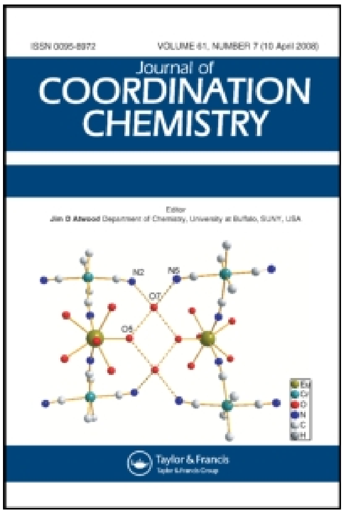

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THE FLUORIDE COMPLEXES OF THE TRIVALENT FIRST-ROW METAL IONS, WITH SPECIAL REFERENCE TO THE FLUORIDE COMPLEXES OF V(III) AND Sc(III)

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A fluoride ion-selective electrode is used to study the Sc^{III} and V^{III} fluoride systems log β_n = 6.18, 11.52, and 15.8 for n = 1,2, and 3 respectively was obtained in 0.5 mol.dm^{-3} NaClO at 25°C for Sc^{III}. A better fit to the potentiometric data was obtained by inclusion of the species $Sc_2F_3^{3+}$, for which log β_{32} = 19.0 was indicated by the computer program (MINIQUAD) used for analysing the data. Inclusion of a variety of other polymers of similar composition also gave nearly as good an improvement in fit, so that this value must be regarded with some caution. The other constants determined were not very sensitive to the inclusion of these polymers, however. V^{3+} ions were generated in solution by electrochemical reduction of VO^{2+}, and log K_1 = 5.00 determined for the V^{3+}/F^- system in 1.0 mol.dm^{-3} $NaClO_4$ at 25°C. It is shown that log $K_1(F^-)$ for the first row trivalent transition metal ions Sc^{III} to Ga^{III} show an inverse order of stability as compared with that usually observed, which is interpreted in terms of the lower position of F^- in the spectrochemical series than the solvent water with which it is competing for coordination sites. This inverted stability order suggests that the very low value of log $K_1(F^-)$ estimated for Co^{III} using a dual basicity type of equation is reasonable.

The observation of particular stability orders, such as the Irving–Williams stability order,[1] has often been rationalised in terms of ligand-field theory.[2] In a recent paper,[3] a correlation observed for the formation constants of F^-, OH^-, and NH_3 complexes suggested that the formation constant of the fluoride complex of Co(III) would be rather lower (log K_1 = 3.3) than log $K_1(F^-)$ for other trivalent metal ions of the first transition period. This reversal of the normal situation, where the cobalt(III) complex is more stable than those of the other first-row M(III) ions, suggests that one might observe a reversal of the usual stability order expected from ligand-field stabilisation arguments for the various M(III) ions. The following data are available in the literature,[4,5] from which, where possible, values were taken at μ = 0 and 25°C. For Mn(III), where values at μ = 0 are not available, these were estimated from the data available by use of the Davies modification of the Debye–Hückel equation.

M(III ion	Sc	Ti	V	Cr	Mn	Fe	Co	Ga
log $K_1(F^-)$	7.1	–	–	5.2	5.6	6.0	(3.3)	5.9

Apart from the estimated value for Co(III), the impression of a reversal of the usual stability order for first-row M(III) ions rests rather heavily on the value[5] for Sc(III). It was decided that this determination should be repeated so as to confirm this value. At the same time, a study of the V(III) fluoride system was undertaken so that the available data for first-row M(III) complexes with fluoride could be expanded. Confirmation of a reverse ligand-field order, which would be due to the fact that the position of the fluoride ion is lower in the spectrochemical series than that of the solvent water, with which it is competing for coordination sites, would strongly support the estimated value[3] of log K_1 for the fluoride complex of Co(III).

EXPERIMENTAL

Materials

(a) Scandium(III). Approximately 2.5 g of B.D.H. Sc_2O_3 was dissolved in conc HCl, and evaporated to dryness three times on a hot-plate. The resulting

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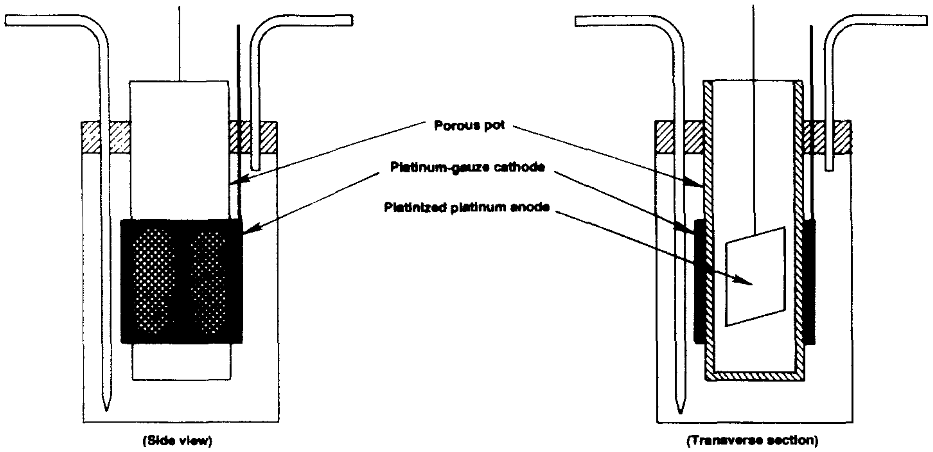

