554. *The Infrared Spectra of Alkali Salts of Complex Fluoro-acids.*

By R. D. PEACOCK and D. W. A. SHARP.

The infrared spectra of a large number of alkali-metal salts of complex fluoro-acids have been recorded. The frequencies of the observed peaks are discussed in terms of the position of the central atom of the anion in the Periodic Table. It is concluded that complex fluorides, even in perovskite structures, show some covalent bonding in the central atom–fluorine bond. The infrared spectra of some complexes of unknown stereochemical configuration are discussed briefly.

ALTHOUGH much has been written about the metal–ligand bonding in complexes there are, in fact, few data on the bond strengths, most of the values being derived from stability constants of complexes in solution.[1] Since the stability constant of a complex is a measure of the free-energy change, this method of evaluating bond strengths involves the assumption that the entropy changes are approximately constant, and it is interesting to compare these

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[1] Irving and Williams, *J.*, 1953, 3192.

values of bond strengths with values derived from a different method. The force constant for the symmetrical stretch of a metal–ligand bond should give some indication of the bond strength [2] but unfortunately the possibility of obtaining such force constants for a wide range of complexes is not great since the measurement of Raman spectra, which would be necessary to obtain the values of the symmetrical bond-stretching frequencies, is very difficult for this type of compound. Metal–oxygen stretching frequencies for a limited number of hydrates are known,[3] and these indicate that the order of stability of the hydrates is $Mn^{2+} < Cu^{2+} > Zn^{2+}$, *i.e.*, in agreement with the normal Irving–Williams order for the stability of complexes. The metal–oxygen symmetrical stretching frequency in acetyl-acetone complexes and benzoylacetone complexes follows the order of stability constants of the complexes.[4] The symmetrical stretching frequencies of a large number of chlorides, bromides, and iodides are known [5,6] and their values change in the same order as the stability constants where these are known. The metal–carbon stretching frequencies in a small number of complex cyanides have been discussed in terms of back-bonding from the metal to the ligand.[7]

Table 1 contains the absorption frequencies of some complex fluoro-anions and related compounds. All values refer to present work except where a reference is given. Except for the cryolites, the peaks are quite sharp and the position of the peak is characteristic of the particular complex fluoro-anion. In particular, it was found that the fluoro-silicate ion, $SiF_6{}^{2-}$, was readily detected by the presence of a very characteristic band at 480 cm.$^{-1}$.

Tetrahedral.—Table 1 contains values for the infrared spectrum of K_2BeF_4 which has a broad peak of low intensity which is split into two components at 773 and 819 cm.$^{-1}$. This peak should be derived from the ν_3 vibration of a tetrahedral molecule, the band being split either because of the interaction of the ions in the unit cell or because of the low site symmetry of the ion in the crystal lattice (cf. the similar splitting of the 1100 cm.$^{-1}$ band of $BF_4{}^-$ in potassium tetrafluoroborate [8,9]). Woodward [6] states that it has so far proved impossible to measure the Raman spectrum of the fluoroberyllate ion, so a precise discussion of the Be–F bond strength is not possible; however, it seems from the values of ν_3 that the $BeF_4{}^{2-}$ ion follows the trend set by the isoelectronic entities $BF_4{}^-$ and CF_4.

Octahedral.—By far the majority of complex fluorides have octahedra of fluoride ions about the central metal atom, these octahedra sometimes sharing corners. An octahedral molecule or ion, $MF_6{}^{n-}$, should have two (ν_3 and ν_4) infrared-active vibrations, and for the lighter atoms, M, two frequencies are observed in the region studied in the present investigation. By analogy with the gaseous molecules, MF_6, the absorption at the higher frequency is due to the vibration ν_3 and that at the lower to the vibration ν_4. Since ν_4 was not observed for all ions the present discussion will be confined to ν_3.

