concentration of negative charge arising from the $(\delta-)$F–P$(\delta+)$ bond dipole and the fluorine lone pairs.

In the series $H_3BP(OMe)_3$, $H_3BPF(OMe)_2$, $H_3BPF_2(OMe)$, the CH_3 and BH_3 protons produce increasing and decreasing ASIS effects, respectively, in both aromatic solvents. Increasing the electronegativity of phosphorus along the series by fluorine substitution of OMe groups would tend to render both the CH_3 and BH_3 protons more acidic and this is also reflected in the increased deshielding of these nuclei in the series (Table I). The reason for the opposite progression of the ASIS effect at fluorine for the last two members of the series in C_6F_6 and C_6D_6 is not clear and it may be related to variations in solvent cluster geometries arising from differing steric requirements of the two solutes and/or a domination of van der Waals solute–solvent interactions.[9]

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Complexes of Nucleophiles with Rare Earth Chelates. I. Gas Chromatographic Studies[1a] of Lanthanide Nuclear Magnetic Resonance Shift Reagents

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Abstract: The present study reports the retention of many different ethers, ketones, alcohols, esters, olefins, and alkanes by gas-chromatographic columns with liquid phases composed of solutions of tris-β-diketonate rare earth chelates in squalane. The dependence of the interaction on the nature of the organic solute, the nature of the chelate ligand, the radius of the metal ion, and the degree of polymerization was investigated. The more nucleophilic organic compounds, for example, tetrahydrofuran (THF), were found to undergo much stronger interaction with the metal chelates than the less basic solutes. The Er(III) chelates of fluorinated β-diketonates (for example, the new ligand 3-trifluoroacetyl-*d*-camphorate anion, facam) underwent a much greater interaction with the nucleophiles than similar nonfluorinated Er(III) compounds. The retention time of THF increases exponentially with the inverse of the metal ionic radius in the facam chelates. The data indicate that this effect is due to a decrease in the extent of polymerization of the chelates with decreasing radius. In squalane, over the concentration range studied, the polymeric form of $Tb(facam)_3$ appears to be a dimer; molecular weight determinations support this conclusion. The regularities observed in the gc data can be used to predict the efficacy of various rare earth chelates as nmr shift reagents. Since the structure of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)erbium(III) is trigonal prismatic in the solid state, a reaction scheme is postulated in which a fused monocapped trigonal-prismatic dimer dissociates in solution to yield a monomer with a trigonal-prismatic structure. It is this monomer to which a donor becomes bonded to form a monocapped trigonal-prismatic adduct in both the gc and nmr studies.

Specific interactions between solutes and stationary phases have been employed in gas chromatography (gc) to resolve many mixtures which have proven difficult to separate by other means.[2–12] The formation of hydrogen-bonded associates was used in resolving racemic mixtures on asymmetric phases.[3] Metal salts and complexes have been found very useful in resolving other mixtures. For example, the affinity of the Ag(I) ion for the π electrons of olefins was used to efficiently separate alkenes from alkanes.[4] The association constants of the unstable Ag(I) olefin complexes have been measured as a function of the alkene structures,[6–8] and the equilibrium constant for the association of Cl^- with $SbCl_3$ has been measured as a function of the size of the alkali metal ion in the liquid phase.[5]

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(1) (a) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969. (b) Author to whom correspondence should be addressed at the Chemistry Department, The Weizmann Institute of Science, Rehovoth, Israel.

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Many discrete metal complexes and salts undergo specific interactions with a large number of organic compounds. The majority of such complexes are insoluble in organic solvents and/or unstable above their melting temperatures and thus can be used only as solid stationary phases.[9] However, some complexes and salts have been used successfully as liquid phases above their melting temperatures,[10,11] including some transition and representative metal β-diketonates.[12] Fortunately, many β-diketonate chelates possess the property of solubility in organic solvents and are thermally stable above their melting temperatures. In addition, a number of such complexes exhibit Lewis acid character.[13]

The present study deals with the interaction of alkanes, alkenes, ethers, ketones, esters, and alcohols with various tris(β-diketonato) rare earth complexes. Formally these chelates are coordinately unsaturated; the three bidentate ligands supply six donor atoms while the rare earth ions usually tend to have coordination numbers of at least 7.[14] The behavior of an organic donor D toward the chelates $\mathrm{LnL_3}$ can thus formally be represented by the equation

$$[(\mathrm{LnL_3})_n]_{7\text{-co}} \rightleftharpoons (\mathrm{LnL_3})_{6\text{-co}} \underset{-\mathrm{D}}{\overset{+\mathrm{D}}{\rightleftharpoons}} (\mathrm{LnL_3D})_{7\text{-co}}$$

where the subscripts 6-co and 7-co refer to 6 and 7 coordination, respectively. We are aware, however, that 6 coordination is extremely unusual but not unknown (*vide infra*) for the rare earth ions[14] and that even rare earth chelates with very bulky ligands (*e.g.*, tris(2,2,6,6-tetramethylheptanedionato)praseodymium(III)[15]) exist in the solid state as 7-coordinate dimers. Nevertheless, the concept of additional ligation embodied in the above equation is a useful one,[16] as it does express the well-known tendency of many rare earth chelates to form adducts with a wide variety of donor molecules.[14,17] This tendency, coupled with the generally high solubility of the chelates in organic solvents and good thermal stability, might cause these chelates to be very useful in resolving difficultly separable mixtures, including the separation of racemic solutes by gas–liquid chromatography. Several aspects of the interaction between such metal chelates and organic compounds were investigated: specifically, the dependence on the nature of the β-diketonate ligand, the nature of the nucleophile, the radius of the metal ion, and the degree of aggregation of the chelate.

Experimental Section

Organic Solutes. All organic solutes used in this study were obtained commercially.

