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Ternary complexes of Al^{3+} and F^- with a third ligand

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Contents

Abstract

Al^{3+} binds fluoride more strongly than sixty other metal ions. Binary stability constants are recommended for four ionic strengths from 0.0 to 0.5 M. Ternary complexes with hydroxide become important in neutral solutions. Competition between fluoride and hydroxide occurs for scarce sites on a metal ion highly chelated by a ligand such as EDTA. Under the conditions of experiments with G-proteins, the main solution species are hexacoordinate $(H_2O)_2(HO)AlF_3^-$ at pH 7.5 and hexacoordinate $(H_2O)_2AlF_4^-$ at pH 6.0. Crystal structure determinations show that on a G-protein a β-phosphate oxygen substitutes for a water molecule on the species in solution.

Keywords: Ternary complexes; Al^{3+}; F^-; G-protein

Abbreviations

CDTA	cyclohexane-1,2-diaminetetracetate
EDTA	ethylenediaminetetracetate
EGTA	ethylenebis(oxyethylenenitrilo)tetracetate
GDP	guanosine diphosphate
HEDTA	2-hydroxyethylethylenediaminetriacetate
NDP	nucleoside diphosphate
NTA	nitrilotriacetate

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1. Introduction

Of more than sixty metal ion species, Al^{3+} binds F^- the most strongly (except for the marginally stronger Sc^{3+}) [1]. Though fluoride is the "hardest" ligand, there is only a weak qualitative correlation of stability constants with metal ion hardness; metal ion electronegativity, ionization potential, and electron affinity all give better correlations [2]. Al^{3+} forms much stronger complexes with fluoride than with any other halide. When present, Al(III) is the main complexing agent of F^- in drinking water [3]. Naturally occurring fluoride reduces the toxicity of Al(III) to fish [4]. Fluoride also ameliorates Al(III) toxicity in plants such as tea [5] and wheat [6]. In humans Al(III) is neurotoxic [7] and fluoride in drinking water is reported to reduce the incidence of dementia [8]. Additionally, many investigators have added the two ions to G-proteins with the idea of generating AlF_4^- as a pseudophosphate linked to protein bound guanosine diphosphate. This proposal will be discussed at the end of this review. The ternary complexes formed by Al^{3+}, F^-, and a variety of third ligands including hydroxide form the subject of the first part.

Comparisons among metal ions and between ligands suggest that the binding of F^- to Al^{3+} is unusually strong. For most ligands including hydroxide the stability order is $Fe^{3+} > Ga^{3+} > Al^{3+}$ [9], while for fluoride ion Al^{3+} moves to the front of the list: $Al^{3+} > Fe^{3+} > Ga^{3+}$. F^- alone of all common ligands binds more strongly (10-times) to Al^{3+} than to Fe^{3+}.

Because it is at least 10^{11}-times more basic, we may expect hydroxide to bind more strongly than fluoride ($pK_a = 3.0$). It does so, but to Al^{3+} by a factor of only 10^2 to 10^4 (Sections 3 and 4). Comparing the reaction of $Al^{3+} + F^- \rightleftarrows AlF^{2+}$ [10, 11], with $Al^{3+} + OH^- \rightleftarrows AlOH^{2+}$ [12], we find virtually identical large positive entropy changes and small heat changes favoring the hydroxide reaction by about 11 kjoule $mole^{-1}$ (1.9 log units). In the binary complexes, owing to cooperativity in hydroxide binding [13], successive binding of hydroxides becomes more favored over fluorides.

