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Mixed Ligand Complexes of Trivalent Metal Ions with an Amine-*N*-polycarboxylate and Fluoride

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The formation constants of the mixed ligand complexes MLF(M: Al^{3+}, Ga^{3+}, In^{3+}, Fe^{3+}, Sc^{3+}, Y^{3+}, La^{3+}; L: nta^{3-}, $hedta^{3-}$, $edta^{4-}$, $cdta^{4-}$) were determined. Reactivity of a trivalent metal ion with fluoride generally decreases by the coordination of an amine-*N*-polycarboxylate. From the decrease the structures of the parent and mixed ligand complexes are discussed.

Fluoride ion is a unique ligand in that it shows almost pure electrostatic interactions with metal ions in solution. Since the fluoride ion-selective electrode was developed in 1966,[1] the formation constants of nearly every metal fluoro complexes have been determined.[2]

Recently we have found the general presence of the mixed ligand complexes containing fluoride in the equilibrium study on the reaction of aluminum fluoro complexes with masking reagents.[3] Such complexes have never been reported so far as we know. In this paper, the formation constants of a series of the mixed ligand complexes MLF (M: Al^{3+}, Ga^{3+}, In^{3+}, Fe^{3+}, Sc^{3+}, Y^{3+}, La^{3+}; L: nta^{3-}, $hedta^{3-}$, $edta^{4-}$, $cdta^{4-}$; charges of complexes are omitted)[4] are determined.

Experimental

Reagents and Equipments. Aluminum, gallium, lanthanum and iron solutions were prepared by dissolving their nitrates in dilute nitric acid. Indium, scandium, and yttrium solutions were obtained by reacting metallic indium, scandium oxide and yttrium oxide with nitric acid, respectively. All these solutions were standardized against EDTA. Potassium fluoride was dried for 24 h at 110 °C. Fluoride solutions were stored in polyethylene containers. Potassium nitrate was recrystallized twice. Carbonate-free potassium hydroxide solution was prepared as described in the literature.[5] All other chemicals used were of reagent grade.

Throughout this work the ionic strength was adjusted to 0.1 mol dm^{-3} with potassium nitrate. A measuring cell made of polypropylene was placed in a water bath thermostated at 25±0.1 °C. A fluoride ion-selective electrode (Denki Kagaku Keiki Co.; DKK type 7200), a HF-resistant glass electrode (Ohkura electric Co.; GP 1200) and two reference electrodes with a junction made of porous Teflon (DKK type 4400) were soaked in the sample solution, and potentials were measured to 0.1 mV with two potentiometers (DKK IOC-10). The fluoride ion-selective electrode was calibrated with several potassium fluoride solutions between 10^{-2}—10^{-6} mol dm^{-3} made by serial dilution, whereas the glass electrode was calibrated with several nitric acid solutions. Both electrodes gave Nernstian responses. Before and after a series of measurements standard potentials of these electrodes were determined with a 1.00×10^{-2} mol dm^{-3} potassium fluoride solution and a 1.00×10^{-2} mol dm^{-3} nitric acid solution, respectively. The presence of complexing reagents did not affect the standard potential of the fluoride ion-selective electrode.

Procedure. Stability constants of simple metal fluoro complexes and protonation constants of metal amine-*N*-polycarboxylate complexes were determined by the conventional methods.[2] When ternary systems were studied, 10% excess of a ligand against a metal ion was added to suppress the dissociation of an amine-*N*-polycarboxylate complex but not to form a bis complex, ML_2. With a dilute nitric acid or a potassium hydroxide solution, $-\log[H^+]$ was adjusted. This solution being titrated with potassium fluoride solution, $-\log[H^+]$ and $-\log[F^-]$ were measured after each addition. Constant potentials were obtained within 10 min. In the systems containing aluminum, potentials were read after 24 h using a batch method.

