

## Nickel(II) Complex with a Tridentate ONS-Schiff Base Ligand: X-Ray Structure, VIS and NIR Solution Spectra and Kinetics of Ligand Substitution

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### Abstract

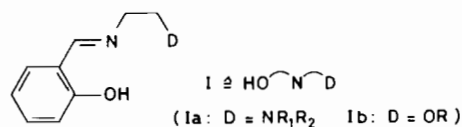
The ligand N-(3-thia-n-pentyl)salicylaldimine (Hsalen-SEt) and its green nickel(II) complex Ni(salen-SEt)<sub>2</sub> was prepared. The complex crystallizes in the orthorhombic space group *Pbca* with  $a = 2538.3(4)$  pm,  $b = 1490.0(3)$  pm,  $c = 1163.5(2)$  pm and  $Z = 8$ . The coordination sphere of the nickel is a distorted octahedron with two oxygen atoms in a *cis*-position, two nitrogen atoms in a *trans*-position and two sulfur atoms in a *cis*-position. The two Ni–O distances were 197.8 and 198.1 pm, the two Ni–N distances 201.8 and 200.6 pm, whereas the two Ni–S distances are 272.0 and 266.3 pm. The magnetic susceptibility of Ni(salen-SEt)<sub>2</sub> was measured in the temperature range 2.6–281 K, the magnetic moment being  $\mu_{\text{eff}} = 3.02 \mu_{\text{B}}$ .

The VIS and NIR solution spectra of the complex in different solvents indicate that the two tridentate ONS-ligands are coordinated as bidentate ON-ligands, the coordination geometry being square-planar (*trans*-N<sub>2</sub>O<sub>2</sub>) in non-coordinating solvents (*e.g.*, toluene) and octahedral in coordinating solvents (*e.g.*, pyridine), due to addition of two solvent molecules. From spectrophotometric titration the individual complex formation constants for the species Ni(salen-SEt)<sub>2</sub>·py ( $K_1$ ) and Ni(salen-SEt)<sub>2</sub>·2py ( $K_2$ ) were found to be  $K_1 = 1.76 \pm 0.40 \text{ M}^{-1}$  and  $K_2 = 145 \pm 34 \text{ M}^{-1}$ . The kinetics of the reaction Ni(salen-SEt)<sub>2</sub> + H<sub>2</sub>salen → Ni(salen) + 2Hsalen-SEt as studied in acetone by stopped-flow spectrophotometry follow the rate law, rate = ( $k_S + k_{H_2\text{salen}} [\text{H}_2\text{salen}]$ ) × [Ni(salen-SEt)<sub>2</sub>] with  $k_S = 0.038 \pm 0.013 \text{ s}^{-1}$  and  $k_{H_2\text{salen}} = 17.2 \pm 0.4 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C. The spectroscopic and kinetic properties of Ni(salen-SEt)<sub>2</sub> are compared with those of bis(N-alkyl-salicylaldiminato)-nickel(II) complexes.

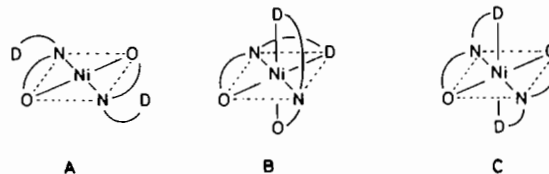
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### Introduction

Tridentate Schiff bases of type I and their nickel(II) complexes have been studied by several groups, one of the interesting aspects being the mode of

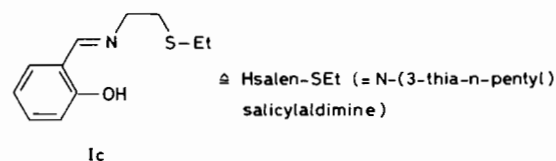


coordination. For D = NR<sub>1</sub>R<sub>2</sub> Sacconi *et al.* [1] reported that depending on the nature of the groups R<sub>1</sub>



and R<sub>2</sub> octahedral nickel(II) complexes (type B, meridional ligand arrangement) or square-planar complexes (type A) are formed. For D = OMe it was found by Holm *et al.* [2] that the potentially tridentate ligand prefers bidentate coordination, thus forming a four-coordinate complex (type A). Type C complexes with facially-coordinated ligands I have not been observed so far.

