THERMODYNAMICS OF MOLECULAR ASSOCIATION BY GAS–LIQUID CHROMATOGRAPHY

σ-DONOR MOLECULES AND DIMERIC 3-TRIFLUOROACETYLCAMPHOR-ATES OF Mn(II), Co(II) AND Ni(II)

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SUMMARY

A simplified gas chromatographic technique has been developed for measuring the thermodynamics of 1:1 molecular associations between Group V and VI σ-donor molecules and the title metal chelates in non-coordinating squalane solution. Employing a squalane reference column and an inert reference standard, stability constants, $K_{(m)}$, were obtained from solute retention parameters according to the equation $K_{(m)} \cdot m_A = r/r_0 - 1 = R'$, where r_0 is the relative retention of the solute with respect to the inert reference standard on a squalane column and r is the relative retention of the solute with respect to the inert reference standard on a column containing a molal concentration m_A of the metal chelate in squalane. R' has been defined as "retention increase" due to complexation. Gibbs–Helmholtz parameters have been obtained from the ln K *vs.* $1/T$ plot, both graphically and by a computerized non-linear regression analysis.

Thermodynamic data for 1:1 σ-donor–metal acceptor adduct formation have been measured in a non-polar medium where solvation effects are virtually absent. Stability constants decrease in the order alcohols > cyclic ethers > ketones > esters > aldehydes > ethers for oxygen donors with Ni(II) ≫ Co(II) > Mn(II) at 100 °C. $\Delta H°$ and $\Delta S°$ values of the 1:1 association of 30 σ-donor molecules with [Ni(tfacCam)₂]₂ in squalane at 75–125 °C have been measured. All adduct formations are exothermic and accompanied by loss of entropy. No linear relationship between $\Delta H°$ and $\Delta S°$ has been observed.

The data have been used to discuss the nature of interactions involved. Comparison of $\Delta H°$ values for oxygen and sulfur donors with Ni(II) revealed that the nickel chelate is a borderline acid with regard to the hard–soft acid–base concept of

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Pearson. The data imply pronounced electrostatic interactions in the adduct formations. Merits and restrictions of the gas chromatographic technique for studying ligand–transition metal interactions are discussed in detail.

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INTRODUCTION

The thermodynamics of molecular association have recently been extensively studied by gas–liquid chromatography (GLC) in non-electrolytic solutions. If a 1:1 molecular complex is formed rapidly and reversibly between a volatile compound B and a non-volatile compound A, e.g.:

$$A + B \overset{K}{\rightleftharpoons} AB$$
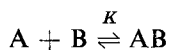
the stability constant, K, can be obtained from GLC retention data[1–3]. From the temperature dependence of ln K, all terms of the Gibbs–Helmholtz equation ($\Delta H°$, $\Delta S°$, $\Delta G°$) can also be calculated[4]. In practice, the volatile compound B, hereafter called the solute, is eluted through a column containing pure complexing agent A or, preferably, a dilute solution of A in an inert non-volatile solvent S.

This method has been used successfully for the thermodynamic study of molecular associations as a result of hydrogen bonding[4–14], charge-transfer interaction[15–22] and olefin–transition metal complexation[1–4,23–27]. The approach is claimed[3,11,21,22] to be strongly competitive with other commonly used methods for determining chemical equilibria (calorimetry and IR, UV, visible and NMR spectroscopy). Obvious advantages are accuracy, speed, simplicity, reproducibility and the absence of self-association of the solute applied at infinite dilution and highest purity.

At present, there appear no comprehensive thermodynamic data available on the association equilibria of Group V and VI σ-donor molecules with metal coordination compounds in non-polar non-coordinating media. We consider GLC to be a useful means of obtaining such data.

Selective complex-forming inorganic column materials have been widely applied for analytical purposes in gas chromatography, employing the metal complexes (viz., carboxylates[28–31], salicylaldimines and glyoximes[32,33], β-diketonates[34–36], phthalocyanins[37]) either as solids[29,33,34], polymers[38], dispersions[28,30,37] or solutions in coordinating[31] and non-coordinating[35,36] solvents. The above systems are, however, not suitable for a thermodynamic study of the σ-donor–metal ion acceptor association equilibria involved.

In order to obtain thermodynamic data according to the Purnell (class A) GLC approach[3], the metal chelates employed should meet the following requirements: (a) non-volatility and high thermal stability; (b) solubility in a non-coordinating solvent suitable for GLC (e.g., squalane); (c) reversible and rapid complexation with σ-donor molecules of distinct stoichiometry (1:1); (d) sufficient complexing strength at elevated temperatures and in high dilution ($<10^{-1} m$); (e) absence of dissociation or polymerization equilibria over a broad concentration range.

The number of metal coordination compounds satisfying the above conditions

will obviously be small. The closest approach has been made by Castells and Catoggio[31], who studied the molecular association of amines with metal stearates. However, the solvent used (quadrol) itself complexes with the metal ions and therefore no meaningful data for the formation constants were obtained. More recently, Sievers and co-workers[35,36] studied the association of a number of σ-donor molecules with dilute solutions of lanthanide tris-β-diketonates in squalane. However, no linear relationship between the substrate retention data and the metal chelate concentration was observed owing to a dissociation equilibrium of the dimeric metal chelates involved in solution[35].

It had earlier been found[39] that nickel bis-3-trifluoroacetylcamphorate, Ni(tfacCam)$_2$, dissolved in squalane provides an excellent system for the GLC study of the association with σ-donor solutes. Essentially, all of the criteria outlined above are met by this chelate. The association equilibria of σ-donor solutes with nickel and related metal chelates of 3-trifluoroacetylcamphor (tfacCam) have now been studied in detail. A simplified GLC technique described earlier[24,25] employing relative retention data has been used for a comprehensive thermodynamic study of the equilibria involved.

EXPERIMENTAL

Metal chelates

Bis-3-trifluoroacetylcamphorato (tfacCam) chelates of Mn(II), Co(II) and Ni(II) were obtained from the corresponding metal chloride hydrates and barium bis-3-trifluoroacetylcamphorate, Ba(tfacCam)$_2$, in ethanol in nearly quantitative yields[39,40]. Purification was accomplished by extraction and recrystallization from *n*-hexane and subsequent sublimation at 100–230 °C and $4 \cdot 10^{-3}$ mm Hg. The anhydrous chelates were stored over phosphorus pentoxide. They are soluble in common organic solvents. Eu(tfacCam)$_3$ was prepared according to ref. 41.

Organic solutes

The solutes used were commercial products obtained from local stores. Inherent to the GLC method, no purification of the substrates was necessary.

Reference solute

Commercial cyclohexane was used throughout as an inert reference standard.

Columns

Two columns (2 m × 1.75 mm I.D., glass) were used for the GLC experiments, as described below.

Reference column (15 wt.-% of squalane on Chromosorb P). A 1-g amount of squalane (Applied Science Labs., State College, Pa., U.S.A.) was dissolved in 5 ml of chloroform and the solution added to 5.8 g of Chromosorb P, 80–100 mesh, acid-washed, DMCS-treated (Johns-Manville, Denver, Colo., U.S.A.). The chloroform was removed *in vacuo* in a rotary evaporator and the material (approximately 2 g) packed into the glass column. The ends of the column were sealed with glass-wool.

Metal chelate-containing columns (15 wt.-% of the required molal concentration

of the metal chelates in squalane on Chromosorb P). In a typical experiment, 55.3 mg of anhydrous $[Ni(tfacCam)_2]_2$ and 1 g of squalane $(5 \cdot 10^{-2} \, m)$ were dissolved in 5 ml of dry chloroform, 5.8 g of Chromosorb P, 80–100 mesh, acid-washed, DMCS-treated, were added, and the mixture was agitated manually until it became homogeneous. The solvent was then removed *in vacuo* and the packing dried over phosphorus pentoxide. The material was subsequently filled into the glass column.

Gas chromatographic procedure

The gas chromatograph used was a Barber Coleman Series 5000 instrument designed for two-column operation. The carrier gas (helium, purified to remove water with molecular sieve) was divided equally between the two columns with a home-built injection port. Simultaneous injection of the solutes on to both columns was thus possible. The columns were connected separately with a flame ionization detector (FID) (250 °C), electrometer and recorder.

