CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
SIR GEORGE WILLIAMS UNIVERSITY, MONTREAL 107, QUEBEC, CANADA

Ligand-Exchange Equilibrium Studies of Some Octacoordinate Yttrium(III)–β-Diketonate Complexes by Hydrogen-1 Nuclear Magnetic Resonance Spectroscopy[1]

BY NICK SERPONE* AND ROUBEN ISHAYEK

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Ligand-exchange equilibria for the [pip][Y(hfac)$_4$]–[pip][Y(tfac)$_4$] system, where pip is piperidinium and tfac and hfac stand for trifluoroacetylacetonate and hexafluoroacetylacetonate, respectively, have been studied in deuteriochloroform by proton nmr spectroscopy. This system has been characterized quantitatively in the methylene proton nmr region. The complex [pip][Y(hfac)$_4$] has not been reported previously. In the temperature range −58 to −16°, the equilibrium quotients for the formation of mixed complexes are 3–5 times larger than statistical assuming a total random distribution of ligands. Deviations from statistical behavior are ascribed to enthalpy changes, entropy changes being zero or nearly zero within experimental error. Relative rates of ligands exchanging between two complexes are discussed in terms of the coalescence behavior of the methylene proton resonances from which it appears that the hexafluoroacetylacetonate ligands exchange faster than the trifluoroacetylacetonate ligands. Downfield shifts of the methylene proton resonances of the five [pip][Y(hfac)$_n$-(tfac)$_{4-n}$] (where n = 0, 1, 2, 3, or 4) complexes with decreasing temperature are attributed to greater solvent–solute interactions at the lower temperatures.

Introduction

Eight-coordinate tetrakis-β-diketonate complexes have been the subject of many interesting studies in the past several years. These studies were directed toward structure elucidation,[2-4] laser action in these chelates,[2,3,5,6] magnetic properties,[7-9] ligand dissociation equilibria,[2,3] volatility and thermal properties,[10-15] kinetics of ligand exchange,[16] vibrational properties,[17] electric field effects on proton chemical shifts,[18] and ligand-exchange equilibria.[19-21] Of special interest are the latter studies in which lability of the β-diketonate ligands in octacoordinate neutral complexes of the type M(dik)$_4$[19,20,22] [M is Zr(IV), Hf(IV), Th(IV), or Ce(IV); dik[23] is acac or tfac] and in octacoordinate ion-pair complexes, [$(C_6H_5)_4$As][Y(dik)$_4$][21] (dik is tfac or hfac), has been demonstrated by proton[19,21] and fluorine[20] nmr spectroscopy. For example, a benzene solution of Zr(acac)$_4$–Zr(tfac)$_4$ contains the mixed complexes Zr(acac)$_3$(tfac), Zr(acac)$_2$(tfac)$_2$, and Zr(acac)(tfac)$_3$ as well as the parent complexes. The mixed complexes appear to be thermodynamically more stable than Zr(acac)$_4$ and Zr(tfac)$_4$. Deviations from a purely random distribution of ligands have been ascribed to entropy effects, enthalpy changes being zero or nearly zero.[20] Fay has emphasized the need for measurement of enthalpy and entropy changes in studies of ligand-exchange equilibria.[24]

Except for Zr(acac)$_4$–Zr(tfac)$_4$,[20] Ga(acac)$_3$–Ga(bzbz)$_3$, and Ga(acac)$_3$–Ga(hfac)$_3$,[25] and Al(AA)$_3$–Al(BB)$_3$[26] systems (where AA and BB are acac, hfac, or dpm), relatively little thermodynamic data are available in the literature for bidentate ligand exchange. Pinnavaia and Nweke[25] have shown that Ga(acac)$_3$–Ga(hfac)$_3$ is the first system observed for which deviations from statistical scrambling are due mainly to enthalpy changes. Similar enthalpy changes can probably be found in cases where the equilibrium quotients are two or more orders of magnitude larger than the expected statistical values.[25,26]

The work reported here was undertaken to characterize quantitatively, by ^{1}H nmr spectroscopy, ligand-exchange equilibria for the [pip][Y(hfac)$_4$]–[pip][Y(tfac)$_4$] system (pip = piperidinium) and to obtain thermodynamic data for this system in order to ascertain whether enthalpy or entropy changes are the driving force behind the exchange reactions.

Experimental Section

Materials and Techniques.—Columbia Organic Chemicals trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione) and hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoro-2,4-pentanedione) were used as purchased without further purification. Yttrium(III) chloride hexahydrate (99.9%) was purchased from Alfa Inorganics. Solvents used in the syntheses were reagent grade. Deuteriochloroform was prepared by the method of Paulsen and Cooke.[27]

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(23) The following abbreviations are used throughout: acac, acetylacetonate; tfac, trifluoroacetylacetonate; hfac, hexafluoroacetylacetonate; bzac, benzoylacetonate; bzbz, dibenzoylmethanate; dpm, dipivaloylmethanate.
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Melting points were measured with a Gallenkamp melting point apparatus and are not corrected.

All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Syntheses.—The compounds were prepared using the general piperidine method.[5,6,18]

Piperidinium Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)-yttrate(III).—This compound was prepared by the same procedure as reported previously;[18] mp 105.5–107.5°; lit.[18] mp 106–108°. *Anal.* Calcd for $C_5H_{12}NY(C_5H_4F_3O_2)_4$: C, 38.13; H, 3.58; N, 1.78; F, 28.97; Y, 11.29. Found: C, 38.03; H, 3.53; N, 1.78; F, 28.81; Y, 11.42.

