iented nematic glasses were obtained according to the method described by Fackler et al.[28] Samples were heated to obtain the isotropic phase and oriented in a magnetic field of 8000 G during the cooling to the nematic phase temperature range. In the next step the temperature was lowered to 77 K. Samples were rotated with respect to the perpendicular to the magnetic field axis to obtain an angular dependence of line intensities. The concentration of the samples used was 0.2 mg/cm³.

Samples were deoxygenated directly in the ESR tube by bubbling with N₂ through Teflon tubing immersed in the sample and sealed with a septum cap. Solutions used for titration were deoxygenated as described by the syringe technique. Gastight syringes were used for titration. Positive pressure of N₂ was kept during addition of reagents. Toluene saturated with sulfur dioxide was used for titration to determine the stiochiometry of the adduct. Nitrogenous bases were added in toluene solutions.

Electrochemical measurements were performed in tetrahydrofurn with tetra-*n*-butylammonium perchlorate (TBAP) as a supporting electrolyte.

Cyclic voltammograms were recorded for the potential scan rate (*v*) ranging from 0.02 to 0.5 V s⁻¹ by using apparatus described previously.[10] The Pt-disk working electrode, Pt-foil axiliary electrode, and SCE (NaCl ‖ 0.1 M TBAP/solvent) reference electrodes were applied. The system was thermostated at 298 K, and the inert-gas atmosphere (Ar, N₂) was kept during the experiments. A Jeol-PS-100 NMR spectrometer was used for magnetic susceptibility measurements by the Evans technique[51] with C₆D₆ solution, with the peak of tetramethylsilane used as a standard. Diamagnetic correction was obtained by using the published values for the constitutive corrections for TPPH₂[52] and Pascal's constants.

(51) Evans, D. F.; James, T. A. *J. Chem. Soc., Dalton Trans.* 1979, 723.
(52) Eaton, S. S.; Eaton, G. K. *Inorg. Chem.* 1980, *19*, 1095.

Contribution from the Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56100 Pisa, Italy, and Istituto di Chimica Analitica Strumentale del CNR, 56100 Pisa, Italy

Spectrophotometric Study of the Equilibria between Nickel(II) Schiff Base Complexes and Ammonium-like Cations or Sodium Tetraphenylborate[1]

Ambrogio Giacomelli,[†] Taddeo Rotunno,[‡] Lucio Senatore,*,[†] and Roberta Settambolo[§]

Received November 14, 1988

The formation constants of the chelate adducts originated from the interactions between [*N,N'*-ethylenebis(salicylideneaminato)]nickel(II) (Ni(salen)) and a series of ammonium-like cations and between bis(*N*-alkylsalicylaldiminato)nickel(II) (Ni(SB–R)₂; R = methyl, ethyl, isopropyl) and the sodium cation in acetonitrile were determined and compared. The general order of increasing stability of these adducts was correlated for the quadridentate Schiff base with the ability of the cations to form pairs of hydrogen bonding, while for the bidentate Schiff base it resulted dependent on the steric hindrance of the alkyl group. Two nonlinear least-squares programs were tested to determine the number of species in the solution and to estimate the stability constants.

Introduction

Quadridentate Schiff base metal complexes (M(SB)) with an N₂O₂ set of donor atoms can act as bidentate chelating ligands for inorganic and organic cations M'⁺ to generate polynuclear systems.[2] This can be exemplified by Scheme 1, where O⌒N⌒N⌒O = salen and S = solvent.

We were attracted by the use of these "inorganic ligands" for complexing various cationic species,[2] by the change of the reactivity of the transition metal as a consequence of such complexation,[3] by the reactivity of the resulting polymetallic systems,[4] and by the use of cationic organic species as complex carriers in organic solvents. For this purpose we have recently started a study[5] of the equilibria between M(SB) and M'⁺ in different organic solvents. The stability and selectivity for cations acting like positively charged spheres were found to depend on the nature of the solvent and of the M(SB) complexes, on the charge of the cation, and on the balance of the electrostatic and steric factors, both conditioned by the O- - -O bite of the chelating ligand. The behavior of the NH₄⁺ ion seems anomalous, and it is reasonable to assume that the anchoring of NH₄⁺ to M(salen) is mainly regulated by the hydrogen-bond formation, in which the directional properties play an important role. This assumption is indirectly supported by the structural study of similar adducts in the solid state,[6,7] but nothing is known in solution. The aim of this paper is to evaluate the role of hydrogen bonding in the formation of these adducts and the different sequestering abilities of the quadridentate and bidentate Schiff bases. These chelate adducts with ammonium-like cations help to understand the biological processes involving organic molecules with the ⋝NH⁺ functional group when hydrogen bonding plays an important role.

