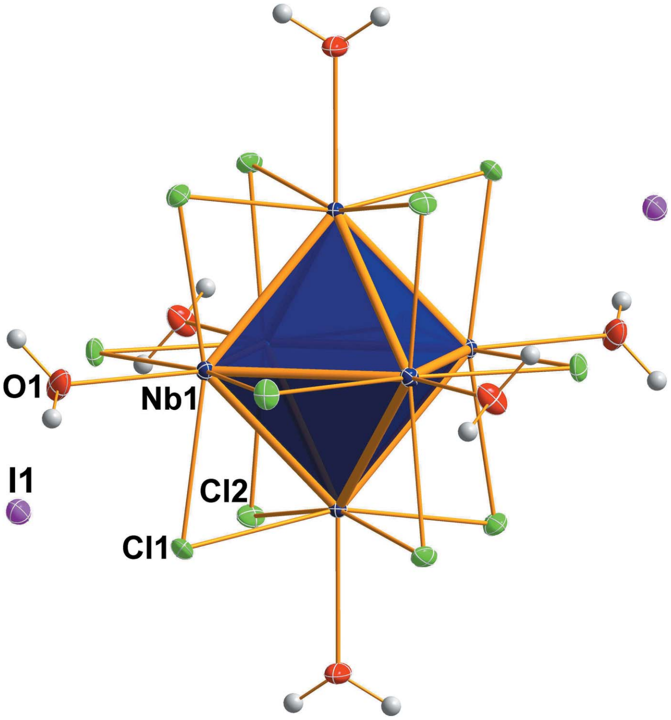


Figure 1
Perspective view of the title compound with atom labelling for the asymmetric unit. Displacement ellipsoids are shown at the 50% probability level.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Nb_6Cl_{12}(H_2O)_6]I_2$
M_r	1344.76
Crystal system, space group	Trigonal, $P\bar{3}1m$
Temperature (K)	123
a, c (Å)	9.3911 (8), 8.6576 (9)
V (Å^3)	661.2 (1)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	6.08
Crystal size (mm)	0.20 × 0.20 × 0.16
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2017)
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	43489, 1059, 1058
$R_{\rm int}$	0.031
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.806
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.013, 0.034, 1.38
No. of reflections	1059
No. of parameters	27
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.72, −0.81

Computer programs: *APEX3* and *SAINT* (Bruker, 2017), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg & Putz, 2019) and *publCIF* (Westrip, 2010).

hydrogen-type bonding contact exists between I1 and O1 with an O1—H1*A*···O1 distance of 3.501 (1) Å.

Synthesis and crystallization

Starting from the compound $[Nb_6Cl_{12}I_2(H_2O)_4]\cdot 4H_2O$ (Schäfer *et al.*, 1972; Brnicevic *et al.*, 1981), the compound $[Nb_6Cl_{12}(H_2O)_6]I_2$ can be synthesized in acceptable yields.

Amounts of 100 mg (72.42 µmol) of $[Nb_6Cl_{12}I_2(H_2O)_4]\cdot 4H_2O$ and 100 mg (667.16 µmol) of NaI were dissolved in 8 ml (444.07 mmol) of degassed water at room temperature and then filtered. The obtained dark-green solution was evaporated in a crystallizing shell for 4 d. Large black single crystals were obtained in remnants of NaI. After washing several times with acetone, 65.0 mg (48.34 µmol, yield: 65%) of $[Nb_6Cl_{12}(H_2O)_6]I_2$ were obtained. The cluster compound was further characterized as follows: Elemental analysis: M $[H_{12}Cl_{12}I_2O_6Nb_6] = 1344.764$: found H = 1.01% (calc. 0.90%); ^{1}H NMR: (MeCN-d_3 was refluxed for several hours with CaH_2 and finally distilled under Schlenk conditions) (MeCN-d_3, 300 MHz, 300 K, p.p.m.): $\delta = 2.14$ (*s*, 12H, *H*$_2$O); IR (300 K, ATR, cm^{-1}): $\nu = 406$ (*s*), 600 (*s*), 692 (*s*), 1587 (*vs*), 3140 (*s*), 3256 (*s*).