2. Binary Al^{3+} and F^- complexes

As a basis for discussion of ternary complexes, binary complex stabilities need to be clarified. Four studies report binary stability constants at 25 °C. The classic study of Brosset and Orring performed experiments with backgrounds of 0.53 M KNO_3 and 0.53 M NH_4NO_3 [14]. Owing to an activity coefficient difference in solutions of the two different inert salts, the formation curves for the two kinds of solutions do not superimpose but are nearly parallel, with that in NH_4NO_3 lying slightly lower. We recalculate the stability constants by non-linear least squares for 16 points of v versus pF results collected from $v = 0.5$ to 3.3 in 0.53 M KNO_3 [14] to find (with one standard deviation in parentheses) $\log K_1 = 6.16(1)$, $\log K_2 = 5.04(2)$, $\log K_3 = 3.88(3)$, and $\log K_4 = 2.74(4)$. Recalculation of 19 points obtained in 0.53 M NH_4NO_3 from $v = 2.2$ to 4.7 yields $\log K_2 = 4.69(8)$, $\log K_3 = 3.80(3)$, $\log K_4 = 2.57(3)$, $\log K_5 = 1.48(5)$, and $\log K_6 = 0.5(2)$. To convert all the values to 0.53 M KNO_3, we

have taken the K_1, K_2, and K_3 values from that solution as fixed, and combined them with the points from the NH_4NO_3 solution with an adjustable parameter to be added to each n value at a given pF. The non-linear least squares results now applicable to 0.53 M KNO_3 are $\log K_4 = 2.76(4)$, $\log K_5 = 1.59(4)$, and $\Delta n = 0.130(15)$. The $\log K_4$ value falls well within one standard deviation of that calculated directly for the same salt solution. Thus the set of successive stability constant logs applicable to 0.53 M KNO_3 is 6.16, 5.04, 3.88, 2.75, 1.59, with $\log K_6$ too uncertain to specify (highest $v = 4.7$), but with an estimated value of 0.4. These refined values for 0.5 M salt are listed in the second column of Table 1. The estimates of the original authors for the successive log stability constants, 6.13, 5.02, 3.85, 2.74, 1.63, and (0.47) [14], agree better with the superior non-linear least squares analysis than do a proposed set of values based on the same data but using only a segment of the formation curve to estimate any one stability constant [11]. The constants in Ref. [14] were also selected in a critical survey [1].

Two additional studies report successive stability constants in 0.5 M salt and three lower ionic strengths. In their study with a KNO_3 background Agarwal and Moreno [15] report values at 0.5 M with $\log K_1 = 6.14$, $\log K_2 = 5.09$, $\log K_3 = 3.93$, but $\log K_4 = 3.68$ (which we ignore), the first three values in excellent agreement with those in Table 1. In a study with an NH_4NO_3 background Baumann [16] reports at 0.5 M somewhat lower successive log stability constants of 6.08, 4.93, 3.69, and 2.50, qualitatively consistent with the ammonium salt difference described above. These two studies provide the basis for estimates of the stability constants at lower ionic strengths.

The ionic strength dependence of the stability constant log may be approximated by

$$\log K_i^I = \log K_i^0 + 0.51\Delta(z_i^2)\sqrt{I}/(1 + 1.5\sqrt{I}) + b_i I$$

where the subscript i represents the number of bound F^-, I the ionic strength, 0.51 the usual Debye–Huckel term for 25 °C, and b_i an adjustable parameter to be fitted. The differences in squares of ionic charges between product and reactants in the complexation reactions, $\Delta(z_i^2)$, are listed in the third column of Table 1. The 1.5 instead of unity term in the denominator is necessary to soften the strong ionic strength dependence due to large values of $\Delta(z_i^2)$ in accord with the observed stability constants at low ionic strengths. From a non-linear least squares analysis of the

Table 1
Binary stability constants for AlF_i complexes at four ionic strengths

i	$\log K_i^{0.5}$	$\Delta(z_i^2)$	$\log K_i^0$	b_i	$\log K_i^{0.10}$	$\log K_i^{0.16}$
1	6.16	−6	7.02	0.32	6.40	6.32
2	5.04	−4	5.62	0.24	5.21	5.15
3	3.88	−2	4.1	0.26	3.91	3.89
4	2.75	0	2.6	0.30	2.63	2.65
5	1.59	2	1.1	0.28	1.35	1.40

above equation over four ionic strengths from the two studies, the most consistent successive zero ionic strength stability constants, log K_i^0, appear in the fourth column of Table 1. These values are recommended as the best zero ionic strength constants at 25 °C. Utilization of the 0.5 M and 0.0 M ionic strength stability constants in the second and fourth columns of Table 1 allows calculation of b_i in the above equation for each complex, and the values appear in the fifth column. With the values of log K_i^0 and b_i now known, log K_i^I may now be calculated for any ionic strength up to about $I=0.5$ M. Such a calculation for 0.10 M ionic strength yields the successive stability constants in the penultimate column of Table 1, in excellent agreement with an independent set of constants at this ionic strength of 6.40, 5.24, 3.86, and 2.7 [17]. A calculation for the 0.16 M ionic strength of body fluids yields the log $K_i^{0.16}$ values tabulated in the last column of Table 1.

