Mechanistic Study of Schiff Base Release from Bis(*N*-phenylsalicylaldiminato)nickel(II) in Acetonitrile†

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The reaction of bis(*N*-phenylsalicylaldiminato)nickel(II) and ammonium or ammonium-like ions has been studied kinetically in acetonitrile solution. The general features of the release of *N*-phenylsalicylaldimine were investigated. Attempts have been made to assign the observed reaction rates to different species existing in solution. The results show that the protonable groups of the Schiff base are involved in an acid–base equilibrium with ammonium ions, in a complex stepwise reaction mechanism. The equilibria also involve stereoisomeric nickel complexes, the free metal ion and the free ligand. The elimination of the first Schiff base shows a rate increase with increasing acidity of the ammonium ions, which can be correlated with their pK_a values. The reaction with $NHEt_3^+$ is approximately three-fold slower than with NH_3Et^+, presumably because of steric hindrance. The formation of diphenyl(*N*-phenylsalicylaldiminato)boron, from the nickel complex and anilinium tetraphenylborate is also briefly discussed.

We have recently reported[1] on the synthetic aspects of the transimination reaction between ammonium or ammonium-like ions and the imino portion of some N-substituted salicylaldiminato-metal complexes, [M(R-sala)$_2$] (M = Ni^{II}, Cu^{II} or Co^{II}). For R = alkyl this reaction takes place rapidly on addition of a slight excess of the ammonium salt to a non-aqueous solution of the complex [equation (1)]. The

$$[M(R\text{-sala})_2] + 2NH_3R'^+ \rightleftharpoons [M(R'\text{-sala})_2] + 2NH_3R^+ \quad (1)$$

mechanistic aspects of this reaction were discussed in the preceding paper.[2] For R = phenyl, the reaction gives the free Schiff base[1] [equation (2)]. The different behaviour of the *N*-phenyl derivative can be ascribed to the destabilizing effect of the substituent, which confers a significant acidity upon both the iminic nitrogen and the phenolic oxygen through mesomeric effects. Although estimated[3,4] in water as solvent, both the pK_{OH} and the pK_{NH} values of *N*-phenylsalicylaldimine are smaller than the corresponding values of *N*-alkyl derivatives.

$$[M(Ph\text{-sala})_2] + 2NH_3R'^+ \rightleftharpoons 2Ph\text{-Hsala} + 2NH_2R' + M^{2+} \quad (2)$$

The interest in the transimination reaction[2] and the lack of literature data regarding the dissociation of Schiff-base complexes promoted the present attempt to ascertain the generality of the reaction mechanism. To the best of our knowledge, this paper represents the first report of an example of this type of reaction in an aprotic solvent.

Experimental

Bis(*N*-phenylsalicylaldiminato)nickel(II)[5] [Ni(Ph-sala)$_2$], bis(*N*-isopropylsalicylaldiminato)nickel(II)[5] [Ni(Pr^i-sala)$_2$], [*N,N'*-*o*-phenylenediaminebis(salicylideneiminato)]nickel(II)[5] [Ni(salphen)], and *N*-phenylsalicylaldimine[4] (Ph-Hsala) were prepared according to the methods described in the literature. Sodium tetraphenylborate and tetra-*n*-butylammonium tetraphenylborate were C. Erba products. The ammonium and ammonium derivative salts were prepared by standard procedures. Special care was devoted to the purification and storage of [NH$_3$Ph]BPh$_4$, which decomposes producing triphenylboron, aniline and benzene. All manipulations of this salt were carried out under dry nitrogen using Schlenk-tube technique. Diphenyl(*N*-phenylsalicylaldiminato)boron[6] was prepared by reaction of BPh$_3$ (Aldrich product; 1.13 g, 4.6 mmol) suspended in anhydrous acetonitrile (80 cm^3) with Ph-Hsala (0.43 g, 2.2 mmol) under a nitrogen atmosphere. The solution was stirred for 24 h at room temperature. The solid obtained was separated by filtration and recrystallized twice from hexane. The same product, identified by elemental analysis, infrared, mass and NMR spectra, was also obtained employing [NH$_3$Ph]BPh$_4$ instead of BPh$_3$ and [Ni(Ph-sala)$_2$] instead of Ph-Hsala. All the reagents were dried at 50 °C under vacuum prior to use. Acetonitrile was carefully purified and dried by standard methods.[7] The procedures for recording the electronic spectra and for kinetic measurements have been described previously,[2] as have the procedures and the experimental conditions used for the pK_a determination.[8] In all cases investigated, the experimental infinity spectra were identical, within experimental errors, to those of the expected products recorded under the same kinetic conditions.

