Ligand Substitution in Bis(*N*-alkylsalicylideneiminato)copper(II) Complexes: Comparison of Activation and Transfer Data obtained from Solvent Mixtures

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Stopped-flow spectrophotometry has been used to study the kinetics of ligand substitution in three bis(*N*-alkylsalicylideneiminato)copper(II) complexes $[Cu(Rsaln)_2]$ (R = Et, Pr^i, or Bu^t) with *N*-ethylsalicylideneimine (H-Etsaln) or *N*-phenylsalicylideneimine (H-Phsaln) in solvent mixtures of methanol–butan-2-ol and methanol–2-methylbutan-2-ol. The rate of substitution follows a two-term rate law, rate = $(k_S + k_{ligand}[\text{ligand}])[\text{complex}]$, although for most systems studied the second-order contribution $k_{ligand}[\text{ligand}]$ is negligibly small, so that rate = $k_S[\text{complex}]$. The determination of k_S, the so-called solvent path, in alcohol mixtures of different composition has led to $\delta\Delta G^\ddagger$. From the temperature dependence of k_S, the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ have been obtained. On the basis of solubilities determined spectrophotometrically, the Gibbs free energy of transfer, δG_{tr}, has been obtained for the various mixtures. An attempt is made to correlate the activation data $\delta\Delta G^\ddagger$ for the solvent path with the transfer data δG_{tr} and this is discussed in terms of ground- and transition-state solvation. The significance of the different co-ordination geometry of the three complexes studied for the kinetics and for solvation is examined. It is shown that there is a correlation between $\ln k_S$ and Reichardt's solvent polarity parameter $E_T(30)$, which is of mechanistic importance.

RECENTLY we reported on the kinetics of ligand substitution in the pseudotetrahedral complex bis(*N*-t-butylsalicylideneiminato)copper(II) by *N*-ethylsalicylideneimine in various alcohols.[1] The substitution is described by equation (i) and follows the two-term rate law (ii), although for most of the alcohols applied as solvent the ligand-dependent term $k_{H\text{-}Etsaln}[\text{H-Etsaln}]$, the so-called ligand path, is negligibly small. The

$$[Cu(Bu^tsaln)_2] + 2\text{H-Etsaln} \longrightarrow [Cu(Etsaln)_2] + 2\text{H-Bu}^t\text{saln} \quad \text{(i)}$$

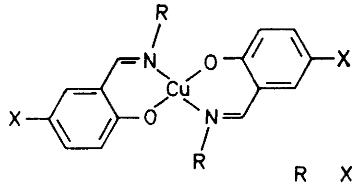
$$\text{Rate} = (k_S + k_{H\text{-}Etsaln}[\text{H-Etsaln}])[Cu(Bu^tsaln)_2] \quad \text{(ii)}$$

ligand-independent term k_S, the so-called solvent path, is mechanistically interpreted as being caused by the attack of an alcohol molecule, the subsequent formation of a kinetically labile solvento complex (*i.e.* an alcoholato-complex), and its fast reaction with the incoming ligand.[1] The high values observed for k_S in alcohol media as compared to aprotic media are obviously due to the fact that an alcohol can provide the proton necessary to cause the co-ordinated ligand to leave. In agreement with this interpretation it was found for dimethyl sulphoxide (dmso)–alcohol solvent mixtures that (*a*) the alcohol-initiated rate contribution is described by a linear term $k_{ROH}[\text{ROH}]$ and (*b*) the size of k_{ROH} is linearly correlated with the pK_a of the alcohols in dmso.

In the last few years several studies dealing with ligand substitution in mixed-solvent systems have been published.[2] The magnitude of the second-order rate constant characterizing the ligand path has been related to the solubilities of the reacting species which are taken as a measure of ground-state solvation. In some cases it has been possible to discriminate between the kinetic significance of either ground- or transition-state solvation.

Alcohols have to be considered as highly structured liquids.[3] If the solvent path of a substitution reaction such as (i) is initiated by a single solvent molecule or by a specifically structured solvent cluster it is to be expected that the addition of a structure-changing co-solvent will be reflected in the kinetics. In the present study we report on some ligand-substitution reactions in binary alcohol mixtures which proceed nearly exclusively through the solvent pathway. An attempt is made to correlate the kinetic data with solubility data obtained for the reacting substrate and to extract information on the mechanism of the solvent pathway from a comparison of activation and transfer data.

