STRUCTURAL STUDIES OF IRON HEXAFLUORIDES: INFRARED SPECTRA OF M_3FeF_6 ($M = Li, Na, K, Rb, Cs, Ag, Tl$)

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ABSTRACT

The IR spectra of a series of M_3FeF_6 compounds ($M = Li, Na, K, Rb, Cs, Ag, Tl$) have been recorded from 4000–40 cm^{-1} . The crystallographic spectra have also been obtained. On the basis of the ensemble of spectral data, a hypothesis has been proposed to explain the nature of crystallographic distortions observed in certain of the compounds. An approximate dipole-induced-dipole calculation provides support for the hypothesis, as well as an explanation of frequency variations observed in the IR spectra.

INTRODUCTION

In the past ten years several structural investigations of $(FeF_6)^{3-}$ complexes have been made. Although many different techniques have been used (crystallography¹⁻², electron-spin resonance³, magnetic measurements⁴⁻⁶, and Mössbauer spectroscopy⁷), until now the medium of absorption spectroscopy has been little exploited. In this paper the IR spectroscopic data obtained for a series of M_3FeF_6 compounds ($M = Li, Na, K, Rb, Cs, Ag, Tl$) will be presented.

This particular series of compounds is of interest because, although the ambient-temperature structures are quite varied (from O_h^5 for Tl_3FeF_6 to C_{2v}^9 for Li_3FeF_6), for each compound except Li_3FeF_6 there exists some temperature at which the structure becomes cubic. It is the purpose of this paper to relate the effects of structural symmetry of the room-temperature phases to the observed IR spectra of the seven compounds and to describe the predominant forces present in these crystals.

Fig. 1. Crystal structures of M_3FeF_6 compounds ($M = Li, Na, K, Rb, Cs, Ag, Tl$).

STRUCTURES AND GROUP ANALYSES

The only compound in the series which has the perfect cubic structure at room temperature is Tl_3FeF_6 . A recent report concerning the synthesis and structural determination² indexed the Tl salt under the space group $O_h^5 (Fm\bar{3}m)$ with four molecules per crystallographic unit cell. As shown in Fig. 1a, the structure is composed of M^+ cations and isolated $(FeF_6)^{3-}$ octahedra. The Bravais cell⁸ is of the form shown in Fig. 1b and contains but one Tl_3FeF_6 unit.

In the point group O_h only the vibrations of species F_{1u} are active in the IR. Therefore, for an isolated octahedral ion, the IR spectrum consists⁹ of a triply degenerate stretching mode ν_4 , and a triply degenerate bending mode ν_3 . In the case of Tl_3FeF_6 , since there is only one Tl_3FeF_6 formula per primitive cell, the IR spectrum, apart from two translatory lattice vibrations of species F_{1u} , does not

TABLE 1
POINT-GROUP CORRELATION SCHEME
(Infrared-active species are underlined)

Isolated FeF_6^{2-}	Ti_3FeF_6 (1 mol)	M_3FeF_6 (1 mol) $\text{M} = \text{K, Rb, Cs, Ag}$	Na_3FeF_6 (2 mol)	Li_3FeF_6 (4 mol)
O_h	O_h	D_{4h}	C_2	C_{2v}
A_{1g} 1(t)	A_{1g} 1(t)	A_{1g} 2(t)	A_g 12(3b, 3c, 3e, 3f)	A_1 24(6a, 9b, 3c, 11f)
A_{2g}	A_{2g}	A_{2g} 1(t)	B_g 12(3b, 3c, 3e, 3f)	A_2 30(6a, 9b, 3c, 12f)
E_g 1(t)	E_g 1(t)	B_{1g} 1(s)		
F_{1g} 1(t)	F_{1g} 1(t)	B_{2g} 2(1b, 1f)		
F_{2g} 1(t)	F_{2g} 2(1b, 1f)	E_g 3(1b, 1c, 1f)		
A_{1u}	A_{1u}	A_{1u}	A_u 17(4b, 3c, 8f)	A_1 24(6a, 9b, 3c, 11f)
A_{2u}	A_{2u}	A_{2u} 4(1b, 1c, 2f)	B_u 16(6b, 3c, 7f)	A_2 24(6a, 9b, 3c, 11f)
E_u	E_u	B_{1u}		
<u>F_{1u} 2(1b, 1c)</u>	<u>F_{1u} 4(1c, 1b, 2f)</u>	<u>B_{2u} 1(b)</u>		
<u>F_{2u} 1(b)</u>	<u>F_{2u} 1(b)</u>	<u>E_u 5(2b, 1c, 2f)</u>		
S B	S B T	S B T	S B T	

