

Disordering of the $[\text{NbOF}_5]^{2-}$ complex anions in bis(glycinium) pentafluoridooxidoniobate(V) and bis(β -alaninium) pentafluoridooxidoniobate(V) dihydrate

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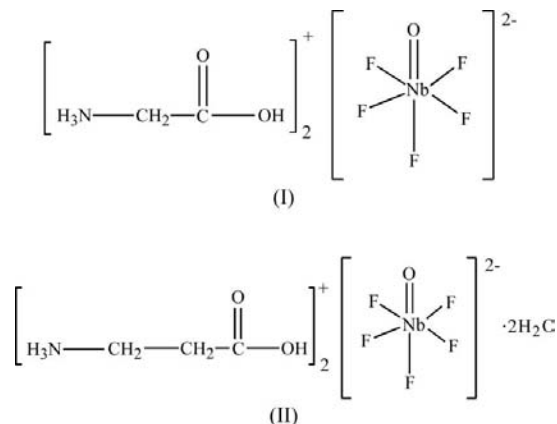
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The title compounds, $(\text{C}_2\text{H}_6\text{NO}_2)_2[\text{NbOF}_5]$, (I), and $(\text{C}_3\text{H}_8\text{NO}_2)_2[\text{NbOF}_5]\cdot 2\text{H}_2\text{O}$, (II), are built from isolated distorted octahedral $[\text{NbOF}_5]^{2-}$ complex anions, amino acid cations and water molecules [for (II)]. In the pentafluoridooxidoniobate(V) anions, the Nb and O atoms, and the F atoms in *trans* positions with respect to the O atoms, are disordered about an inversion centre for both structures. The Nb atoms are shifted from the inversion centres by distances of 0.1455 (1) and 0.1263 (2) Å for (I) and (II), respectively. The Nb=O and Nb–F(*trans*) bond lengths are 1.7952 (3) and 2.0862 (3) Å, respectively, for (I), and 1.8037 (7) and 2.0556 (7) Å for (II). In the crystal structures, cations and water molecules [for (II)] are linked to the $[\text{NbOF}_5]^{2-}$ anions *via* hydrogen bonds. This study demonstrates the possibility of true geometry determination of disordered $[\text{NbOF}_5]^{2-}$ complex anions in centrosymmetric structures.

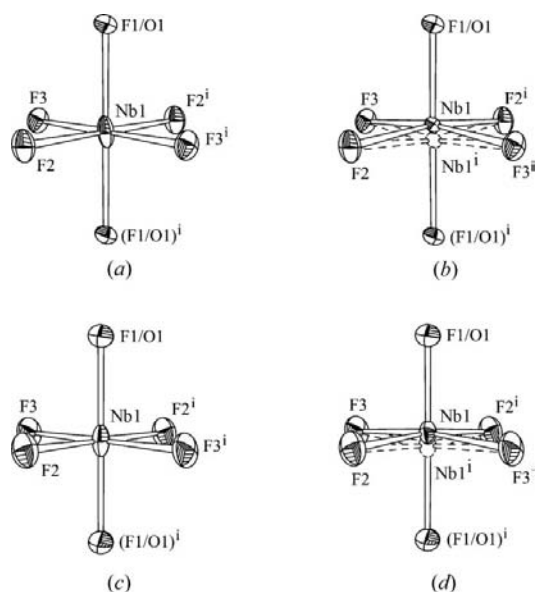
Comment

Recently, hybrid organic–inorganic compounds have been synthesized and intensively studied due to their exceptional importance for designing materials with structure-dependent properties, such as nonlinear optical activity, superionic conductivity, and piezoelectric and ferroelectric properties. Special attention has been given to compounds of the early transition metals with distorted coordination polyhedra in which the metal atoms are displaced from the centre of the polyhedron toward a vertex, edge or face. These metals include niobium, characterized by the displacement of the Nb atom from the centre of the octahedron in the $[\text{NbOF}_5]^{2-}$ anion in the direction of the O atom along the Nb=O bond, caused by electronic effects [‘primary’ distortion (Welk *et al.*, 2002; Izumi *et al.*, 2005)]. Sometimes in the $[\text{NbOF}_5]^{2-}$ anion, the Nb atom is located on or near an element of symmetry

that results in a statistical arrangement of ligands around it and this complicates analysis of the accurate geometry of the complex anions. The present work deals with the determination of the crystal structures of bis(glycinium) pentafluoridooxidoniobate(V), (I), and bis(β -alaninium) pentafluoridooxidoniobate(V) dihydrate, (II), and the study of the disordering of the $[\text{NbOF}_5]^{2-}$ complex anions in these compounds.