Table 1 lists recommended binary AlF_i stability constants appropriate to seawater in column two, fresh water in column four, and extracellular body fluids in the last column. Since the complexation heats are low, less than +5 kjoule mole^{-1} for $i=1$ and smaller for succeeding complexes [10,11], the values in Table 1 may be applied to other temperatures. Complexation for the first five successive AlF_i complexes is entropy driven.

Fig. 1 shows in dashed curves a mole fraction Al(III) distribution diagram plotted from the constants at 0.5 M ionic strength. Since the abscissa contains $pF = -\log[F^-]$, where $[F^-]$ is the ambient fluoride molar concentration, the dashed

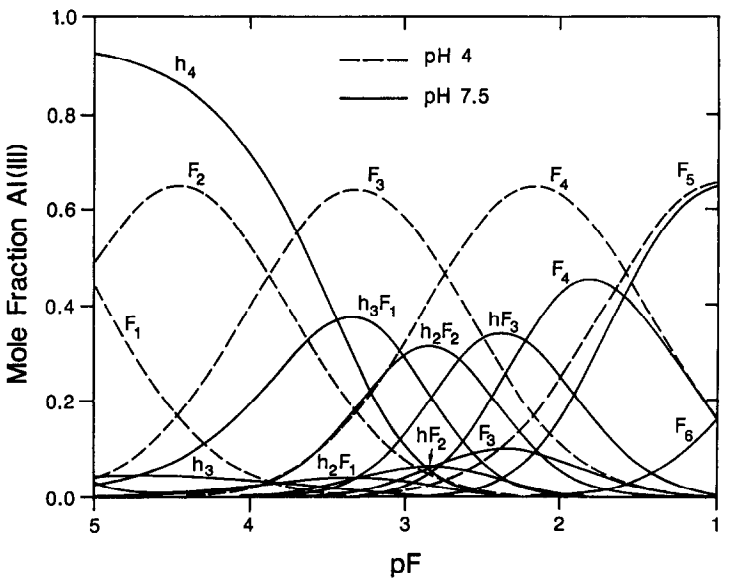

Fig. 1. Mole fraction of total Al(III) versus $pF = -\log[F^-]$, where $[F^-]$ is the ambient fluoride molar concentration, for fluoride complexes of aluminum at two pH values, dashed curves for pH 4 and solid curves for pH 7.5. Symbols on curves designate number of fluoride (F) or hydroxy groups (h) bound to Al(III). Thus h_4 represents $Al(OH)_4^-$; F_4, AlF_4^-; and hF_3, $(HO)AlF_3^-$. Constructed from equilibrium constants mentioned in the text. From Ref. [20], p. 105.

curves are applicable to acidic solutions where HF forms ($pK_a = 3.0$). Applicability of the dashed curves does not extend, however, to solutions more basic than about pH 5 as hydroxo and mixed fluoro, hydroxo complexes form. To these ternary complexes we now turn our attention.

