Preparation and the pH dependent reversible color change of complexes of cobalt(III) and chromium(III) with a hexafluoroacetylacetonato ligand

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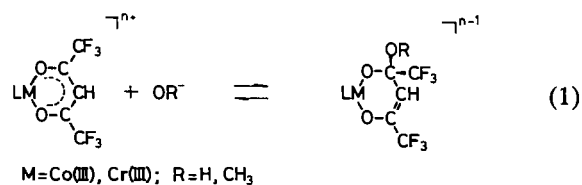
Abstract

Thirteen complexes of Co(III) and Cr(III) with a hexafluoroacetylacetonato (hfac) ligand were newly prepared as perchlorate salts. These are $CoL(hfac)^{2+}$ with $L=(tn)_2$, tren, β-2,3,2-tet, β-3,2,3-tet, $(EtNH_2)_4$, $(n\text{-}PrNH_2)_4$, $(n\text{-}BuNH_2)_4$, $(bpy)_2$, $(phen)_2$; and $CrL(hfac)^{2+}$ with $L=(NH_3)_4$, $(tn)_2$, α-2,3,2-tet, 3,2,3-tet. In these complexes the ligand L occupies four coordination sites and the hfac ligand acts as a bidentate. Aqueous or methanolic solutions of these complexes show a pH dependent rapid and reversible color change; orange in an acid and violet in a base. The origin of this chromism may be a covalent hydration equilibrium, where a lyate anion forms a σ bond with one of the carbonyl carbon atoms of the coordinating hfac ligand. The equilibrium constant in water is $2 \sim 12 \times 10^6$ M^{-1} for Co(III) complexes and $1 \sim 6 \times 10^{10}$ M^{-1} for Cr(III) complexes ($M = mol$ dm^{-3}).

Introduction

Recently, we have studied a unique hydrolysis phenomenon of Co(III) and Cr(III) complexes with a bidentate hfac ligand; $CoL(hfac)^{n+}$ with $L=(NH_3)_4$, $(en)_2$, α-trien, β-trien, i-dtma, α-edda, β-edda, and $Cr(en)_2(hfac)^{2+}$ [1–9]**. The pH dependent reversible color change of these kinds of complexes in water or in methanol has been ascribed to a reversible lyate anion addition to one of the carbonyl carbon atoms of the hfac ligand.

$$M = Co(III), Cr(III); \quad R = H, CH_3$$

This reaction is a novel one in the chemistry of Co(III) and Cr(III) complexes and is worth investigating in more detail. In the present work, we are interested in the effect of a variation of the L ligand on reaction (1). We have prepared thirteen new complex perchlorates of Co(III) and Cr(III) with a bidentate hfac ligand. We have studied the pH dependent UV–Vis absorption spectra and the hydrolysis equilibria of them.

Experimental

Commercially available amines were used without further purification. Analytical data are presented in Table 1. ^{19}F NMR spectra were recorded on a JEOL-GSX270-FT-NMR instrument at the Advanced Instrumentation Center for Chemical Analysis, Ehime University. We could not prepare $[Co(MeNH_2)_4(hfac)](ClO_4)_2$ with a satisfactory elemental analytical result. The difficulty existed in the isolation of $[Co(MeNH_2)_4CO_3]ClO_4$. **Caution:** Although we have experienced no difficulties with the perchlorate salts of the complex mentioned herein, these compounds should be treated as potentially explosive and should be handled with care.

TABLE 1. Analytical data[a]