Chelate Ligands. 2,6-Dimethyl-3,5-heptanedione (diisobutyrylmethane), H(dibm), was obtained commercially (Eastman Organic Chemicals). 2,2,6,6-Tetramethyl-3,5-heptanedione, H(thd), was obtained commercially (Pierce Chemical Co.). 1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione, H(fod), was prepared as reported earlier.[18] 3-Acetyl-*d*-camphor, H(acam), was prepared according to the method of Bruhl.[19] 3-Trifluoroacetyl-*d*-camphor, H(facam), was prepared according to the following method. 3-Bromo-*d*-camphor (127 g, 0.55 mol) and magnesium turnings (13.4 g, 0.55 g-atom) were stirred in 600 ml of absolute ether in a 2-l. three-necked, round-bottom flask fitted with a condenser and a dropping funnel. The mixture was heated to reflux. After about 10 min the solution turned milky, the heating oil bath was removed, and the reaction continued vigorously. After 40 min, most of the magnesium had reacted. The solution was cooled with an ice bath and 85 g (0.6 mol) of ethyl trifluoroacetate was added at a fast dropping rate. A vigorous reaction occurred and the mixture was cooled until the reaction slowed. After stirring for another 20 min at room temperature, the reaction mixture was refluxed for 1 hr and then cooled in an ice bath. Cold 1:1 HCl was slowly added until the aqueous phase had a pH 1. The ether layer was separated, washed with water, and dried over anhydrous $\mathrm{Na_2SO_4}$. After filtering, the ethereal solution was distilled twice under reduced pressure. The fraction boiling at 57° (1.5 mm) was collected: yield, 31%; $[\alpha]^{28}\mathrm{D}$ $-5.99°$ (neat).

Rare Earth Chelates. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)erbium(III), $\mathrm{Er(thd)_3}$, and tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)erbium(III), $\mathrm{Er(fod)_3}$, were prepared as reported earlier.[18,20]

Tris(3-trifluoroacetyl-*d*-camphorato)lanthanide(III), -yttrium(III), and -scandium(III) complexes [$\mathrm{Ln(facam)_3}$, $\mathrm{Y(facam)_3}$, and $\mathrm{Sc(facam)_3}$] were prepared as follows. Two solutions were prepared. For solution A, 15 mmol (3.70 g) of H(facam) was stirred into 100 ml of a 50% alcohol solution. A 10% $\mathrm{NH_4OH}$ solution was added slowly until all of the H(facam) had just dissolved. For solution B, 5 ml of a 1 *M* aqueous solution of metal chloride (5 mmol) was added to 20 ml of alcohol.

Solution A was added dropwise to solution B with vigorous stirring. The precipitate formed was stirred for another hour in the mother liquor after all of solution A had been added. The mixture was filtered and washed with 100 ml of a 50% alcohol solution and air-dried overnight. This procedure yielded almost exclusively solvated tris chelates for Sc(III), Tb(III), Sm(III), Pr(III), and Lu(III); for La(III), Y(III), and Er(III), considerable amounts of the tetrakis chelates were produced as well (*e.g.*, $\mathrm{NH_4La(facam)_4}$). *Anal.* Calcd for $\mathrm{C_{48}H_{60}F_{12}LaNO_8}$: C, 50.31; H, 5.28; N, 1.22; La, 12.12. Found: C, 49.90; H, 5.13; N, 1.30; La, 12.28). The dry precipitates were refluxed in methylcyclohexane (MCH) and filtered. This procedure separated the tris and tetrakis chelates, as the former are soluble in MCH and the latter are not.

The MCH was removed under reduced pressure to isolate the tris chelates. The Sc(III) and Tb(III) chelates were then recrystallized from an alcohol–water mixture. The Sm(III) and Pr(III) chelates were recrystallized from *n*-hexane, and the Lu(III) chelate was recrystallized from MCH. These recrystallizations yielded water- or alcohol-solvated chelates. Ansolvous chelates were obtained by heating *in vacuo* for several hours at ~105°. Final yields were 25–60%.

Thermogravimetric analysis (TGA) data for the tetrakis chelates of La(III) and Er(III) showed that heating at ~200° results in the loss of $\mathrm{NH_4}$ facam: $\mathrm{NH_4Ln(facam)_4} \rightarrow \mathrm{NH_4facam} + \mathrm{Ln(facam)_3}$. Calculated weight losses for this reaction are 22.9% for the La complex and 22.3% for Er. The observed weight losses are ~24% for both La and Er. Thus, the tris chelates of La(III), Er(III), and Y(III) were obtained by decomposition of the tetrakis salts at elevated temperatures. At 250–300° the tris complexes are volatilized with some decomposition. Elemental analyses of the anhydrous tris chelates produced by the above methods are given in Table I.

Bis(diisobutyrylmethanato)(hydroxo)erbium(III), $\mathrm{Er(OH)(dibm)_2}$,[21] was prepared by a modification of the method used for $\mathrm{Er(thd)_3}$. H(dibm) (20 mmol, 3.12 g) was dissolved in 10 ml of pure

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(21) The empirical formula $\mathrm{Er(OH)(dibm)_2}$ is used since the actual structure is not known. This formula is not intended to imply that the Er atom is five-coordinate. The molecular weight data (*vide infra*) indicate that $\mathrm{Er(OH)(dibm)_2}$ is a dimer at low concentrations and that association increases with increasing concentration. The mechanism of association is undoubtedly bridging through the dibm and/or OH oxygen atoms to give at least six-coordinate, and more likely seven-coordinate, rare earth ions.

Table I. Elemental Analyses[a] of the Anhydrous Tris M(facam)$_3$ Chelates

Metal	C, %		H, %		M, %		Mp, °C
	Calcd	Found	Calcd	Found	Calcd	Found	
La(III)	49.10	49.55	4.81	4.81	15.77	16.40	205–207.5
Pr(III)	48.99	48.84	4.80	4.83	15.96	14.14	211.5–213.5
Sm(III)	48.47	47.99	4.75	4.90	16.85	16.84	207.5–208.5
Tb(III)	48.01	47.63	4.70	4.80	17.65	17.77	185–188
Er(III)	47.57	48.69	4.66	4.90	18.40	17.70	(Glass)
Y(III)	52.06	50.60	5.10	5.16	10.70	11.24	207.5–209.5
Ln(III)	47.17	47.09	4.62	4.51	19.09	19.61	223–225
Sc(III)	54.93	54.97	5.38	5.45	5.72	6.22	142.5–145

[a] Obtained by Galbraith Laboratories.