Piperidinium Tetrakis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)yttrate(III).—This compound was prepared by a procedure similar to that used for the corresponding trifluoroacetylacetonate.[18] To a boiling solution of 50 ml of 95% ethanol, 7.80 g of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (32 mmol), and 3.16 ml of piperidine (32 mmol) was added a 30-ml aqueous solution of yttrium(III) chloride hexahydrate (2.43 g, 8 mmol). The mixture was stirred while refluxing for 0.5 hr and the solvent was evaporated (*ca.* 30 ml) by heating over a hot plate for a further 0.5 hr; this evaporation resulted in the formation of an oil which did not crystallize after standing in the cold (0°) for 1 day. The oily lower layer was separated and dissolved in *ca.* 20 ml of dichloromethane and 5 ml of hexane. This solution was concentrated by passing a gentle stream of nitrogen over the surface until the first appearance of crystals. The product was allowed to crystallize in the cold (0°) for 2 days. The crystals were filtered, washed twice with 20-ml portions of hexane, and dried *in vacuo* in a drying pistol (70°) for 8 hr. The yield was 1.0 g (12% of theoretical); in another preparation the yield was 16% of theoretical; mp 130–132°. *Anal.* Calcd for $C_5H_{12}NY(C_5HF_6O_2)_4$: C, 29.92; H, 1.60; N, 1.39; F, 45.44; Y, 8.86. Found: C, 29.89; H, 1.55; N, 1.49; F, 45.63; Y, 9.05.

Preparation of Solutions.—Samples of the [pip][Y(hfac)$_4$]–[pip][Y(tfac)$_4$] mixture were prepared by weighing the appropriate amount of the compounds in a 1.00-ml volumetric flask and then adding deuteriochloroform (with 10% v/v of tetramethylsilane) to the mark. The solutions were shaken vigorously for *ca.* 10–15 min to enhance dissolution of the complexes.[28,29] The solutions were transferred to 9-in. nmr precision tubes and sealed *in vacuo*. Fourteen solutions were thus prepared, each one of which differed from the preceding and subsequent solution by 0.02 g in each of the complexes, while the total weight of the mixture was kept constant at 0.30 g. The three samples richest in [pip][Y(hfac)$_4$] were not used for variable-temperature nmr work because this complex is but slightly soluble at low temperatures.

To check how fast equilibrium is achieved at the low temperatures, a sample 0.48 mol fraction in [pip][Y(hfac)$_4$] was prepared by weighing 0.145 g of [pip][Y(hfac)$_4$] in an nmr tube and adding 0.70 ml of deuteriochloroform; the mixture was frozen by placing the nmr tube in liquid nitrogen. To this frozen mixture was added 0.124 g of [pip][Y(tfac)$_4$] dissolved in 0.30 ml of deuteriochloroform. The nmr tube was sealed *in vacuo* and transferred to an *N,N*-dimethylformamide–Dry Ice bath (−61°). The contents of the tube were shaken vigorously at −61°, but even after 15 min the mixture did not dissolve. The tube was taken out of the cold bath and the contents were vigorously shaken for *ca.* 10–15 sec until a solution was obtained; the sample was then quickly inserted into the variable-temperature nmr probe (already at −58°). The spectrum was recorded 1 min after insertion of the sample.

Nuclear Magnetic Resonance Spectra.—Variable-temperature proton magnetic resonance spectra were obtained with a Varian HA-100 high-resolution spectrometer operating at 100.00 MHz. The spectrometer was equipped with a variable-temperature probe accessory, Model V-4333, and a temperature controller accessory, Model V-6040. The spectra were recorded in the temperature range +50 to −58° in the frequency sweep mode.

Room-temperature and variable-temperature chemical shifts (^{1}H) were measured with the HA-100 spectrometer. The magnetic field sweep of the spectrometer, at room temperature, was checked against a chloroform–TMS reference sample (Varian Part No. 943346-07), a method in agreement with the side-band technique. Room-temperature shifts are believed accurate to ±0.01 ppm; variable-temperature shifts, to ±0.02 ppm.

Measurement of Signal Intensities.—Proton resonance signals were obtained under conditions of low-radiofrequency fields, H_1, such that differences in the product T_1T_2 for the various signals could be neglected.[30]

Signal areas (accurate to ±3%) used in calculating equilibrium quotients were determined using a compensating polar planimeter. In general, five spectra were recorded for each sample at each temperature to reduce errors caused by changes in magnetic field sweep. Each signal was integrated 10 times and the results were averaged. Because of some overlap between resonance signals, the spectra were resolved manually. This manual resolution was checked by resolving and integrating a set of spectra with the Du Pont 310 curve resolver. Equilibrium quotients calculated by planimetric and electronic integration agreed within experimental error.

When the hfac and tfac –CH= proton resonances of the complex [pip][Y(hfac)$_2$(tfac)$_2$], the tfac ring proton resonance of [pip][Y(hfac)$_3$(tfac)], and the hfac –CH= proton resonance of [pip][Y(hfac)(tfac)$_3$] could not be resolved manually because of serious overlap, the total area under these resonance signals was obtained. This area was then subdivided into the area of the appropriate resonance signals since the areas for the tfac –CH= proton resonance of [pip][Y(hfac)$_3$(tfac)] and for the hfac –CH= proton resonance of [pip][Y(hfac)(tfac)$_3$] are known from integration of (hfac)$_3$ and (tfac)$_3$ ring proton resonances, respectively.

Results and Discussion

Proton Nmr Spectra.—Random distribution of ligands in an equilibrium mixture of [pip][Y(hfac)$_4$] and [pip][Y(tfac)$_4$] should give rise to five compounds having the general formula [pip][Y(hfac)$_n$(tfac)$_{4-n}$] where n = 0, 1, 2, 3, or 4. The nmr spectrum of an equilibrium mixture containing all five complexes should reveal a maximum of eight –CH= proton resonance signals and four CH_3 proton resonances. We have chosen to investigate ligand-exchange equilibria in this system using –CH= protons as probes rather than CH_3 protons. The methyl resonances were poorly resolved. The use of the ring protons necessitated more concentrated solutions (0.34 *M*) than would have been required had methyl protons been used.

Attempts to observe geometrical isomers of the mixed complexes (n = 1, 2, or 3) were not successful. Apparently, the rate of the intramolecular exchange process is rapid enough that only the time-averaged chemical shifts of the methylene protons of each of the five compounds are observed.