Qualitatively, the frequency of ν_3 decreases down a group of the Periodic Table and also decreases towards the more electropositive side of the Table. These changes are not completely regular and the slight irregularities will be discussed later. The first of these changes probably reflects the increase in mass of M. The second reflects the increase in the effective ionic radius of M, which is a measure of the decrease in the covalent character in the M–F bonds. The frequency of ν_3 decreases with decrease in valency of M, this trend again reflecting the increasing ionic character of the M–F bond with the increase in effective size of the M^{6-n} ion. The sharing of corners of octahedra does not greatly affect the frequency of ν_3 (see K_3AlF_6 and $KAlF_4$) and there is a regular change in the value of ν_3

[2] Cottrell, " The Strengths of Chemical Bonds," 2nd edn., Butterworths, London, 1958.
[3] Mathieu, *J. Chim. phys.*, 1953, **50**, C79.
[4] Nakamoto, McCarthy, and Martell, *Nature*, 1959, **183**, 459.
[5] Mathieu, *J. Inorg. Nuclear Chem.*, 1958, **8**, 33.
[6] Woodward, *Trans. Faraday Soc.*, 1958, **54**, 1271.
[7] Caglioti, Sartori, and Scrocco, *J. Inorg. Nuclear Chem.*, 1958, **8**, 87.
[8] Coté and Thompson, *Proc. Roy. Soc.*, 1952, **210**, *A*, 217.
[9] N. N. Greenwood, personal communication.

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TABLE 1. *Infrared absorption frequencies of complex fluoro-ions* (cm.⁻¹).

Co-ordination number 4

BeF₄²⁻	BF₄⁻ ᵃ	CF₄ ᵇ
773, 819	1100 (786)	1283 (903)

Co-ordination number 6

(i) Bivalent (measured in perovskites)

Mg	Cr	Mn	Fe	Co	Ni	Cu	Zn
462	481	407	431	439	445	489	437

Ca							Cd
<400							<400

(ii) Tervalent (measured in cryolites)

Al
570 *

Sc	Ti	V	Cr	Mn	Fe	Co	Ga
479	452	511	535, 522	560, 617 w	465 †	480	464

Y	Zr	Nb	Mo	Tc	Ru	Rh	In
<400	—	—	—	—	514, 497	530, 512	446
					479	500	

La							<Tl
<400							400

(iii) Quadrivalent

Si
(656) ᶜ
726 ‡, 480

Ti	V	Cr	Mn	Fe	Co	Ni	Ge
560	583	556	622	—	—	654	600
Zr	Nb	Mo	Tc	Ru	Rh	Pd	Sn
<400	—	—	—	581	589	602	552
Hf	Ta	W	Re	Os	Ir	Pt	Pb
—	—	—	541	548	568	583	502

Th
400

(iv) Quinquevalent

P ᵈ
(741) §
845, 559

V
715

As
700 §, 400

Nb	Mo	Tc	Ru		Sb
580	623	—	640		660
Ta	W	Re	Os	Ir	
580	594	627	616	667	

(v) Sexivalent

S ᵉ
965 (775)
Se ᶠ
787 (710)
Te ᶠ
752 (697)

Mo
741 (741)

W ᶠ	Re ᵍ	Os	Ir ʰ
712 (772)	716 (753)	—	718 (696)
U	Np ⁱ	Pu ⁱ	
640 (656)	624 (648)	615 (628)	

Miscellaneous

AlF₄⁻ *
599

MnF₅⁻
614

ZrF₇³⁻	NbF₇²⁻	MoF₇⁻	Tc	IF₆⁻
<400	524	645	—	624
	TaF₇²⁻	WF₇⁻	ReF₇⁻	AuF₄⁻
	518	620	598	477, 585

Figures in parentheses refer to the symmetrical stretching frequency, ν_1, observed from Raman spectra. All spectra of potassium salts except CsReF₇.

* For the AlF₆³⁻ anion de Lattre ʲ finds 599 cm.⁻¹ for Na₃AlF₆ and records that KAlF₄ is similar.

