Table III. Ring-Closure Rate Constants and Acid Dissociation Constants at 25 °C for Some Platinum(II) Complexes

complex	μ, M	k, s^{-1}	K_a, M	ref
trans-[$PtCl_2$-(en′)(en′)]	1.0	10.4 ± 0.6	(1.2 ± 0.1) × 10^{-8}	2
[PtCl-(en′)en]$^+$	1.0	0.73 ± 0.006	(1.1 ± 0.1) × 10^{-8}	2
[$PtCl_2$-(bama)]	0.4	2.1 ± 0.1	(2.5 ± 0.3) × 10^{-9}	3
[$PtCl_2$-(taa)][a]	0.4	4.3 ± 0.2		3
[$PtCl_3$-(bas)]$^-$	0.4	3.6 ± 0.2		this work
[$PtCl_2$-(bas)]	0.4	0.173 ± 0.005	(5.9 ± 0.4) × 10^{-9}	this work

[a] taa = tris(2-aminoethyl)amine.

compared to that of the nitrogen may make a significant contribution.

The rate constant for the second ring closure is 0.173 ± 0.005 s^{-1}, which can be compared with the values of 2.1 ± 0.1 s^{-1} and 4.3 ± 0.2 s^{-1}, respectively, obtained for [$PtCl_2$(bama)] and [$PtCl_2$(taa)] (Table III). The difference between these latter rates has been attributed to a statistical factor, since the taa complex has two equivalent amine groups available for coordination, whereas the bama complex has only one. Examination of data from crystal structure analyses suggests that the lower rate constant for the bas complex compared to that of the bama derivative is probably due to very severe steric strain associated with the closure of the second ring. We cite, for example, the fact that the [PtBr(dien)]$^+$ cation has two normal Pt–N bond lengths (1.98 and 1.96 Å), but the third Pt–N (associated with a primary amine group) is 2.12 Å,[15] indicating that one five-membered ring is strained. Such strain would be exacerbated in a Pt(II) chelate containing bas, since Pt–S bond lengths are about 2.25 Å.[1,16] The Pt–bas ring closure activation entropies in basic media (Table II) (−8.2 ± 0.8 and −9.0 ± 0.5 cal/(deg mol)) are more positive than those usually found for bimolecular substitution processes in Pt(II) complexes (−14 to −30 cal/(deg mol)),[17] consistent with an intramolecular mechanism. Both the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are less favorable for the second ring closure, which accords with the proposal that more strain is involved in reaching the transition state in this final step.

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Registry No. [$PtCl_3(basH_2)$]Cl, 69551-36-6; [$PtCl_2$(bas·HCl)], 69551-37-7; [PtCl(bas)]Cl, 69551-38-8; [$PtCl_3$(bas)]$^-$, 69551-39-9; [$PtCl_2$(bas)], 69551-40-2.

Supplementary Material Available: Listing of k_{obsd} values for the ring closure reactions (2 pages). Ordering information is given on any current masthead page.

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Kinetic Studies on Four-Coordinate Chelate Complexes of Copper(II): Isotopic Ligand Exchange of Bis(salicylaldiminato)copper(II) in Toluene

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Isotopic exchange technique has been used to study the rate of ligand exchange of a series of ^{131}I-labeled bis(*N*-R-salicylaldiminato)copper(II) complexes (R = ethyl, *n*-propyl, isopropyl, isobutyl, *tert*-butyl, neopentyl) in toluene as a function of the nature of R and properties of substituents X at the salicylaldehyde ring. The rate of exchange follows a two-term rate law, namely, $r_{ex} = (k_S + k_{ligand}[ligand])[complex]$. The occurrence of k_S is found to be due to residual water in toluene, according to $k_S = k_{H_2O}[H_2O]$. The equilibrium constants K(py) for the addition of pyridine to the complexes studied have been measured spectrophotometrically. From the variation of k_S, k_{ligand}, $\Delta H^{\ddagger}(k_S)$, $\Delta H^{\ddagger}(k_{ligand})$, $\Delta S^{\ddagger}(k_S)$, $\Delta S^{\ddagger}(k_{ligand})$, and K(py) with R and X, it is concluded that both the solvent and the ligand term in the observed rate equation can be explained by an associative mode of activation.

Introduction

In recent years only very few kinetic studies based on isotopic exchange experiments have been reported.[1] For most of the kinetic investigations, techniques have been applied which allow on-line measurements.

Isotopic exchange experiments are restricted to slowly exchanging systems because of necessary separation of the exchange partners, and radioisotopes with appropriate half-lives and facile detectability must be available. Apart from these experimental limitations, isotopic exchange experiments possess some very striking advantages: (i) there is no driving force due to free energy changes, and (ii) the exchange reactions are of high symmetry. This latter aspect means that the derivation of the rate law for an isotopic ligand-exchange reaction of a bis complex, for example, can be restricted to considering only half of the reaction as compared to the nonisotopic case. With complexes containing more than two identical ligands, an even greater simplification is possible.

