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Nuclear Magnetic Resonance Studies of Ligand-Exchange Processes. I. Ligand-Exchange Equilibria for Some Gallium(III) β-Diketonates[1]

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The ligand-exchange equilibria that are established in Ga(acac)$_3$–Ga(bzbz)$_3$ and Ga(acac)$_3$–Ga(hfac)$_3$ mixtures, where acac = acetylacetonate, bzbz = dibenzoylmethanate, and hfac = hexafluoroacetylacetonate, have been studied by proton nmr spectroscopy. Equilibrium constants for formation of each mixed-ligand complex from the parent complexes have been determined in benzene solution. For formation of Ga(acac)$_2$(bzbz) and Ga(acac)(bzbz)$_2$, the equilibrium constants, extrapolated to 25°, are only *ca.* 20% smaller than the values expected for a random statistical distribution of ligands. Within experimental error, enthalpy changes are zero or nearly zero and entropy changes are equal to the values expected for a statistical distribution of ligands. In the Ga(acac)$_3$–Ga(hfac)$_3$ system, the mixed-ligand complexes are very strongly favored at the expense of the parent complexes, the equilibrium constants being *ca.* 400 times larger than statistical values. The deviations from statistical behavior are due almost entirely to enthalpy effects.

Introduction

Ligand-exchange reactions for systems in which the exchangeable ligands on the central moiety are monodentate have been studied in considerable detail.[2-5] Relatively little information, however, is available for exchange equilibria of metal chelates.[6] We have undertaken an investigation of exchange reactions of metal β-diketonates for two reasons. First, quantitative studies of exchange between zirconium(IV),[7,8] hafnium(IV),[7] titanium(IV),[9] yttrium(III),[10] aluminum(III),[11] and copper(II)[12] β-diketonates indicate that some ligand systems give equilibrium constants which are quite close to the values expected for a random statistical distribution of ligands, whereas others exhibit equilibria which deviate appreciably from statistical behavior. Except for the zirconium(IV)[8] and titanium(IV) systems, however, enthalpy and entropy contributions to the driving force of the reactions are not known. Second, the mixed-ligand products obtained in the reactions are often suited for studies of rapid configurational rearrangement processes by nmr line-broadening techniques. Some important kinetic and mechanistic information for rearrangement processes of six-coordinated aluminum(III) β-diketonates, for example, has been obtained from nmr studies on mixed-ligand complexes.[11,13,14]

In this paper we quantitatively characterize by nmr spectroscopy the ligand-exchange equilibria which occur in the systems Ga(acac)$_3$–Ga(bzbz)$_3$ and Ga(acac)$_3$–Ga(hfac)$_3$, where acac = acetylacetonate, bzbz = dibenzoylmethanate, and hfac = hexafluoroacetylacetonate. Kinetic studies of configurational rearrangement processes for some of the mixed-ligand products obtained in the exchange reactions are described in the following paper.[15]

Experimental Section

Syntheses.—Gallium(III) acetylacetonate and dibenzoylmethanate were prepared using previously described methods.[16,17] Both compounds were recrystallized from benzene–hexane and dried *in vacuo* at 80° for 0.5 hr: mp for Ga(acac)$_3$ 196–197°, lit. 194–196°,[16] 198°;[18] mp for Ga(bzbz)$_3$ 294–295°, lit.[17] 284°. The descrepancy in melting point for Ga(bzbz)$_3$ necessitated elemental analysis.

Anal. Calcd for Ga(C$_{15}$H$_{11}$O$_2$)$_3$: C, 73.09; H, 4.50; Ga, 9.43. Found: C, 73.19; H, 4.62; Ga, 9.61.

Gallium(III) hexafluoroacetylacetonate has not been previously reported but was readily prepared using the method described for the aluminum(III) analog.[19]

Tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)gallium(III) was obtained as colorless, needle-shaped crystals when recrystallized from benzene–hexane; mp 70–72°.