differ from that of an isolated octahedron. The results of factor-group calculations are presented in Table 1. In each case, the enumeration of vibrations is accompanied by an approximate description of the modes involved.

Crystallographic studies of the K, Rb, Cs and Ag compounds^{2,10}, (hereafter referred to as the tetragonal compounds), which are isostructural, have shown that the unit cells are, in these cases, similar to that of Ti_3FeF_6 , but with a tetragonal distortion. This distortion might be caused by one or both of two effects: (1) elongation of two opposite Fe-F bonds, and/or (2) tilting of the octahedra with respect to the C_4 axis. If one assumes the former explanation, a tetragonal structure (Fig. 1c) is implied, whose resulting symmetry is D_{4h} and which contains two M_3FeF_6 formulas per unit cell. The primitive cell for this structure has half the volume and therefore contains but one M_3FeF_6 "molecule"⁸. The results of the factor-group analysis for the compounds assuming this structure are presented in Table 1. On comparing the second and third columns of Table 1, one sees that the IR spectrum of K_3FeF_6 , for example, should be considerably more complicated than that of the Ti compound, since in passing from O_h to D_{4h} symmetry all bands become split into multiple components. If the latter of the two possibilities considered above is assumed, a structure analogous to that of Na_3FeF_6 is suggested.

The compound Na_3FeF_6 crystallizes in a monoclinic system of space group C_{2h}^5 ($P2_1/n$) with two Na_3FeF_6 formulas per unit cell¹¹⁻¹³. The crystal structure (Fig. 1e) resembles that of the tetragonal compounds with a marked tilting of the octahedra superimposed on the type of distortion which was considered in the tetragonal compounds assuming D_{4h} symmetry. The results of the factor-group calculations for Na_3FeF_6 are given in the fifth column of Table 1.

The recent synthesis and structure determination of the lithium salt completes the M_3FeF_6 series². In Li_3FeF_6 the cation is so small that the cryolite structure is completely distorted into a crystal of space group C_{2v}^9 ($Pna2_1$) having four Li_3FeF_6 formulas per unit cell. This cell, which is also the primitive cell, is identical¹⁴ to that of Li_3AlF_6 , and can be obtained from the cubic structure in the manner shown in Fig. 1f-g. All atoms lie on sites of symmetry C_1 . Factor-group results are presented in the last column of Table 1.

TABLE 2

SITE-GROUP CORRELATION SCHEME

(Infrared-active species are underlined)

By considering the site symmetry of $(\text{FeF}_6)^{3-}$ octahedra in each of the six compounds, an attempt has been made to correlate successive changes which could occur in the internal-mode region of the spectra (Table 2). The stretching and bending modes observed for Tl_3FeF_6 are expected to split into two and three components, respectively, in the spectrum of the tetragonal compounds. In the spectrum

of Na_3FeF_6 , further splitting is predicted and finally, in the spectrum of the Li compound, the stretching and bending-mode fundamentals should be split into six and nine components, respectively, purely on the basis of site-group selection rules.

Below the correlation diagrams in Tables 1 and 2, schematic representations of each spectrum have been drawn. In each case, the new components arising from lowered symmetry have been represented very approximately, since neither band intensities nor frequencies can be easily deduced. However, the general complexity of the spectra can be predicted from symmetry considerations.

