concentration within the transition state can account for some volume reduction. Selecting some examples suggests that the charge concentration effect (on solvent) is greater for negative than for positive charge concentration in aqueous solution; for example, contrast reaction 22 ($\Delta V^* = -22$ cm^3 mol^{-1})[20] to reactions 30 and 32 ($\Delta V^* = -2.2$ and -11.4 cm^3 mol^{-1}, respectively).[24,26] But the situation is not straightforward, as reaction 23, $Co(en)_3^{2+}$ + $Co(en)_3^{2+}$ in water,[21] has $\Delta V^* = -20$ cm^3 mol^{-1}. Hence, from this it can be concluded that the overlap/interpenetration effect contributes to considerable varying extents to the volume decrease and is complex specific. ΔV^* values become more negative as one proceeds from reaction 25 to reaction 29. These increases coincide with an increase in ligand bulkiness and flexibility in the series of reactions.[8] Therefore, the overlap and/or penetration effect contributes more to volume reduction as the volume of reactants increases.

In conclusion, this analysis supports the idea emerging from recent studies that intrinsic volume contractions arising from interpenetration of ligands coordinated to the metal centers of reaction partners or of ligands coordinated to a metal center and an organic substrate can account for the more negative ΔV^* values than expected on the basis of solvation changes due to increase in electrostriction only. This represents another type of an "intrinsic" volume change in addition to the traditional one for various mechanistic features. This means that, notwithstanding the bulkiness of some of the bound ligands in two-metal-center reactions and in metal center–organic substrate redox reactions, there seems to be a specific distance of approach that is required for electron transfer and also facilitates it. The results now available for several series of outer-sphere electron-transfer reactions produce a consistent picture for qualitative arguments and interpretation. An objective in our current research is to choose suitable reactions which allow an evaluation of the factors that seem to be critical in these electron-transfer reactions; ultimately, a quantitative explanation should be possible, and this should be compatible with existing theoretical descriptions of these processes.

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Registry No. $IrCl_6^{2-}$, 16918-91-5; catechol, 120-80-9; 4-*tert*-butylcatechol, 98-29-3; 3,4-dihydroxybenzoic acid, 99-50-3; 2,3-dihydroxybenzoic acid, 303-38-8; adrenaline, 51-43-4; L-dopa, 59-92-7.

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

Kinetic Study on Bis(*N*-alkylsalicylaldiminato)nickel(II) Complexes: Chiral Discrimination in Associatively Controlled Ligand Substitution

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Normal and stopped-flow spectrophotometry was used to study the kinetics of the reaction $NiA_2 + H_2B \rightarrow NiB + 2HA$ in acetone with NiA_2 = Ni(PhEt-sal)$_2$ (bis[*N*-(1-phenylethyl)salicylaldiminato]nickel(II)) and Ni(CyEt-sal)$_2$ (bis[*N*-(1-cyclohexylethyl)-salicylaldiminato]nickel(II)) and with H_2B = H_2salen (1,2-diamino-*N*,*N*′-disalicylideneethane), H_2salpn (1,3-diamino-*N*,*N*′-disalicylidenepropane), H_2sal-Me-en (1,2-diamino-*N*,*N*′-disalicylidenepropane, H_2sal-Me$_2$-en (1,2-diamino-*N*,*N*′-disalicylidene-2-methylpropane, H_2sal-Me,Me-en (2,3-diamino-*N*,*N*′-disalicylidenebutane and H_2sal-Cy-en (1,2-diamino-*N*,*N*′-disalicylidenecyclohexane). The reaction follows a second-order rate law, rate = k_2[NiA$_2$][H$_2$B], and is associatively controlled (A mechanism). For the system Ni(PhEt-sal)$_2$/H$_2$B, the rate constant k_2 (298 K) ranges from 70.2 (H_2salen) to 0.33 M^{-1}s^{-1} (H_2sal-Me$_2$-en). The reactivity of the complex Ni(PhEt-sal)$_2$ is by a factor of approximately 5 greater than that of Ni(CyEt-sal)$_2$. Preparation of the complexes Ni(PhEt-sal)$_2$ and Ni(CyEt-sal)$_2$, respectively, with the *R* and *S* enantiomers of the chiral amines 1-phenylethylamine and 1-cyclohexylethylamine, respectively, leads to the enantiomers "Ni(*RR*)" and "Ni(*SS*)" of the two complexes, which were characterized by their specific rotation in acetone. The *R* and *S* enantiomers of the ligand H_2sal-Me-en were obtained from the racemic ligand by HPLC techniques, and the *R*,*R* and *S*,*S* enantiomers of the ligand H_2sal-Cy-en were prepared from the enantiomers of the chiral amine 1,2-diaminocyclohexane by Schiff base reaction with salicylaldehyde. Ligand substitution in the systems Ni(PhEt-sal)$_2$/H_2sal-Me-en, Ni(PhEt-sal)$_2$/H_2sal-Cy-en, Ni(CyEt-sal)$_2$/H_2sal-Me-en, and Ni(CyEt-sal)$_2$/H_2sal-Cy-en with the various pairs of enantiomers results in the finding that there is chiral discrimination in the sense that rate constant k_2 for the various combinations Ni(*RR*)/(*R*)-ligand and Ni(*SS*)/(*S*)-ligand is by a factor of 1.4–2.1 greater than for the combinations Ni(*RR*)/(*S*)-ligand and Ni(*SS*)/(*R*)-ligand. Activation parameters ΔH^*, and ΔS^* are presented. Equilibrium constants for adduct formation in acetone according to $NiA_2 + 2\,base \rightleftharpoons NiA_2{\cdot}base + base \rightleftharpoons NiA_2{\cdot}2\,base$ for base = pyridine, 2-picoline and (*S*)-(−)-nicotine are presented. The results are discussed in terms of kinetic vs thermodynamic control of the observed chirality effects.

Introduction

Chiral recognition is a phenomenon of utmost importance for the functioning of biological systems and also for chemical synthesis. Stereoselectivity, as resulting from chiral recognition in reactions involving chiral and/or prochiral compounds, may arise from kinetic or thermodynamic sources. When kinetically controlled, stereoselecivity is due to the energetically differentiated formation of diastereoisomeric intermediates and/or transition states, leading to a difference in reaction rates. Thermodynamically controlled stereoselectivity results from the nonstatistical distribution of diastereoisomeric products in an equilibrium situation.