Table II. Molecular Weight Studies of Lanthanide Chelates

Chelate	Solvent	Theoretical for monomer	Found	Ratio	Concn, *m*
La(facam)$_3$	CHCl$_3$	881	1275	1.4	*a*
Pr(facam)$_3$	CHCl$_3$	883	1150	1.3	*a*
Sm(facam)$_3$	CHCl$_3$	892	1050	1.2	*a*
Tb(facam)$_3$	CHCl$_3$	901	970	1.1	*a*
Er(facam)$_3$	CHCl$_3$	909	944[d]	1.0	*a*
Lu(facam)$_3$	CHCl$_3$	917	932	1.0	*a*
Sc(facam)$_3$	CHCl$_3$	787	910	1.2	*a*
Er(fod)$_3\cdot$H$_2$O[b]	*n*-C$_6$H$_{14}$	1071	1100	1.1	0.0346
Er(fod)$_3\cdot$H$_2$O[b]	*n*-C$_6$H$_{14}$	1071	1270	1.19	0.0621
Er(fod)$_3\cdot$H$_2$O[b]	*n*-C$_6$H$_{14}$	1071	1380	1.29	0.0939
Er(OH)(dibm)$_2$	*n*-C$_6$H$_{14}$	495	1000	2.02	0.0208
Er(OH)(dibm)$_2$	*n*-C$_6$H$_{14}$	495	1061	2.14	0.0545
Er(OH)(dibm)$_2$	*n*-C$_6$H$_{14}$	495	1140	2.30	0.0808
Sm(thd)$_3$	*n*-C$_6$H$_{14}$	700	711	1.02	*c*
Tb(thd)$_3$	*n*-C$_6$H$_{14}$	709	720	1.02	*c*
Dy(thd)$_3$	*n*-C$_6$H$_{14}$	712	715	1.01	*c*
Ho(thd)$_3$	*n*-C$_6$H$_{14}$	715	712	0.99	*c*

[a] Determined by Galbraith Laboratories, concentrations unknown. [b] Mp = 104–108°; see ref 18. [c] Concentration not reported; see ref 22. [d] The molecular weight measured in a less polar solvent, benzene, was found to be 1300.

ethanol containing a few drops of H$_2$O. A solution of 20 mmol (0.8 g) of NaOH in 16 ml of 50% ethanol was added to the H(dibm) solution. A test with pH paper indicated that the resulting clear solution was quite basic. As the pH was adjusted to near neutrality (by the addition of HNO$_3$) the solution became somewhat cloudy.

A solution containing 6.7 mmol (2.92 g) of Er(NO$_3$)$_3\cdot$5H$_2$O in 16 ml of 50% ethanol was prepared; 1 *M* NaOH was used to adjust the pH to near neutrality. A clear pink solution resulted upon the addition of the ligand stock solution. When the pH of the reaction mixture was slowly raised, an orange-pink oil which could not be solidified by stirring or air-drying was formed. This oil was dissolved in ~5 ml of boiling *n*-heptane and large pink platelets were formed when the temperature was reduced to ~−5°. After the product was filtered and washed with cold heptane, the yield was 0.8 g. The crystals were dried for 24 hr *in vacuo* over P$_4$O$_{10}$ at room temperature. Most of the sample melted in the broad range, 184–210° (uncorrected). *Anal.* Calcd for Er(OH)(dibm)$_2$, C$_{18}$H$_{31}$ErO$_5$: C, 43.70; H, 6.31; Er, 33.81; H$_2$O, 3.64.[22] Found: C, 43.90; H, 6.49; Er, 35.65; H$_2$O, 3.62.

Bis(3-acetyl-*d*-camphorato)(hydroxo)erbium(III), Er(OH)(acam)$_2$, was synthesized in a manner similar to that for Er(OH)(dibm)$_2$. Solution A was prepared with 5 ml of 1.2 *M* ErCl$_3$, 5 ml of H$_2$O, and 10 ml of ethanol. Solution B was prepared by dissolving 3.52 ml of 3-acetyl-*d*-camphor (18 mmol) and 1.15 ml of concentrated NH$_4$OH (18 mmol) in 30 ml of 50% ethanol. Solution B was added dropwise, with stirring, to solution A. Recrystallization of the crude product from hot acetone yielded pink crystals of Er(OH)(acam)$_2$. *Anal.* Calcd for C$_{24}$H$_{35}$ErO$_5$: C, 50.50; H, 6.18; Er, 29.30. Found: C, 49.82; H, 6.21; Er, 28.69.

Thermal Stability. TGA data for the anhydrous M(facam)$_3$ complexes were obtained with a Du Pont Model 950 thermogravimetric analyzer with a dry helium flow of 60 ml/min and a heating rate of 5°/min. All of these compounds were found to be stable above 220°, *i.e.*, above their melting temperatures which are in the neighborhood of 200°. In the case of Sc and, to some extent, also of Lu, Y, and Er, the vapor pressure is high enough to permit sublimation at a reasonable rate without appreciable decomposition at 250–300°.

Similarly, the solvated chelates, which are initially obtained in the preparation of the Ln(facam)$_3$ chelates, lose their solvent of crystallization in the range 100–130° when heated under the same conditions as above or *in vacuo*. This process was also monitored by infrared spectroscopy. This fact is important in the consideration of the use of these compounds as selective liquid phases for organic nucleophiles.

Molecular Weight Determinations. The concentration dependence of the molecular weight of the Er(fod)$_3\cdot$H$_2$O and the Er(OH)(dibm)$_2$ chelates in *n*-hexane was determined by osmometry on a Mechrolab Model 301A instrument and is shown in Table II. Data for some Ln(thd)$_3$ chelates are also given here,[23] as are the molecular weights of the facam chelates.

Gas Chromatographic Experiments. A mixture of the proper weights of the anhydrous chelates and squalane to give the required molality was diluted with chloroform, the solution added to Gas-Chrom Z (60–80 mesh), and the CHCl$_3$ evaporated to produce a 15% coating. The coated support was packed in a 3-m Teflon column, $^1/_8$ in. i.d. The columns containing the various chelates were conditioned overnight at 100° with helium as a carrier gas.

A Perkin-Elmer Model 800 gas chromatograph equipped with a flame ionization detector was used. Helium (pressure, 20 psi) was used as the carrier gas. The sample solutions consisted of 20% of the organic compound in ether. To minimize the amount of compound injected, a 1-μl syringe was washed with the sample solution and the "wet" empty needle was introduced into the hot injection port. The retention values of the gc peaks were corrected for the dead volume of the column (determined with methane) and were normalized to that of MCH.

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(22) The water content was calculated with the assumption that Karl Fischer reagent completely titrates OH$^-$.

