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Molar Refractivity as a Diagnostic Tool for Determining Composition of Transition Element Fluoride Complexes[1]

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The composition of alkali (and ammonium) fluoride complexes of the tetravalent d- and f-transition elements Zr, Ce, Th, U, and Pt can be determined from their molar refractivities, R. A simple linear rule applies: $R_{n\mathrm{AF}\cdot\mathrm{MF}_4} = nR_{\mathrm{AF}} + R_{\mathrm{MF}_4}$. The absolute value of the refractivity depends on the tetravalent element M and the mole ratio (n) of alkali fluoride (AF) to MF_4. The increment in refractivity per mole of a given alkali fluoride in the complex is a constant. For some 45 compounds it was found that R_{AF} is equivalent to R_{A^+} plus R_{F^-}, Fajans' refractivities for the aqueous ions. Thus, a close estimate of the molar refractivity for many compounds can be obtained by adding multiples of Fajans' aqueous refractivities for the alkali and fluoride ions to the measured refractivity of the tetrafluoride. The $R_{n\mathrm{AF}\cdot\mathrm{MF}_4}$ values for analogous compounds reflect the sequence $R_{\mathrm{CeF}_4} > R_{\mathrm{UF}_4} \approx R_{\mathrm{PtF}_4} > R_{\mathrm{ThF}_4} > R_{\mathrm{ZrF}_4}$. Additivity also applies to $R_{n\mathrm{AF}\cdot\mathrm{MF}_3}$ and $R_{n\mathrm{AF}\cdot\mathrm{MF}_5}$, the molar refractivities of trivalent and pentavalent fluoride complexes. A model for statistical treatment of refractivity data is given.

Introduction

The use of X-ray diffraction to characterize inorganic compounds is of great value. However, with its increasing use there has been a decline in the use of optical crystallography. This is unfortunate, because the two techniques supplement each other in important ways. In particular, use of the polarizing microscope to examine crystals can rather quickly classify them into three major groups: (1) cubic (isotropic, one refractive index); (2) tetragonal or hexagonal (uniaxial, two refractive indices, n_o and n_e); and (3) orthorhombic, monoclinic, or triclinic (biaxial, three refractive indices, n_x, n_y, and n_z). The above classification can be made even if the crystals totally lack faces; classification into subgroups can be made if there are well-developed faces.

Also, there is a distinct relationship between optical properties and the internal structure of a crystal. For example, calcium carbonate and sodium nitrate contain triangular anions whose plane is perpendicular to the threefold rhombohedral axis; they thus show a much higher refractive index parallel to the planar groups than perpendicular to them. This view can be extended to crystals containing the $\mathrm{MF}_6{}^{x-}$ ion which frequently is distorted along its threefold axis, with a consequent effect on the optical properties.

Even less widely utilized by inorganic chemists in the United States is the semiquantitative information concerning stoichiometry provided by the molar refractivity, which can be derived from easily made refractive index and density measurements. In contrast, the usefulness of refractometry in structural chemistry is of current interest in Europe.

The refractivity of inorganic and organic substances in various states has long been the subject of study by Fajans and his school. Indeed, his newest publication[2] comes after 43 years of leadership in this field. While Fajans has emphasized the interpretation of deviations from additivity of Lorentz–Lorenz molar refractivities (see remarks by Fajans in the Correspondence section of this issue), our purpose is to show that in the area of fluoride complexes additivity is sufficiently well obeyed to be of great aid in the study of these complexes. For example, the refractivities of complexes containing different amounts of KF differ by about 5 cm^3/mol of KF, so that deviations from additivity amounting to even several tenths of a cm^3 would seldom cause a gross error in assigning stoichiometry. There is a sufficient body of quantitative information on alkali and ammonium fluoride complexes (particularly for the tetravalent elements) that diagnosis for chemical composition can often be made from refractive index and density measurements alone.

Particularly simplifying is the finding presented here that the refractivity of a complex fluoride, such as $n\mathrm{KF}\cdot\mathrm{MF}_4$, for example, can be estimated by adding the Fajans' refractivities for the aqueous ions K^+ and F^- to the measured refractivity of the particular MF_4.

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

[2] K. Fajans, *Struct. Bonding* (Berlin), **3**, 88 (1967), and references therein.