To our knowledge the ligand exchange of copper(II) salicylaldimines (I) has not yet been investigated kinetically. As

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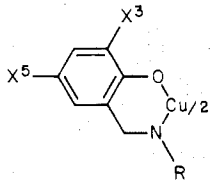
reported recently,[2] the isotopic *metal* exchange in chloroform and methylene chloride solvent is rather fast at room temperature and special techniques for separation of the partners had to be developed.[3] Surprisingly, the isotopic *ligand* exchange according to (1) in toluene as solvent is slower than the corresponding metal exchange by a factor of more than 10^2.

$$Cu(3\text{-}{*}I\text{-}5\text{-}X\text{-}SA{=}NR)_2 + 2(3\text{-}I\text{-}5\text{-}X\text{-}HSA{=}NR) \rightleftharpoons Cu(3\text{-}I\text{-}5\text{-}X\text{-}SA{=}NR)_2 + 2(3\text{-}{*}I\text{-}5\text{-}X\text{-}HSA{=}NR) \quad (1)$$

For the present contribution iodine-131 was chosen as a radioisotope with suitable half-life (8.05 days) and good detectability and availability. The bis(salicylaldiminato)-copper(II) complexes I allow the kinetic study of slight



I = CuL_2

$X^3 = I$, $X^5 = NO_2$: $Cu(INSA{=}NR)_2$

$X^3 = X^5 = I$: $Cu(DISA{=}NR)_2$

modifications of the substrate. Attention was focused mainly on steric aspects in the sense that different organic groups R (as attached to the amine nitrogen) were introduced to obtain complexes I with ranging degrees of shielded copper. The aim was to classify the ligand substitution of four-coordinate copper(II) complexes as associative or dissociative in the nomenclature of Langford and Gray[4] and to collect further information on the kinetic behavior of four-coordinate complexes in aprotic organic solvents. In poorly coordinating media such as toluene, residual nucleophiles in the bulk solvent are of great importance; therefore, the effect of pyridine and water in toluene was studied in detail.

Experimental Section

Preparation of Compounds. 3,5-Diiodosalicylaldehyde (DISA) was synthesized by the method of Bougault et al.[5] ^{131}I-Labeled 3,5-diiodosalicylaldehyde was obtained by two methods.

(i) To a solution of inactive DISA in acetonitrile was added a solution of $Na^{131}I$ (carrier free, Amersham Buchler, Braunschweig) in water. The solvent was evaporated in vacuo. The resulting crystalline mass was kept molten at 115 °C for 15 min, and then it was recrystallized from alcohol upon addition of inactive potassium iodide until the specific activity remained constant.

(ii) Salicylaldehyde was treated with a solution of iodine plus KI containing up to 5-mCi iodine-131 following the method of Bougault et al.[5] Only slight modifications had to be made with regard to the special problems in handling the activity.

The bis(3,5-diiodosalicylaldiminato)copper(II) complexes were obtained by dropwise addition of a solution of copper(II) acetate in water to an alcoholic solution of 3,5-diiodosalicylaldehyde containing a slight excess of the appropriate amine. The complexes were precipitated and recrystallized from a chloroform/petroleum ether mixture. The analytical data have been presented elsewhere.[6] The same procedure was followed in the case of the ^{131}I-labeled compounds.

The Schiff bases were prepared by addition of the amine (20% excess) to a warm alcoholic solution of DISA. The yellow crystals were recrystallized twice from ethanol. The melting points and the analytical data are given in Table I.

3-Iodo-5-nitrosalicylaldehyde (INSA) was obtained by iodination of 5-nitrosalicylaldehyde with ICl in acetic acid according to the following procedure. A solution of 22 mmol of ICl in 14 mL of glacial acetic acid was added dropwise to a solution of 20 mmol of 5-nitrosalicylaldehyde in 50 mL of glacial acetic acid under stirring. After stirring for 2 h at room temperature, the reaction mixture was poured into 200 mL of water. The excess of ICl was reduced with a few milliliters of a concentrated Na_2SO_3 solution. The precipitate was collected on a Büchner funnel, washed chloride-free with water, and twice recrystallized from ethanol: yield 10 mmol; mp 166 °C. Anal. Calcd: C, 28.69; H, 1.38; N, 4.62. Found: C, 28.70; H, 1.38, N, 4.62. NMR (in $CDCl_3$) (ppm): 8.6, 4 H; 8.9, 6 H; 9.93, -C*H*O; 12.43, -O*H*.

Table I. Analytical Data of the Schiff-Base Ligands 3-I-5-X-HSA=NR

R	X^5	mp, °C	% calcd			% found		
			C	H	N	C	H	N
Et	I	115	26.96	2.26	3.49	26.96	2.26	3.36
n-Pr	I	73	28.94	2.67	3.38	28.85	2.70	3.40
i-Pr	I	49	28.94	2.67	3.38	28.92	2.69	3.40
i-Bu	I	71	30.79	3.05	3.26	30.82	2.99	3.35
t-Bu	I	118	30.79	3.05	3.26	30.74	3.05	3.27
neo-Pe	I	132	32.54	3.41	3.16	32.42	3.40	3.18
Et	NO_2	170	33.77	2.83	8.75	33.60	2.75	8.61
n-Pr	NO_2	121	35.95	3.32	8.38	35.89	3.38	8.41
i-Pr	NO_2	153	35.95	3.32	8.38	35.61	3.28	8.32
i-Bu	NO_2	136	37.95	3.76	8.05	37.70	3.79	7.94
t-Bu	NO_2	228	37.95	3.79	8.05	37.94	4.00	7.99
neo-Pe	NO_2	154	39.80	4.17	7.73	39.61	4.12	7.70

^{131}I-Labeled INSA was synthesized by following the same procedure. The activity was introduced by addition of 1 mL of aqueous $Na^{131}I$ solution (5-mCi iodine-131) to the ICl solution in glacial acetic acid. The synthesis was carried out with 1.5 mmol of 5-nitrosalicylaldehyde.

The Schiff bases were prepared as described for the corresponding diiodo compounds. The analytical data are given in Table I.