Ring proton resonance spectra (temperature is −58°) for equilibrium mixtures of [pip][Y(hfac)$_4$] and [pip][Y(tfac)$_4$] in deuteriochloroform solution at various values of mole fraction of [pip][Y(hfac)$_4$] are presented in Figure 1. Six –CH= proton resonance signals are observed; the seventh resonance is masked by one of the more intense signals (*vide infra*). The Y(hfac)$_4^-$ ring proton resonance is not observed[31] at values of mole fractions shown in Figure 1. These spectra are consistent with the presence of [pip][Y(tfac)$_4$] and the three mixed complexes (n = 1, 2, or 3). The two

(28) Care should be taken not to heat the solutions to enhance the rate of dissolution since this can lead to some dissociation of the [pip][Y(dik)$_4$] complex.[29]

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(31) The –CH= proton resonance of [(C$_6$H$_5$)$_4$As][Y(hfac)$_4$] was clearly observed by Cotton and coworkers[21] but not that of [(C$_6$H$_5$)$_4$As][Y(tfac)$_4$] at values of mole fraction >0.29. However, at a mole fraction of 0.17 in Y(hfac)$_4^-$, the ring proton signal of Y(tfac)$_4^-$ was observed at −5.68 ppm (−40°) (S. J. Lippard, private communication, Jan 1971). The difference between our observations and those reported earlier[21] is probably due to slight changes in chemical shifts for the pip$^+$ *vs.* the (C$_6$H$_5$)$_4$As$^+$ salts because of ion pairing and diamagnetic anisotropic effects of the phenyl groups in the latter salts which tend to shift proton resonances upfield (*cf.* ref 20).

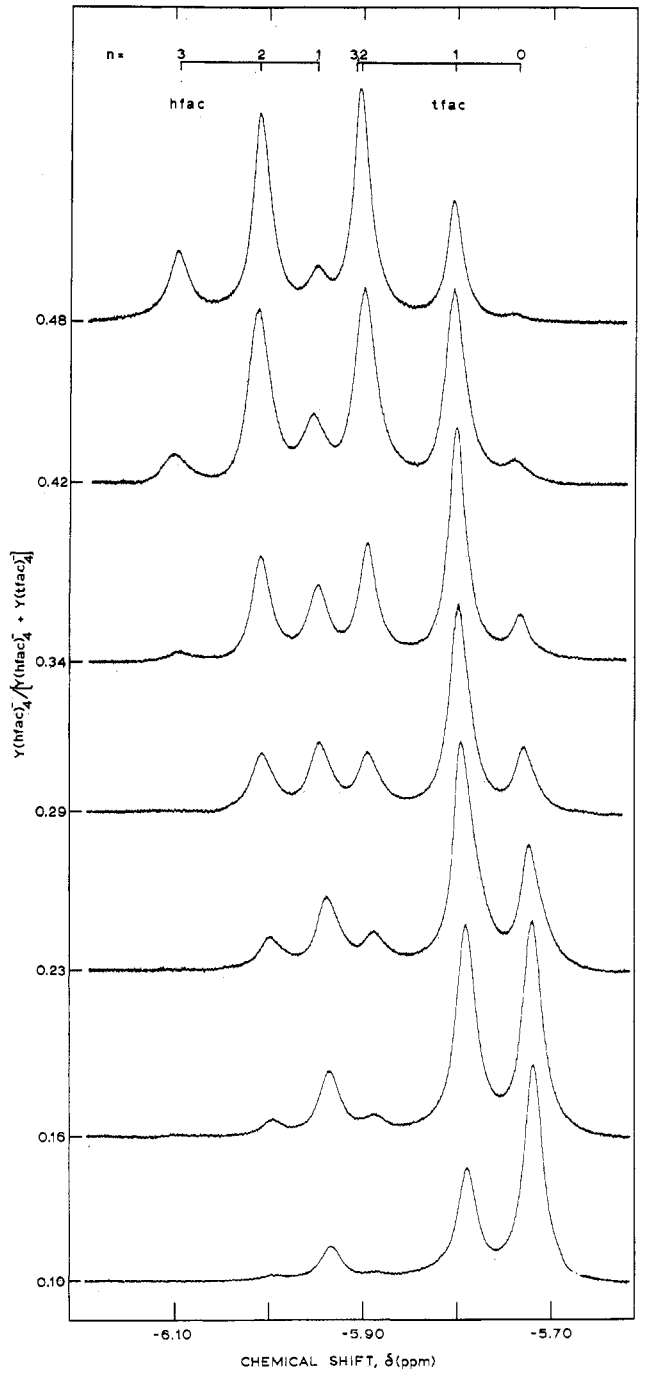

Figure 1.—Ring proton resonance spectra for equilibrium mixtures of [pip][Y(hfac)$_4$] and [pip][Y(tfac)$_4$] in deuteriochloroform at −58.0°; total solute molarity is 0.34 *M*. The resonances are ascribed to [pip][Y(hfac)$_n$(tfac)$_{4-n}$] complexes where n = 0, 1, 2, or 3.