TABLE I

EXPERIMENTAL MOLAR REFRACTIVITIES OF nAF·MF$_4$ COMPLEXES[a]

n	M	A					
		Li	Na	K	Rb	NH$_4$	Cs
5	Th			40.2[3,4]			
4	Ce					42.8[6]	
	Th		24.6[3,7]			42.0	
	U	24.6[3,5]				42.3[6]	
3.5	Th		(23.4)[3,7]				
3	Zr		20.9[10,11]	27.0[3]		32.3[12]	38.4[3]
	Th	21.5[3,8]			(34.4)[3]		42.1[3]
	U	21.9[3]	(24.4)[3]	30.0[3]	(34.6)[3]		(42.6)[3,9]
2	Zr	16.8[3]	β (17.1)[10]				30.2[3]
	Ce					28.4[6]	
	Th		β 20.0[3]	24.0[4,14]	26.5[3,16]		(34.3)[3]
	U		δ 20.5[3,7] β (20.2)[3,7]	24.4[13,14]	27.3[15]	28.6[15]	
	Pt			24.5[17]	27.5[17]		
1.167 (7:6)	Zr		15.5[18]				
	Ce					23.1[6]	
	Th		18.0[7]	20.0[3]	21.8[3]		
	U		18.7[7]	20.4[3]	22.0[3,13]	22.4	
1	Th						(24.6)[3]
	U	17.4[19]					

[a] Values in parentheses were estimated from measured refractive indices, assuming a reasonable value for the molecular volume (see text).

Extension of this approach to fluorides of trivalent and pentavalent elements is also suggested by the data.

Data and Calculations

The data collected here concern primarily fluoride complexes of the tetravalent actinides U and Th with additional data for Zr(IV), Ce(IV), and Pt(IV) compounds as well as for some U(V), Ta(V), and lanthanide(III) compounds. Many of the data were calculated from the results of the extensive fluoride-phase studies made at Oak Ridge National Laboratory. In those classic studies, X-ray and optical data constituted an important part of the results.[3] However, that optical data would be even more useful had density always been measured.

The Lorentz–Lorenz molar refractivity of a substance has the dimension of cubic centimeters (this dimension for R will be understood to apply throughout the remainder of this paper) and is given by eq 1, where n is the index of refraction for a definite wavelength (in this paper the Na D line), M is the formula weight, and d is the density. Frequently, optical data are given

$$R = \frac{n^2 - 1}{n^2 + 2}\left(\frac{M}{d}\right) \tag{1}$$

$$R = \frac{n^2 - 1}{n^2 + 2}\left(\frac{\text{cell volume (Å}^3) \times 0.6025}{\text{formula units per cell}}\right) \tag{2}$$

together with X-ray cell constants and the alternate form, eq 2, is useful, avoiding calculation of formula weight. The refractive index has one value for isotropic crystals. For uniaxial crystals a mean index is used, obtained from $n = (n_o{}^2 n_e)^{1/3}$ or, with good approximation, $(2n_o + n_e)/3$. For biaxial crystals $(n_x n_y n_z)^{1/3}$ is used; when n_y is not known, the geometric mean of the highest and lowest indices $(n_x n_z)^{1/2}$ is used as an approximation for n. In this paper, R denotes the (Lorentz–Lorenz) molar refractivity and its subscript is the substance in question; *i.e.*, $R_{n\text{AF}\cdot\text{MF}_4}$ is the refractivity of the complex containing n mol of alkali fluoride (AF) and 1 mol of tetrafluoride (MF$_4$).

Refractivities of nAF·MF$_4$ Complexes.—In Table I[3–19] are collected refractivities of 44 nAF·MF$_4$ complexes with n ranging from 1 to 5; n is an integer except in the 7:6 class of rhombohedral complexes, which have an "extra AF" per each 6AF·MF$_4$ formula units.[18] In calculating R values for the 7:6 complexes, the formula was taken as 1.167AF·MF$_4$.

In Table I, R values for complexes having different AF:MF$_4$ ratios, n, are listed in the same vertical column for a particular alkali fluoride. From left to right in a given row, a constant AF:MF$_4$ ratio is maintained with change of alkali cation, A.

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In Table II[3,4,20–22] are collected R_{MF_4} values for some d- and f-transition element tetrafluorides, together with a summary of refractive index and cell volume information necessary to calculate R values by eq 2.

