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Thermodynamic Properties for the Adduct Formation of Some Shift Reagents with Aniline

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Equilibrium constants, enthalpies, and entropies of formation of the shift reagent-substrate adducts were determined by the measurement of infrared spectra. Aniline was employed as substrate in most cases since its NH stretching absorption bands (ν_{as}) does not overlap with those of the adducts and suitable to estimate the amount of its free species quantitatively. A series of $Ln(dpm)_3$ and $Ln(fod)_3$ (where Ln=Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Yb) were used as shift reagents. The formation constants (K_1 and K_2), as well as ΔH, decrease in the increasing order of the atomic numbers of the central lanthanoid ions. The results were compared with those on some bis(β-diketonato) complexes of transition metal ions and discussed.

Since the discovery by Hinckley,[1)] various lanthanoid shift reagents have been widely employed to expand the chemical shift range of NMR spectrum without remarkable broadening of the signals. Quite a few examples[2-5)] of their application have been reported, and many new shift reagents, including Ag compounds[6)] for aromatic substrates, have been prepared and used both to resolve the overlapping signals and to determine the stereochemistry of many complex organic compounds by use of the steric factor in the McConnell-Robertson equation.[7,8)] However, the properties of the shift reagent-substrate complexes have not been known very thoroughly. Thus, the shift reagent-substrate complexes were studied quantitatively by the measurement of infrared spectra of the complexes in solution in order to determine their formation equilibrium constants and to estimate the enthalpies and the entropies of their formation.[9)]

Theoretical

In general, 1:1 and 1:2 complexes RS and RS_2 are formed when the lanthanoid shift reagent (R) is added to the solution of the substrate (S). These reactions and their formation constants are expressed by the following equations.

$$\mathrm{R} + \mathrm{S} \rightleftharpoons \mathrm{RS} \qquad K_1 = \frac{[\mathrm{RS}]}{[\mathrm{R}][\mathrm{S}]} \tag{1}$$

$$\mathrm{RS} + \mathrm{S} \rightleftharpoons \mathrm{RS_2} \qquad K_2 = \frac{[\mathrm{RS_2}]}{[\mathrm{RS}][\mathrm{S}]} \tag{2}$$

When the infrared X–H stretching bands are selected as key bands, addition of the shift reagent to the solution of substrate gives rise to new absorption band(s) in addition to the absorption band(s) due to the free species of the substrate, hereby accompanying a decrease in the intensity of the free band. The new bands are assigned to the complexed species RS and/or RS_2. If the measurements are carried out under conditions in which the Lambert-Beer law is valid, the concentration of the free substrate [S] is obtained from the intensity of the band assigned to the free substrate and its molar absorptivity ε_f, which can be determined easily by the measurement on the substrate alone in the same solvent. From the concentration of the free substrate [S] obtained by the infrared measurement, concentrations of the complexed substrate S_b and the free shift reagent [R] are derived by Eqs. 3 and 4, respectively.

$$S_b = (S_t - [\mathrm{S}]) \tag{3}$$

$$[\mathrm{R}] = R_t - (S_t - [\mathrm{S}])/n \tag{4}$$

In these equations, S_t and R_t are stoichiometrical total concentrations of the substrate and the shift reagent, respectively, and n is the number of substrate molecules complexed to a shift reagent molecule.

When the second reaction to form 1:2 adduct is negligible, the first equilibrium constant K_1 is given by Eq. 5.

$$K_1 = \frac{[\mathrm{S}]\{nR_t - (S_t - [\mathrm{S}])\}}{S_t - [\mathrm{S}]} \tag{5}$$

Dissociation constant $K_D(=1/K)$ of the shift reagent-substrate complex RS_n is then given by Eq. 6, by assuming that n molecules of substrate are coordinating to one molecule of the monomeric shift reagent.

$$\frac{S_t - [\mathrm{S}]}{R_t \times [\mathrm{S}]} = \frac{n}{K_D} - \frac{S_t - [\mathrm{S}]}{K_D \times R_t} \tag{6}$$