Results and Discussion

The addition of an excess of ammonium salt [HB$^+$X$^-$; NH$_4^+$, NH$_3$(CH$_2$Ph)$^+$, NH$_3$Ph$^+$, NH$_3$Et$^+$ or NHEt$_3^+$; X$^-$ = BPh$_4^-$ or ClO$_4^-$] to a [Ni(Ph-sala)$_2$] solution in acetonitrile produces in a few seconds a drastic variation of the electronic spectrum, which then remains unchanged even some hours after mixing. For example, Fig. 1 shows the UV/VIS spectra of [Ni(Ph-sala)$_2$] alone (*a*) and after reaction with NH$_4^+$ (*d*), NH$_3$Et$^+$ (*c*) and NHEt$_3^+$ (*b*). With NH$_4^+$ the final spectrum appears to be that of a sample of the Schiff base (Ph-Hsala), in the presence of NH$_4^+$X$^-$, at a concentration which is twice that of the initial complex. Moreover, identical spectra to (*b*) and (*c*) were obtained by monitoring the progress of the reaction with a stoichiometric amount of NH$_4^+$. These observations, in agreement with our previous report,[1] suggest that the addition of the ammonium salts results in Schiff base release, complete with NH$_4^+$ and partial in the other cases, establishing an

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† *Supplementary data available* (No. SUP 56858, 5 pp.): derivation of rate equation. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

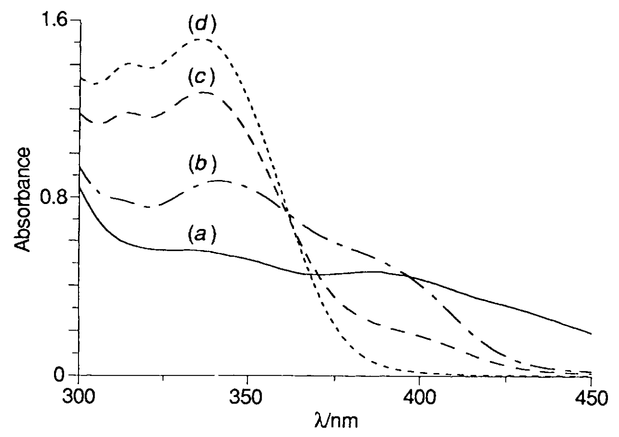


Fig. 1 Absorption spectra of different mixtures of $[Ni(Ph\text{-}sala)_2]$ (6.5×10^{-5} mol dm^{-3}) and $HB^+BPh_4^-$ (0.01 mol dm^{-3}) in acetonitrile at 25 °C: $[Ni(Ph\text{-}sala)_2]$ alone (*a*); $HB^+ = NHEt_3^+$, (*b*); NH_3Et^+, (*c*); NH_4^+ (*d*)

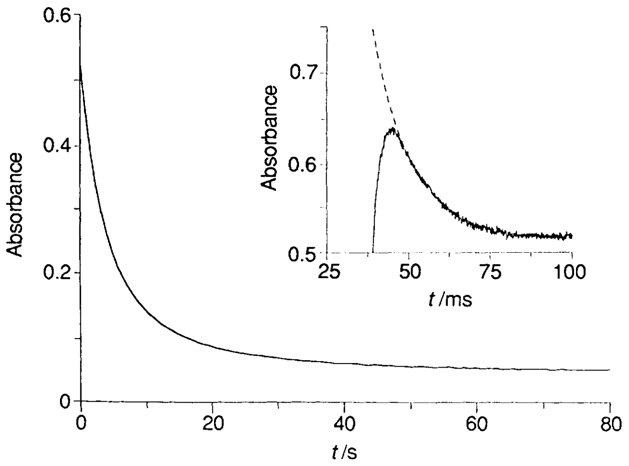


Fig. 2 Stopped-flow record of the reaction of $[Ni(Ph\text{-}sala)_2]$ (1.42×10^{-4} mol dm^{-3}) with NH_4BPh_4 (0.006 mol dm^{-3}) in acetonitrile at 25 °C, $I = 0.03$ mol dm^{-3}, $\lambda = 415$ nm. Over a 100 ms time base (expanded scale) a contribution from a faster phase is apparent. The fit shown (superimposed) has been extrapolated to the experimental absorbance of the nickel complex alone (0.750). The simulated reaction profile of the major phase corresponds to equation (5) and is perfectly superimposable upon the experimental data

