

Ethylenediaminium niobium oxyfluoride

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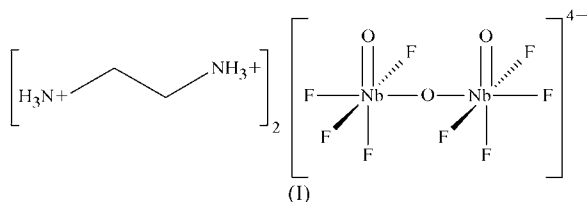
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The title compound, bis(ethylenediaminium) μ -oxo-bis[tetrafluorooxonio niobium(V)], $(C_2H_{10}N_2)_2[Nb_2O_3F_8]$, is a novel organically templated niobium oxyfluoride. It consists of isolated $[Nb_2O_3F_8]^{4-}$ octahedral dimers charge balanced by ethylenediaminium cations, two of which lie about inversion centres. Two NbO_2F_4 octahedra are fused through a common O atom to form the dimers. Characteristic short terminal $Nb=O$ bond lengths and longer $Nb-F$ and bridging $Nb-O$ bond lengths are observed, which result in the out-of-centre distortion of the octahedra, a manifestation of the second-order Jahn–Teller effect. Extensive hydrogen bonding between the dimers and the organic template is exhibited.

Comment

The title compound, (I), is the first organically templated niobium oxyfluoride. It also appears to be the first example of isolated dimeric niobium oxyfluoride units. In purely inorganic niobium oxyfluorides, a variety of building units have been reported: isolated $[NbOF_5]^{2-}$ octahedra are found in Li_2NbOF_5 (Galy *et al.*, 1969), and isolated pentagonal bipyramidal NbF_7 and $NbOF_6$ units are found in $Rb_5Nb_3OF_{18}$ (Agulyanskii *et al.*, 1991) and $Ba_4Nb_2O_3F_{12}$ (Crosnier-Lopez & Fourquet, 1993), respectively. The latter compound also contains *cis* corner-sharing octahedral tetramers. O-Atom-linked *trans* vertex-sharing chains are found in $(NH_4)[NbOF_4]$ (Pakhomov & Kaidalova, 1974). Welk *et al.* (2002) have exploited metal-organic complexes in ‘directing’ otherwise isolated $[NbOF_5]^{2-}$ ions into specific crystallographic orientations.

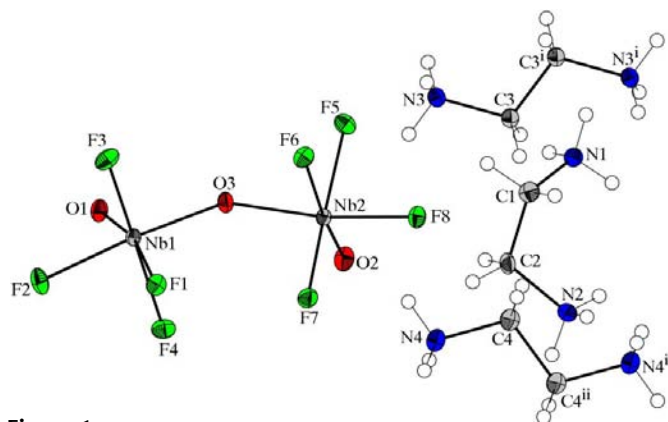


The main feature of most of the previously reported niobium oxyfluorides is the out-of-centre octahedral distortion. Electronic and bond-network effects lead to the char-