The present contribution introduces a new ONS-type ligand I with D = SEt and its nickel(II) complex



Ni(salen-SEt)<sub>2</sub>. The results of an X-ray structure determination are presented, as well as spectroscopic

data describing the state of coordination in solution and rate data describing the kinetic behavior of Ni(salen-SEt)<sub>2</sub> towards ligand substitution.

## Experimental

### Synthesis

The complex Ni(salen-SEt)<sub>2</sub> was prepared in the following way.

To a suspension of 1.42 g (0.01 mol) 2-(ethylthio)-ethylamine hydrochloride (EGA-CHEMIE) in 20 ml EtOH was added 2.5 ml 4 M NaOH (0.01 mol) and then under stirring 1.22 g (0.01 mol) salicylaldehyde (Bayer A.G.) dissolved in 10 ml EtOH. Complex formation was achieved by dropwise addition of a solution of 1.45 g (0.005 mol) Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (reagent grade, Merck) in 10 ml H<sub>2</sub>O/EtOH (1:1), and finally, by slow addition of 15 ml EtOH containing 2.5 ml 4 M NaOH (0.01 mol) under stirring. The green reaction mixture was heated on a water bath to approx. 80 °C and 90 ml of hot water were added, whereupon crystallization began. After cooling the precipitate (thin green scales) was filtered off, washed with EtOH/H<sub>2</sub>O (3:7) and dried in a desiccator (yield: approx. 90%). A melting point determination revealed that the green crystals obtained obviously contain coordinated water (from approx. 90 °C on they begin to change colour and appearance, due to loss of water).

The anhydrous complex Ni(salen-SEt)<sub>2</sub> was obtained in the form of green needles by recrystallization of the hydrated green scales from chloroform/petrol ether (40–80 °C) (1:9). M.P.: 134–135 °C. *Anal.* Found: C, 54.87; H, 5.91; N, 5.90; Ni, 12.45%. Calcd. for C<sub>22</sub>H<sub>28</sub>N<sub>2</sub>NiO<sub>2</sub>S<sub>2</sub>: C, 55.55; H, 5.94; N, 5.89; Ni, 12.35%.

### VIS/NIR Spectra

The absorption spectra were taken on a PERKIN-ELMER spectrophotometer (model 554) and on a ZEISS spectrophotometer (model DMR 22).

### Magnetic Measurements

The susceptibility of the complex Ni(salen-SEt)<sub>2</sub> in the temperature range 2.6–281 K was determined with a vibration magnetometer (Institut für Festkörperphysik, Technische Hochschule, Darmstadt) described elsewhere [3], at a field strength of 10 kG.

### X-ray Structure Determination

The crystal of Ni(salen-SEt)<sub>2</sub> selected for the structural analysis was a needle with a cross section of 0.15 × 0.4 mm. Intensities were measured with a four-circle diffractometer (Siemens-Stoe) using graphite-monochromated Mo K<sub>α</sub> radiation (λ = 71.069 pm). Cell constants were determined by least squares from the 2θ angles of about 50 reflections (T = 24 °C), measured on the same instrument.

The measured intensities were corrected for background and Lp effects; a numerical absorption correction was applied.

TABLE I. Summary of Crystal Data for the Complex Ni(salen-SEt)<sub>2</sub>.

formula	C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> NiO <sub>2</sub> S <sub>2</sub>
mol wt.	475.29
<i>a</i> , pm	2538.3(4)
<i>b</i> , pm	1490.0(3)
<i>c</i> , pm	1163.5(2)
space group	orthorhombic, <i>Pbca</i>
<i>Z</i>	8
<i>d</i> <sub>calc.</sub> , gcm <sup>-3</sup>	1.43
refl. coll. (2θ range up to 50)	4012
sym-indep reflexns	3884
reflexns with <i>F</i> > 2σ ( <i>F</i> )	3349
$R_1 = \sum  F_o - F_c  / \sum  F_o $	0.041
$R_2 = \sum w^{1/2}  F_o - F_c  / \sum w^{1/2}  F_o $	0.031
abs. coeff., cm <sup>-1</sup>	10.26

The structure was solved by direct methods and atomic positions and anisotropic temperature factors refined by least squares to the *R* values given in Table I. Final parameter shifts were less than 0.1 standard deviations. Hydrogen atoms were positioned geometrically (C–H distance 96 pm) and not refined. The crystallographic calculations were performed with a program system developed by H. Langhof at Stoe + Cie. (Darmstadt). Table I summarizes relevant crystallographic data and information on data processing. The final positional parameters are given in Table II, the bond distances and bond angles in Table III.

