Contribution from Anorganische Chemie III, Eduard-Zintl-Institut
der Technischen Hochschule Darmstadt, and Abteilung Strukturforschung,
Institut für Physikalische Chemie der Technischen Hochschule Darmstadt, D-6100 Darmstadt, Federal Republic of Germany

Square-Planar Copper(II) Chelate Complexes of the ONN,X Type (X = Monodentate Ligand): Kinetics of Ligand Substitution As Studied in Acetone and the Effect of Water

Jürgen R. Röper,[†] Helmut Paulus,[‡] and Horst Elias*,[†]

Several four-coordinate copper(II) complexes of the formula LCuX (L = anion of *N*-(2-(diethylamino)ethyl)salicylaldimine; X = Cl, Br, NCS, NO_3, N_3, NCO, ONO), the aqua complex [$LCu(H_2O)$]ClO_4, and the complex L'CuCl (chloro[*N*-(2-(ethylamino)ethyl)salicyldiminato]copper(II)) were prepared and characterized. X-ray structure analysis of LCuNCS ($C_{14}H_{19}Cu$-N_3OS) confirms N-coordination of the thiocyanate ion and a slightly distorted square-planar coordination geometry around the copper. Visible absorption spectra of the complexes LCuX in acetone show a broad d–d band in the range 586–657 nm with ϵ_{max} ranging from 203 to 330 M^{-1} cm^{-1}. According to conductivity measurements in acetone, [$LCu(H_2O)$]ClO_4 ionizes almost completely and $LCuNO_3$ to a considerable extent, whereas for the other complexes LCuX ionization is minor. Spectrophotometric titration of acetone solutions of LCuX with water leads to data for the equilibrium constant K_{aq} describing the aquation of LCuX to form ion pairs $LCu(H_2O)^+$,X^- and ions $LCu(H_2O)^+$(solvd). Normal and stopped-flow spectrophotometry was used to study the kinetics of ligand substitution in LCuX, [$LCu(H_2O)$]ClO_4, and L'CuCl by H_2salen (*N*,*N'*-disalicylidene-1,2-diaminoethane) and H_2Mesalen (*N*,*N'*-disalicylidene-1,2-diaminopropane) in acetone. Under pseudo-first-order conditions ([H_2salen]$_0 \geq$ 10[LCuX]$_0$) substitution in LCuX (X = Cl, NCS, N_3, NCO, Br, TU (thiourea)) is a single-exponential process, the formation of Cu(salen) following a one-term rate law, rate = k[H_2salen][LCuX]. At 298 K the second-order rate constant k ranges from 0.66 ± 0.09 (X = NCO) to 5.46 ± 0.05 M^{-1} s^{-1} (X = Br) for X = anion and rises to k = 256 ± 10 M^{-1} s^{-1} for X = TU. The reaction with H_2Mesalen instead of H_2salen is slower by a factor of 3–4, and L'CuCl reacts with H_2salen 5 times faster than LCuCl. The activation parameters for the reaction of LCuCl with H_2salen are ΔH^* = 9.24 ± 0.88 kcal mol^{-1} and ΔS^* = −26.5 ± 2.9 cal mol^{-1} K^{-1}. The experimental facts support the operation of an associative (A) mechanism. For ligand substitution in LCuX (X = NO_3, ONO) and in $LCu(H_2O)^+$ two-phase kinetics are observed, both single-exponential processes being first-order in H_2salen. At 298 K the two second-order rate constants obtained range from k_1 = 62.6 ± 5.9 (X = ONO) to (10.6 ± 0.8) × 10^3 M^{-1} s^{-1} (X = H_2O) and from k_2 = 11.1 ± 0.4 (X = ONO) to 13.4 ± 0.7 M^{-1} s^{-1} (X = NO_3). Depending on X, these rate constants are assigned to ligand substitution in the species LCuX, $LCu(H_2O)^+$,X^- (ion pair), or $LCu(H_2O)^+$, which are formed due to the presence of residual water in acetone. Experiments carried out in the presence of admixed water provide evidence supporting a mechanistic interpretation according to which the observed two-phase kinetics are due to parallel rather than to consecutive reactions.

Introduction

We reported recently[1] the kinetics of ligand substitution in bis(*N*-alkylsalicylaldiminato)nickel(II) complexes, Ni(R-sal)$_2$, by the tetradentate ligand H_2salen (*N*,*N'*-disalicylidene-1,2-diaminoethane) in acetone according to (1). It was shown that

$$Ni(R\text{-}sal)_2 + H_2salen \rightarrow Ni(salen) + 2R\text{-}salH \quad (1)$$

(1) obeys rate law 2 and follows an associative (A) mechanism.

$$\text{rate} = k[Ni(R\text{-}sal)_2][H_2salen] \quad (2)$$

The size of the second-order rate constant k depends on the nature of the organic group R and ranges from 154 (R = *i*-Pr) to 0.028 M^{-1} s^{-1} (R = *t*-Bu) at 298 K.

The study of (1) with Cu(R-sal)$_2$ ($3d^9$ system) instead of Ni(R-sal)$_2$ ($3d^8$ system) led to the interesting result[2] that k for a given complex Cu(R-sal)$_2$ is considerably smaller than that for the corresponding nickel complex (k_{Ni}/k_{Cu} ranges from 8 × 10^3 to 5, depending on R). Considering the kinetic lability of copper(II) complexes in general, the slowness of (1) for complexes Cu(R-sal)$_2$ is rather remarkable, a possible explanation being found in the mechanism postulated[1] for (1), which implies adduct formation between Ni(R-sal)$_2$ and H_2salen in a fast equilibrium preceding the rate-controlling rupture of the first Ni–O (leaving ligand) bond and proton transfer. As evidenced by the weak interaction between Cu(R-sal)$_2$ and pyridine[3] (compared to that of the system Ni(R-sal)$_2$/py[1]), the copper in Cu(R-sal)$_2$ has only weak acceptor properties, and hence, adduct formation between Cu(R-sal)$_2$ and H_2salen is less favored.

The present study centers on the kinetics and mechanism of reaction 3 in acetone, with LCuX denoting neutral four-coordinate

$$LCuX + H_2salen \rightarrow Cu(salen) + (H_2L)^+X^- \quad (3)$$
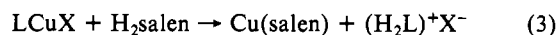
copper(II) complexes, L or L' representing the anion of the tridentate ONN-ligand *N*-(2-(diethylamino)ethyl)salicylaldimine or *N*-(2-(ethylamino)ethyl)salicylaldimine, and X denoting a

monodentate anion (in addition to H_2salen, the C-methylated ligand H_2Mesalen (*N*,*N'*-disalicylidene-1,2-diaminopropane) was also utilized).
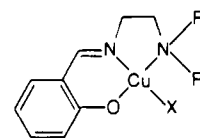
R = R' = Et: LCuX = (sal-enEt$_2$)CuX
R = H; R' = Et: L'CuX = (sal-enNHEt)CuX
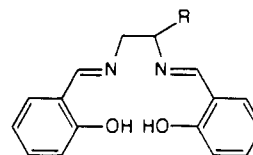
R = H: H_2salen
R = Me: H_2Mesalen

This investigation was undertaken to study the kinetic effects of the labile position X on the formation of Cu(salen) according to (3) and to compare the kinetic behavior of complexes LCuX with that of the symmetrical *trans*-N_2O_2 complexes Cu(R-sal)$_2$ and Ni(R-sal)$_2$ mentioned above.

A minor point of interest was also the rate of reaction 4, which we studied in detail for the corresponding d^8 complexes LPtX[4] and LPdX.[5]

$$LCuX + Y^- \rightarrow LCuY + X^- \quad (4)$$
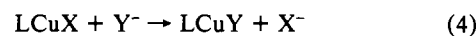
Experimental Section

The solvent acetone (Merck) was analytical grade and was used without further purification. Karl Fischer titration led to [H_2O] = 0.044 M.

