

CO₂ and CaO were. However, the sample which was treated *in an identical manner*, except that it was *not* exposed to the atmosphere, showed *no evidence of reaction*. The original BaO and CaCO₃ were still present despite that fact that the sample had been heated for 20 minutes at 125° above the "reaction temperature."

This same measurement has been made with BaO + CuSO₄, SrO + CaCO₃ and SrO + CuSO₄ with results the same as described. Specifically, no reaction takes place in any of these other three systems when the reactants are prepared, mixed and heated above the "reaction temperature" *in vacuo*. Under conditions which are otherwise identical, the control which is exposed to the atmosphere does react in each case.

It appears, therefore, that the reactions of BaO and SrO as described by Hedvall do not proceed by solid state diffusion processes but occur *via* the liquid phase. Furthermore, the so-called characteristic "reaction temperature" has nothing to do with the oxide itself but is merely the melting point of what is probably a hydroxide containing eutectic as Balarew suggested,³ the presence of which presents a low energy path along which the reaction proceeds very rapidly. This is illustrated in Fig. 2 where hypothetical rate constant temperature curves are shown for the liquid phase and solid state mechanisms by curves I and II, respectively. Below the melting point of the third component (T_M), the only path available is the solid state path¹⁴ where, even

(14) We can, of course, only speculate as to the reaction path in the absence of a liquid phase and a better guess, probably, is that the reac-

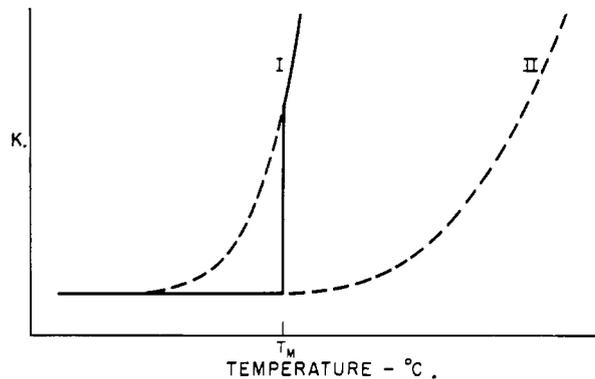


Fig. 2.—Postulated mechanism of the reactions of BaO and SrO. Hypothetical rate constant temperature curves for the liquid phase and solid state mechanisms are shown, respectively, as curves I and II. The reaction path (solid line) follows curve II up to the melting point of the third component at which point the lower energy, liquid phase path becomes available.

at T_M , the reaction rate is so small that it may be considered to be zero for all practical purposes. On sudden appearance of a liquid phase, the system finds itself well up on the steep portion of curve I where, because of its exothermic nature, the reaction proceeds with a burst of heat, leading to the high ΔT 's observed with DTA.

tion will proceed through the gaseous phase. However, for the purpose of the above, this is of no consequence.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

The Fluoride Complexing of Scandium(III) in Aqueous Solution: Free Energies, Heats and Entropies

By JOHN W. KURY, ARMINE D. PAUL, LOREN G. HEPLER AND ROBERT E. CONNICK

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The complexing of Sc(III) in perchlorate solutions at an ionic strength of 0.5 *M* was determined by studying the potential of the ferrous-ferri electrode as a function of the HF, H⁺ and Sc(III) concentrations. The data can be interpreted by assuming the presence of the species ScF⁺⁺, ScF₂⁺, ScF₃(aq) and ScF₄⁻. Equilibrium constants for the formation of these complexes at 15, 25 and 35° were evaluated and from them the heat and entropy changes of the reactions calculated. The scandium fluoride complexes are more stable than those of other trivalent ions of comparable radius. The extra stability of the complex scandium fluorides arises from an irregularity in the heat term, rather than in the entropy term.

Introduction

This investigation was undertaken because of the work of Dodgen¹ who found the scandium fluoride complexes to be more stable than those of other trivalent ions of similar radius. According to Pauling,² In(III) has the same ionic radius (0.81 Å.) as Sc(III). However, the first fluoride complex of Sc(III) is about 280 times more stable than the first fluoride complex of In(III).³ We wished to determine whether the greater stability of the

scandium fluoride complexes arises from the heat term or the entropy term.