### Kinetic Measurements

The kinetics of ligand substitution in the system Ni(salen-SEt)<sub>2</sub>/H<sub>2</sub>salen (=N,N'-disalicylidene-ethylenediamine) was studied in acetone (reagent grade) at 25 °C with a modified [4] DURRUM D110 stopped-flow spectrophotometer in combination with a transient recorder and desk computer. The kinetic runs were done under pseudo-first-order conditions [*H*<sub>2</sub>salen] ≥ 10[Ni(salen-SEt)<sub>2</sub>] and the reaction was monitored at 550 nm. Reproducible runs were evaluated by fitting a total of 100 data points to an exponential function with a computer program based on the least-squares method.

## Results and Discussion

### Preparation of Ni(salen-SEt)<sub>2</sub>

The preparation of the Schiff base ligand **Ic** and its neutral nickel(II) bis complex follows standard procedures and leads to pure Ni(salen-SEt)<sub>2</sub> in good yield. One interesting finding is that recrystallization from

TABLE II. Final Positional Parameters ( $\times 10^4$ ) (Excluding Hydrogens) for the Complex Ni(salen-SEt)<sub>2</sub>.

Atom	x	y	z
Ni	3453(1)	3931(1)	2857(1)
O1	3963(1)	2941(1)	3069(1)
C1	4390(1)	2956(2)	3676(2)
C2	4781(1)	2298(2)	3480(2)
C3	5237(1)	2263(2)	4108(3)
C4	5332(1)	2876(2)	4987(3)
C5	4968(1)	3524(2)	5199(3)
C6	4498(1)	3597(2)	4557(2)
C7	4165(1)	4357(2)	4786(2)
N1	3765(1)	4607(1)	4198(2)
C8	3488(1)	5425(2)	4539(2)
C9	3431(1)	6038(2)	3509(2)
S1	3011(1)	5555(1)	2403(1)
C10	2373(1)	5822(2)	3016(2)
C11	1941(1)	5684(2)	2158(3)
O2	2846(1)	3576(1)	3824(1)
C12	2375(1)	3459(2)	3424(2)
C13	1936(1)	3605(2)	4147(2)
C14	1430(1)	3504(2)	3774(3)
C15	1323(1)	3216(2)	2650(3)
C16	1734(1)	3050(2)	1931(2)
C17	2262(1)	3186(2)	2266(2)
C18	2664(1)	3050(2)	1408(2)
N2	3143(1)	3301(1)	1491(2)
C19	3506(1)	3131(2)	533(2)
C20	3728(1)	4016(2)	113(2)
S2	4058(1)	4652(1)	1230(1)
C21	4705(1)	4150(2)	1231(3)
C22	5064(1)	4667(2)	2034(3)

EtOH/H<sub>2</sub>O leads to the hydrated complex in the form of thin green scales. The water is obviously rather loosely bound; upon heating to approx. 90 °C the crystals begin to lose water. Recrystallization from chloroform/petrol ether leads to the anhydrous complex in the form of thin green needles, which are readily soluble in organic media, the solutions being slightly different in colour. This 'solvatochromic' behaviour (solution in toluene: yellow to olive green; solution in pyridine: green) is related to the state of coordination of the nickel(II) (see 'Spectroscopic Results').

#### X-ray Structure

The crystal data are summarized in Table I. The crystals are orthorhombic with the space group *Pbca*. The structure could be refined to  $R_2 = 0.031$ .

Figure 2 gives a view of the unit cell of the complex projected along [001], which clearly shows that the complex units are non-associated. The meridional ligand arrangement (complex type B; see 'Introduction') follows from Fig. 2 and in more detail from Fig. 1. The nickel(II) is definitely six-coordinate, the octahedron being formed by two oxygen atoms in a *cis*-position, two nitrogen atoms in a *trans*-

TABLE III. Interatomic Distances (pm) and Bond Angles (deg) for the Coordination Core of the Complex Ni(salen-SEt)<sub>2</sub>.