After conditioning the columns at 100 °C under 30 p.s.i.g. of helium for 12 h, gas chromatographic measurements were started. Operating temperatures were 75, 100 and 125 °C. The column bath temperature was controlled and measured to within ± 0.1 °C.

The solutes were injected as diluted vapors together with cyclohexane as the inert reference standard and methane for adjusting for the gas hold-up (dead volume) in the apparatus. It was found important to minimize the amount of solute to be injected: a 10-μl gas-tight syringe was washed with the sample vapor and, after washing it several times with air, approximately 5 μl of the "empty" syringe volume were injected. The minute amount of solute thus introduced prevented overloading of the metal complex with substrate, which otherwise resulted in lowering of retention and peak tailing. The instrument was consequently operated at highest sensitivity with a signal-to-noise ratio of about 10. It was ensured that variation of the sample size (1:50) did not change the relative retention for interacting solutes. No variation of the relative retention of complexing solutes had been observed as a result of different flow-rates of carrier gas, which suggested that the kinetics of complexation were rapid. The stability of the metal chelate-containing stationary phases had been checked throughout the measurements by repeated injection of 2-pentanone, the inert reference standard cyclohexane and methane. No change in the relative retention of the solute was noticed, which suggested that no decomposition of the metal chelates occurred at the operating temperatures. The absolute retention times also remained constant over that period, so that no loss of stationary phase (at 30 p.s.i.g. of helium) through bleeding had taken place. Furthermore, no irreversible loss of solute on the complex-forming stationary phase had been observed, as judged by the identical relative peak areas obtained by simultaneous injection of the solute and reference compound into both columns.

In order to ensure that the column material and the support (Chromosorb P) had no influence on the partition of the solute between the gaseous and complexing liquid phases, two different column types, each containing a $5 \cdot 10^{-2} \, m$ solution of $[Ni(tfacCam)_2]_2$ in squalane, had been prepared. The retention of tetrahydrofuran with respect to cyclohexane was the same $(t_s/t_r = 8.55)$ at 100 °C with a packed column of the type described above and with a 50-m stainless-steel capillary column (0.25 mm I.D.; Handy and Harmon Tube Co., Norristown, Pa., U.S.A.), coated by

the dynamic plug method. In addition, seven different support materials (Chromosorb P), coated with 15 wt.-% of squalane, differing in mesh size and silanization and acid-washing procedures, were also tested. It was found that the support which gave least tailing for polar solutes was Chromosorb P, 80–100 mesh, acid-washed, DMCS-treated, and this material was therefore chosen for all experiments.

The number of theoretical plates of the columns, n, was approximately 1000 per meter for non-interacting solutes, e.g., cyclohexane. This figure decreased with increasing interaction of complexing solutes with the metal chelates. Such an observation had earlier been made with a related complexing system[26].

Calculation of the retention increase (R') and of the thermodynamic data

Retention times, adjusted for the gas hold-up, were measured as the distance between the net maximum peak heights of the solute and the methane peaks. The adjusted retention time of the solute, t_s, was then related to that (t_r) of the inert reference standard, cyclohexane, which was co-injected, i.e., $t_s/t_r = r$ (r = relative retention of a solute with respect to cyclohexane). The relative retention of a solute obtained for a column containing a metal chelate dissolved in squalane, r, and the relative retention of the same solute obtained for the reference column containing pure squalane, r_0, were then used to calculate the retention increase, R', according to the equation $r/r_0 - 1 = R'$. From the plot of R' versus the molal concentration, m_A, $K_{(m)}$ was obtained (see below). $\Delta H°_{(m)}$ and $\Delta S°_{(m)}$ values were obtained from the least-squares best linear fit of ln $K_{(m)}$ versus $1/T$, both graphically and statistically by computer analysis. $\Delta H°_{(m)}$ and $\Delta S°_{(m)}$ values were also obtained from the best non-linear fit together with standard deviations by statistical computer analysis[42,43]. The computer (Hewlett-Packard Calculator, Series 9800) was programmed by Mr. H. R. Karfunkel, Chemistry Department, University of Tübingen, G.F.R. All thermodynamic data thus obtained refer to the molality concentration scale. $K_{(m)}$ values can be converted into the molarity scale by using the equation $K_{(c)} = K_{(m)}/\varrho$, where ϱ is the density of squalane at the temperature of the gas chromatographic measurement. The observed linearity of the density versus temperature plot for straight-chain hydrocarbons[44] had been used to extrapolate the densities of squalane at 75, 100 and 125 °C from relevant literature data[15,19,21].
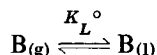
Density of squalane (g/ml):
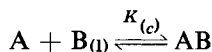75 °C: 0.774
100 °C: 0.757
125 °C: 0.740.

With these figures, the thermodynamic data refering to the molarity concentration scale have been obtained.

THEORETICAL

Consider a volatile solute B, eluting through a column containing a dilute solution of a non-volatile additive A in a non-volatile inert solvent S. For the simplest case, in which a 1:1 complex is formed between A and B, two equilibria occur:

$$B_{(g)} \xrightleftharpoons{K_L°} B_{(l)}$$

and

$$A + B_{(1)} \underset{\longleftarrow}{\overset{K_{(c)}}{\rightleftharpoons}} AB$$

or

$$K_L{}^\circ = \frac{c_{B(1)}}{c_{B(g)}} \tag{1}$$

and

$$K_{(c)} = \frac{a_{AB}}{a_A a_{B(1)}} = \frac{c_{AB}}{c_A c_{B(1)}} \cdot \frac{\gamma AB}{\gamma A \gamma B_{(1)}} \tag{2}$$

where $K_L{}^\circ$ is the partition coefficient of B between the gaseous and pure liquid phase S, $K_{(c)}$ is the thermodynamic stability constant of AB in S and a_i is the activity of the species i, with the convention that $a_i \rightarrow c_i$ as $c \rightarrow 0$ (i.e., the activity coefficient, $\gamma_i \rightarrow 1$ as $c \rightarrow 0$). As both AB and $B_{(1)}$ are infinitely dilute under the conditions of the GLC experiment, eqn. 2 can be rewritten as

$$K_{(c)} \cdot a_A = \frac{c_{AB}}{c_{B(1)}} \tag{3}$$

The total amount of solute present in the liquid phase S is $c_{B(1)} + c_{AB}$.

Hence the apparent partition coefficient K_L, assuming no volume change on dissolution of B, is

$$K_L = \frac{c_{B(1)} + c_{AB}}{c_{B(g)}} \tag{4}$$

This can be rewritten as

$$K_L = \frac{c_{B(1)}}{c_{B(g)}} + \frac{c_{AB}}{c_{B(g)}} = \frac{c_{B(1)}}{c_{B(g)}} + \frac{c_{AB}}{c_{B(1)}\,a_A} \cdot \frac{c_{B(1)}\,a_A}{c_{B(g)}} = K_L{}^\circ + K_L{}^\circ K_{(c)}\,a_A \tag{5}$$

or

$$K_{(c)} \cdot a_A = \frac{K_L}{K_L{}^\circ} - 1 \tag{6}$$

Thus, $K_{(c)}$ can be obtained[1,2] from the plot of K_L versus a_A (eqn. 5). From eqn. 6, a very useful correlation between $K_{(c)}$ and GLC retention data is obtained if a reference column, containing pure solvent S, and an inert non-coordinating reference standard is employed[24,25].

It is also useful to introduce the molality concentration scale, as A is preferably dissolved in a weighed amount of the solvent S. For the determination of the temperature dependence of $\dot{K}$, measurements can therefore be carried out with only one column of known molality as this concentration unit is independent of temperature. If the density ϱ of the solvent S is known precisely at the given temperature, $K_{(c)}$ might be calculated from $K_{(m)}$ according to the equation $K_{(c)} = K_{(m)}/\varrho$.