---

(1) Schumann, M.; Elias, H. *Inorg. Chem.* **1985**, *24*, 3187.
(2) Knoch, R.; Wilk, A.; Wannowius, K. J.; Reinen, D.; Elias, H. To be submitted for publication.
(3) Ewert, A.; Wannowius, K. J.; Elias, H. *Inorg. Chem.* **1978**, *17*, 1691.
(4) Becker, M.; Elias, H. *Inorg. Chim. Acta* **1986**, *116*, 47.
(5) Volz, H. Dr. rer. nat. Thesis, Technische Hochschule Darmstadt, submitted in 1988.

---

†Eduard-Zintl-Institut.
‡Institut für Physikalische Chemie.

Ligands and Complexes. The Schiff base Hsal–enNEt$_2$ [N-(2-(di-ethylamino)ethyl)salicylaldimine (from N,N-diethylethylenediamine and salicylaldehyde)] was prepared as described earlier.[6] The preparation of H$_2$salen and H$_2$Mesalen was carried out according to published methods.[1]

The complexes LCuX (X = Cl, Br, NO$_3$) and LCu(H$_2$O)ClO$_4$ were obtained from CuX$_2$ and Hsal–enNEt$_2$ as described previously.[6] For the preparation of LCuX (X = NCS, NO$_2$, N$_3$, NCO) the following procedure was applied: A solution of 2.59 g (7.5 mmol) of LCuNO$_3$ in 100 mL of EtOH is added dropwise to a stirred solution of 22.5 mmol of NaX in 150 mL of EtOH. The reaction mixture is refluxed for 30 min, and the solvent is evaporated in vacuo. The residue is treated with hot CHCl$_3$, and after filtration, the chloroform is evaporated. The complex LCuX thus obtained is recrystallized in EtOH and dried in vacuo at 60 °C (yield ~90%).

The complex L'CuCl ((sal–enNHEt)CuCl) was obtained by reacting stoichiometric amounts of N-ethylethylenediamine, salicylaldehyde, and CuCl$_2$·2H$_2$O in EtOH in a one-step procedure. Isolation and purification were performed as described for LCuCl.[6]

Warning! Solutions of LCu(H$_2$O)ClO$_4$ and LCuN$_3$ should be handled carefully!

The C, H, and N data obtained from elemental analysis proved the purity of the green complexes LCuX, LCu(H$_2$O)ClO$_4$, and L'CuCl.

Instrumentation. UV/vis spectra were recorded with a diode-array spectrophotometer (Hewlett-Packard 8451 A) in quartz cells. The infrared spectra were obtained from KBr tablets of the complexes (spectrophotometer: Acculab 2, Beckman). The determination of the concentration of water in acetone by Karl Fischer titration was carried out with an automated titration unit (Metrohm). The conductivity data were collected at 298 K and corrected for the conductivity of the medium (conductometer: LF 530, Wissenschaftlich-Technische Werkstätten).

X-ray Structure Determination. Crystals of LCuNCS ((salenNEt$_2$)-CuNCS) were grown from a solution of the material in a methanol–water mixture. The crystal used for the X-ray measurement was broken from the edge of a larger crystal; it had a volume of about 0.026 mm^3. Intensities were measured with a four-circle diffractometer (Stoe-Siemens AED2) using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Cell constants were determined by least-squares from the 2θ angles of 46 reflections (T = 295 K), measured on the same instrument.

Lp and background corrections and a numerical absorption correction were applied. The structure was solved by MULTAN80 and refined to the R values given in Table III. Hydrogen atoms were positioned geometrically (C–H distance 1.08 Å) and not refined. The ethyl groups of both symmetry-independent molecules could not be refined, even with the N–C and the C–C distances fixed; the positions of the methyl carbons did not converge. All crystallographic calculations were performed with the program SHELX76 on a Micro-VAX II computer at Stoe & Cie, Darmstadt, West Germany. Scattering factors for C, H, N, O, and S are stored in SHELX76.[7] The final positional parameters are given in Table IV.

Spectrophotometric Titration. The titration of the acetone solutions of LCuX ([LCuX]$_0$ = 1 × 10^{-4} M) with water ([H$_2$O] = 0.04–23 M) was followed spectrophotometrically (λ = 400–800 nm) at 298 K in quartz cells (1 cm). The data obtained for absorbance A at 450 nm were computer-fitted either to eq 6, describing the addition of water to the complex according to (5), or to eq 8, describing the aquation of LCuX

$$LCuX + nH_2O \rightleftharpoons LCuX \cdot nH_2O \quad K_{ad} \quad (5)$$

$$K_{ad} = \frac{A - A_0}{A_\infty - A} \frac{1}{[H_2O]_0{}^n} \quad (6)$$

according to (7) (the symbols A_0 and A_∞ refer to the absorbance of LCuX

$$LCuX + nH_2O \rightleftharpoons LCu(H_2O)_n{}^+ + X^- \quad K_{aq} \quad (7)$$
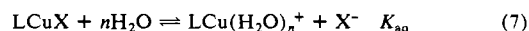
$$K_{aq} = \frac{A - A_0}{A_\infty - A} \frac{[X^-]}{[H_2O]_0{}^n} \quad (8)$$

and the product complex, respectively, at initial and final concentrations). Considering the fact that the titration with water was carried out to a water level as high as 23 M, the application of eq 6 and 8 can be a crude approximation only, since the *activity* of water is required in these aquations instead of its *concentration*.

Kinetic Measurements. Reaction 3 was followed spectrophotometrically (HP 8451 A) at 374 nm (formation of Cu(salen)) in two-chamber

(6) Elias, H.; Hilms, E.; Paulus, H. *Z. Naturforsch.* **1982**, *37B*, 1266.

(7) Data for Cu were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table I. Visible Absorption[a] of the Complexes LCuX[b] in Acetone[c] ([LCuX] = 10^{-2} M)

	X								
	Cl	Br[d]	NCS	NO$_3$	ClO$_4$	N$_3$[e]	NCO	ONO	Cl[f]
λ_{max}, nm	654	657	614	611	600	586	628	612	643
ϵ_{max}, M^{-1} cm^{-1}	240	279	330	207	176	260	238	203	200

[a] All complexes have a strong charge-transfer band (ϵ = 5150–7910 M^{-1} cm^{-1}) in the range 368–376 nm. [b] LCuX = (sal–enNEt$_2$)CuX. [c] Commercial acetone (analytical grade); 0.044 M H$_2$O according to Karl Fischer titration. [d] Shoulder at ~500 nm. [e] Additional absorption band at λ_{max} = 491 nm (ϵ = 323 M^{-1} cm^{-1}). [f] L'CuCl = (sal–enNHEt)CuCl.
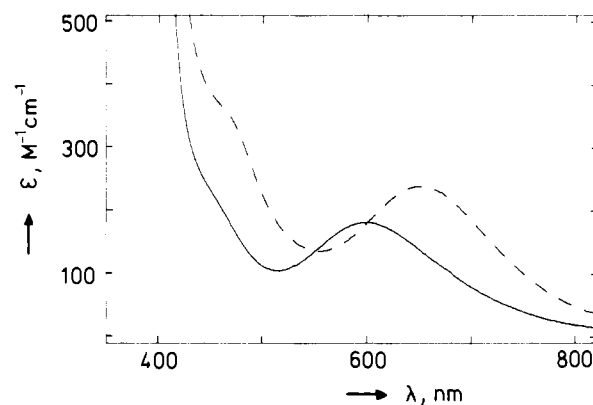
Figure 1. Visible spectra of the species [LCu(H$_2$O)]$^+$ (from [LCu(H$_2$O)]ClO$_4$; solid line) and of the complex LCuCl (generated from [LCu(H$_2$O)]ClO$_4$ by admixing a stoichiometric amount of [Bu$_4$N]Cl; dashed line) in acetone.

quartz cells (2 × 0.439 cm). The faster reactions ($t_{1/2}$ < 1 min) were measured with a modified[8] stopped-flow spectrophotometer (Durrum, D110). In all cases pseudo-first-order conditions were maintained ([H$_2$salen]$_0$ ≥ 10[LCuX]$_0$). The absorbance/time data were computer-fitted to either eq 9 or eq 10 with programs based on the least-squares

$$A = (A_0 - A_\infty) \exp(-k_{obsd}t) + A_\infty \quad (9)$$

$$A = \Delta_1 \exp[(-k_{obsd}(1))t] + \Delta_2 \exp[(-k_{obsd}(2))t] + A_\infty \quad (10)$$

method (A = absorbance; Δ_1, Δ_2 = amplitudes of the two exponentials).