FIGURE 1 Electrolysis cell used for reduction of vanadium(IV) to vanadium(III)

$ScCl_3$ was dissolved in water, and NaOH solution was added to precipitate scandium hydroxide. This precipitate was filtered off and washed at the pump, and the solid hydroxide was then dissolved in a standardized solution of perchloric acid to give a solution of $Sc(ClO_4)_3$ containing excess perchloric acid. The Sc^{3+} in solution was determined as described by Vogel[6] for Al^{3+}.

(b) Vanadium. $VO(OH)_2 \cdot aq$ was prepared from $VO(SO_4) \cdot 5H_2O$ purchased from Merck. A number of literature sources indicated that $VO(OH)_2$ can be precipitated from aqueous solutions of $(VO(H_2O)_4SO_4)$ with sodium hydroxide[7] or ammonia.[8] Preliminary tests were performed with various reagents, and it was found that excess alkali must be avoided owing to the amphoteric properties of the VO^{2+} ion. Washing of the $VO(OH)_2$ precipitate with acetone resulted in changes that were possibly the result of oxidation. Dissolution of the dry hydroxide was slow, and excess acid was used. The vanadyl perchlorate solution obtained in this way was analysed by titration with potassium permanganate.[9] Solutions of vanadium(III) perchlorate were prepared by electrolytic reduction of the vanadyl perchlorate solution of known concentration. A platinum-gauze cathode and a platinized platinum anode were used with a current density of 4.1 mA cm^{-2} of gauze, the current passing for three hours. The anode compartment consisted of a porous pot suspended in the cell, and 1.0 mol dm^{-3} $HClO_4$ was used as the electrolyte. The apparatus is shown in Figure 1. This arrangement allows the electrolysis to be carried out under a nitrogen atmosphere. The solution is conveniently discharged from the vessel by the hydrogen generated in the cell, once the reduction of the vanadium(IV) is complete. The vanadium(III) was analysed after the reduction by re-oxidation with a known quantity of acidified $KMnO_4$ solution to V(V) under a nitrogen atmosphere, and then analysed in the same way as before the electrolytic reduction. The analyses before and after reduction agreed to within 0.4 per cent. The uv-visible spectrum of the vanadium(III) perchlorate solution so produced agreed well with spectra reported in the literature.[10]

Potentiometric Apparatus and Procedure

The stability constants of the M(III) complexes were determined in a jacketed Teflon vessel, an electrochemical cell being used that consisted of an Orion fluoride ion-selective electrode, Model 94–09, and an Orion "single-junction" Ag/AgCl reference electrode, model 90–01, made of epoxy resin. The liquid–junction potentials were kept as constant as possible by ensuring that the ionic strength and hydrogen-ion concentration of the solution in the reaction vessel was the same as that in the reference electrode. The ionic strength of the solutions was made up to μ = 1.0 mol dm^{-3} for the V^{3+}/F^- measurements, and μ = 0.5 mol dm^{-3} for the Sc^{3+}/F^- measurements. Three titrations at different F^-, H^+, and V^{3+} concentrations† were carried out for vanadium(III) under an atmosphere of nitrogen freed from oxygen by passage through a freshly prepared solution of sodium dithionite and indigo-carmine in 10 per cent KOH.[11] The purified nitrogen was then pre-saturated and bubbled through the cell to exclude oxygen and carbon dioxide, and

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†The exact conditions and titration potentiometric results are on file, and can be obtained from the Editors.