TABLE II

REFRACTIVITIES OF SOME TETRAFLUORIDES

MF_4	Geometric mean refractive index	Lorentz–Lorenz function, $(n^2 - 1)/(n^2 + 2)$	Vol/formula unit, Å^3	R_{MF_4}
ZrF_4	1.5879	0.33649	61.0	12.4[3]
CeF_4	1.6308	0.35608	74.0	15.9[21]
ThF_4	1.5173	0.30268	81.1	14.8[22] (15.3)[3,4]
UF_4	1.5779	0.33181	77.4	15.5[3,20]
PtF_4	...	...	63.7	(15.6)[a]

[a] The value for R_{PtF_4} was estimated from R_{UF_4} as a result of the similarity of the pairs $R_{K_2UF_6}$, $R_{K_2PtF_6}$ and $R_{Rb_2UF_6}$, $R_{Rb_2PtF_6}$, given in Table I.

From the data in Table II, it is noted that R_{ZrF_4} is smaller than R_{UF_4} by $\Delta R = 3.1$. In Table I it can be seen that the refractivities of analogous Zr and U complexes reflect this difference. This is demonstrated in Figure 1, as the $R_{nNaF \cdot ZrF_4}$ line is displaced from the $R_{nNaF \cdot UF_4}$ line by an average ΔR of 3.1 (obtained from the two least-squares equations).

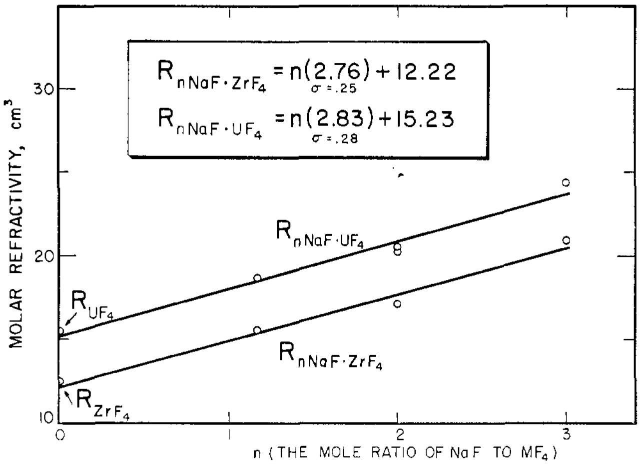

Figure 1.—Molar refractivities of comparable sodium fluoride complexes with zirconium or uranium tetrafluoride. The lines shown are the least-squares lines $R_{nNaF \cdot ZrF_4} = n(2.758) + 12.22$ and $R_{nNaF \cdot UF_4} = n(2.833) + 15.23$, with R as a function of n (σ, standard deviation).

In Figure 2 are shown R values for complexes with different alkalies but with a common tetravalent element, U(IV). It is seen that the slopes of the lines decrease in the order Cs > NH_4 > Rb > K > Na > Li; however, the lines have a common origin, R_{UF_4}. In Figure 1, R values are shown for two series of complexes having a common alkali (Na) but different tetravalent elements (U and Zr); in this latter case the lines have (essentially) a common slope but different intercepts, R_{ZrF_4} and R_{UF_4}.