The "ferri" method of Brosset and Oring⁴ was used. The complexing of Sc(III) was determined indirectly by studying its effect on the ferric fluoride complexing equilibria, as measured potentiometrically through the ferrous-ferri couple.

Experimental

Apparatus.—Descriptions of the cells, electrodes, measuring apparatus and general procedure are given elsewhere.^{3,5,6}

(1) H. W. Dodgen, private communication.

(2) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

(3) L. G. Hepler, J. W. Kury and Z. Z. Hugus, *J. Phys. Chem.*, **58**, 26 (1954).

(4) C. Brosset and J. Oring, *Svensk. Kem. Tid.*, **55**, 101 (1943).

(5) H. W. Dodgen and G. K. Rollefson, *THIS JOURNAL*, **71**, 2600 (1949).

(6) R. E. Connick and M. Tsao, *ibid.*, **76**, 5311 (1954).

Solutions.—A scandium perchlorate-perchloric acid stock solution was prepared by dissolving spectroscopically pure Sc_2O_3 in perchloric acid. The solution was analyzed for scandium by precipitating it as the hydroxide and weighing as Sc_2O_3 . The acidity was determined by precipitating the scandium as ScF_3 and titrating with standard base to the phenolphthalein end-point.

Double vacuum-distilled perchloric acid was diluted with water and the solution standardized against mercuric oxide. Sodium fluoride solutions were prepared by dissolving weighed amounts of the C.P. salt which had been dried at 150° .

A stock solution of sodium perchlorate was prepared by treating C.P. sodium carbonate with an excess of perchloric acid. After boiling to expel the carbon dioxide, the pH was adjusted to 5–6 with carbonate-free sodium hydroxide and the solution then filtered. Aliquots were evaporated to dryness, dried for several hours at 160° , and weighed as NaClO_4 .

A ferrous perchlorate-ferric perchlorate-perchloric acid stock solution was prepared by dissolving a weighed amount of electrolytic iron in a known amount of perchloric acid. A portion of the resulting ferrous perchlorate was oxidized to ferric perchlorate with hydrogen peroxide. The ferrous ion concentration was determined by titration with standard ceric sulfate. The ferric ion concentration and the acidity were determined by difference.

Distilled water was redistilled from alkaline permanganate for use in all solutions.

Procedure.—Three half-cells were used which will be designated A, B and C. Half-cells A and C, and half-cells B and C, were connected by sodium perchlorate-agar agar salt bridges. Each half-cell initially contained the same concentrations of ferrous perchlorate, ferric perchlorate and perchloric acid. Half-cell A contained in addition a known concentration of scandium perchlorate. The ionic strength in each half-cell was adjusted to 0.50 *M* with sodium perchlorate. The volumes were equal.

After the initial zero potentials in each cell became constant, known quantities of sodium fluoride were added to half-cells A and B from a calibrated micropipet, and the potential measured after each addition. The fluoride addition was continued until a potential of about 150 mv. was developed in each cell or until scandium fluoride precipitated. The potential reading became constant to a few hundredths of a millivolt within about one minute after each fluoride addition.

Experimental Data

The initial conditions for each experiment are summarized in Table I.

TABLE I

Temp., °C.	INITIAL EXPERIMENTAL CONDITIONS				
	Sc(ClO ₄) ₃ , moles/l. × 10 ³	HClO ₄ , moles/l.	Fe(ClO ₄) ₂ , moles/l. × 10 ⁴	Fe(ClO ₄) ₃ , moles/l. × 10 ⁴	NaClO ₄ , moles/l.
25	12.73	0.1122	3.553	3.402	0.3087
25	1.387	.05287	3.869	3.705	.4355
25	2.735	.05457	3.831	3.669	.4257
35	1.387	.05277	3.868	3.704	.4350
35	2.741	.05493	3.831	3.668	.4252
35	6.665	.1065	3.721	3.563	.3502
15	1.387	.05277	3.868	3.704	.4350
15	6.665	.1065	3.721	3.563	.3502
15	2.741	.05493	3.831	3.668	.4252

The acidity was varied twofold and the scandium concentration was varied at least fivefold. The maximum stoichiometric fluoride concentration varied from 0.015 to 0.03 *M*,⁷ depending on the particular experiment.