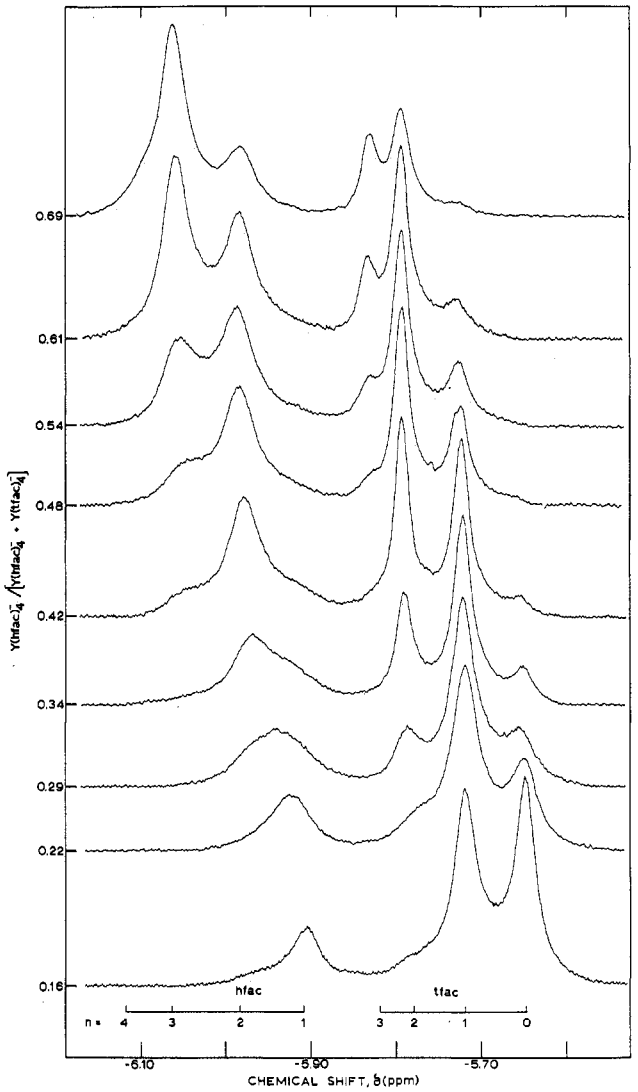

Figure 2.—Ring proton resonance spectra for equilibrium mixtures of [pip][Y(hfac)$_4$] and [pip][Y(tfac)$_4$] in deuteriochloroform solution at −16.0°; total solute molarity is 0.34 *M*. The resonances are ascribed to [pip][Y(hfac)$_n$(tfac)$_{4-n}$] complexes where n = 0, 1, 2, 3, or 4.

equally intense resonances at δ −5.99 and −5.88 ppm are, respectively, assigned to hfac and tfac protons of [pip][Y(hfac)$_2$(tfac)$_2$]. The –CH= signal at δ −5.72 ppm is assigned to [pip][Y(tfac)$_4$]; the chemical shift of the ring proton resonance in a pure sample of [pip][Y(tfac)$_4$] is −5.72 ppm at −58°. The two resonances at −5.92 and −5.78 ppm are ascribed to the –CH= protons of hfac and tfac, respectively, of the [pip][Y(hfac)(tfac)$_3$] mixed complex. The proton signal at −6.07 ppm is assigned to the hfac ring proton of [pip][Y(hfac)$_3$(tfac)]; the corresponding –CH= resonance for the tfac ligand in this mixed complex is masked by the more intense resonances of the [pip][Y(hfac)$_2$(tfac)$_2$] complex. However, inspection of Figure 1 reveals that the –CH= (tfac) resonance of [pip][Y(hfac)$_2$(tfac)$_2$] is slightly more intense than the corresponding hfac –CH= resonance; it is probable that the ring proton resonance of the tfac ligand in [pip][Y(hfac)$_3$(tfac)] occurs at −5.88 ppm. This resonance is clearly observed at −5.82 ppm (−16°) in Figure 2 which presents ring proton spectra at higher values of mole fraction of [pip][Y(hfac)$_4$]. The temperature dependence of the tfac –CH= proton chemical shifts (see below) allows the tfac ring proton resonance for [pip][Y(hfac)$_3$(tfac)] to be identified. The Y(hfac)$_4^-$ ring proton resonance (mole fraction 0.69) is barely discernible on the low-field side of the [pip][Y(hfac)$_3$(tfac)] hfac proton resonance.

Figure 3 shows the temperature-dependent ring proton resonance spectra for the [pip][Y(hfac)$_n$(tfac)$_{4-n}$] complexes. In the low-temperature region (−28.5 to −58°), seven ring proton resonances are observed consistent with the presence of the complexes for n = 0–3. As the temperature is increased, the –CH= resonances for the individual complexes coalesce until only one

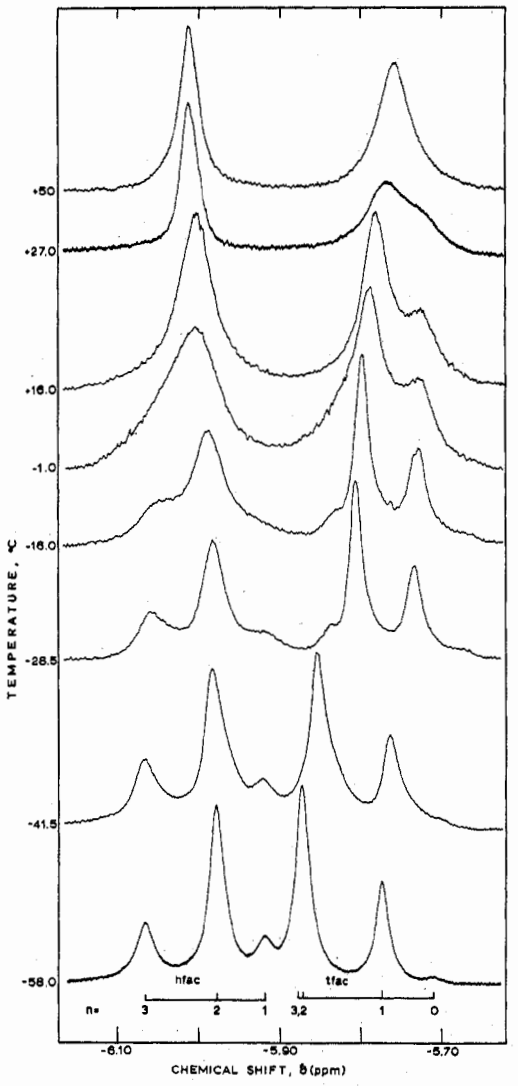

Figure 3.—Temperature dependence of the methylene (-CH=) proton nmr spectra for an equilibrium mixture of [pip][Y(hfac)$_4$] and [pip][Y(tfac)$_4$] in deuteriochloroform; mole fraction in [pip][Y(hfac)$_4$] is 0.48.

hexafluoroacetylacetonate (low-field line) and one trifluoroacetylacetonate peak (high-field line) are observed in the high-temperature limit. This coalescence is attributed to a rapid intermolecular ligand-exchange process which averages the magnetic environment of the individual protons. Similar observations have been reported by others.[19-21]