Equation 6 is often called the Scatchard equation and is used to calculate K_D and n. When $(S_t - [\mathrm{S}])/R_t[\mathrm{S}]$ values are plotted against $(S_t - [\mathrm{S}])/R_t$ values, both K_D and n are obtained from the slope and the intercept of the straight line calculated as the least squares of the plots. Another evidence for the stoichiometry of the complex is obtained when isosbestic points were observed with the concentration dependent spectra. The appearance of isosbestic points excludes the possibility of the coexistence of the 1:1 and 1:2 complexed species in the same solution. Thus the number of the coordinating substrate (n) can be determined by the Scatchard plot (Eq. 6).

When RS and RS_2 are present together in the same solution (apparently $1<n<2$), the following equation (Eq. 7), derived from Eqs. 1 and 2, is useful in evaluating the equilibrium constants K_1 and K_2.[10)]

$$\frac{[\mathrm{S}]^3 + (2R_t - S_t)[\mathrm{S}]^2}{S_t - [\mathrm{S}]} = \frac{1}{K_2} \times \frac{(S_t - [\mathrm{S}] + R_t)[\mathrm{S}]}{S_t - [\mathrm{S}]} + \frac{1}{K_1 K_2} \tag{7}$$

The plot of $\{[\mathrm{S}]^3 + (2R_t - S_t)[\mathrm{S}]^2\}/(S_t - [\mathrm{S}])$ (ordinate) *vs.* $(S_t - [\mathrm{S}] - R_t)[\mathrm{S}]/(S_t - [\mathrm{S}])$ (abscissa) gives the K_1 and K_2 values from its slope and intercept.

In this way, the equilibrium constants are evaluated at various temperatures, the enthalpies and the entropies of formation of the complexes (RS and RS_2) being obtained from the $\log K$ *vs.* $1/T$ plots.

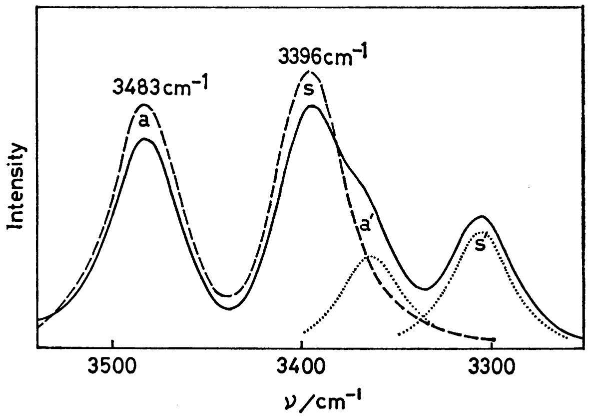

Fig. 1. NH Stretching bands of aniline in CCl_4 in the presence (——) and in the absence (----) of $Pr(dpm)_3$. Symmetric (s′) and asymmetric (a′) NH_2 stretching bands of the complexed species appear in the low frequency region. These bands are separated by the band shape analysis and illustrated by the dotted line (······). The letters a and s denote asymmetric and symmetric stretching bands of the free species, respectively.

$$\ln K = -\frac{\Delta H}{R} \times \frac{1}{T} + \frac{\Delta S}{R} \tag{8}$$

In this investigation, tris(dipivaloylmethanato)- or tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)lanthanoid(III)'s were used as the shift reagents (R) and anilines as the substrates (S). The equilibrium constants were estimated by measuring the intensities of the N–H stretching absorption bands of the free species of aniline as a measure of [S].