The bis(3-iodo-5-nitrosalicylaldiminato)copper(II) complexes were obtained by the method which was described for diiodo compounds. The complexes were recrystallized twice from a chloroform/petroleum ether mixture. Melting points: >300 °C (R = Et), 240 °C (R = *n*-Pr), 295 °C (R = *i*-Pr), 245 °C (R = *i*-Bu), 190 °C dec (R = *t*-Bu), >305 °C (R = *neo*-Pe). The C, H, and N determinations were in agreement with the theoretical formulas. The same procedure was used in the preparation of the ^{131}I-labeled complexes (specific activity: 10^7–5×10^8 cpm/mmol of complex). The complex $Cu(INSA{=}NEt)_2$ could not be studied kinetically because of its low solubility in toluene ($<6 \times 10^{-5}$ M).

Toluene (reagent grade, Merck, Darmstadt) was dried over 4-Å molecular sieves. The residual water content of $[H_2O] = 2 \times 10^{-3}$ M was determined by Karl–Fischer titration. Solutions of the complexes and of the ligands in toluene could be stored over molecular sieves for weeks without decomposition. In the case of the ligand solutions, however, an appreciable amount of ligand was absorbed by the molecular sieves, thus altering their concentrations.

Separation. It was necessary to carry out extensive studies on the separation of complexed and free ligand in toluene solution, because the complexes are relatively instable against aqueous NaOH, which is needed for the extraction of the free ligands. Extraction with aqueous NaOH resulted in a 10–90% transfer of the free ligand into the water phase depending on the molarity of the NaOH solution, the extraction time, and the system under investigation.

The best results were obtained by shaking the toluene solution for 1 min with 1 M NaOH on a laboratory vibrator. In the case of fast reactions, shorter extraction times were used. Under these conditions less than 1% of the coordinated ligand was extracted. In order to reduce the error caused by the instability of the complex, the ligand concentration was held in an at least 10-fold excess over the complex concentration in the kinetic experiments.

Extraction with strongly alkaline solutions causes hydrolysis of the Schiff-base ligands, and the phenolate of 3,5-diiodosalicylaldehyde is extracted into the aqueous phase whereas the amine stays in the organic phase. The aqueous layer was washed three times with toluene to remove traces of the highly radioactive reaction mixture. The alkaline extracts were acidified with 2 N HCl (DISA decomposes slowly in alkaline media), and the DISA was reextracted with 5 mL of reagent grade toluene into the organic phase, which was washed once with 2 N HCl and twice with water (in the presence of pyridine, washing of the toluene with 2 N HCl was done repeatedly). Finally the specific activity of DISA was determined by activity counting in a well-type NaI(Tl)-scintillation counter (Telefunken, MStr 1104) and by spectrophotometric determination of the aldehyde at its absorption maximum at 360 nm (ϵ 3600 ± 52 L mol^{-1} cm^{-1}) with a Zeiss DMR 22 spectrophotometer.

Table II. Isotopic Exchange in the System $Cu(D^*ISA{=}N\text{-}n\text{-}Pr)_2/DIHSA{=}N\text{-}n\text{-}Pr$[a]

$10^3[CuL_2]$, M	$10^7 r_{ex}$, M s^{-1}	$10^4 k_{ex}$, s^{-1}
0.8	4.06 ± 0.16	5.08 ± 0.20
2.0	10.4 ± 0.15	5.18 ± 0.08
4.0	23.8 ± 0.80	5.94 ± 0.20
6.0	36.0 ± 2.4	6.00 ± 0.39
8.0	42.8 ± 2.1	5.35 ± 0.26
		Av 5.51 ± 0.43

[a] In toluene; 40 °C; [DIHSA=N-*n*-Pr] = 0.2 M (constant).

In the case of the INSA=NR complexes, extraction with aqueous 1 M Na_2CO_3 was successful due to the enhanced acidity of the 3-iodo-5-nitrosalicylaldimines. The extraction procedure was the same as described for the diiodo compounds. The concentration of INSA in toluene solution was determined spectrophotometrically at 336 nm (shoulder; ϵ 4350 L mol^{-1} cm^{-1}).

Isotopic Exchange Experiments. Solutions of the reactants were thermostated separately. The reaction was started in a thermostated glass vessel by combining the partners under vigorous stirring. Aliquots of 1–10 mL (depending on the ligand concentration) were pipetted into a wide glass tube containing approximately 20 mL of 1 N NaOH or 20 mL of 1 M Na_2CO_3, respectively. Immediately extraction by shaking was started. In each run, 5–7 samples were taken and the increase in specific activity of the free ligand was followed. The total activity of the reaction solution was determined for standardization.

Determination of the Rate of Exchange. The rate of exchange was determined from the slope of McKay plots[7] ($\log (1 - F) = f(t)$; F = fraction of exchange) with a computer program based on a weighted least-squares approximation. In all cases straight lines were obtained, which sometimes (R = *i*-Pr, *t*-Bu) showed zero-time exchange up to 20%. As mentioned above, this is due to partial decomposition (less than 1%) of the complex during the extraction procedure. In most cases the samples drawn immediately after mixing of the reactants led to practically inactive ligand.

After exchange equilibrium was reached, the specific activity of the ligand was in agreement with the calculated value (applied for the determination of F) within a limit of less than 5%, proving that there are no errors introduced by the separation procedure.

Equilibrium Constants. The equilibrium constants for the addition of pyridine to the complexes were determined from changes in absorbance in the ligand field region upon addition of pyridine to a solution of the complexes in toluene. As outlined elsewhere,[8] the absorbances were treated with a computer program based on a least-squares procedure for the determination of K(py). The occurrence of isosbestic points in the visible region in all cases indicated addition of only one molecule of pyridine.

Stopped-Flow Measurements. The stopped-flow measurements were carried out with a Durrum D110 stopped-flow spectrophotometer in connection with an Aminco-Dasar storage oscilloscope. The ligand-exchange reaction was monitored at 600 nm under pseudo-first-order conditions ($[ligand]_0 \gg [complex]_0$). The absorbances were fitted to an exponential function leading to values for the first-order rate constant k_{obsd}.