Of significance are the relative rates of hexafluoroacetylacetonate and trifluoroacetylacetonate ligand exchange among the five compounds in the equilibrium mixture. Two types of ligand exchange can take place;[19] these are shown in reactions 1 and 2 and in reactions 3 and 4. First, as described in reactions 1 and 2,

$$[pip][Y(hfac)_3(tfac)] + [pip][Y(hfac)(tfac)_3] \rightleftharpoons 2[pip][Y(hfac)_2(tfac)_2] \quad (1)$$

$$[pip][Y(hfac)(tfac)_3] + [pip][Y(hfac)_2(tfac)_2] \rightleftharpoons [pip][Y(hfac)_2(tfac)_2] + [pip][Y(hfac)(tfac)_3] \quad (2)$$

$$[pip][Y(hfac)(tfac)_2(\textit{tfac})] + [pip][Y(hfac)_2(tfac)_2] \rightleftharpoons [pip][Y(hfac)(tfac)_3] + [pip][Y(hfac)_2(tfac)(\textit{tfac})] \quad (3)$$

$$[pip][Y(hfac)(\textit{hfac})(tfac)_2] + [pip][Y(hfac)_3(tfac)] \rightleftharpoons [pip][Y(hfac)_2(tfac)_2] + [pip][Y(hfac)_2(\textit{hfac})(tfac)] \quad (4)$$

a hfac ligand from one complex can intermolecularly exchange with a tfac ligand of another complex. In reaction 1, a hfac ligand in [pip][Y(hfac)$_3$(tfac)] exchanges with a tfac ligand in [pip][Y(hfac)(tfac)$_3$], the result of which is to shift a hfac ligand from [pip][Y(hfac)$_3$-(tfac)] to [pip][Y(hfac)$_2$(tfac)$_2$] and a tfac ligand from [pip][Y(hfac)(tfac)$_3$] to [pip][Y(hfac)$_2$(tfac)$_2$]. In the back-reaction 1, a hfac and a tfac ligand exchange between the two [pip][Y(hfac)$_2$(tfac)$_2$] complexes resulting in a shift of a hfac from [pip][Y(hfac)$_2$(tfac)$_2$] to [pip]-[Y(hfac)$_3$(tfac)] and a tfac ligand from [pip][Y(hfac)$_2$-(tfac)$_2$] to [pip][Y(hfac)(tfac)$_3$]. This intermolecular exchange process should be observed as coalescence of the hfac methylene proton resonances and coalescence of the tfac -CH= resonances in all three complexes involved in reaction 1. If the separations between the resonances in the absence of exchange are equal and the ring proton resonances coalesce at the same temperature, then the rates of exchange of hfac and tfac ligands are the same. In reaction 2, the hfac and tfac ligands exchange between [pip][Y(hfac)(tfac)$_3$] and [pip][Y(hfac)$_2$(tfac)$_2$], a process which should lead to coalescence of hfac and tfac -CH= proton resonances in these two complexes. Other reactions of this type which occur at the same time as reactions 1 and 2 exchange hfac and tfac ligands into [pip][Y(hfac)$_4$] and [pip][Y(tfac)$_4$], respectively. Thus exchange of ligands can occur among all possible sites.

The second type of ligand exchange (reactions 3 and 4) involves exchanging a hfac ligand of one complex with another hfac ligand of another complex and exchanging tfac ligands also between two complexes. In reaction 3, the *tfac* ligand in [pip][Y(hfac)(tfac)$_3$] exchanges with a tfac of [pip][Y(hfac)$_2$(tfac)$_2$], a process which should manifest itself in the coalescence of the tfac -CH= proton resonances. In reaction 4, the *hfac* in [pip][Y-(hfac)$_2$(tfac)$_2$] exchanges with a hfac ligand of [pip]-[Y(hfac)$_3$(tfac)]; this process should be observed as a coalescence of the hfac methylene proton resonances of these two complexes. Relative rates of ligand exchange can be obtained from the temperature dependence of the methylene proton resonances (Figure 3).

Figure 3 reveals that at −58.0° the [pip][Y(hfac)$_3$-(tfac)] and [pip][Y(hfac)$_2$(tfac)$_2$] hexafluoroacetylacetonate -CH= proton resonance separation is 8.9 Hz while the separation is 9.7 Hz for the trifluoroacetylacetonate -CH= proton resonances of [pip][Y(hfac)$_2$-(tfac)$_2$] and [pip][Y(hfac)(tfac)$_3$]; at −16.0° the separation is 6.3 Hz (hfac) and 6.7 Hz (tfac). The coalescence temperatures of the -CH= proton resonances are −1.0° (hfac) and *ca.* 30° (tfac). These data and other hfac and tfac -CH= resonance separations, as well as the higher coalescence temperatures of tfac ring proton resonances (Figure 3), suggest that the hexafluoroacetylacetonate ligands intermolecularly exchange faster than the trifluoroacetylacetonate ligands.

Our presently available data do not permit us to speculate on a possible mechanism; however, the piperidinium cation may play an important role in any mechanism since the two reacting species are anionic.

Ligand-Exchange Equilibria in [pip][Y(hfac)$_4$]-[pip]-[Y(tfac)$_4$] System.—Ligand-exchange equilibria for the [pip][Y(hfac)$_4$]-[pip][Y(tfac)$_4$] system have been quantitatively characterized in deuteriochloroform solution. To describe these ligand-exchange equilibria we are re-

quired to specify three independent equilibrium quotients defined by the reactions

$$[pip][Y(hfac)_4] + [pip][Y(hfac)_2(tfac)_2] \overset{K_1}{\rightleftharpoons} 2[pip][Y(hfac)_3(tfac)] \quad (5)$$

$$[pip][Y(hfac)_3(tfac)] + [pip][Y(hfac)(tfac)_3] \overset{K_2}{\rightleftharpoons} 2[pip][Y(hfac)_2(tfac)_2] \quad (6)$$

$$[pip][Y(hfac)_2(tfac)_2] + [pip][Y(tfac)_4] \overset{K_3}{\rightleftharpoons} 2[pip][Y(hfac)(tfac)_3] \quad (7)$$

Quotients K_2 and K_3 were computed from the relative intensities of the trifluoroacetylacetonate methylene proton resonances. Failure to observe the hexafluoroacetylacetonate –CH= resonance for $[pip][Y(hfac)_4]$ at values of mole fraction <0.69 precluded calculation of K_1.[32]

The dependence of equilibrium molar fractions of total solute, defined by

$$f_{[pip][Y(hfac)_n(tfac)_{4-n}]} = \frac{[[pip][Y(hfac)_n(tfac)_{4-n}]]}{\sum_{n=0}^{4} [[pip][Y(hfac)_n(tfac)_{4-n}]]}$$

on the molar fraction of total ligand as hfac, f_{hfac}, in deuteriochloroform solution at −58.0° (open circles), −37.5° (solid circles), and −16.0° (open rhombi) is presented in Figure 4. Statistical curves yielding com-

