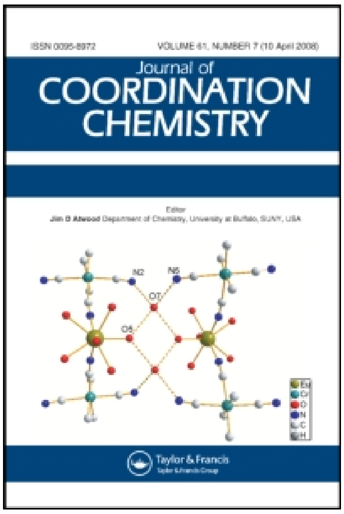

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SOLVENT-DEPENDENT VARIATION OF THE SPIN STATE OF *BIS*(SALICYLALDOXIMATO) NICKEL(II) IN NONAQUEOUS SOLUTIONS

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Magnetic susceptibilities and chemical shifts of salicylaldoxime protons in $CDCl_3$-DMSO-d_6 solutions of *bis*(salicylaldoximato)Ni(II) were analysed according to the equilibrium between diamagnetic square planar $Ni(Saldox)_2$ and paramagnetic solvates $Ni(Saldox)_2 \cdot m$DMSO. Magnetic susceptibility data yield thermodynamic parameters for inner sphere solvation (*i.e.*, formation of the *bis*-solvate $Ni(Saldox)_2 \cdot 2DMSO$): $\Delta H = -18.4 \pm 2.9$ kJ/mol, $\Delta S = -102.1 \pm 9.2$ J/mol K and the magnetic moment of paramagnetic solvate $\mu_{para} = 3.4 \pm 0.2\,\mu B$. The dependences of chemical shifts of salicylaldoxime protons on solvent composition and temperature require more than two DMSO molecules solvating $Ni(Saldox)_2$ for an adequate description. Analysis of these data according to the formation of $Ni(Saldox)_2 \cdot 4DMSO$ yields thermodynamic parameters of both inner-sphere and outer-sphere solvation, namely $\Delta H = -56.5 \pm 1.3$ kJ/mol and $\Delta S = (-249.0 \pm 5.0)$ J/mol K. This shows that outer sphere solvation is connected with higher enthalpies than inner-sphere solvation (38.1 and 18.4 kJ/mol, respectively) of this complex. This phenomenon is explained by the high contribution of electric dipole–dipole interactions of DMSO molecules in the $Ni(Saldox)_2 \cdot 4DMSO$ solvate. Analysis of hyperfine coupling constants of the salicylaldoxime protons shows that the outer-sphere solvation of $Ni(Saldox)_2$ proceeds *via* hydrogen bonding with oxime groups, which breaks intramolecular hydrogen bonds in $Ni(Saldox)_2$. This model produces a good agreement between measured hyperfine coupling constants and ZINDO/1 computed spin-densities on protons. The observed small equilibrium constants of solvation were found to be due to strongly negative entropies of solvation (−102.1 and −145.2 J/mol K, respectively, for inner and outer sphere solvation).

Keywords: Solute-solvent interactions; spin-state transition; nonaqueous solutions; structural variations

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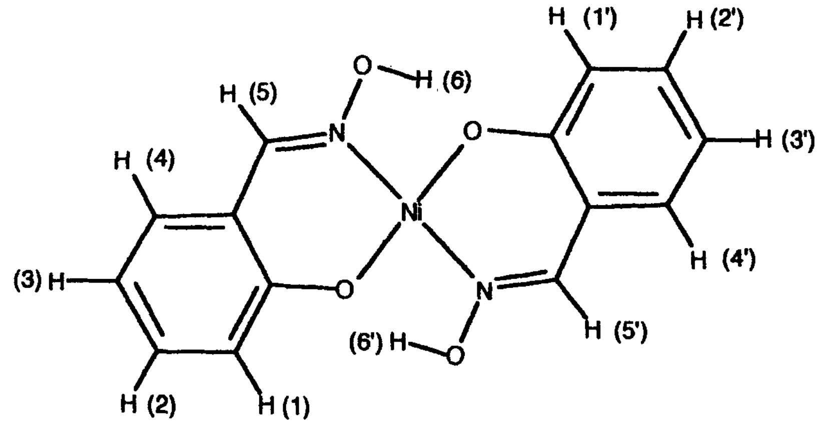
INTRODUCTION