† For the FeF₆³⁻ anion de Lattre ʲ finds 492—458 cm.⁻¹ (diffuse) for Na₃FeF₆ and (NH₄)₃FeF₆.

‡ For the SiF₆²⁻ anion de Lattre ʲ finds 735 and 488 cm.⁻¹ for K₂SiF₆.

§ The absorption bands thus marked have also been recorded previously.ᵏ

ᵃ Edwards, Morrison, Ross, and Schultz, *J. Amer. Chem. Soc.*, 1955, **77**, 266. ᵇ Woltz and Nielsen, *J. Chem. Phys.*, 1952, **20**, 307. ᶜ Siebert, *Z. anorg. Chem.*, 1953, **274**, 34. ᵈ Woodward, *J. Inorg. and Nuclear Chem.*, 1956, **3**, 326. ᵉ Landolt–Börnstein, " Atom- und Molekularphysik," Springer Verlag, Berlin, 1951. ᶠ Burke, Smith, and Nielsen, *J. Chem. Phys.*, 1952, **20**, 447. ᵍ Gaunt, *Trans. Faraday Soc.*, 1954, **50**, 209. ʰ Mattraw, Hawkins, Carpenter, and Sabol, *J. Chem. Phys.*, 1955, **23**, 985. ⁱ Malm, Weinstock, and Classen, *ibid.*, 1955, **23**, 2192. ʲ de Lattre, *J. Chem. Phys.*, 1952, **20**, 1180. ᵏ Sharp and Sharpe, *J.*, 1956, 1855.

from the volatile MF_6 compounds to the perovskites, KMF_3, where the bonding is supposed to be purely ionic. There is no great difference between the frequencies found for transitional and B-group, non-transitional, complexes. These qualitative observations appear to support the formulation of all the $MF_6{}^{n-}$ groups as complexes with a constant, or smoothly changing, order of covalent character. From the mere fact that the infrared spectra of perovskites are observable between 400 and 500 cm.$^{-1}$ it appears that there is some covalent bonding even in these compounds.

Quantitative consideration of these results is much more arbitrary. Ideally one would like to consider the symmetrical stretching force constant of the M–F bond but this can only be derived from Raman spectra. The Tables show that for molecules and ions where ν_3 and ν_1 are both known there is no direct relation between these two frequencies. This is borne out by calculations made on an octahedral group, MX_6, using various force fields.[10,11] The abrupt change in the value of $\nu_1 - \nu_3$ on passing from the series SF_6, SeF_6, TeF_6 to UF_6 has been discussed and tentatively recognised as being due to a change in the type of hybridisation in passing from the B to the A sub-group.[12] The fact that the frequency of ν_1 for MoF_6 is less than the value for WF_6 indicates an unexpected change in the force constant between these two compounds. However, one may hope that for a series of molecules or ions of similar mass, trends in ν_3 should follow trends in ν_1 and that this in turn can be related to changes in the force constant K_1. For example, in the isoelectronic series of ions SF_6, $PF_6{}^-$, $SiF_6{}^{2-}$, and $AlF_6{}^{3-}$ (Table 2) it can be considered that the values of ν_1 and K_1 for $AlF_6{}^{3-}$ would follow the trend set by the other ions, the force constant being smaller than that for the $SiF_6{}^{3-}$ ion.

TABLE 2.

	ν_1 (cm.$^{-1}$)	$10^5 K_1$ (dynes cm.$^{-1}$) [6]	ν_3 (cm.$^{-1}$)
$AlF_6{}^{3-}$	—	—	570
$SiF_6{}^{2-}$	656	4·82	726
$PF_6{}^-$	741	6·14	845
SF_6	775	6·72	965

(For other references see Table 1.)