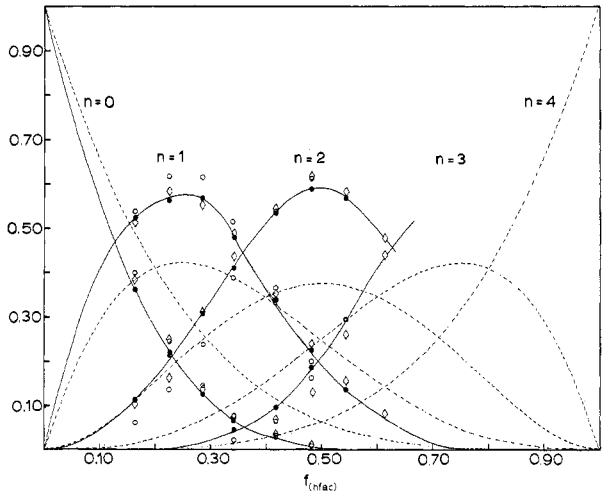

Figure 4.—Equilibrium distribution of $[pip][Y(hfac)_n(tfac)_{4-n}]$ complexes as a function of molar fraction of total ligand in deuteriochloroform solution at −58.0° (open circles), −37.5° (closed circles), and −16.0° (open rhombi). Total solute molarity is 0.34 *M*. Solid lines are experimental curves (−37.5°); dashed lines, theoretical curves assuming a random distribution of ligands.

puted values of $f_{[pip][Y(hfac)_n(tfac)_{4-n}]}$ assuming a completely random distribution of ligands are also included. These curves were calculated using the relation[20,24]

$$f_{[pip][Y(hfac)_n(tfac)_{4-n}]} = (f_{hfac})^n(1 - f_{hfac})^{4-n}\frac{4!}{n!(4-n)!}$$

Comparison of calculated and experimental curves indicates that the mixed complexes $[pip][Y(hfac)_n(tfac)_{4-n}]$ (n = 1–3) are favored at the expense of the parent complexes (n = 0 and 4).

Values of the equilibrium quotients K_2 and K_3 are, within experimental error, independent of ligand composition, f_{hfac}, and total solute concentration. The data, reported in Tables I and II, demonstrate that the values of K_2 and K_3 are 3–5 times larger than those expected assuming a random ligand distribution. The independence of K_2 and K_3 on ligand composition and total solute concentration suggests that the quotients of activity coefficients are constant in the range of concentrations used.[33]

To investigate whether enthalpy or entropy changes are the driving force in these ligand-exchange reactions, we have studied the equilibrium quotients as a function of temperature,[34] data for which are presented in Table III. Enthalpy and entropy changes at 25° were cal-

TABLE I
DEPENDENCE OF EQUILIBRIUM QUOTIENTS FOR THE $[pip][Y(hfac)_4]$–$[pip][Y(tfac)_4]$ SYSTEM ON SOLUTE COMPOSITION[a] AT −16.0°

f_{hfac}	K_2[b]	K_3[b]
0.164	...	6.8 ± 0.3[c]
0.225	...	8.4 ± 1.6
0.286	...	7.2 ± 0.7
0.342	...	7.5 ± 0.4
0.418	...	7.1 ± 1.6
0.482	...	7.0 ± 1.4
0.544	8.4 ± 0.5	...
0.614	6.4 ± 0.4	...
Mean of all spectral measurements	7.4 ± 0.8	7.3 ± 0.3
Statistical equilibrium quotients	2.25	2.67

[a] Solvent is deuteriochloroform; total solute molarity is 0.34 *M*. [b] Average of five spectral measurements. [c] All errors are estimated at the 95% confidence level.

TABLE II
DEPENDENCE OF EQUILIBRIUM QUOTIENTS FOR THE $[pip][Y(hfac)_4]$–$[pip][Y(tfac)_4]$ SYSTEM ON TOTAL SOLUTE COMPOSITION[a] AT −60°

Total molarity	K_2[b]	K_3[b]
0.342	11.9 ± 0.9[c]	8.4 ± 0.5
0.314	10.6[d] ± 3.2	6.8[d] ± 1.8
0.245	10.1 ± 0.9	7.8 ± 0.4
0.199	9.9 ± 1.1	7.8 ± 0.8
Mean of all spectral measurements	10.6 ± 0.6	7.8 ± 0.8
Statistical equilibrium quotients	2.25	2.67

[a] Deuteriochloroform solution; ±2°; f_{hfac} = 0.418. [b] Average of five spectral measurements. [c] All errors are estimated at the 95% confidence level. [d] Average of three spectral measurements.

TABLE III
TEMPERATURE DEPENDENCE OF EQUILIBRIUM QUOTIENTS FOR THE $[pip][Y(hfac)_4]$–$[pip][Y(tfac)_4]$ SYSTEM IN DEUTERIOCHLOROFORM

Temp, °C	K_2[a]	K_3[a]	Temp, °C	K_2[a]	K_3[a]
−58.0	11.4 ± 0.6[b]	10.4 ± 0.6	−37.5	8.2 ± 0.3	7.6 ± 0.4
−50.5	9.5 ± 0.3	7.5 ± 0.4	−28.5	7.7 ± 0.8	6.5 ± 0.3
−41.5	8.3[c] ± 0.7	6.7 ± 0.4	−16.0	7.4 ± 0.8	7.3 ± 0.3

[a] Mean of all spectral measurements; total solute molarity is 0.34 *M*. [b] All errors are estimated at the 95% confidence level. [c] Lit.[21] value 4.0 ± 0.5 at −40°.

(32) In a more dilute solution (total solute concentration 0.026 *M*) and at a mole fraction of 0.91, $[pip][Y(hfac)_4]$ is insufficiently soluble in deuteriochloroform at temperatures below 0° to permit observation of the hfac ring proton resonance and thus calculation of the equilibrium quotient, K_1, of reaction 5.

(33) Although activity coefficients for the five complexes of reactions 5–7 are unknown, they are probably close in value since the complexes are very similar. Under these conditions, the quotient of activity coefficients will be close to unity and the equilibrium quotients will approximately equal the thermodynamic equilibrium constant.