Results and Discussion

Kinetics of Isotopic Ligand Exchange. The isotopic ligand exchange, according to reaction 1 with $X^3 = X^5 = I$, was studied in toluene at 40 °C with R = Et, *i*-Pr, *t*-Bu, *n*-Pr, *i*-Bu, and *neo*-Pe (neopentyl). In each system the dependence of the rate of exchange, r_{ex}, on the concentration of both complex and ligand was investigated. In Table II the data for r_{ex} are presented for R = *n*-Pr at constant ligand concentration. These data prove that the exchange proceeds first order in complex concentration (see (2)).

$$r_{ex} = k_{ex}[CuL_2] \quad (2)$$

The dependence of the first-order rate constant k_{ex} on the concentration of the ligand LH is shown in Figure 1 for all systems studied. In each case a linear relationship is obtained for the concentration range 1×10^{-4}–0.2 M, which can be described by the two-term rate expression (3).

$$k_{ex} = k_S + k_{LH}[LH] \quad (3)$$

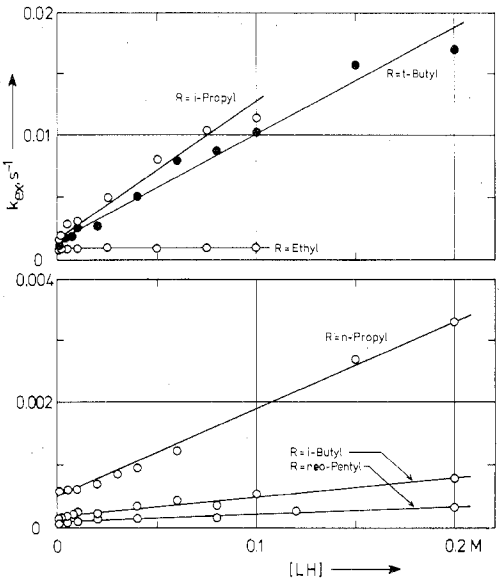


Figure 1. Isotopic ligand exchange of complexes $Cu(D^*ISA{=}NR)_2$ in toluene at 40 °C as a function of ligand concentration (k_{ex} calcualated from r_{ex} according to eq 2; $[CuL_2] = 5 \times 10^{-5}$–$8 \times 10^{-3}$ M).

Hence the ligand exchange follows a rate law which usually is observed for substitution of unidentate ligands at square-planar metal complexes.[9] The exchange occurs formally via both a solvent path (k_S) and a reagent path ($k_{LH}[LH]$). In the case of R = Et, no reagent path could be detected up to [LH] = 0.1 M (see Figure 1).

Experiments carried out at very high ligand concentrations close to saturation (0.2–0.5 M) revealed that k_{ex} does not increase linearly as expected according to (3) but levels off. To account for this effect one would tend to introduce an additional ligand-dependent term in the denominator of (3). From studies on ligand substitution rates in similar systems carried out in methanol/toluene mixtures, it is known,[10] however, that at relatively high methanol content (mole fraction $X_{MeOH} \geq 0.1$) similar deviations from linearity occur. They are presumably due to a breakdown or an alteration of the solvent structure. Therefore, we believe that such a structural breakdown by the ligand (medium effect) is responsible for the observed curvature at ligand concentrations higher than 0.2 M. At the present state it would be inadequate, however, to modify the rate law (3) by taking these effects into account.

As is shown in Figure 1, both rate constants k_S and k_{LH} are markedly influenced by the nature of the *N*-alkyl group R. The straight lines in Figure 1 were computed with a least-squares fit. The resulting values for the intercept and slope are listed in Table III.

The ligand dependence of k_{ex} as it is shown in Figure 1 for 40 °C was determined at a minimum of three additional temperatures in the range 0–75 °C. It was found that the rate equation (3) is valid for all temperatures studied ([LH] ≤ 0.2 M). The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ resulting from the temperature dependence of k_S and k_{LH} are compiled in Table III. In addition, this table contains the k_S values and the corresponding activation parameters for the isotopic ligand exchange of the complex bis(*N*-alkyl-3-iodo-5-nitrosalicylaldiminato)copper(II) ($Cu(INSA{=}NR)_2$). The data for k_S were obtained at low ligand concentrations ($<10^{-3}$ M), where the rate of exchange is practically independent of the ligand concentration ($k_{ex} \approx k_S$).

The effects of substituents $X^3 = X^5 = I$ on the one hand and $X^3 = I$ and $X^5 = NO_2$ on the other hand are rather small (see Table III). The k_S values obtained for the 3-iodo-5-nitro system are somewhat lower than those obtained for the

Table III. Kinetic Parameters for the Isotopic Ligand Exchange of the Complexes $Cu(DISA{=}NR)_2$ and $Cu(INSA{=}NR)_2$ in Toluene