With very dilute solutions of A in the solvent S, the convention holds that

$\gamma_A \to 1$, and thus $a_A \to m_A$, if m_A refers to the molal concentration of A in S. Eqn. 6 can be rewritten as

$$K_{(c)} \cdot \varrho \cdot m_A = K_{(m)} \cdot m_A = \frac{K_L}{K_L{}^\circ} - 1 \qquad (7)$$

The partition coefficient of the solute B in the solvent S, $K_L{}^\circ$, is defined by

$$K_L{}^\circ = \frac{V_N{}^\circ}{V_L{}^\circ}$$

and the apparent partition coefficient observed when complexation occurs is defined by

$$K_L = \frac{V_N}{V_L}$$

where $V_N{}^\circ$ is the corrected net peak maximum retention volume of the solute B in the pure solvent S, V_N is the corrected net peak maximum retention volume of the solute B in the solution of A in the solvent S, $V_L{}^\circ$ is the volume of the pure solvent S, and V_L is the volume of the solution of A in the solvent S. Eqn. 7 can now be rewritten as

$$K_{(m)} \cdot m_A = \frac{V_N}{V_N{}^\circ} \cdot \frac{V_L{}^\circ}{V_L} - 1 \qquad (8)$$

For a non-complexing inert reference standard B*, it is assumed that $K^*{}_{(m)} = 0$. From eqn. 8, it follows for B* that

$$\frac{V_N{}^*}{V_N{}^{\circ *}} \cdot \frac{V_L{}^\circ}{V_L} = 1 \qquad (9)$$

As all column parameters are equal for the solute and reference compound, eqns. 8 and 9 can be combined by substitution for $V_L{}^\circ / V_L$ to give

$$K_{(m)} \cdot m_A = \frac{V_N}{V_N{}^\circ} \cdot \frac{V_N{}^{\circ *}}{V_N{}^*} - 1 = \frac{r}{r_0} - 1 = R' \qquad (10)$$

with

$$\frac{V_N}{V_N{}^*} = \frac{t}{t^*} = r$$

and

$$\frac{V_N{}^\circ}{V_N{}^{\circ *}} = \frac{t^\circ}{t^{\circ *}} = r_0$$

where r is the relative retention of the solute B with respect to the inert reference standard B* with a column containing the molal concentration of the additive A in the solvent S, and r_0 is the relative retention of the same solute with respect to the same reference standard with a reference column containing the pure solvent S. According to eqn. 10, the retention increase R' is linearly related to m_A at a given temperature if a 1:1 molecular complex is formed. As only relative retention data are measured, no

knowledge of gas chromatographic data such as flow-rate of carrier gas, column pressure drop, volume of liquid phase, column length and recorder speed is required. Eqn. 10 is also independent of the type of columns used[40].

Recently, a similar treatment has been used[27,45] in a re-investigation of the classical olefin–silver ion system. As the high concentration of silver nitrate in ethylene glycol is critical in view of a salting-out effect[2], lithium nitrate solutions of the same molality in ethylene glycol have been used as the reference column. Again, the use of an inert reference standard simplifies the GLC approach considerably[45].

RESULTS

The β-keto-enolate anion of 3-trifluoroacetylcamphor (tfacCam)[35] appears to be a unique ligand for metal ions, exhibiting novel and useful properties. Chelates of various metal ions can be conveniently and quantitatively obtained in non-aqueous media by metal exchange with the easily accessible barium bis-tfacCam salt[39,41]. Important features of the tfacCam chelates are their good solubilities in apolar solvents, pronounced stability and strong lone-pair molecular acceptor properties. Thus, lanthanide–tris-tfacCam chelates[35] and $(CO)_2Rh^I(tfacCam)$[24-26,46], dissolved in squalane, have been successfully employed in GLC as stable stationary phases for the interaction with σ-donor solutes[35] and olefins[46], respectively. $Eu(1R\text{-tfacCam})_3$ has recently been introduced as a versatile NMR chiral shift reagent[47].

TfacCam chelates of divalent transition metals have now been obtained for Mn(II), Co(II) and Ni(II)[39,40]. The Fe(II) chelate could not be prepared owing to atmospheric oxidation to $Fe(tfacCam)_3$. $Mn(tfacCam)_2$, $Co(tfacCam)_2$ and $Ni(tfacCam)_2$ are dimeric in n-hexane. The dimeric nature and good solubility in non-coordinating solvents contrast sharply with the properties of the related 3-formylcamphorate chelates of Mn(II), Co(II) and Ni(II), which are trimeric and insoluble in apolar solvents[48]. The dimeric structure of the tfacCam chelates of Mn(II), Co(II) and Ni(II) in apolar media is particularly interesting, as β-diketonate chelates of these ions are usually trimeric[49] or monomeric[50] in the solid state[51] and in solution[52]. A UV spectroscopic study of various concentrations of $[Ni(tfacCam)_2]_2$ in cyclohexane at 25 °C has been made (Table I) in order to verify a possible monomer–trimer association equilibrium. No deviation from Beer's law, however, is observed at concentrations $<10^{-5} M$, which suggests that only one definite structure is present. As molecular weight determinations in apolar solvents by vaporimetry identified the species as dimers[40], it is concluded that the tfacCam chelates of Mn(II), Co(II) and Ni(II) are also dimeric and non-dissociative in the C_{30} hydrocarbon squalane ($\leqslant 5 \cdot 10^{-2} m$). This

TABLE I

UV SPECTROSCOPY OF $[Ni(tfacCam)_2]_2$ IN CYCLOHEXANE

Values given are absorption at the wavelength specified.

Wavelength (nm)	Concentration $(M_{Ni_2}) \times 10^5$			
	0.5	1.5	2.5	3.5
320	0.16	0.36	0.62	0.90
270	0.06	0.17	0.20	0.44

assumption has been verified by GLC experiments (see below) at temperatures between 75 and 125 °C.

The molecular structure shown in Fig. 1 is proposed for the dimers in analogy with intermediate structures that are believed to occur in the association equilibria of Co(II)[53,54], and Ni(II)[55] acetylacetonates with σ-donor substrates. The molecular structure shows that the two free octahedral coordination sites of the two octahedra sharing edges via oxygen bridges may be occupied by σ-donor ligands, L. This structure is likely to break down in strongly coordinating solvents with the formation of the solvent–bis-adducts of the monomer[39]. Under the conditions of the GLC experiment, however, the 1:1 association equilibrium may be observed readily, as only minute amounts of σ-donor solute are applied in a non-polar medium.
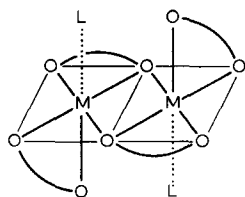

Fig. 1. Proposed molecular structure for [M(tfacCam)₂]₂ (L = σ-donor substrate).

The gas chromatographic behaviour of various σ-donor solutes was studied with columns containing molal solutions of [M(tfacCam)₂]₂ (M = Mn, Co or Ni) in squalane at 100 °C. In all instances, interaction between the solutes and the metal chelates was observed, as shown by an increased retention volume of the solutes compared with that of the squalane reference column (i.e., $R' > 0$). In Table II, results

TABLE II

RETENTION INCREASE, R', OF σ-DONOR MOLECULES WITH [M(tfacCam)₂]₂ OF DIFFERENT MOLAL CONCENTRATIONS IN SQUALANE AT 100 °C

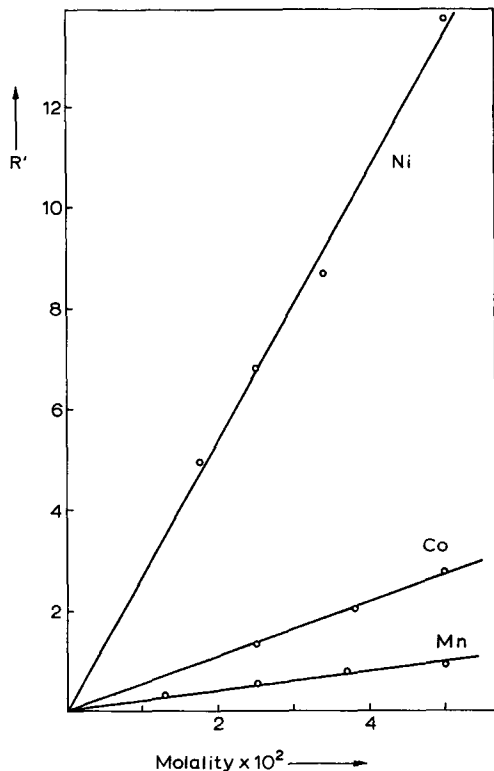| Species	Concentration, $m_A \times 10^2$ (per dimer)	Substrate			
		THF	Trimethylene sulfide	2-Pentanone	Ethyl propionate
[Mn(tfacCam)₂]₂	5.0	0.99	0.04	0.37	0.32
	3.7	0.80	0.02	0.27	0.24
	2.5	0.56	0.01	0.21	0.19
	1.3	0.33	0.01	0.14	0.10
[Co(tfacCam)₂]₂	5.0	2.75	0.35	0.42	0.27
	3.8	2.08	0.26	0.33	0.21
	2.5	1.36	0.18	0.20	0.11
[Ni(tfacCam)₂]₂	5.0	13.72	2.81	1.45	0.68
	3.4	8.67	1.74	0.92	0.45
	2.6	6.80	1.40	0.83	0.38
	1.7	4.96	1.01	0.54	0.25