3. Ternary complexes with OH^-

This ternary system has not been extensively studied so we adopt the approach of combining statistically the results for binary complexes of F^- and those of OH^-. Binary fluoride complexes are discussed above. In solutions more acid than pH < 5, Al(III) exists as an octahedral hexahydrate, $Al(H_2O)_6^{3+}$, usually abbreviated as Al^{3+}. As a solution becomes less acidic, $Al(H_2O)_6^{3+}$ undergoes successive deprotonations to yield $Al(OH)^{2+}$, $Al(OH)_2^+$, and a soluble $Al(OH)_3$, with a decreasing and variable number of water molecules [9,13]. Neutral solutions give an $Al(OH)_3$ precipitate that redissolves, owing to formation of tetrahedral aluminate, $Al(OH)_4^-$, the primary soluble Al(III) species at pH > 6.2. The four successive deprotonations from $Al(H_2O)_6^{3+}$ to yield $Al(OH)_4^-$ squeeze into an unusually narrow pH range of less than one log unit with pK_a values of 5.5, 5.8, 6.0, and 6.2 [18]. The narrow span for Al^{3+} is explained by the cooperative nature of the successive deprotonations due to a concomitant decrease in coordination number from six to four [13]. While Al^{3+} is three log units less acidic than Fe^{3+}, $Al(OH)_4^-$ becomes the dominant species at almost three units lower pH than does $Fe(OH)_4^-$ [13]. For Al^{3+} only two species dominate over the entire pH range, the octahedral hexahydrate $Al(H_2O)_6^{3+}$ at pH < 5.5, and the tetrahedral $Al(OH)_4^-$ at pH > 6.2, while there is a mixture of hydrolyzed species and coordination numbers between 5.5 < pH < 6.2 (distribution curves appear in the references) [13,19–21].

The scheme in Fig. 2 represents the equilibria in mixed fluoride and hydroxide

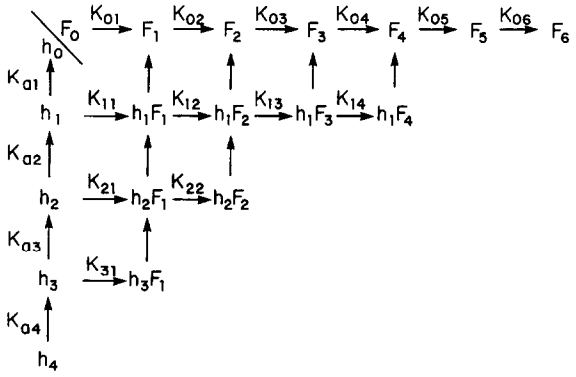

Fig. 2. Scheme for formation of mixed complexes of OH^- and F^- with a metal ion. F^- complexation occurs horizontally and OH^- complexation vertically downward. F signifies fluoride and h hydroxide. Equilibrium constants on horizontal arrows designate F^- stability constants and on vertical arrows represent acidity constants for complexed water deprotonation. From Ref. [22].

complexes of Al^{3+} [22]. Across the top are the successive equilibria for substitution of bound water by F^- at the metal ion with the designated binary equilibrium constants, K_{on}, where $n=1$ to 6. At the left the h_m, with $m=0$ to 4, specify the number of metal ion bound OH^-. Since these binary equilibrium constants are expressed not as addition of hydroxide but as loss of a proton with a pK_{am} value ($m=1$ to 4), the arrows are drawn in an upward direction. Equilibrium constants for fluoride substitution of water, K_{on}, and the pK_{am} values for deprotonation, both occurring at the Al^{3+}, constitute the inputs from the two sets of binary complexes: fluoride and hydroxide.

Ternary or mixed complexes containing both F^- and OH^- as well as Al^{3+} are represented by h_mF_n in Fig. 2. Thus h_1F_3 represents the aluminum complex $(HO)AlF_3^-$. Seven ternary complexes appear in Fig. 2. The system becomes completely defined by the additional evaluation of the seven independent mixed equilibrium constants on the horizontal arrows in the center of Fig. 2. Equilibrium constants on the unlabeled vertical arrows are not independent and may be calculated later from the properties of a cyclic system. Additional complexes beyond those depicted in Fig. 2 occur in negligible amounts.