				solvent path			ligand path		
R	n_R[a]	T, °C	n_T[b]	k_S,[c] s^{-1}	$\Delta H^{\ddagger}(k_S)$, kJ mol^{-1}	$-\Delta S^{\ddagger}(k_S)$, J K^{-1} mol^{-1}	k_{LH},[c] M^{-1} s^{-1}	$\Delta H^{\ddagger}(k_{LH})$, kJ mol^{-1}	$-\Delta S^{\ddagger}(k_{LH})$, J K^{-1} mol^{-1}
				$Cu(DISA{=}NR)_2$					
Et	37	0–75	8	$(0.90 \pm 0.11) \times 10^{-3}$	84 ± 2.3	32 ± 7	no ligand path observed		
i-Pr	33	0–50	4	$(1.55 \pm 0.14) \times 10^{-3}$	49 ± 6.8	139 ± 23	0.111 ± 0.0048	39 ± 4.3	137 ± 14
t-Bu	50	20–50	4	$(1.4 \pm 0.19) \times 10^{-3}$	51 ± 9.5	133 ± 31	0.086 ± 0.0030	37 ± 7.2	147 ± 23
n-Pr	39	40–60	3	$(8.4 \pm 0.89) \times 10^{-5}$	50 ± 10.6	164 ± 33	$(2.33 \pm 0.074) \times 10^{-3}$	66 ± 9.7	84 ± 30
i-Bu	37	40–60	3	$(2.9 \pm 0.40) \times 10^{-5}$	55 ± 2.3	155 ± 7	$(5.2 \pm 0.35) \times 10^{-4}$	62 ± 8.7	110 ± 27
neo-Pe	23	40–60	3	$(1.3 \pm 0.20) \times 10^{-5}$	52 ± 5.1	171 ± 16	$(1.95 \pm 0.20) \times 10^{-4}$	77 ± 4.2	71 ± 13
				$Cu(INSA{=}NR)_2$					
i-Pr	14	20–60	9	$(1.1 \pm 0.2) \times 10^{-3}$	32 ± 3.3	200 ± 11	ligand path not studied		
t-Bu	12	20–60	8	$(1.05 \pm 0.17) \times 10^{-3}$	41 ± 4.3	174 ± 14			
n-Pr	7	20–60	5	$(1.1 \pm 0.2) \times 10^{-4}$	41 ± 4.6	189 ± 15			
i-Bu	9	20–70	5	$(5.3 \pm 0.5) \times 10^{-5}$	41 ± 1.2	197 ± 4			
neo-Pe	10	20–60	3	$(1.5 \pm 0.3) \times 10^{-5}$	49 ± 4.6	181 ± 15			

[a] n_R = number of runs. [b] n_T = number of temperatures. [c] At 40 °C.

3,5-diiodo system for R = *i*-Pr and *t*-Bu. For β-branched alkyl groups such as R = *n*-Pr, *i*-Bu, and *neo*-Pe the reverse is found.

Results from Nonisotopic Ligand Substitution Studies. One inherent disadvantage of isotopic exchange experiments is that in going from one system to another each of the three parameters, entering ligand, leaving ligand, and remaining ligands, is changed simultaneously. As a consequence, it is difficult to specify for a series of systems which of these three parameters is responsible for the observed change in exchange rate. Changes in the ligand-independent term (k_S), however, are necessarily independent of the nature of the entering ligand. For substitution reactions in aqueous solution it is generally accepted to interpret the k_S term as nucleophilic attack of a water molecule at the four-coordinate metal center.[11] Because of the low coordinating power of toluene, the analogous interpretation for toluene as solvent appears to be inadequate.

In a preliminary study we have measured the effect of residual water in toluene on the rate of isotopic ligand exchange. The result was that increasing amounts of water led to a distinct acceleration of the exchange. Since the experimental technique applied in this study was based on extraction with aqueous solutions, it was difficult to keep the water content at a definite and constant level. Therefore, we decided to investigate the kinetic effect of water with a different experimental technique in nonisotopic ligand substitution systems.

The ligand replacement according to (4) in toluene as solvent can be followed by stopped-flow spectrophotometry in the visible region.

$$Cu(SA{=}N\text{-}t\text{-}Bu)_2 + 2HSA{=}NEt \rightleftharpoons Cu(SA{=}NEt)_2 + 2HSA{=}N\text{-}t\text{-}Bu \quad (4)$$

The observed pseudo-first-order rate constants k_{obsd} (excess of ligand) follow the rate equation (5), which is of the same type as (3) (cf. Figure 2).

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

The important addition to what is known from the isotopic exchange experiments is the finding that the ligand-independent term k_S in (5) is directly proportional to the concentration of residual water in the solvent toluene. Relationship 6 is indicated in Figure 2 and follows from Figure 3.

$$k_S = k_{H_2O}[H_2O] \quad (6)$$

Equation 6 clearly rules out that toluene does participate in the k_S path in the sense that there is a toluene path. It is the small amounts of residual water in toluene that bring about an additional reaction path for exchange which formally appears to be a solvent path.

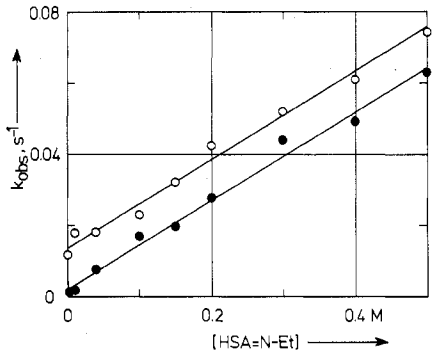


Figure 2. Nonisotopic ligand substitution according to reaction 4 in toluene at 25.5 °C as a function of ligand concentration at $[Cu(SA{=}N\text{-}t\text{-}Bu)_2] = 5 \times 10^{-4}$ M: upper curve, $[H_2O] = 16.3 \times 10^{-3}$ M; lower curve, $[H_2O] = 7.9 \times 10^{-4}$ M.

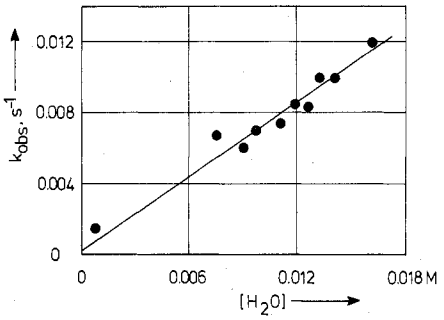


Figure 3. Nonisotopic ligand substitution according to reaction 4 in toluene at 25.4 °C as a function of water concentration ($[Cu(SA{=}N\text{-}t\text{-}Bu)_2] = 5 \times 10^{-4}$ M; $[HSA{=}NEt] = 1 \times 10^{-3}$ M).