Fig. 2. Retention increase, R', of tetrahydrofuran as a function of the molal concentration of [M(tfacCam)$_2$]$_2$ (M = Mn, Co or Ni) in squalane at 100 °C.

for the retention increase, R' (eqn. 10), of four representative solutes at different concentrations of [M(tfacCam)$_2$]$_2$ at 100 °C are listed. In all instances, a linear (zero intercept) relationship between R' and m_A is obtained, as required by eqn. 10. The slope of the lines, passing through the origin, corresponds to the formation constant $K_{(m)}$. This is shown for the solute tetrahydrofuran (THF) in Fig. 2. The stability of the adducts of THF with the dimeric tfacCam chelates of Ni, Co and Mn decreases in the order Ni(II) $\gg$ Co(II) $>$ Mn(II).

From the linear relationship observed between R' and m_A (eqn. 10), it can be concluded that:

(a) a 1:1 molecular complex is formed reversibly between A and B;

(b) the metal chelate dimers retain their structural integrity in dilute (squalane) solution, i.e., no dissociation or association occurs at concentrations $<5 \cdot 10^{-2} m$;

(c) no salting out effect[2] is observed in the concentration range employed;

(d) assumptions and simplifications made in obtaining eqn. 10 are essentially justified.

Thus, eqn. 10 describes well the correlation between $K_{(m)}$, m_A and R' for B. It should be noted that no linear relationship between R' for σ-donor solutes and the molal
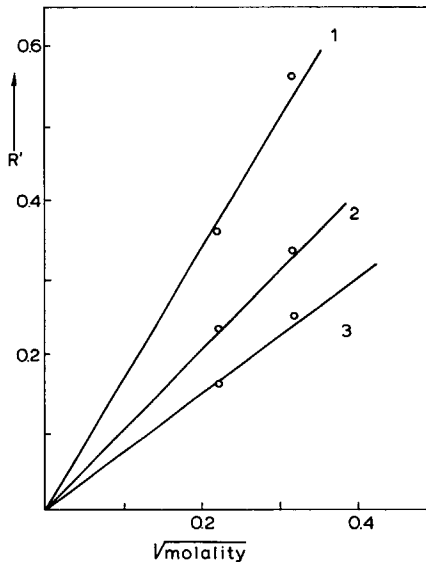
Fig. 3. Retention increase, R', of σ-donor solutes as a function of the square root of the molal concentration of Eu(tfacCam)$_3$ in squalane at 100 °C. 1 = Tetrahydrofuran; 2 = ethyl propionate; 3 = 2-pentanone.

concentration of rare earth metal tris-β-diketonate chelates had been observed[35,36]. Instead, a linear relationship between R' and the square root of the molal concentration was noted. This behaviour has been attributed[35] to a dimer–monomer dissociation equilibrium of the chelates, which persists in squalane at 100 °C, with only the monomer being capable of complexing with the solute. This observation has been verified in this work on the association equilibrium of Eu(tfacCam)$_3$[41,47] and tetrahydrofuran, and the square root relationship, i.e.,

$$K_{(m)} \cdot m_A^{\frac{1}{2}} = R' \tag{11}$$

TABLE III

STABILITY CONSTANTS, $K_{(m)}$ kg/mole*, OF THE MOLECULAR ASSOCIATION OF σ-DONOR SOLUTES WITH [M(tfacCam)$_2$]$_2$ (M = Mn, Co OR Ni) IN SQUALANE AT 100 °C**

Substrate	[M(tfacCam)$_2$]$_2$		
	Mn(II)	Co(II)	Ni(II)
Tetrahydrofuran	20 (2.0)***	55 (0.2)	270 (14)
Trimethylene sulfide	0.5	7.0 (0.3)	53.2 (2.9)
2-Pentanone	7.4 (1.4)	8.4 (0.3)	29.3 (2.0)
Ethyl propionate	6.7 (0.5)	5.4 (0.5)	13.9 (0.7)

* $K_{(c)}$ can be calculated according to the equation $K_{(c)} = K_{(m)}/\varrho$; $\varrho_{\text{Squalane}}^{100} = 0.757$ kg/l.

** Data for $K_{(m)}$ were obtained graphically from the best linear fit of R' vs. m_A with zero intercept (eqn. 10) using the data in Table II.

*** Values in parentheses represent standard deviations.

TABLE IV

RETENTION INCREASE, R', OF σ-DONOR MOLECULES WITH [Ni(tfacCam)$_2$]$_2$ OF DIF-
FERENT MOLAL CONCENTRATIONS IN SQUALANE AT 75, 100 AND 125 °C

Temperature (°C)	Substrate	Concentration, $m_{Ni_2} \times 10^2$			
		5.0	3.4	2.6	1.7
75	Tetrahydrofuran	21.16	14.36	11.48	7.89
	Trimethylene sulfide	4.67	2.92	2.42	1.58
	2-Pentanone	2.18	1.48	1.15	0.84
	Ethyl propionate	0.93	0.64	0.55	0.35
100	Tetrahydrofuran	13.72	8.67	6.80	4.96
	Trimethylene sulfide	2.81	1.74	1.40	1.00
	2-Pentanone	1.45	0.92	0.83	0.54
	Ethyl propionate	0.68	0.45	0.38	0.25
125	Tetrahydrofuran	7.06	4.68	3.65	2.93
	Trimethylene sulfide	1.66	1.09	0.85	0.66
	2-Pentanone	0.93	0.63	0.52	0.39
	Ethyl propionate	0.45	0.31	0.24	0.19
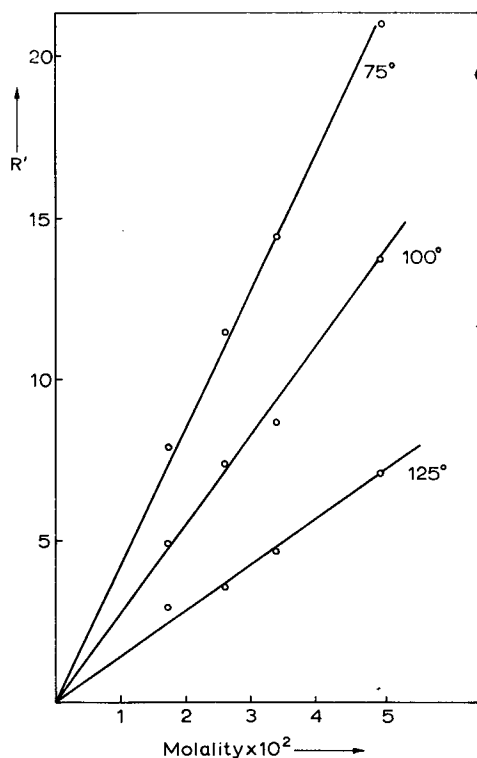
Fig. 4. Retention increase, R', of tetrahydrofuran as a function of the molal concentration of
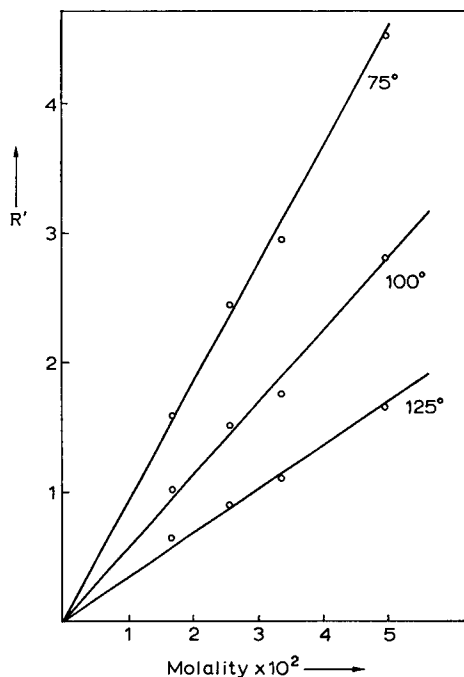[Ni(tfacCam)$_2$]$_2$ in squalane at 75, 100 and 125 °C.