Experimental

Materials. The shift reagents which had not been available commercially were prepared by reacting suitable 1,3-diones with lanthanoid nitrates in aqueous alcoholic solution at suitable pH (adjusted by adding sodium hydroxide).[11–13] Tris (dipivaloylmethanato) complexes of La, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb ($Ln(dpm)_3$), tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato) complexes of La, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb ($Ln(fod)_3$), tris(hexafluoroacetylacetonato) complexes of Eu, Pr, and Yb, and tris(1,1,1-trifluoroacetylacetonato) complexes of Eu, Pr, and Yb were prepared by this method. Two transition metal complexes $Co(dpm)_2$ and $Cu(dpm)_2$ were also prepared by the similar procedures. The hexafluoro- and trifluoroacetylacetonato complexes were sparingly soluble in carbon tetrachloride and, therefore, unsuitable for the measurement. These 1,3-diketonato complexes, together with commercially available ones, were purified by sublimation immediately before use. They were sublimed at temperatures about 10 °C lower than their melting points (100—220 °C for $Ln(fod)_3$ and 160—240 °C for $Ln(dpm)_3$). Then, they were dried for 2 d over phosphours pentaoxide at *ca.* 60 °C and used for the measurement. Commercially available spectro grade solvents were used. They were dried over phosphorus pentaoxide and distilled immediately before use.

Measurement of Infrared Spectra. Infrared spectra were recorded with a Hitachi 225 infrared spectrophotometer usually by use of a 2 cm cell. Temperature of the solution under measurement was controlled by circulating water, and other medium if needed, through the cell jacket from a thermostatic bath. The measurement was carried out with a concentration of *ca.* 3×10^{-3} mol l^{-1} for the shift reagent, changing the concentration of aniline from *ca.* 2×10^{-3} to *ca.* 8×10^{-3} mol l^{-1}. The concentration of the free substrate (aniline) [S] was determined by measuring the intensity of the asymmetric stretching band of NH_2 group appearing at 3483 cm^{-1} in carbon tetrachloride solution. As shown by an example of the spectrum in Fig. 1, the absorption band due to the asymmetric stretching mode of NH_2 vibration (located at the higher frequency) does not overlap with those of the complexed species, hence, being suitable for the determination of [S].

Table 1. The coordination number (n) and the formation constant (K) values for some $Ln(dpm)_3$–aniline complexes in CCl_4

R	S	n	K	t/°C	Ref.
$Pr(dpm)_3$	$C_6H_5NH_2$	0.98	224	25	This work
$Eu(dpm)_3$	$C_6H_5NH_2$	0.90			16
$Dy(dpm)_3$	$C_6H_5NH_2$	0.95	128	25	This work
$Eu(dpm)_3$	t-C_4H_9OH	0.92	348	20	9

Measurement at a far higher concentration is necessary in order to determine the K_2 values for $Ln(dpm)_3$–aniline system. Thus, a variable cell whose length was adjusted to be 0.2 mm was used instead. Since the concentration of aniline can be increased about 100 times larger than that in a 2 cm cell, the equilibrium to form 1:1 adduct lies very far to the product and the second coordination forming 1:2 adduct occurs considerably. In this case, the variable temperature measurement was impossible and the measurement was carried out at 53 °C. Then the K_1's at 53 °C were calculated by assuming the ΔH and ΔS in Table 4. Calculated K_1's and [S]'s from ν_{as} intensities gave K_2 values.

Results

Tris(dipivaloylmethanato)lanthanoid(III)-Aniline Complexes. In our previous report,[14] the composition and the thermodynamic properties of $Eu(dpm)_3$–t-butyl alcohol adduct were investigated by measuring the OH stretching absorption of the alcohol, giving n=0.92 from the Scatchard equation (Eq. 6).[15] The most probable coordination number (n) and the formation constant ($K(=1/K_D)$) were obtained similarly for the $Pr(dpm)_3$–aniline and $Dy(dpm)_3$–aniline complexes by the least squares calculations from the concentration data given in Table 2. The isosbestic points were also observed with the concentration dependent NH_2 absorption intensity data of $Eu(dpm)_3$–aniline in CCl_4.[16]

As expected from the results of the Scatchard plot, the K_1 values obtained by Eq. 1 was nearly constant when the concentrations of the substrate and the shift reagent were changed keeping the temperature constant. Two typical examples are given in Table 2.

