and-dependent pathway with an associative mode of activation (A mechanism). Complexes I–III are subject to a fast configurational equilibrium; planar ⇌ tetrahedral. It follows from the sum of data collected that only the planar isomer is attacked by the entering ligand (attack at the tetrahedral isomer is undetectably small). The planar form of complexes I tends strongly to become octahedral in the presence of nucleophiles such as pyridine. It is clearly shown that the octahedral pyridine adducts of the complexes are inert toward ligand substitution and that substitution occurs exclusively through the four-coordinate planar complex, which in the presence of pyridine is in a fast equilibrium with the octahedral adduct.

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Registry No. I (R = *n*-Pr, $X^5 = OCH_3$), 97403-47-9; I·2py (R = *n*-Pr, $X^5 = OCH_3$), 97403-43-5; I (R = *n*-Pr), 35795-69-8; I·2py (R = *n*-Pr), 35829-38-0; I (R = *n*-Pr, X^5 = Br), 97403-48-0; I·2py (R = *n*-Pr, X^5 = Br), 97403-44-6; I (R = *i*-Pr), 35968-67-3; I·2py (R = *i*-Pr), 35829-39-1; I (R = *i*-Pr, X^5 = Br), 97403-49-1; I·2py (R = *i*-Pr, X^5 = Br), 97403-45-7; I (R = Et), 35968-61-7; I (R = All), 55292-18-7; I (R = *t*-Bu), 40706-02-3; I (R = *n*-Pe), 35968-70-8; I (R = Bz), 68510-29-2; II (R = Me), 15379-97-2; II (R = Et), 14880-23-0; II (R = *n*-Pr), 15391-41-0; II (R = *i*-Pr), 77095-86-4; II (R = All), 97403-41-3; II (R = Ph), 97403-42-4; II (R = Bz), 16828-51-6; III (R = Me), 97465-97-9; III (R = Et), 97465-98-0; III (R = *n*-Pr), 14568-02-6; III (R = *i*-Pr), 41553-43-9; IV (D = Et), 97415-90-2; IV [D = $N(CH_3)_2$], 97415-91-3; IV (D = OMe), 97403-46-8; acetylacetone, 123-54-6; *N,N'*-disalicylideneethylenediamine, 94-93-9.

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Effect of the Coordination Geometry and of Substituent Shielding on the Kinetics of Ligand Substitution in Copper(II) Chelates

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Stopped-flow spectrophotometry has been used to study the kinetics of ligand substitution in bis(*N*-R-salicylaldiminato)copper(II) complexes CuA_2 (R = H, OH, Me, Et, *i*-Pr, *t*-Bu, *neo*-Pe, phenyl) by bidentate ligands HB (*N*-ethylsalicylaldimine, acetylacetone) in methanol and ethylene glycol monomethyl ether at 298 K. A two-term rate law, rate = $(k_S + k_{HB}[HB])$[complex], has been found. The substitution of the first ligand in CuA_2 is rate determining. The relative contributions of the terms k_S and $k_{HB}[HB]$ to the overall rate are controlled by the *N*-alkyl group R in the following sense: (i) small groups R (such as R = Me) favor a planar *trans*-N_2O_2 coordination geometry of the complex, whereas bulky groups (such as R = *t*-Bu) force the complex to become strongly tetrahedrally distorted, and (ii) with increasing extent of tetrahedral distortion (due to the effect of R) the size of k_S increases, whereby the contribution of the term $k_{HB}[HB]$ can become negligibly small. A systematic study of the kinetic effect of substituents X^3 and X^5 (introduced in the 3- and 5-positions of the salicylaldehyde ring) and substituents Y^2, Y^4, and Y^6 (introduced in the 2-, 4-, and 6-positions of the *N*-phenyl ring) reveals that substituents $X^3 = CH_3$, Cl, Br, I, NO_2, which are neighboring to the oxygen donor atom, reduce the size of k_S according to their steric substituent constant E_s. Substituents $Y^2 = CH_3$, F, Cl, Br, I and $Y^2 = Y^6 = CH_3$, Cl (neighboring the nitrogen donor atom in the *N*-phenyl complexes) reduce both k_S and k_{HB}, which can be correlated with the electronic and steric properties of these substituents. The sum of the experimental results supports consistently the following mechanistic interpretation of the observed rate law, namely: (i) the second-order rate constant k_{HB} describes the nucleophilic attack of the entering ligand HB at the copper; (ii) the first-order rate constant k_S describes the attack of a protic solvent molecule, surprisingly not at the copper but at the oxygen donor atom instead.

Introduction

The rate of ligand substitution in square-planar complexes with d^8 metal centers such as platinum(II) and palladium(II) follows a two-term rate law:[1,2]

$$\text{rate} = (k_S + k_L[\text{ligand}])[\text{complex}] \quad (1)$$

The ligand-independent contribution (k_S) and the ligand-dependent contribution (k_L[ligand]) can be mechanistically attributed to the nucleophilic attack of a solvent molecule and ligand molecule, respectively. It is commonly accepted for both the "solvent path" and "ligand path" that nucleophilic attack occurs at the metal center.

It was important to prove but not surprising to find[3] that ligand substitution in planar $3d^8$ nickel(II) complexes is associative in character as well, although so far only for one nickel(II) system was a solvent path shown to exist in addition to the ligand path. This system,[4] in which we studied ligand substitution in bis(*N*-alkylsalicylaldiminato)nickel(II) with bidentate entering ligands, led in addition to an interesting aspect concerning the mechanism of the solvent path. Experimental evidence could be provided supporting the unusual interpretation that solvent attack does not occur at the metal but at the donor oxygen of the coordinated salicylaldimine ligand instead. Moreover, similar studies[5] with the corresponding bis(*N*-alkylsalicylaldiminato)copper(II) complexes ($3d^9$ metal center) revealed that ligand substitution in these complexes again follows rate law 1 and that the data obtained are indeed compatible with solvent attack taking place at the donor oxygen and not at the metal.

The present study was undertaken to further collect experimental data that should allow a more detailed mechanistic interpretation of the two pathways through which ligand substitution in bis(*N*-alkylsalicylaldiminato)copper(II) complexes occurs. This type of complex appears to be especially well suited for such a mechanistic study because of the various possibilities one has to modify the coordination geometry and electron density distribution by the introduction of substituents.

Type I and type II complexes, which basically prefer a square-planar *trans*-N_2O_2 coordination geometry,[6] are subject to the following substituent and R-group effects: (i) substituents

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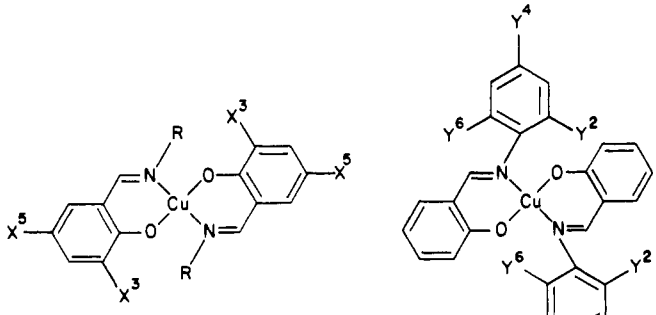

X^5 and Y^4 control the electron density at the donor oxygen (type I) and at the donor nitrogen (type II), respectively; (ii) the effect of substituents X^3 will be electronic and/or steric, the latter in the sense that bulky substituents X^3 can shield the donor oxygen and can lead to tetrahedral distortion of the complex through interaction with large R groups; (iii) the effect of substituents Y^2 and Y^6 will be electronic and/or steric, the latter in a way similar to that described for X^3; (iv) bulky R groups will force the planar arrangement to become tetrahedrally distorted.

