Spectrophotometric Study of the Equilibrium between Sodium Tetraphenylborate and Nickel(II) and Cobalt(II) Schiff Base Complexes

AMBROGIO GIACOMELLI,[1a] TADDEO ROTUNNO,[1b] and LUCIO SENATORE*[1c]

A spectrophotometric investigation has been performed to characterize the equilibrium of the different species formed by adding sodium tetraphenylborate (NaBPh$_4$) to solutions of N,N'-ethylenebis(salicylideneaminato)nickel(II) (Ni(salen)) and of [N,N'-o-phenylenediaminebis(salicylideneaminato)]nickel(II) (Ni(salophen)) in tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and acetonitrile (CH$_3$CN) and of Co(salen) and Co(salophen) in THF. The observed changes in the absorption spectra have been interpreted in terms of formation of chelate adducts with cations and ion pairs. The spectrophotometric data have been processed by a nonlinear least-squares computer program, and the stability constants and the electronic spectra of the different species have been calculated. The enthalpy change for the formation of the [Ni(salen)Na]$^+$ adduct in CH$_3$CN was found to be -3.2 kcal/mol and the entropy change -1.8 eu. The behavior of the Na$^+$ ion has been compared with that of K$^+$, Cs$^+$, NH$_4^+$, and N(C$_2$H$_5$)$_4^+$ cations, in CH$_3$CN. The stability of the adducts and the hypsochromic shifts can be correlated with the cationic radius. The studied complexes have shown a selectivity for Na$^+$ ion.

Introduction

Quadridentate Schiff base metal complexes M(SB) with a N$_2$O$_2$ donor atom set are very well-known to coordinate to inorganic and organic cations to give rise to chelate adducts[2] (Chart I). From this point of view they behave like many complexing agents, both natural (such as enzymes and antibiotics)[3] and synthetic (such as cyclic or linear polyethers),[4] but with the advantage of a greater chemical accessibility. Further interest in the chelate adducts is due to the fact that since they have two metal centers with very different acid–base properties, they promote coordination and activation on small molecules.[5,6] Whereas the structure of these adducts has been thoroughly explored in the solid state,[2,5] very little is known of the nature of the different species and their formation equilibria in solution.

The purpose of this paper is to characterize the interaction between NaBPh$_4$ and some Schiff base metal complexes in nonaqueous solvents and to evaluate the formation constants of their adducts. Moreover, we have tried to highlight the different roles and importance of the transition metal (Co(II), Ni(II)), the nature of the Schiff base (salen, salophen), the solvent (DME, THF, CH$_3$CN), and the dimensions of the added cations (Na$^+$, NH$_4^+$, K$^+$, Cs$^+$, N(C$_2$H$_5$)$_4^+$) with regard to the stoichiometry and the selectivity of the complexation reactions.

Experimental Section

Ni(salen), Ni(salophen), Co(salen), and Co(salophen) complexes were prepared according to the methods described in literature[7] and recrystallized from the same solvents in which they were to be studied. NaBPh$_4$ was a C. Erba product and was recrystallized three times from aqueous

Chart I

salophen = SB
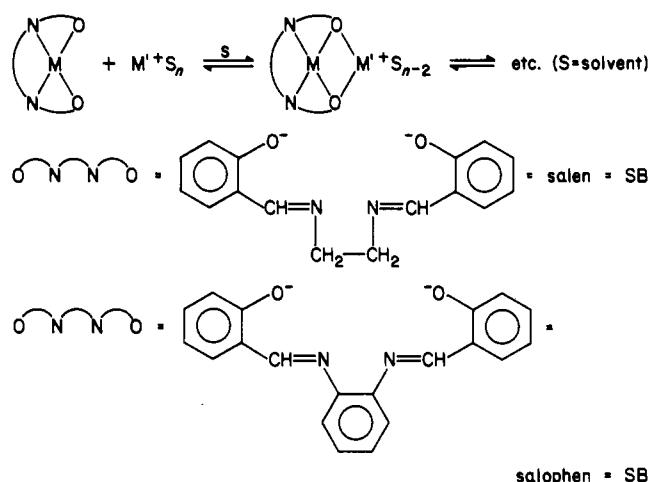
acetone; the other salts, M'(BPh$_4$) (with M' = K$^+$, Cs$^+$, NH$_4^+$, N-(C$_2$H$_5$)$_4^+$), were prepared by precipitation from aqueous solutions of M'Cl with NaBPh$_4$. All the reagents, M(SB), and M'(BPh$_4$) were dried at 50 °C under vacuum; the solvents were carefully purified and dried by standard methods.