Both the Scatchard plot and the constancy of the K_1 values from Eq. 2 show that only the formation of the 1:1 complex (RS) occurs considerably under the experimental conditions in a 2 cm cell. Since the complex formation of a fractional amount of aniline

TABLE 2. THE FORMATION CONSTANTS (K_1) FOR Pr(dpm)$_3$-ANILINE AND Dy(dpm)$_3$-ANILINE COMPLEXES AT VARIOUS CONCENTRATIONS OF THE SUBSTRATE AND THE SHIFT REAGENT (AT 25 °C)

(a) Pr(dpm)$_3$-aniline complex.

Run	$S_t \times 10^3$/mol l^{-1}	$R_t \times 10^3$/mol l^{-1}	[S] $\times 10^3$/mol l^{-1}	K_1/l mol^{-1}
1	3.76	2.75	2.76	207
2	4.65	2.75	3.47	216
3	5.68	2.75	4.41	195
4	6.79	2.75	5.35	205
5	4.69	3.30	3.34	206
			Mean	206
			Standard Deviation	6.7

(b) Dy(dpm)$_3$-aniline complex.

Run	$S_t \times 10^3$/mol l^{-1}	$R_t \times 10^3$/mol l^{-1}	[S] $\times 10^3$/mol l^{-1}	K_1/l mol^{-1}
1	5.89	2.54	4.97	114
2	7.10	2.54	6.04	119
3	4.82	2.54	3.99	121
4	3.88	1.69	3.39	122
			Mean	119
			Standard Deviation	3.1

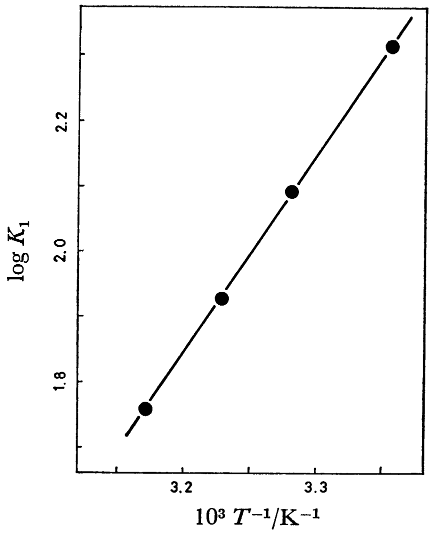

Fig. 2. The log K_1 *vs.* $1/T$ plot for the formation of Pr(dpm)$_3$-aniline adduct.

to the lanthanoid ion is not rationalized from the chemistry involved, the formation of 1:1 complex is supposed to occur actually in the aniline–Ln(dpm)$_3$–CCl$_4$ ternary system. In this case, the formation constants calculated from Eq. 2 should be better than those from the Scatchard plot (Eq. 6). Therefore, the equilibrum constants (K_1's) were estimated by Eq. 2 at various temperatures ranging from 18 to 47 °C. Results with Pr(dpm)$_3$–aniline complex in carbon tetrachloride solution is given in Table 3(a). The change in the K_1 values at varying temperatures is far larger than the variation among those observed at the same temperature (Table 2(a), standard deviation=6.7), which proves the meaningfulness of the temperature dependence measurement. The log K *vs.* $1/T$ plot (Fig. 2) shows a very good linear relation from which the enthalpy and entropy of the complex formation was estimated to be 58.6 kJ mol^{-1} and 152 J mol^{-1}K^{-1}, respectively. Quite similarly ,the enthalpies and the entropies of formation for a series of Ln(dpm)$_3$–aniline complexes were determined as given in Table 4 from the observed K_1's given in Table 3. In addition to the ΔH and ΔS values, the $\nu_s(\mathrm{NH_2})$ frequency shifts caused by the complex formation ($\Delta\nu_s$),[17] as well as ionic radii of trivalent lanthanoid cations (r)[18] are given in Table 4.