Scheme I
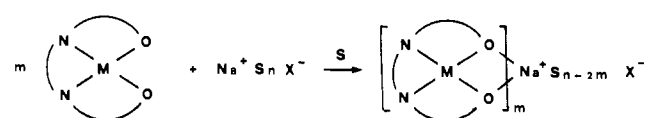
Experimental Section

Ni(salen) and Ni(SB–R)₂ (R = methyl, ethyl, isopropyl) complexes were prepared and purified according to the methods described in liter-

(1) Presented in part at the divisional meeting of the Italian Chemical Society, Camerino, Italy, June 1988.
(2) Gruber, S. J.; Harris, C. H.; Sinn, E. *J. Inorg. Nucl. Chem.* 1968, *30*, 1805. Floriani, C.; Puppis, M.; Calderazzo, F. *J. Organomet. Chem.* 1968, *12*, 209. Sinn, E.; Harris, C. M. *Coord. Chem. Rev.* 1969, *4*, 391. Hobday, M. D.; Smith, T. D. *Ibid.* 1972, 311. Floriani, C.; Calderazzo, F.; Randaccio, L. *J. Chem. Soc., Chem. Commun.* 1973, 384. Bresciani-Pahor, N.; Calligaris, M.; Delise, P.; Nardin, G.; Randaccio, L.; Zotti, E.; Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* 1976, 2310 and reference cited therein. O'Connor, J.; Fryberg, D. P.; Sinn, E. *Inorg. Chem.* 1979, *18*, 1077. Leslie, K. A.; Drago, R. S.; Stucky, G. D.; Kitko, D. J.; Breese, J. A. *Ibid.* 1979, *18*, 1885. Gambarotta, S.; Corazza, F.; Floriani, C.; Zehnder, M. *Ibid.* 1984, 1305. Arena, F.; Floriani, C.; Zanazzi, P. F. *Ibid.* 1987, 183.
(3) Gambarotta, S.; Fiallo, M. L.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* 1982, 503. Floriani, C.; Fiallo, M. L.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* 1987, 1367.
(4) Kurtz, D. N.; Shriver, D. F.; Klotz, I. M. *Coord. Chem. Rev.* 1977, *24*, 145. Ibers, J. A.; Holm, R. H. *Science* 1980, 209. Holm, R. H. *Chem. Soc. Rev.* 1981, *10*, 455. Garner, C. D.; Harrison, P. M. *Chem. Ber.* 1982, 173. Thomson, A. J.; Thorneley, R. N. F. *Ibid.* 1982, 176. Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* 1982, *104*, 5082. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* 1982, 756; *Inorg. Chem.* 1983, *22*, 3966.
(5) Giacomelli, A.; Rotunno, T.; Senatore, L. *Inorg. Chem.* 1985, *24*, 1303.
(6) Giacomelli, A.; Floriani, C.; Perego, G. *J. Chem. Soc., Chem. Commun.* 1982, 650.
(7) Yamada, S. *Coord. Chem. Rev.* 1966, *1*, 415. Sacconi, L.; Paoletti, P.; Del Re, G. *J. Am. Chem. Soc.* 1957, *79*, 4062.

†Università di Pisa.
‡Present address: Dipartimento di Chimica, Università di Bari, Bari, Italy.
§Present address: Istituto di Chimica Quantistica ed Energetica Molecolare del CNR, Pisa, Italy.

