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Key indicators

Single-crystal X-ray study
 $T = 292$ K
Mean $\sigma(\text{C}-\text{C}) = 0.009$ Å
 R factor = 0.037
 wR factor = 0.094
Data-to-parameter ratio = 19.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Hexaaquadodeca- μ -chloro-hexaniobium(II,III) dichloride 2,2'-bipyridine trisolvate

The title compound, $[\text{Nb}_6\text{Cl}_{12}(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 3\text{C}_{10}\text{H}_8\text{N}_2$, is an example of a 'hybrid' inorganic-organic compound, where the inorganic and organic parts do not interact by covalent bonds but are joined by hydrogen bonding. The inorganic part contains a hexanuclear mixed-valence niobium cluster aqua cation $[\text{Nb}_6(\mu\text{-Cl})_{12}(\text{H}_2\text{O})_6]^{2+}$, with the typical $\{M_6X_{12}\}$ structure, and two Cl^- counter-ions. The organic part consists of two crystallographically independent 2,2'-bipyridine molecules; one is planar and lies on a centre of symmetry, and the other is twisted by $42.1(5)^\circ$. The Nb-Nb, Nb-Cl and Nb-O bond distances are close to those found in other salts of this cation. The inorganic and organic parts are joined together by an extended system of hydrogen bonds. Six of the 12 H atoms of the aqua ligands form hydrogen bonds with the N atoms of the bipyridine molecules, and the other six with Cl^- anions. At the same time, the bipyridine molecules use both N atoms in hydrogen bonding with two cluster cations. Each Cl^- anion forms three $\text{Cl} \cdots \text{H}-\text{O}$ bonds with the three cluster cations. The resulting three-dimensional framework shows a non-trivial example of a (12,3,2,2) connected net. The disposition and relative orientation of the cluster cations and the geometric requirements of the hydrogen-bonds dictate the conformations of the bipyridine molecules.

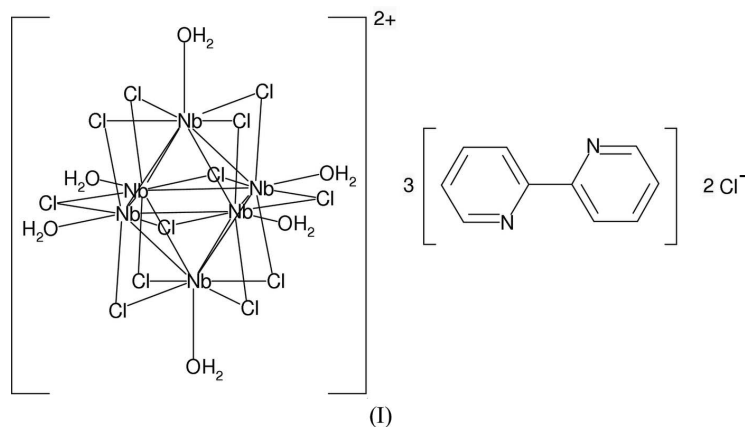
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Comment

The chemistry of niobium clusters has developed rapidly in recent years (Brnicevic, Kojic-Prodic *et al.*, 1995; Brnicevic, Planinic *et al.*, 1995; Brnicevic, 1999; Perrin, 1999; Prokopuk & Shriver, 1999). Facile procedures for the preparation of substituted compounds with an $\text{Nb}_6\text{Cl}_{12}$ cluster core enable new compounds with various apical ligands to be obtained.



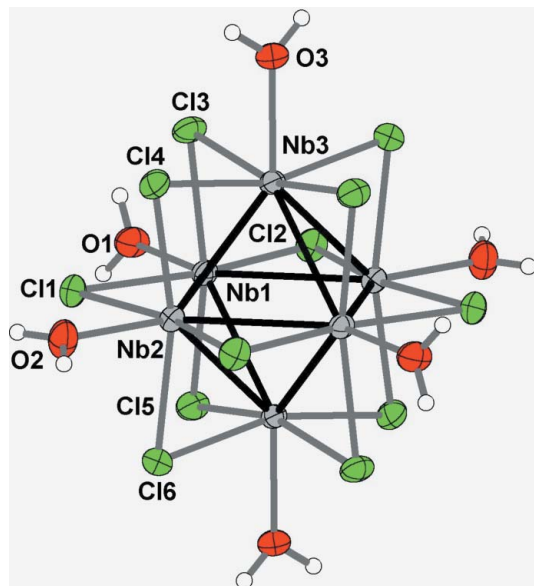


Figure 1
The cluster cation in the crystal structure of (I). Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operation $(-x, -y, -z)$.

