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Intramolecular mobility and phase transitions in ammonium oxofluoroniobates $(NH_4)_2NbOF_5$ and $(NH_4)_3NbOF_6$, a NMR and DFT study

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ABSTRACT

Molecular structure, ionic mobility and phase transitions in six- and seven-coordinated ammonium oxofluoroniobates $(NH_4)_2NbOF_5$ and $(NH_4)_3NbOF_6$ were studied by ^{19}F, ^{1}H NMR and DFT calculations. Equatorial fluorine atoms (F_{eq}) in $[NbOF_5]^{2-}$ and $[NbOF_6]^{3-}$ are characterized by high ^{19}F NMR chemical shifts while axial fluorine atoms (F_{ax}) have those essentially lower. The high-temperature ionic mobility in $(NH_4)_2NbOF_5$ does not stimulate the ligand exchange $F_{eq} \leftrightarrow F_{ax}$, whereas it is observed in $(NH_4)_3NbOF_6$ as pseudorotation typical for seven-coordinated polyhedra. The transformation of pentagonal bipyramidal structure (BP) of $[NbOF_6]^{3-}$ into capped trigonal prismatic (CTP) one takes place during the phase transition (PT) at 260 K. The PT of order-disorder type in $(NH_4)_2NbOF_5$ is accompanied by transition of anionic sublattice to a rigid state. The ^{19}F and ^{1}H NMR data corroborate the independent motions of NH_4 groups and anionic polyhedra in $(NH_4)_2NbOF_5$ while they are coordinated in $(NH_4)_3NbOF_6$.

1. Introduction

The $[NbOF_5]^{2-}$ and $[NbOF_6]^{3-}$ anions are inherently acentric and have polarizable metal–oxygen bonds. In view of this they are potential candidates for use in new second-harmonic-generating (SHG) materials. However, these acentric anions are virtually always found to crystallize in centrosymmetric space groups, thus eliminating possible SHG effects [1]. The O/F ordering in a noncentrosymmetric space group has been achieved with the $[NbOF_5]^{2-}$ anion in inorganic–organic hybrid compounds with cluster [2] and chain motifs [3]. In inorganic solid-state environment, the individual Nb–O and Nb–F bonds were recently found [4] to be ordered in noncentrosymmetric $KNaNbOF_5$ which exhibits the SHG property.

No SHG responses were observed in ammonium oxofluoroniobates $(NH_4)_2NbOF_5$ and $(NH_4)_3NbOF_6$, in spite of the fact that their crystal structures were solved as noncentrosymmetric [5,6]. Both compounds are characterized by orientational dynamic disorder; their structures are of twin nature and appreciably pseudo-centrosymmetric. Noncentrosymmetric space group *F*23 was preferred in the case of $(NH_4)_3NbOF_6$, since the refinement of the structure in the space group *Fm*3*m* yielded abnormally short X–X distances in the pentagonal bipyramid MX_7 (X = F, O). The Nb atom is statistically distributed over the position 24f, so that the pentagonal bipyramid MX_7 has twelve equivalent orientations (four orientations along each of the unit cell axes). The displacement of the Nb atom from the inversion center towards the axial atom X1 by 0.14 Å specifies the latter as oxygen with Nb–O distance of 1.75 Å which is similar to the respective distance in ordered α-$NaNbOF_6$ (1.74 Å) found by Stomberg [7]. One of three crystallographically independent ammonium groups of the structure is disordered over six or twelve equivalent orientations.

Polarized optical [8] and calorimetric studies [9] of $(NH_4)_3NbOF_6$ reveal that during the cooling process the compound undergoes order-disorder phase transitions from cubic to tetragonal and, further, to monoclinic phase with respective entropy changes Rln2.7 and Rln38.3 at around 260 K. To explain such a large entropy change, it is necessary to know the crystal structure of the distorted low-temperature phase; however, structural determination attempted at low temperatures has failed. The diffraction pattern exhibited an overlap of those originating from multiple low-symmetry domains formed by correlated motion of anionic polyhedra and ammonium groups connected via hydrogen bonds.