Three bis(*N*-R-salicylideneiminato)copper(II) complexes (1)—(3) were chosen as substrates, the almost planar one carrying R = Et and the more tetrahedral ones having R = Pr^i or Bu^t.[4] The substitution reactions



		R	X
(1)	$[Cu(Bu^tsaln)_2]$	Bu^t	H
(2)	$[Cu(Pr^isaln)_2]$	Pr^i	H
(3)	$[Cu(Et\text{-}msaln)_2]$	Et	Me

studied correspond to (i), the Schiff-base *N*-ethylsalicylideneimine, H-Etsaln (and sometimes *N*-phenylsalicylideneimine, H-Phsaln), being the incoming ligand and mixtures of methanol and butan-2-ol serving as solvent.

EXPERIMENTAL

The complexes and the ligands were prepared by standard procedures.[5] The elemental analyses agreed with calculated data.

2-Methylbutan-2-ol (Merck-Schuchardt, Munich) was fractionated in a 30-cm Vigreux column. The solvents were dried dynamically with 3- or 4-Å molecular sieves and stored over molecular sieves. The water content was determined by automatic Karl-Fischer titration ($[H_2O] = 10^{-3}$—10^{-2} mol dm^{-3}).

The kinetic measurements were done with a modified[1] Durrum D110 stopped-flow spectrophotometer at 600 nm in combination with an Aminco-DASAR storage oscilloscope. In all cases pseudo-first-order conditions were maintained by applying a $\geqslant$20-fold excess of the ligand. The various solvent mixtures were prepared volumetrically; volume changes upon mixing were neglected.

The solubilities were determined at 25 °C. A saturated solution was equilibrated for at least 72 h, then samples were taken by pipetting 0.1—0.2 ml of the solution through a glass frit. The sample was diluted with the appropriate amount of methanol and the concentration of the substrate was measured by absorption spectrophotometry in the visible or near-u.v. region. The Gibbs free energy for the transfer of a solute from a methanol–butan-2-ol mixture of composition i to pure MeOH (index zero) was determined from the ratio of the corresponding absorbances A_i and A_0 according to (iii). The absolute solubilities s were calculated

$$\delta\mu_{tr}(i \longrightarrow 0) = RT \ln (s_i/s_0) = RT \ln (A_i/A_0) \qquad \text{(iii)}$$

from A on the basis of Beer's law being obeyed in all cases (the ratio of the activity coefficients, γ_i/γ_0, was assumed to be close to unity).

studied the rate follows equation (v), although the second-order ligand path was in some cases too small to be observed. The data in Table 1 show that the two

$$\begin{aligned}\text{Rate} &= k_{obs.}[\text{Cu(Rsaln)}_2] \\ &= (k_S + k_{\text{H-Etsaln}}[\text{H-Etsaln}])[\text{Cu(Rsaln)}_2] \qquad \text{(v)}\end{aligned}$$

rate constants in (v) behave rather differently. The second-order rate constant for ligand attack, $k_{\text{H-Etsaln}}$, is only slightly solvent and complex dependent. Its values differ by less than a factor of three. The first-order rate constant k_S for the solvent path, however, depends considerably on both the solvent and the structure of the complex. The values of the ratio of k_S obtained in MeOH and in Bu^{s}OH demonstrate that the size of k_S is clearly reduced upon replacing the solvent MeOH by Bu^{s}OH, which is probably due to the reduced proton acidity of the latter. The decrease of k_S in the sequence k_S (1) > k_S (2) > k_S (3) parallels the decreasing degree of tetrahedral distortion in these complexes; the effect is more pronounced in MeOH than in Bu^{s}OH. As expected for a solvent path, the k_S values obtained for complex (1) with either H-Phsaln or H-Etsaln as the entering ligand are identical for both solvents within the limits of error.

