754. *Complex Fluorides. Part XII.* The Structures of Some Complex Acid Fluorides.*

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Three compounds of the formula type $M^{I}_3HM^{IV}F_8$ have been studied by *X*-ray powder photography and infrared spectroscopy, and the results are considered in relation to early morphological work, a single-crystal *X*-ray study of K_3HNbOF_7, and the infrared spectrum of potassium hydrogen difluoride. In the solid state these compounds are composed of M^{I+}, $M^{IV}F_6^{2-}$, and HF_2^- ions: K_3HSnF_8 and K_3HPbF_8 are isostructural with monoclinic K_3HNbOF_7, but Na_3HTiF_8 has a different (orthorhombic) structure.

Hoard and Martin's demonstration,[1] by *X*-ray crystallography, that the compound K_3HNbOF_7 is a lattice aggregate of K^+, HF_2^-, and $NbOF_5^{2-}$ ions is the only detailed investigation of the structure of a complex acid fluoride yet reported. The present paper concerns the somewhat similar compounds K_3HPbF_8, K_3HTiF_8, and Na_3HTiF_8; in addition to *X*-ray powder photography, however, infrared spectroscopy has been used to show the presence of HF_2^- ions, and the spectra have been considered in some detail. Early morphological studies [2] of these compounds showed that the two potassium salts have axial ratios very close to those [1,3] of the compound K_3HNbOF_7, and it has been found that their powder photographs can be indexed on the basis of monoclinic unit cells having dimensions similar to those given by Hoard and Martin for the niobium compound (Table 1). The compound Na_3HTiF_8 has an orthorhombic unit cell whose dimensions are closely related to the monoclinic unit cells of K_3HPbF_8, K_3HSnF_8, and K_3HNbOF_7; β is 90° instead of 86—87°, and the *a*-side is shortened. Since the $NbOF_5^{2-}$, PbF_6^{2-}, SnF_6^{2-}, and TiF_6^{2-} ions are all octahedral and almost isodimensional, these results provide strong evidence for the presence of HF_2^- ions in the compounds which have now been investigated. This conclusion is supported by a comparison of the infrared absorption bands of the compounds in Table 2, in which frequencies previously shown [4-7] to be associated with the

Table 1. *X-Ray and morphological crystallographic data.*

Compound	Morphological axial ratios, β	Unit-cell dimensions (Å) *a*	*b*	*c*	β	Axial ratios	*Z*	Density Calc.	Found
K_3HNbOF_7	0·630 : 1 : 0·489 [3] β = 86° 41′	8·82	14·02	6·82	86° 34′	0·629 : 1 : 0·486 [1]	4	2·72	2·68
K_3HPbF_8 ...	0·622 : 1 : 0·482 [2] β = 86° 41′	8·93	14·38	6·93	85° 59′	0·622 : 1 : 0·485	4	3·57	3·51
K_3HSnF_8 ...	0·628 : 1 : 0·493 [2] β = 87° 0′	8·84	14·08	6·83	86° 25′	0·628 : 1 : 0·482	4	3·05	3·00
Na_3HTiF_8	0·517 : 1 : 0·466 [2] β = 90°	7·17	13·96	6·54	90°	0·514 : 1 : 0·469	4	2·73	2·68

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* Part XI, *J.*, 1957, 4804.

[1] Hoard and Martin, *J. Amer. Chem. Soc.*, 1941, **63**, 11.

[2] Groth, "Chemische Krystallographie," Vol. I, Engelmann, Leipzig, 1906, pp. 463—464.

[3] Balke and Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1637.

[4] Coté and Thompson, *Proc. Roy. Soc.*, 1951, *A*, **210**, 206.

[5] Ketelaar and Vedder, *J. Chem. Phys.*, 1951, **19**, 654.

[6] Newman and Badger, *ibid.*, 1951, **19**, 1207.

[7] Ketelaar, Haas, and van der Elsken, *ibid.*, 1956, **24**, 624.