Results

Trivalent Metal Fluoro Complexes. The equilibria of reactions between proton and fluoride were first studied at 25 °C and at 0.1 mol dm^{-3} KNO_3. The results were analyzed as described previously,[6] and the following constants were obtained.

$$H^+ + F^- \rightleftharpoons HF: \quad \log K_{HF} = 2.99 \pm 0.03$$

$$HF + F^- \rightleftharpoons HF_2^-: \quad \log K_{HF_2} = 0.38 \pm 0.08$$

The complexation equilibria of trivalent metal ions with fluoride were studied for the comparison described below. The formation functions of metal fluoro complexes

$$\bar{n} = (C_F - [F^-] - [HF] - 2[HF_2^-])/C_M, \qquad (1)$$

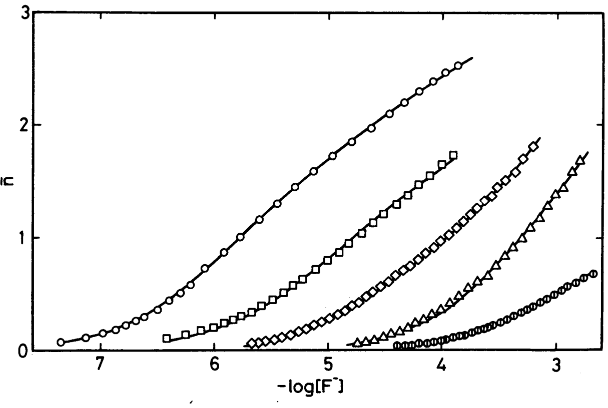

Fig. 1. Plots of $\bar{n}$ vs. $-\log[F^-]$ for trivalent metal fluoro complexes (25 °C, 0.1 mol dm^{-3} KNO_3). Trivalent metal: O, scandium; □, iron; ◇, gallium; Δ, indium; O, proton. Data for aluminum and yttrium complexes are omitted for clarity. The solid curves were calculated with the constants in Table 1.

Table 1. Formation Constants of Trivalent Metal Fluoro Complexes (25 °C; 0.1 mol dm^{-3} KNO$_3$)

Metal ion	Obtained[a]				Literature				Medium	Ref.
	log K_1	log K_2	log K_3	log K_4	log K_1	log K_2	log K_3	log K_4		
Al^{3+}	6.40(1)	5.24(2)	3.86(3)	2.7(10)	6.40	5.19	3.91	2.42	0.1 mol dm^{-3} NH$_4$NO$_3$	b
Ga^{3+}	4.49(2)	3.50(3)			4.40	3.80			1 mol dm^{-3} NaClO$_4$	c
In^{3+}	3.64(3)	2.9(10)			3.69	2.83			1 mol dm^{-3} NaClO$_4$	d
Fe^{3+}	5.30(2)	4.23(2)	3.0(10)		5.16	3.91	2.93		0.5 mol dm^{-3} NaClO$_4$	e
Sc^{3+}	6.22(1)	5.30(2)	3.95(3)		6.22	5.11	3.90		0.5 mol dm^{-3} NaClO$_4$	e
Y^{3+}	3.76(3)				3.91	3.25			0.5 mol dm^{-3} NaClO$_4$	e

a) Numbers in parentheses are estimated errors. b) E. W. Baumann, *J. Inorg. Nucl. Chem.*, **31**, 3155 (1969). c) J. B. Walker, C. R. Twine and G. R. Choppin, *J. Inorg. Nucl. Chem.*, **33**, 1813 (1971). d) T. Ryhl, *Acta Chem. Scand.*, **23**, 2667 (1969). e) A. Aziz and S. J. Lyle, *Anal. Chim. Acta*, **47**, 49 (1969).