Solvation of square planar complexes of Ni(II) by donor molecules is accompanied by the transition from low-spin (diamagnetic) to a high-spin state connected with the change of complex geometry to five- and six-coordinate. These transitions have been studied by magnetic susceptibility measurements and optical spectroscopy[1-4] as well as by NMR spectroscopy[5,6] in a variety of complexes of Ni(II) with acetylacetone and Schiff bases. Magnetic properties of these complexes proved to be sensitive to the nature of the solvent. In non-coordinating solvents such as $CHCl_3$, they exist in a diamagnetic form, while in strongly coordinating solvents, like pyridine, they exhibit paramagnetism, which was interpreted in terms of the equilibria between LS square planar and HS tetrahedral and octahedral states. Among them, *bis*(salicylaldoximato)Ni(II), **1**, is a complex widely used in analytical chemistry.[7] A *trans* configuration for this complex follows from its electronic spectra.[8] It undergoes an LS–HS transition when solvated by donor molecules such as dioxane, pyridine, DMSO and cyclic amines.[1-4,9,10] This transition has been investigated by magnetic susceptibility measurements and optical spectroscopy but chemical shifts in $Ni(Saldox)_2$ adducts have not yet been studied (unlike Ni(II) *bis*(salicylaldiminates) extensively studied by NMR spectroscopy).[11-13]



Pyridine and cyclic amines form stable adducts with $Ni(Saldox)_2$ which can be isolated but its adducts with dioxane and DMSO apparently exist in solution alone. In DMSO solution $Ni(Saldox)_2$ forms a paramagnetic solvate but this reaction is not complete even in pure DMSO.[9] This indicates a low equilibrium constant which does not correspond to the high donor number of DMSO. Elucidation of the mode of solvation of Ni(Saldox)$_2$ by DMSO is of considerable importance because of the wide use of this solvent in analytical practice.

The determination of thermodynamic parameters of this reaction would provide an explanation of weak complexation of Ni(Saldox)$_2$ with DMSO and other donor molecules. This could be advantageously carried out by NMR spectroscopy. Data on contact shifts obtained at different temperatures yield thermodynamic parameters for solvation equilibria as well as hyperfine coupling constants. The structure of the solvate can be investigated by semiempirical molecular orbital optimisation which also provides for the determination of spin densities on protons in the paramagnetic state. The latter can be compared with the experimentally obtained hyperfine coupling constants, indicating the degree of agreement of the computed structure to experimental data. On the other hand, magnetic susceptibility data in solution provide for an independent determination of the solvation equilibrium constant and of the magnetic moment of the paramagnetic solvate.

The presented paper reports the results of an investigation of the solvation of Ni(Saldox)$_2$ in mixed CHCl$_3$-DMSO-d_6 solutions by NMR spectroscopy, analysis of magnetic susceptibility data and semi-empirical MO calculations.

EXPERIMENTAL

Ni(Saldox)$_2$ was synthesised from commercial NiCl$_2$ and salicylaldoxime and purified by recrystallisation from CCl$_4$. CDCl$_3$ (99%$_{at}$) and DMSO-d_6 (99.9%$_{at}$) were obtained from Aldrich and used without further purification. Solutions were prepared by mixing appropriate volumes of the solutions containing 0.003 M Ni(Saldox)$_2$ in CDCl$_3$ and DMSO-d_6. The concentration of DMSO varied over the range 0–100%$_v$.