The experimental absorbance data were obtained with a C. Erba Spectracomp 601 spectrophotometer equipped with a DP-10 Houston plotter and with a teletype for the punching of the data on paper tape. By means of a remote photoreader, the data were input in an IBM VM/370 system for their numerical treatment. The cell compartment of the spectrophotometer was provided with a Peltier cooler thermostatic system that ensured a constancy of temperature of ±0.1 °C.

Aliquots of M'(BPh$_4$) solution were added to the M(SB) solution by a Metrohom 655 Dosimat buret that was claimed to have a precision of 0.003 mL. The resulting solutions were mixed and then transferred to a 1-cm optical path flow cell. All the operations were accomplished in a closed and nitrogen-saturated circuit. The initial concentrations of the M(SB) solutions, for all the experiments here reported, were arranged near 10^{-4} M to ensure a satisfactory scale of absorbance values. The ionic strength of the solutions was not held constant because of the impossibility to find an electrolyte sufficiently soluble in the solvents used, transparent in the explored range of the wavelengths, and inert to the M(SB) complexes. Therefore, the concentration of M'(BPh$_4$) was maintained as low as possible in the range 10^{-6} to 5 × 10^{-4} M. As a matter of fact, in such conditions, for the electrolytes used and for the ion pairs that originate in solution, the equilibrium constants can be considered independent of the ionic strength.[8,9] Moreover, in this concentration range, the formation of triple ions like (BPh$_4^-$, M'$^+$,BPh$_4^-$) and (M'$^+$,BPh$_4^-$)$_2$ can be excluded.[9]

(1) (a) Istituto di Chimica Analitica, Università di Pisa. (b) Istituto di Chimica Analitica Strumentale del CNR di Pisa. (c) Istituto di Chimica Generale, Università di Pisa.

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Calculations

The program used for the calculations reported in this paper, DALSFEK, was developed by Hartley et al.[10] It uses a dumped nonlinear least-squares iterative method to fit equilibrium constants and molar absorption coefficients to spectrophotometric data. The original program[11] was slightly modified to allow the processing of a larger number of experimental data and running on an IBM VM/370 system. The experimental absorbance data were treated by the program as a rectangular matrix $n \times l$, n being the number of solutions examined and l the number of wavelengths where the absorbances had been acquired. The unknown parameters were computed by minimizing the sum of the squared residuals between observed and calculated absorbance values. The iterative procedure of minimization was accomplished by the Marquardt method[12] (a combination of the steepest descent method and methods based on the Taylor series expansion), which has been proven[10,13] to be very effective in obtaining the optimum parameter corrections on each iteration and a smooth convergence to minimum-variance estimates of parameters.

In the present paper, two quantities, S and R, were used to have some measure of the goodness of fit. S is defined as $\sum_{i=1}^{N}(y_{obsd} - y_{calcd})_i^2$, where y_{obsd} and y_{calcd} are the observed and calculated absorbances of the $N = n \times l$ measurements. R, the Hamilton factor, is defined as $[\sum_{i=1}^{N}W_i(y_{obsd} - y_{calcd})_i^2/\sum_{i=1}^{N}W_i(y_{obsd})_i^2]^{1/2}$, W_i being the appropriate weighting factors of the ith absorbance. R is to be compared with the limiting value $R_{lim} = [\sum_{i=1}^{N}W_i\xi_i^2/\sum_{i=1}^{N}W_i(y_{obsd})_i^2]^{1/2}$, where ξ_i are the residuals of the ith equation calculated from pessimistic estimates of the errors in all the experimental quantities using error propagation rules. A fit was judged to be satisfactory if $R < R_{lim}$. Moreover, the different values of R calculated by different equilibrium models were used to test alternative hypotheses. In fact, if the hypothesis H_0 yielded the value R_0 and the hypothesis H_1 the value R_1, then H_1 could be rejected at α significance level if $R_1/R_0 > R_{(m,N-m,\alpha)}$, where m was the number of unknown parameters and $N - m$ the number of degrees of freedom of the least-squares adjustment. Values of $R_{(m,N-m,\alpha)}$ were found in statistical tables.[14,15]