In the field of coordination chemistry, there has been a steady increase in studies involving optically active metal complexes over the past decades.[1] These studies were undertaken mainly to obtain detailed information on the stereochemical aspects of reaction mechanisms and to provide useful information for practical applications, such as separation of enantiomers and development of systems for homogeneous catalysis in enantioselective synthesis.

Electron transfer and ligand substitution represent the two most important types of reactions of metal complexes. Since transition metals are an essential part of the (chiral) active site of many redox-active proteins,[2] numerous investigations deal with stereo-

† This contribution presents part of the results of the Dr.-Ing. Dissertation submitted to the Technische Hochschule Darmstadt in 1991.

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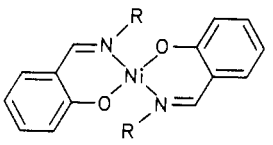
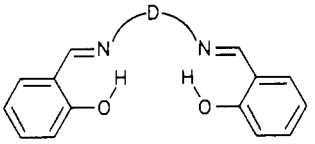
Chart I



Ni(R-sal)$_2$

R	Ni(R-sal)$_2$
*CH(Ph)-CH$_3$	Ni(PhEt-sal)$_2$
*CH(cyclo-C$_6$H$_{11}$)-CH$_3$	Ni(CyEt-sal)$_2$



$H_2salD \hat{=} H_2B$

D	H_2salD
	H_2salen
	H_2salpn
	H_2sal-Me-en
	H_2sal-Me$_2$-en
	H_2sal-Me,Me-en
	H_2sal-Cy-en

selective rate effects in electron-transfer reactions involving chiral metal complexes and metalloproteins. This field, to which the groups of Taube, Lappin, Gray, Sykes, and Bernauer contributed most significantly,[3] has been reviewed very recently by Bernauer.[4] It is somewhat surprising, however, that the kinetic study of chiral recognition in ligand substitution reactions appears to have been neglected so far.

Ligand substitution in transition-metal complexes with an associative mode of activation (A mechanism[5]) is documented best for square-planar complexes with d^8 metal centers such as Pt(II) and Pd(II) and, to a certain extent, Ni(II), Ir(I), and Au(III).[5,6] In these complexes the metal itself cannot be made a chiral center;[7] chirality has to be introduced instead through suitable chiral ligands. Considering the biological relevance of the various d^8 metal centers mentioned above, one realizes that Ni(II) is the one that is biologically essential, e.g. in ureases.[9] From this point

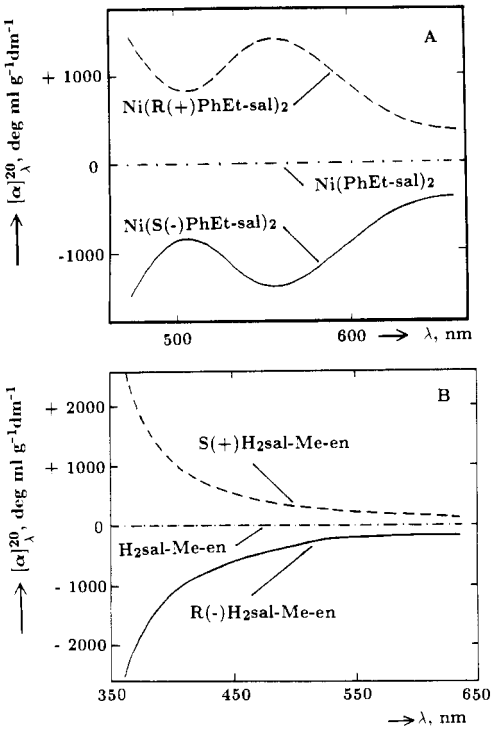


Figure 1. ORD spectra of the enantiomers of the complex Ni(PhEt-sal)$_2$ (A) and of the ligand H_2sal-Me-en (B) in acetone at 293 K.

of view, square-planar nickel(II) complexes suggest themselves for the study of chirality effects in ligand substitution reactions. In addition to this, the chemical and stereochemical variability[8,10] of bis(*N*-alkylsalicylaldiminato)nickel(II) complexes, Ni(R-sal)$_2$, and the knowledge of their kinetic behavior in ligand substitution[11-13] can be taken as further suggestion to use this class of planar *trans*-N_2O_2 complexes, provided with chiral groups R, for such a study.

The present contribution presents kinetic data for reaction 1 as studied in acetone with chiral complexes Ni(R-sal)$_2$ = Ni-

$$Ni(R\text{-}sal)_2 + H_2B \rightarrow NiB + 2R\text{-}salH \qquad (1)$$

(PhEt-sal)$_2$, Ni(CyEt-sal)$_2$, and achiral or chiral tetradentate ligands H_2B = H_2salD of the salen type in which the bridging group D is variable, as shown below in Chart I.

A chiral Schiff base complex such as Ni(PhEt-sal)$_2$ is readily formed when bis(salicylaldehydato)nickel(II) reacts with (1-phenylethyl)amine. Since this preparation can be carried out either with the enantiomers (*R*)-(+)- and (*S*)-(−)-(1-phenylethyl)amine or with racemic (1-phenylethyl)amine, three isomers of the complex have to be considered. In the stereochemical part of the Discussion the simplified notation Ni(*RR*), Ni(*SS*), and Ni(*RS*) ("meso complex") will be used for these isomers. The stereo isomers of the complex Ni(CyEt-sal)$_2$ will be termed analogously.