Results and Discussion

Preparation and Properties of the Complexes LCuX. Four-coordinate complexes of the type LCuX with a ONN,X set of donor atoms were first described by Sacconi et al.[9] in 1965 and later by Muto and Tokii et al.[9] In the present study some of the complexes were prepared directly by reacting stoichiometric amounts of the tridentate Schiff base, copper salt (CuX$_2$), and base as described earlier.[6] Some of the complexes, however, were obtained by anion exchange in ethanol according to (11).[6] With

$$LCuX + Y^-(excess) \rightarrow LCuY + X^- \quad (11)$$
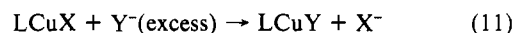
the exception of the perchlorate complex, which was obtained as LCu(H$_2$O)ClO$_4$, the composition of the green complexes was found to be LCuX. One can conclude, therefore, that in the case of X = ClO$_4$ the aqua complex cation LCu(H$_2$O)$^+$ is formed, which is in agreement with the findings of Chakravorty et al.[10]

The visible absorption spectra in acetone are characterized by a d–d band in the range λ = 586 (X = N$_3$)–657 nm (X = Br) with ϵ lying between 176 (aqua complex with X = ClO$_4$) and 330 M^{-1} cm^{-1} (X = NCS) (see Table I). The azido complex has an

(8) Elias, H.; Fröhn, U.; von Irmer, A.; Wannowius, K. J. *Inorg. Chem.* **1980**, *19*, 869.

(9) (a) Sacconi, L.; Bertini, I. *Inorg. Chem.* **1966**, *5*, 1520. (b) Muto, Y.; Tokii, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 139. (c) For a comprehensive compilation of the literature concerning the work of Sacconi et al. and Muto and Tokii et al., see ref 6.

(10) Balundgi, R. H.; Chakravorty, A. *Inorg. Chem.* **1973**, *12*, 981.

Table II. Dissociation of the Complexes LCuX in Acetone[a] Derived from Conductance Data[b]

	Cl	Br	NCS	NO₃	ClO₄	N₃	NCO	ONO	Cl[c]
					X				
α,[d] %	1.0	2.9	3.2	11.4	88	3.3	2.0	4.9	2.6

[a] Commercial acetone (analytical grade); 0.044 M H₂O according to Karl Fischer titration. [b] Data for molar conductivity Λ (corrected for solvent conductivity) taken at 298 K in 5×10^{-5} M acetone solutions of LCuX. [c] L'CuCl = (sal–enNHEt)CuCl. [d] Degree of dissociation as calculated from $\alpha = \Lambda/\Lambda_{\infty}$. The value of $\Lambda_{\infty} = 189\ \Omega^{-1}\ cm^2\ mol^{-1}$ applied for calculating α is the mean obtained for 5×10^{-5} M acetone solutions of [Bu₄N]Cl, [Bu₄N]Br, and [Bu₄N]NO₃.
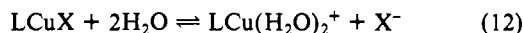
additional band at 491 nm, and for the bromo complex a shoulder is found at ~500 nm. Taking into account the absorption data for complexes LCuCl, LCuBr, and LCuNCS reported earlier,[6] one recognizes a minor, but obviously nonsystematic, solvent effect on the position and intensity of the d–d band upon changing from chloroform to acetone and methanol. It should be pointed out that for all of the complexes a strong CT band at $\lambda = 368$–376 nm is observed ($\epsilon = 5150$–7910 $M^{-1}\ s^{-1}$), the position of which is practically independent of the nature of X. Figure 1 presents the visible spectra of the complexes LCu(H₂O)ClO₄ and LCuCl, the latter being generated by admixing a stoichiometric amount of [Bu₄N]Cl with an acetone solution of LCu(H₂O)ClO₄.

The ligands X = thiocyanate, cyanate, and nitrite are ambidentate, and therefore the question of linkage isomerism arises. The N-coordination of thiocyanate follows from structure analysis (see below) as well as from infrared data,[11] the latter unfortunately being not unambiguous for the cyanate and nitrite complexes. The sum of visible absorption and kinetic data, however, strongly points to N-coordination for cyanate and O-coordination for nitrite.

Considering the fact that, according to X-ray analysis, the coordination geometry in the complexes LCuCl,[6] LCuBr,[6] and LCuNCS (see structure below) is planar (though tetrahedrally distorted), one can conclude from the similarity of the d–d spectra that all LCuX complexes prepared are practically planar four-coordinate copper(II) complexes, with water occupying the fourth position in the case of X = ClO₄.

Conductivity Data and Spectrophotometric Titration. The conductivity measurements in acetone prove (see Table II) that for X = ClO₄ the complex ionizes almost completely ($\alpha = 88\%$), forming the aqua cation LCu(H₂O)⁺. For X = NO₃ the extent of ionization is considerable ($\alpha = 11\%$) whereas for all the other anions X ionization is very limited.

The spectrophotometric titration of acetone solutions of LCuX with water leads to changes in absorbance that can be fitted to either eq 6 (addition of water) or eq 8 (ionization of LCuX) for $n = 2$. The data compiled in Table IX show that both K_{ad} and K_{aq} reflect similar relative changes with X. Considering the experimental fact, however, that the molar conductance of acetone solutions of LCuX increases with increasing water concentration, it is plausible to assume that the spectral changes observed upon stepwise addition of water reflect ionization processes as described by (12) (except for LCu(H₂O)ClO₄). The data for α calculated

$$LCuX + 2H_2O \rightleftharpoons LCu(H_2O)_2^+ + X^- \qquad (12)$$

on the basis of equilibrium constant K_{aq} (see Table IX) agree reasonably well with the corresponding conductance data (see Table II) for X = Cl, Br, and ClO₄, whereas for the other anions the spectrophotometrically determined dissociation appears to be smaller. For the complex LCu(H₂O)ClO₄ the best fit of the

Table III. Crystallographic Data for (sal–enNEt₂)CuNCS

|	
C₁₄H₁₉CuN₃OS	$T = 22\ °C$
fw 340.93	$\lambda = 0.71069\ \text{Å}$
space group $Fdd2$ (No. 43)	$\rho(\text{calcd}) = 1.42\ \text{g cm}^{-3}$
$a = 49.612\ (8)\ \text{Å}$	$\mu = 14.65\ \text{cm}$
$b = 17.645\ (3)\ \text{Å}$	transmissn coeff = 0.690–0.889
$c = 14.602\ (2)\ \text{Å}$	$R(F_o) = 0.0795$
$V = 12783\ \text{Å}^3$	$R_w(F_o) = 0.0753$
$Z = 32$	
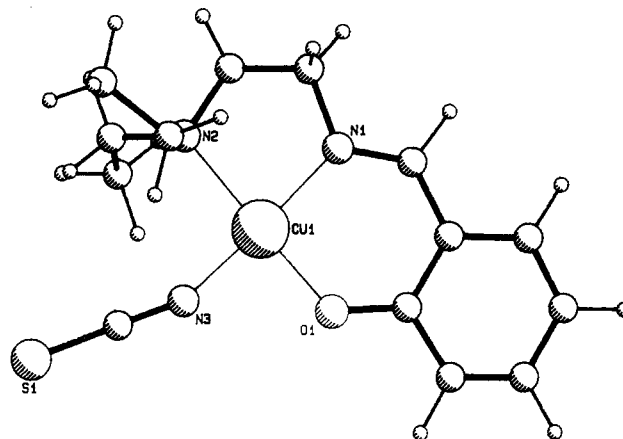
Figure 2. View of the coordination geometry in the complex LCuNCS (molecule I).

absorbance data to eq 8 was obtained for $n = 1$.