HF_2^- ion are listed in the left-hand column, while those observed in this work are denoted by the letter *A* in the right-hand column.

The linear ion HF_2^- has three fundamental frequencies: ν_1 (symmetrical stretching) at about 600 cm.$^{-1}$; ν_2 (doubly degenerate bending) at 1220 cm.$^{-1}$; ν_3 (antisymmetric stretching) at 1425 cm.$^{-1}$. Only ν_2 and ν_3 are infrared-active, but ν_1 appears in combination frequencies. It has recently been found [7] that the infrared spectra of ammonium, potassium, and sodium hydrogen difluorides vary with the conditions under which they are observed; in Nujol mulls the ν_3 fundamental is nearly hidden by a very broad, strong band at 1600 cm.$^{-1}$ whose half-width is about 150 cm.$^{-1}$. The spectra cited in Table 2 were observed for the finely powdered compounds with and without mulling agents.

The half-width of the ν_2 band is no more than 20 cm.$^{-1}$ at room temperature, so that it is more reliable than ν_3 for diagnostic purposes. When its double degeneracy is removed in a dissymmetric crystal lattice, the splitting of ν_2 should be resolvable as long as it exceeds 5 cm.$^{-1}$. In crystalline potassium hydrogen difluoride, the HF_2^- ions are arranged in planes perpendicular to the four-fold axis, and deformations in these planes therefore correspond to a different energy change from those at right angles. This interpretation [4] of the splitting of ν_2 in potassium hydrogen difluoride into two frequencies separated by about 20 cm.$^{-1}$ can be extended to other compounds containing this ion. It has been reported that the lattice of sodium hydrogen difluoride is rhombohedral with one molecule per unit cell; [8,9] the HF_2^- ion lies parallel to the three-fold axis, and ν_2 would therefore be expected to remain degenerate. In fact, a single frequency occurs at 1210 cm.$^{-1}$, and this has no fine structure at room temperature.

The environment of the HF_2^- ion in the monoclinic K_3HNbOF_7 lattice is more complex, but according to Hoard and Martin [1] the hydrogen atom lies at a centre of symmetry. There are six K^+ and six $NbOF_5^{2-}$ ions placed irregularly about it, as well as two HF_2^- ions. The energy of the bending vibration was estimated on a simple electrostatic model, the ion being treated as F^-–H^+–F^-. The difference in energy for vibrations in two perpendicular planes was used to calculate the splitting of this deformation frequency as

TABLE 2. *Infrared frequencies (cm.$^{-1}$) observed at room temperature.*

KHF_2 (lit) [a]	Assgt.	KHF_2	$NaHF_2$	K_3HNbOF_7	K_3HPbF_8	K_3HSnF_8	Na_3HTiF_8	R.I. [e]	E.I. [f]
3890—3660 [b]									
3240 w	$3\nu_1 + \nu_3$								
2670 ms	$2\nu_1 + \nu_3$	2660						vw	*A*
2420 w	$2\nu_1 + \nu_2$	2420						vw	*A*
2060 s	$\nu_1 + \nu_3$	2080	2120	2105	2095	2115	2090	ms	*A*
1870 s	$\nu_1 + \nu_2$	1836	1830	1830	1835	1840	1825	wm	*A*
1700 s		1600 [c]	1600 [c]	1590 [c]	1570 [c]	1600 [c]	1610 [c]	vs	*A*
1425 vs	ν_3	1460		1480 sh	1475 sh	1470 sh	1440 sh	m	*A*
—	—			1310	1310	1310		w	?
		1235 sh		1220	1232	1221	1277		
1238 } vs	ν_2, ν'_2		1210				1251	s	*A*
1220 }		1220		1183	1193	1184	1224		
		K_2TiF_6	Na_2TiF_6						
1170 vw		1020	1035	1015			1026	vw	*B*
—					965		965	w	*B*?
880 vw				918				s	*B*ii
740 vw									
		625 sh	625 sh	630 sh	509 [d]	565 [d]	630 sh		
							580	vs	*B*i
		580	563	550 [d]	490 sh	550 sh	550 sh		
		464						w	*B*?