TABLE 1

Rate constants at 25 °C for substitution reaction (iv) studied in MeOH and in Bu^{s}OH as solvent

Complex/ entering ligand	MeOH		Bu^{s}OH		
	k_{MeOH}/s^{-1}	$k_{\text{H-Etsaln}}$/ dm^3 mol^{-1} s^{-1}	k_{Bu^sOH}/s^{-1}	$k_{\text{H-Etsaln}}$/ dm^3 mol^{-1} s^{-1}	$\frac{k_{MeOH}}{k_{Bu^sOH}}$
[Cu(Bu^{t}saln)$_2$]/H-Etsaln [a]	0.95	[b]	0.012 2	0.004 4	78
[Cu(Pr^{i}saln)$_2$]/H-Etsaln	0.10	[b]	0.001 0	0.002 4	100
[Cu(Et-msaln)$_2$]/H-Etsaln	0.0118	0.0056	0.000 75	0.002 1	16
[Cu(Bu^{t}saln)$_2$]/H-Phsaln [d]	0.91	[b]	0.012 8	0.004 [e]	71

[a] Ref. 1. [b] Not observed. [c] $k^{MeOH}_{\text{H-Etsaln}}/k^{Bu^sOH}_{\text{H-Etsaln}} = 2.7$. [d] Data at 24 °C. [e] Refers to $k_{\text{H-Phsaln}}$.

RESULTS AND DISCUSSION

Ligand Substitution in Pure Alcohols.—It is obvious that the substitution of ligands in complexes such as (1)—(3) has to take place stepwise [equation (iv)]. As

$$[\text{Cu(Rsaln)}_2] \xrightarrow[\substack{+\text{H-Etsaln,}\\ -\text{H-Rsaln}}]{\text{step I}} [\text{Cu(Rsaln)(Etsaln)}] \xrightarrow[\substack{+\text{H-Etsaln,}\\ -\text{H-Rsaln}}]{\text{step II}} [\text{Cu(Etsaln)}_2] \qquad \text{(iv)}$$

shown previously,[1,6] for (1) the first step is rate controlling for both MeOH and Bu^{s}OH as solvent. In the present study it was confirmed for complexes (2) and (3) as well that in reaction (iv) the first step is the slow one, the second one being a fast consecutive reaction. This conclusion is based on two facts: (*i*) the spectrometric signal observed corresponds to pure (1), (2), or (3) at $t = 0$ and to pure [Cu(Etsaln)$_2$] at $t = \infty$; (*ii*) the change in absorbance with time can be fitted to a single exponential function with an accuracy >99%.

The dependence of the pseudo-first-order rate constant $k_{obs.}$ on the concentration of the entering ligand was measured for [H-Etsaln] = 0.01—0.5 mol dm^{-3} at $[\text{Cu(Rsaln)}_2] = 5 \times 10^{-4}$ mol dm^{-3}. In all systems

For a given complex the solvent effect on k_S as measured by k_{MeOH}/k_{Bu^sOH} is considerable (see Table 1). Attempts to correlate the size of k_S with solvent parameters such as fluidity, enthalpy of vaporization, and Taft's parameter σ* were not very satisfactory,[1] whereas the correlation with pK_a values[1] and with Reichardt's $E_T(30)$ values[7] was more convincing. The latter correlation is especially interesting since the $E_T(30)$ values of protic solvents reflect hydrogen-bond formation.[8]

TABLE 2

Solubilities of complexes (1)—(3) in MeOH and in Bu^{s}OH at 25 °C

Complex	Solubility, s/mol dm^{-3}		$\ln\left[\frac{s(\text{MeOH})}{s(\text{Bu}^s\text{OH})}\right]$
	MeOH	Bu^{s}OH	
[Cu(Bu^{t}saln)$_2$]	0.040	0.0215	0.621
[Cu(Pr^{i}saln)$_2$]	0.040	0.0275	0.372
[Cu(Et-msaln)$_2$]	0.025	0.0225	0.104

For a discussion of solvent effects on k_S it appears to be also worthwhile to consider the solvation of the reacting complexes [Cu(Rsaln)$_2$] on the basis of their solubilities. The data in Table 2 show that the solubilities of complexes (1)—(3) are not very different in both solvents.