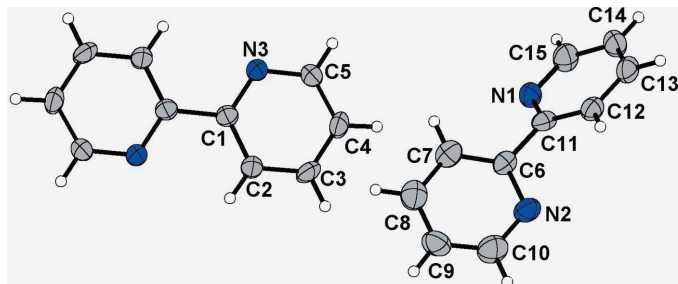


Figure 2
The organic molecules in the crystal structure of (I). Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operation $(-x, 1-y, 1-z)$.

The title compound, (I), is an example of a 'hybrid' inorganic-organic compound, where the inorganic and organic parts do not interact by covalent bonds but are joined by hydrogen bonds. The inorganic part contains a hexanuclear mixed-valence niobium cluster aqua cation, $[\text{Nb}_6(\mu\text{-Cl})_{12}(\text{H}_2\text{O})_6]^{2+}$ (Fig. 1), and two Cl^- counterions. The organic part consists of two crystallographically independent 2,2'-bipyridine molecules (Fig. 2).

The cluster core in the cation has the typical $\{M_6X_{12}\}$ structure of an octahedron of metal atoms with halogen bridges on each edge. In addition, there are six coordinated terminal water molecules, one per Nb atom. The whole cation lies on a centre of symmetry (Wyckoff position $1a$). The Nb–Nb, Nb–Cl and Nb–O bond distances (Table 1) are quite close to those found in other salts of this cation, namely $[\text{Nb}_6\text{Cl}_{12}(\text{H}_2\text{O})_6](\text{CH}_3\text{O})_2 \cdot 8\text{H}_2\text{O}$ (Brnicevic, Planinic *et al.*, 1995) and $[\text{Nb}_6\text{Cl}_{12}(\text{H}_2\text{O})_6](\text{CH}_3\text{O})_2 \cdot 0.25\text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$ (Brnicevic, Kojic-Prodic *et al.*, 1995).

The two crystallographically independent 2,2'-bipyridine molecules possess different conformations: one of them is

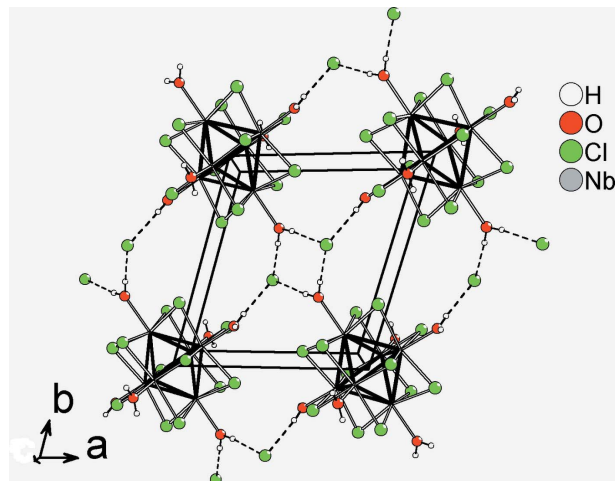


Figure 3
The crystal packing of (I), showing the inorganic layers without the bipyridine molecules. Hydrogen bonds are shown by dashed lines.

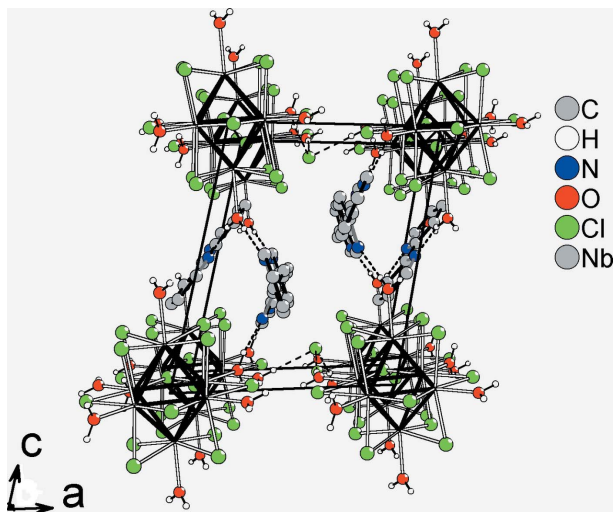


Figure 4
The crystal packing of (I), showing the inorganic layers joined by bipyridine molecules. Hydrogen bonds are shown by dashed lines. The H atoms of the bipyridine molecules have been omitted for clarity.