Distances <sup>a</sup>	
Ni–O(1)	197.8(3)
Ni–N(1)	201.8(3)
Ni–S(1)	272.0(2)
Ni–O(2)	198.1(3)
Ni–N(2)	200.6(3)
Ni–S(2)	266.3(2)
Angles <sup>b</sup>	
O(1)–Ni–N(1)	91.1
O(1)–Ni–S(1)	163.3
O(1)–Ni–O(2)	103.8
O(1)–Ni–N(2)	90.4
O(1)–Ni–S(2)	90.7
S(1)–Ni–O(2)	91.5
S(1)–Ni–N(2)	95.8
S(1)–Ni–S(2)	75.0
N(1)–Ni–S(1)	82.4
N(1)–Ni–O(2)	98.9
N(1)–Ni–N(2)	179.3
N(1)–Ni–S(2)	97.1
O(2)–Ni–N(2)	91.1
O(2)–Ni–S(2)	163.7
N(2)–Ni–S(2)	81.5

<sup>a</sup>The numbering of the atoms follows that shown in Fig. 1.

<sup>b</sup>Error limits  $\pm 0.2$  deg.

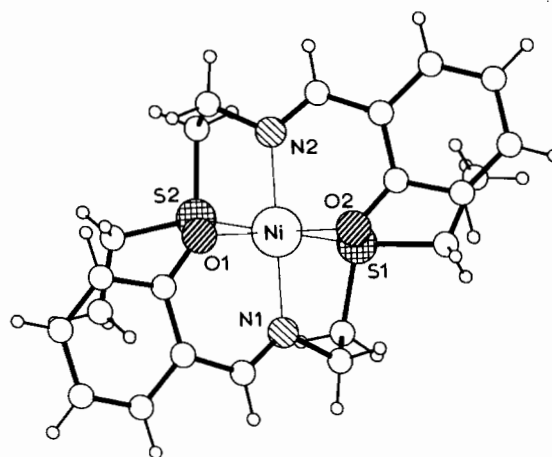


Fig. 1. View of the coordination geometry of the complex Ni(salen-SEt)<sub>2</sub>.

position and two sulfur atoms in a *cis*-position. A closer look at the angles and distances (Table III) reveals, however, that the octahedron is distorted. The N–Ni–N axis is practically linear and the four N–Ni–O angles are very close to 90°, but the O–Ni–O, N–Ni–S, S–Ni–S and O–Ni–S angles

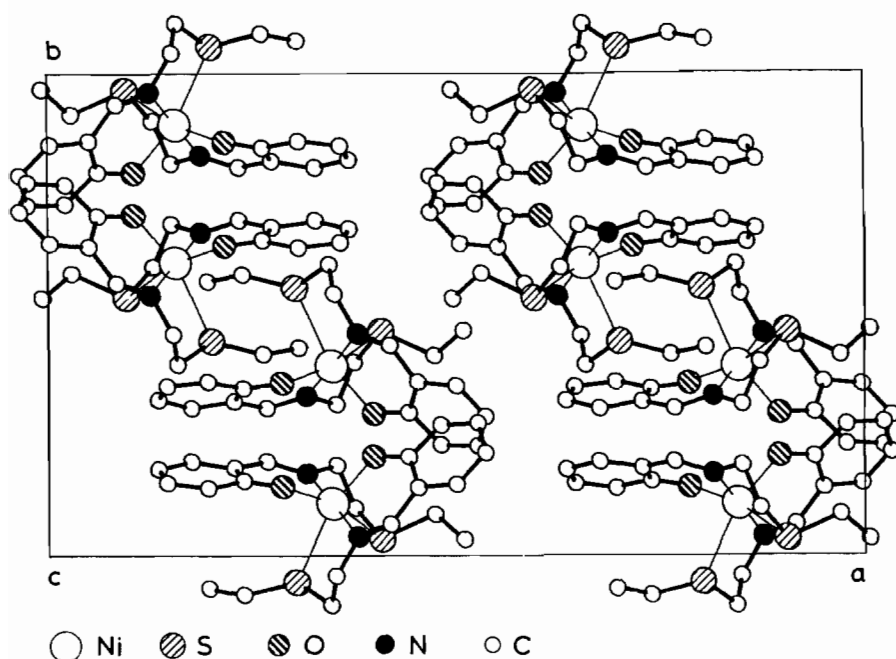


Fig. 2. View of the unit cell of the complex  $\text{Ni}(\text{salen-SEt})_2$  projected along [001].

deviate strongly from  $90^\circ$  and  $180^\circ$ , respectively. The distortion has obviously to do with the very large Ni–S distances of 272 and 266 pm, which contrast the four ‘normal’ Ni–O and Ni–N distances of approx. 200 pm. Considering that a ‘covalent octahedron’ radius of 139 pm can be assigned to nickel(II) [5] and a ‘covalent tetrahedron’ radius of 104 pm to sulfur [5], one would expect a normal Ni–S distance of approx. 240 pm, which is indeed observed for  $\text{NiS}_2$  (Ni–S distance: 242 pm [5]).