TABLE I
Stability constants for the formation of complexes involving V(III) and Sc(III) with the F^- ion, together with the stability constants used to correct for competing reactions

Reaction	log β(obs)	μ/mol dm^{-3}	log β(lit)	μ/mol dm^{-3}
$V^{3+} + F^- = VF^{2+}$	5.00 ± 0.03	1.0	–	-
$Sc^{3+} + F^- = ScF^{2+}$	6.18 ± 0.02	0.5	6.19(13)	0.5
$Sc^{3+} + 2F^- = ScF_2^+$	11.52 ± 0.05	0.5	11.47(13)	0.5
$Sc^{3+} + 3F^- = ScF_3$	15.8 ± 0.4	0.5	15.55(13)	0.5
$2Sc^{3+} + 3F^- = Sc_2F_3^{3+}$	19.0 ± 0.3	0.5	–	–
$H^+ + F^- = HF$	2.95 ± 0.01	0.5	2.93 ± 0.02(5)	0.5
$H^+ + F^- = HF$	–	–	2.95(14)	1.0
$H^+ + 2F^- = HF_2^-$	–	–	3.54(14)	1.0
$V^{3+} + OH^- = V(OH)^{2+}$	–	–	11.42(15)	1.0
$V^{3+} + 2OH^- = V(OH)_2^+$	–	–	21.57(15)	1.0
$Sc^{3+} + OH^- = Sc(OH)^{2+}$	–	–	8.84(16)[a]	0.5
$2Sc^{3+} + 2OH^- = Sc_2(OH)_2^{4+}$	–	–	21.58(16)[a]	0.5
$H_2O = H^+ + OH^-$ (pK_w)	–	–	13.95(17)	1.0
$H_2O = H^+ + OH^-$ (pK_w)	–	–	13.74(18)	0.5

[a] Calculated from data given in reference 16, a value of the pK_w = 13.74 being used for μ = 0.5 mol. dm^{-3}.

the cell potential was measured with a RADIOMETER PHM64 research pH-meter. The experimental conditions were similar for Sc(III), except that ordinary high-purity nitrogen was used without removal of the oxygen. The potentiometric results for Sc(III) are also on file.

RESULTS

The stability constants were calculated with the MINIQUAD program of Sabatini *et al.*[12] Corrections were made for side reactions occurring in the experiment, e.g. hydrolysis of the metal ion and protonation of the ligand, using the constants shown in Table I, which were obtained either by measurement or from the literature. Also shown in Table I are the formation constants determined in this work for the Sc(III) and V(III) fluoride complexes. For the Sc(III)/F^- system, in addition to the mononuclear complexes ScF^{2+}, ScF_2^+, and ScF_3, a fairly substantial improvement was obtained in both the deviation function U, and the goodness-of-fit statistic χ^2,[12] when polynuclear complexes were postulated to be present. Further experiments indicated that for measurements carried out at different overall $(Sc)_T$ concentrations, $\bar{n}$ versus log $[F^-]$ curves for this system do not superimpose which supports the contention that polynuclear species are formed in this system. A number of polynuclear complexes were postulated, and it was found that the 'best' fit to the experimental data was obtained with the complex $Sc_2F_3^{3+}$. Precise identification of the polynuclear species from the potentiometric data given here is problematical. However, it should be noted, that log β_1 for ScF^{2+} varies by no more than ±0.01 of a log unit regardless of which polynuclear species is postulated. This, presumably, reflects the fact that the ScF^{2+} complex forms at an early stage during the titration – where little of the polynuclear species forms at all. From numerous calculations it is estimated that uncertainty in the identification of the polynuclear species introduces an uncertainty of ±0.05 in log β_2 and of ±0.40 in log β_3. The limits of error quoted in Table I for the Sc(III)/F^- complexes incorporate this effect, as well as three times the limits of error produced by the MINIQUAD programme.[12] The results obtained are in good agreement with values reported in the literature.

From the potentiometric data for the V(III)/F^- system, which were obtained at a lower (F^-) than was the case for the Sc(III)/F^- measurements, there was no indication that any complex other than VF^{2+} was formed under the experimental conditions employed.

DISCUSSION

In Figure 2 is shown a plot of log $K_1(F^-)$ for trivalent first-row metal ions versus the number of d-electrons. Values at infinite dilution were estimated by use of