For both structures, the locations of the Nb atoms at the inversion centres were determined by direct methods and confirmed by the Patterson function. Thus, the structures of (I) and (II) were initially solved with the Nb atoms located at centres of inversion [Wyckoff position 2*a* for (I) and 1*a* for (II)] and atoms F1 and O1 occupying the same position. Least-squares refinement with anisotropic displacement parameters for all non-H atoms resulted in an $R [F^2 > 2\sigma(F^2)]$ value of 0.0579 for (I) and 0.0255 for (II). At this stage, the lengths of the Nb–F1/O1 bonds were approximately equal to the


Figure 1

The $[\text{NbOF}_5]^{2-}$ anions, showing the elongated displacement ellipsoids of the Nb1 atoms when situated on the inversion centre [(a) for (I) and (c) for (II)] and the disordered displacement of the Nb1 atoms from the inversion centre [(b) for (I) and (d) for (II)]. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x, -y + 1, -z + 1$, for (I); (i) $-x + 2, -y, -z + 2$, for (II).]

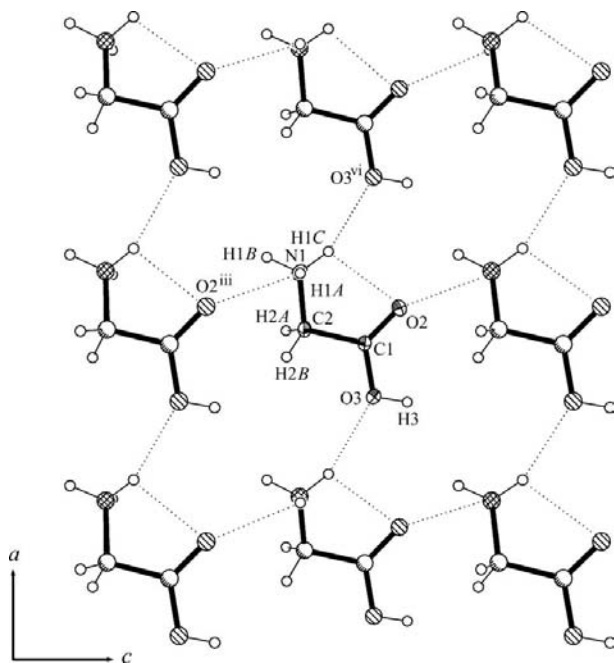


Figure 2

A fragment of the cationic layer of (I), viewed parallel to the ac plane. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dotted lines. [Symmetry codes: (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (vi) $x - 1, y, z$.]

average mean values of Nb=O and Nb–F(*trans*) bonds for ordered structures (Pushilin *et al.*, 2007; Zhu *et al.*, 2005; Zhu & Tang, 2005, 2006; Sarin *et al.*, 1977), namely 1.939 Å for (I) and 1.930 Å for (II). Analysis of the anisotropic displacement parameters showed that the Nb1 atoms had significant thermal displacement along the Nb1–F1/O1 directions in both structures (Fig. 1*a* and 1*c*). The maximal axis of the Nb1 displacement ellipsoid (σ_1) had angles with the Nb1–F1/O1 bond of 8° for (I) and 1° for (II), which make no physical sense, since the Nb=O bond is strongest in $[\text{NbOF}_5]^{2-}$ anions (Kharitonov & Buslaev, 1964; Welk *et al.*, 2002; Izumi *et al.*, 2005). In addition, for difference electron-density syntheses with isotropic displacement parameters for the Nb1 atoms, the highest peaks ($Q1$) [$28 \text{ e } \text{Å}^{-3}$ for (I) and $10 \text{ e } \text{Å}^{-3}$ for (II)] were located along the Nb1–F1/O1 bonds at distances from the Nb1 atoms of 0.33 and 0.47 Å for (I) and (II), respectively. In our opinion, the above factors indicate displacement of the Nb1 atoms from the centres of inversion towards the O atoms along the Nb1–F1/O1 directions. We have checked this assumption by placing the Nb1 atoms approximately in the middle of the Nb1··· $Q1$ distances with half-occupancy of the Nb1 sites. Refinement led to determination of the Nb1 positions at distances of 0.1455 (1) Å for (I) and 0.1263 (2) Å for (II) from the centres of inversion and demonstrated satisfactory anisotropy of the Nb1 atoms (Fig. 1*b* and 1*d*) [the angle between σ_1 and the Nb1–F1/O1 direction is 54° for (I) and 37° for (II)]. The resulting geometric parameters of the $[\text{NbOF}_5]^{2-}$ anion are comparable with those of the same anions for ordered structures. For similar reasons, the Nb atom