[a] Refs. 4, 5, 6, 7, 12. [b] 3890, 3810, 3775, 3715, 3660. [c] Very broad and strong; sh = shoulder. [d] $KNbF_6$, K_2PbF_6, K_2SnF_6 absorb sharply at 580, 502, 552 cm.$^{-1}$ respectively.[10] [e] Relative intensities. [f] Excited ion; *A* hydrogen difluoride frequency; *B* octahedral ion frequency.

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[8] Rinne, Hentschel, and Leonhardt, *Z. Krist.*, 1923, **58**, 629.

[9] Andersen and Hassel, *Z. phys. Chem.*, 1926, **123**, 151.

[10] Peacock and Sharp, *J.*, 1959, 2762.

about 50 cm.$^{-1}$. The observed values (Table 2) show that $\Delta\nu = \nu_2 - \nu'_2$ is approximately constant at 38 ± 5 cm.$^{-1}$; ν_2 and ν'_2 have approximately equal intensities for any given compound.

The infrared spectrum of the compound Na_3HTiF_8 confirms the conclusion, from *X*-ray powder photography, that this substance is not isomorphous with K_3HNbOF_7, K_3HPbF_8, and K_3HSnF_8. The ν_2 frequency is apparently split into three components: ν_2 (1277), ν'_2 (1251), and ν''_2 (1224 cm.$^{-1}$) (all ± 3 cm.$^{-1}$), with relative intensities 1 : 2 : 1, and differences $\Delta\nu$ of 26 and 27 (± 5) cm.$^{-1}$. This suggests that there are two different kinds of HF_2^- ion in the lattice, giving rise to four ν_2 frequencies, two of which happen to coincide at 1251 cm.$^{-1}$.

The bands denoted by *B* in Table 2, which do not correspond to HF_2^- frequencies, and which presumably arise from the octahedral ions, may be considered in two groups, *B*(i) and *B*(ii).

B(i), at 500—630 cm.$^{-1}$, is the more complex and intense. Peacock and Sharp [10] have pointed out that frequencies in this region correspond to ν_3 for the regular MF_6^{n-} species, and that ν_4, the other infrared-active vibration, will rarely appear above 400 cm.$^{-1}$. The tin and lead compounds give rise to very similar absorptions here, the only difference being a shift of the main frequency from 565 to 509 cm.$^{-1}$, corresponding to the increase in atomic weight of the central atom. The spectra of the complex acid fluorides differ from those of $K_2M^{IV}F_6$ in that small shifts in frequency and splitting occur in the former. Thus, K_2SnF_6 and K_2PbF_6 absorb [10] quite sharply at 552 and 502 cm.$^{-1}$ respectively. These small discrepancies and splittings may be ascribed to lower symmetry and more ions in the unit cells of the complex acid fluorides. The spectrum of the $NbOF_5^{2-}$ ion has the principal band at 550 cm.$^{-1}$, whereas the fluoroanion in $KNbF_6$ absorbs [10] at 580 cm.$^{-1}$. Because the natures of the vibrations will be similar in these ions, the small shifts in frequency can be interpreted as indicating a multiple niobium–oxygen bond in the oxyfluoroanion; the addition of an electron to VF_6^-, forming VF_6^{2-}, involves [10] a shift in the absorption from 715 to 583 cm.$^{-1}$.

B(ii) is at 918 cm.$^{-1}$ in the $NbOF_5^{2-}$ spectrum. This ion will have a dipole moment, unlike the regular $M^{IV}F_6^{2-}$ ions, and this frequency will be mainly the O–NbF_5 stretching frequency as long as there is little coupling in the O–Nb(F_2F_2)–F vibration. The energy difference 918 — 550 cm.$^{-1}$ indicates that any coupling will be slight. Absorption at this frequency would then correspond to a force constant of $7{\cdot}3 \times 10^5$ dynes/cm. for the niobium–oxygen bond, which suggests a bond order higher than unity. To confirm that this frequency is due to the $NbOF_5^{2-}$ ion, the compound was partially deuterated; as a result new bands appeared corresponding to the DF_2^- spectrum, but the 918 cm.$^{-1}$ band showed no decrease in intensity and no new band was observed in the range 640—670 ($918/\sqrt{2}$) cm.$^{-1}$.