Experimental Section

The following chemicals were used without further purification: Ni(AcO)$_2$·4H$_2$O (Merck); the solvent acetone (reagent grade, Merck); salicylaldehyde (Bayer AG); (±)-trans-1,2-diaminocyclohexane (99%, Aldrich); 1,2-diaminoethane (99%), 2-picoline p.a. and pyridine p.a. (Merck-Schuchardt); 1,3-diaminopropane and 1,2-diamino-2-methylpropane (99%, Aldrich); (*S*)-(−)-nicotine (96–98%, Jansen-Chimica); (±)-(1-phenylethyl)amine, (*R*)-(+)-(1-phenylethyl)amine and (*S*)-(−)-(1-phenylethyl)amine (98%, Aldrich); (*R*)-(−)-(1-cyclohexylethyl)amine

(3) See corresponding references in ref 4.
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(6) See ref 1, Chapter 4.
(7) One has to be aware of planar, four-coordinate complexes which are subject to a configurational equilibrium planar ⇌ tetrahedral, as enforced by bulky ligands. In such complexes, the metal in the tetrahedral isomer is of course a center of chirality. This aspect was reviewed in ref 8.
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Table I. Visible Absorption and Specific Rotation of the Complexes and Ligands in Acetone

complex/ligand	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})	$[\alpha]^{20}_D$, deg mL g^{-1} dm^{-1}
Ni(PhEt-sal)$_2$	416 (4200); 615 (80)	
Ni(*R*(+)-PhEt-sal)$_2$	416 (4200); 615 (80)	+1180 ± 20
Ni(*S*(−)-PhEt-sal)$_2$	416 (4200); 615 (80)	−1200 ± 20
Ni(*R*(−)-CyEt-Sal)$_2$[a]	410 (sh; ≈3800); 590 (110); 720 (sh); 1450 (22)	+1390 ± 20[a]
Ni(*S*(+)-CyEt-sal)$_2$[a]	410 (sh; ≈3800); 590 (110); 720 (sh); 1450 (22)	−1360 ± 20[a]
Ni(sal-Me-en)	385 (sh); 412 (6900); 450 (sh); 550 (sh; ≈150)	
Ni(sal-Cy-en)	410 (6700); 430 (sh); 550 (120)	
R(−)-H$_2$sal-Me-en	330 (6100); 410 (65)	−232 ± 20
S(+)-H$_2$sal-Me-en	330 (6100); 410 (65)	+214 ± 20
1*R*,2*R*(−)-H$_2$sal-Cy-en	330 (6500); 410 (50)	−522 ± 50
1*S*,2*S*(+)-H$_2$sal-Cy-en	330 (6500); 410 (50)	+508 ± 50

[a] Complex formation turns the negative specific rotation of (*R*)-(−)-1-(cyclohexylethyl)amine into a positive specific rotation and vice versa.

and (*S*)-(+)-(1-cyclohexylethyl)amine (98%, Fluka); 1*R*,2*R*(−)-1,2-diaminocyclohexane and 1*S*,2*S*(+)-1,2-diaminocyclohexane (purum, Fluka).

Complexes. The complex Ni(PhEt-sal)$_2$, described by Terent'ev et al.[14] and Maeda et al.,[15] and the novel complex Ni(CyEt-sal)$_2$ were prepared from Ni(sal)$_2$·2H$_2$O and the corresponding amine according to a procedure reported earlier.[11] The preparation of Ni(CyEt-sal)$_2$ was carried out under N_2. Both complexes tend to include some water, most of which could be removed by drying over P_4O_{10} in vacuo at 65 °C. The complexes were characterized by elemental analysis (CHN), visible spectroscopy, and specific rotation (see Table I). Figure 1A shows the ORD spectra of Ni(*R*(+)-PhEt-sal)$_2$, Ni(*S*(−)-PhEt-sal)$_2$ and the "meso complex".

Ligands H$_2$salD. The tetradentate Schiff bases H$_2$salen, H$_2$salpn, H$_2$sal-Me-en, H$_2$sal-Me$_2$-en, and H$_2$Me,Me-en, and H$_2$sal-Cy-en were prepared from salicylaldehyde and the corresponding diamine in methanol. The yellow solids were recrystallized from methanol.

Separation of the Enantiomers of H$_2$sal-Me-en. The racemic ligand, as prepared from salicylaldehyde and racemic 1,2-diaminopropane, was separated by HPLC on a column (length, 83 cm; inner diameter, 45 mm) filled with microcrystalline cellulosetriacetate (15-25 μm; Merck) at 6 bar (solvent, ethanol/*n*-hexane = 40/60; flow rate, 3 mL/min). The *S*(+) enantiomer came off first, reasonably well separated from the *R*(−) enantiomer. The acetone solutions of the pure enantiomers (see the ORD spectra in Figure 1B) were stable in the sense that racemization was not observed.

Instrumentation. UV/vis spectra: diode array spectrophotometer (Hewlett-Packard, type 8451) and two-beam spectrophotometer (Perkin-Elmer, type 554). ORD spectra: spectropolarimeter (Jasco, type J-20). Specific rotation: polarimeter (Perkin-Elmer, type 241).

Spectrophotometric Titration. The titration of the acetone solutions of Ni(*R*-sal)$_2$ = NiA$_2$ with bases B (pyridine, 2-picoline and (*S*)-(−)-nicotine) according to (2) was followed spectrophotometrically. The

$$NiA_2 \; 2B \overset{K_1}{\rightleftharpoons} NiA_2{\cdot}B + B \overset{K_2}{\rightleftharpoons} NiA_2{\cdot}2B \qquad (2)$$

absorbance/[B] data for a given wavelength were computer-fitted to eq 5, given in ref 11, to obtain K_1 and K_2 (see Table II).

Kinetic Measurements. Reaction 1 was followed spectrophotometrically in two-chamber quartz cells (2 × 0.439 cm) by recording the increase in absorbance of the products Ni(salD). Faster reactions with $t_{1/2} < 2$ min were studied with a modified[16] stopped-flow spectrophotometer (Durrum, D 110). The A/t data (A = absorbance) obtained under pseudo-first-order conditions ([complex]$_0$ ≪ [H$_2$salD]$_0$) were computer-fitted to eq 3, whereas those obtained under stoichiometric

$$A = (A_0 - A_\infty)[\exp(-k_{obsd})] + A_\infty \qquad (3)$$

conditions ([complex]$_0$ = [H$_2$salD]$_0$) were fitted to eq 4, describing an

$$A = A_\infty + (A_0 - A_\infty)/(1 + [\text{complex}]_0 kt) \qquad (4)$$

irreversible second-order reaction. The programs used were based on the least-squares method.