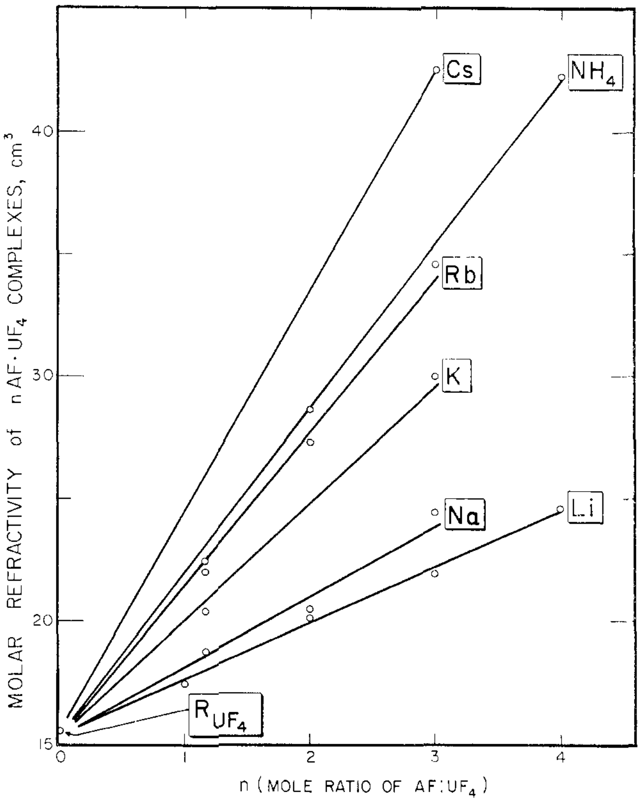

Figure 2.—Molar refractivities of alkali fluoride–uranium tetrafluoride complexes.

Treatment of the Data for $nAF \cdot MF_4$ Complexes.—The refractivity data in Tables I and II are well represented by a series of straight-line plots, such as are given in Figures 1 and 2. By linear regression analysis of the individual data sets, it was established that: (1) the refractivities of $nAF \cdot MF_4$ complexes containing a common alkali fluoride but different tetravalent elements have the same incremental increase in refractivity per mole of alkali fluoride (statistically indistinguishable slopes); (2) for the different alkali fluorides but the same tetravalent element, the functions have a common origin.

Having established these facts above separately, the 49 data points (Tables I and II) were then fitted to a combined linear model which required that the above two findings be met simultaneously by all of the data. In statistical notation, this model may be written $E(Y_{ijk}) = \alpha_i + \beta_j X_{ijk}$, where Y_{ijk} and X_{ijk} are the kth observed values of molar refractivity and mole ratio for the ith tetravalent element and the jth alkali fluoride and $E(Y_{ijk})$ denotes the expected value of the refractivity.

The model successfully predicts the refractivity to better than 1.5% over-all and was as far off as 5% in only a single instance, that of Na_3UF_7; the abnormal volume of this compound is discussed later. Using the 49 data points, the sum of squares of deviations is 12.7 and the weighted variance is 0.33. In the LiF–UF_4 case, for example, this model yields a value for the LiF slope (β_{LiF}) which best represents all of the lithium fluoride–metal tetrafluoride data and not solely the

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LiF–UF_4 data, with the intercept being the value projected, using all of the $n\mathrm{AF}\cdot\mathrm{UF}_4$ data and not just the LiF–UF_4 data.

A Correlation of the Empirical Slopes with Some Refractivities for Alkali and Fluoride Ions.—The best estimate of the incremental increase in $R_{n\mathrm{AF}\cdot\mathrm{MF}_4}$ per mole of a given alkali fluoride is the slope as derived above. These empirical slopes are compared in Table III[12,23,24] with the refractivities of the individual alkali fluorides and with Fajans' classic values for the sum of the ionic refractivities $(R_{\mathrm{A}^+} + R_{\mathrm{F}^-})_{\mathrm{aq}}$ and $(R_{\mathrm{A}^+} + R_{\mathrm{F}^-})_{\mathrm{g}}$. It is seen that the increment in refractivity of these solid complexes per mole of alkali fluoride is in good (and perhaps surprising) agreement with the value obtained using Fajans' ionic refractivities $(R_{\mathrm{A}^+} + R_{\mathrm{F}^-})_{\mathrm{aq}}$. Statistically, there is no significant difference at the 0.05 level between the empirical slope values in column 2 and the $(R_{\mathrm{A}^+} + R_{\mathrm{F}^-})_{\mathrm{aq}}$ values in column 3. The sum of squares of deviations increased only slightly, from 12.7 to 15.2, when the slopes were fixed at the $R_{\mathrm{AF(aq)}}$ values in fitting the data. The sum of squares of deviations increases to 23.1 when the gaseous refractivity values are used and enormously, to 479, when the refractivities of the solid alkali fluorides themselves are used.