Sample data for the second experiment of Table I are given in Table II. Data for all but the last experiment are given by Paul.⁸

(7) The symbol *M* indicates concentrations in moles per liter of solution.

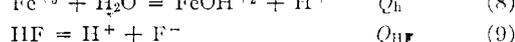
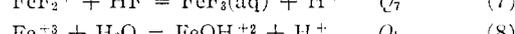
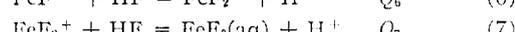
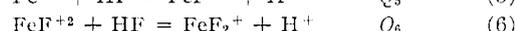
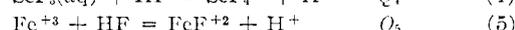
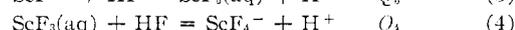
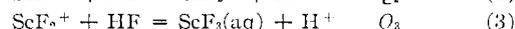
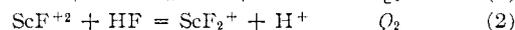
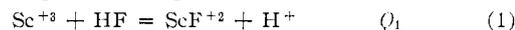
(8) A. D. Paul, Thesis, University of California, 1955; University of California Radiation Laboratory unclassified report UCRL-2926,

TABLE II

DATA FOR SECOND EXPERIMENT OF TABLE I			
Initial vol. = 100.95 ml.		0.4702 <i>M</i> NaF added	
Cell B-C (no Sc ⁺⁺⁺ present)	<i>E</i> (mv.)	Cell A-C (Sc ⁺⁺⁺ present in A)	<i>E</i> (mv.)
NaF added, ml.		NaF added, ml.	
0.0747	13.25	0.0747	0.72
.1494	24.98	.1494	1.74
.2241	34.71	.2241	3.16
.2988	42.84	.2988	5.12
.3735	49.75	.4482	11.15
.4482	55.84	.5976	20.18
.5229	61.24	.8964	41.90
.5976	66.11	1.0458	51.80
.6723	70.53	1.1952	60.60
1.1707	93.67	1.5687	78.68
1.6691	110.77	2.1418	99.97
2.1675	124.57	2.6402	114.89
2.6659	136.10	3.1386	127.61
3.1643	146.80	3.6370	139.00

Analysis of Data

The equilibria in question are



The hydrolysis of scandium ion⁹ and the hydrolytic dimerization of ferric ion¹⁰ were both negligible under the conditions employed here. The *Q*'s are equilibrium quotients expressed in concentrations, for example where the quantities in parentheses

$$Q_1 = \frac{(\text{ScF}^{+2})(\text{H}^+)}{(\text{Sc}^{+3})(\text{HF})} \quad (10)$$

represent the concentrations of the enclosed species in moles per liter. The values at $\mu = 0.5$ of *Q*₅, *Q*₆, *Q*₇, *Q*_h and *Q*_{HF} used in these calculations are given in ref. 11.

The difference between the moles of fluoride added to half-cell A and the moles of fluoride added to half-cell B when the potentials are equal is, to a very good approximation, the moles of fluoride in half-cell A present in the form of scandium fluoride complexes. Division by the volume of solution of half-cell A yields the concentration of fluoride as scandium complexes, symbolized by $\Delta(\Sigma\text{F}^-)$. The moles of fluoride in half-cell B corresponding to each potential reading of A were read from a plot of the former *versus* potential.

From stoichiometry it can be seen that

$$\Delta(\Sigma\text{F}^-) = (\text{ScF}^{+2}) + 2(\text{ScF}_2^+) + 3(\text{ScF}_3) + 4(\text{ScF}_4^-) \quad (11)$$

$$(\Sigma\text{Sc}^{+3}) = (\text{Sc}^{+3}) + (\text{ScF}^{+2}) + (\text{ScF}_2^+) + (\text{ScF}_3) + (\text{ScF}_4^-) \quad (12)$$

April, 1955. The values listed for \bar{n} are slightly in error at high fluoride concentrations because of the use of a poorer approximation than used here in calculating \bar{n} .