$$[Ni(Ph\text{-}sala)_2] + 2HB^+ \rightleftharpoons Ni^{2+} + 2Ph\text{-}Hsala + 2B \qquad (3)$$

equilibrium condition [equation (3)]. The position of the equilibrium seems to depend on the pK_a and on the steric hindrance of the ammonium cation used {see $\varepsilon_{\infty 2} = A_{\infty 2}/[Ni(Ph\text{-}sala)_2]$ values in Table 2}. However, it can be shifted to the left on addition of Ph-Hsala or completely to the right on the addition of NH_4^+.

Reaction (3) appears to be cleanly biphasic as shown in Fig. 2 for $NH_3R' = NH_4$. At 415 nm (Fig. 2) an appropriate expansion of the scale of the initial reaction times clearly shows the existence of two separate processes. The same trend is also found for the other salts, except for anilinium. For the first part of the reaction, pseudo first-order rate plots were obtained showing the reaction to be first order in substrate [equation (4)]. The second, slower variation of the absorbance

$$A_t = A_{\infty 1} + (A_{01} - A_{\infty 1})e^{-k_{obs}t} \qquad (4)$$

appears to be a more complex time function and shows the presence of two kinetically detectable steps according to equation (5); A_t, A_{01}, $A_{\infty 1}$ and $A_{\infty 2}$ in equations (4) and (5)

$$A_t = A_{\infty 2} + a_1e^{-\alpha_1 t} + a_2e^{-\alpha_2 t} \qquad (5)$$

represent the absorbance values at different times, at the start of the reaction, and at 'infinite time' in the first and second parts of the reaction, respectively.

For $NHEt_3^+$, equation (5) describes the overall process with the consequent reduction to only two, instead of three, differentiable reaction steps. Finally, for $[NH_3Ph]ClO_4$, it is possible to measure only one reaction step first order in substrate and zero order in anilinium. The kinetic data for the systems studied are summarized in Tables 1 and 2 and in Fig. 3.

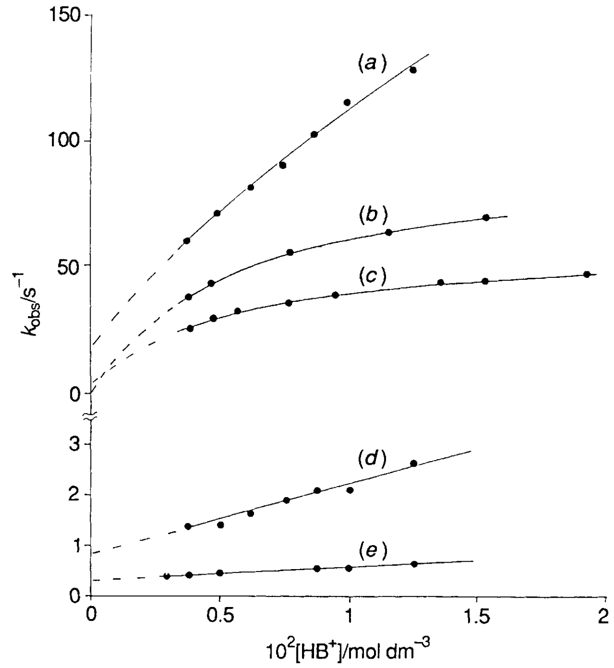


Fig. 3 Observed rate constants for the first phase of the reaction of $[Ni(Ph\text{-}sala)_2]$ with HB^+X^- ($X^- = BPh_4^-$ or ClO_4^-) as a function of cation concentration. $HB^+ = NH_4^+$ (*a*), $NH_3(CH_2Ph)^+$ in the presence of $NH_2(CH_2Ph)$ at constant concentration (0.025 mol dm^{-3}) (*b*), $NH_3(CH_2Ph)^+$ (*c*), NH_3Et^+ (*d*), and $NHEt_3^+$ (*e*). The dotted lines are drawn according to equation (6) and to the computed values in Table 1.