(23) V. A. Mode and G. S. Smith, *J. Inorg. Nucl. Chem.*, **31**, 1857 (1969).

Table III. Relative Corrected Retention Times, α, at 100° [a]

Solute	Squalane	Er(thd)$_3$	Tris chelates Er(fod)$_3$	Tris chelates Er(facam)$_3$	Hydrolyzed chelates Er(OH)(dibm)$_2$	Hydrolyzed chelates Er(OH)(acam)$_2$
Methylcyclohexane	1.000	1.000	1.000	1.000	1.000	1.000
3-Methyl-1-hexene	0.515	0.504	0.519	0.500	0.506	0.510
3-Methylcyclohexene	1.055	1.038	1.023	1.030	1.041	1.040
Diethyl ether	0.123	0.150	0.499	0.152	0.157	0.146
Di-*n*-propyl ether	0.621	0.561	1.115	0.563	0.556	0.558
Di-*n*-butyl ether	2.470	2.391	4.718	2.485	2.416	2.403
Tetrahydrofuran	0.327	0.751	36.96^b	1.040	0.391	0.371
2-Butanone	0.204			0.351		0.242
2-Pentanone	0.420	0.568	20.56^b	0.698	0.463	0.450
2-Hexanone	0.905	1.195		1.500	0.960	0.940
2-Heptanone	1.968			3.110		1.996
3-Pentanone	0.452	0.573	17.33^b	0.699	0.481	0.487
3-Heptanone	1.994			2.964		1.961
4-Heptanone	1.831	2.152		2.766	1.818	1.806
Ethyl propionate	0.480	0.631	32.52^b	0.950	0.519	0.504
Ethyl acetate	0.219			0.476		0.252
n-Butyl acetate	1.039			2.154		1.062
n-Pentyl acetate	2.253			4.487		2.276
n-Hexyl acetate	4.825			9.391^b		4.671
2-Methyl-2-propanol	0.123	0.218	5.613^b	0.264	0.157	0.139
2-Methyl-2-butanol	0.320	0.674	11.92^b	0.663	0.379	0.348
2-Methyl-2-pentanol	0.664	1.373	24.70^b	1.381	0.775	0.689
2-Methyl-2-heptanol		6.010^b		6.050^b	3.230	2.913

[a] The columns: liquid phase, 15% coating of 0.131 *m* solution of the complex in squalane on Gas-Chrom Z; size, 3-m length, 2-mm i.d. The columns were conditioned overnight at 100°; carrier gas, helium. [b] Obtained on a short column, 60 cm × 2 mm.

Results and Discussion

The relative corrected retention times, α, of different organic compounds (hereafter called solutes) were obtained for columns with stationary phases consisting of solutions of Er(thd)$_3$, Er(fod)$_3$, and Er(facam)$_3$ (0.13 *m* in squalane) and of Er(OH)(dibm)$_2$ and Er(OH)(acam)$_2$ (0.17 *m* in squalane).[24] These data are given in Table III. The retention times, corrected for dead volume, were normalized to that of methylcyclohexane because this compound, an alkane, is assumed to undergo no significant specific interaction with the chelates. The data reflect the influence of the ligands on α. Very striking increases in retention occur in the solutions containing perfluoroalkyl substituents attached to the carbonyl carbon atom of the ligand, particularly for the oxygen-containing solutes. While in some instances the squalane solutions of hydrolyzed chelates (*i.e.*, Er(OH)(dibm)$_2$ and Er(OH)(acam)$_2$) give smaller values than pure squalane,[25] a squalane solution of Er(fod)$_3$ gives about an 80-fold increase in the relative corrected retention time of tetrahydrofuran (THF) over that in pure squalane.

The effect of the size of the metal ion of the chelate on the interaction with the solute was also determined. Chelates of H(facam) were chosen because these complexes, having perfluoromethyl groups attached to the carbonyl carbon atoms, show appreciable interaction with the oxygen-containing solutes. In addition, the chromatographic peaks obtained with these phases are symmetrical while those on the others studied show tailing, particularly with the alcohols.

The data presented in Table IV are the α values of different solutes in columns containing 15% coatings of 0.13 *m* solutions of M(facam)$_3$ chelates in squalane on an inert support. A plot of the data for some representative solutes as a function of $1/r$ is reproduced in Figure 1. For the olefins and dialkyl ethers studied α is unaffected by the size of the metal ion in the chelate, indicating negligible interaction between solute and chelate. On the other hand, the α value of THF, a cyclic ether with a greater tendency to act as a ligand toward metal ions, is strongly affected by changes in the ionic radius. A similar behavior is noted for the esters, ketones, and alcohols. For these solutes, the α values increase exponentially with the inverse of the ionic radius, the scandium phases providing consistent exceptions (Table IV).[26] Starting from a value smaller than or equal to that in pure squalane for the larger lanthanides, the α values increase by two- to fourfold as $1/r$ increases by 30%.

This behavior is consistent with the following equilibria

$$\mathrm{D(gas)} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{D(solution)} \tag{1a}$$

$$\mathrm{D(solution)} + \mathrm{chelate} \overset{K_2}{\rightleftharpoons} \mathrm{chelate \cdot D} \tag{1b}$$

where D is the donor solute, (gas) represents the solute in the gas phase, and (solution) refers to the solute in solution but not interacting with the chelate. Equation 1b describes the interaction of the solute with the chelate. In order to account for the symmetrical

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(24) Concentrations are given in molalities since this unit is temperature independent. That is, solutions made up at room temperature will have the same molality at the elevated temperatures in the gas chromatograph whereas the molarity would change because of volume changes of the solution.

(25) This phenomenon is similar to salting out and is probably due to nonspecific interactions in the liquid phase. It should be noted that the gc liquid phases actually contain ~10% by weight of the chelate, and thus the solubility properties of the liquid phases are undoubtedly somewhat different from those of pure squalane. In turn, the solubility of the organic solute in the liquid phase affects its rate of passage through the column.

(26) Normally the strength of interaction (in this case, as estimated by the α values) increases with increasing charge:radius ratio. It is obvious, however, that steric crowding must eventually limit the accessibility of the metal to the donors. The increase in α with increasing $1/r$ thus will ultimately fail to hold true because of a change in structure, and this is evidently the reason that the α values for the scandium chelate (which rarely has a coordination number greater than six) are much smaller than predicted from the rare earth portion of the curve (where the coordination numbers are probably seven).