Results and Discussion

Properties of the Complexes and Ligands. The characteristics of the vis absorption spectra of the green complexes Ni(PhEt-sal)$_2$ and Ni(CyEt-sal)$_2$, prepared from Ni(sal)$_2$·2H$_2$O and the corresponding amines, are compiled in Table I. Planar bis(*N*-alkylsalicylaldiminato)nickel(II) complexes Ni(*R*-sal)$_2$ such as Ni(Ph-(CH$_2$)$_n$-sal)$_2$ (n = 1–4)[13] and Ni(*n*-Pr-sal)$_2$[12] have a strong CT band in the range 410–420 nm and a relatively weak d–d band at approximately 600 nm. These two "planar" absorptions are indeed observed for both Ni(PhEt-sal)$_2$ and Ni(CyEt-sal)$_2$ (see Table I). For the latter complex, however, additional weak absorptions are found at 720 nm (shoulder) and in the near-infrared region at 1450 nm. It follows from a comparison with the well-studied[8] complex Ni(i-Pr-sal)$_2$ that these additional bands are indicative of tetrahedral distortion, typically observed for complexes Ni(*R*-sal)$_2$ with α-branched alkyl groups R.[8] One learns thus that the stereochemical effect of the bulky cyclohexyl group, bound to the α-carbon of an ethyl group R, differs from that of the flat phenyl group, located at the same position. The phenyl complex Ni(PhEt-sal)$_2$ is practically planar, whereas the cyclohexyl complex Ni(CyEt-sal)$_2$ is tetrahedrally distorted. It is well-known for this class of complexes, however, that in solution there is a rapid configurational equilibrium planar ⇌ tetrahedral.[8,12] The typical "planar bands" are thus found in the spectrum as well as the typical "tetrahedral bands".

The absorption properties of the isomeric complexes Ni(*R*-(+)-PhEt-sal)$_2$, Ni(*S*(−)-PhEt-sal)$_2$ and Ni(PhEt-sal)$_2$ ("meso complex") are identical, and the same is true for the enantiomers of the complex Ni(CyEt-sal)$_2$ (see Table I). The salen-type complexes Ni(sal-Me-en) and Ni(sal-Cy-en) with a planar *cis*-N_2O_2 coordination geometry have a characteristic absorption at approximately 550 nm (see Table I), which can be used for monitoring product formation in reaction 1.

The purity of the enantiomers of the complexes Ni(PhEt-sal)$_2$ and Ni(CyEt-sal)$_2$, respectively, is reflected by the data obtained for the specific rotation of the corresponding pairs of enantiomers, which agree (with opposite sign, of course) within the limits of error (see Table I). In addition, the ORD spectrum of Ni(*R*-(+)-PhEt-sal)$_2$ is exactly the mirror image of that obtained for Ni(*S*(−)-PhEt-sal)$_2$ (see Figure 1A). It is noteworthy that, in the case of Ni(CyEt-sal)$_2$, the specific rotation of the optically active amines (*R*)-(−)- and (*S*)-(+)-(1-cyclohexylethyl)amine, used for the synthesis of the complexes, changes sign upon complex formation.

As documented by the data obtained for the specific rotation of *R*(−) and *S*(+)-H$_2$sal-Me-en, the HPLC separation of the racemic Schiff base H$_2$sal-Me-en into its enantiomers was successful. The ORD spectrum of the *S*(+) isomer is the mirror image of the *R*(−) isomer (see Figure 1B).

Equilibrium Constants for Adduct Formation. The tendency of four-coordinate bis(*N*-alkylsalicylaldiminato)nickel(II) complexes to add bases according to (2) and thus become six-coordinate is well-known.[11-13,17,18] It is found for bases such as pyridine that $K_1 < K_2$, which means that six-coordination is clearly preferred over five-coordination. Table II shows this type of behavior for pyridine addition to Ni(PhEt-sal)$_2$ and Ni(CyEt-sal)$_2$, with the latter complex, due to its tetrahedral distortion, being a considerably poorer base acceptor. The ratio K_2/K_1 amounts to 2.4 (Ni(PhEt-sal)$_2$) and 3.5 (Ni(CyEt-sal)$_2$), respectively. As to be expected, the two enantiomeric complexes Ni(*R*(+)-PhEt-sal)$_2$ and Ni(*S*(−)-PhEt-sal)$_2$ do not differ in adduct formation with pyridine. Addition of the base 2-picoline to Ni(PhEt-sal)$_2$ yields weak mono adduct formation only (K_1 = 0.18 M^{-1}). This can be taken as an indication for deformation of the planar N_2O_2Ni

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Table II. Equilibrium Constants for Adduct Formation of Ni(CyEt-sal)$_2$ and Ni(PhEt-sal)$_2$ with Bases B According to (2) in Acetone at 298 K

	B = pyridine			B = 2-picoline[b]	B = (*S*)-(−)-nicotine[c]		
complex[a]	K_1, M^{-1}	K_2, M^{-1}	β_2,[d] M^{-2}	K_1, M^{-1}	K_1, M^{-1}	K_2, M^{-1}	β_2,[d] M^{-2}
Ni(*R*(−)-CyEt-sal)$_2$	3.11 ± 0.62[e]	10.8 ± 2.2[e]	33.6 ± 6.8[e]				
Ni(*R*(+)-PhEt-sal)$_2$	7.7 ± 1.5[f]	18.7 ± 3.8[f]	145 ± 30[f]	0.172 ± 0.024	11.3 ± 2.2	42.3 ± 8.4	477 ± 96
Ni(*S*(−)-PhEt-sal)$_2$	7.7 ± 1.5[f]	18.4 ± 3.7[f]	142 ± 28[f]	0.187 ± 0.010	10.2 ± 2.0	47.5 ± 9.4	482 ± 96

[a] [complex] = 0.004 M. [b] Data obtained from change in absorbance at 416 nm. [c] Data obtained from change in absorbance at 570 nm. [d] $\beta_2 = K_1K_2$. [e] Mean of data obtained from change in absorbance at 584, 602, and 700 nm. [f] Data obtained from change in absorbance at 650 nm.