In this contribution we report on the kinetics of ligand substitution in a variety of complexes CuA_2 of types I and II as studied in methanol or ethylene glycol monomethyl ether according to reactions 2 and 3. The abbreviations Hsal-Et and Hacac represent

$$CuA_2 + 2Hsal\text{-}Et \rightleftharpoons Cu(sal\text{-}Et)_2 + 2HA \quad (2)$$

$$CuA_2 + 2Hacac \rightleftharpoons Cu(acac)_2 + 2HA \quad (3)$$

the ligands *N*-ethylsalicylaldimine and acetylacetone. Modification of CuA_2 was achieved by introduction of different combinations of substituents X^3, X^5, Y^2, Y^4, Y^6, and alkyl groups R as pointed out above.

Experimental Section

Ligands and Complexes. Acetylacetone (Hacac; reagent grade, Merck) was used without further purification. *N*-Ethylsalicylaldimine (Hsal-Et) was prepared and purified as described earlier.[5]

5-Carboxysalicylaldehyde[7] was prepared by heating a solution containing 1 mol of 4-hydroxybenzoic acid dissolved in concentrated NaOH solution (480 g of NaOH dissolved in 1.5 L of water) and 196 g of trichloroacetic acid over a period of 2 h at 100 °C with stirring. The solution was acidified with H_2SO_4 and extracted with ether. The ethereal extracts were shaken with a $KHSO_3$ solution, which was acidified with H_2SO_4. Ether and SO_2 were removed by passing steam through the solution. The free aldehyde precipitated as yellowish crystals. It was recrystallized from $EtOH/H_2O$ (mp 243–244 °C).

Salicylaldehyde-5-carboxylic acid ethyl ester was obtained by refluxing 30 mmol of 5-carboxysalicylaldehyde in absolute ethanol in the presence of 7 g of concentrated H_2SO_4 for 72 h. The solvent was removed in vacuo and the residue poured into ice water. The ester separated together with unreacted carboxylic acid as a white solid. It was extracted with ether, dried with $CaCl_2$, and, after removal of the solvent, fractionated under reduced pressure (yield 52%; mp 68 °C; bp 180 °C (18 mmHg)).

Bis(*N*-*tert*-butyl-5-carbethoxysalicylaldiminato)copper(II) (Cu(sal-tBu)$_2$, X^3 = H, X^5 = COOEt) was obtained by a standard procedure[8] and recrystallized from chloroform (mp 233–235 °C). Anal. Calcd: C, 60.04; H, 6.47; N, 5.00. Found: C, 59.58; H, 6.39; N, 4.96.

Bis(salicylaldiminato)copper(II) (Cu(sal-H)$_2$) was obtained by saturating a warm solution of 20 mmol of salicylaldehyde in 100 mL of EtOH with gaseous ammonia. Upon addition of a warm solution of $Cu(AcO)_2 \cdot H_2O$ (10 mmol in 10 mL of concentrated NH_3) the complex precipitated. Recrystallization from chloroform yielded green scaly crystals (yield 41%; mp 160–161 °C (lit.[9] mp 164–165 °C)). Anal. Calcd: C, 55.35; H, 3.95; N, 9.23. Found: C, 55.20; H, 3.74; N, 9.47.

Bis(*N*-methylsalicylaldiminato)copper(II) (Cu(sal-Me)$_2$). To a warm solution of 20 mmol of salicylaldehyde in 100 mL of EtOH was added a concentrated aqueous solution of $MeNH_2$ in 50% excess. The addition of a warm solution of 10 mmol of $Cu(AcO)_2 \cdot H_2O$ in 10 mL of H_2O yielded green crystals upon cooling to room temperature (yield 36%; mp 153–157 °C (lit.[9] mp 157 °C) from EtOH). Anal. Calcd: C, 57.91; H, 4.83; N, 8.45. Found: C, 57.78; H, 4.62; N, 8.57.

Bis(salicylaldoximato)copper(II) (Cu(sal-OH)$_2$) was obtained quantitatively by the addition of a 1% EtOH solution of salicylaldoxime (reagent grade, Merck) to a solution of $Cu(AcO)_2 \cdot H_2O$ in dilute acetic acid. Recrystallization from EtOH yielded green crystals (yield: 80%; dec pt >70 °C (lit.[9] dec pt >50 °C)). Anal. Calcd: C, 50.07; H, 3.58; N, 8.35. Found: C, 50.36; H, 3.52; N, 8.48.

The preparation, melting points, and analytical data for all the other type I[10,11] and type II[12] complexes have been described earlier. The results of elemental analysis were in good agreement with the calculated data.

Solvents. MeOH and ethylene glycol monomethyl ether (EGMME) (both reagent grade, Merck) were dried dynamically and stored over 3-Å molecular sieves (for measurements with type I complexes). The residual water content as determined by automatic Karl Fischer titration was less than 5×10^{-3} M. For the kinetic runs with type II complexes both solvents were employed without drying. As shown earlier[5], variations in the content of residual water have no significant effect on the rate.

Kinetic Measurements. The kinetic measurements were done with a modified[5] Durrun D 110 stopped-flow spectrophotometer in combination with an Aminco DASAR storage oscilloscope. The kinetic runs were done under pseudo-first-order conditions ([ligand] > 20[complex]) and monitored at 500–600 nm. Reproducible runs were evaluated by fitting a total of 200 data points to an exponential function with a computer program based on the least-squares method. The deviation from ideal first-order kinetics was smaller than 1% (for the complex Cu(sal-*i*-Pr)$_2$ with X^3 = H and X^5 = NO_2 a second step was observed for reaction 2).

Results and Discussion

Coordination Geometry of Type I and Type II Complexes. The neutral bis complexes formed by copper(II) with salicylaldimines basically prefer a planar *trans*-N_2O_2 coordination geometry.[6] It follows from the results of single-crystal X-ray analysis that two types of deviations from this planar arrangement do occur, namely (i) tetrahedral distortion due to steric hindrance imposed by bulky groups R and substituents X^3 and (ii) formation of a "stepped structure". The latter type of deviation is found for the complex Cu(sal-Ph)$_2$, e.g., the displacement being 0.89 Å.[13] The origin of this displacement is not clear, and the occurrence of the "stepped structure" may well be limited to the solid state.

Information on the coordination geometry of type I and type II complexes in solution follows from the UV/vis absorption spectra, which basically confirm the configurational change observed for the solid state upon variation of R, X^3, Y^2, and Y^6.