Complex	C (%)	H (%)	N (%)
[Co(tn)₂(hfac)](ClO₄)₂·H₂O	21.0	3.3	8.8
	(20.9)	(3.3)	(8.9)
[Co(tren)(hfac)](ClO₄)₂	21.6	3.3	9.3
	(21.6)	(3.1)	(9.2)
β-[Co(2,3,2-tet)(hfac)](ClO₄)₂	22.8	3.4	9.1
	(23.0)	(3.4)	(9.0)
β-[Co(3,2,3-tet)(hfac)](ClO₄)₂·H₂O	23.4	3.7	8.8
	(23.7)	(3.8)	(8.5)
[Co(EtNH₂)₄(hfac)](ClO₄)₂	23.9	4.6	9.0
	(24.2)	(4.5)	(8.7)
[Co(n-PrNH₂)₄(hfac)](ClO₄)₂	29.0	5.5	8.2
	(29.1)	(5.3)	(8.7)
[Co(n-BuNH₂)₄(hfac)](ClO₄)₂	33.3	6.2	7.8
	(33.3)	(6.0)	(7.4)
[Co(bpy)₂(hfac)](ClO₄)₂	38.2	2.3	7.2
	(38.6)	(2.2)	(7.2)
[Co(phen)₂(hfac)](ClO₄)₂	41.9	2.3	6.5
	(42.2)	(2.1)	(6.8)
[Cr(NH₃)₄(hfac)](ClO₄)₂	11.8	2.7	11.1
	(11.4)	(2.5)	(10.7)
[Cr(en)₂(hfac)](ClO₄)₂	19.0	3.1	10.4
	(18.7)	(3.0)	(9.7)
[Cr(tn)₂(hfac)](ClO₄)₂	21.6	3.6	9.6
	(21.8)	(3.5)	(9.2)
α-[Cr(2,3,2-tet)(hfac)](ClO₄)₂	23.4	3.4	9.6
	(23.2)	(3.4)	(9.1)
[Cr(3,2,3-tet)(hfac)](ClO₄)₂	24.4	3.6	9.3
	(24.7)	(3.7)	(8.9)

[a]Calculated values are given in parentheses.

[Co(tren)CO₃]ClO₄

This was prepared by treating an aqueous solution of Co(tren)CO₃⁺ with NaClO₄. It was recrystallized from water [10].

[Co(3,2,3-tet)CO₃]ClO₄

This was prepared according to a published method [11].

[Co(bpy)₂CO₃]ClO₄

2,2'-Dipyridyl (1.56 g) was added to a tricarbonatocobaltate solution freshly prepared from CoCl₂·6H₂O (1.2 g) [12]. This solution was stirred at 60 °C for 1 h. The resultant precipitate of [Co(bpy)₂CO₃]Cl was collected on a glass filter. It was dissolved in water and an insoluble substance was removed by filtration. A precipitate of [Co(bpy)₂CO₃]ClO₄ (2.2 g) separated on addition of NaClO₄ (1.8 g) to the filtrate. It was washed with water, ethanol and ether.

[Co(tn)₂CO₃]ClO₄, [Co(EtNH₂)₄CO₃]ClO₄ and [Co(phen)₂CO₃]ClO₄

These were prepared in a similar way to that described for [Co(bpy)₂CO₃]ClO₄, using an appropriate amine.

[Co(n-PrNH₂)₄CO₃]ClO₄

A tricarbonatocobaltate solution (0.05 mol Co) was treated with n-PrNH₂ (30 ml). The resultant pink precipitate was a mixture of blue–violet K[Co(n-PrNH₂)₂(CO₃)₂] and red [Co(n-PrNH₂)₄CO₃]Cl. The latter was extracted with methanol. The extract was mixed with a saturated aqueous solution (10 ml) of NaBr. The mixture was rotoevaporated and [Co(n-PrNH₂)₄CO₃]Br separated. It was washed with water, acetone + ether (1:1) and dried under reduced pressure. A pink perchlorate salt separated from an aqueous solution (1 l) of the bromide (6.1 g) on addition of NaClO₄. It was recrystallized from methanol (0.4 l) by addition of NaClO₄ and washed with ethanol + ether (1:1) (yield 5.7 g).

[Co(n-BuNH₂)₄CO₃]ClO₄

[Co(n-BuNH₂)₄CO₃]Cl was obtained by treating a tricarbonatocobaltate solution with n-BuNH₂ in a similar way to that described for [Co(n-PrNH₂)₄CO₃]Br. Ethanol was used as an extracting solvent and NaCl as a precipitant. A pink perchlorate salt separated from an aqueous solution of the chloride on addition of NaClO₄. It was recrystallized from methanol (yield 26%).