The second equilibrium constants, *i.e.* the formation constants of RS$_2$ from RS and S, were determined at 53 °C (Table 5). Since the formation of RS$_2$ proceeds consecutively following the formation of RS, considerably high concentration of the substrate becomes necessary in order to maintain the concentration of RS high enough to produce RS$_2$ measurably. Thus the measurement was carried out by using a thin cell (optical path length: 0.2 mm) so as to adjust the observed intensity of $\nu_{\mathrm{NH_2}}$ band measurably. Under the conditions for the K_2 determination, more than 90% of Ln(dpm)$_3$ exists as the complexed species. As the K_2 value could not be determined as a function of temperature, the enthalpy and the entropy of formation of RS$_2$ from RS were not known. Under the conditions for the measurement with a 2 cm cell at 53 °C, only less than 1% of the shift reagent was estimated to form 1:2 adduct from the K_1 and K_2 values of Pr(dpm)$_3$–aniline system. The extent of the formation of 1:2 adduct becomes less as the atomic number of central lanthanoid ion increases, showing the assumption for K_1 determination is valid.

Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)lanthanoid–Aniline Adducts. The Ln(fod)$_3$ complexes are so hygroscopic that they absorb the moisture even during the infrared spectral measurement in carbon tetrachloride solutions. Free Ln(fod)$_3$'s are especially sensitive to the moisture, sometimes disturbing remarkably the measurement in use of their solu-

TABLE 3. TEMPERATURE DEPENDENCE OF THE FORMATION CONSTANTS K_1 OF VARIOUS $Ln(dpm)_3$-ANILINE 1 : 1 COMPLEXES IN CCl_4

T/°C	$S_t\times10^3$/mol l^{-1}	$R_t\times10^3$/mol l^{-1}	[S] $\times10^3$/mol l^{-1}	K_1/l mol^{-1}
(a) $Pr(dpm)_3$-aniline				
25.0	4.69	3.30	3.34	206
31.8	3.10	3.12	2.39	124
36.7	3.10	3.12	2.55	84.1
42.3	3.10	3.12	2.68	57.1
(b) $Nd(dpm)_3$-aniline				
27.6	3.80	3.00	2.77	187
31.9	5.52	2.22	4.54	173
32.8	3.80	3.00	2.89	152
37.4	3.80	3.00	3.09	101
38.5	5.52	2.22	4.87	84.0
44.5	5.52	2.22	5.02	56.9
(c) $Sm(dpm)_3$-aniline				
24.0	3.36	3.09	2.38	197
28.6	3.36	3.09	2.50	155
32.6	3.36	3.09	2.63	118
36.5	3.36	3.09	2.77	84.9
40.9	3.36	3.09	2.96	40.8
(d) $Eu(dpm)_3$-aniline				
18.5	4.90	3.49	3.20	296
25.8	4.90	3.49	3.51	190
31.5	4.90	3.49	3.75	131
39.8	4.90	3.49	4.04	80.9
44.3	4.90	3.49	4.32	46.1
(e) $Gd(dpm)_3$-aniline				
21.8	5.77	3.65	3.85	284
27.7	5.77	3.65	4.11	203
31.2	5.77	3.65	4·25	167
45.4	5.77	3.65	4.87	64.8
(f) $Tb(dpm)_3$-aniline				
25.0	6.21	2.87	4.69	241
36.1	3.94	3.17	2.92	164
40.4	3.94	3.17	3.04	131
44.6	3·94	3.17	3.23	89.4
47.7	3.94	3.17	3.25	85.6
(g) $Dy(dpm)_3$-aniline				
19.8	3.33	3.22	2.45	154
25.3	3.33	3.22	2.57	119
30.0	3.33	3.22	2.73	83.8
36.2	3.33	3.22	2.85	61.9
41.6	3.33	3.22	3.01	37.3
(h) $Ho(dpm)_3$-aniline				
19.1	4.21	2.99	3.31	130
25.5	4.21	2.99	3.44	101
30.1	4.21	2.99	3.56	77.9
36.4	4.21	2.99	3.74	49.8
42.3	4.21	2.99	3.89	30.5
(i) $Er(dpm)_3$-aniline				
19.0	4.21	2.89	3.40	115
25.5	4.21	2.89	3.57	79.1
31.7	4.21	2.89	3.70	57.3
42.9	4.21	2.89	3.87	31.3
(j) $Yb(dpm)_3$-aniline				
19.3	3.66	3.09	3.10	71.7
26.2	3.66	3.09	3.24	48.4
33.4	3.66	3.09	3.39	29.1
38.3	3.66	3.09	3.43	24.0