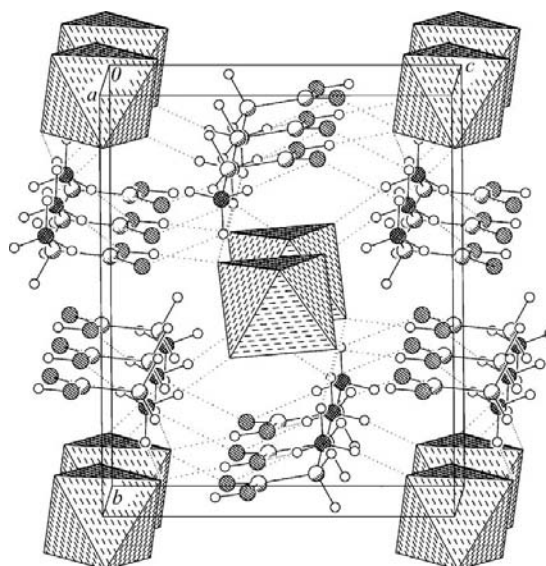


Figure 3

The structure of (I), viewed along the a axis.

was moved from the twofold rotation axis in the $\text{Na}_2[\text{NbOF}_5]$ structure (Stomberg, 1984), which also resulted in a more accurate geometry for the $[\text{NbOF}_5]^{2-}$ anion.

Due to the statistical distribution of the Nb atoms in (I) and (II), one should also expect splitting of the ligand positions. Refinement of models where ligand positions were split into two sites was performed for both structures. However, in our experiments, these positions were indistinguishable within the limits of experimental error. Thus, in (I) and (II) the complex anions are statistically disordered about an inversion centre. The Nb atoms are coordinated by five F atoms and one O atom, forming distorted octahedra. The Nb–F bond in a *trans* position to the Nb=O bond is significantly longer than the other four Nb–F bonds in the polyhedra (Tables 1 and 3). The Nb1 atoms are displaced from the equatorial planes of the octahedra in the direction of the axial O1 atoms by 0.1455 (1) and 0.1263 (2) Å for (I) and (II), respectively.

The asymmetric unit of (I) contains one-half of an $[\text{NbOF}_5]^{2-}$ anion and one glycinium cation. The glycinium cation is protonated on the amine group and thus carries a positive charge. The C1–O3 bonds [1.3169 (4) Å] are much longer than C1–O2 [1.2158 (4) Å], indicating localized single and double bonds, respectively. The glycinium cations are linked by intermolecular N–H···O hydrogen bonds to form layers parallel to the ac plane (Fig. 2). By a combination of N–H···F, N–H···O and O–H···F hydrogen bonds (Table 2 and Fig. 3), some of which are weak and bi- or trifurcated, the layers are linked to the $[\text{NbOF}_5]^{2-}$ anions. It should be noted that the structure includes two short O–H···F/O hydrogen bonds between the hydroxyl groups of the glycinium cations and the axial F1 and O1 atoms having the highest negative charge in the $[\text{NbOF}_5]^{2-}$ anion (Izumi *et al.*, 2005). Also, in the structure of (I), there is a very weak noncovalent interaction, *viz.* F3(δ^-)···C1ⁱⁱⁱ(δ^+) [2.8446 (5) Å; symmetry code: (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$], which is slightly less than the sum of the van der

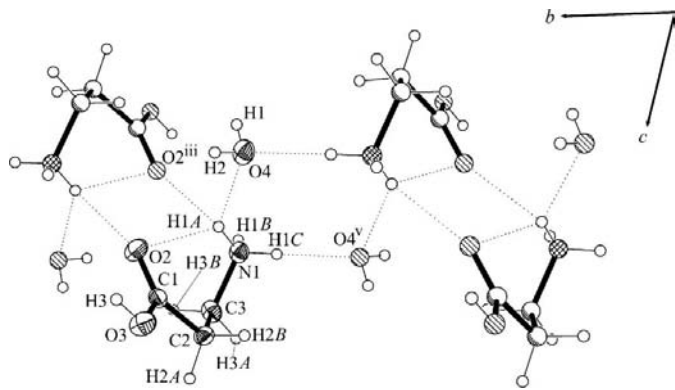


Figure 4
A fragment of the chain of hydrogen-bonded cations and water molecules of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dotted lines. [Symmetry codes: (iii) $-x + 1, -y + 2, -z + 1$; (v) $-x + 1, -y + 1, -z + 1$.]