Table IV. Relative Corrected Retention Time, α, at 100° [a]

Solute	M(facam)$_3$ Sc	La	Pr	Sm	Tb	Er	Y	Lu
Methylcyclohexane	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
3-Methyl-1-hexene	0.516	0.512	0.510	0.506	0.510	0.500	0.512	0.501
3-Methylcyclohexene	1.043	1.050	1.046	1.031	1.033	1.030	1.028	1.022
Diethyl ether	0.150	0.150	0.120	0.142	0.145	0.152	0.152	0.152
Di-*n*-propyl ether	0.556	0.551	0.538	0.559	0.568	0.563	0.565	0.567
Di-*n*-butyl ether	2.444	2.424	2.397	2.430	2.444	2.485	2.432	2.467
Tetrahydrofuran	0.392	0.501	0.494	0.568	0.696	1.040	1.019	1.479
2-Butanone	0.246	0.320	0.251	0.293	0.300	0.351	0.362	0.406
2-Pentanone	0.488	0.575	0.499	0.564	0.610	0.698	0.731	0.812
2-Hexanone	1.026	1.202		1.168	1.300	1.500	1.587	1.772
2-Heptanone	2.123	2.455	2.306	2.450	2.682	3.110	3.275	3.844
3-Pentanone	0.514	0.573	0.532	0.572	0.632	0.699	0.734	0.795
3-Heptanone	2.091	2.246	2.154	2.352	2.593	2.964	3.130	3.392
4-Heptanone	1.920	2.049	1.971	2.153	2.389	2.766	2.923	3.187
Ethyl propionate	0.536	0.685	0.592	0.667	0.768	0.950	1.031	1.164
Ethyl acetate	0.272	0.387	0.312	0.347	0.389	0.476	0.523	0.592
n-Butyl acetate	1.140	1.583	1.334	1.482	1.703	2.154	2.305	2.723
n-Pentyl acetate	2.378	3.299	2.809	3.222	3.577	4.487	4.884	5.747
n-Hexyl acetate	4.888	6.839	5.751	6.462	7.397	9.391	10.23	11.78
2-Methyl-2-propanol	0.1535	0.159	0.176	0.186	0.233	0.264	0.279	0.339
2-Methyl-2-butanol	0.369	0.391	0.380	0.455	0.519	0.663	0.689	0.829
2-Methyl-2-pentanol	0.730	0.798	0.901	0.900	1.074	1.381	1.436	1.742
2-Methyl-2-heptanol	3.109	3.301	3.437	3.770	4.589	6.050	6.248	
2-Propanol	*b*	0.174	0.120	0.179	0.203	0.286	0.300	0.445
2-Butanol	*b*	0.341	0.293	0.372	0.457	0.653	0.680	0.981
2-Pentanol	*b*	0.706	0.626	0.771	0.983	1.440	1.454	2.181
2-Hexanol	*b*	1.436	1.334	1.626	2.077	3.091	3.135	4.830
3-Hexanol	*b*	1.306	1.256	1.484	1.950	2.902	2.950	4.502
3-Methyl-2-butanol	*b*	0.569	0.659	0.637	0.828	1.231	1.254	1.884
3,3-Dimethyl-2-butanol	*b*	0.846	0.960	0.973	1.251	1.823	1.871	2.761
2-Methyl-1-butanol	*b*	1.003		1.222	1.417	2.020	2.044	3.314

[a] The columns: phase, 15% coating of 0.131 *m* solution of the complex in squalane on Gas-Chrom Z; size, 3-m length, 2-mm i.d. The columns were conditioned overnight at 100°; carrier gas, helium. [b] Very strong tailing.

chromatographic peaks, such equilibria must be established rapidly. This is expected for the gas–liquid equilibrium and is a good assumption for the complexation reaction since most similar reactions of rare earth complexes in solution are fast.[27,28] Six-coordinate complexes of the smaller scandium(III) ion with bulky β-diketonates show little tendency to form adducts;[29] for these systems the simplifying approximation that $K_2 = 0$ can be made (except perhaps in those cases where D is a very strong donor).

Since for a given ligand all the chelate phases are quite similar and principally differ only in the size of the metal ion, it may be assumed that the value of K_1 is solely dependent on the nature of the solute. Thus, for a given vapor pressure of a given solute, the same concentration of uncoordinated solute should be observed in each chelate phase. The validity of this assumption is supported by the constancy of α for each individual olefin and dialkyl ether shown in Table IV and Figure 1; in these cases complex formation is negligible.

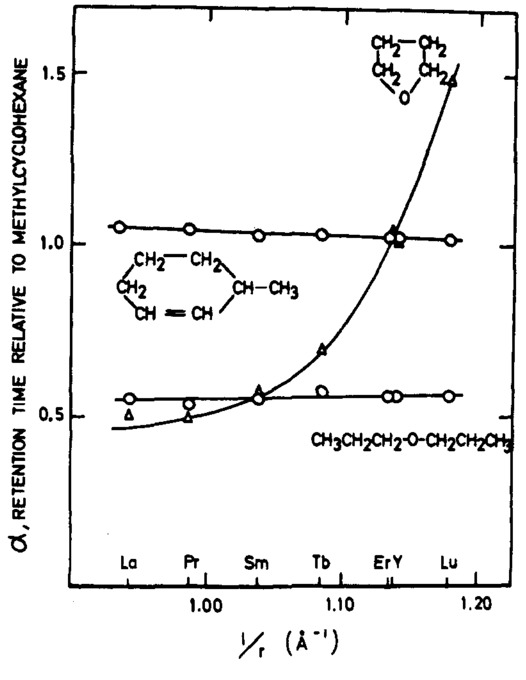

Figure 1. Gas-chromatographic retention data for THF, 3-methylcyclohexene, and di-*n*-propyl ether in liquid phases consisting of solutions of Ln(facam)$_3$ chelates in squalane as a function of the ionic radius of the Ln ion (see Experimental Section for details). Ionic radii for the trivalent rare earth metal ions were taken from N. E. Topp, "The Chemistry of the Rare Earth Elements," Elsevier, New York, N. Y., 1965, p 12; and T. Moeller, "The Chemistry of the Lanthanides," Reinhold, New York, N. Y., 1963, p 20.