TABLE 4. THE ENTHALPIES AND THE ENTROPIES OF FORMATION OF Ln(dpm)$_3$-aniline complexes

Ln	Z$^{a)}$	K_1^{298}/l mol^{-1}	$-\Delta H$/kJ mol^{-1}	$-\Delta S$/J mol^{-1} K^{-1}	$r\times 10$/nm$^{b)}$	$\Delta\nu$/cm^{-1}
Pr	59	214	58.6±4.6	152±15	1.013	86
Nd	60	259	60.7±4.3	157±14	0.995	86.5
Sm	62	197	59.0±6.2	154±21	0.964	87
Eu	63	197	53.1±4.6	134±15	0.950	87
Gd	64	251	49.4±2.5	120± 8	0.938	89.5
Tb	65	263	49.8±4.7	119±16	0.923	90
Dy	66	116	49.0±3.0	125±10	0.908	87
Ho	67	96.3	48.5±4.7	123±16	0.894	89
Er	68	85.7	41.8±1.6	103± 5	0.881	91
Yb	70	54.1	45.2±4.6	118±15	0.858	89
Eu(*p*-toluidine)$^{c)}$		—	49.0±4.2	113±14		
En(*t*-C_4H_9OH)$^{d)}$		—	40.2±3.7	88±12		

a) Atomic numbers. b) See Ref. 18. c) The values for Eu(dpm)$_3$-*p*-toluidine complex. d) The values for Eu(dpm)$_3$-*t*-butyl alcohol complex.

TABLE 5. THE SECOND EQUILIBRIUM CONSTANTS (K_2) FOR Ln(dpm)$_3$-ANILINE AT 53 °C IN CCl_4

Ln	S_t/mol l^{-1}	R_t/mol l^{-1}	[S]/mol l^{-1}	K_1^{326}/l mol^{-1} $^{a)}$	K_2^{326}/l mol^{-1}
Pr	0.373	0.0892	0.211	38.3	29.7
Nd	0.578	0.0778	0.435	31.9	13.9
Sm	0.578	0.155	0.311	25.7	11.4
Eu	0.578	0.158	0.321	32.9	6.6
Gd	0.578	0.153	0.352	45.7	3.1
Tb	0.578	0.0695	0.472	56.1	2.6
Dy	0.578	0.181	0.365	21.4	1.1
Ho	0.578	0.148	0.398	21.3	1.2
Er	0.578	0.136	0.418	20.2	0.95
Yb	0.578	0.169	0.392	11.4	0.99

a) Calculated from ΔH and ΔS in Table 4.