Table I. Stability Constants (M^{-1}) for Systems Ni(salen)/Ammonium (or Ammonium-like) Cations and Ni(SB–R)$_2$/Na$^+$ in CH$_3$CN Calculated by CFTSP and DALSFEK Programs

system	CFTSP[a]		DALSFEK[a]		n	f	K_1/f
	K_1	K_2	K_1	K_2			
Ni(salen)/NH$_4$$^{+}$[b]	48.6 ± 4.2		50 ± 10		4	6	8
	53.1 ± 7.4	13.9 ± 15.1	58 ± 90	40 ± 53			
Ni(salen)/EtNH$_3$$^+$	20.5 ± 1.2		20.1 ± 2.9		3	3	7
	23.6 ± 3.6	7.6 ± 7.9					
Ni(salen)/Et$_2$NH$_2$$^+$	6.4 ± 1.4		6.3 ± 3.1		2	1	6
	6.7 ± 2.2	0.88 ± 3.6					
Ni(salen)/Et$_3$NH$^+$	1.1 ± 0.2		1.3 ± 1.5		1	0	
Ni(salen)/n-C$_7$H$_{15}$NH$_3$$^+$	25.5 ± 1.5		23.2 ± 2.1		3	3	8
Ni(salen)/C(NH$_2$)$_3$$^+$	22.8 ± 2.1		20.0 ± 8.1		6	3	8
			19.9 ± 17.8	99 ± 103			
Ni(salen)/NH$_3$$^+$–NH$_3$$^+$	112 ± 13.1		103.0 ± 3.9		6	15	7
	107 ± 21.4	639 ± 311					
Ni(salen)/H$_3$N$^+$(CH$_2$)$_8$NH$_3$$^+$	28.1 ± 3.4		27.6 ± 0.7		6	6	5
	35.1 ± 7.6	1.1 ± 1.2					
Ni(BS–Me)$_2$/Na^{+}[c]	15.1 ± 2.8		15.8 ± 3.1				
Ni(BS–Et)$_2$/Na$^+$	13.2 ± 2.7		14.0 ± 3.2				
Ni(BS–iPr)$_2$/Na$^+$	4.5 ± 1.5		4.2 ± 2.1				

[a] Only the models that converged with SD ⩽ 2s or $R_H < R_{lim}$ (see text) are reported. [b] K_1 for the system Ni(salen)/Et$_4$N$^+$ < 1. [c] K_1 for the system Ni(salen)/Na$^+$ = 98 ± 1 and for the system Ni(salen)/K$^+$ = 13 ± 7.[5]

ature.[8] Melting point and elemental analysis confirmed the purity of each salt. Sodium tetraphenylborate (NaBPh$_4$) was a Carlo Erba product recrystallized three times from aqueous acetone; the other salts M'BPh$_4$ (M' = NH$_4$$^+$, Et$_4N^+$, Et$_3NH^+$, Et$_2NH_2$$^+$, EtNH$_3$$^+$, n-C$_7H_{15}NH_3$$^+$, C(NH$_2$)$_3$$^+$, N$_2H_6$$^{2+}$, H$_3$N(CH$_2$)$_8NH_3$$^{2+}$) were prepared by precipitation from aqueous solutions of the corresponding chloride with NaBPh$_4$. All the Schiff base complexes and tetraphenylborate salts were dried at 50 °C under vacuum. The acetonitrile solvent was carefully purified and dried by standard methods.

The experimental absorbance data were obtained by using a Perkin-Elmer Lambda-15 spectrophotometer connected to a Gould 32/87 computer for numerical treatment. The reaction vessel and the cell compartment of the spectrophotometer were thermostated at 25 ± 0.1 °C. The procedures and experimental conditions used are those reported in a previous paper.[5]

Calculations

For the computation of the equilibrium parameters of the chemical systems investigated in this paper, we used the two nonlinear regression computer programs DALSFEK[9] and CFTSP.[10] These programs allow computation of the stability constants (K_i) and molar absorptivities (ϵ_i) by a nonlinear least-squares iterative procedure that fits the experimental absorbance data to a defined chemical model. The programs calculate the values of the absorbancies A_i^{calc} of the N data points on each iteration according to the chosen model and with the equilibrium parameter values calculated in the previous cycle; they then adjust the values of the parameters so as to minimize the sum of the squared residuals, $U = \sum_{i=1}^{N}(A_i^{obs} - A_i^{calc})^2$, being the ith weighting factor to be assumed as proportional to the inverse of the variance of A_i^{obs}. DALSFEK accomplishes the minimization of U by the Marquard method, which made it possible[11] to obtain the best parameter estimates. The experimental absorbance data are treated as a rectangular matrix $n \cdot l$, n being the number of solutions with different ratios [M'BPh$_4$]/[Ni(salen)] and l the number of wavelengths where the absorbancies have been acquired. For each of the systems studied, the absorbance data relative to n = 15 solutions and to l = 10 wavelengths were processed.