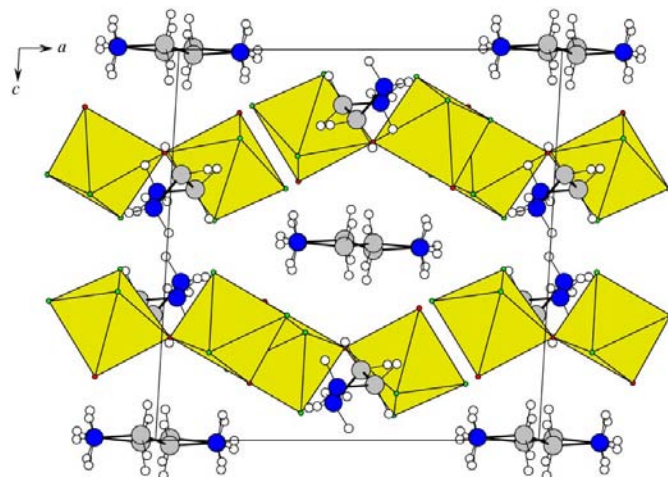
acteristic short $Nb=O$ bond length and the longer $Nb-X$ bond length *trans* to it. Along with non-centrosymmetry, the off-centre distortion is important in the non-linear properties of the structure. In the $[NbOF_5]^{2-}$ anion (*e.g.* Izumi *et al.*, 2005), the Nb atom is displaced from the centre of the octahedron towards the O atom to form a short $Nb=O$ bond and a longer $Nb-F$ bond.

$(C_2H_{10}N_2)_2[Nb_2O_3F_8]$ (Fig. 1) is built up from diprotonated ethylenediamine cations and dimeric $[Nb_2O_3F_8]^{4-}$ units. Each dimer consists of two NbO_2F_4 octahedra, which share corners with each other *via* one O atom.

Bond-valence sums (Table 2) show that some of the F atoms are heavily underbonded, and this is compensated by substantial hydrogen bonding (Table 1) to the organic cations. For example, the two F atoms *trans* to the short $Nb=O$ bonds (F1 and F6) accept three hydrogen bonds, while the two *trans* to the bridging O atom (F2 and F8) accept two each. Similarly, atom O1 is hydrogen bonded to two NH groups, while atom O2 is only bound to one, compatible with a small $s_{(ij)}$ of 1.48


Figure 1

The asymmetric unit of the title compound, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, -y, 1-z$.]


Figure 2

Projection of the structure down $[010]$, showing the stacking of the dimers and cations.

for the Nb1—O1 bond and a larger $s_{(ij)}$ of 1.61 for the Nb2—O2 bond. The bridging O3 atom does not require hydrogen bonding. All H atoms of the ethylenediaminium moieties partake in hydrogen bonding. In one of the octahedra (Nb1) there is a slight tendency for displacement of Nb towards an edge (O1—O3) rather than a vertex of the octahedron.

The complex hydrogen-bonding scheme results in the crystal packing shown in Fig. 2. The dimers are aligned along the [010] direction in a herring-bone fashion.

Experimental

Niobium pentoxide (0.2658 g), water (5 ml) and a 40% solution of HF (0.5 ml) were heated in a polypropylene bottle at 373 K for 1 h. The contents of the bottle were washed into a Teflon-lined steel autoclave with ethylene glycol (5 ml). To this mixture was added ethylenediamine (0.25 ml) to give a pH of 4. The mixture was heated at 463 K for 5 d. The pH increased to 6.5 over this time. The final product was filtered off, washed with water and allowed to dry overnight at room temperature.

Crystal data

$(\text{C}_2\text{H}_{10}\text{N}_2)_2[\text{Nb}_2\text{O}_3\text{F}_8]$	$D_x = 2.374 \text{ Mg m}^{-3}$
$M_r = 510.06$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 72 reflections
$a = 11.7121 (12) \text{ \AA}$	$\theta = 12\text{--}28^\circ$
$b = 10.1984 (10) \text{ \AA}$	$\mu = 1.71 \text{ mm}^{-1}$
$c = 11.9712 (12) \text{ \AA}$	$T = 125 (2) \text{ K}$
$\beta = 93.438 (2)^\circ$	Prism, colourless
$V = 1427.3 (2) \text{ \AA}^3$	$0.1 \times 0.1 \times 0.03 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	2608 independent reflections
φ and ω scans	2419 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	$R_{\text{int}} = 0.022$
$T_{\text{min}} = 0.829$, $T_{\text{max}} = 0.950$	$\theta_{\text{max}} = 25.4^\circ$
9021 measured reflections	$h = -14 \rightarrow 13$
	$k = -12 \rightarrow 12$
	$l = -13 \rightarrow 14$