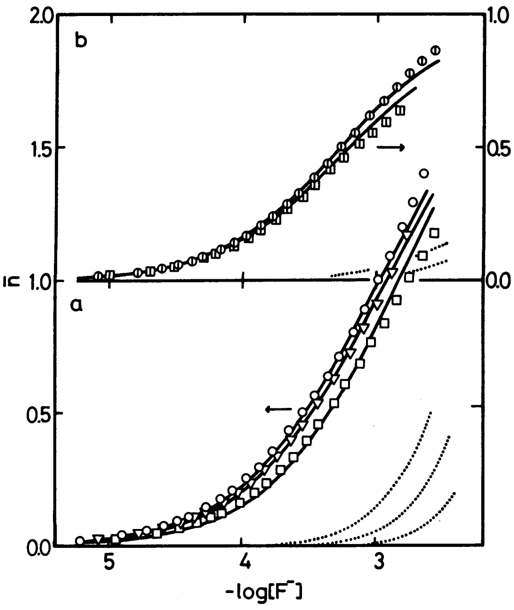

Fig. 2. Plots of $\bar{n}$ vs. $-\log[\mathrm{F}^-]$ for Fe-NTA-F and Fe-HEDTA-F systems (25 °C, 0.1 mol dm^{-3} KNO$_3$). System: a, Fe-NTA-F; b, Fe-HEDTA-F. $-\log[\mathrm{H}^+]$: ○, 2.9; ▽, 3.3; □, 3.85; ○, 2.9; □, 3.2. The solid curves were calculated with the constants in Table 2. The dotted curves were expected by assuming no mixed ligand complex formation.

are plotted against $-\log[\mathrm{F}^-]$ in Fig. 1. The change in the total concentration of a metal ion (from 5×10^{-4} to 2×10^{-3} mol dm^{-3}) or hydrogen ion did not displace the formation functions. Thus neither polymerized fluoro complexes nor hydrolyzed species were formed. The stepwise formation constants of metal fluoro complexes

$$\mathrm{MF}_{m-1} + \mathrm{F}^- \rightleftharpoons \mathrm{MF}_m : K_m,$$

were refined to give a minimum error square sum about $\bar{n}$ (Table 1). Constants smaller than $10^{3.0}$ are less reliable because of low precision of the numerator in Eq. 1. Formation of lanthanum fluoro complexes could not be studied by the same method due to the precipitation of lanthanum trifluoride.

Mixed Ligand Complexes in Fe-NTA-F and Fe-HEDTA-F Systems. Figure 2 shows the formation functions at various $-\log[\mathrm{H}^+]$ in Fe-NTA-F and Fe-HEDTA-F systems.

Table 2. Average Deviation of $\bar{n}$ for Various Combinations of Species in Fe-NTA-F and Fe-HEDTA-F Systems[a]

System	No.	Species considered			$\Delta\bar{n}$
		MLF	MLF$_2$	ML(OH)F	
Fe-NTA-F	1	×	×	×	0.627
	2	○	×	×	0.181
	3	○	○	×	0.042
	4	○	○	○	0.040
Fe-HEDTA-F	1	×	×	×	0.442
	2	○	×	×	0.041
	3	○	○	×	0.040
	4	○	○	○	0.040

a) Numbers of data used for the calculation were 73 for Fe-NTA-F and 67 for Fe-HEDTA-F, respectively.

The parent complex ML hydrolyzes at higher $-\log[\mathrm{H}^+]$.

$$\mathrm{ML(OH)} + \mathrm{H}^+ \rightleftharpoons \mathrm{ML} : K^{\mathrm{H}}_{\mathrm{ML}}$$

These constants were potentiometrically determined to be $10^{3.96}$ for Fe-NTA and $10^{3.86}$ for Fe-HEDTA. On the other hand, the complex is protonated at lower $-\log[\mathrm{H}^+]$.

$$\mathrm{ML} + \mathrm{H}^+ \rightleftharpoons \mathrm{MHL} : K^{\mathrm{H}}_{\mathrm{MHL}}$$

Among these species, ML and MHL react with fluoride to form mixed ligand complexes.[3] It was difficult, however, to study the reactivity of MHL, because MHL forms only in strongly acidic solution where on the addition of fluoride the substitution reaction prevails over the formation of the mixed ligand complex. Thus we adopted the data in the $-\log[\mathrm{H}^+]$ range where only ML and ML(OH) existed.

