Kinetics of Ligand Substitution in Bis(*N*-alkylsalicylaldiminato)nickel(II) Complexes: a Search for Kinetically-effective Aromatic Ring Stacking

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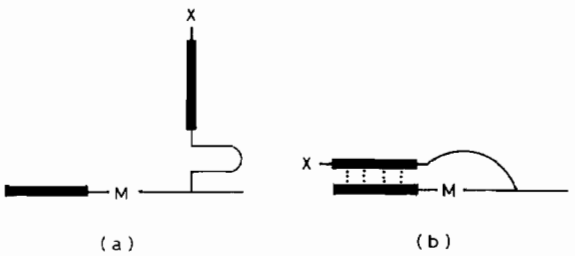
(Received March 28, 1988)

Abstract

The square-planar bis chelate complexes $Ni(R\text{-}sal)_2$ (= bis(*N*-alkyl)salicylaldiminato)nickel(II)) with R = $-(CH_2)_2-Ph$ (**I**; Ph = phenyl), $-(CH_2)_3-Ph$ (**II**), $-(CH_2)_4-Ph$ (**III**) and $-(CH_2)_2-$(4-hydroxyphenyl) (**IV**) were prepared and characterized. Complexes **II** and **III** meet the steric requirements for intramolecular aromatic ring stacking. Stopped-flow spectrophotometry was used to study the kinetics of ligand substitution in complexes **I**–**IV** by H_2salen (= *N,N'*-disalicylidene-ethylenediamine) in acetone. For the substitution of the two bidentate ligands in $Ni(R\text{-}sal)_2$ only one step is kinetically observed which follows a second-order rate law, rate = $k[H_2salen][Ni(R\text{-}sal)_2]$, with k = 43.4 (**I**), 64.0 (**II**), 87.0 (**III**) and 49.5 (**IV**) M^{-1} s^{-1} at 298 K. It is found, therefore, that the size of k does not change significantly upon lengthening of the alkane chain in $Ni(Ph-(CH_2)_n-sal)_2$ from n = 2 to 4 and that there is no kinetic evidence for intramolecular stacking interactions. The equilibrium constants and thermodynamic parameters for the formation of the bis adducts **III**·$(py)_2$ and **III**·$(MeOH)_2$ in acetone are reported.

Introduction

The term 'aromatic ring stacking' refers to the occurrence of intramolecular attractive forces between aromatic ring systems being part of a given molecular species and being oriented in a more or less co-planar fashion. Stacking interactions thus lead to an increase in thermodynamic stability. With respect to planar metal complexes, the following schematic representation describes orientations of ligand moieties without (a) and with (b) stacking interaction (the fat bars characterize aromatic ring systems).



A recent publication by Yamauchi *et al.* [1] gives a good survey on metal complexes, for which such stacking interactions were observed, and also presents a series of ternary palladium(II) complexes with a planar N_4 coordination and with aromatic and aromatic units containing ligands, for which ^1H NMR spectroscopy reveals the existence of intramolecular stacking interactions. The authors prove that substituents X on one of the aromatic ring systems clearly effect the extent of stacking.

Our studies on the dynamic behaviour of planar nickel(II) complexes [2, 3] showed that ligand substitution in square-planar bis(*N*-alkylsalicylaldiminato)nickel(II) complexes $Ni(R\text{-}sal)_2$ as carried out in acetone according to eqn. (1) follows rate law (2) (H_2salen = *N,N'*-disalicylidene-ethylenediamine) [3]

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

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

The mechanism of (1) is associative in the sense that the rate-controlling step is the bimolecular reaction of $Ni(R\text{-}sal)_2$ with H_2salen via the adduct [$Ni(R\text{-}sal)_2$, H_2salen], formed in a fast preequilibrium [3].

The *N*-alkylsalicylaldimines serving as ligands in $Ni(R\text{-}sal)_2$ are aromatic systems. If, therefore, the group R attached to the donor nitrogen carries aromatic moieties (such as in R = benzyl) intramolecular stacking in complexes $Ni(R\text{-}sal)_2$ could, in principle, occur.