(34) Equilibrium in these ligand-exchange reactions is established very rapidly within the time required for temperature equilibration of the sample (*ca.* 10 min) at the prevailing temperature of the nmr probe. In an experiment designed to test this, K_2 = 9.96 in fair agreement with the value of 10.6 ± 0.6 of Table II.

culated from the slope and intercept, respectively, of a plot of log K *vs.* $1/T$. The data of Table III were treated by least-squares analysis including about 10–20 data points (K_2) and about 20–30 data points (K_3) at each temperature. These thermodynamic parameters, along with the free energy changes and the calculated entropy changes assuming statistical behavior, are summarized in Table IV.

TABLE IV
THERMODYNAMIC DATA FOR THE [pip][Y(hfac)$_4$]–[pip][Y(tfac)$_4$] SYSTEM IN DEUTERIOCHLOROFORM SOLUTION AT 25°

Reaction	ΔH, kcal/mol	ΔG, kcal/mol	ΔS, eu	Statistical ΔS, eu
5	...	...	...	1.95
6	-1.14 ± 0.27[a]	-0.95 ± 0.48	-0.61 ± 1.32	1.61
7	-0.79 ± 0.22	-0.98 ± 0.40	0.61 ± 1.11	1.95

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

Experimental entropy changes are less than statistical even at the upper 95% confidence limit and are nearly zero or zero within experimental error. Deviations from statistical behavior cannot be accounted for by these entropy changes. The important driving force in these ligand-exchange reactions is the exothermic enthalpy changes. It appears then that enthalpy changes can also effect deviations from statistical behavior in ligand-exchange reactions where values of equilibrium quotients are less than one order of magnitude larger than the expected statistical values. Further studies on other hfac–tfac systems are being carried out to verify this.

In a recent review, Fay[24] has pointed out that when ligands differ in electronic structure, equilibrium quotients for formation of mixed complexes will probably be appreciably larger than statistical. In addition, electrostatic effects may also contribute to the stability of mixed complexes when these contain both fluorinated and nonfluorinated diketonate ligands because the inductive effect of the fluorine atoms causes the charges on the donor oxygen atoms to differ. In the present system we have a fluorinated ($CF_3COCHCOCF_3$) and a partially fluorinated ($CF_3COCHCOCH_3$) diketonate ligand. Using a point charge model, the stabilization energy for the dodecahedral[4] [pip][Y(hfac)$_2$(tfac)$_2$] mixed complex relative to the parent complexes is given by $(e' - e'')^2/r$,[35] where $(e' - e'')$ is the difference in charge between the donor oxygen atoms of hfac and tfac ligands and r (= 2.32 Å) is the yttrium–oxygen distance. To attain a stabilization energy of 1 kcal/mol the difference in charge between the donor atoms need only be *ca.* 0.08 electron charge unit. Although electrostatic effects may have some stabilizing influence on the mixed complexes, especially [pip][Y(hfac)$_2$(tfac)$_2$], the enthalpy changes cannot be solely attributed to these effects.

Preferential solvation of the mixed complexes by deuteriochloroform over the parent complexes can also contribute to the stability of the mixed species. Figure 3, for example, reveals that the resonances of the tfac –CH= protons are shifted markedly to low field with decreasing temperature (see below) suggesting increased solvent–solute interactions preferentially at the tfac ends of the mixed species. This increased solvation at the lower temperatures stabilizes the mixed-ligand complexes. Although enthalpies and entropies of solvation for these [pip][Y(hfac)$_n$(tfac)$_{4-n}$] complexes in deuteriochloroform are unknown, it appears that the former makes some contribution to the ΔH of the ligand-exchange reactions [*cf.* the Zr(acac)$_4$–Zr(tfac)$_4$ system[20] and Ga(acac)$_3$–Ga(bzbz)$_3$ and Ga(acac)$_3$–Ga(hfac)$_3$ systems[25]].

Proton Chemical Shifts.—It was implied earlier and shown in Figure 3 that ring proton resonances of [pip][Y(hfac)$_n$(tfac)$_{4-n}$] complexes are temperature dependent. The dependence of –CH= proton chemical shifts on temperature is pictured in Figure 5 which also

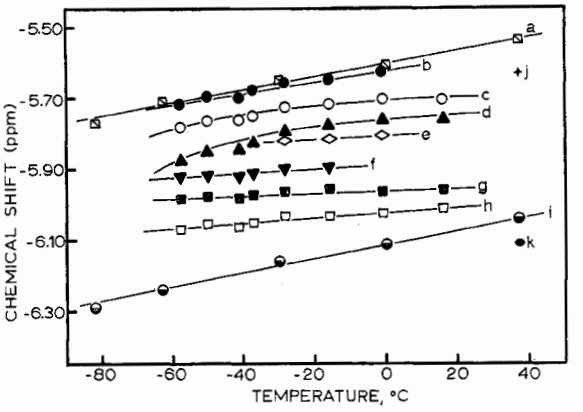

Figure 5.—Variable-temperature chemical shifts in deuteriochloroform solution of the ring proton resonances: (a) Co(acac)$_3$ (in dichloromethane);[30] (b) [pip][Y(*tfac*)$_4$]; (c) [pip][Y(hfac)(*tfac*)$_3$]; (d) [pip][Y(hfac)$_2$(*tfac*)$_2$]; (e) [pip][Y(hfac)$_3$(*tfac*)]; (f) [pip][Y(*hfac*)(tfac)$_3$]; (g) [pip][Y(*hfac*)$_2$(tfac)$_2$]; (h) [pip][Y(*hfac*)$_3$(tfac)]; (i) Ti(acac)$_2$Br$_2$ (in dichloromethane);[30] (j) pure sample of [pip][Y(*tfac*)$_4$]; (k) pure sampe of [pip][Y(*hfac*)$_4$].

shows the temperature-dependent ring proton frequencies for Co(acac)$_3$ and Ti(acac)$_2$Br$_2$ in dichloromethane.[36] Evidently, proton nmr frequencies shift downfield with decreasing temperature, a trend which appears to be general for β-diketonate complexes and which has been attributed to increased solvent–solute interaction *via* hydrogen bonding[21] at the lower temperatures.[36] The greater temperature dependence of the tfac proton frequencies of [pip][Y(hfac)$_2$(tfac)$_2$] allows the tfac ring proton resonance of [pip][Y(hfac)$_3$(tfac)] to be observed at the higher temperatures. It is also apparent that the temperature dependence of the tfac proton resonances is more pronounced than that of the hfac ligands. This would imply that solvent–solute interactions are more effective at the tfac ends of the complexes. This view is supported by chemical shift data in deuteriochloroform and in an "inert" solvent such as carbon tetrachloride. The hfac ring proton frequencies of [pip][Y(hfac)$_4$] are −6.11 ($CDCl_3$) and −6.10 ppm (CCl_4); the tfac –CH= proton chemical shifts of [pip][Y(tfac)$_4$] are −5.63 ($CDCl_3$)[18] and −5.57 ppm (CCl_4).