Fig. 5. Retention increase, R', of trimethylene sulfide as a function of the molal concentration of [Ni(tfacCam)$_2$]$_2$ in squalane at 75, 100 and 125 °C.

has indeed been obtained in squalane at 100 °C (see Fig. 3). This result should be remembered in view of the importance of Eu(tfacCam)$_3$ as a chiral PMR shift reagent[47], indicating that the donor–acceptor chemistry involved in solution is complex.

Table III lists the stability constants, $K_{(m)}$, of the molecular association of four representative σ-donor solutes with [M(tfacCam)$_2$]$_2$ (M = Mn, Co or Ni) in squalane at 100 °C obtained from the data in Table II. The accuracy of the results is estimated to be 5–10%. For the interpretation of the $K_{(m)}$ data, it is useful to obtain the Gibbs–Helmholtz parameters $\Delta H°$ and $\Delta S°$ according to the equation

$$RT \ln K = -\Delta G° = -\Delta H° + T\Delta S° \tag{12}$$

Such data were obtained from a study of the temperature dependence of the association equilibria of σ-donor solutes with [Ni(tfacCam)$_2$]$_2$ in squalane.

Measurements were made for four representative solutes (tetrahydrofuran, trimethylene sulfide, 2-pentanone and ethyl propionate) at 75, 100 and 125 °C for different molal concentrations of [Ni(tfacCam)$_2$]$_2$ in squalane. The results are summarized in Table IV and Figs. 4 and 5. Again, the linear relationship between R' and m_A according to eqn. 10 is strictly observed for all solutes at all temperatures. Stability constants, $K_{(m)}$, were calculated from the slope of the lines obtained graphically from the best linear fit of R' versus m_{Ni} with zero intercept (e.g., Figs. 4 and 5). Data for $K_{(m)}$ for three temperatures (75, 100 and 125 °C) are listed in Table V. The

TABLE V

THERMODYNAMICS OF THE 1:1 MOLECULAR ASSOCIATION OF σ-DONOR MOLE-
CULES WITH [Ni(tfacCam)$_2$]$_2$ IN SQUALANE AT 75–125 °C (MOLALITY CONCENTRA-
TION SCALE)

Substrate	$K_{(m)}$ (kg/mole)*			$-\Delta H°_m$ (kcal/mole)	$\Delta S°_m$ (entropy units)
	75 °C	100 °C	125 °C		
Tetrahydrofuran	432	274	142	6.3	−5.9
Trimethylene sulfide	91.0	55.5	33.5	5.55	−7.1
2-Pentanone	43.5	28.5	18.5	4.7	−6.0
Ethyl propionate	18.5	13.0	9.5	3.75	−4.9

* Graphically extrapolated from the plot of R' vs. m_{Ni} (Table IV) with zero intercept.

accuracy of the $K_{(m)}$ data is estimated to be 5–10%. Assuming $\Delta H°$ is independent of
temperature between 75 and 125 °C, the plot of ln $K_{(m)}$ versus $1/T$ should give straight
lines according to the linear form of the Gibbs–Helmholtz equation, i.e.,

$$\ln K = -\frac{\Delta H°}{R} \cdot \frac{1}{T} + \frac{\Delta S°}{R} \qquad (13)$$

Results obtained for four solutes are shown in Fig. 6. Except for tetrahydro-

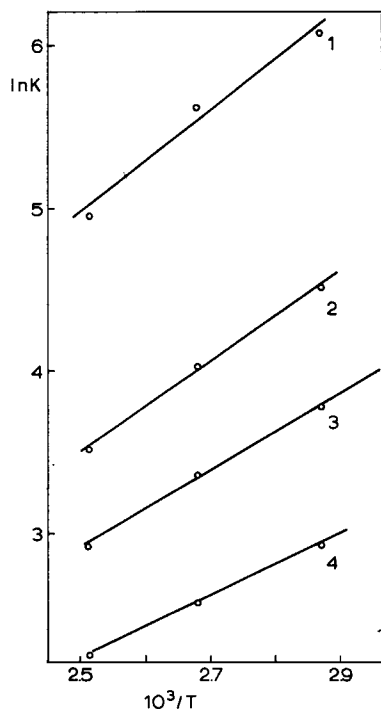

Fig. 6. Plot of ln $K_{(m)}$ vs. $1/T$. 1 = Tetrahydrofuran; 2 = trimethylene sulfide; 3 = 2-pentanone;
4 = ethyl propionate.

furan, the data in Table IV fit the linear plots of ln $K_{(m)}$ *versus* $1/T$ very well, which suggests that the simplified GLC approach based on eqn. 10 can indeed afford reliable thermodynamic parameters. The relevant ΔH° and ΔS° data (molality concentration scale) were obtained graphically from Fig. 6 and the data are listed in Table V.

Thermodynamic data obtained by conventional methods are usually based on the molarity concentration scale. $K_{(c)}$ data were calculated according to the equation $K_{(c)} = K_{(m)}/\varrho$. The densities of squalane, ϱ, at 75, 100 and 125 °C were extrapolated from literature data[15,19,21] (*cf.*, Experimental section). The thermodynamic parameters of the molecular association of σ-donor molecules with [Ni(tfacCam)$_2$]$_2$ in squalane in molarity units are listed in Table VI. The first set of ΔH° and ΔS° data were obtained from the graphically fitted ln $K_{(c)}$ values with $1/T$. The same set of data was obtained statistically from the best linear unweighted fit (least-squares method) by computer analysis.

TABLE VI

THERMODYNAMICS OF THE 1:1 MOLECULAR ASSOCIATION OF σ-DONOR MOLECULES WITH [Ni(tfacCam)$_2$]$_2$ IN SQUALANE AT 75–125 °C (MOLARITY CONCENTRATION SCALE)

Substrate	$K_{(c)}$ (l/mole)*			$-\Delta H^{\circ***}$ (kcal/mole)		$-\Delta S^{\circ***}$ (entropy units)	
	75 °C	100 °C	125 °C	Graph-ical**	Computer analysis	Graph-ical**	Computer analysis
Tetrahydrofuran	594.1	362	192	6.2	5.8 (0.6)§	5.0	3.95 (1.8)§
Trimethylene sulfide	117.6	73.3	45.3	5.2	5.1 (0.2)	5.6	5.25 (0.6)
2-Pentanone	56.2	37.65	25.0	4.4	4.35 (0.2)	4.8	4.5 (0.5)
Ethyl propionate	23.9	17.2	12.85	3.4	3.4 (0.1)	3.5	3.5 (0.1)

* Calculated according to the equation $K_{(c)} = K_{(m)}/\varrho$. For data for ϱ $_{squalane}$, see Experimental section.

** Obtained graphically from the ln K vs. $1/T$ plot.

*** ΔH° and ΔS° values are not corrected for the temperature dependence of the squalaned ensity ϱ.

§ Values in parentheses represent standard deviations.

It should be emphasized that the least-squares method is reliable only if the variance of the experimentally obtained K data is homogeneous over the series of observations, *i.e.*, if the absolute error in K is constant[42]. As K is converted into the natural logarithmic scale, the variance of ln K becomes inhomogeneous over the series of observations and, consequently, the least-squares method of the best unweighted fits is incorrect[43]. The second set of data for ΔH° and ΔS° in Table VI refers accordingly to the best non-linear fit of ln K with $1/T$ (*i.e.*, the best linearly weighted fits with K^2 weight)[42,43], obtained iteratively[43] by computer analysis from the estimates of the first set, together with the relevant standard errors for the refitted estimates.