It often happened that for models with acceptable S and R values the R factor ratio test did not allow a unique choice of the equilibrium model. In this case further considerations were applied:[16] (a) *Simplicity*. The selected model was the simplest possible by excluding poorly defined species, i.e. the species with large standard deviations and with low concentrations (<2%) throughout the examined range of total concentrations. (b) *Similarity*. The model that was in agreement with the previous results of reliable measurements on analogous systems was generally preferred. (c) *Chemical Significance*. The selected model had to fulfil all the requirements (stoichiometry of the species, reasonable reaction pathways, electronic spectra, etc.) that made good chemical sense.

In order to limit the number of hypotheses to be refined with DALSFEK, it was necessary to determine a priori the minimum number of absorbing species. This was accomplished by calculating the rank of the absorbance matrix[17] and by using the approach suggested by Hartley et al.[11] in deciding whether a diagonal element of the matrix was zero.

For each of the studied systems, the unknown parameters were calculated by processing the absorbance data relative to $n = 17$ solutions and referred to $l = 20$ wavelengths.

Results and Discussion

The stoichiometry of the chelate adducts between M(SB) and alkaline cations M'^+ depends in the solid state on the nature of the cation, on the solvent, and on the crystallization conditions.[2] Compounds with M(SB)/M'^+ ratios of 3:1 or 2:1 can be obtained, where M'^+ directly coordinates to the bite O···O of Schiff base. The crystalline structure is composed of discrete BPh_4^- anions and macrocations $[M(SB)]_sM'^+S_p$, where $s = 2$ or 3; S is the solvent, and the alkaline ion is always hexacoordinated. In solution, the spectra recorded by adding $M'(BPh_4)$ to M(SB) complexes varied continuously at increasing concentration of $M'(BPh_4)$ even when

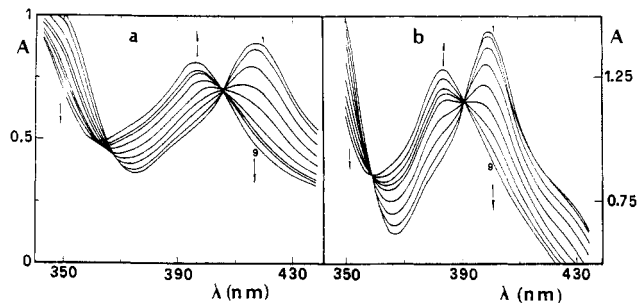(10) Alcock, R. M.; Hartley, F. R., Rogers, D. E. *J. Chem. Soc., Dalton Trans.* **1978**, 115–123.
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Figure 1. Absorption spectra of Ni(salen)/NaBPh$_4$ solutions: (a) in THF solvent, [Ni(salen)] = 1.315×10^{-3} M, [Na$^+$] = 0, 4.953×10^{-5}, 2.017×10^{-4}, 3.792×10^{-4}, 5.927×10^{-4}, 9.251×10^{-4}, 1.465×10^{-3}, 2.373×10^{-3}, 4.250×10^{-3} M, optical path 0.1 cm; (b) in DME solvent, [Ni(salen)] = 2.199×10^{-4} M, [Na$^+$] = 0, 3.561×10^{-5}, 1.592×10^{-4}, 4.019×10^{-3}, 7.878×10^{-4}, 1.331×10^{-3}, 2.032×10^{-3}, 2.893×10^{-3}, 3.987×10^{-3} M, optical path 1 cm.