PMR spectra of Ni(Saldox)$_2$ solutions in mixed CDCl$_3$-DMSO-d_6 were recorded at different temperatures using a Bruker AC-250 spectrometer. Chemical shifts were determined with respect to internal TMS. The spectra of this complex in diamagnetic (CDCl$_3$ solution) and in paramagnetic (DMSO solution) states are shown in Figures 1 and 2. Signals of aromatic protons in the diamagnetic state were easily assigned as additionally split 'doublets' (1 and 4) and 'triplets' (2 and 3). The NOH and HCN protons produce singlets (not shown). The non-assigned narrow lines in the paramagnetic

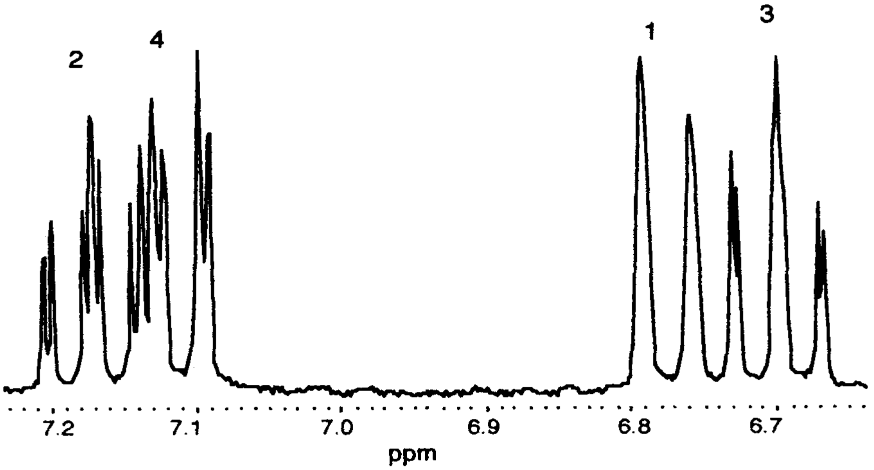


FIGURE 1 Aromatic region of the PMR spectrum of Ni(Saldox)$_2$ in CDCl$_3$ at 298 K.

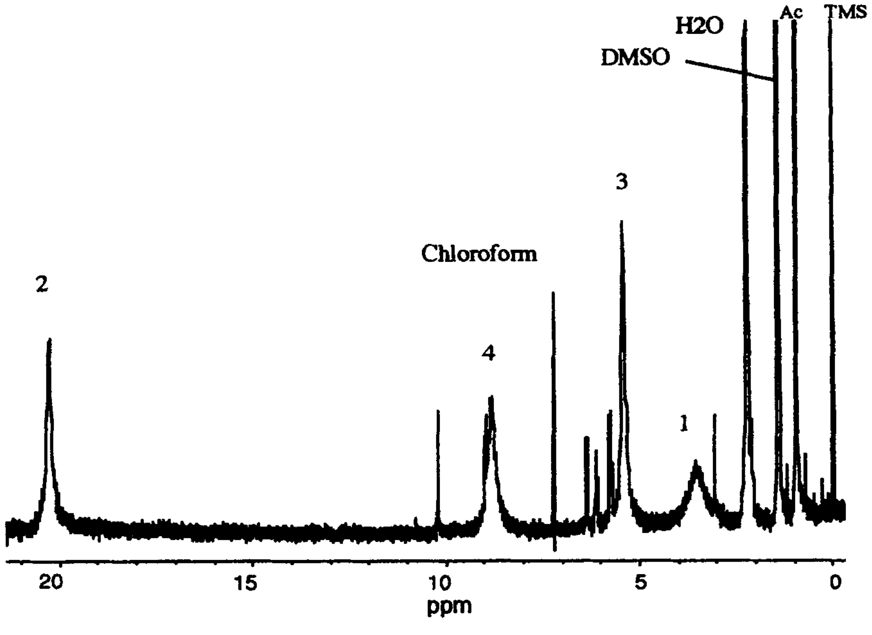


FIGURE 2 PMR spectrum of Ni(Saldox)$_2$ solution in DMSO-d_6 (HCN and NOH protons are not shown).

solutions in DMSO belong to free salicylaldoxime (HSaldox) molecules presumably formed by hydrolysis of the Ni complex. Their integrals are negligibly small compared to those of the dissolved complex. The measured proton chemical shifts are given in Table I.