No fixed hydrogen bonds are formed in the crystal structure of $(NH_4)_2NbOF_5$ at room temperature [5]. Both niobium octahedra and ammonium tetrahedra are reoriented dynamically. Three spatial orientations of $[NbOF_5]^{2-}$ around the pseudo three-fold axis arise from reorientational motion which forces a central atom to displace from the symmetrical position that allows identification

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of O and F atoms in a separate orientation of octahedron. Thus, it becomes possible to distinguish between oxygen and fluorine atoms by X-ray diffraction under dynamic O/F disorder. The Nb–O distances in two crystallographically independent [$Nb1OF_5$] and [$Nb2OF_5$] octahedra are equal to 1.734(1) Å, and equatorial F atoms are disposed at 1.90–1.95 Å from Nb. Niobium is shifted from the equatorial plane towards the O atom by 0.23 and 0.20 Å, respectively, so the *trans* Nb–F bond is longer (2.09–2.12 Å) that is in good agreement with the [$NbOF_5$] geometry in ordered structures [1,4].

As the temperature decreases, the compound undergoes two phase transitions which was confirmed by studying polarization-optical [10], thermal and dielectric properties of $(NH_4)_2NbOF_5$ [11]. It has been established that the structural phase transitions $Cmc2_1 \rightarrow C2 \rightarrow Ia$ observed at the temperatures $T(1) = 258$ K and $T(2) = 219$ K exhibited a nonferroelectric nature. Moreover, barocaloric effect was estimated near structural order-disorder phase transitions in $(NH_4)_2NbOF_5$. It was found that hydrostatic pressure was an effective tool to change the entropy of compounds with ordering ionic groups in the structure and realize the significant caloric effects comparable with the values of electro- and magnetocaloric effects, characteristic for a number of materials, considered as promising solid refrigerants [12,13].

In this paper, phase transitions in $(NH_4)_2NbOF_5$ and $(NH_4)_3NbOF_6$ are considered from the ionic mobility standpoint, since it is clear that changes in dynamic behavior of the complex investigated are responsible for the phase transitions at lower temperatures. The study is focussed on the problem of central ion coordination by different ligands (O^{2-} and F^-) and its influence on the intramolecular dynamics.

2. Results and discussion

2.1. Ionic mobility in $(NH_4)_2NbOF_5$

The ^{19}F NMR spectra of $(NH_4)_2NbOF_5$ and the character of their temperature transformations are presented in Fig. 1. In general, they are similar to those of ammonium oxofluorotitanates $(NH_4)_3TiOF_5$ and Rb_2KTiOF_5 we studied recently [14,15]. At lower temperatures (below 240 K), the observed shape of the ^{19}F NMR spectra (Fig. 2) is determined by structural nonequivalence of fluorine atoms in the $NbOF_5$ octahedron and the chemical shift anisotropy. Experimental and calculated parameters of the ^{19}F NMR chemical shift tensors are shown in Table 1. Only qualitative agreement between experimental and calculated parameters, which can be explained by anionic orientational vibrations and Coulomb compression (pressure) in the crystal lattice, can be observed. The large value of the second moment ($S_2(F) \approx 130$ G^2) at 150–220 K provides the evidence of the rigidity of fluorine positions in the crystal lattice. In the temperature range of 240–270 K, a strong decrease of $S_2(F)$ to 40 G^2 and a sharp change of spectral shape were observed similarly to those of $(NH_4)_3TiOF_5$ which were connected with the phase transition and appearance of local isotropic motions in anionic sublattice. The data obtained are in agreement with the thermo-chemical results for $(NH_4)_2NbOF_5$ [10,11] indicating to two PT at 220 and 260 K.

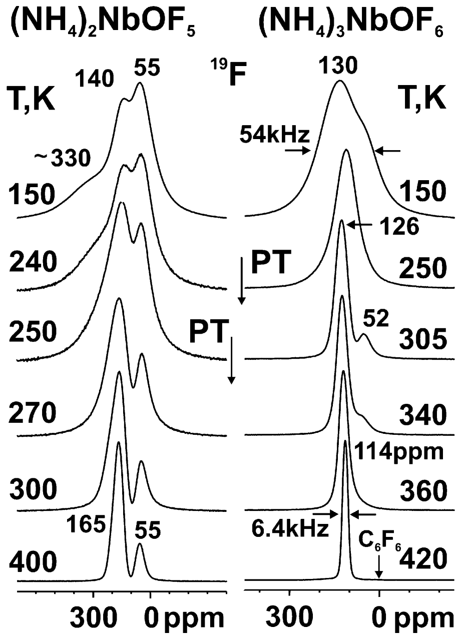

Fig. 1. ^{19}F NMR spectra of $(NH_4)_2NbOF_5$ (left) and $(NH_4)_3NbOF_6$ at some temperatures. Reference: C_6F_6.