planar and located on an inversion centre, while the other is twisted by 42.1° and lies in a general position. The reason for this difference can be found in an analysis of the hydrogen bonding in the crystal, where all possible hydrogen bonds are realised (Table 2). Six of the 12 H atoms of the H_2O ligands form hydrogen bonds with the N atoms of the bipyridine molecules and the remaining six with Cl^- anions. At the same time, the bipyridine molecules use both N atoms in hydrogen bonds with two cluster cations. Each Cl^- anion forms three $\text{Cl} \cdots \text{H}-\text{O}$ hydrogen bonds with three cluster cations.

In the crystal packing one can select 'inorganic' layers of clusters and Cl^- anions joined together by hydrogen bonds (Fig. 3). These layers lie in the (001) plane. The bipyridine molecules join the layers by means of $\text{N} \cdots \text{H}-\text{O}$ hydrogen bonds (Fig. 4). The centrosymmetric planar bipyridine molecule joins clusters in the (0,1,0) and (0,0,1) positions, with a cluster-cluster distance of 14.304 Å. The twisted molecule

joins clusters in the (0,0,0) and (0,0,1) positions with a shorter cluster–cluster distance of 12.258 Å. This difference between the cluster–cluster distances results from the fact that the centre of the planar bipyridine molecule lies exactly on the line between the centres of the cations, while the centre of the twisted molecule is located away from this line (the centre–centre–centre angle is 114.8°). Taking into account the rigid geometry of the cluster cation, one can state that the positions of the cations and their relative orientations, along with the hydrogen-bonding geometry, dictate the conformations of the bipyridine molecules.

The resulting three-dimensional framework shows a non-trivial example of a (12,3,2,2) connected net (O’Keeffe *et al.*, 2000). According to the results of the ADS subprogram of the TOPOS4.0 program set (Blatov *et al.*, 2000) the topology of the hydrogen-bond net can be characterized by the total Schläfli symbol of $\{4^3\}2\{4^8;6^{22};8^{31};10^5\}\{4\}2\{6\}$.

Experimental

An aqueous solution (10 ml) of $K_4Nb_6Cl_{18}$ (50 mg, 0.037 mmol) was mixed with a solution of bpy (34.7 mg, 0.222 mmol) in ethanol (3 ml). The mixture was boiled for 30 min, and then left at room temperature. After one week, a dark-green solid, (I), was obtained. This was decanted, washed with ethanol and dried in air (yield 18.7 mg, 31.0%).

Crystal data

$[Nb_6Cl_{12}(H_2O)_6]Cl_2 \cdot 3C_{10}H_8N_2$	$Z = 1$
$M_r = 1630.41$	$D_x = 2.163 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.1546$ (12) Å	Cell parameters from 3551 reflections
$b = 11.2503$ (15) Å	$\theta = 2.5\text{--}28.2^\circ$
$c = 12.2583$ (11) Å	$\mu = 2.12 \text{ mm}^{-1}$
$\alpha = 74.822$ (4)°	$T = 292$ (2) K
$\beta = 74.551$ (4)°	Prism, dark green
$\gamma = 70.901$ (4)°	$0.09 \times 0.03 \times 0.01 \text{ mm}$
$V = 1251.8$ (3) Å ³	

Data collection

Bruker X8 APEX CCD area-detector diffractometer	5658 independent reflections
ω and φ scans	4317 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$R_{\text{int}} = 0.033$
$T_{\text{min}} = 0.871$, $T_{\text{max}} = 0.980$	$\theta_{\text{max}} = 27.5^\circ$
12802 measured reflections	$h = -13 \rightarrow 13$
	$k = -14 \rightarrow 14$
	$l = -11 \rightarrow 15$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 1.4105P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.094$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 1.27 \text{ e \AA}^{-3}$
5658 reflections	$\Delta\rho_{\text{min}} = -0.67 \text{ e \AA}^{-3}$
298 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