CFTSP is based on a widely used program[12] handling the iterative procedure for the retrieval of values that correspond to the minimum error surface. The program used a modified steepest descent technique and an extrapolation procedure that makes convergence quicker to obtain.

The need to compare the values of the equilibrium parameters obtained by two different computer programs was due to the small change of absorbance shown by the studied chemical systems after adding aliquots of M'BPh$_4$ solutions. In fact for values of the ratio [M'BPh$_4$]/

[(Ni(salen)] from 0.5 to 160 the mean change was too small (only of 0.25 absorbance units) for unambiguous discrimination of the number of equilibrium absorbing species; moreover, the low values of the estimated stability constants made the contributions of the different absorbing species to the total absorbances very low. Owing to these limitations, it was difficult for the CFTSP program to find the equilibrium model best fitting the experimental data; furthermore, they gave rise to ill-conditioning of the normal equations matrix that must iteratively be inverted in the DALSFEK program with consequent severe difficulty of convergence.

Some quantities were computed in both programs, which helpeed to estimate fitness and to test the hypothesis represented by the model used: SD, the standard deviation from regression; χ^2, the value used to perform the χ^2 test; R_H, the Hamilton factor defined as $[\sum_{i=1}^{N}\omega_i(A_i^{obs} - A_i^{calc})^2/\sum_{i=1}^{N}\omega_i(A_i^{obs})^2]^{1/2}$. A fit can be considered satisfactory if SD ⩽ 2s, s being the standard error of the absorbance measurements estimated in absence of systematic errors. The χ^2 test was used to check whether the absorbance residuals distribution was satisfactory.

R_H was compared with the limiting value R_{lim} = $[\sum_{i=1}^{N}\omega_i\mu_i^2/\sum_{i=1}^{N}\omega_i(A_i^{obs})^2]^{1/2}$, where μ_i are the residuals calculated from pessimistic estimates of the errors in all the experimental absorbancies. If $R_{lim} < R_H$, the fit was discarded. The different values of R_H calculated by different equilibrium models were also used to test alternative hypotheses. If the hypotheses H_0 and H_1 yielded values R_0 and R_1, respectively, and if $R_1/R_0 > R_{m,N-m,\alpha}$, the hypothesis H_1 could be rejected at α significance level, where m was the number of unknown parameters and $N - m$ the number of degrees of freedom of the least-squares adjustment. Values of $R_{m,N-m,\alpha}$ may be found in statistical tables.[13]
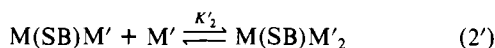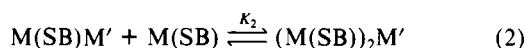
Results and Discussion

By addition of a guanidinium salt (M'BPh$_4$) solution to an Ni(salen) solution, the UV–visible spectrum of the resulting mixture was continuously modified and two sharp isosbestic points appeared at 404 and 360 nm (Figure 1). The absorption spectra for the other systems considered gave similar behavior. The appearance of two isosbestic points indicates the existance of at least two absorbing species, although complementary techniques are needed to evaluate correctly the number of species at equilibrium.[14] We made use of numerical techniques as described under Calculations.

Taking into account the results of a previous paper[5] and the experimental observations, and assuming the complete dissociation of all electrolytes used or formed in acetonitrile,[15] we proposed the following equilibria:

(8) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8.
(9) Hartley, F. R.; Burgess, C.; Alcock, R. M. *Solution Equilibria*; Ellis Horwood Publishers: Chichester, England, 1980.
(10) Lampugnani, L.; Meites, L.; Papoff, P.; Rotunno, T. *Anal. Chim. Acta* **1987**, *194*, 77.
(11) Alcock, R. M.; Hartley, F. R.; Rogers, D. E. *J. Chem. Soc., Dalton Trans.* **1978**, 115.
(12) Meites, L.; Meites, T. *Talanta* **1972**, *19*, 925.