Structure of the Complex LCuNCS. The molecular conformation of the thiocyanato complex LCuNCS is very similar to those of the chloro and bromo complexes described earlier.[6] Due to the thermal motion of the N-ethyl groups, which could not be located precisely, it was not possible to refine the structure to a high degree of accuracy ($R_w = 0.0753$ for LCuNCS (see Table III), 0.042 for LCuCl,[6] and 0.040 for LCuBr[6]). The orthorhombic unit cell contains 32 molecular units, which split into two symmetry-independent sets of 16 molecules each (molecules I and II; see Tables IV and V). Despite the limited accuracy of refinement, the questions concerning the coordination chemistry of the complex LCuNCS can be fully answered; namely, (i) the thiocyanate moiety is definitely N-bonded (see Figure 2), (ii) the coordination geometry around the copper is practically square-planar with a slight tetrahedral distortion (see Table V; torsion angle $\beta = 10.8$ (molecule I) and 10.3° (molecule II) as compared to 15° for LCuCl·CHCl₃[6] and 12.3° for LCuBr·CHCl₃[6]), and (iii) there are obviously no bonding interactions between the molecular units of LCuNCS, although the S–Cu distances between the sulfur atom of I and the copper atoms of II and of another unit of I are rather short (3.36 and 2.92 Å, respectively).

It follows from the distances and bond angles compiled in Table V that the Cu–O and Cu–N distances and bond angles in LCuNCS are very similar to those obtained for LCuCl[6] and LCuBr.[6] The data for the independent molecules I and II are slightly, but not significantly, different.

Kinetic Results. One would expect that the position of the monodentate ligand X in the LCuX complexes is kinetically much more labile than that of the anion of the tridentate Schiff base Hsal–enNEt₂ (N-(2-(diethylamino)ethyl)salicylaldimine). For the d⁸ metal complexes LPt(H₂O)⁺ and LPd(H₂O)⁺ studied in methanol, the ratio of second-order rate constants for the substitution of Y for H₂O is found to be $k(\text{Pd})/k(\text{Pt}) \approx 100/1$ at 293 K,[4,5] and $k(\text{Pt})$ ranges from 1 to 500 $M^{-1}\ s^{-1}$, depending on the nucleophilicity of the entering ligand Y.[4] In line with these results, we found that anation according to (13) is a very rapid

$$LCu(H_2O)^+ + Y \rightarrow LCuY^+ + H_2O \qquad (13)$$
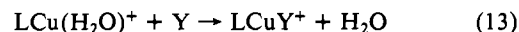
process. For Y = TU (thiourea) and Y = Cl⁻ this reaction is too fast for the stopped-flow time scale, which means that these substitutions proceed with $k \geq 5 \times 10^5\ M^{-1}\ s^{-1}$. So, the ligand X in the LCuX complexes is indeed kinetically very labile.

(11) For the C–N stretching vibration in LCuNCS we find $\bar{\nu} = 2060\ cm^{-1}$, which is close to $\bar{\nu} = 2050\ cm^{-1}$ for N-bonded complexes, whereas for S-bonded complexes a value near 2100 cm⁻¹ is reported.[12] For a review of the literature and the application of infrared methods to the discussion of S or N bonding of the thiocyanate ligand, see ref 12.

(12) (a) Golub, A. M.; Köhler, H.; Skopenko, V. V. *Chemistry of Pseudohalides*; Elsevier: Amsterdam, 1986. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 1986.

Table IV. Atomic Parameters ($\times 10^4$) for (sal–enNEt$_2$)CuNCS (Excluding H)

	molecule I				molecule II		
atom	x	y	z	atom	x	y	z
Cu(1)	1748.9 (3)	9445 (1)	6398	Cu(2)	1151.4 (3)	756 (1)	3402 (1)
O(1)	1482 (2)	9432 (4)	7312 (5)	O(2)	1519 (2)	699 (4)	3009 (6)
C(1)	1230 (2)	9206 (6)	7230 (8)	C(15)	1696 (3)	1255 (9)	2951 (8)
C(2)	1048 (3)	9329 (6)	7962 (10)	C(16)	1963 (3)	1060 (9)	2765 (10)
C(3)	798 (3)	9125 (7)	7922 (11)	C(17)	2147 (3)	1706 (10)	2709 (12)
C(4)	695 (3)	8811 (9)	7124 (14)	C(18)	2062 (4)	2390 (11)	2842 (12)
C(5)	853 (3)	8641 (7)	6416 (11)	C(19)	1812 (3)	2628 (11)	2838 (11)
C(6)	1124 (2)	8843 (6)	6440 (9)	C(20)	1625 (3)	2035 (8)	3064 (9)
C(7)	1284 (3)	8700 (6)	5650 (10)	C(21)	1355 (4)	2280 (7)	3232 (10)
N(1)	1540 (2)	8874 (4)	5525 (6)	N(4)	1149 (2)	1850 (5)	3393 (8)
C(8)	1674 (2)	8697 (6)	4675 (8)	C(22)	889 (3)	2150 (8)	3603 (10)
C(9)	1894 (3)	9221 (8)	4551 (11)	C(23)	708 (3)	1599 (8)	4152 (12)
N(2)	2042 (2)	9399 (5)	5395 (7)	N(5)	732 (2)	824 (6)	3747 (10)
C(10)	2217 (2)	10058 (5)	5221 (13)	C(24)	641 (5)	231 (10)	4385 (10)
C(11)	2070 (3)	10825 (7)	5278 (12)	C(25)	395 (6)	226 (24)	5026 (22)
C(12)	2204 (3)	8764 (7)	5749 (17)	C(26)	606 (4)	710 (12)	2844 (9)
C(13)	2474 (5)	8663 (17)	5244 (20)	C(27)	308 (5)	933 (18)	2719 (27)
N(3)	1988 (3)	9821 (8)	7258 (10)	N(6)	1128 (2)	−333 (6)	3201 (7)
C(14)	2175 (3)	10217 (9)	7488 (12)	C(28)	1140 (2)	−970 (6)	3019 (8)
S(1)	2452 (1)	10576 (3)	7900 (4)	S(2)	1166 (1)	−1853 (2)	2801 (3)