It is interesting, however, that the decrease in the parameter ln[s(MeOH)/s(Bu^{s}OH)] (which is proportional to the Gibbs free energy of solvation) corresponds qualitatively with the decrease in k_S (see Table 1) as observed for the sequence (1) ⟶ (2) ⟶ (3).

Kinetic Results obtained in Solvent Mixtures.—The rate constants $k_{obs.}$ obtained for the ligand substitution in complexes (1)—(3) according to (iv) in mixtures of MeOH and Bu^{s}OH at 25 °C are shown in Figure 1. As pointed out earlier, the conditions were such that any second-order rate contribution could be neglected, so that $k_{obs.} = k_S$ [*cf.* (v)]. Confirmation of this lies in the fact that the data obtained for systems (1)–H-Etsaln and -H-Phsaln coincide.

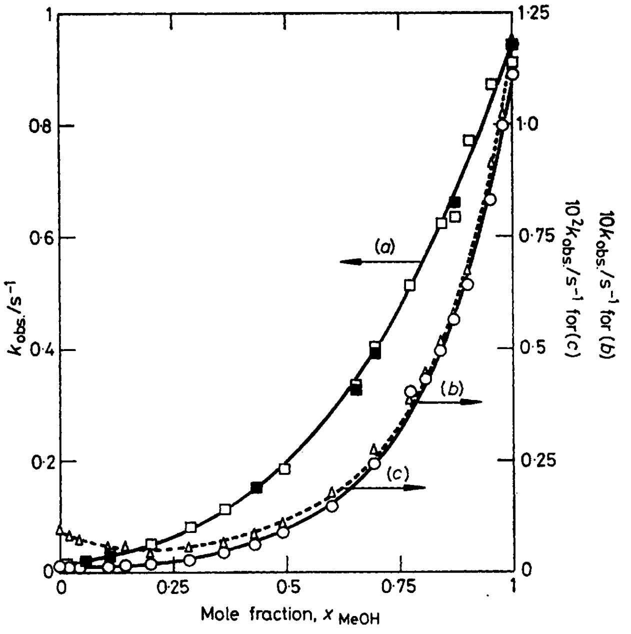


FIGURE 1 Observed rate constant $k_{obs.}$ in the solvent system MeOH–Bu^{s}OH: (*a*), (1) + H-Phsaln (□), (1) + H-Etsaln (■); (*b*), (2) + H-Etsaln (○); (*c*) (broken line), (3) + H-Etsaln (△). Conditions: [complex] = 5 × 10^{-4} mol dm^{-3}, [ligand] = 0.04 mol dm^{-3}, and T = 298 K

The curvature in all three systems is non-ideal in the sense that the transition from $k_{obs.}$(Bu^{s}OH) to $k_{obs.}$(MeOH) is non-linear. The deviations are negative, *i.e.* the observed values are lower than expected. Presumably, these deviations are due to a specific association between molecules of MeOH and Bu^{s}OH in the mixtures. Unfortunately, in the literature [9] there are no activity-coefficient data in MeOH–Bu^{s}OH mixtures. From mixtures of MeOH with Pr^{i}OH and Bu^{n}OH [9] it can be inferred, however, that activity coefficients alone cannot account for the observed deviations.

Addition of a less associated alcohol such as Bu^{s}OH to MeOH reduces the number of MeOH monomers by the formation of mixed species such as MeOH,Bu^{s}OH.* Therefore, the finding that the rate decreases considerably upon addition of even small amounts of Bu^{s}OH points to MeOH monomers (with ' free ' hydroxyl groups) being operative in the solvent path. With rising temperature the curves become more linear (see Figure 2), which is obviously due to a breakdown of solvent structure as a consequence of increased thermal motion.