EXPERIMENTAL

All of the compounds were synthesized in this laboratory using the methods described by Tressaud et al.². As it has not been possible to obtain single crystals, powdered samples were prepared as Nujol emulsions between KRS-5 or polyethylene windows. Infrared spectra were measured using a Model 521 Perkin-Elmer grating spectrometer ($2000\text{--}250\text{ cm}^{-1}$) and an RIIC vacuum interferometer ($400\text{--}40\text{ cm}^{-1}$). Although all spectra were repeated at liquid nitrogen temperatures, no significant changes were observed. Infrared spectra of M_3FeF_6 ($\text{M} = \text{Li, Na, Ag, K, Rb, Cs, Tl}$) are reproduced in Fig. 2. Crystallographic powder spectra, which were obtained using Fe $K\alpha$ radiation with a Philips spectrogoniometer, are given in Fig. 3.

DISCUSSION

An analysis will now be made of the IR and crystallographic spectra, and then, on this basis, an attempt will be made to clarify the structural characteristics of the tetragonal compounds.

In the internal-mode region of the spectrum of Tl_3FeF_6 (Fig. 2), two rather simple bands are found which are assigned to the ν_4 stretching mode (448 cm^{-1}) and the ν_3 bending mode (268 cm^{-1}). For the tetragonal compounds, by means of either the site-group or factor-group analysis, splitting of these bands is predicted (see Table 2). The experimental results show that there is no apparent difference between the forms of ν_4 and ν_3 observed for Tl_3FeF_6 and the forms of the analogous bands observed for the Cs compound. However, in the spectra of the Rb, K, and Ag compounds, there is evidence of structure on the bands due to the stretching and bending modes. The splitting which was previously predicted might be the cause of the apparent broadening of the two bands. Since neither the degree of broadening nor the spectral contour changes very much in the case of Na_3FeF_6 , one might suspect that there is a similarity between the structure of the Na com-

Fig. 2. Infrared spectra of M_3FeF_6 compounds.

pound and that of the tetragonal compounds. Support for this hypothesis might be looked for in the lattice-mode region.

From the correlation scheme shown in Table 1, some deductions can be made concerning the external modes. Both of the translatory modes found for the Tl compound should be split into two components in the spectrum of the tetragonal compounds if the symmetry is D_{4h} ; a total of fifteen components should appear in the spectrum of Na_3FeF_6 .

Although the individual components predicted by the factor-group analysis are not resolved, the region over which the translatory modes extend does become increasingly broad in passing from Tl_3FeF_6 to the tetragonal compounds and finally to Na_3FeF_6 . If the change in spectral complexity were due only to polarizabilities or ionic radii of the cations, the spectrum of the K compound would be expected to be considerably more complicated than that of the Rb compound. However, comparison of the observed spectra does not bear out this prediction.

Fig. 3. X-ray diagrams of M_3FeF_6 compounds.

The spectra seem to indicate that the tetragonal deformation observed crystallographically in the Cs, Rb, K and Ag compounds as an elongation of one edge of the cube, is due not only to an elongation of two opposite Fe-F bonds, which would give decreasing symmetry in the order $Cs > Rb > K > Ag$ (obtained from observed unit cell dimensions), but also to tilting of the octahedra, the second explanation proposed above. This conclusion is clearly based on the analogy of these compounds with Na_3FeF_6 in which the octahedra are known¹¹ to be tilted by an angle of about 15° .

The general conclusions based on the interpretations of the IR spectra receive some support from crystallographic data. The principal lines observed in the powder spectrum of Tl_3FeF_6 (Fig. 3) become split in the spectra of all of the tetragonal compounds. Because of the instability of Ag_3FeF_6 , it was difficult to obtain crystallographic spectra of the Ag salt of quality high enough to observe the expected splitting.

Combining the crystallographic data and the results of the IR spectra (particularly the external mode region, which seems more sensitive to distortion), it seems, indeed, that the effect of tilting of the octahedra is being observed. Moreover, there is indication that if the octahedra are untilted in the Tl compound, there is very little tilting of the octahedra in the Cs compound. Apparently the angle is

appreciable in the case of the Rb, K, Ag and, of course, the Na compound. Actually, tilting of the octahedra is a more logical explanation of the tetragonal distortion than an elongation of certain Fe-F bonds, because Fe^{3+} has an electronic high spin $3d^5$ structure which favors six equivalent bonds.