Anal. Calcd for Ga(C$_5$HF$_6$O$_2$)$_3$: C, 26.08; H, 0.44; F, 49.50; Ga, 10.09. Found: C, 26.03; H, 0.50; F, 49.70; Ga, 9.94.

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Preparation of Solutions.—Reagent grade benzene was dried by refluxing over calcium hydride for at least 24 hr. In general, vigorous shaking for 1–3 hr at room temperature was required for dissolution of $Ga(acac)_3$–$Ga(bzbz)_3$ and $Ga(acac)_3$–$Ga(hfac)_3$ mixtures at the concentrations and ligand compositions studied. Dissolution of some mixtures was hastened by warming. Special care, however, was exercised in warming all $Ga(acac)_3$–$Ga(hfac)_3$ mixtures. When these latter mixtures were heated above the melting point of $Ga(hfac)_3$, the undissolved crystals formed an immiscible oil, which then dissolved, and under these conditions unidentified decomposition products were observed in the nmr spectra of the solutions. If oil formation was avoided in the dissolution step, then mixtures stable at temperatures even as high as 120° were obtained. The rather long time required for dissolution at room temperature is attributed to the low rate at which the less soluble component, $Ga(bzbz)_3$ or $Ga(hfac)_3$, is consumed in the ligand-exchange reaction. For example, after an equimolar mixture of $Ga(acac)_3$–$Ga(bzbz)_3$ was dissolved in benzene at a concentration of 0.05 *M* at room temperature, an additional 45 min was required to achieve equilibrium at 36°. Less than 15 min was required to achieve equilibrium in the $Ga(acac)_3$–$Ga(hfac)_3$ system under similar conditions.

Nmr Spectra.—Proton magnetic resonance spectra were obtained using a Varian A-60 analytical spectrometer at 60.000 MHz. The instrument was equipped with a Varian variable-temperature controller, Model V-6040. Temperatures were determined by measuring the chemical shift difference for methanol (low temperatures) or ethylene glycol (elevated temperatures). The magnetic sweep width was checked using the audio-frequency side-band technique or a standard sample containing seven compounds with chemical shifts uniformly distributed over a sweep width of 500 Hz.

Measurement of Signal Intensities.—Signal areas used in the determination of equilibrium constants were determined by electronic integration. The integrations were checked by planimetry, and the equilibrium constants obtained by both methods agreed within experimental error. In general, each spectrum was integrated 12–25 times and the results were averaged in order to reduce errors caused by variations in magnetic field sweep. Errors due to saturation effects were avoided by employing small radiofrequency fields.

Results and Discussion

Equilibrium mixtures of $Ga(acac)_3$ and $Ga(bzbz)_3$ and of $Ga(acac)_3$ and $Ga(hfac)_3$ each should contain four compounds with formulas $Ga(acac)_n(dik)_{3-n}$, where $n = 0, 1, 2,$ or 3, and dik = bzbz or hfac. Compounds with $n = 1$ or 3 are expected to exhibit one methyl proton resonance line, but two lines of equal intensity are expected for compounds with $n = 2$. The nonequivalent methyl group environments for the $Ga(acac)_2(dik)$ complexes are illustrated in Figure 1. No methyl resonances, of course, can be observed for complexes with $n = 0$. Therefore, a total of four methyl resonances should be observed for an equilibrium mixture.

Methyl proton resonance spectra for equilibrium mixtures of $Ga(acac)_3$ and $Ga(bzbz)_3$ in benzene solution at various values of ligand composition are shown in Figure 2. The ligand composition is specified by the quantity f_{acac}, which is defined as the molar fraction of total ligand present as acetylacetonate. A total of four methyl resonances are observed, as is expected. The two lines of equal intensity at τ 8.13 and 8.32 are assigned to $Ga(acac)_2(bzbz)$; the lines at τ 8.19 and 8.25, respectively, are assigned to $Ga(acac)(bzbz)_2$ and $Ga(acac)_3$.