Table V. Selected Distances (Å) and Bond Angles (deg) of (sal–enNEt$_2$)CuNCS

molecule I		molecule II	
Cu(1)–O(1)	1.88 (1)	Cu(2)–O(2)	1.91 (1)
Cu(1)–N(1)	1.93 (1)	Cu(2)–N(4)	1.93 (1)
Cu(1)–N(2)	2.07 (1)	Cu(2)–N(5)	2.14 (2)
Cu(1)–N(3)	1.85 (2)	Cu(2)–N(6)	1.95 (2)
O(1)–Cu(1)–N(1)	94.5 (5)	O(2)–Cu(2)–N(4)	93.2 (5)
O(1)–Cu(1)–N(2)	176.6 (4)	O(2)–Cu(2)–N(5)	176.1 (6)
O(1)–Cu(1)–N(3)	88.7 (6)	O(2)–Cu(2)–N(6)	87.8 (4)
N(1)–Cu(1)–N(2)	83.7 (5)	N(4)–Cu(2)–N(5)	86.5 (6)
N(1)–Cu(1)–N(3)	168.8 (6)	N(4)–Cu(2)–N(6)	170.2 (6)
N(2)–Cu(1)–N(3)	92.5 (5)	N(5)–Cu(2)–N(6)	91.8 (5)
N(3)–C(14)	1.21 (2)	N(6)–C(28)	1.16 (2)
C(14)–S(1)	1.63 (2)	C(28)–S(2)	1.59 (2)
Cu(1)–N(3)–C(14)	152.5 (16)	Cu(2)–N(6)–C(28)	172.0 (10)
N(3)–C(14)–S(1)	167.2 (17)	N(6)–C(28)–S(2)	177.6 (12)
β^a = 10.8		β^a = 10.3	

$^a \beta$ is the torsion angle between the O(1)–Cu(1)–N(3) plane and the N(1)–Cu(1)–N(2) plane in molecule I (and the corresponding planes in molecule II) describing the degree of tetrahedral distortion.
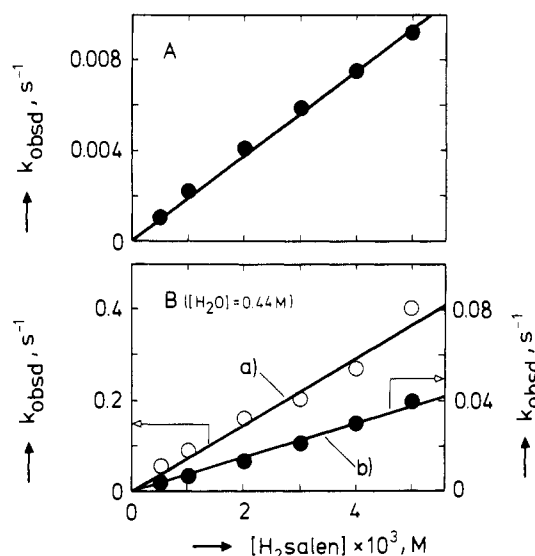
The study of reaction 3 led to the overall kinetic result that for the group of ligands X = Cl, NCS, N$_3$, NCO, TU, and Br (in the presence of [Bu$_4$N]Br) ligand substitution in LCuX by H$_2$salen in acetone follows a one-term rate law, whereas for X = H$_2$O, ONO, NO$_3$, and Br (in the absence of [Bu$_4$N]Br) there are two pathways. Furthermore, in the case of X = Cl admixing water with the solvent acetone produces a second pathway.

Ligand Substitution in LCuX (X = Cl, NCS, N$_3$, NCO, TU, Br). For this group of complexes the absorbance/time data obtained upon reaction with an excess of H$_2$salen in acetone can be fitted

Figure 3. Plot of the experimental rate constant k_{obsd} (298 K) vs the concentration of the entering ligand for the systems LCuCl/H$_2$salen/acetone (A) and LCuCl/acetone/water (B; the slopes of curves a and b correspond to rate constants k_1 and k_2, respectively).

to one exponential according to (9); i.e., the substitution is first-order in LCuX. Figure 3A presents for X = Cl the curve typically obtained when the experimental rate constant k_{obsd} is plotted vs [H$_2$salen]. Since no intercept is found, rate law 14

$$\text{rate} = \text{d}[\text{Cu(salen)}]/\text{d}t = k_{obsd}[\text{LCuX}] = k[\text{LCuX}][\text{H}_2\text{salen}] \quad (14)$$

applies, and the resulting second-order rate constants k are sum-

Table VI. Second-Order Rate Constants^{a,b} for Ligand Substitution in LCuX Complexes in Acetone^c at 298 K According to Reaction 3 (Single-Exponential Kinetics)

	X						
	Cl	Br^d	NCS	N$_3$	NCO	TU^e	Cl^f
k, M^{-1} s^{-1} (H$_2$salen)^g	1.88 ± 0.05 2.15 ± 0.05^h	5.46 ± 0.05	2.15 ± 0.04	1.83 ± 0.03	0.660 ± 0.094	256 ± 10	8.79 ± 0.59
k, M^{-1} s^{-1} (H$_2$Mesalen)^j	0.616 ± 0.013	i	0.570 ± 0.010	i	i	i	1.41 ± 0.05

^{a} Rate constant k resulting from the slope of the straight line obtained by plotting the experimental rate constant k_{obsd}^{b} vs the concentration of the entering ligand. ^{b} For each complex k_{obsd} was determined in six runs at different concentration of the entering ligand in the concentration range 5 × 10^{-4}–5 × 10^{-3} M at [LCuX] = 5 × 10^{-5} M. ^{c} Commercial acetone (analytical grade); 0.044 M H$_2$O according to Karl Fischer titration. ^{d} Obtained in the presence of [Bu$_4$N]Br (10^{-2} M). ^{e} TU = thiourea; cation LCu(TU)$^+$ generated by adding a 10-fold excess of TU to an acetone solution of LCu(H$_2$O)ClO$_4$. ^{f} L'CuCl = (sal–enNHEt)CuCl. ^{g} Entering ligand: H$_2$salen. ^{h} Determined conductometrically. ^{i} Not determined. ^{j} Entering ligand: H$_2$Mesalen.

Table VII. Activation Parameters for the Complex LCuCl Reacting with H₂salen According to (3) in Acetone[a]

temp, K	k,[b] M^{-1} s^{-1}	temp, K	k,[b] M^{-1} s^{-1}
289.5	0.99 ± 0.02	303.2	2.18 ± 0.07
293.2	1.30 ± 0.03	308.2	2.81 ± 0.11
298.2	1.88 ± 0.05		

$$\Delta H^{\ddagger} = 9.24 \pm 0.88 \text{ kcal mol}^{-1};$$
$$\Delta S^{\ddagger} = -26.5 \pm 2.9 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

[a] Commercial acetone (reagent grade); 0.044 M H₂O according to Karl Fischer titration. [b] Obtained from k_{obsd} according to footnotes a and b of Table VI.

marized in Table VI. They range from 0.66 (X = NCO) to 5.46 M^{-1} s^{-1} (X = Br) for anionic ligands X and peak for X = TU (thiourea); the cationic complex $LCu(TU)^+$ reacts with k = 256 M^{-1} s^{-1}. One learns therefore that for the neutral complexes LCuX there is only a minor leaving group effect when X = Cl, Br, NCS, N₃, or NCO.

In general, reaction 3 was followed spectrophotometrically. Since the formation of Cu(salen) liberates 1 equiv of acid HX (which forms the salt $H_2L^+X^-$ with the leaving Schiff base; see eq 3), conductometric monitoring should be possible as well. It is worthwhile to note that for LCuCl the conductometrically determined rate constant (k = 2.15 ± 0.05 M^{-1} s^{-1}) agrees acceptably with the spectrophotometrically determined one (k = 1.88 ± 0.05 M^{-1} s^{-1}; see Table VI).

There are two important findings favoring the interpretation of (3) as an associative reaction: namely, (i) the sterically less crowded complex L'CuCl (one N-ethyl group less than in LCuCl) reacts approximately 5 times faster with H₂salen than LCuCl, and (ii) the sterically more crowded ligand H₂Mesalen reacts with LCuCl and L'CuCl slower than H₂salen (factors of 3 and 6, respectively). This is in line with analogous steric effects[4] observed for ligand substitution in LPtX and L'PtX following an A mechanism.