Formation of the mixed ligand complex MLF$_n$ is expressed by

$$\mathrm{MLF}_{n-1} + \mathrm{F}^- \rightleftharpoons \mathrm{MLF}_n : K^{\mathrm{F}}_{\mathrm{MLF}_n}.$$

For each experimental point, two simultaneous equations in [M] and [L] were solved,

$$C_\mathrm{M} = [\mathrm{M}] + [\mathrm{ML}] + [\mathrm{ML(OH)}] + \Sigma[\mathrm{MF}_m] + \Sigma[\mathrm{MLF}_n], \tag{2}$$

$$C_\mathrm{L} = [\mathrm{L}]\alpha_{\mathrm{L(H)}} + [\mathrm{ML}] + [\mathrm{ML(OH)}] + \Sigma[\mathrm{MLF}_n], \tag{3}$$

Table 3. Total Concentrations of M and F^-, Concentrations of F^- and HF, $-\log[H^+]$, $\bar{n}$ and the Calculated Formation Constants of the Mixed Ligand Complex in Ga-NTA-F System[a)]

	$10^4 C_M$ / mol dm^{-3}	$10^4 C_F$ / mol dm^{-3}	$10^4[F^-]$ / mol dm^{-3}	10^4[HF] / mol dm^{-3}	$-\log[H^+]$	$\bar{n}$	$\log K^F_{MLF}$ [b)]
1	8.963	0.648	0.125	0.272	2.650	0.028	3.365
2	8.960	0.972	0.188	0.405	2.655	0.042	3.373
3	8.957	1.295	0.254	0.542	2.661	0.056	3.366
4	8.954	1.619	0.318	0.674	2.664	0.070	3.373
5	8.951	1.942	0.385	0.806	2.669	0.084	3.376
6	8.948	2.265	0.454	0.938	2.674	0.098	3.377
7	8.945	2.588	0.524	1.074	2.677	0.111	3.375
8	8.939	3.232	0.670	1.352	2.684	0.135	3.368
9	8.933	3.877	0.810	1.617	2.689	0.162	3.377
10	8.924	4.841	1.035	2.019	2.699	0.200	3.382
11	8.915	5.804	1.272	2.425	2.710	0.236	3.385
12	8.904	7.084	1.601	2.957	2.723	0.283	(3.392)
13	8.892	8.361	1.945	3.483	2.737	0.329	(3.402)
14	8.874	10.27	2.496	4.248	2.759	0.397	(3.420)
15	8.857	12.17	3.092	5.022	2.779	0.457	(3.435)
16	8.834	14.69	3.905	5.960	2.806	0.546	(3.487)
17	8.811	17.20	4.744	6.883	2.828	0.631	(3.557)
18	8.782	20.32	5.946	7.857	2.868	0.740	(3.680)
19	8.748	24.04	7.482	8.831	2.918	0.880	(3.992)

a) Formation of HF_2^- is negligible in this system. b) Calculated with Eqs. 2′ and 5.

Table 4. Formation Constants for the Coordination of the First Fluoride to ML

Metal ion	$\log K^F_{MLF}$ for various L[a)]					Ionic radius
	None	nta^{3-}	hedta^{3-}	edta^{4-}	cdta^{4-}	
Al^{3+}	6.40	5.41(2)	5.53(2)	4.95(2)	3.14(2)	0.50
Ga^{3+}	4.49	3.37(2)	3.15(2)	2.3(10)	2.1(10)	0.62
In^{3+}	3.64	2.0(10)	2.0(10)	1.6(10)	2.1(10)	0.81
Fe^{3+}	5.30	3.46(2)	3.31(2)	1.7(10)	1.5(10)	0.64
Sc^{3+}	6.22	3.90(5)	3.62(5)	1.9(10)	2.5(10)	0.81
Y^{3+}	3.76	2.62(5)	1.8(10)	1.5(10)	1.6(10)	0.93
La^{3+}	2.69[b)]	2.0(10)	1.7(10)	1.4(10)	1.8(10)	1.15

a) Numbers in parentheses are estimated errors. b) At ionic strength 0.5 mol dm^{-3} $NaClO_4$. A. Aziz and S. J. Lyle, *J. Inorg. Nucl. Chem.*, **32**, 1925 (1970).