Scheme I
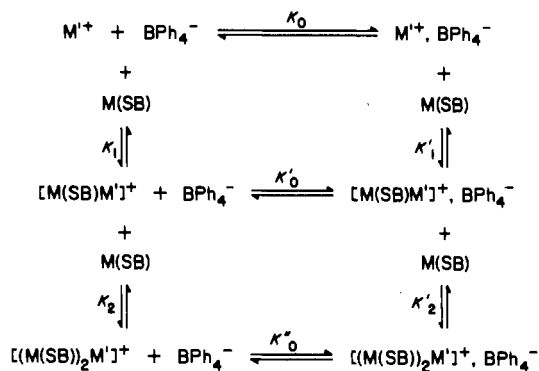
a high value of the $M'(BPh_4)/M(SB)$ ratio (~ 1000) had been reached. The most significant variations of absorbance took place in the near-UV–visible region of the spectrum where M(SB) exhibits a band of maximum absorption that is essentially due to the electronic transitions involving metal–ligand bonds.[18] By addition of $M'(BPh_4)$, this band tended to disappear, and a new one appeared at lower wavelengths. Some examples of spectra for the Ni(salen)/NaBPh$_4$ system in THF and DME are reported in Figure 1. The other systems gave spectra similar to those reported in Figure 1. The spectra in DME and CH$_3$CN showed two sharp isosbestic points, which was a strong indication of the presence of only two absorbing species, while the spectra in THF solution did not show any sharp isosbestic points. It is worth pointing out that the existence of isosbestic points is only indicative of the presence of at least two independent absorbing species.[19] Therefore, for a more correct conclusion on the number of the absorbing species present in solution, the application of complementary techniques was required (see Calculations). On the basis of experimental observations and the behavior of these complexes in the solid state, we have proposed and tested the equilibria given in Scheme I.

The values of formation constants K_0 of NaBPh$_4$ at 20 °C were assumed DME. be 10.580 M^{-1} in THF and 17.820 M^{-1} in DME. In CH$_3$CN, all electrolytes were assumed to be completely dissociated.[8] In this scheme no distinction was made between contact ion pairs and ion pairs separated by the solvent,[20] and for the sake of clarity the solvation molecules were omitted. However, this assumption does not affect the validity of our conclusions.

As an example of the method used to test the different hypotheses and to choose the model that best fulfilled the statistical and chemical criteria, we shall illustrate the system Ni(salen)/Na$^+$ in THF.

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Table I. Application of DALSFEK Program to the Experimental Data for the System Ni(salen)/NaBPh₄ in THF[a]

	(1)	(1,0')	(1,0',2)	(1,0',2,0'')	(1,2)	(1')
K_1	14115 ± 3420	6240 ± 610	7672 ± 7.4 × 10³	22800 ± 2.1 × 10⁴	9773 ± 2.6 × 10³	
K'_0		6478 ± 503	7670 ± 8.1 × 10³	3670 ± 4.3 × 10³		
K_2			480 ± 1.2 × 10⁴	4020 ± 4.2 × 10³	4950 ± 2.7 × 10³	
K''_0				180 ± 3.8 × 10²		
K'_1						22500 ± 1.1 × 10⁴
S	3.514 × 10⁻³	2.191 × 10⁻⁴	1.626 × 10⁻⁴	8.018 × 10⁻⁴	5.611 × 10⁻³	1.226 × 10⁻²
R	1.849 × 10⁻²	1.303 × 10⁻³	1.084 × 10⁻³	4.220 × 10⁻³	1.467 × 10⁻²	3.955 × 10⁻²

[a] Only the models that converged with $R < R_{lim}$ (see text) are reported.