Table 1

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

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N1—H9...F1 ⁱⁱⁱ	0.91	2.05	2.831 (3)	142
N1—H10...F4 ^{iv}	0.91	1.82	2.697 (3)	161
N1—H9...F4 ⁱⁱⁱ	0.91	2.17	2.922 (3)	140
N1—H11...O1 ^v	0.91	2.04	2.830 (3)	144
N2—H12...F6 ^{vi}	0.91	2.02	2.857 (3)	153
N2—H13...F2 ^v	0.91	1.93	2.752 (3)	150
N2—H14...F6 ^{iv}	0.91	1.87	2.690 (3)	148
N3—H15...F6	0.91	2.13	2.889 (3)	140
N3—H15...F8	0.91	2.16	2.862 (3)	133
N3—H16...O2 ⁱⁱⁱ	0.91	1.83	2.719 (3)	164
N3—H17...F4 ^{vii}	0.91	2.03	2.779 (3)	139
N3—H17...F3 ^{viii}	0.91	2.09	2.792 (3)	133
N4—H18...O1 ^{vii}	0.91	2.32	3.005 (4)	132
N4—H18...F8	0.91	2.37	2.909 (3)	118
N4—H18...F7	0.91	2.40	2.927 (3)	117
N4—H19...F2 ^{ix}	0.91	1.87	2.759 (3)	165
N4—H19...F1 ^{ix}	0.91	2.53	3.113 (3)	122
N4—H20...F5 ^{vi}	0.91	1.90	2.791 (3)	165

Symmetry codes: (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (v) $x + 1, y, z$; (vi) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (viii) $-x, -y + 1, -z + 1$; (ix) $-x, -y, -z + 1$.

Table 2

Bond valence parameters.

Atom	$\Sigma s_{(ij)}$	Atom	$\Sigma s_{(ij)}$
Nb1	5.22	F6	0.44 ^b
Nb2	5.29	F7	0.81 ^b
F1	0.54 ^b	F8	0.74 ^b
F2	0.60 ^b	O1	1.48 ^a
F3	0.82 ^b	O2	1.61 ^a
F4	0.77 ^b	O3	1.95 ^a
F5	0.76 ^b		

Notes: $s_{(ij)}$ values calculated for $B = 0.37$; (a) empirical (Brown & Altermatt, 1985); (b) extrapolated (Bresé & O'Keeffe, 1991).

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2 + 3.2384P]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.060$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.52 \text{ e \AA}^{-3}$
2608 reflections	$\Delta\rho_{\text{min}} = -0.57 \text{ e \AA}^{-3}$
190 parameters	
H-atom parameters constrained	

Crystals of (I) are monoclinic, in the space group $P2_1/n$, which was chosen from the systematic absences. H atoms were refined as riding on their carrier atoms [$\text{C—H} = 0.99 \text{ \AA}$, $\text{N—H} = 0.91 \text{ \AA}$, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{N})$].

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997) and SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 2001); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1851). Services for accessing these data are described at the back of the journal.

References

- Agulyanskii, A. I., Zavodnik, V. E., Kuznetsov, V. Ya., Sidorov, N. V., Stefanovich, S. Yu., Tsikaeva, D. V. & Kalinnikov, V. T. (1991). *Izv. Akad. Nauk SSSR Neorg. Mater.* **27**, 1055–1060.
- Brandenburg, K. (2001). *DIAMOND*. Version 2.1. Crystal Impact GbR, Bonn, Germany.
- Bresé, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Bruker (1997). *SMART*, *SAINTE* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Crosnier-Lopez, M. P. & Fourquet, J. L. (1993). *J. Solid State Chem.* **103**, 131–138.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Galy, J., Andersson, S. & Portier, J. (1969). *Acta Chem. Scand.* **23**, 2949–2954.
- Izumi, H. K., Kirsch, J. E., Stern, C. L. & Poeppelmeier, K. R. (2005). *Inorg. Chem.* **44**, 884–895.
- Pakhomov, V. I. & Kaidalova, T. A. (1974). *Kristallografiya*, **19**, 733–736.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. Release 97-2. University of Göttingen, Germany.
- Sheldrick, G. M. (1999). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Welk, M. E., Norquist A. J., Arnold, F. P., Stern, C. L. & Poeppelmeier, K. R. (2002). *Inorg. Chem.* **41**, 5119–5125.