(13) Hamilton, W. C. *Statistics in Physical Science*; Ronald Press: New York, 1964; pp 205–222. Freund, J. E. *Mathematical Statistics*; Prentice-Hall: Englewood Cliffs, NJ, 1962; pp 199–215.
(14) Nowicka-Iankowska, T. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2043.
(15) Carvajal, C.; Tölle, K. I.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1965**, *87*, 5548. Kay, R. L.; Hales, B. J.; Cunningam, G. P. *J. Phys. Chem.* **1967**, *71*, 3925. Yeager, H. L.; Kratochril, B. *Can. J. Chem.* **1975**, *53*, 3448.

$$M(SB) + M' \xrightleftharpoons{K_1} M(SB)M' \tag{1}$$

$$M(SB)M' + M(SB) \xrightleftharpoons{K_2} (M(SB))_2M' \tag{2}$$

$$M(SB)M' + M' \xrightleftharpoons{K'_2} M(SB)M'_2 \tag{2'}$$

where $M(SB) = Ni(salen)$ or $Ni(SB-R)_2$ and the ionic charges are omitted for simplicity.

For each system the models tested by nonlinear regression analysis were those involving the following: only equilibrium 1, model 1; equilibria 1 and 2, model 1,2; equilibria 1 and 2', model 1,2'; equilibria 1, and 2, and 2', model 1,2,2'. Models 1,2' and 1,2,2' were discarded for all the systems because their fits with both the programs either diverged (with wide oscillations in the sum of the squares of the residuals) or reached an unreliable convergence with $R_H \gg R_{lim}$. Table I summarizes the results of the fittings that gave acceptable convergence with $R_H \ll R_{lim}$. The equilibrium parameters obtained by fitting model 1 to the experimental absorbances data showed satisfactory agreement with both programs, and this was a valid proof of the correctness of the model 1.

As for model 1,2, the DALSFEK program gave a good convergence only for the systems where M' is NH_4^+ or $C(NH_2)_3^+$, while the CFTSP program was unable to yield reliable convergences for the systems with $M' = NH_4^+$, $EtNH_3^+$, $Et_2NH_2^+$, $H_3N^+-NH_3^+$, or $H_3N^+(CH_2)_8NH_3^+$. In the cases where the fits of model 1,2 converged reliably, both the standard deviations from regression and the R_H factor values were lower or comparable with the analogous values obtained in the fits of the model 1; however, they were insufficient to reject model 1 with respect to model 1,2. Neverless, we decided to choose model 1 as the most correct equilibrium model for all the studied systems because (a) the standard deviations on the parameters K_2 and ϵ_2, relative to the species $(M(SB))_2M'$, are of the same order if not larger than the parameter values and the $(M(SB))_2M'$ concentration is very low (<2% throughout the examined range of total concentrations and with large standard deviations) and (b) the values of K_2 and ϵ_2 undergo large oscillations when small changes are made in the initial estimates of the parameters. Experience leads us to discard the constants' calculated values and to reject the whole model 1,2.