Figure 2 illustrates the appropriate theoretical vapor pressure diagrams of a solute in equilibrium with two phases in the limit of infinite dilution. One phase is a solution of Sc(facam)$_3$ in squalane and the second is an equally concentrated solution of Ln(facam)$_3$ in squalane,[30] where the latter chelate is one which interacts with the solute. At infinite dilution of the solute ($X = 0$), the two curves have different slopes (Henry's

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[27] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968, p 155.

[28] S. J. Lippard, *Progr. Inorg. Chem.*, 8, 156 (1967).

[29] R. E. Sievers, K. J. Eisentraut, C. S. Springer, Jr., and D. W. Meek, *Advan. Chem. Ser.*, No. 71, 141 (1968).

[30] The symbol Ln represents any of the lanthanide metals, and, because Y(III) behaves similarly to the Ln(III) ions, it will also represent Y(III) here but not Sc(III).

Table V. Complexation Constants, K_2', for Solutes with Ln(facam)$_3$ Chelates[a]

Solute	Pr	Sm	Tb	Er	Y	Lu
Tetrahydrofuran	0.261	0.451	0.775	1.654	1.600	2.775
2-Hexanone		0.139	0.268	0.463	0.548	0.728
2-Heptanone	0.086	0.154	0.263	0.465	0.543	0.810
n-Pentyl acetate	0.181	0.355	0.504	0.887	1.054	1.417
n-Hexyl acetate	0.176	0.322	0.513	0.921	1.093	1.409
2-Methyl-2-pentanol	0.233	0.233	0.470	0.889	0.967	1.386
2-Methyl-2-heptanol	0.105	0.213	0.476	0.946	1.009	

[a] 0.13 *m* solutions of Ln(facam)$_3$ in squalane at 100°.

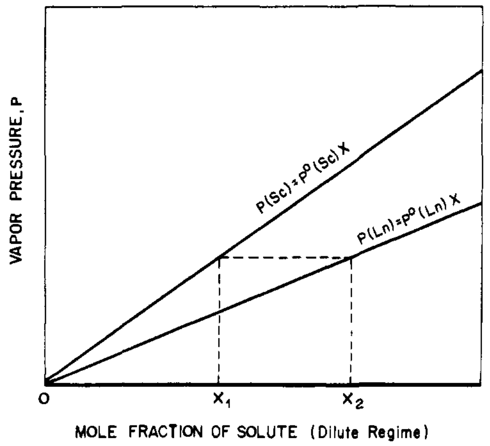

Figure 2. Theoretical phase diagram of the dilute solution of a volatile solute.

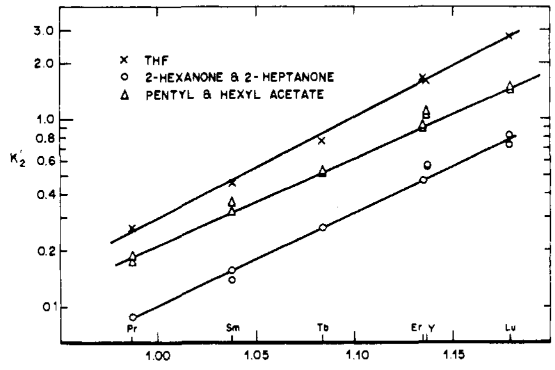

Figure 3. Plot of the log of the complexation constants, K_2', of THF, 2-hexanone, 2-heptanone, pentyl acetate, and hexyl acetate with Ln(facam)$_3$ chelates as a function of the ionic radius. Sources of ionic radii are the same as for Figure 1.

law constants, P^0(Sc) and P^0(Ln)). In the case of Sc, all the dissolved solute is assumed to be uncoordinated to the chelate. On the other hand, for the phase containing the Ln compound, the vapor pressure is reduced because an appreciable fraction of the dissolved molecules is complexed with the chelate. The ratio of the concentrations of complexed solute to uncomplexed solute is

$$\frac{[\mathrm{D(complexed)}]}{[\mathrm{D(solution)}]} = \frac{X_2 - X_1}{X_1} = \frac{P^0(\mathrm{Sc}) - P^0(\mathrm{Ln})}{P^0(\mathrm{Ln})} \quad (2)$$

Substitution of eq 2 in the equilibrium expression for eq 1b gives

$$K_2' = K_2[\mathrm{chelate}] =$$

$$\frac{[\mathrm{D(complexed)}]}{[\mathrm{D(solution)}]} = \frac{P^0(\mathrm{Sc})}{P^0(\mathrm{Ln})} - 1 = \frac{\alpha(\mathrm{Ln})}{\alpha(\mathrm{Sc})} - 1 \quad (3)$$

where α(Ln) and α(Sc) are the normalized corrected retention times in the Ln and Sc columns, respectively, which are inversely proportional to the Henry's law constants. The limit of infinite dilution of the solute in the stationary phase is approached in those glc experiments involving symmetrical peaks arising from extremely small quantities of solutes ($<10^{-5}$ g). Thus K_2' becomes a constant, since the concentration of the chelate is in such great excess that its concentration can be considered to remain unchanged during the interaction with the solute.

The calculated values of K_2' are summarized in Table V for the heavier homologs of each series. For the example of THF on Lu(facam)$_3$, the K_2' value of 2.8 indicates that a THF molecule spends 73% of its time, while in the liquid phase, complexed with the Lu chelate.

Figure 3 shows that the plot of log K_2' *vs.* $1/r$ is a straight line for 2-alkanones, alkyl acetates, and THF. Two different hypotheses, separately or in combination, can be advanced to explain the relationship between log K_2' and $1/r$. (1) The Ln(facam)$_3$ chelates exist in squalane in the monomeric form and the complexation constant, K_2, is inversely proportional to the radius of the metal ion. This would be compatible with charge density arguments.[31] (2) The Ln(facam)$_3$ chelates exist in squalane in the form of aggregates with the degree of polymerization being a function of the radius, as in the case of the rare earth tropolonate chelates.[32] The change of the extent of aggregation with $1/r$ could then either affect K_2 or change the concentration of the reactive chelate species (assumed to be the monomer in eq 1b and 3) to produce the observed behavior.