For the benzyl complex **V** (n = 1; see Fig. 1) it follows from an inspection of the molecular model

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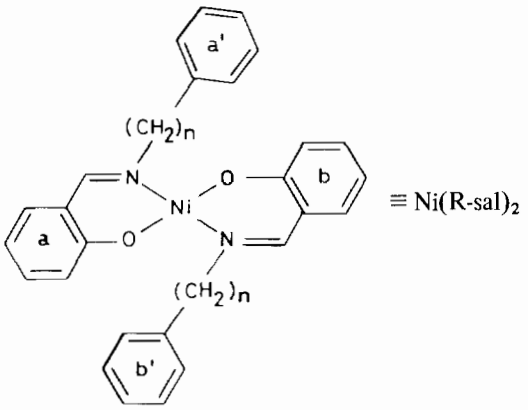

≡ Ni(R-sal)$_2$

Complex	n	X	R
I	2	H	$-(CH_2)_2-Ph$
II	3	H	$-(CH_2)_3-Ph$
III	4	H	$-(CH_2)_4-Ph$
IV	2	OH	$-(CH_2)_2-C_6H_4-OH$
V	1	H	$-CH_2-Ph$

Fig. 1. Structural formula of complexes Ni(R-sal)$_2$ and characterization of complexes **I**–**V**.

that the phenyl group of R cannot get close enough to the aromatic ring of the opposite salicylaldimine ligand, *i.e.* one methylene bridge is not enough to allow intramolecular ring stacking. In the case of $n = 3$ and $n = 4$, however, the bridge $-(CH_2)_n-$ is long enough to admit close coplanar proximity of the aromatic rings for ab′ and a′b interaction, respectively (the meaning of a, a′, b and b′ follows from Fig. 1).

In the present contribution the kinetics of reaction (1) were studied for complexes **I**–**IV** in the solvent acetone at 25 °C (the corresponding data for complex **V** were collected earlier [3]). The study was undertaken as a search for the occurrence of stacking interactions in these complexes and for possible kinetic, *i.e.* rate-reducing effects of such interactions.

Experimental

Synthesis

The ligand H_2salen [3] and the complex Ni(sal)$_2$·2H_2O (= bis(salicylaldehydato)nickel(II) dihydrate) [4] were prepared as described earlier. The amines 2-phenylethylamine, 3-phenylpropylamine, 4-phenylbutylamine and 2-(4-hydroxyphenyl)ethylamine were commercially available (Aldrich). The solvent acetone (Merck) was reagent grade.

The complexes Ni(R-sal)$_2$ were prepared by reacting 1 mmol of Ni(sal)$_2$·2H_2O with 2.5 mmol of the corresponding amine R-NH_2 in 50–80 ml of hot $CHCl_3$ (in the case of complex **IV** a 1:1 mixture of $CHCl_3$/MeOH was used instead of $CHCl_3$). Crystallization was induced by addition of petroleum ether (boiling point 40–80 °C). Twofold recrystallization of the green complexes was carried out in $CHCl_3$ (complex **IV**: $CHCl_3$/MeOH, 1:1). Melting point: (m.p.): 202(**I**), 203(**II**), 144–145(**III**), 231(**IV**) °C.

Anal. Found for **I**: C, 70.92; H, 5.44; N, 5.45. Calc. for **I** = $C_{30}H_{28}N_2NiO_2$: C, 71.03; H, 5.56; N, 5.45%. Found for **II**: C, 71.72; H, 5.95; N, 5.18. Calc. for **II** = $C_{32}H_{32}N_2NiO_2$: C, 71.80; H, 6.03; N, 5.23%. Found for **III**: C, 72.60; H, 6.29; N, 4.95. Calc. for **III** = $C_{34}H_{36}N_2NiO_2$: C, 72.49; H, 6.44; N, 4.97%. Found for **IV**: C, 64.76; H, 5.57; N, 5.05. Calc. for **IV** = $C_{30}H_{28}N_2NiO_4$: C, 66.82; H, 5.23; N, 5.19. Calc. for **IV** = $C_{30}H_{28}N_2NiO_4 \cdot H_2O$: C, 64.66; H, 5.43; N, 5.03%.