The variation in k_S observed upon variation of R at constant concentration of residual water (see Table III) proves that the nature of R characterizes the nature of the complex and that the latter is reflected by the size of k_S.

Equilibrium Studies. In a detailed study on the Lewis acid properties of the metal in copper(II) complexes of the salicylaldiminato type, it has been shown[8] that these complexes add only one molecule of pyridine and that its addition is facilitated by electron-withdrawing groups in the ligand moiety. The inverse but less pronounced effect was observed with branching at the α or β carbon of the organic group attached to the amine nitrogen of the Schiff-base ligand (R). From a similar study with the present complexes, it follows (see Table IV) that (i) substituents at the aromatic ring facilitate the addition of pyridine, according to H < 3,5-diiodo < 3-iodo-5-nitro and (ii) the Lewis acid strength of the copper decreases with increasing branching of R.

Table IV. Equilibrium Constants for the Addition of Pyridine at 25 °C According to

$$CuL_2 + py \overset{K(py)}{\rightleftharpoons} CuL_2 \cdot py$$

	$X^3 = X^5 = H$[a]			$X^3 = X^5 = I$			$X^3 = I, X^5 = NO_2$		
R	$K(py)$, M^{-1}	$-\Delta H^\circ_{298}$, kJ mol^{-1}	$-\Delta S^\circ_{298}$, J K^{-1} mol^{-1}	$K(py)$, M^{-1}	$-\Delta H^\circ_{298}$, kJ mol^{-1}	$-\Delta S^\circ_{298}$, J K^{-1} mol^{-1}	$K(py)$, M^{-1}	$-\Delta H^\circ_{298}$, kJ mol^{-1}	$-\Delta S^\circ_{298}$, J K^{-1} mol^{-1}
Et	0.54 ± 0.023	9.2 ± 2.1	36 ± 7	4.72 ± 0.080	20.3 ± 1.1	55 ± 8			
i-Pr	0.21 ± 0.014	−0.3 ± 3.1	12 ± 10	2.4 ± 0.33	11.9 ± 0.42	33 ± 2	14.8 ± 0.40	23.9 ± 0.53	58 ± 5
t-Bu	0.31 ± 0.089								
n-Pr	0.51 ± 0.015	8.7 ± 0.6	35 ± 2	3.75 ± 0.10	24.2 ± 1.2	70 ± 6	18.6 ± 0.96	28.4 ± 3.2	71 ± 11
i-Bu	0.36 ± 0.015	5.6 ± 1.3	27 ± 5	2.68 ± 0.034	22.0 ± 2.0	66 ± 12	13.7 ± 0.56	24.4 ± 1.6	60 ± 6
neo-Pe	0.17 ± 0.038	0.4 ± 9.7	16 ± 33	1.27 ± 0.025	17.9 ± 1.7	58 ± 8	5.7 ± 0.20	16.4 ± 1.3	41 ± 6

[a] A. Ewert, K. J. Wannowius, and H. Elias, *Inorg. Chem.*, 17, 1691 (1978).

The equilibrium constants compiled in Table IV prove that the complexes under study are able to coordinate a further ligand such as pyridine. This finding supports a mechanistic interpretation of the k_S path of ligand exchange as being initiated by the coordination of a water molecule to the copper. In the case of pyridine, the rate of addition according to (7) is too fast to be measured by stopped-flow techniques.

$$CuL_2 + py \overset{K(py)}{\rightleftharpoons} CuL_2 \cdot py \qquad (7)$$

By analogy it is assumed, therefore, that for the water-initiated path of ligand exchange, the rate-determining step is not the addition of water but the subsequent loss of a ligand molecule. As a consequence, k_{H_2O} in (6) should more properly be described as $k_{H_2O} = k'_{H_2O}K(H_2O)$, with k'_{H_2O} being the rate constant for any slow subsequent step after addition of water according to equilibrium 8 (the formation of $CuL_2(H_2O)_2$ instead of $CuL_2 \cdot H_2O$ is excluded on the basis of the findings with pyridine as donor[8]).

$$CuL_2 + H_2O \overset{K(H_2O)}{\rightleftharpoons} CuL_2 \cdot H_2O \qquad (8)$$

If one regards the $K(py)$ values of Table IV as being representative for the analogous addition of water as well, the observed changes in k_S (see Table III) can only be partially explained by corresponding changes in $K(py)$.

The activation enthalpies for the solvent path are clearly smaller for the complexes $Cu(INSA{=}NR)_2$ than for the complexes $Cu(DISA{=}NR)_2$ (see Table III). If it is true that the ligand exchange occurs via the water adduct formed according to (8), then the enthalpy of reaction 8 contributes to the activation energy. Unfortunately, $K(H_2O)$ and hence its temperature dependence could not be measured by absorption spectrophotometry. The results obtained for the very similar reaction (7) with pyridine instead of water can be taken as a crude measure, however. It follows from these results (see Table IV) that the higher the equilibrium constant the more negative the enthalpy becomes; thus the more negative values of ΔH° observed for the complexes $Cu(INSA{=}NR)_2$ seem to be responsible for the smaller values of $\Delta H^\ddagger$ derived for this type of complex (see Table III).

As was shown previously,[8] the more exothermic according to reaction 7 is the addition of pyridine the higher is the corresponding loss in entropy. This is also true for the complexes compiled in Table IV. If one takes the reaction enthalpy ΔH° as a measure for the bond strength, stronger bonding between copper and pyridine (i.e., shorter bond length Cu–N) is paralleled by more restriction in mobility (i.e., free rotation), as is indicated by the more negative ΔS° values.

