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Hydrogen bonds in mixed bifluoride–nitrate salts of ammonium and potassium

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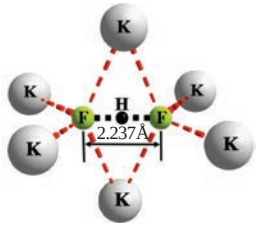
The salts $(NH_4)_2(HF_2)(NO_3)$ and $K_3(HF_2)(NO_3)_2$ were isolated by crystallization from aqueous bifluoride and nitrate solutions. The crystal structures of the ammonium and potassium salts contain short hydrogen bonds in bifluoride anions $(HF_2)^-$ with F···F distances of 2.277(5) and 2.237(1) Å, respectively, and the latter is the shortest among all ever reported hydrogen bonds in metal bifluorides.



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The bifluoride and nitrate salts of alkali metals and ammonium are important reagents in large-scale inorganic synthesis and chemical industry. The mixed bifluoride/nitrate double salts of ammonium or potassium can be formed in the production of fertilizers.[1] The synthesis of the double salts $(NH_4)_2(HF_2)(NO_3)$ and $K_2(HF_2)(NO_3)$ was described, and data on their thermal behavior and X-ray powder diffraction analysis were reported.[1] The synthesis included the mixing of a moistened $NH_4(HF_2)$ or $K(HF_2)$ component with a corresponding nitrate in a ratio of 1 : 1 and the grinding of the mixtures followed by drying at room temperature.

Here, we report the synthesis and crystal structure investigation of $(NH_4)_2(HF_2)(NO_3)$ and $K_3(HF_2)(NO_3)_2$.

The crystalline $(NH_4)_2(HF_2)(NO_3)$ and $K_3(HF_2)(NO_3)_2$ were synthesized by crystallization from aqueous solutions of a bifluoride and a nitrate in stoichiometric amounts, which were concentrated and cooled. The crystalline phases were separated by decantation and dried in air at room temperature. As found by X-ray diffraction analysis, the ammonium double salt with a 1 : 1 stoichiometry was formed, whereas the potassium compound had a bifluoride/nitrate ratio of 1 : 2. Note that the calculated powder diffraction patterns are inconsistent with the patterns reported previously[1] for the 1 : 1 double salts of ammonium and potassium. Therefore, we assume that the samples studied in ref.1 contained either other modifications of double salts or compound mixtures.

Figure 1 shows the structure of $(NH_4)_2(HF_2)(NO_3)$, which can be formally represented as the layers of HF_2^- and NO_3^- anions alternating in the *a* direction, which are connected by ammonium cations *via* N–H···F and N–H···O hydrogen bonds. Each ammonium cation connects two HF_2^- anions and two NO_3^- anions. The hydrogen bonds N(1)–H(2)···F(1) and N(1)–H(3)···F(2) are 2.840(4) and 2.776(4) Å long, respectively, which can be compared with similar bonds in ammonium bifluoride, 2.797(2)–2.822(3)[2] or 2.7964(6)–2.8094(7) Å.[3] The hydrogen bonds N–H···O of 2.926(5) and 2.951(4) Å have usual lengths as, for example, those in ammonium nitrate, 2.879–2.928 Å.[4] The bond F(1)–H(1)···F(2) of 2.277(5) Å belongs, despite its asymmetry,

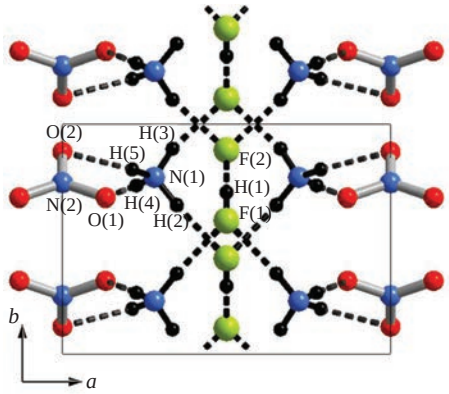

Figure 1 Projection of the crystal structure of $(NH_4)_2(HF_2)(NO_3)$ along the *c* axis. Dashed lines denote hydrogen bonds of the types H···F and H···O. The systems of H-bonded units repeat by a translation of 0.5 *c*, accompanied by a half rotation around *z*.