Table III. Second-Order Rate Constant k_2 (M^{-1} s^{-1}) for the Reaction of the Complex Ni(PhEt-sal)$_2$ with Tetradentate Ligands H_2B of the Salen-Type in Acetone at 298 K According to (1)[a]

H_2B	Ni(*R*(+)-PhEt-sal)$_2$	Ni(*R*,*S*(±)-PhEt-sal)$_2$	Ni(*S*(−)-PhEt-sal)$_2$
H_2salen	69.7 ± 4.3	71.1 ± 3.2	69.7 ± 0.7
H_2salen	13.1 ± 0.3[b]		13.9 ± 0.4[c]
H_2salpn	34.4 ± 0.7	33.9 ± 1.0	
H_2sal-Me-en[d]	36.2 ± 2.0	32.7 ± 0.5	31.8 ± 1.8
H_2sal-Me-en[d]	31.6 ± 0.5[e]		33.7 ± 1.0[e]
H_2sal-Me-en[d]	6.53 ± 0.65[b]		6.64 ± 0.11[c]
H_2sal-Me$_2$-en	0.313 ± 0.006	0.354 ± 0.007	0.326 ± 0.005
H_2sal-Me,Me-en[f]	1.52 ± 0.07	1.34 ± 0.06	
H_2sal-Cy-en[g]	0.49 ± 0.02	0.45 ± 0.02	0.48 ± 0.01

[a] Experiments carried out under pseudo-first-order conditions ([complex]$_0 \leq 0.1[H_2B]_0$) at five different concentrations of H_2B in the range 0.005–0.1 M. Rate constant k_{obsd} obtained by fitting the A/t data to eq 3, with rate constant k_2 resulting from the plot of $k_{obsd} = k_2[H_2B]_0$. [b] Rate constant refers to Ni(*R*(−)-CyEt-sal)$_2$ instead of Ni(*R*(+)-PhEt-sal)$_2$. [c] Rate constant refers to Ni(*S*(+)-CyEt-sal)$_2$ instead of Ni(*S*(−)-PhEt-sal)$_2$. [d] Racemic ligand, as prepared from salicylaldehyde and racemic 1,2-diaminopropane. [e] Rate constant obtained under stoichiometric conditions ([complex]$_0$ = [H_2B]$_0$) by fitting the A/t data to eq 4. [f] Meso form of the ligand; prepared from salicylaldehyde and *meso*-2,3-diaminobutane, as obtained from diacetyl dioxime according to: Gullotti, M.; Pasini, A.; Fantucci, P.; Ugo, R.; Gillard, R. *Gazz. Chim. Ital.* **1972**, *102*, 855. [g] Racemic ligand, as prepared from salicylaldehyde and racemic *trans*-1,2-diaminocyclohexane.

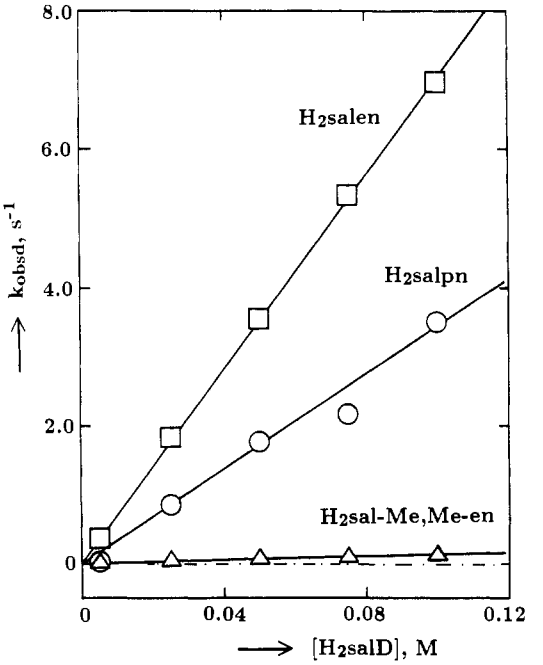

Figure 2. Plot of the experimental rate constant k_{obsd} (298 K) vs the concentration of the entering ligands H_2salD for the complex Ni(*R*(+)-PhEt-sal)$_2$ reacting according to (1) in acetone.

coordination core being necessary to make the addition of the sterically hindered base 2-picoline possible.

The most important result of the spectrophotometric titration studies with bases is the finding that there is no chiral recognition when the optically active base (*S*)-(−)-nicotine is added to the enantiomers Ni(*R*(+)-PhEt-sal)$_2$ and Ni(*S*(−)-PhEt-sal)$_2$. The data obtained for K_1, K_2, and β_2 agree within the limits of error, which is an interesting detail for the kinetic discussion following later. It is important to point out that coordination of the base nicotine occurs through the pyridine nitrogen.[19] Compared to the base pyridine, the equilibrium constants K_1 and K_2 obtained for the addition of nicotine are clearly greater, which points to an increase in pyridine basicity as caused by the introduction of the *N*-methylpyrrolidine group in the 3-position.

Kinetics of Ligand Substitution with Optically Inactive Ligands H_2B. To establish the rate law, ligand substitution according to (1) with Ni(R-sal)$_2$ = Ni(PhEt-sal)$_2$ was studied with a series of optically inactive ligands H_2B first (see Table III). It was found that, under pseudo-first-order conditions ([complex]$_0 \ll$ [H_2B]$_0$), the reaction goes to completion and the A/t data obtained at different wavelengths can be well fitted to eq 3. The experimental rate constant k_{obsd} follows relationship (5), as shown in Figure

$$k_{obsd} = k_2[H_2B] \quad (5)$$

2 for three ligands H_2B. Substitution according to (1) obeys therefore rate law (6), which describes an irreversible second-order

$$\text{rate} = -\text{d}[\text{NiA}_2]/\text{d}t = \text{d}[\text{NiB}]/\text{d}t = k_2[\text{NiA}_2][H_2B] \quad (6)$$

reaction. Further proof for this comes from the fact (see Table III) that rate constant k_2, as obtained for the system Ni(PhEt-sal)$_2$/H_2sal-Me-en under stoichiometric conditions ([NiA_2]$_0$ = [H_2B]$_0$) by fitting the A/t data to eq 4, agrees within error with k_2 derived from measurements under pseudo-first-order conditions.