Further support for an interpretation of (3) as an associative process comes from the negative activation entropy ($\Delta S^{\ddagger}$ = −26.5 ± 2.9 cal mol⁻¹ K⁻¹) obtained from the temperature dependence of k for the complex LCuCl (see Table VII).

The sum of these kinetic results is consistent with the kinetics typically found for ligand substitution in square-planar d^8 metal complexes.

The simple rate law (14) is followed by LCuX complexes that, according to Table II, are subject to minor ionization in solution (α = 1–3%).[13] The fact that a small conductance in acetone solutions of these complexes is measured at all is probably due to residual water being present at a concentration of 0.044 M (the complete removal of residual water by drying with molecular sieves is in principle possible, but exposure of such acetone solutions to air reestablishes a certain water concentration immediately). The nucleophile water equilibrates with LCuX to form an ion pair $LCu(H_2O)^+,X^-$, which dissociates partially according to (15) (the

$$LCuX \underset{}{\overset{H_2O}{\rightleftharpoons}} LCu(H_2O)^+,X^- \underset{}{\overset{H_2O}{\rightleftharpoons}} LCu(H_2O)^+ + X^- \quad (15)$$
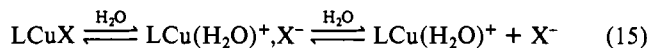
degree of dissociation will very critically depend on the dielectric constant of the medium, which is controlled by the concentration of water present). The fact that only one exponential is observed for these systems can be explained by assuming that the kinetic contribution of the species $LCu(H_2O)^+,X^-$ and $LCu(H_2O)^+$ reacting with H₂salen is too small to be experimentally observed. This interpretation raises of course the question of how fast equilibrium 15 is established compared to the rate of substitution by H₂salen (see discussion below).

Comparing finally the reactivity of LCuX complexes in ligand substitution with H₂salen (eq 3) with that of Cu(R-sal)₂ complexes

(13) As pointed out by James,[14] the solution power of acetone for ions is very limited and, hence, acetone solutions of salts such as LiClO₄ tend to form ion pairs.
(14) James, D. W. *Prog. Inorg. Chem.* **1985**, *33*, 353.

Table VIII. Second-Order Rate Constants[a] for Ligand Substitution in LCuX Complexes with H₂salen in Acetone[b] at 298 K According to Reaction 3 (Two-Exponential Kinetics)

complex	[H₂O], M	k_1, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}
LCuCl	0.044[b]	c	1.88 ± 0.05
	0.44[d]	74.2 ± 3.2	7.56 ± 0.21
	0.88[d]	119 ± 5	22.9 ± 0.9
LCuBr	0.044[b]	75.9 ± 1.9	12.7 ± 0.4
	0.044[b]	17.4 ± 0.7[e]	2.68 ± 0.07[e]
	0.44[d]	134 ± 5	c
LCuNO₃	0.044[b]	157 ± 5	13.4 ± 0.7
	0.044[b]	63.7 ± 1.8[e]	6.47 ± 0.50[e]
LCu(H₂O)ClO₄	0.044[b]	(10.6 ± 0.8) × 10³[g]	1.64 ± 0.4[f]
LCuONO	0.044[b]	62.6 ± 5.9	11.1 ± 0.4

[a] See footnotes a and b of Table VI. [b] Commercial acetone (analytical grade); 0.044 M H₂O according to Karl Fischer titration. [c] Not observed. [d] Water concentration adjusted by adding H₂O to commercial acetone (see footnote b). [e] Entering ligand H₂Mesalen instead of H₂salen. [f] For the complex LCu(H₂O)ClO₄ the experimental rate constant k_{obsd}(2) (which describes the slow step) is independent of [H₂salen] and averages to a first-order rate constant k_{obsd}(2) = 1.64 ± 0.4 s⁻¹. [g] The plot of k_{obsd}(1) vs [H₂salen] leads to a straight line with a slope of k_1 = 10.6 × 10³ M^{-1} s⁻¹; in contrast to the other systems, however, a small intercept of 3.6 ± 1.2 s⁻¹ is observed.

according to (1)² yields the following results: (i) both types of complexes follow the same rate law (eq 14) in their reaction with H₂salen in acetone and (ii) LCuX complexes, depending on X, react with rate constant k ranging from approximately 1 to 5 M^{-1} s^{-1} (see Table VI), whereas Cu(R-sal)₂ complexes, depending on R, react with k ranging from 0.001 (R = neopentyl) to 0.4 M^{-1} s^{-1} (R = phenyl).² So, the presence of the labile position X in LCuX clearly enhances the rate of substitution.

Ligand Substitution in LCuX (X = ClO₄, NO₃, ONO, Br). For this group of complexes the absorbance/time data obtained for reaction 3 can be fitted most properly to two exponentials according to (10). Both of the two experimental rate constants obtained, k_{obsd}(1) and k_{obsd}(2), follow relationship 16, and the

$$k_{obsd} = k[\text{H}_2\text{salen}] \quad (16)$$

resulting second-order rate constants k_1 and k_2 are compiled in Table VIII. The values for k_1 range from 63 (X = ONO) to 10.6 × 10³ M^{-1} s^{-1} (X = ClO₄), and those for k_2, from 11 (X = ONO) to 13.4 M^{-1} s^{-1} (X = NO₃). It is again found that the reaction with the sterically more crowded ligand H₂Mesalen is slower than that with H₂salen, the rate reducing factor being approximately 4.5 for LCuBr and 2.3 for LCuNO₃. It is important to note that both k_1 and k_2 are subject to this effect.

The data presented in Table VIII have to be discussed in some detail: (i) The complex LCuBr is listed in Table VI and in Table VIII because the simple kinetic behavior of this complex (one-term rate law) is found only in the presence of admixed [Bu₄N]Br (see Table VI). In the absence of additional bromide ions, two exponentials are observed (see Table VIII) with rate constant k_2 for the slower reaction (12.7 M^{-1} s^{-1}) being of the same order of magnitude as rate constant k (5.46 M^{-1} s^{-1}; see Table VI). (ii) The complex LCuCl is also listed in Table VIII because an increase in water concentration introduces a second reaction pathway, both k_1 and k_2 depending on [H₂salen] as shown in Figure 3B. (iii) The crucial role of water also follows from the fact that for LCuBr two exponentials are observed for [H₂O] = 0.044 M and only one exponential is observed for [H₂O] = 0.44 M.

General Mechanistic Interpretation. The sum of the kinetic results obtained in the present study can be rationalized best by taking into account that the four-coordinate copper(II) complexes studied are basically square-planar complexes. It is not surprising, therefore, that ligand substitution in those LCuX complexes that do not ionize in acetone solution follows the simple kinetic pattern observed for planar d^8 metal complexes such as those of Pt(II) and Pd(II). The operation of an associative mechanism is in line with the tendency of these complexes to become at least five-coordinate.[15] For those LCuX complexes that ionize in solution
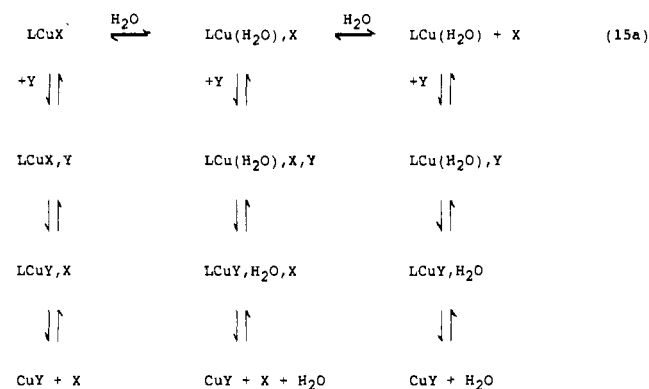
Table IX. Equilibrium Constants[a] for the Addition of Water to LCuX Complexes in Acetone at 298 K According to Reactions 5 and 7

|					X				
	Cl	Br	NCS	NO_3	ClO_4	N_3	NCO	ONO	Cl[b]
K_{ad},[c] M^{-1}	0.045	0.14	0.023	0.64	4.4[d]	0.0068	0.0019	0.011	0.11
K_{aq},[c] M^{-1}	1.9×10^{-6}	8.0×10^{-6}	7.0×10^{-7}	2.9×10^{-5}	5.1×10^{-3}[d]	9.3×10^{-8}	4.5×10^{-10}	1.6×10^{-6}	5.8×10^{-6}
α,[e] %	0.85	1.74	0.52	3.3	84.2	0.19	0.013	0.78	1.49