Theories on bond strengths for transition-metal–ligand bonds use two approaches. The ionic radius [13] and thus the interatomic separation [14] can be considered in terms of the crystal-field stabilisation of the complex. For octahedral ions this would predict a maximum contraction, *i.e.*, maximum bond strength, for d^3 and d^8 configurations, with complications arising from the Jahn–Teller distortion of the d^4 and d^9 configurations. Results on $M^{2+} \ldots F^-$ separations [14] follow crystal-field predictions but there are notable gaps at the d^4 and d^9 configurations since meaningful octahedral radii cannot be obtained for Cr^{2+} and Cu^{2+}. The alternative approach is to relate the bond strength to the tendency towards covalent-bond formation [1,15] between ligand and cation, this tendency being measured by the appropriate ionisation potential. Williams [15] points out that the crystal-field approach as applied to the stability of complexes leaves much to be desired, especially when considering the d^4 and d^9 configurations. Qualitatively, for $MF_6{}^{4-}$ and $MF_6{}^{3-}$ ions the observed values of ν_3 follow the $M^+ \longrightarrow M^{2+}$ and $M^{2+} \longrightarrow M^{3+}$ ionisation potentials respectively, the agreement being particularly good over the d^4 to d^{10} configurations. There appear to be irregularities for the d^0 and d^1 ($ScF_6{}^{3-}$ and $TiF_6{}^{3-}$) configurations for the $MF_6{}^{3-}$ ions and for the d^2 ($CrF_6{}^{2-}$) configuration for the $MF_6{}^{2-}$ series but the appropriate

[10] Venkateswarlu and Sundaram, *Z. phys. Chem. (Frankfurt)*, 1956, **9**, 174.
[11] Pistorius, *J. Chem. Phys.*, 1958, **29**, 1328.
[12] Heath and Linnett, *Trans. Faraday Soc.*, 1949, **45**, 264.
[13] Hush and Pryce, *ibid.*, 1957, **26**, 143.
[14] Hush, *Discuss. Faraday Soc.*, 1958, **28**, 145.
[15] Williams, *ibid.*, p. 123.

ionisation potentials are not accurately known. It seems, therefore, that the present measurements are in accordance with the idea of electron transfer from ligand to cation.

As stated, d^4 and d^9 configurations should show Jahn–Teller splitting resulting in distortion of the regular octahedral co-ordination.[14] Such distortion might cause splitting in the vibrational frequencies. No splitting is observed with the complexes $KCrF_3$ and $KCuF_3$ (preliminary experiments[16] showed a splitting but re-preparation removed the extra bands which must have been due to hydrolysis) and it must be assumed either that the extra bands are too weak or that the splitting is too small for observation. Crystallographically $KCrF_3$[17] and $KCuF_3$[18] are not isostructural with the perovskites. K_3MnF_6, which seems to show distortion in its crystal structure,[19] does have an extra infrared band at 617 cm.$^{-1}$.

Observations could not be made on all possible quadrivalent complexes. The d^4 complex, K_2FeF_6, does not exist and the d^5 complex Cs_2CoF_6, does not give good infrared spectra. K_2NiF_6 is the only element in the first transition series to give a spin-paired complex fluoride.[20] The position of the peak cannot be adequately compared with that expected for a spin-free complex as this would involve extrapolation over a gap of two elements but a simple comparison indicates that the change from a spin-free to a spin-paired configuration does not greatly affect the bond strength as estimated by the present method.

In addition to the weak extra peak observed for K_3MnF_6, the main peak in many other cryolites is split into several components of approximately equal intensity. It has been noted that cryolite structures are particularly prone to slight departures from ideality, these distortions being variously explained as being due to changes of composition[21] or to temperature effects causing rotation of the MF_6^{3-} octahedra.[22] The first of these effects might cause splitting of the fundamental vibrations because of the lowering of site symmetry of the complex ion; rotation effects should tend to increase the symmetry of the complex ion. The presence of more than one molecule in the unit cell might cause splitting of the infrared peaks.

The second- and third-period transition elements show fairly regular trends across the Periodic Table. The rather large drop in the observed infrared frequency on passing from K_2TiF_6 to K_2ZrF_6 is probably due to the change in co-ordination number of M from 6 to 8 in going from titanium to zirconium;[23] K_3ZrF_7, where zirconium is heptaco-ordinate, also has a low value. For pairs of elements where the lanthanide contraction is showing its maximum effect (*e.g.*, Nb, Ta), the observed infrared peaks are close together.