The K_1 values reported in Table I show that, in addition to the electrostatic interaction, the stabilizing effect due to hydrogen bonds formation is to be considered. In our opinion, this explains why the calculated value of K_1 for the formation of [Ni(salen)-NH_4]$^+$ is higher ($\sim$5 times) than the formation constant of [Ni(salen)K]$^+$ and why the values for [Ni(salen)Et$_4$N]$^+$ is the lowest in the homologous series (Table I).[16] The values of K_1 for the homologous derivatives of R_4N^+ (with R = Et and/or H) decrease with the decreasing number of hydrogen atoms bonded to the nitrogen atom of the cation. However, this dependence cannot be attributed only to the number of hydrogens, in particular when the guanidinium ion and the bivalent ions are involved. A correct analysis of the K_1 values should take into account the influence of the various cofactors that help to determine the interaction process in the solution, i.e. the charge density of the various cations, the number of positively charged N atoms, the total number of H atoms able to produce hydrogen bonds, etc. A direct linear correlation was noticed between the values of the formation constants, K_1, and a "statistical factor" that takes into account the possible combinations between the pair of oxygen atoms of the Schiff base and the pairs of hydrogen atoms located on each cation at appropriate distance for coupling. The values of the statistical factor n and of the ratio K_1/n are reported in the last two columns of Table I. This correlation is worth pointing out (without too much emphasis), since it unifies the behavior of
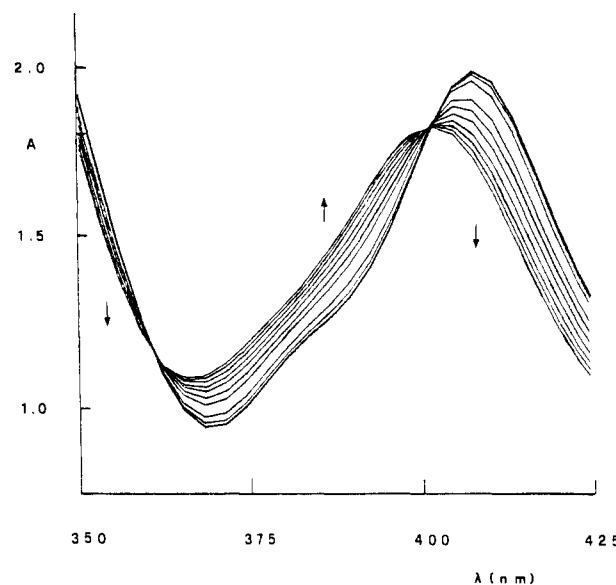

Figure 1. Absorption spectra of $Ni(salen)/C(NH_2)_3BPh_4$ solutions in acetonitrile: $[Ni(salen)] = 3.06 \times 10^{-4}$ M; $[C(NH_2)_3^+] = 0, 1.14 \times 10^{-3}, 3.47 \times 10^{-3}, 9.65 \times 10^{-3}, 1.43 \times 10^{-2}, 2.00 \times 10^{-2}, 2.67 \times 10^{-2}, 3.40 \times 10^{-2}, 4.16 \times 10^{-2}, 4.94 \times 10^{-3}$ M; optical path 1 cm.

the different ammonium-like ions and confirms the fundamental role of hydrogen bonding on the stabilization of these adducts.

The formation of the adducts by the Ni bidentate Schiff bases deserves a special comment. The interaction with ammonium or ammonium-like cations involves a true reaction of transimination with exchange of the groups N-bonded to the imine and to the ammonium. On the mechanism of this reaction we refer elsewhere.[17] Therefore, this study is limited to the interaction between Na^+ and Ni bidentate Schiff bases with alkyl substituents of different steric hindrance. The UV–visible spectra recorded at different ratios of $[Ni(SB-R)_2]/[NaBPh_4]$ were similar to those reported in Figure 1 but showed lower absorbance changes for equal variations of the ratio of concentrations. The values of the equilibrium constant are significantly lower than the corresponding values for Ni(salen).[5] This is probably due to the different spatial disposition of the two negative ends of the Ni–O dipoles. For quadridentate Schiff base complexes these dipoles are placed on the same side (cis), determining a bite able to trap the Na^+ ion. For square-planar bidentate base complexes, the thermodynamically more stable trans disposition involves that only one dipole at a time can "see" the Na^+ ion in its action range. Since this interaction type is very weak (of the order of 1–2 kcal/mol[5]), it cannot induce a trans $\rightarrow$ cis transition, which is instead reported in the literature[18] for some Cu complexes in the presence of cupric ions. It is also worth noting that the charge density on the oxygen atom of the bidentate Schiff base Ni complexes seems lower than that of the analogous quadridentate complexes.[19] Finally, the stability of the adducts with the bidentate complexes in solution is strongly influenced by the steric hindrance of the R groups in $Ni(SB-R)_2$, and this explains the lowest value of K_1 when R = isopropyl substituent (see Table I). For this complex the steric hindrance seems to be much more important than the opposing effect (greater stability) deriving from its pseudotetrahedral geometry[20] with respect to planar-square geometry (R = Me, Et).[21] The pseudotetrahedral configuration should produce a complex–

---

(16) For the system $Ni(salen)/Et_4N^+$, very low absorbance changes were observed even with very high values of the ratio $[Ni(salen)]/[Et_4N^+]$ compatible with solubility. This did not allow a correct elaboration of the collected absorbance data but made it possible to define a limit value for $K_1 < 1$, above which the fitting programs were unable to give convergence.