These thermodynamic arguments are of importance for the kinetic findings too. The small k_S values for complexes with R = *neo*-Pe could be due to the fact that both (i) the Lewis acidity of the coordinated copper is reduced, thus leading to a water adduct in which the copper–water bond is rather weak, and (ii) in addition, the weakly bonded water molecule is rather mobile (small $-\Delta S^\circ$ value), so that a proper orientation for proton transfer to the ligand is not a preferred one; therefore, the high value for $-\Delta S^\ddagger(k_S)$ in Table III is not unexpected.

Table V. Effect of Pyridine on the Isotopic Ligand Exchange in Toluene as Solvent

ligand	[py], M	$10^3 k_{ex}$, s^{-1}	$10^3 k_{py}$, M^{-1} s^{-1}
INHSA=N-*i*-Pr[a]	0.0002	1.13 ± 0.10	52.3 ± 3.0
	0.001	1.41 ± 0.062	
	0.005	1.56 ± 0.057	
	0.05	3.87 ± 0.017	
DIHSA=NEt[b]	0.002	1.87 ± 0.058	2.65 ± 0.27
	0.05	2.10 ± 0.062	
	0.1	2.28 ± 0.15	
	0.3	2.88 ± 0.098	
	0.5	3.20 ± 0.077	

[a] $[CuL_2] = 1 \times 10^{-4}$ M; $[LH] = 2 \times 10^{-4}$ M; $T = 40$ °C.
[b] $[CuL_2] = 2 \times 10^{-3}$ M; $[LH] = 5 \times 10^{-3}$ M; $T = 40$ °C.

Mechanism of Ligand Exchange. At this stage of the discussion the question has to be raised as to what role protons possibly play. It is conceivable that the availability of protons is a necessary condition for the solvent path to occur. If so, the pK_S value of coordinated water or any other protic partner (such as the ligand) would be one of the parameters controlling k_S. Data on the acid strength of water in toluene are not available in the literature. There is good reason to believe, however, that water in bulk toluene and also as coordinated water are stronger acids than bulk water (an interesting observation is, e.g., that a solution of $Cu(SA{=}N\text{-}t\text{-}Bu)_2$ in methanol containing 0.03 M water is stable for weeks, whereas in toluene slow decomposition occurs when 0.03 M water is present). Measurements on the kinetic effect of water in different protic and aprotic organic media are under way.[12]

In a further study the effect of a typical aprotic donor molecule such as pyridine on the isotopic exchange was investigated. At constant ligand concentration an increase in pyridine concentration accelerates the exchange (see Table V). Equation 9 describes this effect quantitatively.

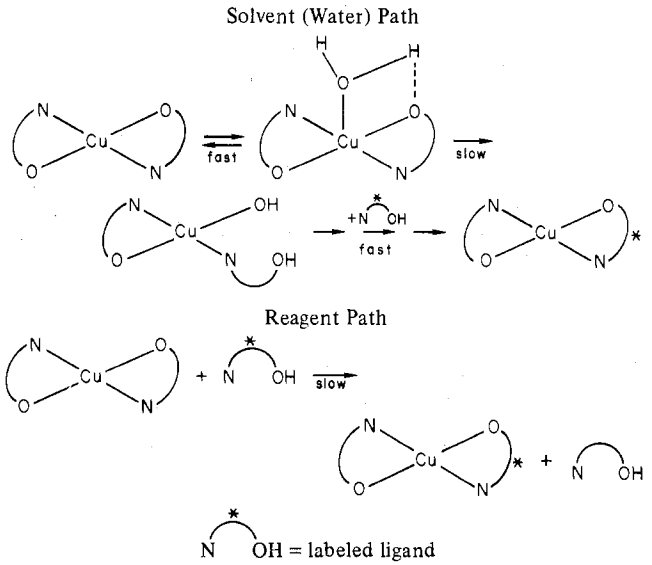
$$k_S = k_{H_2O}[H_2O] + k_{py}[py] \qquad (9)$$

The values calculated for the second-order rate constant k_{py} are given in Table V. It is interesting to note that k_{py} is approximately 20 times greater for the exchange system with the ligand INSA=N-*i*-Pr than for that with the ligand DISA=NEt. Despite the fact that the organic group R is also changed, one would prefer to ascribe this effect at least partly to the greater Lewis acidity of the complex $Cu(INSA{=}N\text{-}i\text{-}Pr)_2$ (see Table IV).

The question of the role of protons is not answered conclusively by these experiments with added pyridine. Either the availability of protons is not a necessary condition for the initiation of an exchange via the solvent path or the specific effect of pyridine is to favor the attack by a ligand molecule.

An interesting aspect of the experiments with pyridine added to toluene is the finding that the presence of 0.1 M pyridine

Scheme I



leads to the occurrence of a ligand path $k_{LH}[LH]$ for the exchange system with LH = DIHSA=NEt (k_{LH} = 0.135 ± 0.0083 M^{-1} s^{-1} at 40 °C). As is shown in Figure 1, there is no ligand path in the absence of pyridine, and $\Delta H^{\ddagger}$ for the solvent path is greater by more than 30 kJ/mol than for the other complexes (see Table III). The reason for this exceptional behavior of the complex $Cu(DISA{=}NEt)_2$ is not yet known. It might be possible that in toluene solution molecular association occurs to some extent, as it is observed in the case of certain nickel(II) complexes of the type $Ni(SA{=}NR)_2$ with R being a small organic group[13] (attempts to determine the molecular weight of $Cu(DISA{=}NEt)_2$ in toluene osmometrically failed because of the poor solubility of the complex). In the presence of pyridine the formation of dimeric units would be less favored because of the vacant coordination sites partially being occupied by pyridine molecules. The value found for k_{LH} in the presence of 0.1 M pyridine seems to be "normal" as compared to the cases for the other complexes (cf. Table III).