[Co(bpy)₂(H₂O)₂](ClO₄)₃

A suspension of [Co(bpy)₂CO₃]ClO₄ in 6 M HClO₄ was warmed. After the evolution of CO₂ gas finished, the solution was cooled in ice. The resultant orange needle crystal was quickly collected and recrystallized from hot water by addition of 6 M HClO₄. It was washed with ethanol + ether (1:1) and air dried.

[Co(phen)₂(H₂O)₂](ClO₄)₃

A red–orange granular crystal was obtained from [Co(phen)₂CO₃]ClO₄ in a similar way to that described for [Co(bpy)₂(H₂O)₂](ClO₄)₃.

[Co(tn)₂(hfac)](ClO₄)₂·H₂O, [Co(tren)(hfac)]-(ClO₄)₂, β-[Co(3,2,3-tet)(hfac)](ClO₄)₂·H₂O, [Co(EtNH₂)₄(hfac)](ClO₄)₂ and [Co(n-PrNH₂)₄-(hfac)](ClO₄)₂

These complex salts were prepared in a similar way to that described for [Co(en)₂(hfac)](ClO₄)₂ using the corresponding carbonato complex as a starting material[1]. In the case of the 3,2,3-tet complex, an oily layer separated from the reaction mixture. It became homogeneous on addition of acetone to the mixture. A cinnabar crystal separated after further reaction at 70 °C for 1 h. The EtNH₂ and n-PrNH₂ complexes were recrystallized from methanol by addition of HClO₄ + NaClO₄.

[Co(bpy)₂(hfac)](ClO₄)₂

[Co(bpy)$_2$(H$_2$O)$_2$](ClO$_4$)$_3$ (0.71 g) was dissolved in water (5 ml). To this solution at 50 °C, an aqueous solution of Hhfac (0.21 g) + NaOH (0.04 g) was added drop by drop. The resultant pink precipitate was washed with acetone and air dried. It was dissolved in 6 M HClO$_4$ (3 ml). On cooling the solution, an orange crystal separated. It was re-crystallized from acetone by addition of 2 M HClO$_4$. It was washed with water and ethanol + ether (1:9) (yield 0.1 g).

[Co(phen)₂(hfac)](ClO₄)₂

[Co(phen)$_2$(H$_2$O)$_2$](ClO$_4$)$_3$ (0.78 g) was dissolved in water (5 ml). To this solution at 50 °C, an aqueous solution of Hhfac (0.21 g) + NaOH (0.04 g) was added drop by drop. The resultant orange crystal was recrystallized from acetone by addition of 2 M HClO$_4$ (yield 0.1 g).

[Co(n-BuNH₂)₄(hfac)](ClO₄)₂

A suspension of [Co(n-BuNH$_2$)$_4$CO$_3$]ClO$_4$ (1.0 g) in 2 M HClO$_4$ (2.5 ml) became dissolved on addition of methanol. When the evolution of CO$_2$ finished at 50 °C, the blue–violet solution was diluted to 20 ml by water. To this solution, a mixture of Hhfac (0.4 g) and 1 M NaOH (2 ml) was added slowly. It was stirred at 40 °C for 3 h. The orange oily layer was extracted with acetone. Drops of water were added to the extract. An orange crystal separated on evaporation. It was washed with water and air dried. It was recrystallized three times from a small amount of methanol by addition of HClO$_4$ + NaClO$_4$ and was dried on P$_2$O$_5$ (yield 0.45 g).

β-[Co(2,3,2-tet)(hfac)](ClO₄)₂

trans(R,S)-[Co(2,3,2-tet)Cl$_2$]Cl · HCl (3.62 g) was dissolved in water (20 ml) [13]. Li$_2$CO$_3$ was added to saturation and the complex was digested at 60 °C for 30 min. Solid Li$_2$CO$_3$ was removed and AgNO$_3$ (6.8 g) was added to the filtrate. AgCl was removed and a small amount of NaI was added. AgI was removed and the filtrate was neutralized by HNO$_3$. The resultant solution was mixed with a solution of Hhfac (2.1 g) + NaOH (0.5 g). The mixture was stirred at 60 °C for 2 h. An yellow–brown precipitate separated on addition of NaClO$_4$ to the cooled solution. It was recrystallized from ethanol.