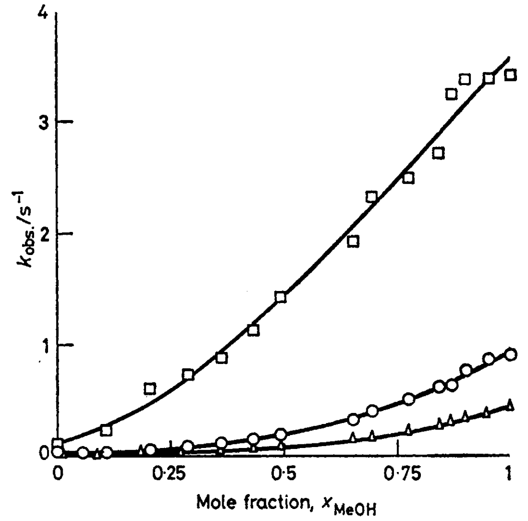


FIGURE 2 Observed rate constant $k_{obs.}$ in the solvent system MeOH–Bu^{s}OH for the reaction (1) + H-Phsaln. T = 318 (□), 297 (○), or 288 K (△). Other conditions as in Figure 1

The activation parameters for the system (1)–H-Etsaln as determined from the temperature dependence of $k_{obs.}$ for various mixtures of MeOH and Bu^{s}OH are collected in Table 3. Interestingly, the entropy of activation is more or less independent of solvent composition for $x_{MeOH} \geqslant 0.2$, as reflected by the constant value of the parameter $T\delta\Delta S^‡$. This means that the observed decrease in rate with increasing fraction of Bu^{s}OH is mainly determined by an increase in $\Delta H^‡$. The reaction being thus isoentropic one could argue that the solvation of the transition state is more or less constant.

TABLE 3

Activation parameters for system (1)–H-Etsaln in MeOH–Bu^{s}OH mixtures

x_{MeOH}	$\Delta H^{‡\,a}$/ kJ mol^{-1}	$-\Delta S^{‡\,a}$/ J K^{-1} mol^{-1}	$\delta\Delta H^{‡\,b}$/ kJ mol^{-1}	$T\delta\Delta S^{‡\,c}$/ kJ mol^{-1}
0	74 ± 1.1	33 ± 3.5	13 ± 1.2	2.6 ± 1.1
0.11	72 ± 1.7	34 ± 5.5	11 ± 1.8	2.5 ± 1.7
0.20	67 ± 1.3	45 ± 4.3	6 ± 1.4	−0.9 ± 1.4
0.43	65 ± 0.3	44 ± 2.1	4 ± 0.8	−0.6 ± 0.8
0.69	63 ± 1.0	42 ± 3.1	2 ± 1.1	0 ± 1
0.87	60 ± 1.2	48 ± 3.9	−1 ± 1.3	−1.8 ± 1.3
1	61 ± 0.5	42 ± 1.6	0 ± 0.7	0 ± 0.4

[a] Determined from six measurements in the range 25—50 °C; [Cu(Bu^{t}saln)$_2$] = 0.001, [H-Etsaln] = 0.04 mol dm^{-3}. [b] $\delta\Delta H^‡ = \Delta H^‡(x_{MeOH}) - \Delta H^‡(x_{MeOH} = 1)$. [c] $T\delta\Delta S^‡ = 298 [\Delta S^‡(x_{MeOH}) - \Delta S^‡(x_{MeOH} = 1)]$.

In addition to the finding that in the pure solvents k_S decreases in the series (1) > (2) > (3), Figure 1 demonstrates that the deviation from ideal behaviour increases

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* In the last decade many papers on the association of alcohols in non-polar solvents have been published; see, for example, ref. 10.

in the series (1) < (2) ≈ (3). For complex (3) even a minimum in k_S is observed at $x_{MeOH} \approx 0.25$ [see Figure 1(*c*)]. These deviations might be due to preferential solvation of the complex.

The rate constant k_S obtained for mixtures of MeOH and Bu^{s}OH may be expressed as in (vi). Since $k_{MeOH}/k_{Bu^sOH} \gg 1$ (see Table 1), the term k_{Bu^sOH} in (vi) is

$$k_S = k_{obs.} = k_{Bu^sOH} + k_{MeOH} \qquad \text{(vi)}$$

negligibly small at high concentrations of MeOH. For small values of x_{MeOH}, however, the contribution of k_{Bu^sOH} has to be taken into account. For a complete description of the data observed it is reasonable, therefore, to introduce relationship (vii) ($k^0_{Bu^sOH}$, k^0_{MeOH} = rate constants for the pure solvents). This equation is

$$\begin{aligned} k_{obs.} &= k^0_{Bu^sOH} \cdot f(x_{Bu^sOH}) + k^0_{MeOH} \cdot f(x_{MeOH}) \\ &= k^0_{Bu^sOH} \cdot f(1 - x_{MeOH}) + k^0_{MeOH} \cdot f(x_{MeOH}) \qquad \text{(vii)} \end{aligned}$$

based on the assumption that both MeOH and Bu^{s}OH are equally responsible for the observed non-ideal behaviour of the solvent mixtures as characterized by $f(x_{Bu^sOH})$ and $f(x_{MeOH})$.