TABLE 6. THE ENTHALPIES AND THE ENTROPIES OF FORMATION OF Ln(fod)$_3$-ANILINE COMPLEXES

Ln	K_1^{298}/l mol^{-1}	$-\Delta H_1$/kJ mol^{-1}	$-\Delta S_1$/J mol^{-1} K^{-1}
Eu	4340	67.8±1.6	158± 6
Gd	1296	57.8±1.8	134± 6
Dy	1160	51.0±2.7	113± 9
Yb	1152	54.4±3.5	124±12

tions as references. Thus the measurement on Ln(fod)$_3$–aniline were repeated several times at a temperature, and only statistically meaningful data were used in the subsequent calculation of the enthalpies and the entropies of the adduct formation. Another difficulty arises from the fact that Ln(fod)$_3$ forms a considerable amount of the 1:2 adduct, in addition to the 1:1 adduct, at a low concentration. The K_1 and K_2 values can be estimated, in principle, from the concentration dependence data by use of Eq. 7. However, the $\{[S]^3+(2R_t-S_t)[S]^2\}/(S_t-[S])$ *vs.* $(S_t-[S]-R_t)/(S_t-[S])$ plot deviate remarkably from the regression line calculated statistically, giving only a fair linear relationship.[19] Rough estimation by Eq. 7 of the formation constants gave $K_1=124$ and $K_2=242$ for La(fod)$_3$–aniline (at 30.4 °C), $K_1=124$ and $K_2=56$ for Pr(fod)$_3$–aniline (at 27.5 °C), and $K_1=279$ and $K_2=45$ for Gd(fod)$_3$–aniline (at 30.2 °C).[20] As the formation of the 1:2 adduct is remarkable with the Ln(fod)$_3$ containing lower series of lanthanoid elements, the formation constant calculated by assuming that the 1:1 adduct is solely formed is somewhat less reliable with the complex of lower lanthanoid than with those of higher lanthanoid and also than that of corresponding Ln(dpm)$_3$. The K_1 values for some Ln(fod)$_3$–aniline adducts were given in Table 6. Except the case of the Pr(fod)$_3$ adduct, the effect of the second coordination was estimated to be rather unimportant (containing less than 5% of RS_2) under the conditions for measurement.

β-Diketonato Complexes of Some Transition Metal Ions. In order to compare the coordinational behavior of lanthanoid β-diketonato complexes with those of transition metal ions, some bis(β-diketonato) complexes of cobalt, nickel, and copper were prepared. The measurements similar to those on the lanthanoid shift reagents were carried out again on these complexes, the results being given in Table 7.

Discussion

As a whole, the formation constants of the 1:1 adducts (RS) and their enthalpies of formation (shown in Table 4) gradually decrease as the atomic number of the central lanthanoid ion increases. Evidently the entropic term also decreases accompanying the decrease in the enthalpy according to the general principle of

TABLE 7. THERMODYNAMIC PARAMETERS FOR THE FORMATION OF THE ANILINE ADDUCTS OF VARIOUS BIS(β-DIKETONATO) COMPLEXES OF SOME TRANSITION METAL IONS[a)]

	K_1^{298}/l mol^{-1}	$-\Delta H_1$/kJ mol^{-1}	$-\Delta S_1$/J mol^{-1} K^{-1}	K_2^{298}/l mol^{-1}	$-\Delta H_2$/kJ mol^{-1}	$-\Delta S_2$/J mol^{-1} K^{-1}
Co(acac)$_2$	290	59.8±6.3	154±21	88	46.0±5.0	117±17
Co(dpm)$_2$	15.1	63.6±5.1	191±17	—	—	—
Co(tfa)$_2$	54500	66.9±7.0	134±23	889	31.8±5.7	50±19
Ni(tfa)$_2$	9720	50.2±5.4	88±18	203	24.5±4.5	38±15
Cu(tfa)$_2$	19	20.7±4.1	45±14	—	—	—
Cu(hfa)$_2$	4870	41.0±6.2	67±20	31	34.7±4.8	88±16

a) acac = Acetylacetonato, tfa = 1,1,1-trifluroacetylacetonato, and hfa = hexafluoroacetylacetonato.