[Cr(tn)₂(H₂O)₂](ClO₄)₃

A solution (30 ml) of trans-[Cr(tn)$_2$Cl$_2$]Cl (10 g) in 1 M NaOH was warmed on a water bath [14]. A precipitate separated on addition of 6 M HClO$_4$ (30 ml) to the cooled solution. It was a mixture of orange crystals and green crystals. When this mixture

was treated with water, only the orange crystals dissolved. The resultant solution was concentrated by an air blow. An orange precipitate separated on addition of NaClO$_4$. This product was a mixture of the major orange cis isomer and the reddish trans isomer [15].

[Cr(NH₃)₄(hfac)](ClO₄)₂

An aqueous solution of cis-[Cr(NH$_3$)$_4$(H$_2$O)$_2$](ClO$_4$)$_3$ (10.9 g) was combined with a solution (8 ml) of Hhfac (5 g) in 3 M NaOH [16]. The resultant violet needle crystal (1) (9.7 g) was dried on P$_2$O$_5$. This intermediate product 1 (2.3 g) was suspended in methanol and was treated with several drops of 9 M HClO$_4$. It was stirred at room temperature. The solution color turned from violet to orange. An orange precipitate was recrystallized from methanol (yield 1.6 g).

[Cr(en)₂(hfac)](ClO₄)₂

In a previous report, we described a preparation of [Cr(en)$_2$(hfac)](PF$_6$)(ClO$_4$) [9]. In its course, a violet needle crystalline intermediate product (2) had been isolated. This intermediate 2 (2.5 g) was treated in methanol with several drops of 9 M HClO$_4$. The resultant orange precipitate was recrystallized from methanol (yield 1.2 g).

[Cr(tn)₂(hfac)](ClO₄)₂

An aqueous solution of [Cr(tn)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ (2.7 g) was mixed with an aqueous solution of Hhfac (1.04 g) + NaOH (0.2 g). The mixture was stirred for 1 h at 50 °C. Its color turned to violet on addition of several drops of 1 M NaOH. An insoluble substance was removed. The violet filtrate was treated with 6 M HClO$_4$. The solution color turned to orange. The resultant orange needle crystal was recrystallized from 1 M NaOH by addition of 6 M HClO$_4$ (yield 0.5 g).

α-[Cr(2,3,2-tet)(hfac)](ClO₄)₂

An aqueous solution (1 ml) of cis-[Cr(2,3,2-tet)Cl$_2$]Cl (0.38 g) was stirred at 45 °C for 1 h [13]. This solution was combined with a solution of Hhfac (0.21 g) + NaOH (0.04 g). It was stirred at 45 °C for 1 h. The resultant violet precipitate was treated with 6 M HClO$_4$ until it became a paste. The orange precipitate was recrystallized from acetone (yield 0.1 g).

[Cr(3,2,3-tet)(hfac)](ClO₄)₂

A suspension of cis-[Cr(3,2,3-tet)Cl$_2$]ClO$_4$ (8 g) in water (10 ml) was stirred for 1 h at 80 °C [17]. The brownish green precipitate of trans-[Cr(3,2,3-tet)Cl$_2$]ClO$_4$ was removed. The red filtrate was com-

bined with a solution of Hhfac (4 g) in 1 M NaOH (20 ml). It was stirred for 1 h at 45 °C. A violet precipitate separated on addition of 1 M NaOH (2 ml) + NaClO$_4$ (5 g). It was dissolved in acetone (2 ml) and treated with 9 M HClO$_4$ (0.5 ml). The solution color turned from violet to orange. An orange precipitate separated on addition of water (4 ml). It was recrystallized from acetone by addition of water (1 ml) (yield 2.2 g).