(9) M. Kilpatrick and L. Pocras, *J. Electrochem. Soc.*, **100**, 85 (1953).

(10) R. M. Milburn and W. C. Vosburgh, *THIS JOURNAL*, **77**, 1352 (1955).

(11) R. E. Connick, L. G. Hepler, Z. Z. Hugus, Jr., J. W. Kury, W. M. Latimer and Maak-Sang Tsao, *ibid.*, **78**, 1827 (1956).

where (ΣSc^{+3}) signifies the total stoichiometric concentration of scandium.

Let \bar{n} represent the average number of fluoride ions held by each scandium ion

$$\bar{n} = \frac{\Delta(\Sigma \text{F}^-)}{(\Sigma \text{Sc}^{+3})} \quad (13)$$

Combining equations 12 and 13 with 1, 2, 3 and 4 yields an expression for \bar{n}

$$\bar{n} = \frac{Q_1 \frac{(\text{HF})}{(\text{H}^+)} + 2Q_1Q_2 \frac{(\text{HF})^2}{(\text{H}^+)^2} + 3Q_1Q_2Q_3 \frac{(\text{HF})^3}{(\text{H}^+)^3} + 4Q_1Q_2Q_3Q_4 \frac{(\text{HF})^4}{(\text{H}^+)^4}}{1 + Q_1 \frac{(\text{HF})}{(\text{H}^+)} + Q_1Q_2 \frac{(\text{HF})^2}{(\text{H}^+)^2} + Q_1Q_2Q_3 \frac{(\text{HF})^3}{(\text{H}^+)^3} + Q_1Q_2Q_3Q_4 \frac{(\text{HF})^4}{(\text{H}^+)^4}} \quad (14)$$

In order to obtain values for Q_1 , Q_2 , Q_3 and Q_4 , it is necessary to know the value of $(\text{HF})/(\text{H}^+)_A$ for each value of \bar{n} , that is, as a function of E_{A-C} . At the same potential, the ratio $(\text{HF})/(\text{H}^+)$ in half-cells A and B is the same to a very good approximation. This ratio can be calculated from the data of cell B-C and the known ferric fluoride complexing constants by solving equation 15 by means of successive approximations. The observed potential is E and \mathcal{F} is Faradays' constants. The derivation of this equation and the assumptions are given in ref. 3.

$$\left(1 + \frac{Q_h}{(\text{H}^+)}\right)(e^{\mathcal{F}E/RT} - 1) = Q_5 \frac{(\text{HF})}{(\text{H}^+)} + Q_5Q_6 \frac{(\text{HF})^2}{(\text{H}^+)^2} + Q_5Q_6Q_7 \frac{(\text{HF})^3}{(\text{H}^+)^3} \quad (15)$$

Knowing \bar{n} and $(\text{HF})/(\text{H}^+)$ it is possible to calculate Q_1 , Q_2 , Q_3 and Q_4 from equation 14. This was done by plotting \bar{n} versus $\log (\text{HF})/(\text{H}^+)$, reading from the smoothed curve four points chosen at appropriate intervals, and solving the four simultaneous equations 14 for Q_1 , Q_2 , Q_3 and Q_4 . It then was verified that the remaining data were consistent with this set of constants. A plot of \bar{n} versus $\log (\text{HF})/(\text{H}^+)$ for the experiments at 25° is shown in Fig. 1. The solid curve represents the curve calculated using the Q 's listed in Table III. It can be seen that all the experimental points fall very close to the theoretical curve.

Results

The values obtained in this investigation for Q_1 , Q_2 , Q_3 and Q_4 at 15, 25 and 35° at $\mu = 0.50 M$ are summarized in Table III.

TABLE III

SUMMARY OF EQUILIBRIUM QUOTIENTS AT $\mu = 0.5 M$				
Temp., °C.	$Q_1 \times 10^{-3}$	Q_2	Q_3	Q_4
15	2.12 ± 0.17	288 ± 22	16.8 ± 1.6	0.7 ± 0.2
25	$1.91 \pm .15$	233 ± 18	14.6 ± 1.4	$.85 \pm .2$
35	$1.63 \pm .13$	182 ± 14	11.4 ± 1.1	$.5 \pm .2$

The uncertainties were calculated by refitting the \bar{n} versus $\log (\text{HF})/(\text{H}^+)$ curve assuming an error of 0.02 in \bar{n} at the point most important in determining the particular Q . The values which Dodgen¹ gives for Q_1 , Q_2 , Q_3 and Q_4 at 25° and the same ionic strength are 1750, 242, 12.7 and 0.88, respectively.