TABLE I Proton chemical shifts in Ni(Saldox)$_2$ solutions in CDCl$_3$-DMSO-d_6

C_{DMSO} (%v)	T/K	Proton no.						T/K	Proton no.					
		6	5	4	3	2	1		6	5	4	3	2	1
0	298	10.58	8.29	7.11	6.68	7.21	6.76	303	10.53	8.21	7.12	6.68	7.19	6.75
10	298	10.91	9.93	7.17	6.67	7.33	6.74	303	10.81	9.54	7.16	6.67	7.30	6.74
20	298	12.09	14.21	7.27	6.66	7.67	6.71	303	11.69	13.19	7.25	6.66	7.57	6.71
30	298	15.20	26.21	7.47	6.64	8.57	6.58	303	14.24	22.88	7.41	6.64	8.28	6.62
40	298	20.83	49.21	7.78	6.62	10.18	6.37	303	19.17	42.24	7.68	6.61	9.66	6.43
50	298	29.72	83.09	8.25	6.59	12.59	6.03	303	26.02	68.94	8.05	6.57	11.58	6.15
60	298	38.90	116.33	8.68	6.55	14.97	5.67	303	33.92	100.16	8.48	6.52	13.81	5.82
70	298	45.48	146.360	9.13	6.54	17.13	5.42	303	40.57	127.6	8.87	6.51	15.80	5.53
80	298	50.92	165.440	9.33	6.51	18.49	5.10	303	44.57	145.7	9.11	6.45	17.08	5.31
90	298	53.74	183.390	9.60	6.51	19.79	4.880	303	49.78	164.41	9.38	6.51	18.44	5.10
100	298	57.17	192.210	9.76	6.48	20.57	4.740	303	53.62	178.0	9.54	6.45	19.41	4.99
0	308	10.51	8.13	7.10	6.68	7.18	6.75	313	10.49	8.07	7.09	6.68	7.18	6.75
10	308	10.74	9.29	7.15	6.67	7.27	6.74	313	10.66	9.05	7.14	6.67	7.25	6.74
20	308	11.53	12.47	7.23	6.66	7.51	6.71	313	11.35	11.83	7.22	6.66	7.45	6.72
30	308	13.44	20.49	7.37	6.64	8.09	6.66	313	13.00	18.69	7.34	6.64	7.94	6.65
40	308	17.76	36.58	7.60	6.61	9.24	6.49	313	16.63	32.40	7.56	6.60	8.92	6.53
50	308	23.50	59.31	7.93	6.56	10.88	6.25	313	21.53	51.10	7.83	6.56	10.28	6.32
60	308	30.42	87.32	8.32	6.52	12.87	5.94	313	27.72	75.62	8.17	6.52	12.04	6.06
70	308	36.79	111.82	8.66	6.47	14.66	5.67	313	32.54	96.14	8.46	6.49	13.54	5.82
80	308	40.99	129.04	8.91	6.47	15.90	5.49	313	37.12	113.84	8.72	6.47	14.84	5.63
90	308	45.74	146.98	9.14	6.48	17.21	5.28	313	41.79	132.39	8.96	6.43	16.15	5.46
100	308	49.69	161.71	9.36	6.48	18.23	5.15	313	44.90	145.83	9.19	6.43	17.13	5.24

Data on the temperature dependence of the magnetic susceptibility of Ni(Saldox)$_2$ in DMSO-d_6 (Evans method[14]) were taken from Ref. 9 and corrected for the temperature dependence of the density of solvent. Quantum chemical (ZINDO/1) and molecular mechanics calculations were performed using the HyperChem3 (Autodesk™) program. By a judicious choice of initial configurations of DMSO molecules in solvates Ni(Saldox)$_2 \cdot m$DMSO it was found possible to obtain optimised (to residual forces on atoms of 0.8 kJ/A and lower) structures which still contain planar Ni(Saldox)$_2$ moieties, notwithstanding a typical trend of HyperChem optimisers to convert them into non-planar configurations. Molecular mechanics calculations were used to find. possible orientations of solvating molecules when m was greater than two.