Results and discussion

Preparative course

The general preparative course is that the hfac anion reacts with the corresponding diaquo complex, which may be derived from the carbonato or dichloro complex. In the case of Cr(III), violet intermediates are formed which can be isolated (1 and 2). The UV–Vis absorption spectrum of 1 differs from that of [Cr(NH$_3$)$_4$(hfac)](ClO$_4$)$_2$ under the same conditions. Therefore, 1 is not the salt [Cr(NH$_3$)$_4$(hfacOH)](ClO$_4$), where hfacOH acts as a bidentate. Similarly, it can be noticed from the absorption spectrum of 2 that 2 is not the salt [Cr(en)$_2$(hfacOH)](ClO$_4$). In the absorption spectrum of 1 or 2 in an acid, absorption intensity around 345 nm increases gradually with time. The final spectrum of 2 is an overlapping of the spectrum for Co(en)$_2$(hfac)$^{2+}$ and of the spectrum 484 nm (67), 367 nm (42.5) for cis-Co(en)$_2$(H$_2$O)$_2$$^{3+}$ [18]. From this spectral evidence, we got an idea to treat the violet intermediates in a non-aqueous media, where diaquo species might not be formed. As expected, the treatment of 1 and 2 by HClO$_4$ in methanol resulted in a good yield of [Cr(NH$_3$)$_4$(hfac)](ClO$_4$)$_2$ and [Cr(en)$_2$(hfac)](ClO$_4$)$_2$, respectively. Anal. 1: Found: C, 12.8; H, 3.5; N, 12.4. Calc. for Cr(NH$_3$)$_4$(hfac)(OH)(ClO$_4$)(H$_2$O): C, 13.0; H, 3.5; N, 12.1%. 2: Found: C, 20.4; H, 4.1; N, 10.8. Calc. for Cr(en)$_2$(hfac)(OH)(ClO$_4$)(H$_2$O)$_{1.5}$: C, 20.6; H, 4.1; N, 10.7%. The possible construction of 1 and 2 may be [Cr(NH$_3$)$_4$(hfacOH)(H$_2$O)](ClO$_4$) and [Cr(en)$_2$(hfacOH)(H$_2$O)](ClO$_4$)·0.5H$_2$O, respectively, where the hfacOH ligand acts as monodentate. On the other hand, usually one does not notice any sign of an intermediate formation in the preparative course of the hexafluoroacetylacetonato Co(III) complex. Only in one case, a pink intermediate was isolated, which yielded [Co(bpy)$_2$(hfac)](ClO$_4$)$_2$ on treatment by HClO$_4$. We speculate that the perchlorate salt of the Co(III) intermediate with a monodentate hfacOH ligand is usually too soluble to be isolated.

^{19}F NMR spectra

Two isomers (α-cis and β-cis) are possible for ML(hfac)$^{2+}$ with L = 2,3,2-tet or 3,2,3-tet.

α isomer   β isomer
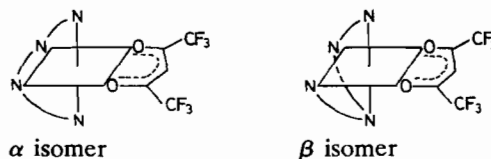
The two CF$_3$ groups in the α isomer experience the same field, whereas those in the β isomer are in different fields. Therefore, the ^{19}F NMR spectrum of the α isomer will be a singlet, that of the β isomer a doublet. The results are summarized in Table 2. In the case of [Cr(3,2,3-tet)(hfac)](ClO$_4$)$_2$, we could not find any ^{19}F NMR peak.

Color change

All the complex salts with a bidentate hfac ligand obtained in this work are orange colored in the solid state. The solutions of these complexes are also orange colored and turn to violet on addition of a base. The tone depends more or less on the respective complex. This color change is fast enough, but is not instantaneous. On the successive addition of an acid to the solution, the color returns to the original one.