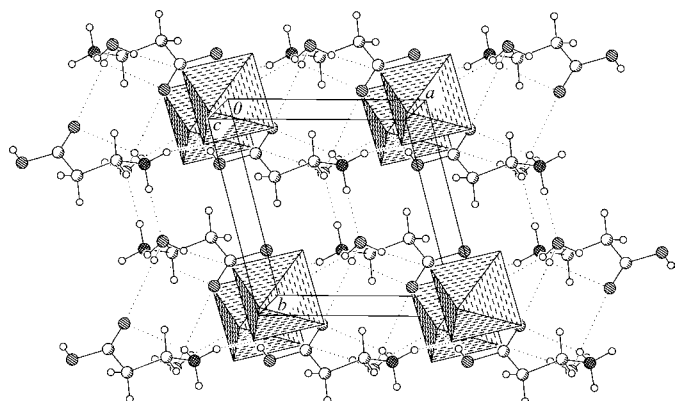


Figure 5
The structure of (II), viewed along the *c* axis.

Waals radii of F and C atoms (3.17 Å; Bondi, 1964). Similar short contacts between the F atom and the C atom of a carboxyl group are also present in the structures of bis(DL-valinium) pentafluoridooxidoniobate(V) (2.840 Å; Pushilin *et al.*, 2007), sodium tris(glycinium) bis(hexafluorosilicate) glycine trisolvate (2.870 Å; Narayana *et al.*, 2007) and 4-methylbenzoic acidium hexafluoroarsenate *p*-toluic acid (2.920 and 2.940 Å; Lindeman *et al.*, 2005).

The asymmetric unit of (II) contains one-half of an $[\text{NbOF}_5]^{2-}$ anion, one β -alaninium cation and one water molecule. The positive charge of the cation is localized on the amine group. The single (C1–O3) and double (C1=O2) bonds in the carboxyl group are 1.3270 (11) and 1.2097 (10) Å, respectively. The cations and water molecules are linked by N–H···O hydrogen bonds to form chains along the *b* axis and these chains are packed into layers parallel to the *ab* plane (Fig. 4 and Table 4). The anions, cations and water molecules are linked by a network of O–H···F and N–H···F hydrogen bonds into a three-dimensional framework (Fig. 5). As in (I), the shortest hydrogen bonds are formed with atoms F1 and O1 of the $[\text{NbOF}_5]^{2-}$ anion.

Experimental

Compound (I) was synthesized by the reaction of Nb_2O_5 (1.33 g, 5 mmol) with glycine (1.50 g, 20 mmol) in a solution of hydrofluoric acid (48%, 40 ml). The solution was allowed to evaporate slowly at room temperature. After a few days, colourless crystals suitable for X-ray diffraction were obtained. These were separated from the solution, washed with a small amount of acetone and dried to a constant weight in air. Compound (II) was synthesized using a route similar to that for the preparation of (I), *viz.* by the reaction of Nb_2O_5 (1.33 g, 5 mmol) with β -alanine (1.78 g, 20 mmol) in a solution of hydrofluoric acid (48%, 40 ml).

Compound (I)

Crystal data

$(\text{C}_2\text{H}_6\text{NO}_2)_2[\text{NbOF}_5]$
 $M_r = 356.07$
Monoclinic, $P2_1/c$
 $a = 5.3532$ (1) Å
 $b = 10.8585$ (3) Å
 $c = 8.9913$ (2) Å
 $\beta = 90.022$ (1)°

$V = 522.64$ (2) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 1.24$ mm⁻¹
 $T = 173$ (2) K
0.28 × 0.14 (radius) mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: for a sphere (SADABS; Bruker, 2003)
 $T_{\min} = 0.669$, $T_{\max} = 0.723$

19292 measured reflections
5525 independent reflections
5027 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.075$
 $S = 1.11$
5525 reflections

85 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 1.00$ e Å⁻³
 $\Delta\rho_{\min} = -0.95$ e Å⁻³

Table 1

Selected bond lengths (Å) for (I).