Table III

Incremental Increase in Refractivity for $n\mathrm{AF}\cdot\mathrm{MF}_4$ Compounds per Mole of Alkali Fluoride. Comparison with Ionic Refractivities[a] and Those of the Solid Alkali Fluorides

AF	Empirical slopes and std dev	$(R_{\mathrm{A}^+} + R_{\mathrm{F}^-})_{\mathrm{aq}}$[23]	$(R_{\mathrm{A}^+} + R_{\mathrm{F}^-})_{\mathrm{g}}$[24]	$R_{\mathrm{AF(c)}}$[12]
LiF	2.34 (0.11)	2.28	2.52	2.34
NaF	2.70 (0.10)	2.80	2.92	3.01
KF	4.97 (0.10)	4.85	4.69	5.05
RbF	6.36 (0.13)	6.39	6.23	6.49
NH_4F	6.78 (0.09)	6.91	6.75	7.21
CsF	9.16 (0.12)	9.13	8.97	9.30

[a] Fajans' refractivities for the aqueous ions[23] are (values for the gaseous species[24] are enclosed in parentheses): Li^+, −0.32 (0.08); Na^+, 0.20 (0.48); K^+, 2.25; Rb^+, 3.79; NH_4^+, 4.31; Cs^+, 6.53; F^-, 2.60 (2.44).

Molar Refractivities of $\mathbf{AF\cdot UF_5}$ Compounds.—In Table IV[23,25-28] are collected measured values for alkali fluoride–uranium pentafluoride compounds of stoichiometry $\mathrm{AF}:\mathrm{MF}_5 = 1:1$.[25] Optical data are known for the 1:1 complexes only, and the refractivities are tabulated in Table IV, column 2. Fajans' aqueous R_{A^+} was then subtracted from each, to give the net $R_{\mathrm{UF}_6^-}$ value for this anion in the various compounds.

Molar Refractivities of $\mathbf{n AF\cdot MF_3}$ Complexes.—For the lanthanides, data for $\mathrm{AF}:\mathrm{MF}_3 = 1:1$ are known only for $\mathrm{LiF}\cdot\mathrm{MF}_3$ and $\mathrm{NaF}\cdot\mathrm{MF}_3$ compounds.[3,29] (Note: the R_{MF_3} data in ref 29 are not correctly listed.) The tetragonal $\mathrm{LiF}\cdot\mathrm{MF}_3$ compound types are formed only with the heavier lanthanides, while the hexagonal $\mathrm{NaF}\cdot\mathrm{MF}_3$ types form throughout the series.[29] There is nearly a constant difference ($\Delta R \approx 2.6$) between R_{MF_3} and $R_{\mathrm{LiF}\cdot\mathrm{MF}_3}$ (M = Eu–Lu). The $\mathrm{NaF}\cdot\mathrm{MF}_3$ compounds, however, have R values which do not parallel those of the R_{MF_3} values but show a difference, $R_{\mathrm{NaF}\cdot\mathrm{MF}_3} - R_{\mathrm{MF}_3}$, decreasing from 3.4 to 2.9 as atomic number increases from 57 to 71. The sodium flouride–lanthanide trifluoride systems containing between 35 and 50 mol % NaF are complicated by several factors, including cubic, hexagonal, and orthorhombic symmetries and, apparently, interstitial fluoride.[29] Further work on structure and refractometry is indicated here.

Table IV

Experimental Molar Refractivities of Alkali Fluoride–Uranium Pentafluoride Compounds[25]

	R_{AUF_6}	R_{A^+}[23]	Net $R_{\mathrm{UF}_6^-}$	Remarks
$LiUF_6$	19.7	−0.3	20.0	Rhombohedral, 6-coord $LiSbF_6$ type
$NaUF_6$	20.7	+0.2	20.5	Rhombohedral, 6-coord $LiSbF_6$ type
($NaUF_6$)	(22.5)[a]	0.2	(22.3)[a]	Fcc, 6-coord $NaSbF_6$ type
KUF_6	22.7	2.3	20.4	Orthorhombic, 8-coord $RbPaF_6$ type
$RbUF_6$	24.6	3.8	20.8	Orthorhombic, 8-coord $RbPaF_6$ type
NH_4UF_6	24.8	4.3	20.5	Orthorhombic, 8-coord $RbPaF_6$ type
$CsUF_6$	26.8	6.5	20.3	Rhombohedral, 6-coord $KOsF_6$ type

[a] This high value accompanies the abnormally high molecular volume of this phase. High molecular volumes are generally found in cubic phases of other $NaMF_6$ complexes of group Va elements.[26,27] This must indicate an effect other than stoichiometry error and, in fact, is a result of inefficient packing. Note that in oxides, Shockley has shown that the polarizability increases parallel to the volume occupied by oxygen.[28] However, Professor Zachariasen brought to the author's attention the fact that the cubic $NaSbF_6$ structure type, because of the linear Na–F–M(V) linkage, contains very large holes into which other ions (for example K^+) can be packed. For example, K_2NaAlF_6 has nearly the same cell volume.