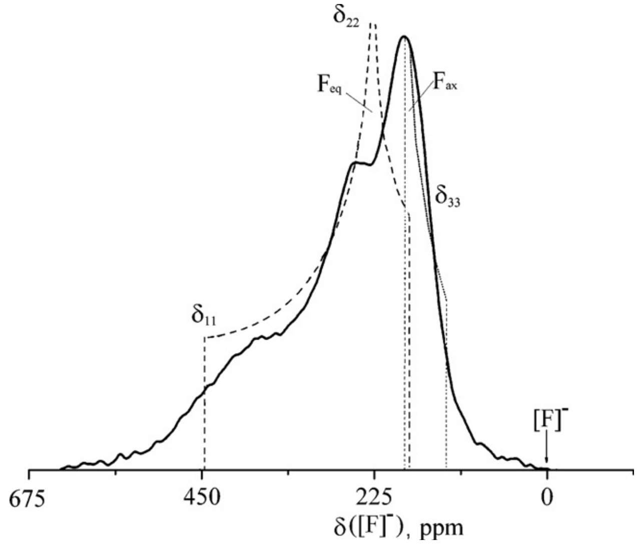

Fig. 2. ^{19}F NMR spectrum of $(NH_4)_2NbOF_5$ at 150 K. Reference: $[F]^-$. Solid line – experimental; dotted line – idealized fine structure caused by chemical shift anisotropy.

Above 270 K, the spectrum is described by two lines at a distance of 110 ppm that allows observing a well resolved two-component spectrum with the intensities ratio of ≈4:1 (Fig. 1). Taking into account the NMR data for $(NH_4)_3TiOF_5$) [14,15], these two lines can be attributed to equatorial and axial fluorines (F_{eq} and F_{ax}) in octahedral $[NbOF_5]^{2-}$. The data obtained also confirm the absence of any $F_{eq} \leftrightarrow F_{ax}$ exchange and intramolecular dynamics of the pseudorotaion type (Bailar twist [16]) in $(NH_4)_2NbOF_5$ below 400 K.

The F_{ax} chemical shift (55 ppm) does not virtually change in the temperature range of 150–400 K. Since these fluorine atoms are also characterized by the C_4 axial symmetry, they should be met the equation: $\delta_{11}([F]^-) = \delta_{22}([F]^-) = \delta_{\perp}([F]^-)$. The chemical shift anisotropy of this component is insignificant, so all three main components of the second rank tensor are equal, and a line shape is determined mainly by dipole–dipole interaction of magnetic nuclei.

Another situation is in the case of the F_{eq} component at lowering the temperature from 300 to 150 K. Below 200 K, the ^{19}F NMR spectrum is characterized by "fine" structure which permits determining the value of two components of the chemical shift tensor, $\delta_{11}([F]^-)$ and $\delta_{22}([F]^-$, corresponding to the magnetic field orientation perpendicular to the Nb–F bond. A value of the third component $\delta_{33}([F]^-)$ can be calculated from the formula for

Table 1
Experimental and calculated parameters of main components of CS F ^{19}NMR tensors (in ppm) in *cis*-positions in $[NbOF_5]^{2-}$ and $[NbOF_6]^{3-}$ complex anions.

Compound/anion	$\delta_{11}([F_{eq}]^-)$	$\delta_{22}([F_{eq}]^-)$	$\delta_{33}([F_{eq}]^-)$	$\delta_{iso}([F_{eq}]^-)$	$\delta_{iso}([F_{ax}]^-)$
$(NH_4)_2NbOF_5$ (exper.)	450 ± 25	264 ± 10	153 ± 20	289 ± 3	179 ± 3
$[NbOF_5]^{2-}$ (calc. C_{4v})	432	140	118	230	100
$(NH_4)_3NbOF_6$ (exper.)	–	260 ± 20	–	250 ± 3	175 ± 3
$[NbOF_6]^{3-}$ (calc. C_{5v})	283	200	56	180	45

Reference: $[F]^-$.

