

SbF²⁺ AS LEWIS ACID IN Na(SbF)PO₄·nH₂O (n = 1-2) AND NH₄(SbF)PO₄·H₂O

R. Mattes* and K. Holz

Institut of Inorganic Chemistry, University of Münster (F.R.G.)

SbF₃ is a strong acceptor to fluoride ions and oxoanions like sulfate or nitrate [1,2]. Recently complexes of the composition M(SbF₂)SO₄ (M=Rb,Cs) [2] and K(SbF₂)HPO₄ [3] have been described. Here the SbF₂⁺ group is linked to different oxoanions through 2 short (~217pm) Sb-O bonds. The new compounds Na(SbF)PO₄·nH₂O (n=1-2) (I) and NH₄(SbF)PO₄·H₂O (II) have been prepared by reaction of SbF₃ and Na₂HPO₄ or (NH₄)₂HPO₄ in water. Their structures have been determined by single crystal X-ray diffraction. I: monoclinic, a=656.2(1), b=654.1(1), c=867.9(1) pm; β=92.43(2)°; space group P2₁/m, Z=2; R=0.044 (R_w=0.064) for 884 reflections. II: tetragonal, a=656.5(2), c=1439.8(5) pm; space group I4, Z=4; R=0.025 (R_w=0.035) for 646 reflections. I and II contain the so far unknown SbF²⁺ group, which originates from SbF₃ by fluoride ion abstraction. The structures consist of layers with the overall composition [SbFPO₄]⁻. The SbF²⁺-group is a strong acceptor towards the oxygen atoms of 4 different PO₄³⁻-ions. Its strong Lewis acidity is shown by the rather short Sb-O bonds of 216-222 pm length. Sb(III) is coordinated pseudooctahedrally by the stereochemically active lone pair, by one fluorine atom trans to the lone pair (Sb-F: 193 pm) and by 4 oxygen atoms in the equatorial plane. The layers represent a rare example of a simple planar net of tetrahedra and (pseudo)octahedra which both share 4 vertices. Between the layers, which are stacked differently in I and II, the cations and water molecules are situated. The structure is also reflected in the vibrational spectra and 121-Sb Mössbauer data. The isomer shift is less negative than in SbF₃, the quadrupole coupling constant smaller. This is due to the more regular environment of Sb(III) in I and II compared to SbF₃.

- 1 R.L. Davidovich, L.A. Zemnukhova, L.V. Samarats, V.I. Kostin, *Koord. Khim.* **5**, 1014 (1979)
- 2 R. Fourcade, M. Bourgault, B. Bonnet, B. Cucourant, J. *Solid State Chem.* **43**, 81 (1982)
- 3 S. Hürter, R. Mattes, D. Rühl, J. *Solid State Chem.* **46**, 204 (1983)