There are two series, KF–CeF_3 and NaF–ScF_3, which do form compounds having $\mathrm{AF}:\mathrm{MF}_3$ mole ratios up to 3. The KF–CeF_3 data are given in the next section. In the sodium fluoride–scandium trifluoride system, $R_{\mathrm{ScF}_3} = 9.43$, $R_{\mathrm{NaF}\cdot\mathrm{ScF}_3} = 12.56$, and $R_{3\mathrm{NaF}\cdot\mathrm{ScF}_3} = 17.97$.[30] These values give a slope $R_{\mathrm{NaF}} = 2.83$ ($\sigma = 0.11$).

Comparison of $\mathbf{R}$ Values for $\mathbf{KF\cdot MF_x}$ ($\mathbf{x = 3}$–$\mathbf{5}$) Complexes.—The data for a series of potassium fluoride complexes with CeF_3, ZrF_4, ThF_4, TaF_5, and UF_5 are plotted in Figure 3. The data again suggest that the slopes for a given alkali fluoride are the same, with the intercepts being the R_{MF_x} values. The value

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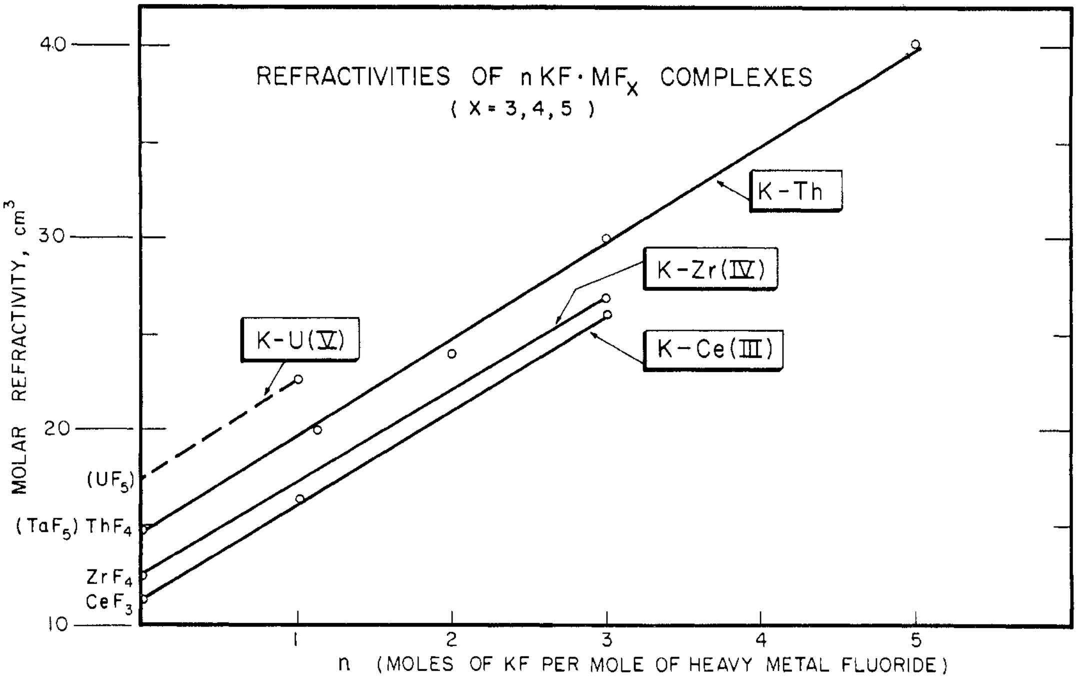

Figure 3.—Refractivities of potassium fluoride complexes with some tri-, tetra-, and pentavalent metals.