The first mechanistic consideration is drawn from the curves in Fig. 3. While for NH_4^+ and $NH_3(CH_2Ph)^+$ it is possible to identify a non-linear dependence of k_{obs} on their concentration, for the other two ions (NH_3Et^+ and $NHEt_3^+$) the dependence is linear over the concentration range studied. The plots in Fig. 3, with the exception of (*b*) $[NH_3(CH_2Ph)]^+$ in presence of $NH_2(CH_2Ph)$], have non-zero intercepts which are outside the experimental error and which are suggestive of an equilibrium condition in the rate-determining step. On the other hand, the experimental $A_{\infty 1}$ values are independent of ammonium salt concentration in spite of the substantial contribution of the intercepts to the values of k_{obs}. These apparently conflicting facts and the dependence of k_{obs} on [ammonium ion] can be rationalized by admitting the existence of additional fast equilibria. The position of the overall equilibrium essentially lies towards the products in this reaction phase. The values of the kinetic parameters obtained for the systems studied are strongly dependent on the pK_a and, to a certain extent, on the steric hindrance of the cation used.

All the experimental data seem to favour a mechanism which implies: (*a*) the existence of the above-mentioned equilibria; (*b*) the involvement of only one ammonium ion in the rate-determining step, represented by equation (4) (Scheme 1); (*c*) two further parallel equilibria described by equation (5) (Scheme 2).

Table 1 Rate constants for the first phase of the reaction between $[Ni(Ph\text{-}sala)_2]$ and different ammonium salts (HB^+X^-) in acetonitrile at 25 °C.[a]

HB^+ (pK_a)[b]	$10^2[HB^+]$/mol dm^{-3}	k_{obs}[c]/s^{-1}	k_{-2}/s^{-1}	k'[d]/dm^{-3} mol^{-1} s^{-1}	K[d]/dm^3 mol^{-1}
NH_4^+ (16.46)	0.375	59	18 ± 4.5	(1.17 ± 0.16) × 10^4	25 ± 11
	0.50	71			
	0.625	81			
	0.75	89.5			
	0.875	102			
	1.00	115			
	1.25	127.5			
$NH_3(CH_2Ph)^+$[e] (16.76)	0.385	25	2.8 ± 0.8	(9.61 ± 0.11) × 10^3	170 ± 8
	0.48	28			
	0.58	32			
	0.77	34.5			
	0.96	38			
	1.34	43			
	1.53	43			
	1.92	46.5			
	0.385[f]	38	4×10^{-8} $\pm 8 \times 10^{-4}$	(1.67 ± 0.04) × 10^4	174 ± 8
	0.46[f]	43			
	0.77[f]	56			
	1.15[f]	64			
	1.54[f]	70			
NH_3Et^+ (18.40)	0.375	1.38	0.82 ± 0.06	136 ± 10	
	0.50	1.38			
	0.625	1.61			
	0.75	1.86			
	0.875	2.06			
	1.00	2.10			
	1.25	2.58			
$NHEt_3^+$[g] (18.46)	0.30	0.385	0.31 ± 0.01	26 ± 1.5	
	0.375	0.405			
	0.50	0.47			
	0.875	0.55			
	1.00	0.56			
	1.25	0.63			

[a] $[Ni(Ph\text{-}sala)_2] = (0.9\text{–}1.3) \times 10^{-4}$ mol dm^{-3}, X = BPh_4, $I = 0.03$ mol dm^{-3} (NBu_4BPh_4), $\lambda = 415$ nm. Standard errors were calculated by the VARPAR program.[2] [b] Acid dissociation constant of HB^+ in acetonitrile.[9] [c] Mean value of at least three kinetic measurements at a single salt concentration. [d] $k' = k_2K_1K_1 \ldots$; $K = K_1 + K_1K_1 + \ldots$ [see equation (6)]. [e] $X^- = ClO_4$. [f] In the presence of $NH_2(CH_2Ph)$ 0.025 mol dm^{-3}. [g] $\lambda = 380$ nm.