The precision of the ΔH° and ΔS° values is evident from the small standard deviation from the linear ln K *versus* $1/T$ Gibbs–Helmholtz plot (less than 5% for ΔH° and less than 10% for ΔS°). In order to assess these data, it should be mentioned that, inherent in eqn. 12, small errors in K produce large errors in ΔH and even larger errors in ΔS. For example, the deviation from the linearity of ln K *versus* $1/T$ for THF

TABLE VII

STABILITY CONSTANTS, $K_{(c)}$, OF THE 1:1 MOLECULAR ASSOCIATION OF σ-DONOR
SOLUTES WITH [M(tfacCam)$_2$]$_2$ (M = Mn, Co OR Ni) (5·10^{-2} m) IN SQUALANE AT 75 °C
$\varrho^{75}_{Squalane}$ = 0.774 g/ml.

Substrate	$K_{(c)}$ (l/mole)		
	Mn(II)	Co(II)	Ni(II)
Methyl formate	2.64	2.35	19.64
Ethyl formate	4.08	5.40	21.60
Methyl acetate	8.27	9.62	32.92
Ethyl acetate	12.14	13.52	41.14
Vinyl acetate	2.58	3.64	9.10
Methyl propionate	7.00	6.74	18.99
Ethyl propionate	10.05	9.10	23.90
Methyl butyrate	7.55	7.06	19.46
Ethyl butyrate	10.78	9.82	27.96
Propanone	11.94	18.55	60.16
2-Butanone	10.60	14.47	54.0
2-Pentanone	11.68	17.42	56.2
Acetaldehyde	3.13	5.30	31.76
Acrolein	4.86	7.96	25.84
Propanal	3.10	7.08	31.12
Butanal	3.72	7.57	30.03
Isobutanal	3.00	6.98	29.33
Diethyl ether	2.92	6.40	21.03
Di-n-propyl ether	1.32	2.20	8.01
Diisopropyl ether	0	0	0.35
Propylene oxide	7.36	16.15	53.23
Tetrahydrofuran	33.85	131.52	594.1
p-Dioxane	18.81	93.0	782.9
Furan	0.16	0	0.78
Pyrrole	1.50	3.23	6.43
Thiophene	0.2	0.8	0.4
Benzene	0.15	0.6	0.5
Nitromethane	0.83	2.92	9.43
1-Nitropropane	1.58	1.81	3.85
Dimethyl sulfide	1.58	19.30	178.0
Diethyl sulfide	1.50	16.72	126.6
Propylene sulfide	1.03	6.66	51.16
Ethanol	159.2	165.1	>200
1-Propanol	175.9	185.5	>200
2-Propanol	99.5	102.8	189.4
1-Butanol	187.3	212.9	>200
2-Butanol	83.7	86.1	151.95
2-Pentanol	89.4	94.6	156.6

(Fig. 5) causes great uncertainty in the ΔH and ΔS values. Nevertheless, the data ob-
tained from GLC are considered to be competitive with, if not better than, those
obtained by spectroscopic means. The large experimental error in K for THF probably
results from the strong interaction of this solute with Ni(II) and subsequent overload-

ing at the high retention time involved. Better results for this solute are predicted if columns with lower concentrations of Ni(II) chelate are used. On the other hand, the data for the solutes trimethylene sulfide, 2-pentanone and ethyl propionate show that GLC is an excellent method for obtaining thermodynamic parameters of 1:1 association equilibria based on the simplified eqn. 10.

Once the linear relationship of R' versus m_A had been established for a number of representative solutes, it was considered possible to obtain thermodynamic data for a large number of solutes in short time at only a single concentration of the metal chelates. With this approach, only one column for the given metal chelate is required, together with the squalane reference column. If several solutes are injected on to the

TABLE VIII

THERMODYNAMIC PARAMETERS OF THE 1:1 MOLECULAR ASSOCIATION OF σ-DONOR MOLECULES WITH $5 \cdot 10^{-2} m$ [Ni(tfacCam)$_2$]$_2$ IN SQUALANE (MOLALITY CONCENTRATION SCALE)

Substrate	$K_{(m)}$ $(kg/mole)^*$			$-\Delta H_{(m)}^0$ $(kcal/mole)^{**}$	$-\Delta S_{(m)}^0$ $(entropy\ units)^{**}$
	75 °C	100 °C	125 °C		
Methyl formate	15.20	11.30	7.32	3.75 (0.5)***	5.4 (1.6)***
Ethyl formate	16.40	11.30	7.54	4.15 (0.25)	6.35 (0.7)
Methyl acetate	25.48	16.76	10.80	4.6 (0.25)	6.8 (0.65)
Ethyl acetate	31.84	22.42	14.38	4.15 (0.45)	5.05 (1.25)
Vinyl acetate	7.04	4.66	3.76	3.65 (0.45)	6.6 (1.3)
Methyl propionate	14.70	10.32	6.98	4.0 (0.25)	6.05 (0.75)
Ethyl propionate	18.70	13.54	9.0	3.85 (0.4)	5.2 (1.15)
Methyl butyrate	15.06	10.12	7.06	4.15 (0.1)	6.55 (0.1)
Ethyl butyrate	21.64	14.06	10.0	4.3 (0.1)	6.3 (0.3)
Propanone	46.56	32.40	24.24	3.65 (0.1)	2.8 (0.2)
2-Butanone	41.76	25.90	17.24	4.9 (0.1)	6.65 (0.1)
2-Pentanone	43.58	28.90	18.56	4.55 (0.15)	5.6 (0.75)
Acetaldehyde	24.58	18.92	14.12	3.0 (0.2)	2.2 (0.6)
Acrolein	20.0	16.02	12.16	2.65 (0.25)	1.65 (0.75)
Propanal	24.08	15.56	11.70	4.1 (0.3)	5.5 (0.85)
Butanal	23.24	15.90	10.70	4.15 (0.2)	5.7 (0.55)
Isobutanal	22.70	15.40	10.36	4.2 (0.2)	5.95 (0.5)
Diethyl ether	16.28	9.10	6.42	5.4 (0.5)	10.05 (1.4)
Di-n-propyl ether	6.20	3.46	2.32	5.5 (0.2)	12.25 (0.5)
Diisopropyl ether	0.26	0.26	0.22		
Propylene oxide	41.20	27.22	18.64	4.35 (0.1)	5.1 (0.15)
Tetrahydrofuran	423.2	274.4	141.2	5.5 (0.9)	3.6 (3.0)
Furan	0.6	0.5	0.44	1.75 (0.9)	6.0 (0.3)
Pyrrole	4.98	2.86	1.50	6.25 (0.5)	14.75 (1.4)
Nitromethane	7.30	5.26	3.28	4.1 (0.6)	7.85 (1.65)
1-Nitropropane	2.98	1.88	1.14	5.1 (0.3)	12.5 (0.85)
Dimethyl sulfide	137.8	81.6	46.6	5.75 (0.3)	6.75 (0.9)
Diethyl sulfide	98.0	55.6	29.4	6.3 (0.4)	9.0 (1.25)
Propylene sulfide	39.6	26.2	15.54	4.85 (0.5)	6.6 (1.45)
Trimethylene sulfide	91.0	55.5	33.5	5.5 (0.25)	6.45 (0.65)

* Mean of two measurements.
** Obtained by computer analysis (best non-linear fit).
*** Standard deviations from the linear Gibbs–Helmholtz plot.

column simultaneously or in close succession, a considerable amount of thermodynamic information can be gained in short time. Thus, the stability constants of the association of 38 σ-donor molecules with $5 \cdot 10^{-2}$ m [M(tfacCam)$_2$]$_2$ (M = Mn, Co or Ni) in squalane at 75 °C were determined. The results are given in Table VII, and show that $K_{(c)}$ can easily be determined in the range $1-2 \cdot 10^2$ l/mole at metal chelate concentrations of $5 \cdot 10^{-2}$ m. It should be pointed out that for the interpretation of ligand–metal interactions, a comparison of relative stabilities of a number of association equilibria is often more instructive than absolute data for stability constants. The GLC method can provide such data with great accuracy and speed. Even in cases where the actual concentration m_A of the metal chelate is not known precisely, the relative stabilities of interacting species nevertheless give considerable insight into the nature of the interactions involved[24,25]. The results in Table VII yield comprehensive information about the affinities of σ-donor solutes for transition metal chelates, which cannot be obtained as readily by other methods of measuring stability constants.