(17) Carbonaro, L.; Giacomelli, A.; Isola, M.; Senatore, L. Manuscript in preparation.

(18) Harris, C. M.; Sim, E. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2723. Grauber, S. J.; Harris, C. M.; Sinn, E. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 107.

(19) De Alti, G.; Galasso, V.; Bigotto, A. *Inorg. Chim. Acta* **1972**, *6*, 131; **1972**, *6*, 153.

(20) Sacconi, L.; Ciampolini, M.; Nardi, N. *J. Am. Chem. Soc.* **1964**, *86*, 819. Takenchi, A.; Yamada, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3046.

(21) The positive check of Lambert–Beer law verified for each $Ni(SB-R)_2$ complex solution excluded the possibility of any process of association or isomerism, at least in the concentration ranges used in this paper.

Na$^+$ interaction very similar to that with Ni(salen). Similar explanations are reported in literature to explain why the Ni complexes with high steric hindrance are unable to form associated species or to coordinate two molecules of pyridine giving the octahedral complex Ni(SB–R)$_2$·2Py.[22]

(22) Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 4683. Shumann, M.; Holturn, A.; Wannowius, J.; Elias, H. *Inorg. Chem.* **1982**, *21*, 606.

Contribution from the Dipartimento di Chimica Analitica, Università di Torino, 10125 Torino, Italy, Istituto di Chimica Generale, Inorganica e Analitica, Università di Cagliari, 09124 Cagliari, Italy, and Dipartimento di Scienze Chimiche, Università di Catania, 95125 Catania, Italy

Ligand–Ligand Interactions in Metal Complexes. Thermodynamic and Spectroscopic Investigation of Simple and Mixed Copper(II) and Zinc(II) Substituted-Malonate Complexes with 2,2'-Bipyridyl in Aqueous Solution

Paola Amico,[1a] Raffaele P. Bonomo,*[1b] Rosario Calì,[1c] Vincenzo Cucinotta,[1c] Pier G. Daniele,*[1a] Giorgio Ostacoli,[1a] and Enrico Rizzarelli*[1c]

The influence of side-chain residues on the thermodynamic properties of simple and mixed complexes has been investigated by potentiometric and calorimetric methods for ML, ML$_2$, and M(bpy)(L), where M = Cu(II) and Zn(II), bpy = 2,2'-bipyridyl, and L = malonate, methylmalonate, *n*-propylmalonate, isopropylmalonate, *n*-butylmalonate, isobutylmalonate, dimethylmalonate, di-*n*-propylmalonate, and di-*n*-butylmalonate. The presence of noncovalent ligand–ligand interaction is indicated by a more favorable enthalpy change accompanying the complex formation of mixed zinc(II)–2,2'-bipyridyl species with *n*-propyl-, isobutyl-, *n*-butyl-, di-*n*-propyl- and di-*n*-butylmalonates. The EPR parameters of mixed copper(II) complexes show that the metal ion reaches the same geometry and coordination number with little or no influence of side-chain groups. This result together with the thermodynamic data indicates that, in the mixed copper(II) complex, solvophobic ligand–ligand interaction is not present. The diagnostic character of a thermodynamic approach is confirmed by ^{1}H NMR data on mixed zinc(II) complexes, which show an upfield shift only for those species having more exothermic $\Delta H°$ formation values.

Introduction

Noncovalent interactions between molecules or side-chain groups of macromolecules are known to provide the specificity and flexibility required in most important biological processes[2–10] and have been also invoked to explain drug biological activity.[11] Many model systems have been studied, such as molecules of low molecular weight containing nucleic acid bases connected by polymethylene chains.[12] Analogously, since indirect interactions mediated through metal cations have been found in biological systems,[13–15] a number of metal complexes with noncovalent interactions between side-chain groups have been investigated.[16–22]

In the model systems the above-mentioned interactions play an important role, providing distinct features in stability,[23] reactivity,[24] selective synthesis,[25] racemate resolution,[26] and thermodynamic stereoselectivity.[27,28]

On the basis of calorimetric data and EPR parameters, we revealed the presence of side-chain interactions in mixed complexes of metal ions containing ATP and amino acids[29,30] or biofunctional ligands such as histamine[31] and in copper(II) complexes of linear dipeptides.[32] The enthalpy change was found to become more favorable and the entropy change less favorable if the side chains