In order to hypothesize on the nature of the equilibria, as in point (*a*), it should be reminded that in previous work[8] we showed that in a solution containing a bi- or tetra-dentate Schiff base–nickel(II) complex, a charge/dipole interaction is established between an added cation and the two Ni ••• O dipoles of the complex. This phenomenon was studied for some systems unable to undergo further chemical reactions. For NH_4^+ or ammonium-like ions the anchoring to the complex is mainly regulated by hydrogen-bond formation, in which the directional properties and the total number of N–H bonds play an important role.[8] Indirect evidence for the equilibria suggested in Scheme 1 (K_1 and K_1) can be obtained by comparing the spectral changes induced by an 'inert' cation such as Na^+ on the UV/VIS spectra of $[Ni(Ph\text{-}sala)_2]$, [Ni(salphen)] and $[Ni(Pr^i\text{-}sala)_2]$ (Fig. 4). These changes are too fast to be measured even on the stopped-flow time-scale. For $[Ni(Ph\text{-}sala)_2]$ remarkable spectral changes are observed, whereas the other two complexes show a weak ipsochromic effect, similar to that induced by polar solvents.[10] In the case of $[Ni(Ph\text{-}sala)_2]$ the different and more intense change in the spectrum indicates a more complex phenomenon which accompanies the charge/dipole interaction. This behaviour can be interpreted by invoking a *trans-cis* isomerization of the complex which assumes a pseudo-tetrahedral configuration, showing both the dipoles Ni ••• O to the Na^+ ion. Conversely, for [Ni(salphen)] and $[Ni(Pr^i\text{-}sala)_2]$ the isomerization induced by Na^+ cannot take place since the former complex exists in a rigid *cis*-planar conformation and the latter is already essentially in a tetrahedral form.[11] By changing the temperature of a $[Ni(Ph\text{-}sala)_2]$ solution, in the absence of Na^+, similar reversible spectral changes are observed in agreement with those ascribed in literature[11] to planar–tetrahedral equilibria. The spectral changes which should appear immediately before the rate-determining step of reaction (3) should be more evident around 380 nm, in agreement with the trends in Fig. 4. At this wavelength a small but measurable difference (≈10%) is observed between the absorbance extrapolated at time zero using equation (4) and that of the complex in the absence of salt.

The unusual instability of $[Ni(Ph\text{-}sala)_2]$, owing to the electronic effects exerted by the phenyl groups bound to the iminic nitrogens, allows the release of the ligand by protonation of phenolic oxygen by the ammonium ion. The base thus produced may occupy an axial position on the nickel complex, giving rise to a five-co-ordinated species **I** whose existence is well documented for d^8 complexes.[12] The ligand protonation and co-ordination of the base B should occur by a concerted mechanism (Scheme 1). The successive transformation of the intermediate **I** into $\mathbf{I_1}$ represents the rate-determining step.

The dependence of k_{obs} upon $[HB^+]$, when HB^+ is NH_4^+ or $NH_3(CH_2Ph)^+$ [curves (*a*)–(*c*) of Fig. 3], is not linear over the range of concentrations studied and, in agreement with Scheme 1, is given by equation (6). For $HB^+ = NHEt_3^+$ and NH_3Et^+,

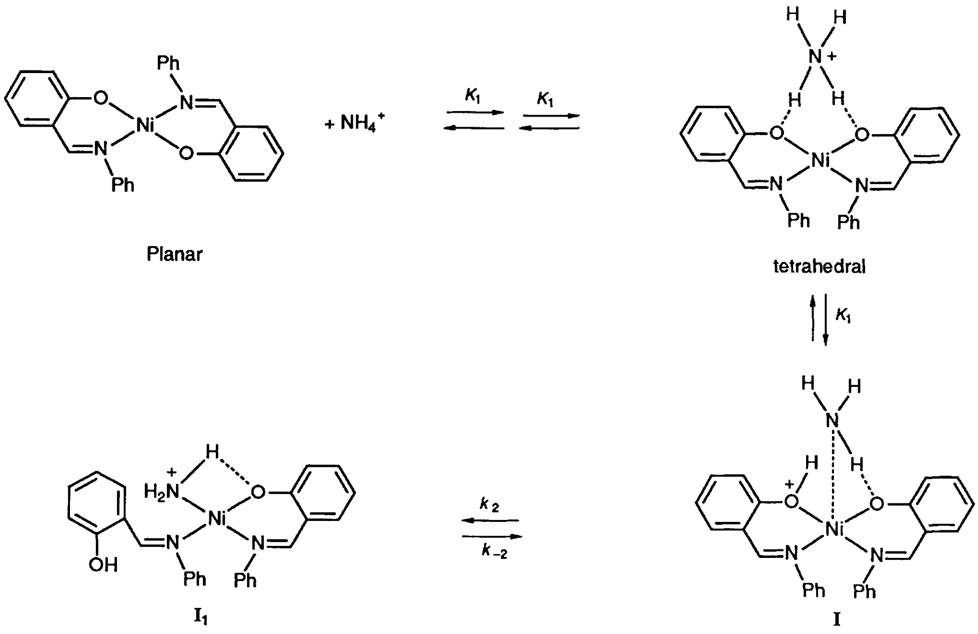
$$k_{obs} = k_{-2} + k_2 \cdot \frac{K_1K_1 \ldots [HB^+]}{1 + (K_1 + K_1K_1 + \ldots)[HB^+]} \qquad (6)$$