The strong interaction of σ-donor molecules with [Ni(tfacCam)$_2$]$_2$ warranted further efforts to determine the Gibbs–Helmholtz parameters of the molecular association equilibria involved. Measurements were carried out for 30 σ-donor solutes with a column containing $5 \cdot 10^{-2}$ m [Ni(tfacCam)$_2$]$_2$ in squalane and a squalane reference column at 75, 100 and 125 °C. $\Delta H°$ and $\Delta S°$ values were obtained iteratively[43] by computer analysis of $K_{(m)}$ data calculated from eqn. 10 providing also the standard deviations from the linear Gibbs–Helmholtz plot (ln K versus $1/T$) (eqn. 12). Table VIII shows that the precision of the $\Delta H°$ and $\Delta S°$ values is reasonably good, even though only two sets of measurements at only one concentration of the chelate were carried out (c.f., results in Table VI). It follows that the simplified GLC approach described here is a simple method for obtaining thermodynamic parameters of the molecular association of σ-donor molecules with metal chelates, the accuracy of which might be surpassed only by use of the time-consuming thermometric titration calorimetry[56]. With the results in Table VIII, a large amount of thermodynamic information on the molecular association of σ-donor solutes with a Ni(II) β-diketonate in a non-polar non-coordinating solvent is now available for the first time.

DISCUSSION

The nature of interactions

Electronically and coordinatively unsaturated β-keto-enolates of divalent transition metal ions, ML$_2$, are strong Lewis acids for σ-donor molecules[51]. Adduct formation between Lewis bases and metal β-diketonates was observed as early as in 1904[57]. Frequently, the chelates ML$_2$ react with themselves, usually with the formation of trimeric associates in which the metal atoms are bridged by oxygen[49,52]. The non-dissociative dimeric structure, [ML$_2$]$_2$, observed for the 3-trifluoroacetylcamphorates of Mn(II), Co(II) and Ni(II) in non-polar solvents[40] is a new example of this self-association. The following equilibria may occur for a 1:1 molecular association of σ-donor molecules, B, with a metal chelate dimer, [ML$_2$]$_2$:
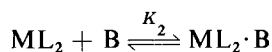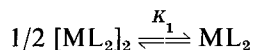
(a) associative mechanism:

$$[ML_2]_2 + B \underset{}{\overset{K}{\rightleftharpoons}} [ML_2]_2 \cdot B$$
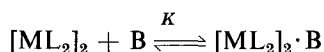
(b) one-step associative–dissociative mechanism:

$$[ML_2]_2 + B \overset{K'}{\rightleftharpoons} ML_2 \cdot B + ML_2$$

(c) two-step dissociative–associative mechanism:

$$1/2 \ [ML_2]_2 \overset{K_1}{\rightleftharpoons} ML_2$$

$$ML_2 + B \overset{K_2}{\rightleftharpoons} ML_2 \cdot B$$

The occurrence of mechanisms (b) or (c) can be disregarded as a close linearity of the plot of R' *versus* m_A (eqn. 10) has been observed for the molecular association studied in this work (*cf.*, Fig. 2). Furthermore, the UV electronic absorption spectra of different concentrations of $[Ni(tfacCam)_2]_2$ in cyclohexane indicated that only one species is present at concentrations $<10^{-4} \ M$ (Fig. 1). Mechanism (c) or (b) evidently occurs for the association of σ-donor solutes with $[Ln(tfacCam)_3]_2$ (Ln = lanthanide ion)[35].

In order to differentiate between mechanisms (a) and (b) or (c), a UV spectroscopic electronic absorption study of the molecular association of tetrahydrofuran and ethyl propionate with $[Ni(tfacCam)_2]_2$ ($2.5 \cdot 10^{-5} \ M$ in cyclohexane) at 25 °C was carried out and the results are shown in Figs. 7 and 8. For varying concentrations of the donor
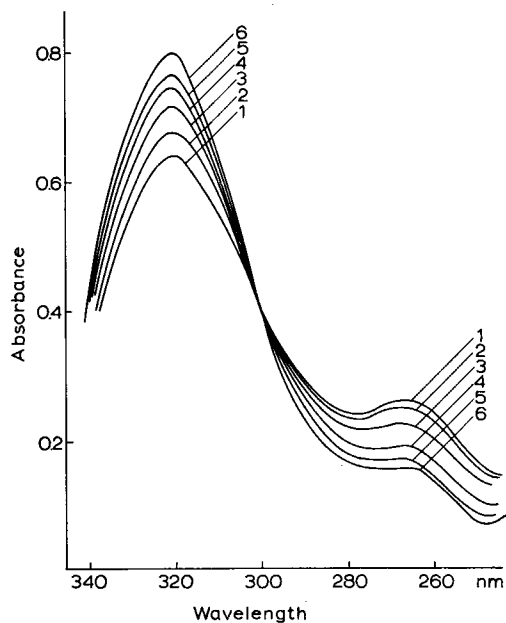

Fig. 7. UV spectrum of $[Ni(tfacCam)_2]_2$ in cyclohexane at 25 °C with increments of tetrahydrofuran added. Ni concentration: $2.5 \cdot 10^{-5} \ M$. THF concentration: 1, 0; 2, $1 \cdot 10^{-3} \ M$; 3, $5 \cdot 10^{-3} \ M$; 4, $1 \cdot 10^{-2} \ M$; 5, $5 \cdot 10^{-2} \ M$; 6, $1 \cdot 10^{-1} \ M$. Isosbestic point at 303 nm.
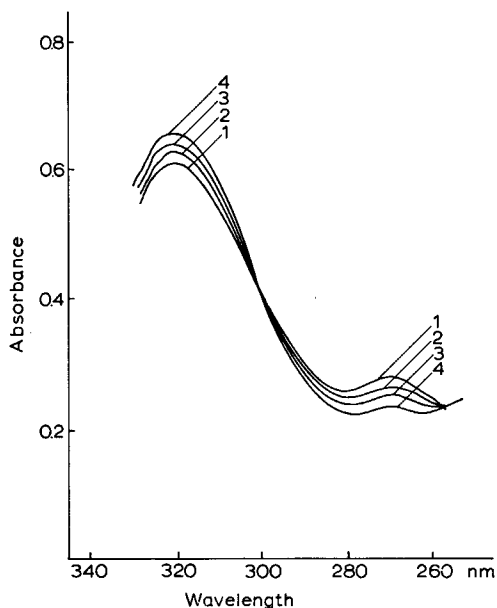
Fig. 8. UV spectrum of [Ni(tfacCam)$_2$]$_2$ in cyclohexane at 25 °C with increments of ethyl propionate added. Ni concentration: $2.5 \cdot 10^{-5}$ M. Ethyl propionate concentration: 1, 0; 2, $7 \cdot 10^{-4}$ M; 3, $2.1 \cdot 10^{-2}$ M; 4, $7 \cdot 10^{-2}$ M. Isosbestic point at 300 nm.

substrates (10^{-1}–10^{-3} M), curves with a sharp isosbestic point were observed, which indicated the presence of only two species in equilibrium (*i.e.*, the chelate dimer and the 1:1 adduct) at the concentration range employed. Mechanism (a) is also supported by the isolation of adducts of the type [ML$_2$]$_2 \cdot$ B for the complexation of pyridine with Co(II) and Ni(II) bis(pentane-2,4-dionate)[53,55].

The following discussion of thermodynamic parameters for the molecular association of σ-donor molecules with [M(tfacCam)$_2$]$_2$ (M = Mn, Co or Ni) in squalane, obtained by GLC, is based on the premise that a 1:1 association equilibrium of type (a) is involved.