† *Crystal data.* The X-ray single crystal data for $(NH_4)_2(HF_2)(NO_3)$ and $K_3(HF_2)(NO_3)_2$ were collected at 100 and 160 K on an IPDS (Stoe) image plate diffractometer and a STADI4 (Stoe) single-point diffractometer, respectively, using graphite-monochromated Mo-Kα radiation (λ = = 0.71073 Å). The crystal structures were solved by direct methods and refined with SHELXL.

$(NH_4)_2(HF_2)(NO_3)$, orthorhombic, $Pmc2_1$, a = 8.2804(12), b = 5.7924(11) and c = 5.7548(10) Å, V = 276.02(8) Å^3, Z = 4. The position of H(1) in a bifluoride anion was fixed in the mirror plane, whereas all hydrogen atoms of the ammonium cation were freely refined. A refinement with 698 reflections and 59 parameters converged to wR_2 = 0.123 and R_1 = 0.046 for 691 reflections with $I > 2\sigma(I)$.

$K_3(HF_2)(NO_3)_2$, orthorhombic, *Pbam*, a = 7.861(1), b = 9.646(1) and c = 5.382(1) Å, V = 408.1(1) Å^3, Z = 2. The position of the hydrogen atom H(1) was fixed at 0.5 0.5 0.5. A refinement with 648 reflections and 40 parameters converged to wR_2 = 0.037 and R_1 = 0.015 for 617 reflections with $I > 2\sigma(I)$.

CSDs 1978443 and 1978444 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

to very strong hydrogen bonds, and it has the same length as symmetric F···H···F bonds in $(NH_4)(HF_2)$, 2.278(1) and 2.281(1) Å.[3] Similarly, in the crystal structure of diphenylguanidinium bifluoride $[(PhNH)_2CNH_2](HF_2)$, the formation of four N–H···F hydrogen bonds (two by each F atom) results in a strong slightly asymmetric F–H···F bond with a short F···F distance of 2.293(3) Å.[5] In the structure of guanidinium bifluoride $[C(NH_2)_3](HF_2)$, the F···F distance in a symmetric F···H···F bond is even shorter [2.273(2) Å].[6] The very strong symmetric F···H···F hydrogen bonds of similar lengths are present in the crystal structures of alkali metal bifluorides: 2.277(1) (Na),[3] 2.277(6) (K),[7] and 2.280(4) Å (Rb).[3]

It is well known that D–H···A hydrogen bonds are weakened by additional interactions of a donor (D) or an acceptor (A) atom, such as additional donor or acceptor functions in the crystal structures. For example, F–H···F hydrogen bonds in $K(H_2F_3)$ [2.29–2.35(5) Å][8] are longer than those in $K(HF_2)$[7] because the central F atom acts as a double acceptor. Moreover, even longer F···F distances of 2.49(1) Å are present in HF crystals, where all F atoms in zigzag chains act as hydrogen donors and hydrogen acceptors.[9] Thus, very short F···F distances in $(NH_4)_2(HF_2)(NO_3)$ double salt and the bifluorides of alkali metals and ammonium suggest that the weakening influence of a cationic environment in ionic structures is the same as the formation of two N–H···F hydrogen bonds on both sides of a F–H···F or F···H···F bifluoride anion.

Figure 2 shows the crystal structure of $K_3(HF_2)(NO_3)_2$, where atoms are situated in crystallographic mirror planes, which alternate at a distance of 2.691 Å in the *c* direction. In this way, the layers of K(1) cations and nitrate groups alternate with the layers composed of K(2) cations and bifluoride anions. Among close contacts (Coulomb interactions) of potassium atoms with O and F atoms, the contacts with O atoms prevail: 6O + 4F for K(1) and 8O + 2F for K(2).