UV/Vis Spectra

The spectra were taken on a diode array single beam spectrophotometer (Hewlett-Packard, 8451 A). In the range 350–700 nm the following data for λ_{max}(nm)/ϵ(M^{-1} cm^{-1}) were obtained for acetone solutions: complex **I**, 416/4660 and 620/90; complex **II**, 416/4260 and 616/78; complex **III**, 416/4590 and 620/87; complex **IV**, 416/4840 and 614/70.

The spectrophotometric titration of complex **III** with pyridine (= py) in acetone was carried out at 38, 25, 0, −20 and −40 °C with [**III**] = 1×10^{-4} M and [py] ranging from 1×10^{-4} to 1 M. The addition of increasing amounts of pyridine in up to 24 steps lead to a decrease in the absorption at 416 nm and to an increase at 375 nm. The equilibrium constant β_2 for the formation of the bis adduct **III**·(py)$_2$ according to (3) was obtained by least-squares computer fitting of eqn. (4) [2] to the data for the absorbance A_{380} at different concentrations of pyridine

$$\mathbf{III} + 2\text{py} \rightleftharpoons \mathbf{III}\cdot(\text{py})_2;\ \beta_2 \qquad (3)$$

$$A = (A_0 + A_\infty\beta_2[\text{py}]^2)/(1 + \beta_2[\text{py}]^2) \qquad (4)$$

The addition of the nucleophile methanol to complex **III** in acetone was studied in the same way, with [MeOH] ranging from 1×10^{-4} to 22 M. The results are compiled in Table I.

Kinetic Measurements

Reaction (1) was followed at 465 nm (formation of Ni(salen)) with a modified [5] stopped-flow spectrophotometer at 5 different concentrations of H_2salen under pseudo-first-order conditions ([Ni(R-sal)$_2$] = 0.5×10^{-4} M; [H_2salen] = 10^{-3}–0.1 M). A single exponential function was fitted to the absorbance/time data obtained with a computer program based on the least-squares method, the error of the experimental rate constant k_{obs} being ≤1%. The results are compiled in Table II.

TABLE I. Equilibrium Constants and Thermodynamic Parameters[a] for the Addition of Pyridine to Complexes Ni(R-sal)$_2$ According to Eqn. (3)

Complex	Solvent	β_2 (at 25 °C) (M^{-2})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J K^{-1} mol^{-1})	Reference
III	Acetone	147 ± 11	−53.8[c]	−142[d]	this work
III[b]	Acetone	(6 ± 3) 10^{-3}	−31.8[c]	−22.1[d]	this work
Ni(n-Pr-sal)$_2$[e]	Acetone	27.2 ± 3.5			3
Ni(n-Pr-sal)$_2$[e]	Toluene	146 ± 3			2
Ni(Ph-sal)$_2$[f]	Toluene	975 ± 96			2

[a]$\Delta H°$ was calculated from the slope of the function ln β_2 = f(1/T) and $\Delta S°$ from the relationship $\Delta S° = (\Delta H° + RT \ln \beta_2)T^{-1}$. [b]Data refer to the addition of MeOH instead of pyridine. [c]Error approx. ±10%. [d]Error approx. ±25%. [e]Bis(*N*-n-propyl-salicylaldiminato)nickel(II). [f]Bis(*N*-phenyl-salicylaldiminato)nickel(II).