Nb1–O1	1.7952 (3)	Nb1–F2 ⁱ	1.9484 (3)
Nb1–F1 ⁱ	2.0862 (3)	Nb1–F3 ⁱ	1.9233 (3)
Nb1–F2	1.9218 (3)	Nb1–F3	1.9264 (3)

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

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<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>
O3–H3···(F1/O1) ⁱⁱ	0.84	1.69	2.5268 (4)	174
N1–H1A···O2 ⁱⁱⁱ	0.91	2.45	2.9149 (5)	112
N1–H1A···(F1/O1) ^{iv}	0.91	2.25	2.8259 (4)	120
N1–H1A···F3 ^v	0.91	2.25	2.8640 (4)	124
N1–H1B···F2	0.91	1.84	2.7264 (4)	164
N1–H1C···O3 ^{vi}	0.91	2.21	3.0707 (4)	158
N1–H1C···O2	0.91	2.27	2.7121 (4)	109

Symmetry codes: (ii) $x + 1, y, z - 1$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (iv) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (v) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x - 1, y, z$.

Table 3

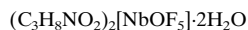
Selected bond lengths (Å) for (II).

Nb1–F1 ⁱ	2.0556 (7)	Nb1–F2 ⁱ	1.9443 (7)
Nb1–O1	1.8037 (7)	Nb1–F3	1.9420 (7)
Nb1–F2	1.9186 (7)	Nb1–F3 ⁱ	1.9129 (7)

Symmetry code: (i) $-x + 2, -y, -z + 2$.

Compound (II)

Crystal data

 $M_r = 420.15$ Triclinic, $P\bar{1}$ $a = 6.9552$ (8) Å $b = 7.2092$ (8) Å $c = 8.0205$ (9) Å $\alpha = 74.609$ (2)° $\beta = 86.223$ (2)° $\gamma = 74.016$ (2)° $V = 372.74$ (7) Å³ $Z = 1$ Mo $K\alpha$ radiation $\mu = 0.90$ mm⁻¹ $T = 203$ (2) K $0.27 \times 0.25 \times 0.24$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2003)

 $T_{\min} = 0.794$, $T_{\max} = 0.814$

4033 measured reflections

2215 independent reflections

2114 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.021$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.025$ $wR(F^2) = 0.064$ $S = 1.15$

2215 reflections

108 parameters

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.53$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.56$ e Å⁻³

Table 4

Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3-H3 \cdots (F1/O1)^{ii}$	0.83	1.79	2.6143 (9)	170
$N1-H1A \cdots O2$	0.90	2.29	2.9159 (11)	126
$N1-H1A \cdots O4$	0.90	2.37	3.0766 (12)	135
$N1-H1A \cdots O2^{iii}$	0.90	2.45	2.8660 (10)	108
$N1-H1B \cdots F2^{iv}$	0.90	2.04	2.8069 (10)	142
$N1-H1C \cdots O4^v$	0.90	1.90	2.8019 (12)	175
$O4-H1 \cdots (F1/O1)^v$	0.761 (14)	1.979 (15)	2.7201 (9)	164.6 (15)
$O4-H2 \cdots F3^{vi}$	0.836 (16)	1.967 (16)	2.7923 (10)	168.9 (16)

Symmetry codes: (ii) $-x+2, -y+1, -z+1$; (iii) $-x+1, -y+2, -z+1$; (iv) $-x+1, -y+1, -z+2$; (v) $-x+1, -y+1, -z+1$; (vi) $x, y+1, z-1$.

The Nb1 atoms were refined with site occupancies of 0.5. Atoms F1 and O1 were refined together, assuming that their positional and displacement parameters were the same, with site occupancies of 0.5. For the glycinium and β -alaninium cations, after checking their presence in difference maps, all H atoms were placed in geometrically

idealized positions and refined in the riding-model approximation, with C—H = 0.99 or 0.98 Å, N—H = 0.91 or 0.90 Å and O—H = 0.84 or 0.83 Å, and with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C,N,O})$. For the water molecules, the H atoms were located in a difference map and refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

For both compounds, data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: XP in SHELXTL; software used to prepare material for publication: publCIF (Westrip, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3082). Services for accessing these data are described at the back of the journal.

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