EXPERIMENTAL

Preparations.—Fluorotitanates were made from titanium dioxide, hydrofluoric acid, and alkali-metal carbonates by the standard methods. Titanium was determined as TiO_2; the acid salt was also analysed for hydrolysable fluoride by potentiometric titration according to the equation $Na_3HTiF_8 + 5OH^- = 3NaF + TiO_2 + 5F^- + 3H_2O$ (Found: Ti, 23·0. Calc. for Na_2TiF_6: Ti, 23·1. Found: Ti, 20·1. Calc. for K_2TiF_6: Ti, 20·0. Found: Ti, 17·7%; hydrolysable F^-, 4·95 g.-ion/mole. Calc. for Na_3HTiF_8: Ti, 17·7%; hydrolysable F^-, 5·0 g.-ion/mole).

The compound K_3HNbOF_7 was made by dissolving niobium pentoxide in 40% hydrofluoric acid and adding potassium carbonate until the solution was only slightly acidic; the product was recrystallised from dilute hydrofluoric acid (Found: Nb, 25·6. Calc. for K_3HNbOF_7: Nb, 25·8%).

Deuteration was effected by crystallisation from deuterium oxide to which a trace of the aqueous acid had been added. The compounds K_3HSnF_8 and K_3HPbF_8 were made by a modification of Mathers's method [11] for the latter compound. The dioxides were fused with

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[11] Mathers, *J. Amer. Chem. Soc.*, 1920, **42**, 1309.

potassium hydrogen difluoride in a platinum dish; the difluoride was regenerated by treatment with anhydrous hydrogen fluoride and the fusion was then repeated. The process was continued until the reaction mixture contained very little unchanged oxide. The acid salts were extracted with hot 50% hydrofluoric acid, from solutions in which they crystallise on being cooled. Tin was determined as the dioxide, and lead by reduction with iodide in concentrated hydrochloric acid followed by an Andrews's titration of the excess of iodide (Found: Sn, 30·7%; hydrolysable F^-, 5·03 g.-ion/mole. Calc. for K_3HSnF_8: Sn, 30·5%; hydrolysable F^-, 5·0 g.-ion/mole. Found: Pb, 43·5%; hydrolysable F^-, 4·82 g.-ion/mole. Calc. for K_3HPbF_8: Pb, 43·4%; hydrolysable F^-, 5·0 g.-ion/mole).

Infrared Spectra.—These were measured with a Perkin-Elmer double-beam continuously-recording spectrophotometer, with sodium chloride and potassium bromide optics. The solids were examined as Nujol and hexachlorobutadiene mulls, and as fine powders between sodium chloride plates in the absence of mulling agent.

X-*Ray Powder Photographs.*—These were obtained with a 19 cm. camera and Cu-K_α radiation. Samples were contained in thin-walled Pyrex tubes sealed with picein wax, except for the lead compound which attacks glass readily. This substance was mixed with gum tragacanth and moistened with 40% aqueous hydrofluoric acid, and the resulting paste was smeared on a very fine glass rod.

The photographs of K_3HSnF_8 and K_3HPbF_8 were indexed by analogy with the known lattice parameters of K_3HNbOF_7. All the lines could be accounted for in this way, and in each case a consistent set of lattice parameters was calculated. The photograph of Na_3HTiF_8 was indexed with the help of the morphological axial ratios.

I thank Drs. A. G. Sharpe and N. Sheppard for help and encouragement, and the Department of Scientific and Industrial Research for a maintenance grant.

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[12] Ketelaar, *J. Chim. phys.*, 1948, **45**, 72.