this dependence becomes linear [Fig. 3(*d*) and (*e*)] and can be

Table 2 Kinetic data for the second phase of the reaction between $[Ni(Ph\text{-}sala)_2]$ and different ammonium salts (HB^+X^-) in acetonitrile at 25 °C[a]

HB^+	$10^2[HB^+]$/mol dm^{-3}	$10\alpha_1$/s^{-1}	$10\alpha_2$/s^{-1}	$10^3\varepsilon_{\infty 2}$[b]/dm^3 mol^{-1} cm^{-1}
NH_4^+[c]	0.375	1.92	0.37	0.09
	0.62	1.99	0.40	0.05
	0.75	2.14	0.44	0.06
	1.05	2.22	0.51	0.02
	1.50	2.26	0.55	0.00
$NH_3(CH_2Ph)^+$[d]	0.32	0.44	0.13	0.71
	0.38	0.37	0.10	0.49
	0.63	0.42	0.14	0.34
	0.63	0.41	0.14	0.33
	0.95	0.40	0.14	0.22
	1.27	0.43	0.16	0.24
NH_3Et^+[c]	0.375	1.10	0.49	2.52
	0.50	1.22	0.51	2.26
	0.50	1.19	0.51	2.24
	0.625	1.25	0.53	2.22
	0.625	1.38	0.55	2.22
	0.75	1.39	0.56	2.09
	0.875	1.39	0.56	2.00
	1.00	1.35	0.56	1.87
	1.25	1.31	0.56	1.76
$NHEt_3^+$[c]	0.375	—	0.19	3.01
	0.50	—	0.15	3.01
	0.625	—	0.14	2.95
	0.75	—	0.14	2.86
	1.00	—	0.12	2.75
	1.25	—	0.17	2.88
		k_{obs}/s^{-1}		$A_{\infty 2}$
NH_3Ph^+[d,e]	0.42	32.3		0.415
	0.84	31.0		0.496
	1.20	29.8		0.533
	2.40	30.5		0.582
	5.50	31.0		0.834

[a] $[Ni(Ph\text{-}sala)_2]$ = (0.49–1.8) 10^{-4} × mol dm^{-3}, I = 0.03 mol dm^{-3} (NBu_4BPh_4), λ = 415 nm. The relative standard deviation for each fit was $\leqslant 3 \times 10^{-3}$. [b] $\varepsilon_{\infty 2} = A_{\infty 2}/[Ni(Ph\text{-}sala)_2]$. [c] $X^- = BPh_4$. [d] X = ClO_4. [e] Without adding NBu_4BPh_4, λ = 380 nm.