Table II. Stability Constants (M⁻¹) and λmax (nm) for the M(SB)–M'(BPh₄) Complexes

system	solvent	λmax M(SB)	λmax M(SB)M'⁺	λmax M(SB)M'⁺, BPh₄⁻	$10^{-3}K_1$	$10^{-3}K'_0$	$10^{-3}K'_1$
Co(salen)/Na⁺	THF	413	400	396	5.5 ± 0.2	8.4 ± 0.3	4.4 ± 0.5[b]
Co(salophen)/Na⁺	THF	386	375	370	4.5 ± 0.5	6.1 ± 0.7	2.6 ± 0.4[b]
Ni(salophen)/Na⁺	THF	485	465	462	2.4 ± 0.2	2.8 ± 0.2	0.6 ± 0.1[b]
	DME	483		462			0.28 ± 0.03
	CH₃CN	475	465		0.074 ± 0.002		
Ni(salen)/Na⁺	THF	417	396	394	6.2 ± 0.6	6.5 ± 0.5	3.3 ± 0.7[b]
	DME	415		394			0.99 ± 0.01
	CH₃CN	407	396		0.098 ± 0.001[a]		
Ni(salen)/K⁺	CH₃CN	407	405		0.013 ± 0.007		
Ni(salen)/NH₄⁺	CH₃CN	407	404		0.05 ± 0.01		
Ni(salen)/Cs⁺	CH₃CN	407	~406		~0.005		
Ni(salen)/N(C₂H₅)₄⁺	CH₃CN	407	~406		~0.002		

[a] At 5 °C, $K_1 = 131 ± 3$, and at 38.9 °C, $K_1 = 70 ± 2$; $\Delta H = -3.2$ kcal/mol and $\Delta S = -1.8$ eu.　[b] Values calculated as $K'_1 = K_1 K'_0/K_0$.

The experimental spectra of this system, Figure 1a, gave rise to a broad isosbestic point near 406 nm. The absorbance matrix rank analysis suggested the presence of a minimum of three absorbing species. The results of the DALSFEK fittings of different models that gave convergence with $R < R_{lim}$ are reported in Table I. It may be observed that, except for the model (1,0',2,0''), the larger the number of species involved in the model, the lower is the value of S and R, and according to this trend the best model should be (1,0',2). The R factor ratio test allowed us to reject all the other hypotheses, but it was not clear enough for a unique choice between the models (1,0') and (1,0',2). Despite its favorable quantitative conclusions, we rejected the model (1,0',2) because (a) the standard deviations (see Table I) were of the same order if not larger than the relative values of the parameters; (b) the features of the calculated and experimental spectra of Ni(salen) were rather different; and (c) the introduction of the species [(Ni(salen))₂Na]⁺ made the concentration of [Ni(salen)Na]⁺ badly definable, since it was never greater than 0.5% of the total concentration of Ni(salen).

The calculated electronic spectra of the individual absorbing species for the chosen model (1,0') are reported in Figure 2. An analogous procedure was used for all the other systems, and the values of the stability constants and the wavelength of the maximum absorption of the individual species, λmax, for the best selected models are summarized in Table II.

Some comments should be made on the systems Ni(salen)/Na⁺ and Ni(salophen)/Na⁺ in DME for their peculiar behavior. The absorbance matrix rank analysis suggested the presence of at least two absorbing species. The DALSFEK elaboration gave satisfactory convergences with $R < R_{lim}$ only for the models (1) and (1'), and the R factor ratio analysis indicated that the hypothesis (1) could be rejected with respect to (1') at the 99.95% confidence level. Other indications led us to choose (1'). This model, for which $K'_1 = K_1 K'_0/K_0$, implies the predominance, in the explored range of concentrations, of the absorbing species Ni(salen) and [Ni(salen)Na]⁺,BPh₄⁻ in the equilibrium solution, and this agrees to some extent with the weak dissociating properties of the DME solvent. However, we cannot exclude the existence of the species [Ni(salen)Na]⁺ since the equilibrium dissociation constants of NaBPh₄ in THF and DME are not very different. The fitting of the model (1,0') was probably unsuccessful because, with the concentration of [Ni(salen)Na]⁺ too low, the sum of the square
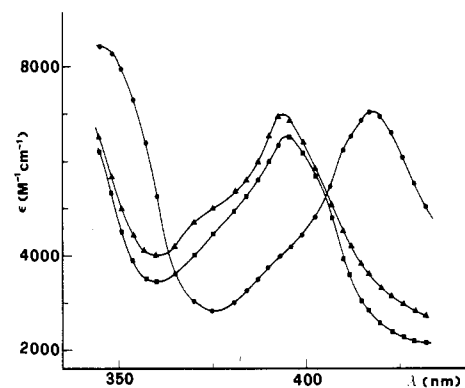