$\delta_{iso}([F]^-)$:

$$\delta_{iso}([F]^-) = \frac{1}{3}[\delta_{11}[(F)^-] + \delta_{22}([F]^-) + \delta_{33}([F]^-)] \qquad (1)$$

Inequality of $\delta_{11}([F]^-)$ and $\delta_{22}([F]^-)$ is the evidence of non-axial Nb–F chemical bonds which are described by the asymmetry parameter of the chemical shift tensor η:

$$\eta = \frac{[\delta_{11}([F]^-) - \delta_{22}([F]^-)]}{\delta_{iso}([F]^-) - \delta_{33}([F]^-)} \qquad (2)$$

The ^{1}H NMR spectra of $(NH_4)_2NbOF_5$ consist of a single symmetrical line the width (ΔH) of which decreases from 31.8 to ≈23 kHz during the temperature rising from 180 to 450 K. The observed line shape and width are typical for isotropic reorientations of ammonium groups which contribute mainly into ionic mobility in cationic sublattice of this compound at 180–450 K. Decreasing of S_2(H) at rising the temperature (Fig. 3) is induced, most probably, by the H–F dipole–dipole interactions as a result of the high ionic mobility in fluoride sublattice above 250 K. In accordance with our structural data [5], no hydrogen bonds are formed at RT, and NH_4 groups and $NbOF_5$ octahedra reorient independently. At lower temperature, two hydrogen bonds are formed after the first PT and octahedral rotation is absent (rigid anionic sublattice) while ammonium groups are not fully ordered. Below the second PT, all structural units are ordered in the crystal.

2.2. Ionic mobility in $(NH_4)_3NbOF_6$

The ^{19}F NMR low temperature spectrum of $(NH_4)_3NbOF_6$ (at 150 K) is represented by asymmetric line with the line width of ≈54 kHz (Figs. 1 and 4) and the second moment of ≈40 G^2, that indicates that the anionic state of fluoride sublattice is close to rigid lattice. The spectrum simulation on two symmetrical lines with the chemical shifts of 146 and 56 ppm (relatively to C_6F_6) and the intensities ratio of 2:1 (Fig. 4) corresponds to $[NbOF_6]^{3-}$ in the form of capped trigonal prism of C_{2v} symmetry.

When the temperature rises, the observed transformation of spectrum shape (Fig. 1) and decreasing of S_2(F) (Fig. 5) indicate to the appearance of ionic mobility in the fluoride sublattice. At 150–220 K, the spectrum narrows to 26 kHz and its asymmetry disappears. At further temperature increasing to 250 K, the ΔH and S_2(F) values remain virtually unchanged (Figs. 1 and 5). The other decrease of S_2(F) begins above 250 K, and a symmetrical line transforms into the two-component one that is consistent with the PT of order-disorder type [8,9] connected, most probably, with the transition of anionic polyhedron from the rotation around local four-fold axis (or around two-fold axis of molecule) to isotropic reorientations. The 280–320 K ^{19}F NMR spectra consist of two lines with the integral intensities ratio of ≈5:1 with chemical shifts of 126 and 52 ppm, respectively (Fig. 1). Such a transformation indicates to the structural change of coordination polyhedron from CTP to PB (pentagonal bipyramid) of C_{5v} symmetry in accordance with our X-ray data for $(NH_4)_3NbOF_6$ [6]. The PB geometry is essentially non-ideal with five Nb–F_{eq} of 1.98–2.11 Å and Nb–F_{ax} of 2.03 Å.

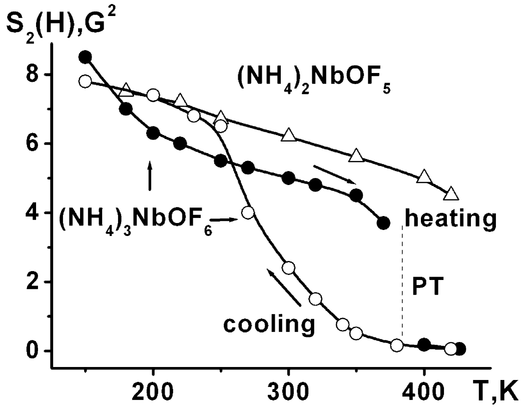

Fig. 3. Temperature dependences of the second moment of the ^{19}F NMR spectra for ammonium oxofluoroniobates $(NH_4)_2NbOF_5$ and $(NH_4)_3NbOF_6$ (B_o = 7.05 T).