On the basis of the single-crystal X-ray data available in the literature[6] or through our own studies[14] and on the basis of the absorption data for solutions found in the literature[10,15–17] or collected as part of this contribution, one is able to classify the complexes studied with respect to their coordination geometry in noncoordinating or weakly coordinating solvents such as toluene or chloroform.

For the series of nonsubstituted (X^3 = X^5 = H) complexes of type I with different alkyl groups R the following crude assignments can be made: OH, P; H, P; Me, P; Et, P; *i*-Pr, TD; *t*-Bu, T; *n*-Pr, T; *i*-Bu, P*; *neo*-Pe, P*. The symbols applied refer to P = practically planar, T = almost tetrahedral, and TD = slight tetrahedral distortion. The asterisk indicates considerable shielding of the copper through β-branched alkyl groups R. It should be

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Table I. Effect of Substituents X^5 on Rate Constants[a] for the Ligand Substitution in Type I Complexes of Different Coordination Geometry according to Reaction 2 Studied in Methanol[b]

		R = Et (P[d])		R = *i*-Pr (TD[d])		R = *t*-Bu (T[d])		R = *neo*-Pe[e] (P[d])
X^5	σ_p[c]	10^2k_S, s^{-1}	10^2k_{HB}, M^{-1} s^{-1}	$10k_S$, s^{-1}	$10k_{HB}$, M^{-1} s^{-1}	k_S, s^{-1}	k_{HB}, M^{-1} s^{-1}	10^3k_S, s^{-1}
OCH_3	−0.268	1.25 ± 0.10	1.35 ± 0.30	1.44 ± 0.10	not obsd	1.19 ± 0.024	not obsd	5.7 ± 0.1
CH_3	−0.170	1.20 ± 0.053	0.4 ± 0.2	1.36 ± 0.10	not obsd	0.889 ± 0.024	not obsd	4.3 ± 0.2
H	0			1.22 ± 0.089	not obsd	0.919 ± 0.016	not obsd	4.6 ± 0.2
F	0.062			1.33 ± 0.038	not obsd	0.896 ± 0.026	not obsd	
Cl	0.227	1.32 ± 0.10	1.16 ± 0.20	1.16 ± 0.045	not obsd	1.36 ± 0.024	not obsd	
Br	0.232			1.13 ± 0.033	not obsd	1.29 ± 0.021	not obsd	
I	0.276			1.16 ± 0.033	not obsd	1.23 ± 0.015	not obsd	
COOEt	0.45					1.03 ± 0.013	not obsd	
NO_2	0.778			0.81 ± 0.16 (I)[f]	8.84 ± 1.0 (I)	1.52 ± 0.056	1.81 ± 0.20	
				13.2 ± 1.8 (II)	55 ± 10 (II)			

[a] From measurements at seven different concentrations in the range $[HB]_0 = 0.01–0.5$ M; $k_{obsd} = k_S + k_{HB}[HB]$. [b] Conditions: $[Cu(X^5\text{-sal-R})_2] = 5 \times 10^{-4}$ M (for X^5 = I, NO_2: 2.5×10^{-4} M); $[HB]_0 = [Hsal\text{-}Et]_0 = 0.01–0.5$ M; $T = 298$ K; $\lambda = 530–580$ nm. [c] See ref 24. [d] The coordination geometry of the complex is characterized by P = practically planar, TD = slight tetrahedral distortion, and T = almost tetrahedral. [e] A ligand-dependent path $k_{HB}[HB]$ is not observed: $k_{HB} < 10^{-3}$ M^{-1} s^{-1}. [f] For this reaction two steps, I and II, are observed.

pointed out that in a more polar solvent such as methanol a solvent molecule may be coordinated by the copper, thus reducing the extent of tetrahedral distortion.

It is not to be expected that the introduction of substituents X^5 in type I complexes has any steric effect. Substituents X^3, however, if large enough, will shield the donor oxygen of the coordinated ligand. For X^3 = I, Br (and probably CH_3) it is to be expected, therefore, that the donor oxygen is less easily accessible, which is an additional effect in the sense that it is independent of the tetrahedral distortion as enforced by bulky alkyl groups such as R = *t*-Bu, *i*-Pr.

The type II complexes with R = phenyl are slightly distorted; i.e., they are of the TD type. In $Cu(sal\text{-}Ph)_2$ the planes of the two salicylaldehyde rings are twisted against each other by an angle of 18°.[13] It is important to note that in $Cu(sal\text{-}Ph)_2$ and in other type II complexes the orientation of the two phenyl rings is nearly perpendicular to the planes of the salicylaldehyde rings, which means that ortho substituents Y^2 and Y^6, respectively, are found above and below the copper. As a consequence, for $Y^2 = Y^6 = CH_3$, Cl the copper thus becomes shielded from nucleophilic attack.[18] Substituents Y^4 in type II complexes, like substituents X^5 in type I complexes, have an effect on the electron density of the donor atoms but do not lead to steric consequences.

The UV/vis absorption spectrum of the type II complex with $Y^2 = OCH_3$ shows clearly that at least one of the methoxy groups is coordinated by the copper.[19]

Experimental Rate Law. Ligand substitution according to (2) and (3) is of the general type (4) (HB ≙ Hsal-Et, Hacac). Under

$$CuA_2 + 2HB \rightleftharpoons CuAB + HA + HB \rightleftharpoons CuB_2 + 2HA \quad (4)$$

excess conditions ($[CuA_2]_0 << [HB]_0$) the course of this two-step substitution process can be described satisfactorily by a single-exponential function; i.e., rate $= -d[CuA_2]/dt = k_{obsd}[CuA_2]$. The observed change in absorbance covers the complete range from CuA_2 to CuB_2, which means that substitution of the first of the two leaving ligands is rate controlling. The experimental first-order rate constant k_{obsd} follows relationship 5. In many cases the

$$k_{obsd} = k_S + k_{HB}[HB] \quad (5)$$

ligand-dependent term $k_{HB}[HB]$, called the "ligand path", is negligibly small as compared to the ligand-independent contribution k_S, called the "solvent path" ($k_{obsd} \approx k_S$). Figure 1 presents some typical data. As shown earlier for protic solvents,[5,20] the size of k_S depends on the nature of the solvent and is subject to mass-law retardation.[21] The fact that k_S can be correlated with

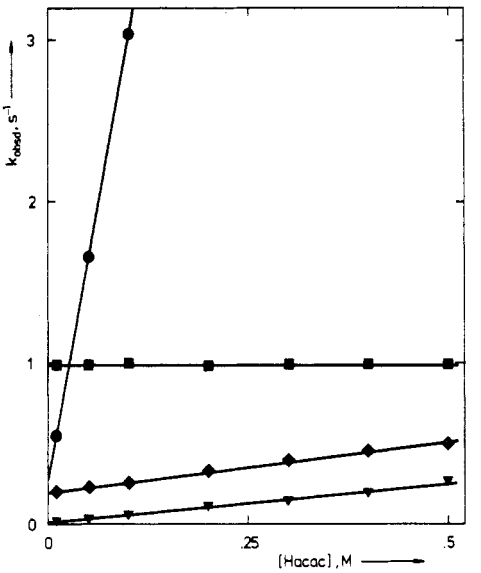

Figure 1. Dependence of k_{obsd} on the ligand concentration for ligand substitution in $Cu(sal\text{-}R)_2$ at 298 K in methanol according to (3) for R = Ph (●), *t*-Bu (■), *i*-Pr (♦), and Et (▼) at $[Cu(sal\text{-}R)_2]_0 = 5 \times 10^{-4}$ M.

the solvent polarity parameter $E_T(30)$[22,23] is of importance for the mechanistic interpretation (see later).