Absorption spectra in water

The UV–Vis absorption spectra of the aqueous solution were recorded for water soluble complex salts. The spectral features are analogous to those already presented for Co(en)$_2$(hfac)$^{2+}$ and Cr(en)$_2$(hfac)$^{2+}$ [1, 9]. The absorption maxima are summarized in Table 3. In acidic conditions the first band exists at around 490 nm for the Co(III) complex and at 460–473 nm for the Cr(III) complex. In basic conditions the first band of the Co(III) complex shifts to lower energy by c. 30 nm and that of the Cr(III) complex by c. 50 nm. The shift is more pronounced in the latter. The second band exists at around 345 nm and may be assigned to a t$_{2g}$(metal) → π*(ligand) charge transfer transition [1]. It disappears in basic solution, which may be taken as evidence for the delocalization of the π electron system of the hfac ligand. Thus, this pH dependent

TABLE 2. ^{19}F NMR spectra and isomeric assignment[a]

Complex	Peak (ppm)	Assignment
Co(2,3,2-tet)(hfac)$^{2+}$	76.02, 76.12	β
Co(3,2,3-tet)(hfac)$^{2+}$	75.98, 76.10	β
Cr(2,3,2-tet)(hfac)$^{2+}$	87.83	α

[a]Measured in 0.01 M DCl (D$_2$O) at 270 MHz.

TABLE 3. Absorption maxima in water

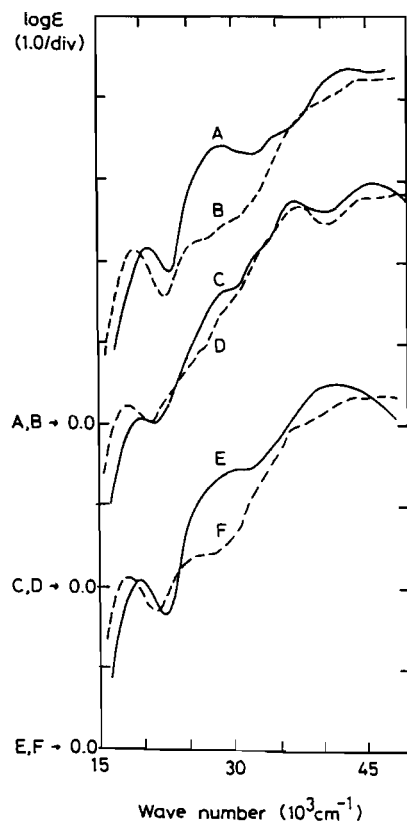| Complex	λ (nm) (ϵ)	
	In acid	In base
$Co(tn)_2(hfac)^{2+}$	490 (93), 345 (2430)	520 (96)
$Co(tren)(hfac)^{2+}$	487 (173), 343 (2530)	512 (138)
β-$Co(2,3,2$-$tet)(hfac)^{2+}$	487 (173), 348 (2090)	519 (161)
β-$Co(3,2,3$-$tet)(hfac)^{2+}$	492 (107), 345 (1740)	525 (110)
$Cr(NH_3)_4(hfac)^{2+}$	473 (50), 341 (4350)	523 (46)
$Cr(tn)_2(hfac)^{2+}$	460 (69), 343 (4320)	510 (59)
α-$Cr(2,3,2$-$tet)(hfac)^{2+}$	473 (133), 347 (3910)	520 (87)
$Cr(3,2,3$-$tet)(hfac)^{2+}$	472 (120), 347 (4690)	518 (86)

Fig. 1. Absorption spectra in methanol (optical path length = 1 cm). A: $Co(en)_2(hfac)^{2+}$ in 0.005 M HCl, B: $Co(en)_2(hfac)^{2+}$ in 0.01 M $NaOCH_3$, C: $Co(bpy)_2(hfac)^{2+}$ in 0.4 M HCl, D: $Co(bpy)_2(hfac)^{2+}$ in 0.05 M $NaOCH_3$, E: $Co(n$-$BuNH_2)_4(hfac)^{2+}$ in 0.4 M HCl, F: $Co(n$-$BuNH_2)_4(hfac)^{2+}$ in 0.05 M $NaOCH_3$.

spectral change may be ascribed to the shift of eqn. (1) with R = H.