TABLE 4

Coefficients a_i for the function f(*x*) in equation (vii) for the solvent system MeOH–Bu^{s}OH

System	θ_c/°C	$k^0_{Bu^sOH}$/s^{-1}	k^0_{MeOH}/s^{-1}	Coefficients
(1)–H-Phsaln	15	0.007 57	0.447	$a_1 = 0.380$, $a_2 = -0.662$, $a_3 = 1.282$
	24	0.012 8	0.944	$a_1 = 0.164$, $a_2 = 0.165$, $a_3 = 0.670$
	45	0.109	3.58	$a_1 = 0.331$, $a_2 = 1.118$, $a_3 = -0.45$
(2)–H-Etsaln	25	0.001 16	0.109	$a_2 = 0.334$, $a_4 = -0.111$, $a_6 = 0.777$
(3)–H-Etsaln	25	0.000 94	0.0117	$a_2 = 0.433$, $a_4 = -0.472$, $a_6 = 1.039$
(1)–H-Etsaln [a]	25	0.001 1 [b]	0.961	$a_1 = 0.133$, $a_2 = -0.518$, $a_3 = 1.385$

[a] Solvent system methanol–2-methylbutan-2-ol. [b] k^0 for 2-methylbutan-2-ol.

The values for $f(x_{MeOH})$ and $f(1 - x_{MeOH})$ at the various compositions of the mixture are obtained by fitting the experimental data of Figure 1 to the power series $f(x) = a_2x^2 + a_4x^4 + a_6x^6$ [for (2) and (3)] or $f(x) = a_1x + a_2x^2 + a_3x^3$ [for (1)] with *x* being either x_{MeOH} or $(1 - x_{MeOH})$. The coefficients a_i resulting from such a least-squares fit are compiled in Table 4. The knowledge of $f(x_{MeOH})$ and $f(1 - x_{MeOH})$ in (vii) allows the calculation of the partial reactivities k_{Bu^sOH} and k_{MeOH} in (vi).

If the solvent path is a bimolecular reaction the pseudo-first-order rate constant $k_{obs.} = k_S$ has to be divided by the concentration of MeOH to obtain the second-order rate constant $k^{II}_{MeOH} = k_{MeOH}/[\text{MeOH}]$ for any composition x_{MeOH}. $\delta\Delta G^‡$ is the difference between the Gibbs free energy of activation obtained for two different solvents. When MeOH is the attacking molecule, $\delta\Delta G^‡$(MeOH) is calculated on the basis of (viii) (subscript 0 refers to pure MeOH). In Figure 3 the values for

$$\begin{aligned} \delta\Delta G^‡(\text{MeOH}) &= \Delta G^‡(\text{MeOH}) - \Delta G^‡_0(\text{MeOH}) \\ &= RT \ln k^{II}_{MeOH}/k^{II,0}_{MeOH} \qquad \text{(viii)} \end{aligned}$$

$\delta\Delta G^‡$(MeOH) are plotted *versus* x_{MeOH}. An increase in the fraction of Bu^{s}OH raises the difference between the Gibbs free energies of activation. For the tetrahedral complex (1) this effect is less pronounced than for the others.

Gibbs Free Energies of Transfer and their Correlation with Kinetic Data.—The difference in solvation energy for a solute in two solvents is given by the Gibbs free energy of transfer according to (iii). In the present study such transfer data have been determined for complexes (1)—(3) dissolved in various MeOH–Bu^{s}OH mixtures; they are presented in Figure 3 as δG_{tr} data. The discussion of these data in terms of solubility reveals: (*i*) the complexes are less soluble in Bu^{s}OH than in MeOH; (*ii*) this difference in solubility decreases in the series (1) ⟶ (2) ⟶ (3); and (*iii*) there is a maximum in solubility in MeOH-rich mixtures which is greatest for the planar complex (3). It has been pointed out [11] that extrema in δG_{tr} stem from specific solvation effects due to the solvent structure.