If hypothesis 1 were true or if K_2 were unaffected by the extent of the aggregation of the chelate postulated in hypothesis 2, K_2' would be a linear function of the chelate concentration for any given metal ion. On the other hand, if hypothesis 2 were the case, the function would not necessarily be linear owing to variations in the extent of aggregation with concentration. Furthermore, the measured K_2' could have contributions from the different interactions of the solute with the monomer and each of the oligomeric forms of the chelate present.

In Table VI, the α values of THF in Sc(facam)$_3$ and Tb(facam)$_3$ columns at different concentrations and temperatures are summarized, and from them the

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(31) Reference 17, p 388.

(32) E. L. Muetterties, H. Roesky, and C. M. Wright, *J. Amer. Chem. Soc.*, **88**, 4856 (1966).

Table VI. Temperature and Concentration Dependence of α(THF)[a] in Sc(facam)$_3$ and Tb(facam)$_3$ Columns

Chelate	Concn,[b] m	60°	70°	80°	90°	100°
Sc(facam)$_3$	0.0315	0.298	0.308	0.318	0.335	0.352
Sc(facam)$_3$	0.0633	0.304	0.320	0.333	0.353	0.368
Sc(facam)$_3$	0.1382	0.346	0.354	0.363	0.376	0.390
Tb(facam)$_3$	0.0320	0.432 (0.298)[c]	0.445 (0.308)[c]	0.459 (0.318)[c]	0.473 (0.335)[c]	0.486 (0.352)[c]
Tb(facam)$_3$	0.0650	0.505 (0.305)[c]	0.512 (0.321)[c]	0.523 (0.333)[c]	0.535 (0.354)[c]	0.548 (0.369)[c]
Tb(facam)$_3$	0.1307	0.691 (0.341)[c]	0.686 (0.351)[c]	0.681 (0.360)[c]	0.682 (0.374)[c]	0.692 (0.388)[c]

[a] Normalized against methylcyclohexane. [b] Solution in squalane. [c] The interpolated value of α(THF) on a column of Sc(facam)$_3$ of the same molality.

complexation constants, K_2', were calculated and are presented in Table VII.

Table VII. Temperature and Concentration Dependence of the Complexation Constant for THF, K_2'(THF), with Tb(facam)$_3$

Column	60°	70°	80°	90°	100°
0.0320 m Tb(facam)$_3$	0.450	0.445	0.443	0.412	0.381
0.0650 m Tb(facam)$_3$	0.656	0.595	0.571	0.511	0.485
0.1307 m Tb(facam)$_3$	1.026	0.954	0.892	0.924	0.783

By plotting K_2' *vs.* chelate concentration in the THF-Tb(facam)$_3$ system (Figure 4), it was found that K_2' is a linear function not of the concentration but of its square root. Thus $K_2' = K_2\sqrt{[\text{chelate}]}$. A simple explanation of this behavior is that, in solution, the principal associative equilibrium is that of dimerization.

$$2\text{Tb(facam)}_3 \underset{}{\overset{K_3}{\rightleftharpoons}} (\text{Tb(facam)}_3)_2 \tag{4}$$

If it is assumed that only the monomeric form gives appreciable association with the solute and that, in squalane in the concentration range of 0.03–0.13 m, most of the chelate is in the dimeric form, then

$$K_2' = K_2[\text{monomer}] = \frac{K_2}{\sqrt{K_3}}\sqrt{[\text{dimer}]} \approx \frac{K_2}{\sqrt{K_3}}\sqrt{\frac{[\text{chelate}]}{2}} \tag{5}$$

A plot of log K_2' *vs.* $1/T$ (°K) gives the reaction enthalpy.

$$\frac{\partial \ln K_2'}{\partial(1/T)} = \frac{\partial\left[\ln K_2' - \dfrac{\ln K_3}{2}\right]}{\partial(1/T)} = \frac{1}{R}\left[\frac{\Delta H_3{}^\circ}{2} - \Delta H_2{}^\circ\right] \tag{6}$$

For the 0.13 m solution of Tb(facam)$_3$ in squalane, $\Delta H_3{}^\circ/2 - \Delta H_2{}^\circ = 1.59$ kcal/mol. This small value indicates that the enthalpy necessary to form 1 mol of monomeric Tb(facam)$_3$ from the dimer ($-\Delta H_3{}^\circ/2$) is almost counterbalanced by the enthalpy resulting from the formation of one THF–Tb(facam)$_3$ bond ($\Delta H_2{}^\circ$).

Further supporting evidence for the existence of a trend in the association of the Ln(facam)$_3$ chelates is seen in the molecular weight data in Table II. The relationship between dimer formation and size of the central atom for the facam chelates parallels that implicit in our interpretation of the previous results. It seems, therefore, that the concentration of the active monomeric species increases with $1/r$, a behavior consistent with the dominating influence of K_3 on the complexation constant, K_2'.

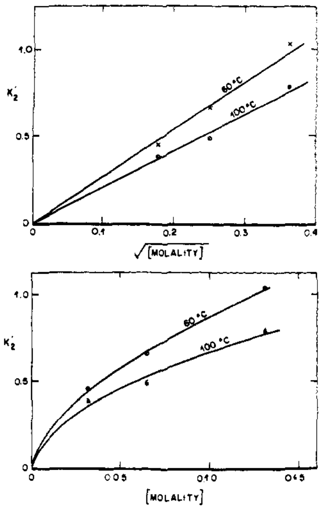

Figure 4. Bottom: complexation constant, K_2', of THF with Tb(facam)$_3$ as a function of the concentration of Tb(facam)$_3$ in the liquid phase. Top: complexation constant, K_2', of THF with Tb(facam)$_3$ as a function of the square root of the concentration of Tb(facam)$_3$ in the liquid phase.

The fact that Er(thd)$_3$ undergoes a greater interaction with the complexing solutes than Er(OH) (dibm)$_2$, even though the ligands are bulkier in the former chelate, can possibly be explained in a similar manner. The molecular weight data in Table II indicate that the monomeric structure probably predominates for Er(thd)$_3$ in solution. On the other hand, the solution molecular weight data in Table II indicate that the less sterically crowded compound, Er(OH)(dibm)$_2$, is strongly associated and is dimeric at the concentrations at which monomeric Er(thd)$_3$ predominates. The bulky thd ligands would be expected to be much more effective in preventing association with another large chelate than the approach of a smaller solute molecule. Qualitatively, this comparison indicates that the Er(thd)$_3$ dimer (if such exists) is more easily broken apart than the Er(OH)(dibm)$_2$ dimer (or higher polymer). The dimerization constant K_3 is undoubtedly much larger for Er(OH)(dibm)$_2$ than for Er(thd)$_3$, and reference to eq 5 shows that K_2' (and ultimately α) is correspondingly reduced for Er(OH)(dibm)$_2$.