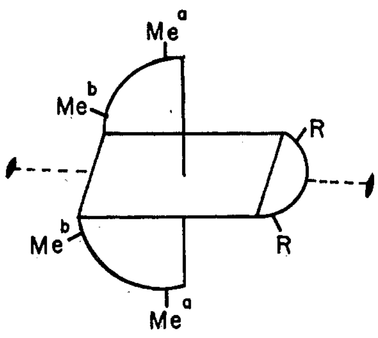

Figure 1.—Nonequivalent methyl group environments (a and b) in $Ga(acac)_2(bzbz)$, R = C_6H_5, and $Ga(acac)_2(hfac)$, R = CF_3.

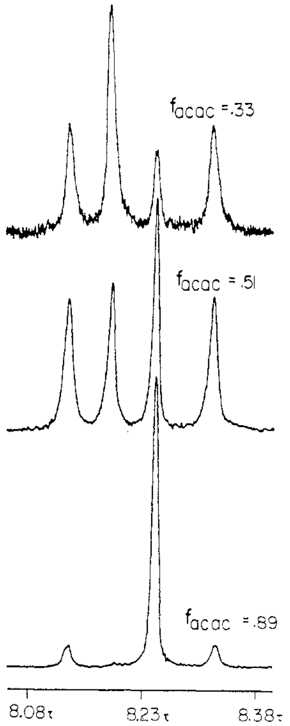

Figure 2.—Methyl proton resonance spectra for equilibrium mixtures of $Ga(acac)_3$ and $Ga(bzbz)_3$ in benzene at 36°. Total solute molarity is 0.10 *M*.

Typical methyl proton spectra for equilibrium mixtures of $Ga(acac)_3$ and $Ga(hfac)_3$ are presented in Figure 3. Unlike the $Ga(acac)_3$–$Ga(bzbz)_3$ system, a total of only three lines is observed in benzene solution at 36°. Based on the dependence of signal intensities on ligand composition, the lines at τ 8.25, 8.38, and 8.52, respectively, are assigned to $Ga(acac)_3$, $Ga(acac)_2(hfac)$, and $Ga(acac)(hfac)_2$. The existence of a single, sharp line for $Ga(acac)_2(hfac)$ is attributed to a rapid intramolecular configurational rearrangement process which exchanges methyl groups between the two nonequivalent environments.[15]

Resonance lines due to —CH= protons on the diketonate rings and phenyl protons in the case of the dibenzoylmethanates are of little interest in the pres-

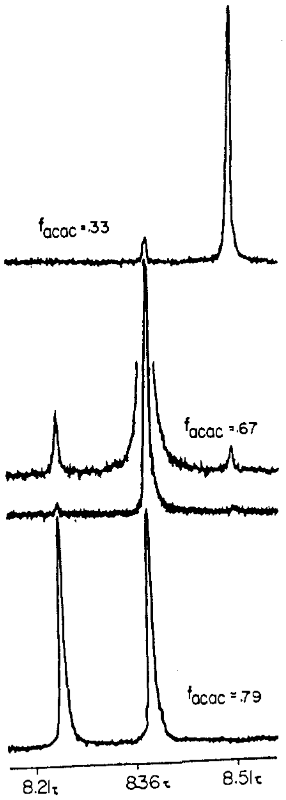

Figure 3.—Methyl proton resonance spectra for equilibrium mixtures of Ga(acac)$_3$ and Ga(hfac)$_3$ in benzene at 36°. Total solute molarity is 0.10 *M*. The two spectra shown for f_{acac} = 0.67 differ only in spectrum amplitude.