Absorption spectra in methanol

The UV–Vis absorption spectra of water insoluble complex salts were recorded in methanol. Typical results are shown in Fig. 1. The first band shifts to lower energy in basic conditions. In the case of

$Co(en)(hfac)^{2+}$ (A, B) and $Co(n$-$BuNH_2)_4(hfac)^{2+}$ (E, F), the second band disappears in basic conditions. In the case of $Co(bpy)_2(hfac)^{2+}$ (C, D), the pH dependence of the second band is obscured owing to the strong absorption of the bpy ligand. Nevertheless, it can be noticed that the absorption around 30000 cm^{-1} decreases in basic conditions. The spectra of $Co(phen)_2(hfac)^{2+}$ are similar to those of $Co(bpy)_2(hfac)^{2+}$. The spectra of $Co(EtNH_2)_4(hfac)^{2+}$ and $Co(n$-$PrNH_2)_4(hfac)^{2+}$ are similar to those of $Co(n$-$BuNH_2)_4(hfac)^{2+}$. The results are summarized in Table 4. The origin of this pH dependence of the spectra in methanol will be the shift of eqn. (1) with R = CH_3 [8].

Equilibrium constant in water

The equilibrium constant (K) of eqn. (1) with R = H was estimated for water soluble complexes. A 0.004 M solution (10 ml) of the Co(III) complex was titrated with 0.1 M NaOH at 28 °C [4]. For the Cr(III) complex, K was estimated at 15 °C as described in the previous report [9]. The pH value and absorption intensity at 460 nm were measured for a solution which contained 0.0025–0.005 M complex and 0.0006 ~ 0.00375 M NaOH. The results are summarized in Table 5. The K value ranges from

TABLE 4. Absorption maxima in methanol

Complex	λ (nm) (ϵ)	
	In acid	In base
$Co(EtNH_2)_4(hfac)^{2+}$	505 (122), 320$_{sh}$ (3000)	540 (120)
$Co(n$-$PrNH_2)_4(hfac)^{2+}$	507 (131), 320$_{sh}$ (3040)	544 (115)
$Co(n$-$BuNH_2)_4(hfac)^{2+}$	507 (127), 325$_{sh}$ (2760)	545 (128)
$Co(bpy)_2(hfac)^{2+}$	497 (119), 327$_{sh}$ (5060)	537 (163)
$Co(phen)_2(hfac)^{2+}$	495 (115), 327$_{sh}$ (4670)	537 (168)

TABLE 5. Equilibrium constants for $ML(hfac)^{2+}$ + $OH^- = ML(hfacOH)^+$

Complex	K (M^{-1})	Reference
$Co(NH_3)_4(hfac)^{2+}$	5.0×10^6	4
$Co(en)_2(hfac)^{2+}$	3.0×10^6	4
$Co(tn)_2(hfac)^{2+}$	3.7×10^6	
$Co(tren)(hfac)^{2+}$	12×10^6	
α-$Co(trien)(hfac)^{2+}$	4.6×10^6	4
β-$Co(trien)(hfac)^{2+}$	2.3×10^6	4
β-$Co(2,3,2$-$tet)(hfac)^{2+}$	2.0×10^6	
β-$Co(3,2,3$-$tet)(hfac)^{2+}$	4.0×10^6	
$Cr(NH_3)_4(hfac)^{2+}$	1.7×10^{10}	
$Cr(en)_2(hfac)^{2+}$	5.6×10^{10}	9
$Cr(tn)_2(hfac)^{2+}$	1.1×10^{10}	
α-$Cr(2,3,2$-$tet)(hfac)^{2+}$	3.5×10^{10}	
$Cr(3,2,3$-$tet)(hfac)^{2+}$	1.0×10^{10}	

$2-12 \times 10^6$ M^{-1} for the Co(III) complex and from $1-6 \times 10^{10}$ M^{-1} for the Cr(III) complex. It depends significantly on the kind of central metal ion and is rather independent of the kind of L ligand. In a previous report, we pointed out that one C–C single bond length (1.366 Å) of the ethylenediamine ligand is abnormally short in [Co(en)$_2$(hfacOH)]Br·H$_2$O [6]. On this basis, we speculated that the L ligand might more or less concern the σ bond formation between the hydroxide ion and the coordinating hfac ligand and that the magnitude of K might be affected by the variation of the L ligand. But, the K value is rather independent of the kind of L ligand as can be seen in Table 5. Only in one case of L=tren, is it a little large, which might be explained by the tripoid coordination mode of the tren ligand.

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