of R_{UF_5} = 17.8 was obtained by subtracting R_{AF} from each of six $R_{AF \cdot UF_5}$ values in Table IV. The values[31] R_{TaF_5} = 14.8 and $R_{K_2TaF_7}$ = 23.9 are so close to the thorium values, R_{ThF_4} and $R_{K_2ThF_6}$, respectively, that they are not shown in the figure. The values $R_{KF \cdot CeF_3}$ = 16.5 and $R_{3KF \cdot CeF_3}$ = 26.2 were calculated from data supplied by Thoma and Brunton.[32]

Applications.—For $n\mathrm{NH_4F \cdot MF_4}$ complexes, a subject of current interest to us, values of the molar refractivity for the 4:1, 3:1, 2:1, and 7:6 $NH_4F:MF_4$ ratios (Table I) are clearly distinguishable. This was useful in our recent work with compounds in the NH_4F–CeF_4–H_2O system which established $(NH_4)_4CeF_8$ as the highest complex[6] rather than $(NH_4)_3CeF_7$, as was reported recently.[33] In our study, the known $(NH_4)_4UF_8$ X-ray powder diffraction data also corroborated the molar refractivity results, since $(NH_4)_4CeF_8$ is isostructural with $(NH_4)_4UF_8$.

A stricter test of the simplicity and usefulness of the molar refractivity method was demonstrated in connection with our study of $(NH_4)_4ThF_8$.[34] The $(NH_4)_4MF_8$ type of compound is monoclinic and isostructural for M = Ce(IV) and Pa(IV) through Am(IV).[35] However, from a saturated NH_4F–ThF_4–H_2O solution, needlelike crystals of a compound, later shown to be triclinic $(NH_4)_4ThF_8$, were obtained which gave an X-ray powder pattern entirely different from that of $(NH_4)_4UF_8$. As initially there were not enough crystals to analyze chemically, the following approach was used. Flotation of crystals in mixtures of diiodomethane (d = 3.3 g/cm³) and *sym*-tetrabromoethane (d = 2.95 g/cm³) on a microscope slide established that the density was just slightly above 3.0. The extreme refractive indices of this biaxial compound were found to be n_x = 1.456 and n_z = 1.474 giving an estimate for the Lorentz–Lorenz function of 0.2764. Because the crystals should contain only NH_4, F, and Th (hydrates being virtually unknown), formula weights could be calculated for different $NH_4F:ThF_4$ ratios. These, when divided by the density and multiplied by 0.2764, gave the following estimates of R: $(NH_4)_2ThF_6$, 35.2; $(NH_4)_3ThF_7$, 38.6; $(NH_4)_4ThF_8$, 42.0. Clearly, the first two values are far above the NH_4F–UF_4 line of Figure 2, whereas the value estimated for $(NH_4)_4ThF_8$ lies very close to it. Thus, from optical measurements and a simple density determination, the stoichiometry was shown to be $(NH_4)_4ThF_8$ rather than $(NH_4)_3ThF_7$ or $(NH_4)_2ThF_6$. The formula $(NH_4)_4ThF_8$ was later confirmed by chemical analysis and a structure determination.[34]

The molar refractivities of the complexes $2KF \cdot PtF_4$ and $2RbF \cdot PtF_4$ are nearly coincident with the values for the corresponding UF_4 complexes. This suggests that the values of U(IV)–F complexes, more of which are known than of the Pt(IV) complexes, could serve as a basis for an estimate for $R_{nAF \cdot PtF_4}$ and for R_{PtF_4} itself. Extension of this approach to other transition element complexes is suggested when the data become available. For example, the anticipated value for R_{TbF_4} would be expected to be lower than R_{CeF_4} because $R_{TbF_3} < R_{CeF_3}$.

Since the slope in Figures 1–3 is a known constant for a given AF, a single measurement should establish the line for an element M in a particular valence state. Indeed, the earlier R value for ThF_4 (15.3) shown in Table II was clearly closer to that of UF_4 (15.5) than

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expected on the basis of the average difference 0.4 ± 0.15 between ten pairs of U(IV)– and Th(IV)–F complexes. In fact, a recent redetermination of the cell constants for ThF_4 gave a lower R value, 14.8.[22] Furthermore, the values for nLiF·UF_4 are very close to those of the corresponding nNaF·ThF_4 complexes. The increased refractivity of Na^+ over Li^+ essentially compensates for the lower refractivity of ThF_4 *vs.* UF_4.