where $\alpha_{L(H)}$ is the side reaction coefficient taking account of the protonation of L. Using [M], [L], $[H^+]$, and $[F^-]$, $\bar{n}$ was calculated.

$$\bar{n}_{\rm cald} = \frac{\sum m[MF_m] + \sum n[MLF_n]}{C_M} \qquad (4)$$

Various combinations of the mixed ligand complexes were assumed and $K^F_{MLF_n}$ values in each set were refined to give a minimum error square sum, $\Delta\bar{n}=(\sum(\bar{n}_{\rm obsd}-\bar{n}_{\rm cald})^2/N)^{1/2}$ (Table 2).

When no mixed ligand complex was assumed there were large systematic deviations (dotted curves in Fig. 2 or No. 1 in Table 2). By considering the formation of MLF satisfactory agreement between experimental and calculated values was obtained in Fe-HEDTA-F system but not in Fe-NTA-F system (No. 2), where presence of MLF_2 must also be taken into account (No. 3). Further improvement was not obtained by assuming the formation of ML(OH)F (No. 4).

Other Systems. As the K^H_{ML} values of the other complexes are larger than those of Fe(nta) and Fe(hedta),[7)] $-\log[H^+]$ can be adjusted so that only ML exists in the solution containing a metal ion and an excess ligand: the concentration of ML(OH) as well as those of MHL and free M is low. When small amounts of fluoride are added to such solutions, formation of MF_m and MLF_n ($n>1$) is negligible. Then Eq. 2 is simplified as

$$C_M = [ML] + [MLF], \qquad (2')$$

and [MLF] is obtained by

$$[MLF] = C_F - ([F^-] + [HF] + 2[HF_2^-]). \qquad (5)$$

The K^F_{MLF} values can be calculated only with these equations.

Table 3 gives some of the data in Ga-NTA-F system. At lower total concentrations of fluoride (until No. 11) K^F_{MLF} values are constant. On the other hand, $\bar{n}$ and thus K^F_{MLF} abruptly increases at higher C_F because of the dissociation of the ligand from the complex accompanied by the formation of GaF_m. The K^F_{MLF} values thus obtained are given in Table 4.

Discussion

Metal Fluoro Complexes. Correlation between $\log K_1$ and $Z_+/(r_+ + r_-)$, where Z_+ is the charge of a metal ion and r_+ and r_- are the radii of the metal and fluoride ions, respectively, has been suggested from a simple electrostatic consideration,[8] but it is not satisfactory. For example, Al^{3+} and Sc^{3+} have almost the same formation constants in spite of very different ionic radii. The role of the solvent is completely neglected in this consideration.

As shown in Table 1, the ratio K_2/K_3 is larger than K_1/K_2, and this indicates the irregular change in the solvation during the stepwise complexation,[9] which cannot be quantitatively evaluated at this stage.

M-NTA-F and M-HEDTA-F. Reactivity of a trivalent metal ion with fluoride generally decreases by the coordination of an amine-*N*-polycarboxylate. As NTA and HEDTA complexes hold more than one coordinated water molecules, formation of their mixed ligand complexes corresponds to substitution of water molecules with fluoride ions as in the formation of simple fluoro complexes. The decrease in the reactivity is thus ascribed to the decrease in the statistical factor, the neutralization of the positive charge on the metal ion by the ligand and the decrease in the degree of solvation.

The first effect is not expected to contribute so much but certainly operates so that small decreases in K^F_{MLF} are observed from NTA complexes with tetradentate chelation to HEDTA complexes with pentadentate chelation. The second effect is more decisive but would be relieved for larger ions because positive charges on these ions can only locally be neutralized. This is the case for scandium group and the difference between K^F_{MF} and K^F_{MLF} decreases in the order of $Sc^{3+} > Y^{3+} > La^{3+}$. But the reverse order is found for aluminum group, where again the third effect must prevail.