TABLE II. Rate Constants[a] for Ligand Substitution in Complexes I to V According to Eqn. (1) as Studied in Acetone at 25 °C

Complex	k_{obs} (s^{-1}) at [H_2salen] (M)						k_s (s^{-1})	k (M^{-1} s^{-1})
	0.001	0.01	0.02	0.05	0.08	0.1		
I	0.0554	0.526	1.11	2.76	3.60	4.36	0.18 ± 0.15	43.4 ± 2.7
II	0.0792	0.737	1.52		4.81	6.76	0.08 ± 0.19	64.0 ± 3.3
III	0.0831	0.790	1.79	3.54	6.36	9.15	−0.17 ± 0.33	87.0 ± 5.7
IV	0.0496	0.496	1.00	2.44	4.36	4.7	0.02 ± 0.15	49.5 ± 2.6
V[b]		0.541	1.06	2.52	3.92	4.86	0.061 ± 0.034	48.8 ± 1.5

[a]Calculated by least-squares fitting of the function $k_{obs} = k_s + k$[H_2salen] to the data obtained for k_{obs} at different concentrations of H_2salen. [b]Data taken from ref. 3b; see also ref. 3a.

Results and Discussion

Properties of Complexes Ni(R-sal)$_2$

The preparation of the complexes **I**–**IV** from Ni(sal)$_2$·2H_2O and R-NH_2 is straightforward and leads to crystalline products. The analytical data found for C, H and N are in good agreement with the calculated ones. The only remarkable exception is complex **IV** with substituent X = OH, which, not unexpectedly, picks up one molecule of water per complex unit upon crystallization.

On the basis of the published [6] single-crystal X-ray structure determinations for Ni(Me-sal)$_2$ and Ni(Et-sal)$_2$ one would expect a planar *trans*-N_2O_2 coordination geometry for complexes **I**–**V**, all of which form green crystals. The absorption spectra taken in acetone solution confirm this expectation in the sense that in the range λ = 350–700 nm the spectra are practically identical with a strong charge-transfer band at λ = 416 nm (ϵ = 4.260–4.840 M^{-1} cm^{-1}) and a d–d band at λ = 614–620 nm (ϵ = 70–90 M^{-1} cm^{-1}). Tetrahedral distortion as found for Ni(i-Pr-sal)$_2$ and for Ni(t-Bu-sal)$_2$ [3] produces characteristic changes with absorptions at $\lambda > 700$ nm which are not observed for complexes **I**–**V**.

Further proof of planar N_2O_2 coordination comes from the spectroscopically monitored formation of octahedral bis adducts upon addition of nucleophiles such as pyridine and methanol to acetone solutions of complex **III** (see Table I). As found calorimetrically for other neutral four-coordinate bis chelate complexes of nickel(II) [7, 8], complex **III** forms the adduct **III**·(py)$_2$ in an exothermic reaction ($\Delta H° = -53.8$ kJ mol^{-1}), which is associated with a loss in entropy ($\Delta S° = -142$ J K^{-1} mol^{-1}). The ratio β_2(MeOH)/β_2(py) = 4 × 10^{-5} for complex **III** (see Table I) reflects the much weaker donor capacity of methanol as compared to pyridine. The fact that the addition of pyridine to Ni(n-Pr-sal)$_2$ and to complex **III**, respectively, leads to the ratio β_2(**III**)/β_2(Ni(n-Pr-sal)$_2$) = 5.4 (see Table I) is probably due to the electronic properties of the phenyl group, which exerts its electron-withdrawing influence even through the –$(CH_2)_4$– chain in **III** and thus makes the nickel in **III** a stronger Lewis acid than in Ni(n-Pr-sal)$_2$. This effect is paralleled by the β_2 values found for Ni(n-Pr-sal)$_2$ and Ni(Ph-sal)$_2$ in toluene (see Table I). Alternatively, these findings could be due to stacking interactions between pyridine and the phenyl groups in **III** and Ni(Ph-sal)$_2$, respectively.

Kinetics of Ligand Substitution

As reported earlier [3] the kinetics of ligand substitution in complexes Ni(R-sal)$_2$ by H_2salen as studied in acetone follows rate law [5]. The contribution of the ligand-independent, solvent-initiated k_s term was found to be negligibly small. Fitting of

$$\text{rate} = (k_s + k[H_2\text{salen}])[\text{Ni(R-sal)}_2] \quad (5)$$

eqn. (5) to the data obtained for k_{obs} in the present study leads to rate constants k_s and k as compiled in Table II. As compared to the size of the term $k[H_2$-salen] even at low concentrations of H_2salen the numbers obtained for k_s are indeed very small. Considering, in addition, the scattering of the k_s data and their large errors*, it is therefore adequate to neglect the contribution of the k_s term in (5) and to describe the kinetics of reaction (1) as being governed by the simple rate law (2).