In Table IV are presented the equilibrium quotients at 25° for $\mu = 0.5$ and $\mu = 0$ for reactions

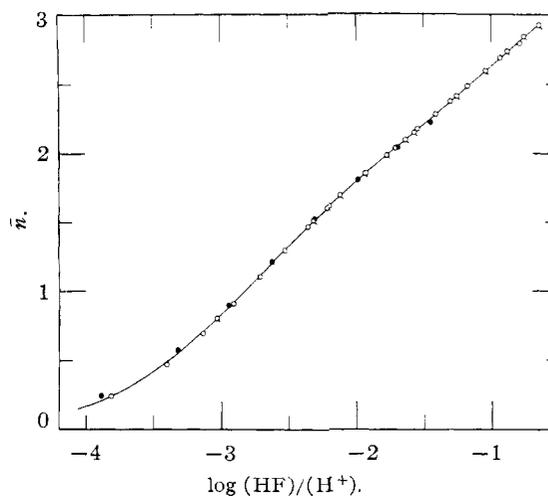


Fig. 1.—Data for \bar{n} as a function of $(\text{HF})/(\text{H}^+)$ at 25°: ●, 0.0127 M $\text{Sc}(\text{ClO}_4)_3$ run; ○, 0.00139 M $\text{Sc}(\text{ClO}_4)_3$ run; ◐, 0.00274 M $\text{Sc}(\text{ClO}_4)_3$ run.

1, 2, 3 and 4 written in terms of fluoride ion rather than HF.

TABLE IV

EQUILIBRIUM QUOTIENTS AT 25° FOR REACTIONS WRITTEN IN TERMS OF FLUORIDE ION

Reaction	Q' ($\mu = 0.5$)	K ($\mu = 0$)
$\text{Sc}^{+3} + \text{F}^- = \text{ScF}^{+2}$	1.55×10^6	1.2×10^7
$\text{ScF}^{+2} + \text{F}^- = \text{ScF}_2^+$	1.89×10^5	6.4×10^5
$\text{ScF}_2^+ + \text{F}^- = \text{ScF}_3(\text{aq})$	1.19×10^4	3.0×10^4
$\text{ScF}_3(\text{aq}) + \text{F}^- = \text{ScF}_4^-$	7×10^2	7×10^2

The values of Q' were obtained by dividing the Q values of Table III by the ionization constant of HF at $\mu = 0.5$ ¹¹. The true equilibrium constants at $\mu = 0$ were estimated using empirical relations of Rabinowitch and Stockmayer¹² and Nasanen,¹³ for activity coefficient corrections.

Table V summarizes the free energy, heat and entropy changes for reactions 1, 2 and 3 at an ionic strength of 0.5 M .

TABLE V

SUMMARY OF THERMODYNAMIC FUNCTIONS OF SCANDIUM FLUORIDE COMPLEXES ($\mu = 0.5$)

Reaction	ΔF_{298} , kcal./mole	ΔH_{298} , kcal./mole	ΔS_{298} , e.u.
$\text{Sc}^{+3} + \text{HF} =$			
$\text{ScF}^{+2} + \text{H}^+$	-4.48 ± 0.05	-2.3 ± 1.0	7 ± 3
$\text{ScF}^{+2} + \text{HF} =$			
$\text{ScF}_2^+ + \text{H}^+$	$-3.23 \pm .05$	-4.1 ± 1.0	-3 ± 3
$\text{ScF}_2^+ + \text{HF} =$			
$\text{ScF}_3(\text{aq}) + \text{H}^+$	$-1.59 \pm .05$	-3.4 ± 1.2	-6 ± 4

The heats and entropies may be converted to those for the reactions written in terms of fluoride ion by subtracting the heat and entropy of ionization of HF from the values in Table V. Hepler, Jolly and Latimer¹⁴ report the heat and entropy of ionization of HF at infinite dilution. Estimation of the correction to $\mu = 0.5$ gives -2.6 kcal./mole and -22 e.u., respectively.