(1) (a) Università di Torino. (b) Università di Cagliari. (c) Università di Catania.
(2) Frieden, E. *J. Chem. Educ.* **1975**, *52*, 754.
(3) Hélène, C. *Stud. Biophys.* **1976**, *57*, 211.
(4) Hélène, C.; Lancelot, G. *Prog. Biophys. Mol. Biol.* **1982**, *39*, 1.
(5) Lohman, T. M.; De Haseth, P. L.; Record, M. T., Jr. *Biochemistry* **1980**, *19*, 3522.
(6) Behmoaras, T.; Toulme, J. J.; Hélène, C. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 926.
(7) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984.
(8) Cantor, C. R.; Schimmel, P. R. *Biophysical Chemistry*; W. H. Freeman: San Francisco, 1982.
(9) Lipscomb, W. N. *Acc. Chem. Res.* **1970**, *3*, 81.
(10) Jencks, W. P. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1975**, *43*, 219.
(11) Delben, F.; Quadrifoglio, F.; Crescenzi, V. *Biopolymers* **1982**, *21*, 331.
(12) Leonard, N. J. *Acc. Chem. Res.* **1979**, *12*, 424.
(13) Hélène, C. *Nucl. Acids Res.* **1975**, *2*, 961.
(14) Lipscomb, W. N.; Reeke, G. N.; Hartsuck, J. A.; Quiocho, F. A.; Bethge, P. H. *Philos. Trans. R. Soc. London, B* **1970**, *257*, 177.
(15) Arnone, A.; Bier, C. J.; Cotton, F. A.; Day, V. W.; Hazen, E. E.; Richardson, D. C.; Yonath, A. *J. Biol. Chem.* **1971**, *246*, 2302.
(16) Sigel, H. In *Coordination Chemistry-20*; Banerjea, D., Ed.; Pergamon Press: New York, 1980; p 27.
(17) Sigel, H.; Fischer, B. E.; Farkas, E. *Inorg. Chem.* **1983**, *22*, 925.
(18) Yamauchi, O. *J. Mol. Catal.* **1984**, *23*, 255.
(19) Yamauchi, O. *Inorg. Chim. Acta* **1985**, *100*, 165.
(20) Sigel, H.; Malini-Balakrishnan, R.; Haring, U. K. *J. Am. Chem. Soc.* **1985**, *107*, 5137.
(21) Sigel, H.; Scheller-Krattiger, K. H.; Prijs, B. *J. Am. Chem. Soc.* **1986**, *108*, 4171.
(22) Arena, G.; Rizzarelli, E. In *Metal Complexes In Solution*; Jenne, E. A., Rizzarelli, E., Romano, V., Sammartano, S., Eds.; Piccin: Padua, Italy, 1986; p 105.
(23) Mitchell, P. R.; Prijs, B.; Sigel, H. *Helv. Chim. Acta* **1979**, *62*, 1723.
(24) Cayley, G. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, 1002.
(25) Nakamura, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3377.
(26) Davankov, V. A.; Bochkov, A. S.; Kurganov, A. A. *Chromatographia* **1980**, *13*, 677.
(27) Impellizzeri, G.; Bonomo, R. P.; Calì, R.; Cucinotta, V.; Rizzarelli, E. *Thermochim. Acta* **1984**, *72*, 263.
(28) Impellizzeri, G.; Bonomo, R. P.; Calì, R.; Cucinotta, V.; Rizzarelli, E. *Thermochim. Acta* **1984**, *80*, 275.
(29) Arena, G.; Calì, R.; Cucinotta, V.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *J. Chem. Soc., Dalton Trans.* **1983**, 1271.
(30) Arena, G.; Calì, R.; Cucinotta, V.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *Thermochim. Acta* **1984**, *74*, 77.
(31) Arena, G.; Calì, R.; Cucinotta, V.; Musumeci, S.; Rizzarelli, E.; Sammartano, S. *J. Chem. Soc., Dalton Trans.* **1984**, 1651.
(32) Bonomo, R. P.; Calì, R.; Cucinotta, V.; Impellizzeri, G.; Rizzarelli, E. *Inorg. Chem.* **1986**, *25*, 1641.