Effect of Substituents X^5 in Type I Complexes. Rate constants k_S and k_{HB} obtained for type I complexes with different substituents X^5 reacting in methanol according to (2) are listed in Table I. The fact that the data for the complexes with R = Et, *neo*-Pe, and strongly electron-withdrawing substituents X^5 are missing is due to their low solubility in methanol.

It follows from the data in Table I that for a given substituent X^5 such as $X^5 = OCH_3$ rate constant k_S clearly depends on the nature of the *N*-alkyl group, which governs the degree of tetrahedral distortion:

$$k_S(R = t\text{-Bu}):k_S(R = i\text{-Pr}):k_S(R = Et):k_S(R = neo\text{-Pe}) \approx 200:25:2:1$$

The size of k_S increases considerably with increasing tetrahedral distortion.

For a given *N*-alkyl group R however there is practically no effect of substituents X^5 on the size of k_S. The same is true for rate constant k_{HB} as obtained for the complexes $Cu(X^5\text{-sal-Et})_2$. (The fact that a ligand-dependent pathway as described by k_{HB} is not observed for the complexes with R = *i*-Pr, *t*-Bu, *neo*-Pe is

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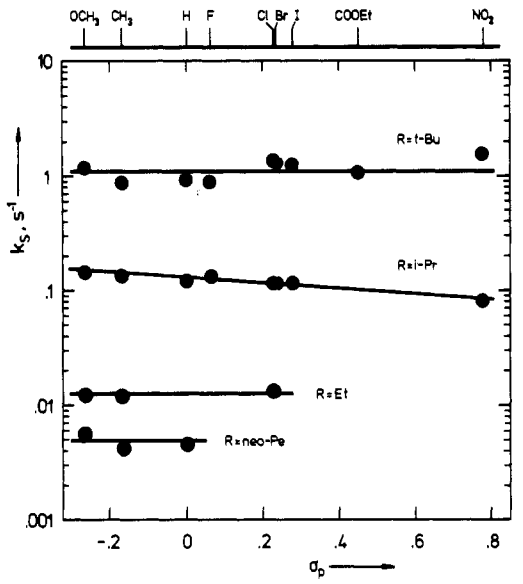

Figure 2. Effect of substituents X^5 on rate constant k_S for the ligand substitution in type I complexes Cu(sal-R)$_2$ (R = Et, *i*-Pr, *t*-Bu, *neo*-Pe) according to (2) in methanol at 298 K (σ_p = Hammett's substituent constant; see Table I and ref 24).

Table II. Rate Constants for Ligand Substitution in the Complex [Cu(X^5-sal-*t*-Bu)$_2$] according to Reaction 2 in Toluene at 298 K[a]

X^5	10^2k_0, s^{-1}	10^2k_{HB}, M^{-1} s^{-1}	X^5	10^2k_0, s^{-1}	10^2k_{HB}, M^{-1} s^{-1}
OCH_3	8.9 ± 0.1	7.9 ± 0.2	I	1.2 ± 0.1	3.7 ± 0.1
CH_3	5.1 ± 0.2	1.7 ± 0.8	COOEt	1.1 ± 0.2	2.5 ± 0.5
H	2.0 ± 0.1	3.3 ± 0.2	NO_2	0.72 ± 0.1	6.7 ± 0.3

[a] From measurements at six different concentrations in the range $[Hsal\text{-}Et]_0 = [HB]_0 = 0.05$–$0.5$ M at [complex] = 5×10^{-4} M; $k_{obsd} = k_0 + k_{HB}[HB]$.

obviously due to the consequences of tetrahedral distortion and shielding (R = *neo*-Pe); only in a planar coordination geometry and for a nonshielding *N*-alkyl group R such as R = Et is the copper sufficiently accessible for the weak nucleophile Hsal-Et.)

Figure 2 shows plots of k_S vs. σ_p, Hammett's substituent parameter[24] (as listed in Table I). As one can see, the slope of these plots (=reaction constant ρ) is practically zero (R = *t*-Bu, Et) or very small (R = *i*-Pr, *neo*-Pe). This finding of a nonexisting or very small substituent effect of X^5 on k_S is contrasted by the distinct effect that substituents X^5 have on the Lewis acidity of the copper in type I complexes as measured by the equilibrium constant K_{py} for reaction 6

$$CuA_2 + py \rightleftharpoons CuA_2{\cdot}py \quad K_{py} \qquad (6)$$

in toluene. The corresponding plot of log K_{py} vs. σ_p leads to ρ = 1.19 for type I complexes and ρ = 0.97 for type II complexes[25] upon variation of Y[4]. This means that in toluene transfer of electron density from the donor atoms to the copper does actually take place.

An explanation for the unexpectedly small electronic effect of substituents X^5 on k_S lies probably in the properties of the solvent. An electron-withdrawing substituent X^5 such as the nitro group will certainly reduce the stability of the Cu–O bond. The electron density at the oxygen donor atom, however, is decreased so that proton transfer from the solvent methanol to the phenolic oxygen is less favored. Experiments with the complex Cu(sal-*t*-Bu)$_2$ demonstrate (see Table II) that in toluene the ligand-independent path k_0 (as initiated by trace amounts of residual water in toluene[26]) clearly depends on the type of substituent X^5. The solvent methanol obviously exerts a leveling effect in the sense that variations in electron density on the donor oxygen become kinetically less effective.

The two complexes Cu(sal-*i*-Pr)$_2$ and Cu(sal-*t*-Bu)$_2$ with X^5 being the nitro group represent exceptions for two reasons: (i) for Cu(sal-*i*-Pr)$_2$ the second, faster step (CuAB → CuB_2; see (4)) is also observed, and (ii) the experimental rate constant k_{obsd} depends on the concentration of the entering ligand Hsal-Et. A possible explanation for this deviating behavior may be the clearly increased Lewis acidity of these complexes with $X^5 = NO_2$.[25] Proton transfer from the attacking ligand Hsal-Et to the nitro group might take place, and the formation of the *aci*-nitro species could then cause the cleavage of the Cu–O bond.