(12) E. Rabinowitch and W. H. Stockmayer, *THIS JOURNAL*, **64**, 335 (1942).

(13) R. Nasanen, *Acta Chem. Scand.*, **4**, 140, 816 (1950).

(14) L. G. Hepler, W. L. Jolly and W. M. Latimer, *THIS JOURNAL*, **75**, 2809 (1953).

Discussion

In Table VI are presented the thermodynamic data for the corresponding reactions of Fe(III),¹¹ Al(III)^{4,15} and In(III)³ at an ionic strength of 0.5.¹⁶

TABLE VI

THERMODYNAMIC FUNCTIONS OF Fe(III), Al(III) AND In ⁺ 3 FLUORIDES FOR AN IONIC STRENGTH OF 0.5 ^a			
Reaction	ΔF_{298}° , kcal.	ΔH_{298}° , kcal.	ΔS_{298}° , e.u.
Fe ⁻³ + HF = FeF ⁺² + H ⁺	-3.09	-0.65	8.2
FeF ⁺² + HF = FeF ₂ ⁺ + H ⁺	-1.38	-1.2	0.6
FeF ₂ ⁺ + HF = FeF ₃ (aq) + H ⁺	~0		
Al ⁺³ + HF = AlF ⁻² + H ⁺	-4.40	-1.45	9.9
AlF ⁻² + HF = AlF ₂ ⁺ + H ⁺	-2.88	-1.8	3.6
AlF ₂ ⁺ + HF = AlF ₃ (aq) + H ⁺	-1.28	-2.4	-3.8
In ⁺³ + HF = InF ⁺² + H ⁺	-1.14	-0.51	2.1
InF ⁺² + HF = InF ₂ ⁺ + H ⁺	0.41	1.0	2

^a See footnote 16.

A comparison of Tables V and VI shows that the entropies of complexing agree well and show the expected trend toward less positive values with increasing radius of the metal ion. The heat term for the Sc(III) complexes, however, is considerably more negative than for the Al(III), Fe(III) and In(III) complexes. Thus the greater stability of the scandium complexes arises from the more negative heat term, rather than from an entropy effect.

It has been shown previously⁶ that the complexing of a number of positive ions by fluoride ion agrees qualitatively with an ionic picture in which the fluoride ion is held to the positive ion by an electrostatic attraction. For example, for positive ions of a given charge the equilibrium constants run roughly in the order of their ionic radii. Scandium appears to be an exception to this correlation. If the ionic radii of Sc(III), Fe(III), Al(III) and In(III) are taken to be 0.83, 0.67, 0.55 and 0.95 Å., respectively,¹⁷ it is obvious from a comparison of Tables V and VI that although Sc(III) is larger than either Al(III) or Fe(III), the fluoride complexes of Sc(III) are more stable than those of Al(III) and Fe(III). If one assumes the fluoride complexes to be purely ionic, which seems to be a reasonable assumption since the fluoride ion has a low polarizability, one would expect the scandium complexes to be stronger than those of indium but weaker than those of iron and aluminum.

The correlation of stability with interionic distance⁶ by means of ionic radii is subject to uncertainty because of the variability of ionic radii. Instead of radii we may use interatomic distances measured by X-ray diffraction for fluoride containing compounds of the elements of interest. In Table VII are given such values. In all compounds the cation was 6-fold coordinated. Aluminum compounds were chosen for which the interatomic

(15) W. M. Latimer and W. L. Jolly, *THIS JOURNAL*, **75**, 1548 (1953).

(16) The ΔF values for aluminum were measured at an ionic strength of 0.53 while the ΔH values were measured at an ionic strength varying between 0.06 and 0.2 *M*. The entropy values were calculated from the ΔF and ΔH values without correction for the differences in ionic strength.

(17) R. W. G. Wyckoff, "Crystal Structure," Interscience Publishers, Inc., New York, N. Y., 1951, Chapter III, Table, p. 15.

distances were believed to be most accurately determined.