The purely statistical approach for evaluating the ternary equilibrium constants is based upon the known equilibrium constant values for the binary complexes. The relevant equations for evaluating the seven unknown ternary constants take on an especially concise form in terms of the commonly used β symbolism for products of equilibrium constants; e.g., $\beta_{02}=K_{01}K_{02}$. The seven equations are as follows: $\beta_{11}=2(\beta_{20}\beta_{02})^{1/2}$, $\beta_{21}=3(\beta_{30}^2\beta_{03})^{1/3}$, $\beta_{12}=3(\beta_{30}\beta_{03}^2)^{1/3}$, $\beta_{31}=4(\beta_{40}^3\beta_{04})^{1/4}$, $\beta_{13}=4(\beta_{40}\beta_{04}^3)^{1/4}$, $\beta_{22}=6(\beta_{40}\beta_{04})^{1/2}$, and $\beta_{14}=5(\beta_{50}\beta_{05}^4)^{1/5}$. The numerical factors before the parentheses arise because of the greater number of ways of forming mixed complexes and correspond to the numbers in Pascal's triangle.

The argument for considering that mixed fluoro–hydroxo complexes occur to an extent suggested statistically rests upon the identical charge and comparable size of F^- and OH^-. An objection is that while there is no reduction in coordination number from octahedral aqueous Al^{3+} upon binding of up to six F^- in octahedral AlF_6^{3-}, there is a limit of only four bound OH^- in tetrahedral $Al(OH)_4^-$. This difference is typical of third row elements; consider the following additional pairs: SiF_6^{2-} and $Si(OH)_4$, PF_6^- and PO_4^{3-}, and SF_6 and SO_4^{2-}. Agreement between the statistical and experimental equilibrium constants validates the statistical approach.

Combination of the binary constants for fluoride at 0.5 M ionic strength in column 2 of Table 1 and the binary hydroxide constants listed at the beginning of this section yields the following seven ternary equilibrium constants: $\log K_{11}=5.8$, $\log K_{12}=4.5$, $\log K_{13}=3.3$, $\log K_{14}<1$, $\log K_{21}=5.3$, $\log K_{22}=4.0$, and $\log K_{31}=4.7$. An experimental study performed at 0.1 ionic strength reports $\log K_{11}=6.1$, $\log K_{12}=4.2$, and $\log K_{31}=4.8$ [23]. The agreement with the statistical approach is excellent; the difference in the first constant accords with the ionic strength difference. Environmental chemists have been slow to consider mixed complexes of hydroxide and fluoride with Al^{3+} in fresh waters. A similar analysis of ternary hydroxo–fluoro complexes has also been given for Be^{2+} [22].

Fig. 1 shows as solid curves the species distribution at pH 7.5 and 0.5 M ionic

strength as a function of the free fluoride ion concentration using the above constants [20,22]. The greater number of species compared to the dashed curves at pH 4 is immediately evident. Inclusion of ternary hydroxide complexes has a major impact on the species distribution at pH 7.5 and less than 20 mM ambient F^-. From 0.3 to 10 mM F^- eight different complexes appear and none attains 40% of the total aluminum present. The main starting species on the left at high pF (low ambient F^-) is the tetrahedral complex $Al(OH)_4^-$ (labeled h4, where the low case h represents a hydroxide group). Addition of fluoride successively replaces hydroxide groups to give as the predominant species $(HO)_3AlF^-$, $(HO)_2AlF_2^-$, $(HO)AlF_3^-$, and AlF_4^-, which holds bound water and is no longer tetrahedral. (The respective labels in the figure are h_3F_1, h_2F_2, hF_3 and F_4.) Further addition of fluoride results in the substitution of coordinated water molecules about hexacoordinate Al(III) to yield AlF_5^{2-} and finally AlF_6^{3-} just as at lower pH. Owing to intervention by bound hydroxide, at the higher pH, a greater fluoride concentration is required to obtain the same number of bound fluorides.

At the 1 ppm that F^- is added to drinking water, p$F = 4.3$, and according to Fig. 1 the main Al(III) containing species becomes AlF_2^+ in acidic solutions and $Al(OH)_4^-$ at pH 7.5. A 4-times greater F^- concentration has been reported to protect against Alzheimer's disease [24,25]. Fluoride does not enhance leaching of Al(III) from cooking utensils [26].

The monohydroxo species $Al(OH)^{2+}$ reacts many times more rapidly than Al^{3+} with F^- and other ligands [27]. Owing to formation of ternary complexes, fulvic acid abets F^- complexation by Al^{3+} [28].