The spectrum of Li_3FeF_6 is rather complicated because the Li^+ ion is so light that the frequency of the lattice modes is shifted into the internal-mode region of the spectrum. Nevertheless, the principal features of the band due to the stretching mode are evident.

In the internal-mode regions of the spectra it might be noticed that not only do both of the fundamentals show a progressive shift in frequency with change in cation but, in addition, the frequency of the bending mode changes more rapidly than that of the stretching mode. In order to explain this effect, the following model has been developed.

In the course of a normal coordinate calculation (to be published) using the Shimanouchi adaptation of the Wilson GF method¹⁵, expressions for the force constants have been derived in terms of internal coordinates for a cubic crystal of Ti_3FeF_6 structure. Thus, in this treatment the distortions in the structures of the Ag, K, Rb, Cs salts have been neglected. (The structures of the Na and Li salts are so distorted from cubic symmetry that they were not considered in this section.) By use of the method of separation of high and low frequencies¹⁶, the stretching and bending modes for an $(\text{FeF}_6)^{3-}$ octahedron in the O_h^5 unit cell can be expressed very approximately as:

$$\lambda_s = (K + f + 4fx^2 - K''')\mu_F \quad (1)$$

and:

$$\lambda_b = \left(2 \frac{(H - H''')}{r_0^2} + 4 \frac{(H' - H'')}{r_0^2} + 4fy^2 \right) \mu_F \quad (2)$$

respectively, where K , H , K''' , f , H''' , H' and H'' are defined in Fig. 4 and $\lambda = 4\pi^2\nu^2c^2$. In the above equations, r_0 is the Fe-F bond length, μ_F the reciprocal mass of F, and x and y are dimensionless geometrical parameters which are related to the distances between the F atoms and the cations along the C_3 axis and which can be defined by the expressions:

$$x = \frac{d - r_0}{\sqrt{2d^2 + (d - r_0)^2}} \quad \text{and} \quad y = \frac{d}{\sqrt{2d^2 + (d - r_0)^2}} \quad (3)$$

where d is one fourth of the length of the crystallographic unit cell. Since f , y^2 and x^2 are the only quantities which change with the nature of the cation, variations of λ_s and λ_b can be reduced to:

$$\Delta\lambda_s = \lambda_s - \lambda_s^0 = \mu_F f(1 + 4x^2) = 8\pi^2\nu_s^0 c^2 \Delta\nu_s \quad (4)$$

and:

$$\Delta\lambda_b = \lambda_b - \lambda_b^0 = \mu_F 4fy^2 = 8\pi^2\nu_b^0 c^2 \Delta\nu_b \quad (5)$$

Fig. 4. Definitions of force constants.

where the superscript zero refers to a hypothetical, isolated $(\text{FeF}_6)^{3-}$ ion. An approximate value of f can be calculated on the basis of dipole-induced-dipole forces. The system shown in Fig. 5 was used, where Fe was assumed to have an infinite mass and the cation possesses a polarizability α ; the perturbing potential is then of the form:

$$V' = \frac{\alpha \mu^2}{R^6} (1 + 3 \cos^2 \theta) = \frac{\alpha}{R_0^6} (1 + 3 \cos^2 \theta) [\mu_0 + \mu'_0 \Delta r]^2 \quad (6)$$

where μ is the effective dipole moment of the Fe-F bond and μ' is its first derivative.

Using the geometrical relationship:

$$q^2 = R^2 + r^2 - 2Rr \cos \theta, \quad (7)$$

and assuming constant θ and small vibrations, the expression for f becomes:

$$f = \frac{\alpha q_0^2}{R_0^8} \left[\frac{12\mu'^2}{\left(\frac{r_0\sqrt{3}}{R_0} - 1\right)^2} - \frac{24\mu_0\mu'}{r_0\left(\frac{r_0\sqrt{3}}{R_0} - 1\right)} + \frac{3\mu_0^2}{r_0^2} \right] \quad (8)$$

Fig. 5. Representation of dipole-induced-dipole system.