The fact that the Er(III) chelates of the fluorinated ligands, H(fod) and H(facam), show much greater interactions with the complexing solutes than the nonfluorinated Er(thd)$_3$ chelate is most likely due to an increase in complex acidity (which in turn is due to a decrease in ligand basicity).[33] Differences in association between the fod, facam, and thd chelates are probably

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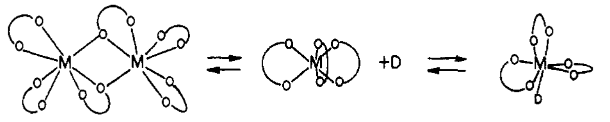
(33) Reference 17, p 411.



I. FUSED MONOCAPPED TRIGONAL PRISMATIC DIMER

II. TRIGONAL PRISMATIC MONOMER

III. MONOCAPPED TRIGONAL PRISMATIC ADDUCT

Figure 5. Postulated structural features accompanying interaction of donors with lanthanide chelates in gas-chromatographic experiments and in nuclear magnetic resonance shift reagent appliations.

small and play only a minor role in the increased interactions.

Recent X-ray structural determinations[15,34–36] make it possible to postulate the nature of the species involved in the interactions within the chromatographic column. Figure 5 shows the anticipated structures of β-diketonates of the type studied here. As we have suggested might be the case,[37] $Er(thd)_3$ has a trigonal-prismatic structure[34] rather than octahedral. The six-coordinate momomer is expected to be more active as a Lewis acid than the dimer which is already seven coordinate. In our model the structural precedent for the fused monocapped trigonal-prismatic dimer is $Pr_2(thd)_6$.[15] Two structural precedents exist for the monocapped trigonal-prismatic adduct: $Dy(thd)_3(H_2O)$[35] and $Lu(fod)_3(H_2O)$.[36] The energy required to dissociate the dimer in some cases may not be very great. Simply dissolving the complex in a solvent may be sufficient to make the monomeric species predominate in solution for some complexes, while for others, oligomerized species may be dominant. It should also be noted that the crystal structures further support our contentions concerning the trend of dimerization with ionic radius. The larger lanthanides from La to Gd form dimeric thd complexes, $Ln_2(thd)_6$, Tb and Dy form both dimers and monomers, $Ln(thd)_3$, and the smaller members from Ho to Lu form monomers.[34]

In conclusion, we would like to note the relevance of these gc studies to other areas of chemistry. A field which has attracted great attention in the last year or so is the use of rare earth chelates as nmr shift reagents.[38,39] It has been reasoned in the nmr studies that the rare earth ion exerts its effect on the spectra by coordination to the organic donor molecule. Due to rapid exchange the resulting "shifted" spectra are actually the average of the spectra of the free and complexed species. The present gc work provides independent confirmation that such coordination occurs in solution, so that higher coordinate lanthanide complexes are formed. The thd chelates, $Eu(thd)_3$ in particular, were the first to be widely used as shift reagents. But, as seen in the gc studies, the fod chelates show interactions with a wider variety of donors than do the thd chelates; furthermore, the $Ln(fod)_3$–organic donor complexes were judged to be more stable than the corresponding thd complexes because of the much larger retention times of the donors on the $Ln(fod)_3$ columns. We thus expected $Eu(fod)_3$ to be a more effective shift reagent than $Eu(thd)_3$. This expectation has been fully confirmed experimentally.[39]

The gc results can thus be used to make the following predictions regarding the efficacy of various rare earth chelates as nmr shift reagents. (1) Chelates containing fluorinated ligands (*e.g.*, fod) should be better shift reagents than chelates with nonfluorinated ligands (*e.g.*, thd). (2) Chelates with little tendency to polymerize, *e.g.*, those with bulky ligands, $Ln(thd)_3$ and $Ln(fod)_3$, are preferable to those which are strongly polymerized (*e.g.*, chelates with small ligands or hydrolyzed chelates, $Ln(dibm)_2OH$ and $Ln(acam)_2OH$).

Finally, we note the applicability of the gc method to a problem of widespread synthetic and practical interest—that of separating enantiomers of a given organic compound. In several of the systems which we examined, the solute spends most of its time in the liquid phase associated with the chelate. If a chelate containing an enantiomeric ligand is chosen as the liquid phase, racemic solutes might be resolved. In this connection, we note that an nmr shift reagent study shows that such a chelate, tris[3-(*tert*-butylhydroxymethylene)-*d*-camphorato]europium(III), preferentially coordinates the *R* isomer of *d*-phenylethylamine in an $R + S$ mixture.[40] This occurs even though the solution probably contains a mixture of all possible diastereomers (with respect to configuration about the metal) of the chelate because of its kinetic lability.[41]

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(34) J. P. R. de Villier and J. C. A. Boeyens, *Acta Crystallogr.*, in press.

(35) C. S. Erasmus and J. C. A. Boeyens, *J. Cryst. Mol. Struct.*, **1**, 83 (1971).

(36) J. C. A. Boeyens and J. P. R. de Villier, *ibid.*, **1**, 297 (1971).

(37) (a) J. E. Sicre, J. T. Dubois, K. J. Eisentraut, and R. E. Sievers, *J. Amer. Chem. Soc.*, **91**, 3476 (1969); (b) C. S. Springer, Jr., Ph.D. Dissertation, The Ohio State University, 1967, p 85.

(38) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(39) R. E. Rondeau and R. E. Sievers, *ibid.*, **93**, 1522 (1971), and references cited therein.

(40) G. M. Whitesides and D. W. Lewis, *ibid.*, **92**, 5625 (1970).

(41) NOTE ADDED IN PROOF. The recent interesting report [H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *ibid.*, **93**, 5913 (1971)] that trifluoroacetyl-*d*-camphor complexes interact with a wide range of optically active alcohols, ketones, esters, epoxides, and amines confirms our earlier data[1a] and offers a broadly useful approach to the determination of enantiomeric compositions.