Increasing branching at the β carbon of R causes a decrease in the rate of both the solvent path and the ligand path. It is interesting to note that there is a good linear correlation between log k_S and log k_{LH} with a slope of m = 1.2. This linearity points to a similar mechanism for the attack of either a ligand molecule or a solvent molecule (i.e., water molecule) at the complex. The exchange appears to be also dependent on the nature of the incoming ligand; otherwise the slope should be m = 1.0.

As mentioned above, the first step in the exchange reaction is likely to consist of the addition of a water molecule (solvent path) or a ligand molecule (reagent path) at the fifth coordination site of the complex. In the visible region, however, no spectral changes could be observed upon addition of up to 0.5 M of the appropriate ligand to the complex dissolved in toluene ($[CuL_2]$ = 10^{-3} M). The equilibrium constants for the addition of a third ligand molecule are obviously very small.

As is indicated by a red shift and intensity increase in the dd spectra,[6] an increasing pseudotetrahedral distortion of the preferentially square-planar complexes I occurs with R = Et < *i*-Pr < *t*-Bu. The continuous drop in the size of k_S and k_{LH} in the series R = *n*-Pr, *i*-Bu, and *neo*-Pe and the very similar values for k_S and k_{LH} for R = *i*-Pr and *t*-Bu give good evidence for an exchange mechanism proceeding via an associative mode of activation. Interestingly, the screening of the copper by increasingly β branched R groups is only poorly reflected by the thermodynamic data ($\Delta H°$ and $\Delta S°$) for equilibrium 7, whereas it is convincingly demonstrated by the decreasing size of the rate constants.

In summary, the sequence of relevant steps leading to isotopic ligand exchange is given in Scheme I. In previous studies[2b] on the isotopic metal exchange of the same complexes in chloroform, a similar dependency of the rate of exchange on the organic group R was observed. Both metal and ligand exchange can obviously be initiated by the attack of protic partners such as water, alcohols, and phenolic ligands. The higher exchange rate of metal compared to ligand exchange is probably due to the different properties of the media (toluene and chloroform) and to the higher content of protic species such as water and ethanol in chloroform. Unfortunately, a direct comparison by metal-exchange studies in toluene was not possible due to extremely low solubility of mono(pyridine)copper(II) acetate in this solvent. On the other hand, ligand exchange in chloroform was faster than in toluene but led to data of very poor reproducibility. The rate of metal–ligand bond rupture in the case of the metal exchange[2b] decreases upon variation of R in the same way as it is observed for the ligand exchange (see Table III).

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Registry No. 3-I-5-I-HSA=NEt, 69897-48-9; 3-I-5-I-HSA=N-*n*-Pr, 69897-49-0; 3-I-5-I-HSA=N-*i*-Pr, 69897-50-3; 3-I-5-I-HSA=N-*i*-Bu, 69897-51-4; 3-I-5-I-HSA=N-*t*-Bu, 59275-66-0; 3-I-5-I-HSA=N-*neo*-Pe, 69897-52-5; 3-I-5-NO_2-HSA=NEt, 69927-27-1; 3-I-5-NO_2-HSA=N-*n*-Pr, 69897-53-6; 3-I-5-NO_2-HSA=N-*i*-Pr, 69897-54-7; 3-I-5-NO_2-HSA=N-*i*-Bu, 69897-55-8; 3-I-5-NO_2-HSA=N-*t*-Bu, 69897-56-9; 3-I-5-NO_2-HSA=N-*neo*-Pe, 69897-57-0; $Cu(DISA{=}NEt)_2$, 53479-90-6; $Cu(DISA{=}N\text{-}i\text{-}Pr)_2$, 53479-92-8; $Cu(DISA{=}N\text{-}t\text{-}Bu)_2$, 53479-94-0; $Cu(DISA{=}N\text{-}n\text{-}Pr)_2$, 53479-91-7; $Cu(DISA{=}N\text{-}i\text{-}Bu)_2$, 53479-93-9; $Cu(DISA{=}N\text{-}neo\text{-}Pe)_2$, 62389-55-3; $Cu(INSA{=}N\text{-}i\text{-}Pr)_2$, 69897-72-9; $Cu(INSA{=}N\text{-}t\text{-}Bu)_2$, 69897-73-0; $Cu(INSA{=}N\text{-}n\text{-}Pr)_2$, 69927-36-2; $Cu(INSA{=}N\text{-}i\text{-}Bu)_2$, 69897-74-1; $Cu(INSA{=}N\text{-}neo\text{-}Pe)_2$, 69897-75-2; $Cu(DISA{=}NEt)_2{\cdot}py$, 69897-76-3; $Cu(DISA{=}N\text{-}i\text{-}Pr)_2{\cdot}py$, 69897-77-4; $Cu(DISA{=}N\text{-}n\text{-}Pr)_2{\cdot}py$, 69897-78-5; $Cu(DISA{=}N\text{-}i\text{-}Bu)_2{\cdot}py$, 69897-79-6; $Cu(DISA{=}N\text{-}neo\text{-}Pe)_2{\cdot}py$, 69897-80-9; $Cu(INSA{=}N\text{-}i\text{-}Pr)_2{\cdot}py$, 69897-81-0; $Cu(INSA{=}N\text{-}n\text{-}Pr)_2{\cdot}py$, 69897-82-1; $Cu(INSA{=}N\text{-}i\text{-}Bu)_2{\cdot}py$, 69897-83-2; $Cu(INSA{=}N\text{-}neo\text{-}Pe)_2{\cdot}py$, 69897-84-3.

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