For large values of R_0 , the quantity within brackets approaches a constant which is a function only of the properties of the Fe-F bond. In this limit:

$$\Delta v_s = \frac{f \mu_F (1 + 4x^2)}{8\pi^2 v_s^0 c^2} \simeq \frac{x q_0^2}{R_0^8} \frac{\mu_F (1 + 4x^2)}{8\pi^2 v_s^0 c^2} \quad (9)$$

and:

$$\Delta v_b = \frac{f \mu_F (4y^2)}{8\pi^2 v_b^0 c^2} \simeq \frac{x q_0^2}{R_0^8} \frac{\mu_F (4y^2)}{8\pi^2 v_b^0 c^2} \quad (10)$$

Therefore, in the limit of large R_0 , v_s and v_b become linear functions of $xq_0^2(1+4x^2)/R_0^8$ and $xq_0^2(4y^2)/R_0^8$, respectively. The value of $4y^2$ is approximately 40% larger than that of $1+4x^2$; therefore, the observation that in the IR spectra the bending-mode frequency changes more rapidly than the frequency of the stretching mode with the nature of the cation is attributed to the geometrical factors x and y .

The linearities of eqns. (9) and (10) are tested in Fig. 6 for each of the five compounds. It should be recalled that this calculation was set up on the basis of a perfect cubic Tl_3FeF_6 -like structure, i.e. with no consideration of possible tilting of the octahedra. From Fig. 6, it is evident that the bending-mode function is linear

Fig. 6. Variation of internal frequencies with geometrical parameters and cation properties.

and therefore completely insensitive to any distortion which has been proposed in certain compounds. On the other hand, the stretching-mode function displays a marked departure from linearity. On consideration of the changes in the values of x and y which may result if the octahedra are allowed to tilt with respect to the C_4 axis, it can be shown that in the limit of small tilt-angles, the value of y remains unchanged, while the value of x is quite sensitive to any displacement. Thus, these results can be used as a final indication that the octahedra in the tetragonal compounds are tilted.

CONCLUSIONS

The IR spectra of a series of M_3FeF_6 compounds ($M = Li, Na, Ag, K, Rb, Cs, Tl$) have been given. Similarity in the complexity observed in the far-infrared region of the spectra for some of the compounds (Rb, K, Ag, Na) has been used as an indication of the existence of a similar structure for the tetragonal compounds (Cs, Rb, K, Ag) and Na_3FeF_6 . The interpretation of the crystallographic spectra being in agreement with the translatory-mode data, a hypothesis has been proposed that the tetragonal distortion observed crystallographically for the Ag, K, Rb and Cs compounds is caused by a tilting of the $(FeF_6)^{3-}$ octahedra in the lattice.

The vibrational problem has been set up for an undistorted octahedral crystal in terms of internal coordinates in GF form. Of the constants, $f(M-F)$, x^2 and y^2 have been found to have dominant effects on the shift of the internal modes. Moreover, this effect should be stronger for the bending mode than for the stretching mode, thus explaining the observed spectral data. As a result of a calculation of dipole-induced-dipole forces, f has been shown to be a function of geometrical parameters in the crystal, as well as of the cation polarizability. Consideration of the plots of $\alpha q_0^2(1+4x^2)/R_0^8$ and $\alpha q_0^2(4y^2)/R_0^8$ versus v_s and v_b , respectively, for five of the compounds, showed that tilting of the octahedra in the tetragonal compounds must be postulated to explain the ensemble of IR and crystallographic data.

ACKNOWLEDGMENTS

We should like to thank Professor P. Hagenmuller for his continued interest and his helpful advice and discussions of this work. The infrared spectra were obtained with the cooperation of the Laboratoire de Spectroscopie Infrarouge, Faculté des Sciences de Bordeaux. We should like to acknowledge the advice and assistance of Professors J. Lascombe and G. Turrell of that laboratory.

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