Effect of Substituents X^3 in Type I Complexes. The rate constants obtained for ligand substitution according to (2) in type I complexes Cu(sal-Et)$_2$, Cu(sal-*i*-Pr)$_2$, and Cu(sal-*t*-Bu)$_2$ with $X^5 = CH_3$ and different substituents X^3 are summarized in Table III. In all cases the complexes with X^3 = H is the fastest. Both electron-withdrawing substituents (such as $X^3 = NO_2$) and electron-releasing substituents (such as $X^3 = CH_3$) decrease the size of k_S. In principle, the effect of substituents X^3 (neighboring the phenolic donor oxygen) can be electronic and steric as well. Considering that the electronic effect of substituents X^5 is negligibly small in methanol (see Table I), one has to conclude that the observed rate effect of substituents X^3 in methanol is primarily steric. This means that substituents in positions ortho to the donor oxygen shield this donor atom. Since it is well documented for alcohol solvents[5,21] that the ligand-independent k_S path in eq 5 is initiated by solvent attack, the conclusion is that the solvent methanol attacks at the donor oxygen and not at the copper.

The steric demands of substituents can be described by their "steric substituent constant" E_s as introduced by Taft.[27] The E_s values of the different substituents X^3 are presented in Table III. For the complexes Cu(sal-*i*-Pr)$_2$ with $X^5 = CH_3$ and X^3 = variable, fitting of k_S to the relationship log $k_S(X^3)$ – log $k_S(X^3 = H) = \delta E_s$ leads to δ = 0.73 ± 0.06. This correlation supports the interpretation that the rate-reducing effect of substituents X^3 is of steric origin.

It is interesting to note (see Table III) that the shielding effect of substituents X^3 such as $X^3 = CH_3$ is related to the coordination geometry of the complex in the sense that the methyl group in the 3-position hinders solvent attack in the planar complex (R = Et) more than in the tetrahedral one (R = *t*-Bu), although the copper is more easily accessible in the planar complex (the ratio $k_S(X^3 = H)/k_S(X^3 = CH_3)$ changes from 6.3 (R = Et) to 4.4 (R = *i*-Pr) and to 3.6 (R = *t*-Bu)). So, both the decrease of k_S with increasing size of substituents X^3 and (for a given substituent X^3) its increase with increasing tetrahedral distortion strongly support the interpretation that the k_S term in eq 5 describes a reaction path initiated by methanol attack at a lone electron pair of the phenolic oxygen. This attack occurs probably through hydrogen bonding since it was shown earlier[23] that k_S can be correlated with the solvent polarity parameter $E_T(30)$.

The interpretation given above for the solvent path k_S favors the conception of one of the two lone electron pairs of the phenolic oxygen being in a sp^2 hybrid orbital and thus in plane with the aromatic ring of the ligand (the second lone electron pair would then occupy the p_z orbital). The rate-reducing steric effect of substituents X^3 would be most plausible if the methanol attack occurred at the sp^2 hybrid orbital.

The kinetic effect of substituents X^3 on the ligand-dependent k_{HB} pathway is somewhat less clear (see Table III). On the one hand, this pathway is completely covered by the solvent pathway for Cu(sal-*i*-Pr)$_2$ and Cu(sal-*t*-Bu)$_2$ with $X^5 = CH_3$ and X^3 = H, CH_3. For the planar complex Cu(sal-Et)$_2$ the k_{HB} term in eq 5 is observed, but the effect of $X^3 = CH_3$ and X^3 = I instead of X^3 = H on k_{HB} is small and not very characteristic, if the error limits for the values obtained are taken into account. For the complex Cu(sal-*i*-Pr)$_2$ with $X^5 = CH_3$ and X^3 = Cl, Br, I, a k_{HB} term is observed and the size of k_{HB} decreases slightly with decreasing inductive effect of the halogen. Unexpectedly large is the increase

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(27) Unger, S. H.; Hansch, C. *Prog. Phys. Org. Chem.* **1976**, *12*, 91.

Table III. Effect of Substituents X^3 on Rate Constants[a] for the Ligand Substitution in Type I Complexes of Different Coordination Geometry according to Reaction 2 Studied in Methanol[b]

			R = Et (P[c])		R = *i*-Pr (TD[c])		R = *t*-Bu (T[c])	
X^3	X^5	$E_s(X^3)$[d]	10^3k_S, s^{-1}	10^3k_{HB}, M^{-1} s^{-1}	10^2k_S, s^{-1}	10^3k_{HB}, M^{-1} s^{-1}	$10k_S$, s^{-1}	$10k_{HB}$, M^{-1} s^{-1}
H	CH_3	0	12.0 + 0.5	4 ± 2	13.6 ± 1.0	not obsd	8.89 ± 0.24	not obsd
CH_3	CH_3	−1.24	1.9 ± 0.03	1.1 ± 0.1	3.1 ± 0.1	not obsd	2.46 ± 0.13	not obsd
Cl	CH_3	−0.97	...	...	1.75 ± 0.036	8.97 ± 1.3	...	
Br	CH_3	−1.16	...	...	1.51 ± 0.005	6.87 ± 0.18	...	
I	CH_3	−1.4	1.14 ± 0.01	2.6 ± 0.1	1.17 ± 0.005	4.83 ± 0.19	...	
NO_2	CH_3	−1.01[e]			2.66 ± 0.10	428 ± 16	...	
H	NO_2						15.2 ± 0.56	18.1 ± 2.0
I	NO_2						3.48 ± 0.17	15.2 ± 0.8

[a] From measurements at seven different concentrations in the range $[Hsal\text{-}Et]_0 = [HB]_0 = 0.01\text{–}0.5$ M; $k_{obsd} = k_S + k_{HB}[HB]$. [b] Conditions: $[complex]_0 = 5 \times 10^{-4}$ M; $[HB]_0 = [Hsal\text{-}Et]_0 = 0.01\text{–}0.5$ M; $T = 298$ K; $\lambda = 570\text{–}600$ nm. [c] Legend: P = practically planar, TD = slight tetrahedral distortion, T = almost tetrahedral. [d] E_s = Taft's steric substituent constant.[27] [e] E_s value of the "thickness" of the nitro group.[27]

Table IV. Effect of the Alkyl Group R on Rate Constants[a] for the Ligand Substitution in Type I Complexes according to Reaction 3 in Methanol and Ethylene Glycol Monomethyl Ether (EGMME)[b]

		EGMME		MeOH	
R	coord geom[c]	10^2k_S, s^{-1}	10^2k_{Hacac}, M^{-1} s^{-1}	10^2k_S, s^{-1}	10^2k_{Hacac}, M^{-1} s^{-1}
OH	P	10.3 ± 0.2	not obsd	...[d]	...[d]
H	P	0.34 ± 0.07	1.74 ± 0.21	...[d]	...[d]
Me	P	2.20 ± 0.28	17.5 ± 1.0	...[d]	...[d]
Et	P	1.11 ± 0.02	9.10 ± 0.07	1.0 ± 0.5	50 ± 3
i-Pr	TD	6.5 ± 0.1	16.9 ± 0.5	20.0 ± 2	64 ± 3
t-Bu	T	21.4 ± 0.1	not obsd	99.0 ± 5	not obsd
n-Pr	P	0.775 ± 0.049	10.3 ± 0.2	2.82 ± 0.17	79.7 ± 2.5
i-Bu	P*[e]	0.283 ± 0.025	6.02 ± 0.09	1.46 ± 0.18	37.9 ± 0.6
neo-Pe	P*	0.196 ± 0.005	0.709 ± 0.019	0.777 ± 0.022	2.83 ± 0.11
Ph[f]	TD	31.5 ± 1.9	360.5 ± 6.7	28.2 ± 0.4	2485 ± 50

[a] From measurements at seven different concentrations in the range $[Hacac]_0 = 0.01\text{–}0.5$ M; $k_{obsd} = k_S + k_{Hacac}[Hacac]$. [b] Conditions: $[Cu(sal\text{-}R)_2]_0 = 5 \times 10^{-4}$ M; $T = 298$ K; $\lambda = 520\text{–}560$ nm. [c] Legend: P = practically planar; TD = slight tetrahedral distortion; T = almost tetrahedral. [d] Complex is not sufficiently soluble in methanol. [e] The asterisk indicates considerable shielding of the copper through β-branched group R. [f] Type II complex.