Thermodynamics of interactions

The thermodynamics of the molecular associations of σ-donor molecules with transition metal chelates are important for the elucidation of the nature of the metal–ligand bond and for determining the factors that influence its stability. The recognition of certain trends in reactivity is of fundamental importance in designing experiments and in developing new syntheses. However, an unambiguous interpretation of thermodynamic data for this purpose appears to be feasible only if the following requirements are fulfilled:

(1) $\Delta H°$ and $\Delta S°$ parameters are not obscured by structure-forming and -breaking solvation effects in coordinating media;

(2) the activity coefficients of donor and acceptor are close to unity (*i.e.*, $a_i \to c_i$);

(3) no multiple association (*i.e.*, 2:1) and no intermolecular interactions occur.

The GLC approach for studying association equilibria of σ-donor molecules with [Ni(tfacCam)$_2$]$_2$ described here meets all of the above requirements as only minute amounts of solute and low concentrations of metal chelate ($<5 \cdot 10^{-2} M$) in the non-polar non-coordinating hydrocarbon squalane are applied. It has been pointed out[58-60] that the thermodynamics in non-polar solvents approximate closely to those in the gas phase, where naturally solvation effects are absent. At present, only a limited number of thermodynamic studies of association equilibria of σ-donor molecules with transition metal chelates in poorly solvating media have been reported. Enthalpy data for the association of tertiary amine oxides with bis-(2,4-pentanedionato)oxo-vanadium(IV) in dichloromethane and chloroform have been measured by calorimetry[61].

A strong dependence of the $\Delta H°$ data upon the choice of solvent has been noticed[61]. Pronounced solvent effects have also been detected in the enthalpies of association of σ-donor molecules with bis-(hexafluoro-2,4-pentanedionato)copper(II) in poorly solvating media[62]. Unfortunately, different solvents had to be employed owing to solubility requirements of the substrates. The heats of association of a limited number of bases with methylcobaloxime have also been reported recently[63].

The solubility properties of solutes are not important in the GLC approach described here and hence the stability constants of a large number of association equilibria of different functional σ-donor molecules with [M(tfacCam)$_2$]$_2$ could be measured. According to Table VII, the stability of the adducts of oxygen donor molecules at 75 °C decreases in the order alcohols > cyclic ethers > ketones > esters > aldehydes > ethers with the chelates Ni(II) ≫ Co(II) > Mn(II).

A strong selectivity of the metal ions is observed with cyclic ethers, for which the interaction strongly decreases in the above order. No such preference of Ni(II) compared with Mn(II) and Co(II) is found for alcohols, however. A comparison of the stability constants of oxygen and sulfur donor molecules, *i.e.*, propylene oxide/propylene sulfide and diethyl ether/diethyl sulfide, with the metal chelates is interesting. The decrease in selectivity of metal ions for sulfur donors is greater by approximately a factor of 10 than for oxygen donors in the order Ni(II) > Co(II) > Mn(II).

Obviously, the Lewis acceptor properties of the metal ions for "soft" ligands decrease in the same order. This observation might in part be explained by an increasing importance of π back-bonding interaction as the number of d-electrons increases (*i.e.*, Ni(II),d^8 > Co(II), d^7 > Mn(II), d^5). It should be mentioned that a striking selectivity of Pd(II) for sulfur donor molecules has been observed with the square-planar chelate Pd(tfacCam)$_2$ (ref. 40).

The interactions of Mn(II), Co(II) and Ni(II) with benzene and five-membered heteroaromatics is negligible. The basicity of oxygen is greatly reduced when oxygen is part of a quasi-aromatic system. This trend is manifested in the large stability differences between tetrahydrofuran and furan adducts.

Stability constants reflect only the free energy change of the species involved in the association equilibrium. Thus, a knowledge of the Gibbs–Helmholtz parameters $\Delta H°$ and $\Delta S°$ is important if conclusions are to be drawn regarding the nature and strength of the metal–ligand bond as well as steric requirements of the adduct formations.

A comprehensive set of data is now available for the association of σ-donor molecules with $[Ni(tfacCam)_2]_2$ in the non-polar solvent squalane. From the data in Table VIII, it follows that all 1:1 adduct formations are exothermic and are accompanied by loss of entropy. The favorable enthalpy term observed throughout accounts for an overall gain in free energy. The data imply that the stability constants decrease with increasing temperature. The parameters can be used in order to predict stability constants at room temperature, provided that ΔH° is independent of temperature between 25 and 125 °C. Evaluation of the data in Table VI leads to the prediction that the THF adduct of Ni(II) may be isolated at room temperature. The negative change of entropy is consistent with an association equilibrium (a) (see above), as individual vibrational and rotational freedom is lost during association. It is important to note that no straightforward parallel between ΔH° and ΔS° data and hence between strength of bonding and amount of complexation is observed. For instance, a strong destabilization through an unfavorable entropy term can be detected when comparing the decrease of stability constants for diethyl ether/di-n-propyl ether, dimethyl sulfide/diethyl sulfide, nitromethane/1-nitropropane and cyclic ethers/ethers with Ni(II). The influence of steric factors, as manifested in the entropy term, can readily be recognized. The poor coordination tendency of open-chain ethers compared with cyclic ethers follows the same trend. The strong negative entropy term observed for pyrrole–Ni(II) is striking, and can be explained by difficult steric requirements of association due to the presence of an essentially coplanar (sp^2) nitrogen atom in the molecule.

If the data of Table VIII are interpreted in the terms of the HSAB (hard–soft acid–base) model of Pearson[64,65], it follows that $[Ni(tfacCam)_2]_2$ may be regarded as a borderline acid exhibiting both "soft" and "hard" character. Thus, contrary to expectation, the nickel chelate undergoes strong electrostatic interactions with σ-donor molecules.

CONCLUSION

Within the limits of the experimental technique used and some assumptions made in obtaining eqn. 10, GLC appears to be a most efficient and convenient method for determining association constants in apolar solvents. Obvious merits of the GLC method for studying ligand–transition metal interactions carried out in this work (see also refs. 3, 11, 21 and 22) are:

(a) association equilibria are measured in non-polar non-coordinating media and in inert gas atmosphere (helium);

(b) because of the low concentration of the metal chelate, A, employed, no serious concentration dependence of K occurs as the change in the activity of A is small;

(c) because of the minute amount of solute B employed, no self-association occurs and only 1:1 association is measured;

(d) solubility criteria of B in S are not important and also highly volatile substrates (gases) can easily be measured;

(e) solutes B undergo high purification by virtue of the separation properties of the GLC column;

(f) variations of working temperature and concentration m_A permit the

quantitative assessment of both small and strong interactions, *i.e.*, $1 < K_{(m)}$ (kg/mole) $<10^6$ (ref. 3);

(g) the GLC method allows equilibria to be determined simultaneously or in close succession in a wide and easily controllable temperature range;

(h) the GLC method is simple, rapid, accurate and reproducible.

Disadvantages of the GLC method result from the following requirements:

(a) the 1:1 association equilibria have to be established rapidly and must be reversible;

(b) the metal chelate has to satisfy the conditions outlined previously, *i.e.*, solubility in non-polar solvents, involatility, stability and chemical integrity;

(c) the solute B must be volatile and thermally stable;

(d) the solute B must not be highly polar (ammonia, methanol);

(e) the solvent S must be involatile and non-polar.

These criteria do not restrict the usefulness of the method as such, but they seriously limit the number of equilibria that can be investigated.

The precision of the stability constants obtained by GLC depends on the accuracy of the gas chromatographic retention data, constancy of carrier gas flow-rate and temperature, as well as on detection sensitivity. As the technique of GLC has steadily been refined in recent years, the use of up-to-date GLC equipment connected with on-line computerized retention data processing facilities should greatly enhance the precision of thermodynamic parameters, notably in connection with high-resolution complexing open tubular columns[26].

The gas chromatography of association equilibria has also a very important analytical aspect. The observed selectivity, which is the result of chemical affinity criteria, may solve difficult analytical problems of separation. The selective and stable (chiral) stationary phases used in this work might also be applied for the separation of mixtures that possess only slight differences in structure and properties such as isotopes or enantiomers[26,35]. Investigations along these lines are being pursued.

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