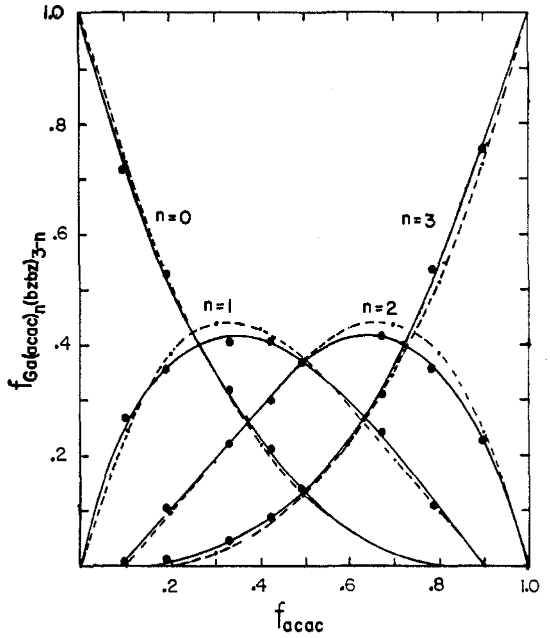

Figure 4.—Equilibrium distributions of Ga(acac)$_n$(bzbz)$_{3-n}$ complexes as a function of ligand composition in benzene at 36°. Total solute molarity is 0.10 *M:* solid lines, experimental curves; dashed lines, calculated curves assuming a random statistical distribution of ligands.

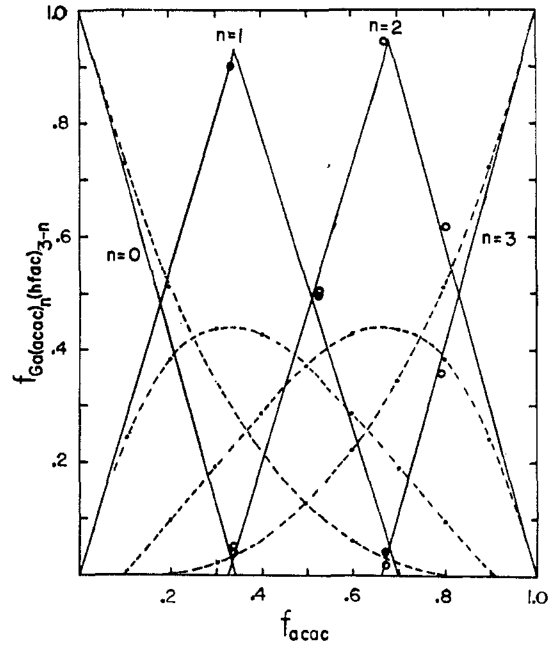

Figure 5.—Equilibrium distributions of Ga(acac)$_n$(hfac)$_{3-n}$ complexes as a function of ligand composition in benzene at 36°. Total solute molarity is 0.10 *M:* solid lines, experimental curves; dashed lines, calculated curves assuming a random statistical distribution of ligands.

ent study. It is noted, however, that each Ga(acac)$_n$(dik)$_{3-n}$ complex with n = 1, 2, or 3 exhibits a single, sharp resonance line due to —CH= protons on the acac rings and that this result is consistent with the stereochemistry of the complexes.

The equilibrium concentrations of complexes containing acac were determined by integration of their methyl proton resonance signals. Concentrations of Ga(bzbz)$_3$ and Ga(hfac)$_3$ were determined by difference. The equilibrium molar fraction of each Ga(acac)$_n$(dik)$_{3-n}$ complex

$$f_{\text{Ga(acac)}_n(\text{dik})_{3-n}} = [\text{Ga(acac)}_n(\text{dik})_{3-n}] \Big/ \sum_{n=0}^{3}[\text{Ga(acac)}_n(\text{dik})_{3-n}]$$

was studied as a function of ligand composition. For a completely random statistical distribution of ligands, the dependence of $f_{\text{Ga(acac)}_n(\text{dik})_{3-n}}$ on ligand composition is given by

$$f_{\text{Ga(acac)}_n(\text{dik})_{3-n}} = f_{\text{acac}}{}^n(1 - f_{\text{acac}})^{3-n}\frac{3!}{n!(3-n)!}$$

The observed equilibrium molar fractions of Ga(acac)$_n$(bzbz)$_{3-n}$ complexes are plotted *vs.* ligand composition in Figure 4. Curves calculated assuming a random scrambling of ligands are also shown. Analogous plots for the Ga(acac)$_n$(hfac)$_{3-n}$ complexes are shown in Figure 5. It is readily seen that the Ga(acac)$_3$–Ga(bzbz)$_3$ system behaves nearly statistically, whereas the equilibria in the Ga(acac)$_3$–Ga(hfac)$_3$ system deviate markedly from statistical behavior, the mixed-ligand complexes being strongly favored at the expense of the parent complexes.