Above 340 K, the spectrum transforms into a single line with the chemical shift of 114 ppm, the width of which decreases with the temperature rising. It should be noted that the line position corresponds to the center of gravity of two-component spectrum, $\langle\delta\rangle = 1/6\ (5 \times 126 + 52) \approx 114$ ppm. This means that the fast $F_{eq} \leftrightarrow F_{ax}$ intramolecular exchange takes place at higher temperatures. It is also worth mentioning that the chemical shift of high-temperature line corresponds to the center of gravity position of low-temperature spectrum, $\langle\delta\rangle = 1/3\ (2 \times 146 + 56) = 116$ ppm, which is consistent with the experiment (taking into account the error of δ determination at low temperatures). The data obtained indicate definitely to non-rigidity of $[NbOF_6]^{3-}$ polyhedron with the $F_{eq} \leftrightarrow F_{ax}$ intramolecular dynamics when local symmetry rises from C_{2v} to C_{5v}.

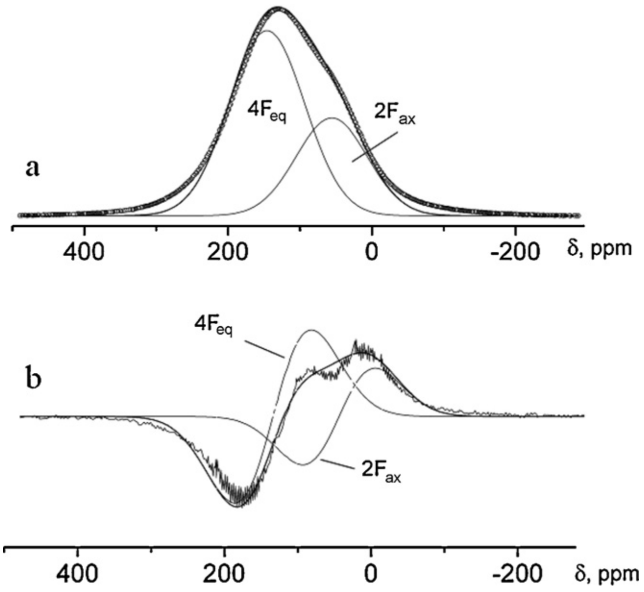

Fig. 4. ^{19}F NMR spectrum of $(NH_4)_3NbOF_6$ (a) and its first derivative (b). T = 150 K. Reference: C_6F_6. Continuous lines – the best fit to experiment.

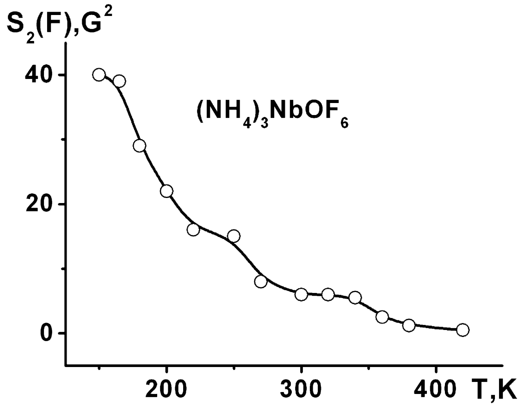

Fig. 5. Temperature dependence of second moments S_2 of ^{19}F NMR spectra of $(NH_4)_3NbOF_6$ (B_o = 7.05 T).