Table V. Effect of Substituents Y^4 on Rate Constants[a] for the Ligand Substitution in Type II Complexes according to Reaction 2 Studied in Methanol

Y^4	$10k_S$, s^{-1}	$10k_{HB}$, M^{-1} s^{-1}	Y^4	$10k_S$, s^{-1}	$10k_{HB}$, M^{-1} s^{-1}
H	1.19 ± 0.12	7.06 ± 0.42	I	1.04 ± 0.09	9.84 ± 0.33
H[b]	0.91 ± 0.03	4.47 ± 0.11	CN	1.66 ± 0.08	5.37 ± 0.20
CH_3	0.94 ± 0.03	3.89 ± 0.11	H[c]	0.288 ± 0.010	0.975 ± 0.036
Cl	0.85 ± 0.03	9.75 ± 0.67	CH_3[d]	0.102 ± 0.003	0.070 ± 0.011

[a] From measurements at seven different concentrations in the range $[Hsal\text{-}Et]_0 = [HB]_0 = 0.01\text{–}0.5$ M and $[complex]_0 = 2 \times 10^{-4}\text{–}1 \times 10^{-3}$ M; $k_{obsd} = k_S + k_{HB}[HB]$. [b] $X^5 = CH_3$ instead of $X^5 = H$. [c] $Y^2 = CH_3$ instead of $Y^2 = H$. [d] $Y^2 = Y^6 = CH_3$ instead of $Y^2 = Y^6 = H$.

in k_{HB} for the complex Cu(sal-*i*-Pr)$_2$ with $X^3 = NO_2$ ($X^5 = CH_3$). In the case of the complex Cu(sal-*t*-Bu)$_2$ with $X^5 = NO_2$ the substitution of $X^3 = I$ for $X^3 = H$ reduces k_S and leaves k_{HB} practically unchanged (see Table III).

Effect of the Alkyl Group R in Type I Complexes. The rate effect of aliphatic groups R on reaction 3 was studied in methanol and also in EGMME because of the low solubility of the complexes Cu(sal-OH)$_2$, Cu(sal-H)$_2$, and Cu(sal-Me)$_2$ in methanol. The use of acetylacetone (Hacac) (reaction 3) instead of *N*-ethylsalicylaldimine (Hsal-Et) (reaction 2) led to greater changes in absorbance to be observed.

It follows from Table IV that a given complex reacts faster in methanol than in EGMME (the type II complex Cu(sal-Ph)$_2$ is the only exception); both k_S and k_{Hacac} are larger in methanol. Independent of that, the trends observed upon variation of R are the same in both solvents, namely (i) α branching in R (Et → *i*-Pr → *t*-Bu) increases k_S, (ii) β branching in R (Et → *n*-Pr → *i*-Bu → *neo*-Pe) decreases k_S, (iii) k_{Hacac} is more or less of similar size for R = Me, Et, *n*-Pr, *i*-Pr and vanishes for R = *t*-Bu, and (iv) β branching in R (*n*-Pr → *i*-Bu → *neo*-Pe) reduces k_{HB} even more than k_S.

These findings can be convincingly correlated with the coordination geometry of the complexes in solution. If the attack of the entering Hacac takes place at the copper, it is obvious that such an attack is strongly hindered for the tetrahedral complex Cu(sal-*t*-Bu)$_2$ (as a consequence, k_{Hacac} is not observed at all). The decrease in k_{Hacac} upon β branching in R is a consequence of steric crowding close to the copper and, hence, shielding of the copper from nucleophile attack by Hacac. Finally, the increase in k_S with increasing tetrahedral distortion corresponds perfectly to the mechanistic interpretation of the solvent-initiated pathway k_S given above. If the attack of the solvent methanol does indeed take place at the (probably sp^2-hybridized) lone electron pair of the donor oxygen, then any tetrahedral distortion of the complex will reduce the shielding of the oxygen through the opposite alkyl group R and, hence, make the oxygen more accessible. On these grounds, it also becomes understandable why k_S (R = Me) > k_S(R = Et). Both complexes are planar, but the interligand shielding of the oxygen is less for the small methyl group than for the ethyl group. The finding that the argument of interligand shielding of the oxygen does not hold for the complexes Cu(sal-H)$_2$ and Cu(sal-OH)$_2$ (they react slower than Cu(sal-Me)$_2$) is probably due to the existence of oligomeric units in solution, which are less reactive (the formation of oligomeric units has been shown to take place in the solid state[6]).

Ligand substitution in the type II complex Cu(sal-Ph)$_2$ takes place much more rapidly than in type I complexes, especially through the k_{Hacac} pathway. This is probably due to the electron-withdrawing effect of the phenyl group, making the copper a better Lewis acid.

Effect of Substituents Y in Type II Complexes. It follows from Table V that the effect of substituents Y^4, which are expected

Table VI. Effect of Substituents Y^2 on Rate Constants[a] for the Ligand Substitution in Type II Complexes according to Reaction 3 Studied in Ethylene Glycol Monomethyl Ether

Y^2	Y^4	Y^6	$\sum\sigma_p$[b]	$\sum E_s$[c]	$10^2 k_S$, s^{-1}	$10^2 k_{Hacac}$, M^{-1} s^{-1}
H	H	H	0	0	31.9 ± 0.5	317 ± 2
CH_3	H	H	−0.170	−1.24	13.2 ± 1.1	83.9 ± 4.0
F	H	H	0.06	−0.46	3.91 ± 0.04	17.9 ± 0.2
CH_3	CH_3	CH_3	−0.510	−2.48	2.05 ± 0.10	12.8 ± 0.4
Cl	H	H	0.227	−0.97	1.47 ± 0.03	5.53 ± 0.10
Br	H	H	0.232	−1.16	1.48 ± 0.01	4.91 ± 0.03
I	H	H	0.276	−1.40	1.89 ± 0.03	3.93 ± 0.12
Cl	H	Cl	0.454	−1.94	0.270 ± 0.003	0.392 ± 0.009
OCH_3	H	H			0.576 ± 0.006	0.878 ± 0.021

[a] From measurements at seven different concentrations in the range $[Hacac]_0$ = 0.01–0.5 M and $[complex]_0$ = 2.5 × 10^{-4}–5.0 × 10^{-4} M; $k_{obsd} = k_S + k_{Hacac}[Hacac]$; T = 298 K; λ = 480–560 nm. [b] See ref 24. [c] See ref 27.