TABLE VII

INTERATOMIC DISTANCES IN FLUORIDE SALTS			
Cation	M-F, Å.	Compound	Ref.
Al ⁺³	1.80	Av. for AlF ₃ , KAlF ₄ , RbAlF ₄ , TlAlF ₄ , Na ₃ AlF ₆	<i>a</i>
Sc ⁻³	2.02	ScF ₃	<i>b</i>
Fe ⁺³	2.07	FeF ₃	<i>a</i>
In ⁺³	2.07	InF ₃ ·3H ₂ O	<i>c</i>

^a R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1951. ^b W. Nowacki, *Z. Krist.*, **101A**, 273 (1939). ^c G. B. Bokii and T. S. Khodashova, *Kristallografiya*, **1**, 197 (1956).

For the other elements, data on only the fluoride compounds tabulated are available, except for iron. In the latter case, in addition to FeF₃, one can approximate Fe-F distances from the lattice parameters¹⁸ of alkali double fluorides of the formula M₃FeF₆ using Pauling's¹⁹ structure determination and subtracting off the appropriate M-F distance as determined from ionic radii. The resulting estimates give Fe-F distances appreciably greater than the value of 2.07 for FeF₃.

The interatomic distances of Table VII are not consistent with Pauling's ionic radii² or those given by Wyckoff¹⁷ in that ferric ion appears to be larger than Sc⁺³ and the same size as In⁺³. Presumably such discrepancies arise because ionic radii are not truly constant. In any case it may be concluded that the greater stability of scandium fluoride complexes relative to ferric complexes may be consistent with an ionic picture which would require a smaller metal-fluoride distance in the case of scandium.

The greater stability of the scandium complexes compared to aluminum cannot be similarly explained in that the radius of aluminum is surely smaller than that of scandium. Although the correlation between radius and stability of fluoride complexes of cations of the same charge is clearly not perfect in other cases, this discrepancy between scandium and aluminum seems to be particularly marked. It may be noted also that the greater stability of scandium complexes compared to aluminum complexes is also found for hydrolysis,^{8,20,21} *i.e.*, formation of the hydroxide complex and apparently for the thiocyanate complexes.²²

The relatively greater stability of the scandium fluoride complex is almost certainly not due to covalent bond formation since such ions as Fe⁺³ and In⁺³ would be expected to deviate even further, and they do not. It is unlikely that the polarizability of scandium ion is responsible, because all of these positive ions have very small polarizabilities. Unfortunately, the polarizabilities are not known with sufficient accuracy to permit a definite conclusion to be drawn.

One obvious explanation is that there may be a change in the coordination number of scandium

(18) W. Minder, *Z. Krist.*, **A96**, 15 (1937).

(19) L. Pauling, *THIS JOURNAL*, **46**, 2738 (1924).

(20) M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, **100**, 85 (1953).

(21) J. Faucherre, *Compt. rend.*, **227**, 1367 (1948).

(22) R. Bock, *Z. anal. Chem.*, **133**, 110 (1951).

which enhances the stability of the fluoride complexes. Thus if Sc^{+3} has a highly strained, co-ordinated layer of eight water molecules around it, replacement of a water by the slightly smaller fluoride ion would relieve this strain and lead to an unusually stable complex. It would be necessary that additional strain be relieved as each of the next three replacements of water by fluoride ion occur because the first four complexes are known to be exceptionally stable. This explanation, however, is contrary to the fact that scandium shows only a co-ordination number of six in its solids² and that the radius ratio² fits a co-ordination number of six with oxygen.

It is possible that it is the aluminum complex which has unusually low stability relative to the stability expected from an ionic model. Such a decrease in stability could arise from steric repulsion. Aluminum ion is on the borderline between fourfold and sixfold co-ordination by fluoride ion²;

consequently, there should be strong steric repulsion for sixfold co-ordinated aluminum ion. Since the water molecules on the hydrated ion are held considerably less tightly than the fluoride ions, the net effect of steric repulsion would be to decrease the binding of the fluorides and lower the values of the complexing constants. It is not apparent, however, how such an effect would lead to equilibrium constants for the aluminum complexes which are actually smaller than for scandium.