Cationic motion in $(NH_4)_3NbOF_6$ at 150–350 K is isotropic reorientations of NH_4 groups in accordance with the ^1H NMR line width and second moment value. The spectrum is represented by symmetrical line, the shape and width of which are temperature dependent (Fig. 6). The sharp changes of the ^1H NMR spectral parameters above 370 K are due to proton diffusion. The narrow symmetrical line (75% Lorentz) at 420 K with $\Delta H \approx 1.3$ kHz and $S_2(H) \leq 0.05$ G^2 confirm the dominant role of diffusion in proton subsystem. One should mention that similar diffusion (above 280 K) was observed in $(NH_4)_3TiOF_5$ after PT at around 265 K [14]. The spectral hysteresis is observed while the sample is cooled from 420 to 300 K (Fig. 3) that is, probably, connected with the PT above 360 K with the formation of metastable phase of $(NH_4)_3NbOF_6$.

2.3. DFT calculations

The calculated and experimental interatomic distances of $[NbOF_5]^{2-}$ and $[NbOF_6]^{3-}$ are listed in Table 2. In both cases, the calculated structural parameters agree quite well with the experimental values. The PB state of $[NbOF_6]^{3-}$ anion is the most stable. This geometry predominates for seven-coordinated mono-oxofluoro species with the central atom of both main group elements and transition metals: IOF_6^- [17], $TeOF_6^{2-}$ [18,19]; $ReOF_6^-$ [20], $NbOF_6^{3-}$ [7], $TaOF_6^{3-}$ [21]. IOF_6^- and $ReOF_6^-$ are rigid anions in which intramolecular exchange processes are suppressed [20]. Nevertheless, non-rigidity is a common feature of the most seven-coordinated complexes which are fluxional due to dynamics of pseudorotation type [22–25]. A well pronounced example of similar behavior is our $(NH_4)_3NbOF_6$. A strong intramolecular ligand exchange due to isotropic reorientations of the PB anion proceeds at higher temperatures. After the PT of order–disorder type at lower temperature, the C_{5v} polyhedron converts to the CTP anion of C_{2v} symmetry. On the other hand, the $[NbOF_5]^{2-}$ anion demonstrates the behavior of a rigid unit.

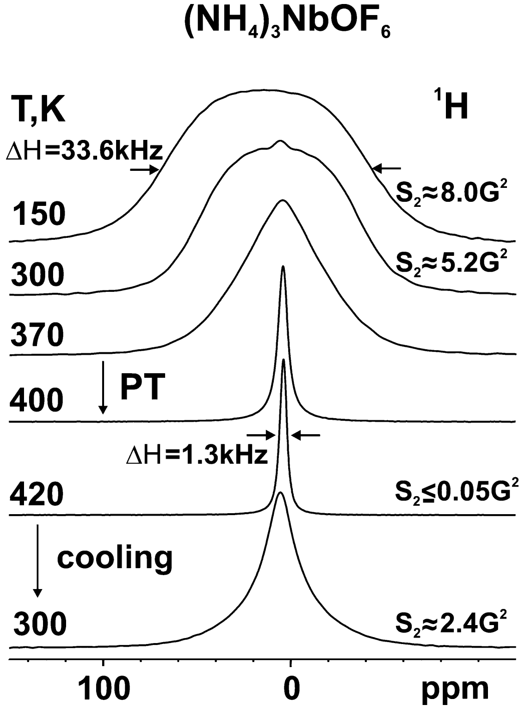

Fig. 6. Transformation of the ^1H NMR spectra of $(NH_4)_3NbOF_6$ during heating and cooling.

Table 2
Experimental and calculated geometric parameters of $[NbOF_5]^{2-}$ and $[NbOF_6]^{3-}$ complex anions.

Compound/ anion	D(Nb–O), Å	D(Nb–F_{eq}), Å	D(Nb–F_{ax}), Å	∠(O–Nb–F_{eq}),°
$(NH_4)_2NbOF_5$ (exper.)	1.73	1.90–1.95	2.09–2.12	95.5–98.9
$[NbOF_5]^{2-}$ (calc.C_{4v})	1.772	2.005	2.111	94.81
$(NH_4)_3NbOF_6$ (exper.)	1.75	1.98–2.11	2.03	93.7–94.5
$[NbOF_6]^{3-}$ (calc.C_{5v})	1.781	2.105	2.177	93.83