The ligand-exchange equilibria in each system are quantitatively described by specifying two arbitrary, independent equilibrium constants. The constants chosen for direct determination are defined by the reactions

$$\text{Ga(dik)}_3 + \text{Ga(acac)}_2\text{(dik)} \xrightleftharpoons{K_1} 2\text{Ga(acac)(dik)}_2 \qquad (1)$$

$$\text{Ga(acac)(dik)}_2 + \text{Ga(acac)}_3 \xrightleftharpoons{K_2} 2\text{Ga(acac)}_2\text{(dik)} \qquad (2)$$

These are the constants that can be determined most accurately in both ligand systems. It will be convenient, however, to discuss the equilibria in terms of the formation of the mixed-ligand complexes from the parent complexes

$${}^1/_3\text{Ga(acac)}_3 + {}^2/_3\text{Ga(dik)}_3 \xrightleftharpoons{K_{f1}} \text{Ga(acac)(dik)}_2 \qquad (3)$$

$${}^2/_3\text{Ga(acac)}_3 + {}^1/_3\text{Ga(dik)}_3 \xrightleftharpoons{K_{f2}} \text{Ga(acac)}_2\text{(dik)} \qquad (4)$$

where $K_{f1} = K_1^{2/3}K_2^{1/3}$ and $K_{f2} = K_1^{1/3}K_2^{2/3}$.

The data in Tables I and II show that values of K_1 and K_2 for the Ga(acac)$_3$–Ga(bzbz)$_3$ system are constant within experimental error over fairly wide ranges of solute composition and total solute molarity. Therefore, the activity quotients do not vary over the ranges studied, and the solutions are probably nearly ideal.

TABLE I

DEPENDENCE OF K_1 AND K_2 FOR THE Ga(acac)$_3$–Ga(bzbz)$_3$ SYSTEM ON SOLUTE COMPOSITION[a]

	Av values[b]	
f_{acac}	K_1	K_2
0.291	2.22 ± 0.25[c]	...
0.387	2.40 ± 0.16	2.48 ± 0.19
0.420	2.60 ± 0.17	2.52 ± 0.17
0.490	2.38 ± 0.23	2.58 ± 0.18
0.598	...	2.63 ± 0.15
0.813	...	2.54 ± 0.22

[a] In benzene at 36°; total solute molarity is 0.050 *M*. [b] Average of at least 12 spectral measurements. [c] All errors are estimated at the 95% confidence level.

TABLE II

DEPENDENCE OF K_1 AND K_2 FOR THE Ga(acac)$_3$–Ga(bzbz)$_3$ SYSTEM ON TOTAL SOLUTE MOLARITY[a]

	Av values[b]	
Total molarity	K_1	K_2
0.05	2.38 ± 0.23[c]	2.58 ± 0.18
0.13	2.51 ± 0.10	2.62 ± 0.11
0.18	2.54 ± 0.20	2.57 ± 0.08
0.20	2.50 ± 0.37	2.62 ± 0.25

[a] In benzene at 36°; f_{acac} = 0.490. [b] Average of at least 12 spectral measurements. [c] All errors are estimated at the 95% confidence level.