Nb1–Nb2 ⁱ	2.9213 (6)	Nb2–Cl1	2.4641 (12)
Nb1–Nb2	2.9239 (6)	Nb2–Cl2 ⁱ	2.4522 (12)
Nb1–Nb3	2.9128 (6)	Nb2–Cl4	2.4656 (13)
Nb1–Nb3 ⁱ	2.9141 (6)	Nb2–Cl6	2.4673 (13)
Nb1–Cl1	2.4731 (13)	Nb2–O2	2.228 (4)
Nb1–Cl2	2.4724 (13)	Nb3–Cl3	2.4679 (12)
Nb1–Cl3	2.4581 (13)	Nb3–Cl4	2.4621 (13)
Nb1–Cl5	2.4622 (12)	Nb3–Cl5 ⁱ	2.4719 (11)
Nb1–O1	2.214 (3)	Nb3–Cl6 ⁱ	2.4619 (13)
Nb2–Nb3 ⁱ	2.9204 (7)	Nb3–O3	2.219 (4)
Nb2–Nb3	2.9246 (7)		
Cl1–Nb1–Nb2 ⁱ	143.90 (3)	Cl6–Nb2–Nb1	96.85 (3)
Cl1–Nb1–Nb2	53.54 (3)	Cl6–Nb2–Nb3 ⁱ	53.58 (3)
Cl1–Nb1–Nb3	96.25 (3)	Cl6–Nb2–Nb3	143.20 (4)
Cl1–Nb1–Nb3 ⁱ	96.02 (3)	O2–Nb2–Nb1 ⁱ	135.36 (9)
Cl2–Nb1–Nb2 ⁱ	53.30 (3)	O2–Nb2–Nb1	134.99 (9)
Cl2–Nb1–Nb2	143.65 (3)	O2–Nb2–Nb3 ⁱ	135.54 (11)
Cl2–Nb1–Nb3	96.07 (3)	O2–Nb2–Nb3	134.82 (11)
Cl2–Nb1–Nb3 ⁱ	95.92 (3)	Cl3–Nb3–Nb1	53.59 (3)
Cl3–Nb1–Nb2 ⁱ	96.81 (3)	Cl3–Nb3–Nb1 ⁱ	143.59 (3)
Cl3–Nb1–Nb2	95.73 (3)	Cl3–Nb3–Nb2 ⁱ	96.61 (3)
Cl3–Nb1–Nb3	53.91 (3)	Cl3–Nb3–Nb2	95.50 (3)
Cl3–Nb1–Nb3 ⁱ	143.89 (3)	Cl4–Nb3–Nb1	96.75 (3)
Cl5–Nb1–Nb2 ⁱ	96.43 (3)	Cl4–Nb3–Nb1 ⁱ	95.65 (3)
Cl5–Nb1–Nb2	96.15 (3)	Cl4–Nb3–Nb2 ⁱ	144.00 (3)
Cl5–Nb1–Nb3	143.95 (3)	Cl4–Nb3–Nb2	53.65 (3)
Cl5–Nb1–Nb3 ⁱ	53.95 (3)	Cl5 ⁱ –Nb3–Nb1	143.65 (3)
O1–Nb1–Nb2 ⁱ	134.23 (11)	Cl5 ⁱ –Nb3–Nb1 ⁱ	53.65 (3)
O1–Nb1–Nb2	135.41 (11)	Cl5 ⁱ –Nb3–Nb2 ⁱ	96.02 (3)
O1–Nb1–Nb3	134.36 (10)	Cl5 ⁱ –Nb3–Nb2	96.13 (3)
O1–Nb1–Nb3 ⁱ	135.64 (10)	Cl6 ⁱ –Nb3–Nb1	95.42 (3)
Cl1–Nb2–Nb1 ⁱ	143.47 (3)	Cl6 ⁱ –Nb3–Nb1 ⁱ	97.23 (3)
Cl1–Nb2–Nb1	53.83 (3)	Cl6 ⁱ –Nb3–Nb2 ⁱ	53.75 (3)
Cl1–Nb2–Nb3 ⁱ	96.07 (3)	Cl6 ⁱ –Nb3–Nb2	144.08 (3)
Cl1–Nb2–Nb3	96.15 (3)	O3–Nb3–Nb1	135.15 (10)
Cl2 ⁱ –Nb2–Nb1 ⁱ	53.94 (3)	O3–Nb3–Nb1 ⁱ	134.84 (10)
Cl2 ⁱ –Nb2–Nb1	143.58 (3)	O3–Nb3–Nb2 ⁱ	134.47 (11)
Cl2 ⁱ –Nb2–Nb3 ⁱ	96.33 (3)	O3–Nb3–Nb2	135.17 (11)
Cl2 ⁱ –Nb2–Nb3	96.11 (3)	Nb2–Cl1–Nb1	72.63 (3)
Cl4–Nb2–Nb1 ⁱ	95.39 (3)	Nb2 ⁱ –Cl2–Nb1	72.77 (3)
Cl4–Nb2–Nb1	96.38 (3)	Nb1–Cl3–Nb3	72.50 (3)
Cl4–Nb2–Nb3 ⁱ	143.17 (3)	Nb3–Cl4–Nb2	72.81 (4)
Cl4–Nb2–Nb3	53.54 (3)	Nb1–Cl5–Nb3 ⁱ	72.40 (3)
Cl6–Nb2–Nb1 ⁱ	95.09 (3)	Nb3 ⁱ –Cl6–Nb2	72.66 (4)
N3–Cl1–Cl1 ⁱⁱ –N3 ⁱⁱ	180.000 (1)	N1–Cl11–Cl6–N2	137.9 (5)