As discussed previously [3] the second-order rate constant k describes the release of the first of the two bidentate ligands in Ni(R-sal)$_2$, the loss of the second one being a fast consecutive step. Since the complexes Ni(R-sal)$_2$ are 16-electron systems and since their Lewis acid properties can be clearly shown by the addition of nucleophiles such as pyridine (see above), it is very plausible to assume that, mechanistically, reaction (1) is initiated by nucleophilic attack of H_2salen at the metal. If so, this mechanism would imply that any shielding of the nickel by stacking interactions of the aromatic ring systems would necessarily lead to a decrease in rate, *i.e.* to smaller numbers for rate constant k.

Considering the steric situation in the complexes studied by looking at their molecular models one comes to the following conclusions: (i) in principle, two types of stacking interactions are possible, namely, the a′b′ type and the a′b (or ab′) type (see Fig. 1); (ii) an interaction of the a′b′ type, however, which is possible for complexes **II** and **III** (n = 3 and 4, respectively), would shield the nickel with its planar coordination on *one* side only, leaving the other side open to nucleophilic attack; (iii) stacking interactions of the a′b and b′a type are sterically possible for complexes **I** (or **IV**), **II** and **III**, the coplanar overlap of the aromatic ring systems decreasing in the order **I** ≪ **II** < **III**; (iv) double intramolecular ring stacking of the a′b and b′a type, occurring on *both* sides of the planar complexes, would shield the nickel very effectively; (v) double stacking of the type described in (iv) could, in principle, also take place on *one* side of the complex only, again leaving the other side open (see (ii)); and (vi) for complex **V** stacking interactions are not conceivable at all.

The numbers obtained for second-order rate constant k at 25 °C (see Table II) do not differ significantly and do not provide convincing experimental evidence for what is expected. Whereas for **I**, **IV** and **V** the data for k agree practically within the limits of error (43.4, 49.5 and 48.8), k obtained for **II** and **III** is somewhat higher (64.0 and 87.0, respectively). The difference between complex **V** (stacking not possible at all) and complex **III** (maximum stacking expected) is so small, however, that it cannot be taken as serious argument. In addition, k(III) is slightly higher than k(V), which contradicts the expectation.

So, there is no experimental evidence for the occurrence of rate-reducing aromatic ring stacking expected for complexes **I** (**IV**), **II** and especially **III** for steric reasons. The overall result is that lengthening of the alkane chain $-(CH_2)_n-$ in complexes Ni(Ph–$(CH_2)_n$–sal)$_2$ does not affect the rate of the associatively controlled ligand substitution according to (1) significantly. Several arguments can be raised to explain this finding. For the a′b (or ab′) type of interaction stacking is expected to occur between a phenolate ring (a or b) and a phenyl ring (a′ or b′). The results obtained by Yamauchi *et al.* [1] clearly show that stacking between an aromatic unit such as 2,2′-bipyridine and benzene-like units decreases in the order phenol > benzene > phenolate. So, the aldimines derived from *o*-hydroxynaphthaldehydes might be a better choice than those derived from salicyladehyde. Another argument could be (see above) that the stacking expected does take place on *one* side of the planar complexes only. Also conceivable is the effect of solvation in the sense that the axial positions of the complexes Ni(R-sal)$_2$ are occupied by solvent molecules, which would create different steric conditions. Finally, the dynamics of stacking could be such that the equilibrium stacked ⇔ unstacked is a fast one, so that nucleophilic attack at the unstacked form is always possible.

*The aprotic solvent acetone is obviously not able to open a solvent-initiated, ligand-independent reaction channel for reaction (1). The very small and not really reproducible k_s values obtained are probably due to protic trace impurities such as residual water or alcohol.

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft and the 'Verband der Chemischen Industrie e.V.' for support. Salicylaldehyde was kindly provided by Bayer AG, Leverkusen.

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