The constants K_1 and K_2 for both ligand-exchange systems were studied as a function of temperature. The results are presented in Tables III and IV. Enthalpy and entropy changes for the corresponding exchange reactions were obtained from the slope and intercept, respectively, of the log *K vs.* $1/T$ plots. The data were treated by least-squares analysis including 25 data points at each temperature. Values of K_1 and K_2 at 25° were calculated from the least-squares straight line. These data were then used to calculate the equilibrium constants, enthalpies, and entropies for formation of the mixed-ligand complexes from the parent complexes, as defined by reactions 3 and 4. The results, along with calculated values of the equilibrium constants and entropies, assuming a random statistical distribution of ligands, are presented in Tables V and VI.

TABLE III

TEMPERATURE DEPENDENCE OF K_1 AND K_2 FOR THE Ga(acac)$_3$–Ga(bzbz)$_3$ SYSTEM IN BENZENE

	Av values[a]	
Temp, °C	K_1[b]	K_2[c]
5.7	2.60[d] ± 0.19[e]	2.49[f] ± 0.13
16.0	2.77 ± 0.19	2.24 ± 0.19
30.3	2.50 ± 0.27	2.42 ± 0.19
43.0	2.90 ± 0.16	2.27 ± 0.22

[a] Average of 25 spectral measurements. [b] f_{acac} = 0.340; total molarity is 0.10 *M* unless otherwise noted. [c] f_{acac} = 0.667; total molarity is 0.20 *M* unless otherwise noted. [d] Total molarity is 0.076 *M*. [e] All errors are estimated at the 95% confidence level. [f] Total molarity is 0.10 *M*.

TABLE IV

TEMPERATURE DEPENDENCE OF K_1 AND K_2 FOR THE Ga(acac)$_3$–Ga(hfac)$_3$ SYSTEM IN BENZENE[a]

	Av values[b]	
Temp, °C	$10^{-2}K_1$[c]	$10^{-2}K_2$[d]
36.0	8.88 ± 1.10[e]	...
58.5	4.81 ± 0.81	...
63.3	...	5.54 ± 0.21
78.9	3.98 ± 0.53	3.77 ± 0.51
98.0	3.22 ± 0.33	2.89 ± 0.33

[a] Total molarity is 0.25 *M*. [b] Average of 25 spectral measurements. [c] f_{acac} = 0.335. [d] f_{acac} = 0.671. [e] All errors are estimated at the 95% confidence level.

TABLE V

THERMODYNAMIC DATA FOR THE Ga(acac)$_3$–Ga(bzbz)$_3$ SYSTEM IN BENZENE AT 25°

				Statistical values	
Reaction	K_f	ΔH, kcal/mol	ΔS, eu	K_f	ΔS, eu
3	2.59 ± 0.11[a]	0.32 ± 0.25	2.98 ± 0.74	3.00	2.18
4	2.47 ± 0.10	0.04 ± 0.24	1.91 ± 0.71	3.00	2.18

[a] All errors are estimated at the 95% confidence interval.

TABLE VI

THERMODYNAMIC DATA FOR THE Ga(acac)$_3$–Ga(hfac)$_3$ SYSTEM IN BENZENE AT 25°

				Statistical values	
Reaction	$10^{-3}K_f$	ΔH, kcal/mol	ΔS, eu	K_f	ΔS, eu
3	1.12 ± 0.21[a]	−4.1 ± 0.8	0.1 ± 2.4	3.00	2.18
4	1.22 ± 0.27	−4.5 ± 1.0	−0.9 ± 2.9	3.00	2.18

[a] All errors are estimated at the 95% confidence level.

Equilibrium constants for formation of Ga(acac)(bzbz)$_2$ and Ga(acac)$_2$(bzbz) from the parent complexes are only *ca.* 20% lower then the values expected for a random scrambling of ligands. Within experimental error, enthalpy changes for the exchange reactions are zero or nearly zero and the entropy changes are equal to the values expected for a random scrambling of ligands. The confidence level estimates of error indicate that either small enthalpy or entropy effects could account for the slight deviations of the equilibrium constants from statistical values.