Table VII. Parameters ρ and δ Obtained by Fitting Rate Constants k_S and k_{Hacac} of Table VI to Eq 7

	ρ	δ
k_S	−1.53 ± 0.34	0.750 ± 0.070
k_{Hacac}	−2.38 ± 0.39	1.01 ± 0.08

to alter the electron density at the donor nitrogen in type II complexes, is very similar to that of substituents X^5 in type I complexes; i.e., the size of k_S is only very slightly affected. The same is true for rate constant k_{HB}, which ranges from 0.39 M^{-1} s^{-1} ($Y^4 = CH_3$) to 0.98 M^{-1} s^{-1} (Y^4 = I).

The kinetic effects of substituents Y^4 and Y^2 in the *N*-phenyl ring of type II complexes parallel indeed the effects of substituents X^5 and X^3 in type I complexes, namely (i) negligibly small electronic effects of the para substituents Y^4 and X^5 on rate constant k_S and (ii) substantial steric effects of the ortho substituents Y^2 (as well as Y^6) and X^3 on k_S. The introduction of one methyl group ($Y^2 = CH_3$) or two methyl groups ($Y^2 = Y^6 = CH_3$) in the *N*-phenyl ring reduces k_S by a factor of 4.1 and 9.2, respectively (see Table V).

The data summarized in Table VI present a more systematic study on the effects of substituents Y^2 and Y^6 in type II complexes reacting in EGMME according to (3). Both k_S and k_{Hacac} are clearly reduced when substituents Y^2 and Y^6 are introduced. One recognizes that the rate-reducing effect of substituents Y^2 and Y^6 cannot be ascribed to the steric demands of these substituents only. An attempt was made, therefore, to consider both steric and electronic effects of substituents Y^2 and Y^6 by fitting the rate constants obtained to the two-parameter relationship (7). As a

$$\log (k(Y)/k(Y = H)) = \rho\sum\sigma + \delta\sum E_s \qquad (7)$$

first approximation it was assumed that $\sigma_p \approx \sigma_o$. The values for $\sum\sigma$ (=sum of substituent constants[24] of all substituents Y present) and for $\sum E_s$ (=sum of steric substituent constants[27] of all orthosubstituents Y present) are given in Table VI. Table VII presents the values obtained for ρ and δ by fitting the rate constants to eq 7.

In parts a and b of Figure 3 the logarithms of rate constants k_S and k_{Hacac} (corrected for $\rho\sum\sigma$, the sum of the electronic effects) are respectively plotted vs. $\sum E_s$, the sum of the steric substituent constants. In both cases satisfying linearity is observed, except for the complex with Y^2 = F. The deviation for Y^2 = F is probably due to nonvalidity of the assumption $\sigma_o \approx \sigma_p$, since fluorine has a strong inductive effect.

The fitting parameters ρ and δ (see Table VII) are smaller for the k_S path than for the k_{Hacac} path, which means that the ligand-dependent pathway is more sensitive to steric and electronic effects introduced by substituents in the *N*-phenyl ring. The negative sign of ρ proves that electron-withdrawing substituents Y^2 and Y^6 such as the halogens decrease the rate of reaction. One could imagine that the proximity of an electron-rich halogen atom makes nucleophilic attack less easy.

There is spectroscopic evidence[19] that in the type II complex with $Y^2 = OCH_3$ the methoxy groups are at least partially coordinated to the copper. The inconsistently strong rate-reducing

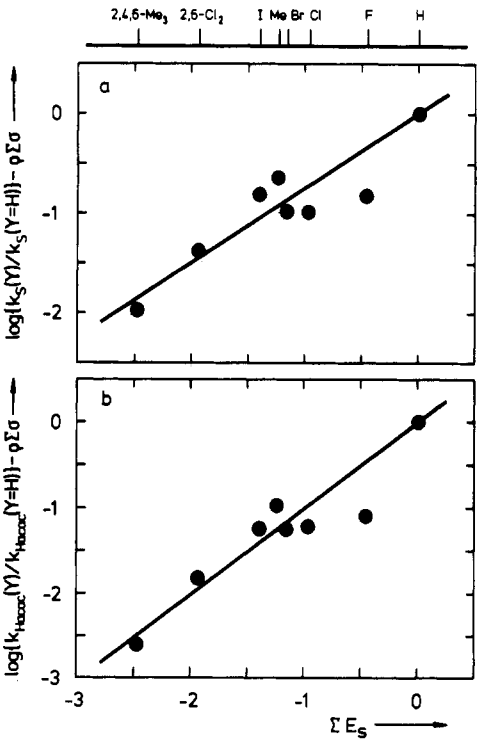


Figure 3. Relative steric effect of substituents Y^2 on rate constants (a) k_S and (b) k_{Hacac} for the ligand substitution in type II complexes Cu(sal-Ph)$_2$ according to (3) in ethylene glycol monomethyl ether at 298 K (correction for electronic effects according to (7); $\sum E_s$ = sum of steric effects; see Table VI and ref 27).

effect of $Y^2 = OCH_3$ on k_S and k_{Hacac} (see Table VI) is not surprising, therefore. It is well-known[4] for the corresponding nickel complexes Ni(sal-R)$_2$ that any increase in coordination number (e.g., by addition of pyridine) decreases the rate of ligand substitution.

Mechanistic Interpretation and Conclusions. The mechanistic interpretation of rate law 8, which is observed for ligand substitution in copper(II) complexes of types I and II according to (2) and (3) has to be based on the following general pattern of kinetic behavior: (i) substitution of the first of the two leaving

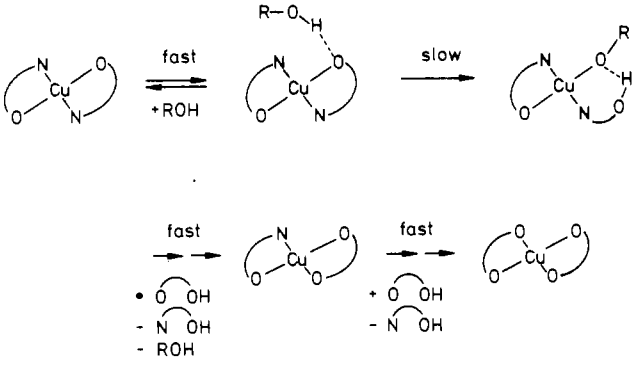
$$\text{rate} = -d[MA_2]/dt = (k_S + k_{HB}[HB])[MA_2] \qquad (8)$$

ligands is rate controlling, and the step $CuAB \rightarrow CuB_2$ is a fast consecutive step; (ii) the stepwise introduction of tetrahedral distortion in a planar type I complex CuA_2 through bulky alkyl groups R increases k_S, by which the term $k_{HB}[HB]$ in (8) becomes more or less "covered"; (iii) substituents X^3 reduce k_S according to their size, and this rate-reducing steric effect is more pronounced in planar and less pronounced in tetrahedral type I complexes CuA_2; (iv) in type II complexes CuA_2 substituents Y^2 and Y^6 reduce both k_S and k_{HB} according to their size.