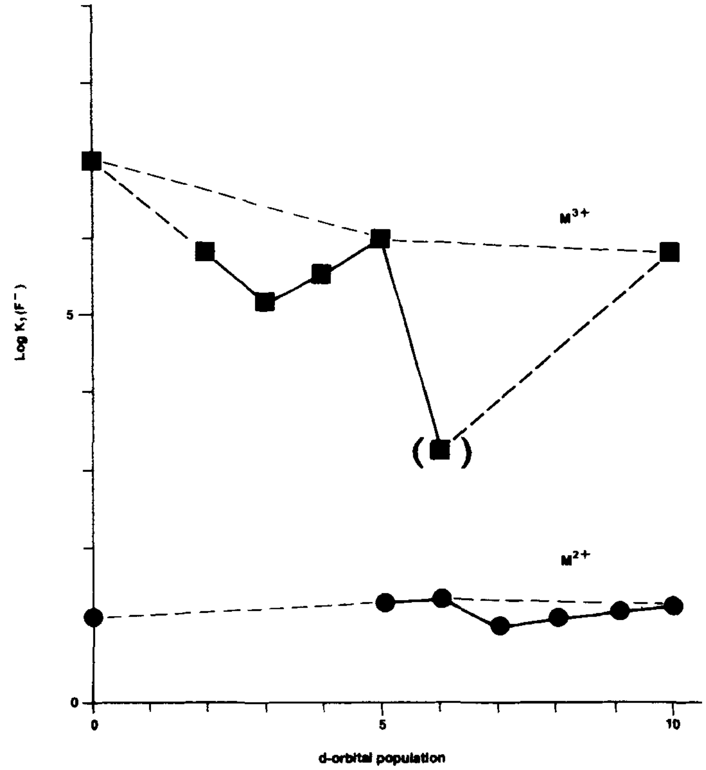

FIGURE 2 Variation of log K_1 (F⁻) (μ = 0, 25°C) with *d*-orbital population for M(II) and M(III) ions

the Davies[19] form of the extended Debye–Hückel equation from results reported at other ionic strengths. It can be seen that log K_1(F⁻), which we determined for vanadium(III), once corrected to infinite dilution, fits in exactly where expected from an inverse ligand field stability order, supporting quite strongly the low value for log K_1 (F⁻) predicted for Co(III)[3]. The method of prediction was to use a form of the Drago[20] "*E* and *C*" Eq. (1) where parameters *E* and *C* represent the tendency towards ionic or covalent bonding respectively, on the part of the Lewis acid *A* or base *B*.

$$\log K_1 = E_A E_B + C_A C_B \qquad (1)$$

E_B = 1 and C_B = 0 were set for fluoride ion, and E_B = 0 and C_B = 14 were set for hydroxide.[3] Thus, for any particular metal ion, E_A is given, approximately, by log K_1(F⁻), and C_A is given, approximately, by log K_1(OH⁻)/14. Values for *E* and *C* are given only approximately by log K_1 for fluoride and hydroxide, respectively, because the values are adjusted to a best fit considering other ligands as well. In principle, though, one could estimate values for parameters *E* and *C* knowing only log K_1 for these two ligands. The log K_1 (OH⁻) values for the first-row M(III) ions are as follows[4,5] (μ = 0, 25°C)

M(III) ion	Sc	Ti	V	Cr	Mn	Fe	Co	Ga
logK_1 (OH⁻)	9.7	12.7	11.7	10.1	(12.9)[a]	11.8	(12.7)[b]	11.4

These log K_1 values do not show any pattern that might be related to ligand-field theory. However, it is difficult for values to be determined for log K_1 (OH⁻) even under favourable circumstances, and, with the susceptibility of the Ti(III) and V(III) complexes to oxidation to the far more acidic M(IV) ions, one must seriously doubt the accuracy of these results. It is, therefore, probably not worth while for these values to be used in the estimation of *E* and *C* values for the V(III) or Ti(III) ions.

The variation of log K_1(F⁻) with d-orbital population observed in Figure 2 for the M(III) ions suggests that a reverse Irving–Williams stability order should also be observed for the M(II) ions with fluoride. The dependence of log K_1(F⁻) for the M(II) ions on *d*-orbital population is also included in Figure

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[a] – corrected from μ = 4.0 mol dm⁻³

[b] – corrected from μ = 3.0 mol dm⁻³

2. It is seen that there may possibly be a reverse order, although certainly not as strongly marked as for the M(III) ions; certainly the usually marked Irving–Williams stability order is not followed. It is of interest for the Irving–Williams stability order to be interpreted in terms of the E and C equation, as well as in terms of a model of the chelate effect proposed previously.[21] For the divalent metal ions Mn(II) to Zn(II), C parameters vary strongly in the same order as the Irving–Williams stability order, whereas the E parameters show only a very weak reverse dependence. The latter order is therefore not easily upset by variation in the hardness, or covalent/ionic nature, of the bond formed. With attempts to extend the order by including other divalent metal ions, such as Pb(II), it is found that their E and C values appear at different places in the series, so that their positions in the order, as in the order of Mellor and Maley,[22] will vary very much with the hardness of the ligand considered. Since the formation constants of polydentate ligands are related by simple equations[21] to those of their monodentate analogues, it follows then that the M(II) complexes of polydentate ligands should also follow the Irving–Williams stability order. Of course, it is debatable just how useful it is for a diagram such as Figure 2 to be interpreted in terms of ligand-field theory. The latter approach ignores the fact that the ligand-field stabilisation energy constitutes only some 10 per cent[2] of the total energy of bond formation. In addition, it serves to promote the artificial separation of the transition from the non-transition elements in bonding theories, as though ligand-field stabilisation were something over and above normal bonding forces, when a consideration of molecular orbital theory shows that it is merely a measure of the separation between a bonding and an anti-bonding energy level, which may not necessarily bear any simple relation to the overall bonding energy.

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