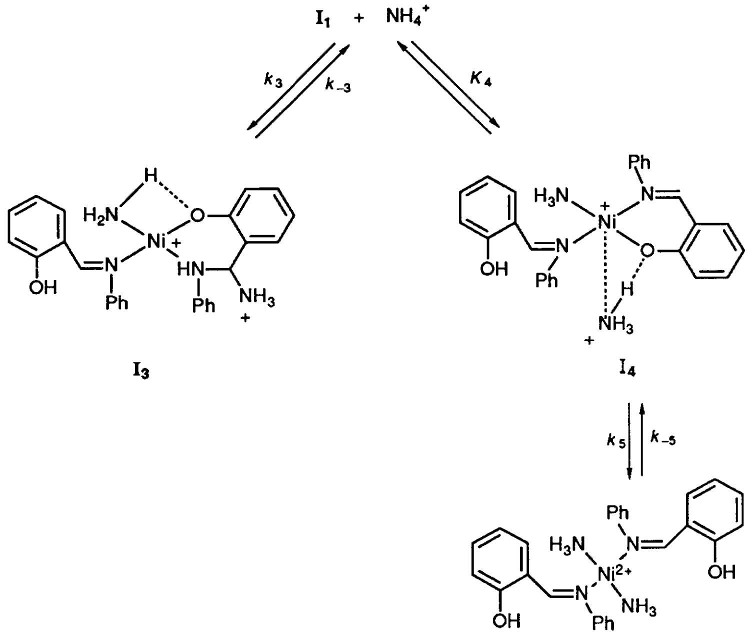


Scheme 1

expressed by equation (7) derived from (6) by assuming (K_1 +

$$k_{obs} = k_{-2} + k_2K_1K_1 \ldots [HB^+] \qquad (7)$$

$K_1K_1 \ldots$)$[HB^+] \ll 1$. The values of k_{-2}, $k = k_2K_1K_1$ and $K = K_1 + K_1K_1$ are reported in Table 1. According to Scheme 1, the k_{-2} values are expected to give indications of the lability of the oxygen–metal bond with respect to the pK_a of the cation. The trend is in accord with our expectations, since k_{-2} decreases with increasing pK_a. When log k_{-2} values (Table 1) for NH_4^+, $NH_3(CH_2Ph)^+$, NH_3Et^+ are plotted *vs.* pK_a an approximately straight line with a slope of −0.7 is observed. The depression



Scheme 2

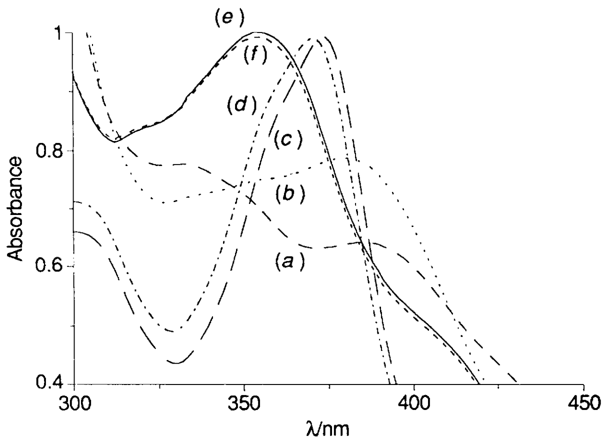


Fig. 4 Absorption spectra in acetonitrile at 25 °C of (*a*) [Ni(Ph-sala)$_2$], (*b*) [Ni(Ph-sala)$_2$] + NaBPh$_4$, (*c*) [Ni(salphen)], (*d*) [Ni(salphen)] + NaBPh$_4$, (*e*) [Ni(Pr^i-sala)$_2$] and (*f*) [Ni(Pr^i-sala)$_2$] + NaBPh$_4$. Salt concentration ≈0.5 mol dm^{-3}, nickel complex concentration ≈10^{-4} mol dm^{-3}

of k_{obs} and k_{-2} found for $NHEt_3^+$ (Fig. 3, Table 1) could be due to a number of concomitant causes: low charge density, remarkable steric hindrance, only one hydrogen atom available to form the hydrogen bond. Finally, for the $NH_3(CH_2Ph)^+$/$NH_2(CH_2Ph)$ system the k_{-2} value is negligible, probably because of the electronic release exerted by benzylamine when it occupies the axial site in the [Ni(Ph-sala)$_2$] complex. This leads to an acceleration of the slow step (k_2) and a corresponding decrease in k_{-2}.*

The second part of the reaction is represented by the kinetic law (5), characterized by the coefficients a_1, a_2, α_1 and α_2. These are complex expressions[14] which depend on the values of the rate constants and on the molar absorbance coefficients of the different species implied in the equilibria. The absorbance recorded at 'infinite time' ($A_{\infty 2}$) appears to depend on the concentration of the reagents and on the pK_a of the cation, while α_1 and α_2 are almost independent of [HB$^+$] (Table 2). In the light of our present knowledge, we believe that Scheme 2 (shown for HB$^+$ = NH_4^+) better expresses the results collected.