[a] Resulting from computer fitting of the absorbance data (450 nm) obtained at 12–15 different water concentrations ($[H_2O] = 4 \times 10^{-2}$–23 M) to eq 6 for $n = 2$ (K_{ad}) and to eq 8 for $n = 2$ (K_{aq}). [b] L'CuCl = (sal–enNHEt)CuCl. [c] Error $\sim \pm 20\%$. [d] Obtained according to footnote a for $n = 1$ instead of $n = 2$. [e] Degree of dissociation as calculated from K_{aq} for $[LCuX] = 5 \times 10^{-5}$ M and $[H_2O] = 0.044$ M according to the equilibrium $LCuX + 2H_2O \rightleftharpoons LCu(H_2O)_2^+ + X^-$.

Scheme I. Simplified Reaction Scheme for Product Formation

$$
\begin{array}{ccccccc}
LCuX & \underset{}{\overset{H_2O}{\rightleftharpoons}} & LCu(H_2O),X & \underset{}{\overset{H_2O}{\rightleftharpoons}} & LCu(H_2O) + X & & (15a) \\
{}^{+Y}\downarrow\uparrow & & {}^{+Y}\downarrow\uparrow & & {}^{+Y}\downarrow\uparrow & & \\
LCuX,Y & & LCu(H_2O),X,Y & & LCu(H_2O),Y & & \\
\downarrow\uparrow & & \downarrow\uparrow & & \downarrow\uparrow & & \\
LCuY,X & & LCuY,H_2O,X & & LCuY,H_2O & & \\
\downarrow\uparrow & & \downarrow\uparrow & & \downarrow\uparrow & & \\
CuY + X & & CuY + X + H_2O & & CuY + H_2O & &
\end{array}
$$

(especially in the presence of admixed water) biphasic kinetics are observed. It is important to note, however, that both pseudo-first-order rate constants obtained are ligand-dependent (e.g., see Figure 3B), which points to the presence of two species reacting associatively with H_2salen in a parallel fashion. The occurrence of two species has to be attributed to the presence of water, which obviously equilibrates with LCuX according to (15), the extent of ion-pair formation and final ionization being controlled by the strength of the Cu–X bond and the amount of water present. For the formation of the product Cu(salen) one has to consider the relative contributions of the complex LCuX, of the ion pair $LCu(H_2O)^+$, X^-, and of the solvated ion $LCu(H_2O)^+$. Scheme I attempts to rationalize and summarize the results obtained in a simplified way (charges and protons involved in ligand substitution are omitted for clarity; Y represents the tetradentate ligand H_2salen or H_2Mesalen in its protonated or deprotonated form; species separated by a comma are considered to be part of an ion-pair or outer-sphere complex).

In acetone solutions of the complexes, the species LCuX, $LCu(H_2O)^+,X^-$, and $LCu(H_2O)^+$ are equilibrated according to (15) and (15a), respectively. When these solutions are mixed with the solution of the attacking ligand H_2salen (Y), the reaction of Y with LCuX, $LCu(H_2O),X$, and $LCu(H_2O)$, respectively, is obviously faster than equilibration according to (15a) (see discussion below). For X = Cl, NCS, N_3, NCO, TU, or Br the species LCuX is dominating and simple kinetics according to (14) are observed. Mechanistically, LCuX forms an outer-sphere complex, LCuX,Y, with Y in an axial position. The rate of product formation is controlled either by rearrangement of LCuX,Y to LCuY,X (with Y bound in the coordination plane in a monodentate fashion) or by the displacement of L and X by Y in the species LCuY,X. This mechanism would allow for the observed minor leaving ligand effect on k (see Table VI).

For X = NO_3, ONO, or Br biphasic kinetics are observed, with rate constant k_2 obviously describing the reaction of LCuX with Y and rate constant k_1 a faster reaction of Y with either the ion pair $LCu(H_2O),X$ or the ion $LCu(H_2O)^+$. The fact that $k_1 > k_2$ is probably due to water being a better leaving ligand than X. Mechanistically, the reactions of $LCu(H_2O),X$ and $LCu(H_2O)^+$
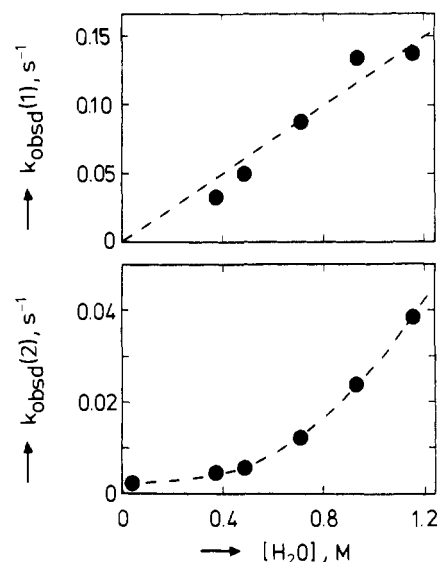
Figure 4. Plot of the experimental rate constants $k_{obsd}(1)$ and $k_{obsd}(2)$ vs the concentration of water for the system $LCuCl/H_2salen/acetone/water$ ($[CuLCl]_0 = 5 \times 10^{-5}$ M; $[H_2salen]_0 = 1 \times 10^{-3}$ M; $T = 298$ K).

with Y are probably very similar to that of LCuX with Y in the sense that the rate-controlling step can either be the entrance of Y into the coordination plane or the displacement of L by Y in the species $LCuY,H_2O,X$ or $LCuY,H_2O$, respectively. An unambiguous assignment of rate constant k_1 to the reaction of either the ion pair $LCu(H_2O),X$ or the solvated ion $LCu(H_2O)^+$ appears to be very difficult. Depending on X (i.e., the strength of the Cu–X bond), the given amount of residual water in acetone ($[H_2O] = 0.044$ M) can either favor ion-pair formation or lead to ionization.

The additional information resulting from experiments in the presence of admixed water is very interesting, though not conclusive (see Table VIII). The addition of water to the system $LCuCl/Y/acetone$ introduces a second pathway for product formation, whereas in the system $LCuBr/Y/acetone$ the pathway involving the species LCuBr disappears at $[H_2O] = 0.44$ M. In addition, rate constants k_1 and k_2 clearly increase with increasing water concentration. Figure 4 demonstrates for the system $LCuCl/Y/acetone/H_2O$ that k_1 appears to increase linearly with increasing water concentration, whereas the dependence $k_2 = f([H_2O])$ is more complex.