M-EDTA-F and M-CDTA-F. The K^F_{MLF} values of Ga(edta), Fe(edta), and Sc(edta) are much smaller than those of their HEDTA and NTA complexes, respectively. This suggests that one carboxylato group must become free on the formation of the mixed ligand complex and also that the parent complexes involve the complete hexadentate chelation of EDTA irrespective of the coordination number of metal ions.[10] On the other hand, for aluminum, similar large decrease in K^F_{MLF} is rather found between EDTA and CDTA complexes. This means the weak coordination of one carboxylato group in Al(edta) complex, which agrees with the fact that $K^H_{MH(edta)}$ of aluminum complex ($10^{2.8-3.4}$) is definitely higher than those of other trivalent metal complexes (less than 10^2 except for large metal ion complexes).[7]

If a CDTA complex of a metal also forms the mixed ligand complex with the pentadentate chelation, $K^F_{M(edta)F}$ is expected to be smaller than $K^F_{MH(edta)F}$, because CDTA has a more rigid skeleton and must have more difficulty in detaching one carboxylato group. This is the case for aluminum, gallium, and iron, but the reverse order is found for indium, scandium, yttrium and lanthanum. As these ions have larger ionic radii, fluoride can coordinate to a metal ion with keeping the hexadentate chelation of the ligand as in the reaction of Co(II)(cdta) with cyanide.[16]

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References

1) M. S. Frant and J. W. Ross, *Science,* **154**, 1553 (1966).

2) A. M. Bond and G. T. Hefter, "Critical Survey of Stability Constants and Related Thermodynamic Data of Fluoride Complexes in Aqueous Solution," IUPAC, Pergamon (1980).

3) A. Yuchi, K. Ueda, H. Wada, and G. Nakagawa, *Anal. Chim. Acta,* **186**, 313 (1986).

4) Ligand abbreviation: NTA, nitrilotriacetic acid (H_3nta); HEDTA, *N′*-(2-hydroxyethyl)ethylenediamine-*N,N,N′*-triacetic acid (H_3hedta); EDTA, ethylenediamine-*N,N,N′,N′*-tetraacetic acid (H_4edta); CDTA, 1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetic acid (H_4cdta).

5) J. E. Powell and M. A. Hiller, *J. Chem. Educ.,* **34**, 330 (1957).

6) K. Srinivasan and G. A. Rechnitz, *Anal. Chem.,* **40**, 509 (1968).

7) a) L. G. Sillen and A. E. Martell, "Stability Constants of Metal-Ion Complexes, and Supplement No. 1," The Chemical Society, London (1964 and 1971); b) D. D. Perrin, "Stability Constants of Metal-Ion Complexes Part B," IUPAC, Pergamon (1979).

8) G. Hefter, *Coord. Chem. Rev.,* **12**, 221 (1974).

9) S. Ahrland, *Pure Appl. Chem.,* **51**, 2019 (1979) and references therein; S. Ahrland, *Pure Appl. Chem.,* **54**, 1451 (1982) and references therein.

10) Fe(edta) is seven coordinate both in the solid[11] and in the solution[12] with a coordinated water. But it is ascribed to the unbalanced affinities to amino nitrogen and carboxylate oxygen rather than the size of ionic radius.[13] Once the ligand becomes pentadentate, the metal becomes six coordinate with relaxation of ring constrain as seen in $[Fe(hedta)]_2O$ and $Fe(Hedta)H_2O$.[14,15] This agrees with our observation that the highest species were $Fe(nta)F_2$ and Fe(hedta)F.

11) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.,* **3**, 34 (1964).

12) J. Oakes and E. G. Smith, *J. Chem. Soc., Faraday Trans. 1,* **79**, 543 (1983).

13) J. J. Stezowski, R. Countryman, and J. L. Hoard, *Inorg. Chem.,* **12**, 1749 (1973).

14) S. J. Lippard, H. Schugar, and C. Walling, *Inorg. Chem.,* **6**, 1825 (1967).

15) C. H. L. Kennard, *Inorg. Chim. Acta,* **1**, 347 (1967).

16) J. P. Jones and D. W. Margerum, *Inorg. Chem.,* **8**, 1486 (1969).