Although some of the above suggestions offer possible, partial explanations of the apparent unusual stability of the scandium fluoride complexes, none of them is really satisfying. The reason for this degree of failure of the simple ionic model is not clear.

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BERKELEY, CALIFORNIA

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The Stereochemistry of Complex Inorganic Compounds. XXIII. Double Optical Isomerism and Optical-Geometric Isomerism in Cobalt(III) Complexes¹

BY WILLIAM E. COOLEY, CHUI FAN LIU AND JOHN C. BAILAR, JR.

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Double optical isomerism, in which both the whole complex and one of its ligands are asymmetric, exists in the *cis*-dinitroethylenediamine-2,3-butylenediamine-cobalt(III) ion. This kind of isomerism exerts a stereospecific effect, and some of the four optically active isomers are less stable against racemization in solution than the others. Optical-geometric isomerism, in which the whole complex is asymmetric and a symmetric ligand is so constituted that it may be oriented in either of two ways, exists in the *cis*-dinitroethylenediamine-isobutylenediamine-cobalt(III) ion. The geometric isomerism modifies the optical isomerism so that this ion also has four optically active isomers, but there is no evidence of preferential stability. The crystals of two of the optical-geometric isomers appear different from those of the other two, but all the double optical isomers have like crystals. The absorption spectra of these *cis* complexes are different from those of the corresponding *trans* complexes in a way analogous to the behavior of other dinitro complexes of cobalt(III). A study of the preparation of the optically active complexes led to an improved method of preparing the non-electrolyte trinitrotriammine-cobalt(III).

In the preparation of complex compounds containing optically active ligands, stereospecific effects often appear, with the result that some of the possible isomers of such compounds occur as small fractions of the total yield, or they do not occur at all. For example, Hürlimann² prepared the dinitro-bis-(propylenediamine)-cobalt(III) ion, $[\text{Co pn}_2(\text{NO}_2)_2]^+$. There are twelve possible isomers of the *cis* form of this ion, corresponding to the two optical isomers of propylenediamine, three geometric orientations of the two propylenediamine molecules, and two optical forms of the whole complex. The *trans* form has four possible isomers, corresponding to the two isomers of propylenediamine and two geometric orientations. More isomers of both *cis* and *trans* form are theoretically possible, of course, if the two propylenediamine molecules in each complex ion are permitted to have either the same or opposite optical configuration. Concluding that he had prepared

the *cis* form, Hürlimann found that only two isomers, *Dll* and *Ldd*,³ could be isolated instead of twelve. Rotatory dispersion studies by O'Brien, McReynolds and Bailar⁴ have shown that Hürlimann probably worked with the *trans* form but, even so, the theoretically possible number of isomers was not realized.

Similarly, Smirnoff⁵ was able to isolate only the *Dlll* and *Lddd* isomers of the tris-(propylenediamine)-platinum(IV) ion, $[\text{Pt pn}_3]^{4+}$. Smirnoff also showed that the analogous cobalt(III) complex, $[\text{Co pn}_3]^{3+}$, is stable only when all three of the propylenediamine molecules have the same optical configuration. Bailar, Stiegman, Balthis and Huffman⁶ concluded that "mixed" isomers containing both configurations of propylenediamine may form but that they rearrange to form the two products

(1) This article is based on portions of dissertations submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois.

(2) Hürlimann, Thesis, University of Zurich, 1918. Reviewed in F. M. Jaeger, "Optical Activity and High Temperature Measurements," McGraw-Hill Book Co., Inc., New York, N. Y., 1930, pp. 157-168.

(3) The optically active complexes of this type are designated here and later by such symbols as *Dll* and *Dlll*, where the capital letter symbolizes the direction of rotation of the complex as a whole, while the small letters symbolize the number and rotation of the optically active ligands.

(4) T. D. O'Brien, J. P. McReynolds and J. C. Bailar, Jr., THIS JOURNAL, **70**, 749 (1948).

(5) O. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

(6) J. C. Bailar, Jr., C. A. Stiegman, J. H. Balthis, Jr., and E. H. Huffman, THIS JOURNAL, **61**, 2402 (1939).