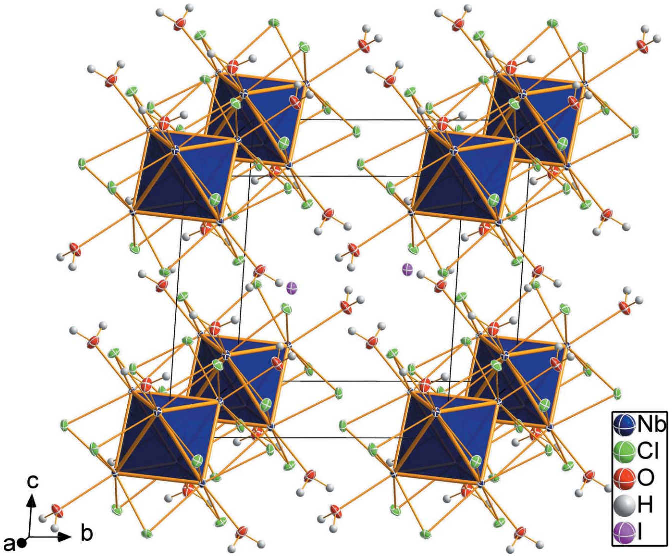


Figure 2
Packing of the cluster cations and iodide anions in the crystal of the title compound.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Two reflections (001 and 010) were omitted from the structure refinement because their intensities were affected by the beam stop.

Acknowledgements

We gratefully acknowledge the maintenance of the XRD equipment through Dr Alexander Villinger (University of Rostock).

Funding information

Funding for this research was provided by: Deutsche Forschungsgemeinschaft (grant No. KO1616-8 to MK).

References

Brandenburg, K. & Putz, H. (2019). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Brnicevic, N., Kojic, B. & Plavsic, D. (1981). *Z. Anorg. Allg. Chem.* **472**, 200–204.

Bruker (2017). *APEX3*, *SADABS* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cotton, F. A. (1964). *Inorg. Chem.* **3**, 1217–1220.

Lemoine, P., Halet, J.-F. & Cordier, S. (2019). In *Ligated Transition Metal Clusters in Solid-State Chemistry: The Legacy of Marcel Sergent*, edited by J.-F. Halet, pp. 143–190. Berlin, Heidelberg: Springer.

Schäfer, H., Plautz, B. & Plautz, H. (1972). *Z. Anorg. Allg. Chem.* **392**, 10–22.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Simon, A. (1988). *Angew. Chem.* **100**, 163–188.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

full crystallographic data

IUCrData (2021). **6**, x210696 [https://doi.org/10.1107/S2414314621006969]

Hexaaquadodeca-μ_2-chlorido-*octahedro*-hexaniobium diiodide

Florian Schröder and Martin Köckerling

Hexaaquadodeca-μ_2-chlorido-*octahedro*-hexaniobium diiodide

Crystal data

$[Nb_6Cl_{12}(H_2O)_6]I_2$
M_r = 1344.76
Trigonal, $P\bar{3}1m$
a = 9.3911 (8) Å
c = 8.6576 (9) Å
V = 661.2 (1) Å^3
Z = 1
F(000) = 616

D_x = 3.377 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9268 reflections
θ = 2.5–34.9°
μ = 6.08 mm^{-1}
T = 123 K
Block, black
0.20 × 0.20 × 0.16 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: microfocus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS, Bruker, 2017)

43489 measured reflections

1059 independent reflections
1058 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 35.0°, θ_{min} = 3.4°
$h = -15 \rightarrow 15$
$k = -15 \rightarrow 15$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.013
$wR(F^2)$ = 0.034
S = 1.38
1059 reflections
27 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.005P)^2 + 1.1433P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} < 0.001$
$\Delta\rho_{\text{max}}$ = 0.72 e Å^{-3}
$\Delta\rho_{\text{min}}$ = −0.81 e Å^{-3}
Extinction correction: SHELXL, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0071 (3)

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.