4. Ternary complexes with multidentate ligands; F^- vs. OH^-

Competition between fluoride and hydroxide binding for a limited number of binding sites on a chelated metal ion may occur. Whether by addition or substitution of a coordinated water the $Al(EDTA)^-$ complex may take on F^- or OH^- ions. For the ternary fluoro complex we write

$$Al(EDTA)^- + F^- \rightleftarrows FAl(EDTA)^{2-}$$

for which $\log K_F = 4.95$ [17]. The multidentate ligand complex bearing a net negative charge binds F^- almost as strongly as does AlF^{2+} ($\log K_2$ in Table 1). Other metal ions bind F^- to their EDTA complex relatively more weakly when compared with their binary complexes. Writing the hydroxo reaction as deprotonation of coordinated water, we have

$$(H_2O)Al(EDTA)^- \rightleftarrows H^+ + (HO)Al(EDTA)^{2-}$$

for which $pK_{OH} = 5.9$ [29]. Thus in neutral solutions the ternary hydroxo complex becomes the dominant species and any F^- must compete with OH^- for a binding site on $Al(EDTA)^-$.

The molar ratio of ternary fluoro to hydroxo complexes is given by

$$\log \frac{[\mathrm{FAl(EDTA)^{2-}}]}{[\mathrm{(HO)Al(EDTA)^{2-}}]} = 10.9 - \mathrm{pH} + \log [\mathrm{F^-}]$$

where the numerical value on the right is the sum of $\log K_F + pK_{OH}$. Thus even at pH 7.4 it requires only 0.3 mM ambient fluoride for a solution to contain equimolar amounts of the two ternary complexes. Since most experiments with these components have contained greater than 1 mM F^-, at pH 7.4 the ternary fluoro complex, $FAl(EDTA)^{2-}$, is the main complex species present.

The numerical sum term on the right of the last equation may also be evaluated for EDTA complexes of other metal ions for which the ternary F^- and OH^- stability constants are known [17,30–32]. In order of decreasing sums we find $Nd^{3+} > Sc^{3+} > Th^{4+} > Al^{3+}$, $Zr^{4+} > In^{3+} > Fe^{3+} > Ga^{3+}$, where each inequality sign represents about a 10-fold decrease in stability constant sum. Relatively stronger binding of F^- yields a greater sum and stronger binding of OH^- a lesser sum. With the lowest sum, the often used Ga^{3+} appears a poor surrogate for Al^{3+} in biological systems.

A further comparison is possible between the stability constants for F^- and OH^- binding to Al^{3+} already chelated by multidentate amine-*N*-polycarboxylate ligands. The strength of OH^- binding is usually reported as the pK_a for water deprotonation [29]. A plot of this pK_{OH} vs. $\log K_F$ for fluoride binding to Al^{3+} complexes of NTA, HEDTA, EDTA, and CDTA [17] yields a straight line of slope -1.20 and an intercept of 11.6 on the pK_{OH} axis at $\log K_F = 0$. Similar plots yield straight lines through most points with slopes of -2.0 for Fe^{3+}, -1.3 for Ga^{3+}, and -1.57 for Th^{4+}. (EGTA aside, thorium gives an arrow-straight line through points for four ligands with $\log K_F$ values from Ref. [30].) Only for Ga^{3+} does the point for the aqueous ion fall near the straight line defined by the chelated complexes. These greater than unit slopes provide further evidence that there is a more profound interaction between metal ions and hydroxide than fluoride. Since NTA is only a quadridentate ligand, a quaternary complex $(OH)FAl(NTA)^{2-}$ seems likely in neutral solutions.

5. Ternary complexes with nucleoside diphosphates; G-proteins

Investigators have added Al^{3+} and excess fluoride to protein systems such as G-proteins and have observed a peak effect at about 5 mM added fluoride. Inspection of the classic dashed curves at pH 4 in Fig. 1 revealed AlF_4^- as the dominant species at the corresponding $pF = 2.3$, and the results have been interpreted as showing this species serving as a tetrahedral pseudophosphate. However, in aqueous solution the AlF_4^- complex should be hexacoordinate with two bound waters. Moreover, most such experiments were performed near pH 7.5, where the match with the solid curves in Fig. 1 suggests the predominant species to be $(OH)AlF_3^-$ with three fluorides.