Miscellaneous.—Addition of a fluoride ion to an MF_6^{n-} anion lowers the observed infrared frequency. It cannot be said whether the observed vibration bears any relation to the infrared frequencies observed for octahedral ions. The observation of an infrared peak for $KMnF_5$ at 614 cm.$^{-1}$ as compared with 622 cm.$^{-1}$ for K_2MnF_6 suggests that the co-ordination is octahedral in the $KMnF_5$; a discrete MnF_5^- ion should give absorption at a frequency very much higher than that observed for the MnF_6^{2-} ion (cf. NbF_7^{2-} and NbF_6^-). The presence of only one peak in the spectrum of KIF_6 suggests a fairly symmetrical structure for the IF_6^- ion; the structure of this ion should be heptaco-ordinate with one position occupied by a lone pair of electrons. The ions of similar electronic structures, $TeCl_6^{2-}$, $TeBr_6^{2-}$, appear to be effectively spherical in the crystalline state even if they are not actually octahedral (for a discussion of the structure of these ions see reference 24).

[16] Sharp, *Discuss Faraday Soc.*, 1958, **28.**, 186.
[17] Edwards and Peacock, unpublished observations.
[18] Martin, Nyholm, and Stephenson, *Chemistry and Industry*, 1956, 83.
[19] Peacock, *J.*, 1957, 4684.
[20] Klemm and Huss, *Z. anorg. Chem.*, 1949, **258**, 221.
[21] Brosset, *Arkiv Kemi, Min., Geol.*, 1946, **21**, *A*, 142.
[22] Bode and Voss, *Z. anorg. Chem.*, 1957, **290**, 1.
[23] Bode and Teufer, *Acta Cryst.*, 1956, **9**, 929.
[24] Eméleus and Sharpe, *J.*, 1949, 2206.

$KAuF_4$ shows two distinct infrared peaks. This salt appears isomorphous with $KBrF_4$,[25] having square planar co-ordination about the central gold atom. This structure, however, does allow further interaction between gold and fluorine atoms belonging to another AuF_4^- group to give distorted octahedral symmetry about the gold atom (cf. the structure of $KBrF_4$ [26]); such a structure would be expected to show extra infrared bands. It has recently been pointed out [27] that similar distorted octahedra can be considered to occur in the complexes $Cs_2AgCl_2AuCl_4$ and $Cs_2AuCl_2AuCl_4$.[28]

EXPERIMENTAL

The complex fluorides were prepared by the standard literature methods. Infrared spectra were measured in Nujol or hexachlorobutadiene mulls, and, where the salts were stable to traces of moisture, in potassium bromide pressed discs. Mulls were prepared in the dry-box. Spectra were recorded on a Perkin-Elmer Model 21 recording spectrophotometer with rock-salt or potassium bromide optics. Specimens of K_3NiF_6 and K_3CuF_6 would not give good infrared spectra. The infrared band of K_3CoF_6 is extremely broad and it is believed that the peaks of the present compounds are so broad as to preclude observation. Cs_2CoF_6 immediately attacked Nujol and satisfactory infrared spectra could not be obtained.

CHEMISTRY DEPARTMENT,
    UNIVERSITY OF BIRMINGHAM,
        EDGBASTON, BIRMINGHAM, 15 (R. D. P.).
INORGANIC CHEMISTRY RESEARCH LABORATORIES,
    IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
        LONDON, S.W.7 (D. W. A. S.).   *[Received, April 24th, 1959.]*

[25] Peacock, unpublished observations.
[26] Sly and Marsh, *Acta Cryst.*, 1957, **10**, 378.
[27] Harris, *J.*, 1959, 682.
[28] Elliot and Pauling, *J. Amer. Chem. Soc.*, 1938, **60**, 1846.