Rate law (6) is compatible with associatively controlled ligand substitution, as typically found for square-planar complexes with d^8 metal centers.[1] The fact that there is no ligand-independent, solvent-initiated reaction channel points to the very weak nucleophilicity of acetone compared to that of the attacking ligand H_2salD. If reaction (1) follows an A mechanism, the size of k_2 should depend on the nature of the attacking ligand, which is indeed observed. Rate constant k_2 for the reaction of Ni(PhEt-sal)$_2$ with ligands H_2salD varies drastically when the entering ligand is modified by variation of the bridge D (see Table III). The reaction is fastest for H_2B = H_2salen (k_2 = 70 M^{-1} s^{-1}) and slowest for H_2B = H_2sal-Me$_2$-en (k_2 = 0.33 M^{-1} s^{-1}). The following sequence is found (k_2, relative):

H_2sal-Me$_2$-en (1) < H_2sal-Cy-en (1.4) < H_2sal-Me,Me-en (4.6) < H_2sal-Me-en (100) < H_2salpn (103) < H_2salen (212)

Especially the introduction of more than one methyl group in the ethylene bridge of H_2salen (see H_2sal-Me$_2$-en and H_2sal-Me,-Me-en) and the presence of a cyclic structure (see H_2sal-Cy-en) reduces the flexibility of H_2salen so much that the rate of substitution drops by a factor of up to 212. Interestingly enough, the rate of isotopic copper exchange in systems Cu(salD)/*Cu^{2+} drops in a similar fashion upon variation of the bridge D.[20]

Rate constant k_2 for the reaction of H_2salen (and H_2sal-Me-en, respectively) with Ni(PhEt-sal)$_2$ is by a factor of approximately 5 greater than for the reaction with Ni(CyEt-sal)$_2$. In addition to steric arguments, an explanation for this reduced reactivity of Ni(CyEt-sal)$_2$ compared to Ni(PhEt-sal)$_2$ could come from an

(19) Muralidharan, S.; Nagaraja, K. S.; Udupa, M. R. *Indian J. Chem., Sect. A* **1987**, *26*, 348.

(20) Köhler, G.; Elias, H. *Inorg. Chim. Acta* **1979**, *34*, L215.

Table IV. Second-Order Rate Constant k_2 (M^{-1} s^{-1}) for the Reaction of the Enantiomers of the Complexes Ni(PhEt-sal)$_2$ and Ni(CyEt-sal)$_2$ with the Enantiomers of the Ligands H_2sal-Me-en and H_2sal-Cy-en in Acetone at 298 K According to (1)[a]

	H_2sal-Me-en				H_2sal-Cy-en			
	k_2				k_2			
Ni(R-sal)$_2$	*R*(−)	*S*(+)	ratio[b]	[ee],[c] %	*R*,*R*(−)	*S*,*S*(+)	ratio[b]	[ee],[c] %
Ni(*R*(+)-PhEt-sal)$_2$	40.0 ± 4.0	22.8 ± 2.3	1.69	25.8	0.60 ± 0.06[d]	0.31 ± 0.03[d]	1.94	31.9
	41.3 ± 4.1[d]	25.2 ± 2.5[d]						
Ni(*S*(−)-PhEt-sal)$_2$	25.5 ± 2.6	40.7 ± 4.1	1.69	25.7	0.29 ± 0.03[d]	0.64 ± 0.06[d]	2.21	37.6
	24.2 ± 2.4[d]	43.3 ± 4.3[d]						
Ni(*R*(−)-CyEt-sal)$_2$	7.8 ± 0.8	5.0 ± 0.5	1.56	21.9	0.180 ± 0.018[d]	0.083 ± 0.008[d]	2.17	36.9
Ni(*S*(+)-CyEt-sal)$_2$	5.9 ± 0.6	7.8 ± 0.8	1.32	13.9	0.088 ± 0.009[d]	0.162 ± 0.016[d]	1.84	29.6

[a] See footnote *a* of Table III. [b] Ratio of rate constants, k_{fast}/k_{slow}, with k_{fast} being the averaged rate constant for the faster reacting pair of enantiomers and vice versa. [c] [ee] = enantiomeric excess = $(k_{fast} - k_{slow})/(k_{fast} + k_{slow})100$, %. For the definition of k_{fast} and k_{slow}, see footnote *b*. [d] See footnote *e* of Table III.

earlier study[12] on ligand substitution in bis chelate complexes of nickel(II) that are subject to the configurational equilibrium planar ⇌ tetrahedral. It was shown for these complexes that the reaction with H_2salen takes place exclusively through the planar isomer.[12] As following from the vis absorption spectra (see Discussion above) the complex Ni(CyEt-sal)$_2$ is tetrahedrally distorted, and the concentration of the planar species is thus smaller than the total complex concentration.

In summary, the variation in k_2 observed upon variation of the nature of the attacking ligand supports the interpretation that reaction 1 is associatively controlled. As to be expected, the two rate constants k_2, obtained for the reaction of a given achiral ligand H_2B (such as H_2salen and H_2sal-Me$_2$-en) with the two enantiomers of Ni(PhEt-sal)$_2$ (i.e., Ni(*RR*) and Ni(*SS*)), are identical within error. The scattering of these data allows the realistic estimate that the maximum limits of error for rate constant k_2 are approximately ±5%.

A notable feature of the system Ni(PhEt-sal)$_2$/H_2B (achiral) arises from the rate data obtained with the "meso complex" Ni(*RS*). It is well-known from complex formation with optically active α-amino acids[21] that, in solution, equilibration occurs according to 2M(*RS*) ⇌ M(*RR*) + M(*SS*). One has thus to consider that, for statistical reasons, the solution of *meso*-Ni(PhEt-sal)$_2$ is one with approximately 50% of Ni(*RS*), 25% of Ni(*RR*), and 25% of Ni(*SS*). The experimental rate constant $k_2(RS)_{exp}$ should therefore be a composite parameter according to $k_2(RS)_{exp} = 0.25k_2(RR) + 0.25\,k_2(SS) + 0.5k_2(RS)$. The data obtained for the ligand H_2B = H_2sal-Me$_2$-en (see Table III) lead thus to $k_2(RS) = 0.388$ M^{-1} s^{-1} with $k_2(RR) \approx k_2(SS) = 0.32$ and $k_2(RS)_{exp} = 0.354$ M^{-1} s^{-1}. The ratio $k_2(RR)/k_2(RS)$ (or $k_2(SS)/k_2(RS)$, respectively) amounts to 0.82, clearly indicating greater reactivity of the meso complex. This means in more general terms that stereochemical discrimination in ligand substitution can occur not only with optically active complexes and the enantiomers of an optically active entering ligand but also with the optically active and the meso complex reacting with any ligand, be it optically active or not. For H_2B = H_2salen and H_2sal-Cy-en these effects are less pronounced (see Table III).