Considering a metal complex in which ligand substitu-

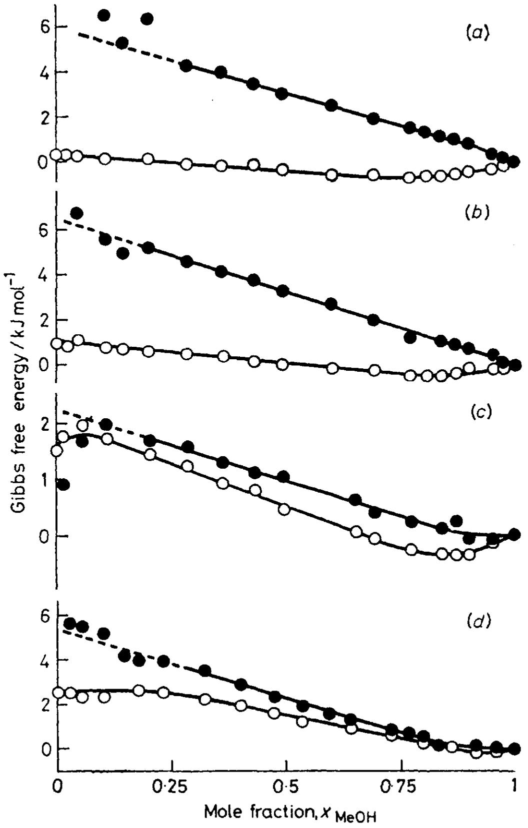

FIGURE 3 Plot of $\delta\Delta G^‡$(MeOH) (●) and $-\delta G_{tr}$ (○) *versus* mole fraction x_{MeOH} (for *T* = 298 K); (*a*), (3) + H-Etsaln in MeOH–Bu^{s}OH; (*b*), (2) + H-Etsaln in MeOH–Bu^{s}OH; (*c*), (1) + H-Phsaln in MeOH–Bu^{s}OH; (*d*), (1) + H-Etsaln in MeOH–2-methylbutan-2-ol

tion occurs through an associative mechanism and, hence, as a second-order rate process, one would expect that strong solvation of the reacting partners in the ground state would not favour the reaction. It is important to note that for such a second-order ligand substitution in solvent mixtures the parameter δG_{tr} is given by the sum of $\delta\mu_{tr}$ (complex) + $\delta\mu_{tr}$ (incoming nucleophile) (in general: $\delta G_{tr} = \Sigma\delta\mu_{tr}$). Several second-order inorganic substitution reactions have been studied in solvent mixtures and correlations of $\delta\Delta G^{\ddagger}$ and δG_{tr} have been made.[2]

A different situation arises when ligand substitution occurs through a solvent path, *i.e.* is independent of the incoming ligand. In this case δG_{tr} should be given only by $\delta\mu_{tr}$ (complex) because (*i*) the incoming ligand is not involved in the formation of the rate-controlling transition state and (*ii*) the contribution of the solvent, although involved in transition-state formation, can be neglected as long as the Gibbs free excess energies are small. As pointed out earlier, there are no data in the literature [9] for activity coefficients in MeOH–Bu^{s}OH mixtures. On the basis of the known data for MeOH–Bu^{n}OH mixtures a Gibbs free excess energy of $G^E \leqslant 0.15$ kJ mol^{-1} is calculated, which is indeed negligibly small.

On a qualitative basis one would expect that for a solvent pathway, in contrast to the second-order ligand pathway, strong solvation of the complex should be paralleled by high reactivity for ligand substitution as long as hydrophobic interactions are neglected. In this case the solvent molecules are assembled in close vicinity of the metal centre, and can therefore readily induce the reaction by solvento complex formation.