Figure 2. Calculated electronic spectra of Ni(salen)/NaBPh₄ adducts for the (1,0') model; circle, Ni(salen); square, [Ni(salen)Na]⁺; triangle, [Ni(salen)Na]⁺,BPh₄⁻.

of the errors, S, underwent large oscillations instead of steady convergence to a minimum value.

Finally, the K_1 and λmax values of Ni(salen)/Cs⁺ and Ni(salen)/N(C₂H₅)₄⁺ in CH₃CN (Table II) should be considered only rough estimates of those parameters because of the very small changes of absorbance exhibited by these systems upon adding aliquots of M'(BPh₄) solutions. In fact, for values up to 100 of the ratio M'(BPh₄)/M(SB) the maximum change was 0.020 absorbance unit, that is, about 5 times the claimed precision of the used spectrophotometer, and the quality of these data did not allow the program DALSFEK to obtain reliable convergences.

Electronic Spectra. The UV–visible spectra of Ni(salen), Ni(salophen), Co(salen), and Co(salophen), together with their magnetic moments measurements, show that in these complexes, and in the examined solvents, the N and O atoms of the ligand are coplanar with the metal center.[7,18,21] The λmax of these complexes are reported in Table II. By increasing the polarity of the solvent, the absorption maxima undergo hypsochromic shifts with a decrease of the intensity of the absorption bands. This trend agrees with the values of λmax measured in the solvents CHCl₃

(21) Hobday, M. D.; Smith, T. D. *Coord. Chem. Rev.* **1972–1973**, *9*, 311–337.

and CH_3OH^{18} and supports the view that the central metal, M, depending on its nature, i.e. Co(II) vs. Ni(II), may to some extent be coordinated by solvent molecules, which modify the electronic transitions. The added Na^+ gives rise to an analogous effect on λ_{max}, as a consequence of the coordination to the oxygens of Schiff base. The absorption bands of $[M(SB)Na)]^+$ are lower in intensity (see Figure 2) and shifted toward lower wavelengths (Table II) than those of M(SB). The intensity of the absorption bands of $[M(SB)Na]^+,BPh_4^-$ increases as a consequence of the reduced electrostatic effect of Na^+ on the complex. Finally, the hypsochromic effect appears to depend also on the dimension of the cation of the electrolyte $M'(BPh_4)$, as it decreases at increasing ionic radius: i.e., $Na^+ > K^+ > Cs^+ \simeq N(C_2H_5)_4^+$ (for NH_4^+ see below). This effect is mainly due to the greater destabilization of the ground state, compared to that of the excited state, when the cation interacts with the complex. This perturbation depends on the electrostatic interaction energy, and therefore its magnitude is approximately proportional to the reciprocal of the cation radius.[20] The increase of energy of the electrostatic transitions due to Na^+ was estimated to be 2 kcal/mol. The sequence of the hypsochromic shifts of Table II suggests an "intimate" interaction between Ni(salen) and M'^+ without interposition of the molecules of the solvent. This hypothesis is supported by the electronic spectra of $[M(SB)Na]^+$ and $[M(SB)Na]^+,BPh_4^-$ in the examined solvents where λ_{max} appears to be independent of the nature of the solvent, despite the large dielectric constant difference.