Refinement. The H atom was located in a difference maps, but refined using a riding model with O—H = 0.85 Å and with U(H) = 1.5 U_{eq}(O).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Nb1	0.0000	0.17816 (2)	0.13652 (2)	0.00709 (5)
Cl1	−0.21059 (3)	0.21059 (3)	0.0000	0.01203 (9)
Cl2	0.21271 (6)	0.21271 (6)	0.32300 (6)	0.01238 (9)
O1	0.0000	0.3770 (2)	0.2816 (2)	0.0167 (3)
H1A	0.0851	0.4473	0.3300	0.025*
I1	0.333333	0.666667	0.5000	0.01368 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nb1	0.00681 (8)	0.00640 (6)	0.00821 (8)	0.00340 (4)	0.00	−0.00114 (4)
Cl1	0.0111 (1)	0.0111 (1)	0.0173 (2)	0.0082 (2)	−0.0021 (1)	−0.0021 (1)
Cl2	0.0136 (2)	0.0136 (2)	0.0106 (2)	0.0072 (2)	−0.0044 (1)	−0.0044 (1)
O1	0.0135 (7)	0.0154 (5)	0.0205 (7)	0.0067 (3)	0.00	−0.0085 (5)
I1	0.01186 (7)	0.01186 (7)	0.0173 (1)	0.00593 (4)	0.00	0.00

Geometric parameters (Å, º)

Nb1—O1	2.250 (2)	Nb1—Nb1^{i}	2.8960 (4)
Nb1—Cl1	2.4502 (4)	Nb1—Nb1^{ii}	2.8980 (4)
Nb1—Cl1^{i}	2.4502 (4)	Nb1—Nb1^{iv}	2.8980 (4)
Nb1—Cl2^{ii}	2.4605 (4)	Cl1—Nb1^{iii}	2.4501 (4)
Nb1—Cl2	2.4605 (4)	Cl2—Nb1^{iv}	2.4605 (4)
Nb1—Nb1^{iii}	2.8960 (4)	O1—H1A	0.8500
O1—Nb1—Cl1	80.29 (4)	Nb1^{iii}—Nb1—Nb1^{i}	60.04 (1)
O1—Nb1—Cl1^{i}	80.28 (4)	O1—Nb1—Nb1^{ii}	135.94 (3)
Cl1—Nb1—Cl1^{i}	88.699 (7)	Cl1—Nb1—Nb1^{ii}	96.180 (6)
O1—Nb1—Cl2^{ii}	82.02 (4)	Cl1^{i}—Nb1—Nb1^{ii}	143.773 (8)
Cl1—Nb1—Cl2^{ii}	88.26 (1)	Cl2^{ii}—Nb1—Nb1^{ii}	53.922 (8)
Cl1^{i}—Nb1—Cl2^{ii}	162.30 (1)	Cl2—Nb1—Nb1^{ii}	96.56 (1)
O1—Nb1—Cl2	82.02 (4)	Nb1^{iii}—Nb1—Nb1^{ii}	59.977 (5)
Cl1—Nb1—Cl2	162.30 (1)	Nb1^{i}—Nb1—Nb1^{ii}	90.0
Cl1^{i}—Nb1—Cl2	88.26 (1)	O1—Nb1—Nb1^{iv}	135.94 (3)
Cl2^{ii}—Nb1—Cl2	89.35 (3)	Cl1—Nb1—Nb1^{iv}	143.773 (8)
O1—Nb1—Nb1^{iii}	134.05 (4)	Cl1^{i}—Nb1—Nb1^{iv}	96.180 (6)
Cl1—Nb1—Nb1^{iii}	53.773 (8)	Cl2^{ii}—Nb1—Nb1^{iv}	96.56 (1)
Cl1^{i}—Nb1—Nb1^{iii}	96.23 (1)	Cl2—Nb1—Nb1^{iv}	53.922 (8)
Cl2^{ii}—Nb1—Nb1^{iii}	96.00 (1)	Nb1^{iii}—Nb1—Nb1^{iv}	90.0
Cl2—Nb1—Nb1^{iii}	143.919 (8)	Nb1^{i}—Nb1—Nb1^{iv}	59.977 (5)
O1—Nb1—Nb1^{i}	134.05 (4)	Nb1^{ii}—Nb1—Nb1^{iv}	60.0
Cl1—Nb1—Nb1^{i}	96.23 (1)	Nb1^{iii}—Cl1—Nb1	72.45 (2)
Cl1^{i}—Nb1—Nb1^{i}	53.773 (8)	Nb1—Cl2—Nb1^{iv}	72.16 (2)

Cl2^{ii}—Nb1—Nb1^{i}	143.919 (8)	Nb1—O1—H1A	122.0
Cl2—Nb1—Nb1^{i}	96.01 (1)		

Symmetry codes: (i) *y*, −*x*+*y*, −*z*; (ii) −*y*, *x*−*y*, *z*; (iii) *x*−*y*, *x*, −*z*; (iv) −*x*+*y*, −*x*, *z*.