3. Conclusions

Ionic mobility and phase transitions in six- and seven-coordinated ammonium oxofluoroniobates $(NH_4)_2NbOF_5$ and $(NH_4)_3NbOF_6$ have been studied by ^{19}F, ^1H NMR and DFT calculations. The rigid $[NbOF_5]^{2-}$ octahedral and fluxional $[NbOF_6]^{3-}$ pentagonal bipyramids are dynamically disordered in the crystal lattices at room and higher temperatures. At lower temperatures, both compounds undergo the PT of order–disorder type accompanied by significant changes of ionic mobility. Interestingly, these changes coincide in regard to the temperature range (at about 260 K) for both cases. In the first compound $(NH_4)_2NbOF_5$, the transition from dynamic motion to rigid anionic sublattice occurred, whereas in the second one $(NH_4)_3NbOF_6$, isotropic reorientation of heptacoordinated polyhedra transforms, most probably, into uniaxial one around the four-fold local axis. This is corroborated by the transformation of the $[NbOF_6]^{3-}$ PB into the CTP form of C_{2v} symmetry. Importantly, it is the first case of heptacoordinated polyhedron in the CTP form for monooxofluoro species and a striking example of pseudorotation similar to that of Berry type.

4. Experimental

The $(NH_4)_2NbOF_5$ and $(NH_4)_3NbOF_6$ complexes were obtained from fluoride aqueous solutions by the methods described in [5,6]. Their transparent crystals were used for NMR experiment. The NMR spectra were measured on a multinuclear Bruker AV-300 spectrometer at Larmor frequencies ν_L = 282.404 MHz (for ^{19}F nuclei) and ν_L = 300.13 MHz (for ^1H nuclei) in the temperature range 150–420 K. The temperature adjustment accuracy was ±2 K. The second moment calculations of NMR spectra (S_2 in G^2) were carried out by the original program with the use of formulae presented in [26]. The line width at half height (ΔH in kHz), chemical shifts (δ in ppm) and integral intensities of spectral components were measured with errors not higher than 3%. The ^{19}F NMR chemical shifts were measured using C_6F_6 as a reference, and the accuracy was ~3%. The chemical shift of C_6F_6 is −589 ppm relatively to gaseous F_2 ($\delta(F_2) = 0$ ppm). For the sake of convenience, the values of chemical shifts were recalculated relatively to free fluoride ion ($\delta[F]^- = -713$ ppm relatively to F_2) to compare them with the calculated data. Thus, $\delta(C_6F_6)$ is equal to 124 ppm relatively to $[F]^-$.

Theoretical calculations of free anions $[NbOF_5]^{2-}$ and $[NbOF_6]^{3-}$ were done at the density functional theory (DFT) [27] using the program complex ADF-2008 [28]. The model Hamiltonian of density functional as a sum of local density functional LDA [29] and gradient exchange functional GGA [29,30] was used. The calculations were done with a set of coreless triple-ζ Slater-type orbitals TZP/ADF2008 [31]. The GIAO-DFT method [32,33] was used for the calculation of main component values of the ^{19}F NMR chemical shift tensors for optimized structures of the $[NbOF_5]^{2-}$ and $[NbOF_6]^{3-}$ anions.