Stability Constants. A correlation between the nature of the central transition metal and the stability of the chelate adducts is not deducible by comparing the equilibrium constants; rather, the influence of the nature of Schiff base appears. In fact the adducts of M(salen) are more stable than those of M(salophen). This depends on the higher geometrical flexibility of salen compared to that of salophen. Because of this characteristic, salen adapts better to the cationic species. More influential seems to be the natue of the solvent, but it is hard to correlate this effect with the many parameters that are generally utilized to characterize the solvent. In Table II, one can observe that the solvent is able to stabilize or destabilize the adducts. Thus, the DME solvent inhibits the formation of the intermediate ionic species $[M(SB)Na]^+$, and CH_3CN inhibits the formation of the associated species $[M(SB)Na]^+,BPh_4^-$ to such an extent that it is impossible, in the experimental conditions used here, to evaluate the relative formation constants. The hypsochromic shifts on M(SB), due to the solvent, mainly depend on the coordination of the solvent on the central transition metal. The changes of λ_{max} in the three solvents THF, DME, and CH_3CN allow a quantitative estimate, about 2 kcal/mol, of the energy changes related to this effect, which is of the same order of magnitude as the energy changes relative to the interactions between M(SB) and Na^+. In this respect, M(SB) can be considered as solvent molecules that compete with DME or THF or CH_3CN molecules in solvating Na^+. Small differences of these energies related to different properties of the solvent are likely to produce very significant "relative" changes and may strongly affect these competition equilibria. For instance, the values of K and K'_1 clearly decrease

when changing THF with CH_3CN or DME, respectively. The trend of the K'_1 values in Table II outlines the chelating nature of the DME solvent, owing to the presence of the two oxygen atoms giving rise to a greater entropic effect. In fact, the replacement of one molecule of DME "chelated" to Na^+ with one molecule of M(SB) requires more energy than that involved in the analogous replacement of two THF molecules.

The thermodynamic parameters for the Ni(salen)/Na^+ system in the CH_3CN solvent are reported in the footnotes of Table II. CH_3CN was chosen as solvent for the simplicity of the system. The endothermic effect of the desolvation of Na^+ is well compensated by the exothermic effect due to the coordination of the Ni(salen) bidentate ligand. The chelating effect of M(SB) seems to be responsible for the negative value of ΔS and to compensate the increase of entropy due to the release of two CH_3CN molecules. The ΔH is comparable with those values calculated for similar processes of Na^+ solvation.[22]

Under the same conditions (solvent, M(SB) complexes, charge of the cation) we can try to evaluate the selectivity of the O⋯O bite of Schiff base vs. the dimension of cation M'^+. The data reported in Table II clearly show the preference of Ni(salen) in the chelation of Na^+. Stability and selectivity depend, among others, on the balance of electrostatic and steric factors, both conditioned by the O⋯O bite of the chelating ligand. The behavior of the NH_4^+ ion seems anomalous since the $[Ni(salen)NH_4]^+$ adduct is more stable than $[Ni(salen)K]^+$, despite the larger dimension of NH_4^+. Also, directional effects due to the presence of hydrogen bonds are likely to play an important role. This was clearly shown in the adduct formation between Ni(salen) and guanidinium cation to form $\{[Ni(salen)]_3[C(NH_2)_3]\}^+$.[2b] The results outlined above for NH_4^+ and guanidinium cations suggest further investigation of this relevant type of complexation by using Schiff base complexes as ligands for amino acids.

Finally, a comparison between the results here reported and those found in literature for the cyclic and linear polyethers[4] is interesting. The cyclic polyethers, or crown ethers, are very strong binding complexing agents with values of the stability constants greater than 10^7 M^{-1} and whose selectivity basically depends on the diameter of the cation and the hole of the macrocycle. The linear polyethers, which are referred to as glymes, have smaller stability constant values ranging from 1.2 M^{-1} for the system glyme-3/Na^+ up to 800 M^{-1} for glyme-7/Na^+ in THF. Therefore, the complexes investigated here take a place between these two classes of cation carriers.

(22) Burgess, J. "Metal Ions in Solution"; Wiley: New York, 1978; Chapter 7.