According to Schemes 1 and 2, α_1 and α_2 should show a non-linear dependence on [HB$^+$]. In fact, $\alpha_1 = (r + s)/2$ and $\alpha_2 = (r - s)/2$, where r and s are defined in equations (8) and (9) with $K^* = [\mathbf{I}_1]/[\mathbf{S}][HB^+] = K_1K_1'K_1''K_2$ and $K_4 = [\mathbf{I}_4]/[\mathbf{I}_1][HB^+]$ (**S** represents the starting complex). Nevertheless, such a dependence can become insignificant if some of the terms of equations (8) and (9) can be considered negligible. For

$$r = k_{-3} + k_{-5} + (k_3 + k_5K_4) \cdot \frac{K^*[HB^+]^2}{1 + K^*[HB^+] + K^*K_4[HB^+]^2} \quad (8)$$

$$s = \left(r^2 - 4\left\{k_{-3}k_{-5} + (k_3k_{-5} + k_{-3}k_5K_4) \cdot \frac{K^*[HB^+]^2}{1 + K^*[HB^+] + K^*K_4[HB^+]^2}\right\}\right)^{\frac{1}{2}} \quad (9)$$

example, α_1 and α_2 are independent of [HB$^+$] if $1 + K^*[HB^+] \ll K^*K_4[HB^+]^2$, which corresponds to $[\mathbf{S}] + [\mathbf{I}_1] \ll [\mathbf{I}_4]$. This condition is plausible in the second phase of the reaction if the equilibrium between $\mathbf{I}_1$ and $\mathbf{I}_4$ is shifted towards $\mathbf{I}_4$.

The release of the second Schiff base should take place through a reaction path which seems to be a repetition of that discussed above for the loss of the first ligand. The lower rate of this last step can be reasonably interpreted in terms of a more difficult attack by the NH_4^+ on the positively charged species $\mathbf{I}_1$ and would allow the establishment of another equilibrium due to the addition of ammonium to the double iminic bond. The geminal diamine $\mathbf{I}_3$ formed represents the intermediate of the transimination reaction.[2] However, in this case the reaction does not proceed in the direction of substitution of the phenyl group, owing to the high acidity of the >N-Ph nitrogen with respect to the other geminal nitrogen. In the case of $NHEt_3^+$, its addition to the double iminic bond would be scarcely effective because of the steric hindrance, causing the disappearance of one of the two reaction paths (k_3/k_{-3}). In Schemes 1 and 2 the NH_3 and Ph-Hsala molecules are shown to be bound to nickel, but they can belong to the primary solvation shell of the metal with no modification of the kinetic orders found.

The zero-order found for [NH_3Ph]ClO_4 (Table 2) can be

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* In this case the release of Ph-Hsala is followed by a transimination reaction with benzylammonium ion and consequent formation of $PhCH_2$-Hsala.[13]

explained by assuming that the high acidity of this cation (pK_a = 10.56)[9] makes it possible to add two protons to the starting complex in fast steps. Decomposition of the adduct leads to the final product through a single kinetically detectable phase. Taking the dead-time into account, the zero-time absorbance at 380 nm was evaluated to possess a value 30–60% higher than that of the initial complex, depending on the NH_3Ph^+ concentration. Such a high variation, not recorded for the other systems studied, cannot be attributed to the charge/dipole interaction, but to the protonation and breaking of the two Ni–O bonds, followed by rapid and extensive protonation of the free Schiff base (whose pK_a we evaluated to be 8.8).

Finally, we consider noteworthy the unexpected results obtained by using anilinium tetraphenylborate. We observed that, in an acetonitrile solution of $[NH_3Ph]BPh_4$, decomposition takes place to afford BPh_3 and C_6H_6, as reported for aqueous warm solutions of BPh_4^- salts upon treatment with mineral acids.[15] When [Ni(Ph-sala)$_2$] was treated with an excess of $[NH_3Ph]BPh_4$, the first rapid release of the Schiff base was followed by a slower reaction, which in about 1 h led to the formation of a product identified as diphenyl(*N*-phenylsalicylaldiminato)boron. The same product, along with C_6H_6, was also obtained from the reaction of the Schiff base with BPh_3. These results suggest that the conversion of the nickel complex into the organoboron compound probably proceeds *via* BPh_3 generated *in situ*, which then reacts with the released Schiff base. However, the same organoboron derivative was obtained upon treatment of the nickel complex with BPh_3, in spite of the lack of a phenolic proton able to perform the protodeboronation reaction. Thus, the previous suggestion is invalid in this case and further work is needed to clarify the preparative and mechanistic aspects of this reaction.

Acknowledgements

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