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y + 1, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1–H11 \cdots N1 ⁱⁱⁱ	0.80 (4)	1.94 (5)	2.720 (5)	167 (6)
O1–H12 \cdots N3 ^{iv}	0.83 (4)	1.96 (2)	2.768 (5)	165 (6)
O2–H21 \cdots Cl7 ^v	0.84 (5)	2.31 (5)	3.136 (4)	170 (6)
O2–H22 \cdots N2 ^{vi}	0.83 (4)	1.93 (3)	2.740 (6)	162 (6)
O3–H31 \cdots Cl7 ^{iv}	0.82 (5)	2.27 (5)	3.095 (4)	172 (6)
O3–H32 \cdots Cl7 ^{vii}	0.82 (4)	2.34 (2)	3.145 (4)	167 (6)

Symmetry codes: (iii) $-x + 1, -y + 1, -z$; (iv) $-x, -y + 1, -z$; (v) $x - 1, y - 1, z$; (vi) $x - 1, y - 1, z - 1$; (vii) $x - 1, y, z$.

C-bound H atoms were positioned geometrically and refined as riding, with $C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H atoms of the coordinated water molecules were located in a difference electron-density map and refined with $U_{\text{iso}}(\text{H})$ fixed at 0.05 \AA^{-2} and O—

H bonds restrained to 0.82 (2) Å. The highest residual peak of 1.27 e Å⁻³ is situated 0.51 Å from atom Cl7.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Bruker, 2005); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: local programs.

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References

- Blatov, V. A., Shevchenko, A. P. & Serezhkin, V. N. (2000). *J. Appl. Cryst.* **33**, 1193.
- Brnicevic, N. (1999). *Metal Clusters in Chemistry*, Vol. 3, edited by P. Braunstein, L. A. Oro & P. R. Raithby, pp. 1551–1562. Weinheim: Wiley-VCH.
- Brnicevic, N., Kojic-Prodic, B., Luic, M., Kashta, A., Planinic, P. & McCarley, R. E. (1995). *Croat. Chem. Acta*, **68**, 861–875.
- Brnicevic, N., Planinic, P., McCarley, R. E., Antolic, S., Luic, M. & Kojic-Prodic, B. (1995). *J. Chem. Soc. Dalton Trans.* pp. 1441–1446.
- Bruker (2005). *APEX2* (Version 1.27), *SADABS* and *SHELXTL* (Version 6.22). Bruker AXS Inc. Madison, Wisconsin, USA.
- O’Keeffe, M., Eddaoudi, M., Li, H., Reineke, T. & Yanhi, O. M. (2000). *J. Solid State Chem.* **152**, 3–20.
- Perrin, C. (1999). *Metal Clusters in Chemistry*, Vol. 3, edited by P. Braunstein, L. A. Oro & P. R. Raithby, pp. 1563–1590. Weinheim: Wiley-VCH.
- Prokopuk, N. & Shriver, D. F. (1999). *Adv. Inorg. Chem.* **46**, 1–49.