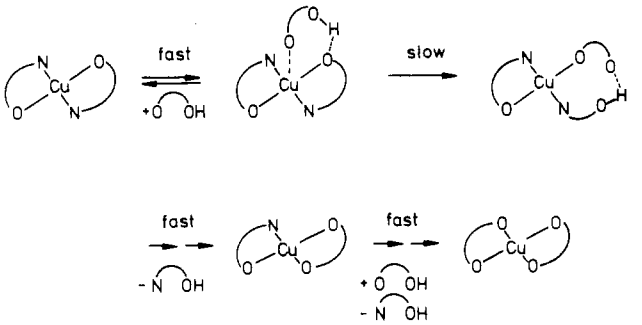
As shown earlier[5,21] for protic solvents, the term k_S in rate law 8 is initiated by solvent attack and is therefore called the solvent

Scheme I

(a) Mechanism of the Solvent Path



(b) Mechanism of the Ligand Path



path. The findings of this contribution lead to mechanistic interpretations of the k_S term and of $k_{HB}[HB]$, which differ fundamentally in the question of where (i.e., at which site of the complex) the reaction starts.

Scheme Ia describes the solvent-initiated reaction channel k_S. In a fast preequilibrium a solvent molecule ROH (=MeOH, EGMME) *adds to a lone electron pair of the donor oxygen*, probably through hydrogen bonding. The slow and rate-controlling step then is the breaking of the Cu–O bond, transfer of the solvent proton to the leaving ligand, and coordination of the alkoxide anion. The species thus formed is highly labile. It reacts quickly with an incoming ligand such as Hacac (abbreviated as HO⁀O) to form the mixed-ligand complex, which is converted to the product in a series of fast consecutive steps.

As shown in Scheme Ib, the ligand-initiated reaction channel $k_{HB}[HB]$ starts with a fast preequilibrium, in which *the incoming nucleophile Hacac adds to the copper*. The slow and rate-controlling step again is the breaking of the Cu–O bond, followed by fast formation of the mixed-ligand complex and, finally, of the product.

These interpretations of the solvent path and of the ligand path are the only that are consistently in agreement with the sum of the experimental facts. Tetrahedral distortion of a planar complex CuA_2 makes the copper less accessible for the incoming ligand (reduction in k_{HB}) and the donor oxygen better accessible for the attacking solvent (increase in k_S). The substituent effects are in line with Scheme I.

One might argue that the discussion on solvent attack at oxygen vs. ligand attack at copper is more academic than really important. One should consider however that it is only the site of attack which explains that distorted copper complexes of type I prefer to react faster through the k_S pathway. In addition, several rather unexpected results can be rationalized now. When ligand substitution according to eq 3 in methanol is carried out with the nickel complex Ni(sal-*t*-Bu)$_2$ instead of Cu(sal-*t*-Bu)$_2$, k_S dominates in both cases and the values obtained are almost identical (k_S = 0.90 s^{-1} for the nickel complex[4] and k_S = 0.99 s^{-1} for the copper complex). Methanol attack occurs at the donor oxygen, and the strengths of the Ni–O and Cu–O bonds obviously are similar. When, however, the two planar complexes Ni(sal-Et)$_2$ and Cu(sal-Et)$_2$ are compared, the ligand path contributes in both systems, but k_{Hacac} for the nickel complex is 4000 times larger[4] than that for the copper complex, since ligand attack occurs at the metal center and since the tendency to increase the coordination number is much stronger for nickel(II) than for copper(II).[4,25]

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Registry No. I (R = Et, X^5 = OMe), 61476-41-3; I (R = Et, X^5 = Me), 61490-46-8; I (R = Et, X^5 = Cl), 61176-43-0; I (R = *i*-Pr, X^5 = OMe), 56192-36-0; I (R = *i*-Pr, X^5 = Me), 15379-85-8; I (R = *i*-Pr), 14077-14-6; I (R = *i*-Pr, X^5 = F), 56234-94-7; I (R = *i*-Pr, X^5 = Cl), 24613-45-4; I (R = *i*-Pr, X^5 = Br), 24728-76-5; I (R = *i*-Pr, X^5 = I), 56192-32-6; I (R = *i*-Pr, X^5 = NO_2), 15413-31-7; I (R = *t*-Bu, X^5 = OMe), 56192-37-1; I (R = *t*-Bu, X^5 = Me), 15379-84-7; I (R = *t*-Bu), 36748-28-4; I (R = *t*-Bu, X^5 = F), 56192-28-0; I (R = *t*-Bu, X^5 = Cl), 15390-16-6; I (R = *t*-Bu, X^5 = Br), 56192-30-4; I (R = *t*-Bu, X^5 = I), 36509-03-2; I (R = *t*-Bu, X^5 = COOEt), 97704-68-2; I (R = *t*-Bu, X^5 = NO_2), 15390-19-9; I (R = *neo*-Pe, X^5 = OMe), 61462-34-8; I (R = *neo*-Pe, X^5 = Me), 61462-33-7; I (R = *neo*-Pe), 61462-27-9; I (R = Et, X^3 = X^5 = Me), 61476-37-7; I (R = Et, X^3 = I, X^5 = Me), 61476-35-5; I (R = *i*-Pr, X^3 = X^5 = Me), 56192-24-6; I (R = *i*-Pr, X^3 = Cl, X^5 = Me), 56192-17-7; I (R = *i*-Pr, X^3 = Br, X^5 = Me), 56234-98-1; I (R = *i*-Pr, X^3 = I, X^5 = Me), 56192-20-2; I (R = *i*-Pr, X^3 = NO_2, X^5 = Me), 56235-00-8; I (R = *i*-Pr, X^3 = I, X^5 = NO_3), 69897-72-9; I (R = *t*-Bu, X^3 = X^5 = Me), 56192-25-7; I (R = OH), 41942-15-8; I (R = H), 21673-65-4; I (R = Me), 26194-22-9; I (R = Et), 26194-23-0; I (R = *n*-Pr), 37703-49-4; I (R = *i*-Bu), 36748-27-3; I (R = Ph), 26194-27-4; II (X^5 = Me), 36423-15-1; II (Y^4 = Me), 29933-35-5; II (Y^4 = Cl), 53177-49-4; II (Y^4 = I), 14688-82-5; II (Y^4 = CN), 33699-99-9; II (Y^2 = Me), 31204-81-6; II (Y^2 = Y^4 = Y^6 = Me), 31204-94-1; II (Y^2 = F), 14972-95-3; II (Y^2 = Cl), 53177-47-2; II (Y^2 = Br), 22881-84-1; II (Y^2 = I), 97704-69-3; II (Y^2 = Y^6 = Cl), 97704-70-6; II (Y^2 = OMe), 31204-86-1; acetylacetone, 123-54-6; *N*-ethylsalicylaldimine, 5961-36-4.