The explanation for the unusually large Ni–S distances observed for the complex  $\text{Ni}(\text{salen-SEt})_2$  lies probably in the steric restrictions of the tridentate chelate ligand **1c**. After formation of the six membered  $\overline{\text{O-Ni-N}}$  chelate ring, the ‘bite’ of the fragment  $\overline{\text{N-CH}_2\text{-CH}_2\text{-S}}$  is obviously too small to form a five membered  $\overline{\text{N-Ni-S}}$  chelate ring free of strain. This behaviour is paralleled by unusually large M–N distances in the corresponding copper(II) and palladium(II) complexes of ligand **1a** ( $\text{D} = \text{NEt}_2$ ) [6].

In conclusion, the two ligands **1c** in the complex  $\text{Ni}(\text{salen-SEt})_2$  are coordinated as tridentate ligands in a meridional fashion, forming a distorted octahedron. It follows from the large Ni–S distances that the two Ni–S bonds are rather weak.

#### Magnetic Susceptibility of $\text{Ni}(\text{salen-SEt})_2$

The susceptibility was studied in the temperature range 2.6–281 K. Figure 3 presents the data according to the Curie law. The dependence  $1/\chi = f(T)$  is linear down to approx. 70 K, the slope of the straight line leading to  $\mu_{\text{eff}} = 3.02 \mu_{\text{B}}$ . This value sup-

ports the results of the structure determination in the sense that for an octahedral nickel(II) complex a ‘spin-only’ magnetic moment of  $2.83 \mu_{\text{B}}$  is to be expected. A magnetic moment of  $3.02 \mu_{\text{B}}$  is also in good agreement with the data obtained for the corresponding octahedral nickel(II) complexes with ligands **1a**, which have the group  $\text{D} = \text{NR}_1\text{R}_2$  instead of  $\text{D} = \text{SEt}$ . Depending on  $\text{R}_1$ ,  $\text{R}_2$  and substituents in the aromatic system, magnetic moments of  $2.83\text{--}3.28 \mu_{\text{B}}$  were found [1a].

#### Spectroscopic Results

Table IV summarizes the absorption characteristics of the complex  $\text{Ni}(\text{salen-SEt})_2$  for the visible and near infrared part of the spectrum. It is obvious that the type of solvent plays a major role. In an aprotic, practically non-coordinating solvent such as toluene, a simple spectrum is observed, with a rather strong absorption band at 614 nm and a very weak one at 950 nm. Considering that the X-ray studies indicate very weak Ni–S bonds and that the  $^1\text{H-NMR}$  spectrum of  $\text{Ni}(\text{salen-SEt})_2$  in toluene- $d_8$  does not show any significant paramagnetic shift for the proton signals of the free ligand, the assumption of square-planar  $\text{Ni}(\text{salen-SEt})_2$  in toluene solution (coordination type A, see ‘Introduction’) appears to be justified. The strong absorption at 614 nm probably represents the  $^1\text{A}_{2g} \leftarrow ^1\text{A}_{1g}$  transition ( $\nu_2$ ), the more intense band ( $\nu_3$ ) expected at higher wavenumbers [7] obviously being hidden under strong charge transfer bands extending into the visible range. The spectrum of  $\text{Ni}(\text{salen-SEt})_2$  in toluene is thus very similar (see Table IV) to that of the complex