Kinetics of Ligand Substitution with Pairs of Enantiomers. Table IV summarizes the data obtained for rate constant k_2 resulting from the reaction of chiral complexes Ni(R-sal)$_2$ with chiral ligands H_2B according to (1). It is found for the system Ni(PhEt-sal)$_2$/H_2sal-Me-en that, in short notation, the reaction of the enantiomer Ni(*RR*) (Ni(*R*(+)-PhEt-sal)$_2$) with the *R* isomer of the ligand H_2sal-Me-en (*R*(−)-H_2sal-Me-en) is clearly faster than the reaction of the enantiomer Ni(*SS*) with the *R* isomer of the entering ligand and vice versa. Rate constants k_2 for the combinations Ni(*RR*)/*R* and Ni(*SS*)/*S* are the same within error (mean: 41.3 M^{-1} s^{-1}) and the same is true for the combinations Ni(*SS*)/*R* and Ni(*RR*)/*S* (mean: 24.4 M^{-1} s^{-1}). Even with a maximum error of ±10% for k_2, the two sets of rate constants averaging at 41.3 and 24.4 M^{-1} s^{-1} are definitely different and reflect the greater reactivity of the Ni(*RR*)/*R* and Ni(*SS*)/*S* pairs of enantiomers compared to that of the corresponding Ni(*SS*)/*R* and Ni(*RR*)/*S* pairs. Figure 3 with the plot of the relationship $k_{obsd} = k_2[H_2$sal-Me-en] is in line with this. So, the phenomenon of chiral discrimination is indeed observed in the sense that *R*- or *S*- configurated partners react faster than mixtures of both. The ratio of the corresponding rate constants amounts to 1.69 for the system Ni(PhEt-sal)$_2$/H_2sal-Me-en and the enantiomeric excess, [ee], is 26% (see Table IV). When the enantiomers of Ni(PhEt-sal)$_2$ react with the enantiomes of the ligand H_2sal-Cy-en, the same type of cross-relationship for k_2 is observed, when an even greater ratio of rate constants (approximately 2.1) and [ee] = 35% (mean).

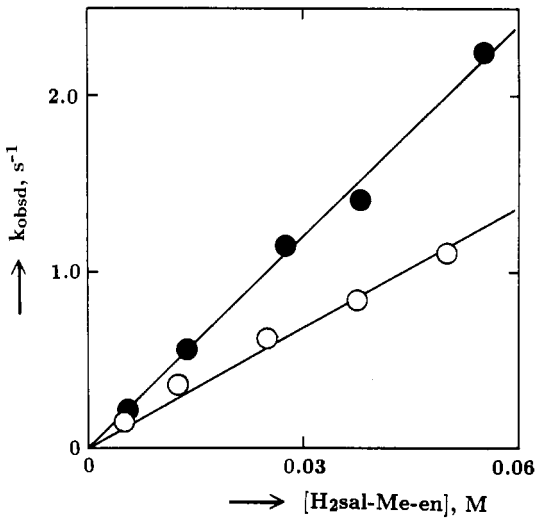

Figure 3. Plot of the experimental rate constant k_{obsd} (298 K) vs the concentration of the entering ligand H_2sal-Me-en for the reaction of the complex Ni(*R*(+)-PhEt-sal)$_2$ with the enantiomers *R*(−)-H_2sal-Me-en (●) and *S*(−)-H_2sal-Me-en (○) according to (1) in acetone.

The chiral effects found for the systems Ni(CyEt-sal)$_2$/H_2sal-Me-en and Ni(CyEt-sal)$_2$/H_2sal-Cy-en (see Table IV) are of the same order of magnitude and analogous in the sense that the Ni(*RR*)/*R* and Ni(*SS*)/*S* pairs of partners react faster than the Ni(*SS*)/*R* and Ni(*RR*)/*S* ones.

On the basis of the obvious and for other nickel systems well-established[11-13] interpretation that the ligand substitution under study, (7), follows the A mechanism according to (8) and

$$NiA_2 + H_2B \rightleftharpoons NiB + 2HA \qquad (7)$$

(9), rate law (10) applies for irreversible conditions (excess of H_2B)

$$NiA_2 + H_2B \rightleftharpoons \{NiA_2,H_2B\} \quad K_{os} \qquad (8)$$

$$\{NiA_2,H_2B\} \xrightarrow{k_{rds}} NiB + 2HA \qquad (9)$$

$$\text{rate} = -d[NiA_2]/dt = k_{rds}K_{os}[NiA_2][H_2B]_0/(1 + K_{os}[H_2B]_0) \qquad (10)$$

and the experimental rate constant k_{obsd} should follow relationship (11). As shown in Figure 2, the dependence of k_{obsd} on $[H_2B]_0$

$$k_{obsd} = k_{rds}K_{os}[H_2B]_0/(1 + K_{os}[H_2B]_0) \qquad (11)$$

(21) Morris, P. J.; Martin, R. B. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2891.