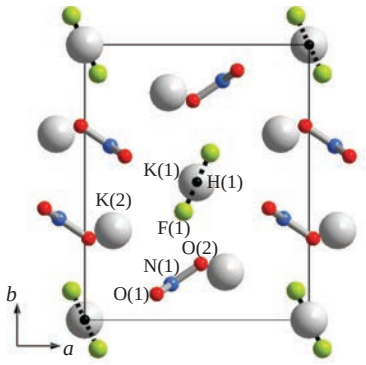

Figure 2 Projection of the crystal structure of $K_3(HF_2)(NO_3)_2$ along the *c* axis. All atoms except for O(1) lie in mirror planes, which are parallel to (*xy*0). Atoms K(1), N(1) and O(2) lie at the heights with $z = 0$ and 1, whereas atoms K(2), F(1) and H(1) have $z = 0.5$. Three K(1) atoms are removed from their positions to show F···H···F bonds presented by dashed lines.

The linear bifluoride anion is characterized by a symmetric position of the hydrogen atom and a very short F···F distance of 2.237(1) Å. Such short F···F distances have never been observed in crystal structures of metal bifluorides. Typical values of 2.28 ± 0.01 Å were found in the bifluorides of alkali metals and ammonium (see above), whereas a noticeably shorter F···F distance of 2.256(2) Å is characteristic of $[N(CH_3)_4](HF_2)$ due to weaker interactions of $(HF_2)^-$ anions with large tetramethylammonium cations.[10] In the (L-agrinine)(HF_2) salt with a bulky cation, two crystallographically independent, asymmetric biflouride anions possess very short F···F distances of 2.233(2) and 2.248(3) Å.[11]

The reasons for shortening the F···H···F bonds in the crystal structure of $K_3(HF_2)(NO_3)_2$ can be simply rationalized on the basis of structural data. The environment of bifluoride anions in the crystal structure of $K(HF_2)$ consists of eight K^+ cations, by four of both sides of the HF_2^- anion, at distances of 2.769 Å.[7] The cationic environment of the bifluoride anion in $K_3(HF_2)(NO_3)_2$ is quite different: both F atoms have distorted tetrahedral coordination with four potassium cations, two K(2) at distances of 2.559 and 2.576 Å and two K(1) at equal distances of 2.914 Å. While the F(1)···K(2) interactions on both sides of the F···H···F anion weaken the hydrogen bond, two F(1)···K(1) interactions act as cationic bridges thus contributing to its shortening. This geometric situation is due to the location of K(1) atoms just above and below H(1) atom on the projection along the *c* axis.

In summary, in the crystal structures of the bifluoride/nitrate double salts $(NH_4)_2(HF_2)(NO_3)$ and $K_3(HF_2)(NO_3)_2$, bifluoride $(HF_2)^-$ anions are characterized by a very short [2.277(5) Å] and an extremely short [2.237(1) Å] hydrogen bonds, respectively.

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References

1 A. Ya. Tavrovskaya, N. L. Portnova, P. M. Zaitsev and T. F. Abashkina, *Russ. J. Appl. Chem.*, 1979, **52**, 481.
2 T. R. R. McDonald, *Acta Crystallogr*., 1960, **13**, 113.
3 S. I. Troyanov, *Crystallogr. Rep*., 2005, **50**, 773.
4 C. S. Choi and H. J. Prask, *Acta Crystallogr*., *Sect. B*: *Struct. Sci.*, 1983, **39**, 414.
5 M. R. Silva, J. A. Paixão, A. M. Beja and L. A. da Veiga, *J. Fluorine Chem*., 2001, **107**, 117.
6 I. M. Shlyapnikov, E. A. Goreshnik and Z. Mazej, *Eur. J. Inorg. Chem*., 2018, 5246.
7 J. A. Ibers, *J. Chem. Phys*., 1964, **40**, 402.
8 J. D. Forrester, M. E. Senko, A. Zalkin and D. H. Templeton, *Acta Crystallogr*., 1963, **16**, 58.
9 M. Atoji and W. N. Liscomb, *Acta Crystallogr*., 1954, **7**, 173.
10 S. I. Troyanov, I. V. Morozov and E. Kemnitz, *Z. Anorg. Allg. Chem*., 2005, **631**, 1651.
11 M. R. Silva, J. A. Paixão, A. M. Beja and L. A. da Veiga, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, 104.

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