For an assumed 1:1 complex, for example, between a Y(tfac) ring and $CDCl_3$, Abraham[37] has put forth a method by which the equilibrium constant K for the equation *solvent* + *solute* ⇄ *complex*, and the enthalpy and entropy of formation can be evaluated from the temperature-dependent chemical shift data. If f

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is the fraction of complexed solute, the equilibrium constant is given by

$$K = \frac{f}{1-f} = \exp\left(\frac{-\Delta H^\circ}{RT}\right)\exp\left(\frac{\Delta S^\circ}{R}\right)$$

The value of f at any temperature is taken equal to $(\delta_t - \delta_0)/(\delta_c - \delta_0)$ where δ_t and δ_c are the observed chemical shifts at temperature t and the proton resonance frequency in the pure complex at 0°K, respectively; the proton chemical shift in an "inert" solvent such as carbon tetrachloride is taken to give δ_0. From the slope of a plot of log K against $1/T$, the enthalpy of complex formation can be estimated. To calculate these thermodynamic parameters, we have used the temperature-dependent ring proton frequencies (δ_t) of [pip][Y(tfac)$_4$] in the equilibrium mixture (Figure 5) to get δ_c (−6.06 ppm); δ_0 was taken as − 5.57 ppm, the chemical shift of [pip][Y(tfac)$_4$] −CH= resonance in carbon tetrachloride. The intercept and the slope of the log K *vs.* $1/T$ plot produced an entropy of formation of −12.9 ± 2.5 eu and an enthalpy of formation of −2.5 ± 0.6 kcal/mol, a value similar to the value of −2.7 ± 0.5 kcal/mol reported for a 1:1 complex between chloroform and acetone,[38] in which complex formation occurs *via* hydrogen bonding between the $CHCl_3$ proton and the carbonyl oxygen of acetone. It is tempting to suggest that hydrogen bonding occurs between $CDCl_3$ deuterium and the carbonyl oxygen atoms of the β-diketonate ligand in these metal–diketonate complexes.[39,40] However, the values of entropy and enthalpy of formation should be taken with caution in view of the assumptions[37] for and the criticisms[41] of this model.

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(40) Studies are being carried out in this laboratory to elucidate further whether hydrogen bonding occurs between the $CHCl_3$ proton and the carbonyl oxygens or between the $CHCl_3$ proton and the π electrons of the β-diketonate ring. Previous studies have not been conclusive as to the site of hydrogen bonding [*cf.* T. S. Davis and J. P. Fackler, Jr., *Inorg. Chem.*, **5**, 242 (1966)].
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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, ST. LOUIS UNIVERSITY, ST. LOUIS, MISSOURI 63103, AND ARIZONA STATE UNIVERSITY, TEMPE, ARIZONA 85281

The Syntheses and Properties of β,β′,β″-Triaminotriethylamine Chelates of the Tripositive Lanthanide Ions

BY JOHN H. FORSBERG,*[1a] THOMAS M. KUBIK,[1a] THERALD MOELLER,[1b] AND KENNETH GUCWA[1b]

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The reaction of β,β′,β″-triaminotriethylamine with a lanthanide(III) nitrate salt in anhydrous acetonitrile yields solid compounds of the type [Ln(tren)$_2$](NO$_3$)$_3$, [Ln(tren)$_2$NO$_3$](NO$_3$), and [Ln(tren)(NO$_3$)$_3$]. Nitrate ion coordination in several of the complexes is established by infrared data. Conductivity data indicate that [Ln(tren)(NO$_3$)$_3$] is the thermodynamically favored species in acetonitrile solutions containing the nitrate salts. However, nmr data establish Ln(tren)$_2^{3+}$ as the stable species in solutions containing the perchlorate salts. The enthalpy changes observed upon complexation of the lanthanide perchlorate salts in acetonitrile establish tetradentate coordination by the amine.

Introduction

High-coordinate lanthanide complexes derived from the strongly basic nitrogen donors ethylenediamine,[2] 1,2-propanediamine,[3] and diethylenetriamine[4] were isolated recently utilizing a nonaqueous solvent as the reaction medium. These species are rapidly hydrolyzed and must be handled under anhydrous conditions. Of special significance is the observation that these cationic complexes are enthalpy stabilized and possess considerable thermodynamic stability in acetonitrile.[4,5]

Coordination numbers of 6 through 12 have been observed in lanthanide complexes.[6,7] That such a wide variation occurs may be attributed to steric factors and electrostatic forces of attraction and repulsion, rather than bond orientation by the well-shielded 4f orbitals of the metal ion. Thus the large size of the lanthanide ions allows coordination of four bidentate ethylenediamine or 1,2-propanediamine molecules and three tridentate diethylenetriamine molecules. In the latter example, increased steric crowding was observed in the tris chelates with decreasing metal ion radius. Additional anion coordination was established in the tetrakis-ethylenediamine and -propanediamine chelates and was found to be dependent upon both anion size and metal ion size.

We report here the syntheses of the first lanthanide complexes derived from the tetradentate N donor β,β′,β″-triaminotriethylamine (tren) isolated as mono and bis chelates of the nitrate salts. The total coordination number in these species and its variation across the lanthanide series were determined by elemental analysis and infrared spectroscopy. Further characterization in solution was accomplished utilizing conductivity mea-

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