The results of the present contribution do not allow a detailed interpretation of the observed dependencies $k_1 = f([H_2O])$ and $k_2 = f([H_2O])$. As pointed out above, the addition of appreciable amounts of water to acetone (as a solvent of low dielectric constant) definitely produces major medium effects. It is not possible at this stage to split the observed rate effects of admixed water into general medium effects and/or specific coordination effects in the inner sphere of the copper. The kinetic significance of the data obtained for K_{aq} from spectrophotometric titration with water (see Table IX) is therefore limited. The fact that fitting of the absorbance data to eq 8 is best for $n = 2$ does not necessarily mean that the species $LCu(H_2O)_2^+$, thus postulated, is kinetically really effective. One would prefer to argue instead that the type of monodentate ligand X occupying the fourth coordination site in the planar species LCuX is kinetically more important. If X is a "strong" ligand such as azide, the neutral species $LCuN_3$ does

(15) Spectrophotometric titration of the bis(*N*-alkylsalicylaldiminato) complexes Cu(R-sal)$_2$ with pyridine in toluene confirms the formation of the adduct Cu(R-sal)$_2\cdot$py. See: Ewert, A.; Wannowius, K. J.; Elias, H. *Inorg. Chem.* **1978**, *17*, 1691.

Table X. Second-Order Rate Constants[a] for the Reaction of the Cation $LCu(TU)^{+}$[b] with H_2salen in Acetone[c] at 298 K According to (3) in the Presence of Additional Thiourea

$[TU]_0$, M	$[TU]_0/$ $[LCu(H_2O)ClO_4]_0$	k_1, $M^{-1} s^{-1}$	k_2, $M^{-1} s^{-1}$
2.5×10^{-5}	1	$(5.66 \pm 0.15) \times 10^{3}$[d]	439 ± 42[d]
2.5×10^{-4}	10	e	256 ± 10
5.0×10^{-4}	20	e	153 ± 7
1.0×10^{-3}	40	e	94.6 ± 5.7

[a] See footnotes a and b of Table VI. [b] Prepared by adding TU (thiourea) to acetone solutions of $LCu(H_2O)ClO_4$. [c] Commercial acetone (analytical grade); $[H_2O] = 0.044$ M according to Karl Fischer titration. [d] The plot of k_{obsd} vs $[H_2salen]$ leads to a straight line with a small intercept of 2.02 ± 0.24 s^{-1} ($k_{obsd}(1)$) or 0.27 ± 0.07 s^{-1} ($k_{obsd}(2)$). [e] Not observed.

Table XI. Experimental Rate Constants k_{obsd}[a] for the Complex LCuCl Reacting with H_2salen According to (3) in Acetone[b] at Different Concentrations of Water

$[H_2O]$, M	$10^2 k_{obsd}(1)$, s^{-1}	$10^3 k_{obsd}(2)$, s^{-1}
0.044[b]	c	2.14 ± 0.03
0.44[d]	8.95 ± 0.34	6.81 ± 0.03
0.44[e]	c	6.76 ± 3.0
0.88[d]	12.6 ± 0.9	18.3 ± 0.1
0.88[e]	c	13.2 ± 0.1

[a] Obtained at 298 K with $[LCuCl] = 5 \times 10^{-5}$ M and $[H_2salen] = 1 \times 10^{-3}$ M. [b] Commercial acetone (analytical grade); 0.044 M H_2O according to Karl Fischer titration. [c] Not observed. [d] The acetone solutions of LCuCl and H_2salen were 0.44 and 0.88 M, respectively, in water before the experiment. [e] The acetone solution of LCuCl was 0.044 M in water before the experiment; the acetone solution of H_2salen was 0.88 and 1.76 M, respectively, in water before the experiment.

not ionize in acetone, is relatively kinetically inert, and behaves as a "normal" square-planar complex in ligand substitution. For the "weak" ligand X = NO_3, the complex $LCuNO_3$ ionizes in acetone to a considerable extent and the planar species $LCu(H_2O)^{+}$ thus formed (either as an ion pair or a solvated ion) is kinetically much more labile. Admixing water with the acetone favors the formation of the species $LCu(H_2O)^{+}$ and increases its reactivity by further solvation and/or ionization.

Important information is provided by two additional experiments. The first one concerns ligand substitution in the species $LCu(TU)^{+}$ (as produced by addition of thiourea to $LCu(H_2O)-ClO_4$) by H_2salen, which follows rate law 14 when $[TU] \geq 10 \cdot [LCu(H_2O)^{+}]$. It is found that the second-order rate constant k decreases with increasing concentration of TU (see Table X; $k_2 \triangleq k$). This mass-law retardation effect strongly supports the existence of the equilibria shown in Scheme I for the LCuX species reacting with Y. The second additional experiment provides information concerning the relative rate of aquation according to (15a) as compared to the rate of ligand substitution with Y. It was carried out in such a way that the final concentration of water in the reaction mixture, $[H_2O]_{mix}$, was either preset in the solutions of *both* partners to be reacted (type A experiment) or produced during the experiment such that the solution of H_2salen had a water concentration of $2[H_2O]_{mix}$ and the solution of LCuCl was blank (type B experiment). The results as compiled in Table XI show that even for $[H_2O]_{mix} = 0.88$ M the "type B experiments" lead to single-exponential kinetics as observed in the absence of additional water (the values for $k_{obsd}(2)$ being

slightly higher though than in the absence of additional water). These findings clearly prove that equilibration of LCuCl with water does not compete kinetically with ligand substitution and that the observed two-exponential kinetics should indeed be interpreted as being due to parallel rather than to consecutive reactions.

The results obtained for the complex $LCu(H_2O)ClO_4$ are rather exceptional in the following sense: (i) the conductance data point to almost complete ionization in acetone ($[H_2O] = 0.044$ M), (ii) rate constant k_1 is by a factor of approximately 100 higher than for any other LCuX complex, and (iii) rate constant k_2 is "normal" (as compared to those of the other LCuX complexes), though independent of $[H_2salen]$ (see Table VIII). There seems to be no straightforward explanation for these findings. The perchlorate ion clearly is the most "innocent" anion studied, and one could argue, therefore, that the high value of $k_1 = 10.6 \times 10^3$ M^{-1} s^{-1} reflects the reactivity of the non-ion-paired species $LCu(H_2O)^{+}$. This interpretation, however, is not in line with the finding that rate constant k_1 is by a factor of approximately 100 smaller than for all the other ligands X even at water concentrations as high as 0.44 M where ionization (i.e., formation of $LCu(H_2O)^{+}$) is very considerable.

Conclusions

In the solvent acetone (with a concentration of residual water of 0.044 M) LCuX complexes, depending on the nature of the anion X, can form a variety of species such as LCuX, $LCu-(H_2O)^{+},X^{-}$ (ion pair), and $LCu(H_2O)^{+}$. Due to the presence of residual water, for X = Br, ONO, and NO_3 equilibria 15 are established with one or two of the various copper species dominating. When these solutions are reacted with H_2salen, each copper species can react with H_2salen to form Cu(salen) in a second-order process following an associative mechanism. The species LCuX has the lowest reactivity.

When only one copper species (such as LCuX) is predominantly present, ligand substitution follows a one-term rate law. In the presence of two copper species, two-exponential kinetics are observed, both terms deriving from ligand-dependent second-order reactions. It has been experimentally shown that the two exponentials observed have to be ascribed to parallel rather than to consecutive reactions. Mechanistically this means that the aquation according to (15) cannot compete kinetically with the reaction of the various copper species with H_2salen present in excess.

From the point of formal kinetics, the planar d^9 complexes LCuX very much resemble the d^8 complexes $LPtX^4$ and $LPdX^5$ in the sense that the coordination site occupied by the monodentate ligand X is the most labile one. The substitution of X in LCuX is by at least 3 orders of magnitude faster, however, than in LPdX.

Supplementary Material Available: Tables SI–SIV, listing complete crystallographic data, calculated coordinates of hydrogens, thermal parameters, and interatomic distances not listed in Table V (4 pages); Table SV, listing observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.