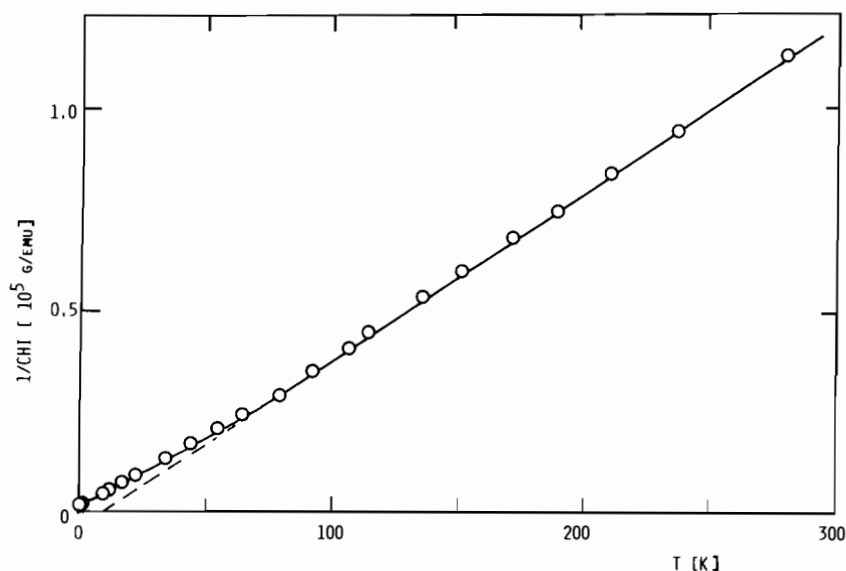


Fig. 3. Temperature dependence of the magnetic susceptibility of Ni(salen-SET)<sub>2</sub> according to the Curie law with a slope yielding  $\mu_{\text{eff}} = 3.02 \mu_{\text{B}}$ .

TABLE IV. Absorption Data for the Complex Ni(salen-SET)<sub>2</sub> in the Wavelength Range 460–1400 nm in Different Solvents.

Solvent	$\lambda_{\text{max}}$ , nm( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )
Toluene	614(72.4); 950(6)
Dimethylformamide	604(51.6); 856(20)
Acetone	604(49.5); 945(18)
Chloroform	603(49.4); 858(22)
Dimethylsulfoxide	594(44.7); 940(33.3)
Ethanol	584(33.4); 854(29.4)
Toluene (2 M py)	575(12.8); 1000(11.8)
Acetone <sup>a</sup>	619(69)

<sup>a</sup>Complex Ni(sal-nPe)<sub>2</sub> instead of Ni(salen-SET)<sub>2</sub>; 800–1400 nm range not studied.

Ni(sal-nPe)<sub>2</sub> (= bis-(*N*-*n*-pentylsalicylaldiminato)-nickel(II)), the square-planar *trans*-N<sub>2</sub>O<sub>2</sub> coordination geometry of which has been proven by spectroscopic and kinetic studies as well [8].

An increase of the donor capacity of the solvent leads to characteristic changes of the solution spectra (see Table IV). Replacement of toluene by dimethylformamide, acetone, chloroform, dimethylsulfoxide, ethanol and pyridine (2 M in toluene) causes a stepwise blue-shift of the  $\nu_2$  band from 614 to 575 nm. Simultaneously, the intensity of this band is reduced from 72.4 to 12.8 M<sup>-1</sup> cm<sup>-1</sup>, whereas the intensity of the weak NIR band is increased. This behaviour is typical for planar four-coordinate nickel(II) complexes being converted to six-coordinate octahedral complexes. Obviously, two molecules of a sufficiently nucleophilic solvent Nu are coordinated according to (1):

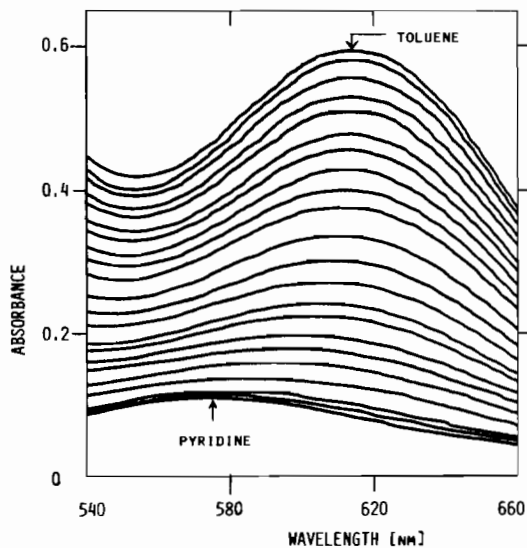
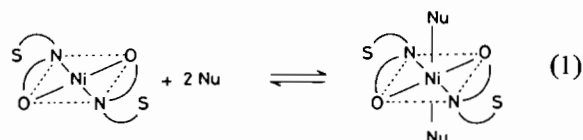
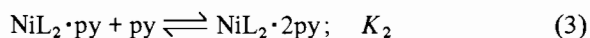


Fig. 4. Spectrophotometric titration of the complex Ni(salen-SET)<sub>2</sub> in toluene with pyridine at 25 °C ([Ni(salen-SET)<sub>2</sub>] =  $4 \times 10^{-3}$  M;  $d = 2$  cm; [py] = 0.01 ÷ 0.4 M).