In Figure 3 both $\delta\Delta G^{\ddagger}$ and δG_{tr} are plotted as a function of x_{MeOH} for all three complexes. Qualitatively, good solubility indeed parallels high reactivity. On a quantitative basis it is found, however, that only for the pseudotetrahedral complex (1) do the data for $\delta\Delta G^{\ddagger}$ and $-\delta G_{tr}$ really parallel each other [see Figure 3(*c*)]. Obviously, the co-ordination geometry and structure of the complexes plays a role, because for the less distorted complex (2) [see Figure 3(*b*)] and the planar complex (3) [see Figure 3(*a*)] there is no such close correlation. Interestingly, the results obtained for the pseudotetrahedral complex (1) in mixtures of MeOH and 2-methylbutan-2-ol [see Figure 3(*d*)] are more similar to those found for (1) than to those found for (2) or (3) in MeOH–Bu^{s}OH mixtures. This, again, points to the significance of the structure of the complex.

The complexes studied are of the *trans*-N_2O_2 type. Due to the orientation of the *N*-alkyl group the phenolic oxygen atoms are more or less shielded and much less accessible in the planar N_2O_2 arrangement than in the pseudotetrahedral one. If the accessibility of these oxygen atoms is kinetically important this would mean that for the mechanism of the solvent path the MeOH or Bu^{s}OH molecule approaches the complex at the oxygen-donor sites. This approach is easier for the small MeOH than for the Bu^{s}OH molecule. In addition to this steric argument there is evidence that the interaction between MeOH or Bu^{s}OH and the phenolic oxygen occurs through hydrogen-bond formation. Figure 4 presents a plot of the relative change in ln $k_{obs.}$ for complexes (1)—(3) as well as a plot of the relative change in $E_T(30)$ *versus* x_{MeOH}. The obvious similarity between the two types of plot for the strongly distorted complexes (1) and (2) can be taken as an indication that the solvent forms hydrogen bonds with the phenolic oxygen in Reichardt's dye no. 30 as well as in the complexes studied. Due to the reduced accessibility of the phenolic oxygen in the square-planar arrangement of complex (3), the deviation between $E_T(30)$ and ln $k_{obs.}$ is not surprising.

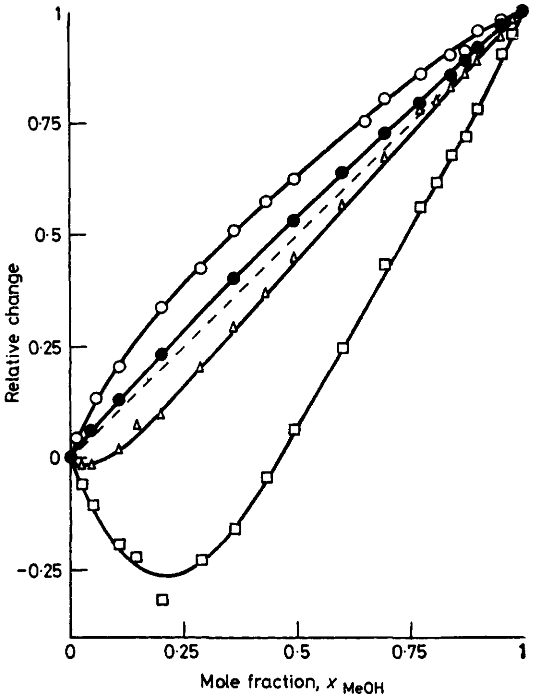

FIGURE 4 Relative change in Reichardt's $E_T(30)$ values (●, ref. 7) and in ln $k_{obs.}$ as a function of x_{MeOH} in MeOH–Bu^{s}OH (T = 298 K) for (1) + H-Phsaln (○), (2) + H-Etsaln (△), and (3) + H-Etsaln (□). The broken line indicates a slope of 1

The general question of how useful is the concept of ground-state–transition-state solvation [2] for the treatment of a solvent path is difficult to answer. First, there is the problem that δG_{tr} refers to both components of the solvent mixtures and $\delta\Delta G^{\ddagger}$ only to the MeOH path [see equation (viii)]. Another argument could be that the type of complex studied in this work is unusual in the sense that the solvent path is initiated by solvent attack at a donor atom and not at the metal.[12]

Finally, one could argue that the comparison and correlation of solvation data (δG_{tr}) and kinetic data ($\delta\Delta G^{\ddagger}$) is fully adequate only for a substrate in which the solvation sites and the reaction sites are identical.

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