Table V. Activation Parameters[a] for the Reaction of the Enantiomers of the Complex Ni(PhEt-sal)$_2$ with the Enantiomers of the Ligand H$_2$sal-Me-en in Acetone According to (1)

complex	ligand	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J mol^{-1} K^{-1}
Ni(*R*(+)-PhEt-sal)$_2$	*R*(−)-H$_2$sal-Me-en	23.3 ± 1.8	−136 ± 13
Ni(*R*(+)-PhEt-sal)$_2$	*S*(+)-H$_2$sal-Me-en	23.1 ± 0.9	−141 ± 10
Ni(*S*(−)-PhEt-sal)$_2$	*R*(−)-H$_2$sal-Me-en	22.8 ± 0.6	−139 ± 15
Ni(*S*(−)-PhEt-sal)$_2$	*S*(+)-H$_2$sal-Me-en	23.4 ± 2.3	−134 ± 16

[a] From the temperature dependence of k_2 (as obtained under stoichiometric conditions, $[\text{complex}]_0 = [\text{ligand}]_0$) at four to six temperatures in the range 290–315 K.

is strictly linear up to $[H_2B]_0 = 0.1$ M, which indicates that $K_{os}[H_2B]_0 \ll 1$, probably due to $K_{os} \leq 1\ M^{-1}$. This means that the experimentally obtained second-order rate constant k_2 is a composite parameter, $k_2 = k_{rds}K_{os}$.

The activation parameters derived from the temperature dependence of k_2 for the four combinations of stereoisomeric complexes and ligands in the system Ni(PhEt-sal)$_2$/H$_2$sal-Me-en are compiled in Table V. The negative entropy of activation is in line with an associative mechanism. The data for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, however, agree within the limits of error for both the "fast" and the "slow" combinations, which might also be due to the small temperature range covered (25 K). So, in contrast to kinetic studies on the electron transfer between optically active cobalt(III) complexes and spinach ferredoxin[22] (or other metalloproteins[4]) the present activation data are not accurate enough to reflect a fine structure, suitable for detailed mechanistic conclusions.

The composite character of rate constant k_2 raises of course the question of what the origin of the observed chiral discrimination is. If $k_2 = k_{rds}K_{os}$, the differentiation could be related either to outer-sphere complex formation in (8), as characterized by equilibrium constant K_{os}, or to the rate-determining step (9), as characterized by rate constant k_{rds}. The equilibrium constants K_1 and K_2, as obtained for adduct formation between the enantiomers Ni(*R*(+)-PhEt-sal)$_2$ and Ni(*S*(−)-PhEt-sal)$_2$, respectively, and the optically active base (*S*)-(−)-nicotine (see Table II), agree within the limits of erorr. This finding would suggest therefore that the observed chiral discrimination is not thermodynamic, but kinetic in origin, i.e., related to the formation of slightly different diastereoisomeric transition states in the rate-controlling step (9). On the other hand, one could argue that the addition of nicotine is not a good model reaction to discriminate between kinetic vs thermodynamic control in the present system. A more crucial approach would be the study of an analogous system[23] in which the chiral nickel complex is such a strong Lewis acid that the entering ligand H_2B is more firmly coordinated, so that $K_{os}[H_2B]_0 \geq 1$ (see eq 11). When this condition is fulfilled, both parameters k_{rds} and K_{os} can be obtained as such.

Conclusions

Ligand substitution in *trans*-N_2O_2 Schiff base complexes bis(*N*-alkylsalicylaldiminato)nickel(II), Ni(alkyl-sal)$_2$, by tetradentate ligands of the salen type is a second-order process (rate = k_2[complex][ligand]), which is associatively controlled. The use of the *R* and *S* enantiomers of chiral alkylamines in complex formation leads to the enantiomeric complexes "Ni(*RR*)" and "Ni(*SS*)", the chirality centers of which are located in the ligand sphere. These enantiomers complexes react with the *R* and *S* enantiomers of chiral salen-type ligands stereospecifically in the sense that second-order rate constant k_2 is clearly greater for the diastereoisomeric complex/ligand pairs Ni(*RR*)/*R* and Ni(*SS*)/*S* than for the pairs Ni(*RR*)/*S* and Ni(*SS*)/*R*. The ratio of the corresponding rate constants lies in the range 1.4–2.1. To our knowledge, this is the first example of a ligand substitution reaction in planar four-coordinate complexes with chiral discrimination.

Acknowledgment. Sponsorship of this work by the Deutsche Forschungsgemeinschaft and by the Verband der Chemischen Industrie e.V. is gratefully acknowledged. We thank Dr. J. Kinkel for providing access to the HPLC equipment of Merck, Darmstadt, Germany. Salicylaldehyde was kindly provided by Bayer AG.

Registry No. H$_2$salen, 94-93-9; H$_2$salpn, 120-70-7; H$_2$sal-Me-en, 94-91-7; H$_2$sal-Me$_2$-en, 30180-37-1; H$_2$sal-Me,Me-en, 98964-54-6; H$_2$sal-Cy-en, 64346-55-0; *R*(−)-H$_2$sal-Me-en, 19237-25-3; *S*(+)-H$_2$sal-Me-en, 41013-25-6; *R*,*R*-(−)-H$_2$sal-Cy-en, 133695-16-6; *S*,*S*-(+)-H$_2$sal-Cy-en, 41013-28-9; Ni(*R*,*S*(±)-PhEt-sal)$_2$, 136981-79-8; Ni(*R*(+)-PhEt-sal)$_2$, 14323-23-0; Ni(*S*(−)-PhEt-sal)$_2$, 60873-36-1; Ni(*R*(−)-CyEt-sal)$_2$, 136847-35-3; Ni(*S*(+)-CyEt-sal)$_2$, 136891-99-1; Ni(*R*(−)-CyEt-sal)$_2$(pyridine)$_2$, 136847-36-4; Ni(*R*(+)-PhEt-sal)$_2$(pyridine)$_2$, 72767-53-4; Ni(*S*(−)-PhEt-sal)$_2$(pyridine)$_2$, 136892-00-7; Ni(*R*(+)-PhEt-sal)$_2$(2-picoline)$_2$, 136981-82-3; Ni(*S*(−)-PhEt-sal)$_2$(2-picoline)$_2$, 136847-37-5; Ni(*R*(+)-PhEt-sal)$_2$((*S*)-(−)-nicotine)$_2$, 136847-38-6; Ni(*S*(−)-PhEt-sal)$_2$((*S*)-(−)-nicotine)$_2$, 136892-01-8.

(22) Bernauer, K.; Monzione, M.; Schürmann, P.; Viette, V. *Helv. Chim. Acta* **1990**, *73*, 346.

(23) Such a study with the complex Ni(PhEt-sal)$_2$ carrying suitable substituents on the phenyl ring is under way.