In experiments with G-proteins, the presumed tetrahedral pseudophosphate AlF_4^- is postulated to reside adjacent to GDP on the G-protein [33]. Multinuclear

NMR spectroscopy has been used to study the ternary system Al^{3+}, F^-, and nucleoside diphosphates (NDP) in aqueous solutions without protein [34,35]. Since binding is at the phosphates similar results are obtained for all NDP. Under a wide variety of conditions at pH 6, species with compositions $(NDP)AlF_x$ with $x=0$ to 3 have been characterized; no species with $x=4$ was detected. All of these complexes should have hexacoordinate Al^{3+}. The scheme for binary and ternary complexes in the Al^{3+}, F^-, and NDP systems with equilibrium constants is shown in Fig. 3. The successive binary stability constants for binding of NDP to Al^{3+} are $\log K_1=7.82$ and $\log K_2=4.34$ [36].

Formation of the ternary (NDP)AlF complex occurs in a statistical amount: $\log \beta_{11}=11.9$ in Fig. 3 vs. $\log \beta_{11}=0.3+(\log \beta_{20}+\log \beta_{02})/2=11.9$ from the binary equilibrium constants. As a consequence of the statistical distribution of complexes, at low F^- concentrations binary complexes with NDP dominate; as the F^- concentration becomes comparable with that of NDP, ternary complexes dominate; and at high F^- concentrations binary complexes with F^- dominate, freeing NDP from complexation [34].

Under the conditions of the G-protein experiments at pH 7.5 with up to 0.1 mM GDP and a maximum effect at about 5 mM F^-, most Al^{3+} occurs as $(HO)AlF_3^-$; the lesser amount of nucleoside diphosphate is not competitive. Thus, under these conditions, the distribution curves in Fig. 1 apply even to solutions with added nucleotides. Therefore, the proposed G-protein bound ternary complex $(NDP)AlF_4^{4-}$ does not occur to a significant extent in aqueous solutions, where the presumed tetrahedral AlF_4^- is hexacoordinate with two bound water molecules, $(H_2O)_2AlF_4^-$. Recent work with transducin interprets $(OH)AlF_3^-$ as the relevant protein bound species [37].

Two recent crystal structure determinations of the α-subunits of two G-proteins reveal that the protein binds AlF_4^-, which is not tetrahedral but hexacoordinate [38,39]. The crystals were prepared at pH 6.0 (in mixed solvent sytems) near p*F* 2, in this range corresponding closely to the curves for pH 4 in Fig. 1, which shows that $(H_2O)_2AlF_4^-$ is the dominant species in solution. On both G-proteins the four fluorides are bound to hexacoordinate Al^{3+} in a plane; one axial bond interacts with a β-phosphate oxygen of GDP and the other with a water molecule, $GDP–AlF_4^- - OH_2$. Thus, on the G-protein, a β-phosphate oxygen substitutes for a water molecule of the species in solution. (Other interactions contribute to stabilization of the complex on the G-protein.) This basic geometry agrees with the point that AlF_4^-

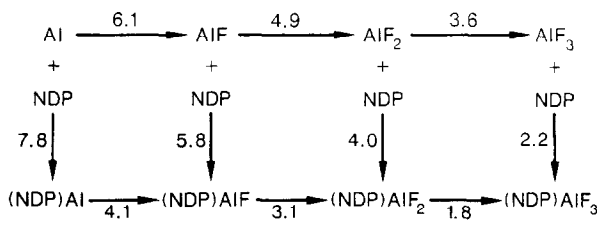

Fig. 3. Stability constant logs for formation of binary and ternary complexes of nucleoside diphosphates (NDP), F^-, and Al^{3+}. The binary constants for fluoride across the top are from an older set in Ref. [34].

species will not be tetrahedral but hexacoordinate [7,19,20,22]. Still to be determined is whether hydroxide substitutes for a fluoride in protein crystals prepared at pH 7.5.

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