Acknowledgments

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References

[1] H.K. Izumi, J.E. Kirsh, C.L. Stern, K.R. Poeppelmeier, Inorg. Chem. 44 (2005) 884–895.
[2] K.R. Heier, A.J. Norquist, C.G. Wilson, C.L. Stern, K.R. Poeppelmeier, Inorg. Chem. 37 (1998) 76–80.
[3] A.J. Norquist, K.R. Heier, C.L. Stern, K.R. Poeppelmeier, Inorg. Chem. 37 (1998) 6495–6501.
[4] R. Marvel, J. Lesage, J. Baek, P.S. Halasyamani, C.L. Stern, K.R. Poeppelmeier, J. Am. Chem. Soc. 129 (2007) 13963–13969.
[5] A.A. Udovenko, N.M. Laptash, Acta Cryst. B64 (2008) 527–533.
[6] A.A. Udovenko, N.M. Laptash, Russ. J. Struct. Chem. 49 (2008) 482–488 (translated from Zh. Strukt. Khim. 49, 550–556).
[7] R. Stomberg, Acta Chem. Scand. A37 (1983) 453–459.
[8] S.V. Mel'nikova, N.M. Laptash, A.L. Zhogal, Phys. Solid State 49 (2007) 958–962 (translated from Fiz. Tverdogo Tela 49, 908–912).
[9] V.D. Fokina, I.N. Flerov, M.V. Gorev, E.V. Bogdanov, A.F. Bovina, N.M. Laptash, Phys. Solid State 49 (2007) 1548–1553 (translated from Fiz. Tverdogo Tela 49, 1475–1479).
[10] S.V. Mel'nikova, N.M. Laptash, K.S. Aleksandrov, Phys. Solid State 52 (2010) 2168–2172 (translated from Fiz. Tverdogo Tela 52, 2023–2027).
[11] V.D. Fokina, E.V. Bogdanov, M.V. Gorev, M.S. Molokeev, E.I. Pogorel'tsev, I.N. Flerov, N.M. Laptash, Phys. Solid State 52 (2010) 781–788 (translated from Fiz. Tverdogo Tela 52, 728–734).
[12] M.V. Gorev, E.V. Bogdanov, I.N. Flerov, V.N. Voronov, N.M. Laptash, Ferroelectrics 397 (2010) 76–80.
[13] M. Gorev, E. Bogdanov, I. Flerov, N. Laptash, J. Phys. Cond. Matter. 22 (2010), Article no. 185901.
[14] V.Ya. Kavun, S.G. Kozlova, I.A. Tkachenko, S.P. Gabuda, Russ. J. Struct. Chem. 51 (2010) 463–470 (translated from Zh. Strukt. Khim. 51, 483–490).
[15] V.Ya. Kavun, S.G. Kozlova, N.M. Laptash, I.A. Tkachenko, S.P. Gabuda, J. Solid State Chem. 183 (2010) 2218–2221.
[16] D. Casanova, J. Cirera, M. Llunell, P. Alemany, D. Avnir, S. Alvarez, J. Am. Chem. Soc. 126 (2004) 1755–1763.
[17] K.O. Christe, D.A. Dixon, A.R. Mahjoub, H.P.A. Mercier, J.C.P. Sanders, K. Seppelt, G.J. Schrobilgen, W.W. Wilson, J. Am. Chem. Soc. 115 (1993) 2696–2706.
[18] K.O. Christe, J.C.P. Sanders, G.J. Schrobilgen, J. Chem. Soc. Chem. Commun. 837 (1991) 837–840.
[19] K.O. Christe, D.A. Dixon, J.C.P. Sanders, G.J. Schrobilgen, W.W. Wilson, Inorg. Chem. 32 (1993) 4089–4093.
[20] S. Giese, K. Seppelt, Angew. Chem. Int. Ed. Engl. 33 (1994) 461–463.
[21] F. Averdunk, R. Hoppe, J. Fluorine Chem. 42 (1989) 413–427.
[22] R. Hoffman, B.F. Beier, E.L. Muetterties, A.O. Rossi, Inorg. Chem. 16 (1977) 511–522.
[23] S.B. Elk, J. Chem. Inf. Comput. Sci. 35 (1995) 858–863.
[24] Z. Lin, I. Bytheway, Inorg. Chem. 35 (1996) 594–603.
[25] S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell, D. Avnir, Coord. Chem. Rev. 249 (2005) 1693–1708.
[26] S.P. Gabuda, Yu.V. Gagarinsky, S.A. Polishchuk, NMR in Inorganic Fluorides, Atomic Energy Press (Atomizdat), Moscow, 1978 (in Russian).
[27] G. Te Velde, F.M. Bickelhaupt, E.J. Baerends, C.F. Guerra, S.J.A. Van Gisbergen, J.G. Snijders, T. Ziegler, J. Comp. Chem. 22 (2001) 931–967.
[28] Amsterdam Density Functional (ADF) Program, Release 2008.02, Vrije Universiteit, Amsterdam, The Netherlands, 2006.
[29] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200–1211.
[30] A.D. Becke, Phys. Rev. A 38 (1988) 3098–3100.
[31] J.P. Perdew, Phys. Rev. B 33 (1986) 8822–8824.
[32] G. Schreckenbach, T. Ziegler, J. Phys. Chem. 99 (1995) 606–611.
[33] G. Schreckenbach, T. Ziegler, Int. J. Quantum Chem. 61 (1997) 899–918.