Estimation of Molecular Volumes in Fluoride Complexes.—To estimate R values for compounds for which optical data and composition are given, but densities or unit cell volumes are not, the following approach may often be used. As an example, using Zachariasen's[36] volume values for NH_4^+ (26 Å^3) and F^- (18 Å^3), we estimate for $(NH_4)_4ThF_8$ 248 Å^3 per formula unit and a density of 3.05 g/cm^3. R values, approximated using such volume estimations,[26,36] are enclosed in parentheses in Table I. This approach does need to be used with some caution, especially with sodium compounds, as was mentioned in connection with $NaUF_6$, Table IV. Also, the compounds Na_3MF_7 have an abnormally high molecular volume, *e.g.*, in Na_3MF_7 there are 14 F's occupying 16 sites, and the molecular volume and R values for Na_3UF_7 are almost identical with those of Na_4ThF_8.[3,36] As was mentioned earlier, the R value for Na_3UF_7 is the farthest (5%) off the calculated function.

Discussion

In UF_4 the coordination of uranium is eight, with all fluorines shared.[20] It is again eight in $(NH_4)_4UF_8$ with no fluorines shared;[37] $(NH_4)_2CeF_6$ represents an intermediate case with four fluorines shared.[38] In Li_4UF_8 uranium is nine-coordinated;[5] in $(NH_4)_4ThF_8$ thorium is also nine-coordinated, and *one fluoride is not involved in a bond to thorium.*[34] The "free" fluoride ion in the lattice does not affect the refractivity in an obvious manner. In the pentavalent uranium complex $CsUF_6$, uranium is six-coordinated[37] and in $RbUF_6$ it is eight-coordinated;[39] the R_{UF_6}- values (Table IV) are only slightly affected (if at all) by the difference in coordination. Batsanov,[40] describing the application of refractometry to structural chemistry, has shown that in general there is only a slight change in molar refractivity in polymorphic modifications of complexes. Also, in the rare earth trifluorides, the molar refractivity is not particularly sensitive to structural differences (shown by Staritzky and Asprey[41] and noted by Levin[42] in his paper on refractivities of rare earth oxides). Thus it appears that the approximate additivity of refractivity values is a generally valid rule in a wide variety of fluoride complexes, showing little effect of coordination or of valence of the central metal. Regarding the effect of valence, the NaF–ScF_3, KF–CeF_3, and AF·UF_5 complexes give the same R_{AF} as was found with the nAF·MF_4 complexes. Including the R values for these MF_3 and MF_5 complexes in the general linear model gives 60 data points to test. When this is done the sum of squares of deviations increases only slightly (from 12.7 to 13.3, and the weighted variance drops from 0.33 to 0.29); the change in R_{AF} values is neligible (average 0.01).

Conclusions

(1) The Lorentz–Lorenz molar refractivities of nAF·MF_4 complexes containing the same tetravalent element are linear functions of the mole ratio (n), fitting the equation $R_{nAF \cdot MF_4} = nR_{AF} + R_{MF_4}$. For different alkali fluorides (AF) they have different slopes (R_{AF}) but a common origin, the refractivity of the pure tetrafluoride, R_{MF_4}.

(2) Refractivities of nAF·MF_4 complexes containing the same alkali (A) but different tetravalent elements (M) have essentially the same incremental increase in refractivity per mole of alkali fluoride (slope), $\Delta R/\Delta n$. The results of pooling the data from 49 compounds (as shown in Table III) give the empirical slopes $\Delta R/\Delta n$ which agree closely with the sum of Fajans' ionic refractivities R_{A^+} and R_{F^-}. Thus to estimate the refractivity for a complex of formula nAF·MF_4, add to the measured R_{MF_4} value n multiples of Fajans' R_{A}- and R_{F}- aqueous refractivities.

(3) For complexes of the type nAF·MF_5 and nAF·MF_3, a linear increase in refractivity per mole of AF is also observed. For the NaF–ScF_3, KF–CeF_3, KF–TaF_5, and AF–UF_5 systems, the increment in $R_{complex}$ per mole of alkali fluoride is the same as that found for the tetravalent complexes.

(4) Fluoride complexes between d- and f-transition elements and the alkali fluorides (or NH_4F) comprise a class of over 1000 potential compounds. Optical data are lacking even for many of the known representatives; refractive index measurements and experimental densities should be part of the data supplied for newly synthesized compounds.[43]

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