"enthalpy-entropy compensation." There are some exceptions, however, in the decreasing sequence of the K_1 values. The K_1's for Gd(dpm)$_3$ and Tb(dpm)$_3$ are larger than expected even when the statistical error is taken into account. On the other hand, the enthalpies of formation decreases monotonously with the increase in atomic number, showing no indication of anomalous behavior. Thus the favorable formation of these two 1:1 adducts is due to the contribution of the entropic term, suggesting sterically favored arrangement of pivaloylmethanato ligands and the substrate in these adducts, though the details of their structure could not be clarified.

The atomic numbers of the central lanthanoid ions affect more pronouncely the formation constants of the 1:2 adducts than the case of the 1:1 adducts. For example, the K$_2$ of Yb(dpm)$_3$–aniline is *ca.* 30 times smaller than that of the similar adduct of Pr, while the difference among K_1's is less than 5 times at the largest. Since the Ln(dpm)$_3$ has a lanthanoid ion surrounded by bulky organic ligands as shown by means of X-ray crystal analyses,[21)] the coordination of the seventh and the eighth ligands, aniline in this case, might be hindered sterically. Important role of the steric effect relative to electronic and other effects has also been pointed out by one of the present authors by determining the coordinating abilities (relative equilibrium constants) towards Eu(dpm)$_3$ of various pyridinoid aza-aromatic compounds.[22)] The ionic radii of trivalent lanthanoid ions decrease with the increasing order of atomic number.[18)] The steric hindrance should become more serious with the lanthanoid complexes of higher atomic numbers because of the contraction of ionic radii. The arrangement of the ligands revealed by the X-ray studies[21)] has only C$_2$ symmetry, suggesting the remarkable bending of metal-ligand bonds. Therefore the steric effect in the first coordination process might be reduced by the bending of metal-ligand bonds towards the direction for minimizing the strain in the adduct molecule. For this reason, the crowdedness due to the contraction of ionic radii restricts more predominantly the approach of the second aniline molecule than that of the first one, which is in consequence with the fact that the K_2 values are more sensitive to the effect of atomic number. The coordination of the second aniline molecule is restricted more severely in Ln(dpm)$_3$ adducts than in Ln(fod)$_3$ adducts. This fact supports the above interpretation concerning the effect of atomic number.

The formation constants and the enthalpies of formation of bis(trifluoroacetylacetonato) complexes of Co, Ni, and Cu also decrease in the increasing order of atomic number. The decrease can be ascribed to the repulsive interaction between the d-electrons of the transition metal ion and the unshared electrons of aniline, since the ionic radii of these ions do not vary regularly with the change in atomic number (0.79 Å for Co^{2+}, 0.84 Å for Ni^{2+}, and 0.76 Å for Cu^{2+}).[23,24)] The similar effect can occur also in the series of the lanthanoid β-diketonato complexes due to the increasing f-electrons. However, the f-electrons occupy the inner electron shell and might interact considerably lesser extent with the unshared electrons of aniline. At present, we cannot conclude either of the effects plays more important role on the decrease of the formation constants and ΔH in the increasing order of atomic number of lanthanoids.

When compared the Eu(dpm)$_3$ adduct of aniline with that of *t*-butyl alcohol, the formation constant of the *t*-butyl alcohol adduct is somewhat larger than that of aniline adduct in spite of its lower enthalpy of formation even in the 1:1 adduct formation process. Since the alcoholic oxygen atom has two pairs of unshared electrons capable of forming the coordinate bond with the lanthanoid ion, the formation of the alcohol–Ln(dpm)$_3$ adduct should be statistically more favored than the formation of the aniline adduct.

The free shift reagents are supposed to exist as dimeric species under certain conditions.[25)] This possi-

$$2\mathrm{R} \rightleftharpoons \mathrm{R}_2 \qquad (9)$$

bility could not be excluded completely in our systems though which consisted of much lower concentrations of the shift reagents than the conditions for NMR measurements. However, the infrared spectra in CCl$_4$ of the shift reagents (in the C=O stretching region) were not dependent on the concentrations, giving no evidence for the equilibrium between monomeric and dimeric species (Eq. 9).

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