In the Ga(acac)$_3$–Ga(hfac)$_3$ system the experimental equilibrium constants for reactions 3 and 4 are *ca.* 400 times larger than the statistical values. Within experimental error, the entropy change for formation of Ga(acac)$(hfac)_2$ is equal to the statistical value; for Ga$(acac)_2$(hfac) the entropy change is probably somewhat less than statistical. However, the driving force for the reactions involves an exothermic enthalpy change that is greater than 3 kcal/mol even at the lower 95% confidence limit. Thus the observed deviations from statistical behavior are due almost entirely to enthalpy effects.

Previous studies[7-12] of ligand-exchange reactions between metal β-diketonates indicate that the mixed-ligand complexes are appreciably favored at the expense of the parent complexes when one ligand contains highly electronegative trifluoromethyl groups and the other ligand is nonfluorinated. The equilibria lie closer to a random statistical distribution of ligands when the two ligands are both fluorinated or both nonfluorinated. The only thermodynamic data reported are for exchange of acetylacetonate and trifluoroacetylacetonate (tfac) between $Zr(acac)_4$ and $Zr(tfac)_4$[8] and between $Ti(acac)_2F_2$ and $Ti(tfac)_2F_2$.[9] In these acac–tfac ligand-exchange systems the equilibrium constants for formation of the mixed diketonate complexes are three to seven times larger than the statistical values, and the deviations from random scrambling are due to entropy effects; enthalpy changes are zero within experimental error. The results reported here are in agreement with the general behavior exhibited by other metal β-diketonate systems. The $Ga(acac)_3$–$Ga(hfac)_3$ system, however, is the first β-diketonate system reported in which deviations from statistical scrambling are due mainly to enthalpy effects. Favorable enthalpy changes can probably be expected for similar systems in which the equilibrium quotients are two or more orders of magnitude larger than statistical values.[11]

Using simple electrostatic arguments, Kida[20] has shown that a decrease in average ligand–ligand repulsive energies will always favor the mixed-ligand species at the expense of the parent complexes whenever the effective charges on the exchangeable ligands differ. Similar electrostatic effects have also been considered by Marcus and Elieser.[21] Fay[6] has pointed out that deviations from statistical behavior for exchange of nonfluorinated and fluorinated diketonates, such as acac and hfac, can be expected to receive some contribution from the difference in effective charge on the donor oxygen atoms of the two ligands, caused by the inductive effect of the fluorine atoms. When the inductive effects of terminal groups on the two ligands are similar, which should be the case for acac and bzbz, little stabilization energy is gained by the mixed complexes, and the equilibrium constants are close to the statistical values.

Based on a point-charge model, the stabilization energy for an octahedral $M(dik)_2(dik')$ complex relative to the parent complexes is $2.621(e - e')^2/r$, where $e - e'$ is the difference in charge on the donor oxygen atoms of dik and dik′, and r is the metal–oxygen distance. For an estimated[22] mean gallium–oxygen distance of 2.0 Å, a difference of *ca.* 0.1 electron charge unit between the donor oxygen atoms of acac and hfac would be sufficient to attain a stabilization energy of 4 kcal/mol for Ga(acac)$(hfac)_2$ and Ga$(acac)_2$(hfac). It probably would not be reasonable, however, to attribute the observed enthalpies for formation of Ga(acac)$(hfac)_2$ and Ga$(acac)_2$(hfac) entirely to lower ligand–ligand repulsive energies in the mixed-ligand complexes. Ga(acac)$(hfac)_2$ and Ga$(acac)_2$(hfac) are expected to have larger net dipole moments than the corresponding $Ga(acac)_n(bzbz)_{3-n}$ complexes; hence, contributions to the enthalpies of reactions 3 and 4 due to differences in solvation energies of reactants and products should be more important for the former complexes.

A considerable amount of additional thermodynamic data is necessary before one can hope to decide on the relative importance of electrostatic effects and differences in solvation energies in stabilizing $M(acac)_n(hfac)_{3-n}$ complexes. Future studies will deal with this topic.

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