Figure 4 demonstrates this process in more detail. Stepwise addition of pyridine to a toluene solution of Ni(salen-SET)<sub>2</sub> shifts the  $\nu_2$  band from 614 to 575 nm and reduces its intensity. On the basis of the change in absorbance  $A$  at 614 nm one can calculate the equilibrium constants  $K_1$  and  $K_2$  ( $\text{NiL}_2 \rightleftharpoons \text{Ni(salen-SET)}_2$ )



by fitting the data to eqn. (4) [8]:

$$A = \{A(\text{NiL}_2) + A(\text{NiL}_2 \cdot \text{py})K_1[\text{py}] + A(\text{NiL}_2 \cdot 2\text{py})K_1K_2[\text{py}]^2\} / \{1 + K_1[\text{py}] + K_1K_2[\text{py}]^2\} \quad (4)$$

Least-square fitting of this equation with the five unknown parameters  $K_1$ ,  $K_2$ ,  $A(\text{NiL}_2)$  ( $= \epsilon(\text{NiL}_2)d[\text{NiL}_2]_0$ ),  $A(\text{NiL}_2 \cdot \text{py})$  ( $= \epsilon(\text{NiL}_2 \cdot \text{py})d[\text{NiL}_2]_0$ ) and  $A(\text{NiL}_2 \cdot 2\text{py})$  ( $= \epsilon(\text{NiL}_2 \cdot 2\text{py})d[\text{NiL}_2]_0$ ) was done with a computer program based on the program 'CURFIT' [8]. The result is:

$$K_1 = 1.76 \pm 0.40 \text{ M}^{-1}$$

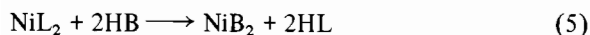
$$K_2 = 145 \pm 34 \text{ M}^{-1}$$

The fact that  $K_2 \gg K_1$  appears to be characteristic for this class of complexes, as shown by the data obtained for the pyridine addition to other bis-(N-alkylsalicylaldiminato)nickel(II) complexes:

alkyl group	$K_1$ ( $\text{M}^{-1}$ )	$K_2$ ( $\text{M}^{-1}$ )	$\beta = K_1K_2$ ( $\text{M}^{-2}$ )	ref.
$-(\text{CH}_2)_2\text{-S-Et}$	1.76	145	255	this work
Et	3.0	52	155	[9]
n-Pr	2.5	61	153	[9]
n-Bu	2.0	77	153	[9]

### Kinetic Studies

It has been shown recently [9] by stopped-flow studies that ligand substitution according to (5) (HL, HB = N-alkyl-salicylaldimines)



takes place as a one-step process and follows rate law (6):

$$\text{rate} = k_{\text{obs.}}[\text{NiL}_2] = (k_S + k_{\text{HB}}[\text{HB}])[\text{NiL}_2] \quad (6)$$

The ligand-independent term  $k_S$  describes a solvent-induced reaction pathway which contributes significantly, especially in the case of protic solvents:

$$k_S(\text{MeOH}) \gg k_S(2\text{-PrOH}) \gg k_S(\text{toluene}) = 0$$

The explanation is that an alcohol molecule can provide a proton to release the first leaving ligand in its neutral form HL [9].

On the basis of these findings, one would expect that for substitution reaction (7) as carried out in acetone ( $\text{H}_2\text{salen} = \text{N,N}'\text{-disalicylidene-ethylenedi-}$

amine) there is no solvent induced reaction channel ( $k_S = 0$ ):

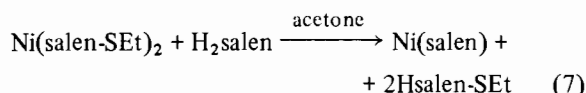


Fig. 5 presents the data obtained for  $k_{\text{obs.}}$  at increasing concentrations of the incoming ligand  $\text{H}_2\text{salen}$ . As a matter of fact,  $k_{\text{obs.}}$  increases linearly with ligand concentration and the ligand-independent contribution (intercept at  $[\text{H}_2\text{salen}] = 0$ ) is very minor, the rate-law being:

$$\begin{aligned} \text{rate} &= k_{\text{obs.}}[\text{Ni}(\text{salen-SEt})_2] \\ &= (k_S + k_{\text{H}_2\text{salen}}[\text{H}_2\text{salen}]) \times [\text{Ni}(\text{salen-SEt})_2] \quad (8) \end{aligned}$$

$$= (0.038 + 17.2[\text{H}_2\text{salen}])[\text{Ni}(\text{salen-SEt})_2] \quad (9)$$

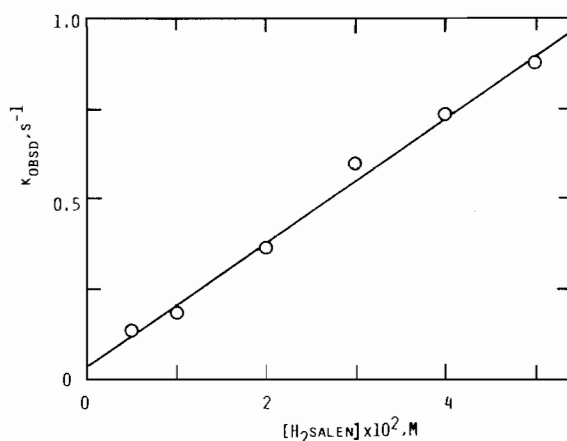
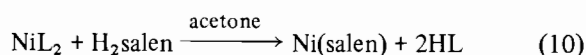


Fig. 5. Plot of the rate constant  $k_{\text{obs.}}$  vs. concentration of the incoming ligand  $\text{H}_2\text{salen} = \text{N,N}'\text{-disalicylidene-ethylenedi-amine}$  ( $[\text{Ni}(\text{salen-SEt})_2] = 5 \times 10^{-4} \text{ M}$ ; solvent: acetone). Least-squares fitting leads to slope =  $17.2 \pm 0.4 \text{ M}^{-1} \text{ s}^{-1}$  and intercept =  $0.038 \pm 0.013 \text{ s}^{-1}$ .

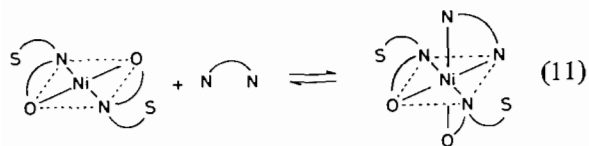
The small contribution  $k_S = 0.038 \text{ s}^{-1}$  is probably due to the presence of protic trace impurities (such as  $\text{H}_2\text{O}$ ) in the aprotic solvent acetone. The main reaction channel, however, is opened by the bimolecular attack of the entering ligand  $\text{H}_2\text{salen}$  at the complex, the breaking of the first Ni-O bond in  $\text{Ni}(\text{salen-SEt})_2$  being the rate-controlling step. It should be pointed out that the kinetic data obtained for reaction (10) (HL = N-n-pentylsalicylaldimine)



are of the same order of magnitude ( $k_S = 0.057 \text{ s}^{-1}$ ;  $k_{\text{H}_2\text{salen}} = 69.2 \text{ M}^{-1} \text{ s}^{-1}$ ). This provides additional support for the interpretation (see 'Spectroscopic Results') that in acetone solution the sulfur atoms of the groups  $-(\text{CH}_2)_2\text{-S-Et}$  are not coordinated.

A final point of interest is the observation that the rate of reaction (7) carried out in the presence of additional 2,2'-bipyridine ( $[\text{bipy}] = 50 [\text{Ni}(\text{salen-SEt})_2]$ ) is reduced considerably ( $k_{\text{obs.}} = 0.035 \text{ s}^{-1}$  instead of  $0.83 \text{ s}^{-1}$  obtained in the absence of bipy). This finding points to an equilibrium such as (11)

( $\text{N} \text{---} \text{N} = \text{bipy}$ ), in which the octahedral adduct is less reactive:



Studies to isolate and further characterize the octahedral adduct are in progress.

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