Besides the optimisation of molecular structure of solvates this program was used for a semi-quantitative (from contour plots) evaluation of spin densities on protons. Spin densities on aromatic protons were found to be extremely sensitive to the choice of convergence limit in MO calculations. In some cases spin density changes its sign when a lower convergence limit is chosen. It was found, however, that at the convergence limits of 10^{-6} and lower, variations of spin densities do not exceed 20%. Therefore spin densities were determined after a single point MO calculation with the convergence limit set to 10^{-6}.

ANALYSIS OF EXPERIMENTAL DATA

Experimental data were analysed according to the solvation equilibrium given in (1).

$$\mathrm{Ni(Saldox)_2} + m\,\mathrm{DMSO} \overset{K}{\rightleftharpoons} [\mathrm{Ni(Saldox)_2} \cdot m\,\mathrm{DMSO}] \qquad (1)$$

The corresponding mass action law equations were simplified taking into account the fact that the concentration of DMSO was always much higher than the concentration of $\mathrm{Ni(Saldox)_2}$ ($C_{\mathrm{DMSO}} \gg C_{\mathrm{Ni}}$).

The mathematical model used in the analysis of the susceptibility measurements was[9]

$$\Delta[\mathrm{ppm}] = (501.9\mu^2_{\mathrm{para}}/T)\,K(T)\,C_{\mathrm{Ni}}\,C^m_{\mathrm{DMSO}}/(1 + K(T)C^m_{\mathrm{DMSO}}) \qquad (2)$$

where Δ is the separation between the TMS signals in solution and in the external standard, C_{Ni} is the concentration of $\mathrm{Ni(Saldox)_2}$ expressed in mol/l and μ_{para} is the magnetic moment (in Bohr Magnetons) of paramagnetic solvate. The equilibrium constant K(T) was expressed as in (3).

$$K(T) = K(273)\exp(Q(1/T - 1/273) \qquad (3)$$

Estimates of μ_{para}, Q and K(273) were obtained using the non-linear regression program OPTIMI.[9]

The mathematical model used for the analysis of chemical shifts was

$$\Delta_i = \delta_i - \delta_i^{\mathrm{dia}} = (B_i/T)(K(T)C^m_{\mathrm{DMSO}}/(1 + K(T)C^m_{\mathrm{DMSO}}) \qquad (4)$$

where δ_i is the chemical shift of the i-th proton of salicylaldoxime in the solution containing C_{DMSO} (mol/l) of DMSO at a given temperature (T), δ_i^{dia} is the chemical shift of the i-th proton in $CDCl_3$ solution at the same temperature and m is the number of DMSO molecules involved in solvation.

Enthalpy and entropy of reaction were calculated from the estimates of Q and K(273) according to

$$\Delta H = -QR \qquad (5)$$

$$\Delta S = R\ln K(273) + \Delta H/273 \qquad (6)$$

All data on the chemical shifts of aromatic, NOH and HC=N protons involving all investigated solutions at four different temperatures were analysed simultaneously using the OPTIMI program which yielded the estimates of B_i, K(273) and Q.

Supposing that the contact shifts in the investigated complex arise from isotropic interactions with unpaired electron it is possible to calculate hyperfine coupling constants A_i of the i-th proton from the estimates of B_i as

$$A_i/h[\mathrm{Hz}] = B_i\, 3k\gamma_N/(2\pi g\mu_B S(S+1)) = 42.2B_i \qquad (7)$$

where $k = 1.38 \cdot 10^{-16}$ erg/K, $\gamma_H = 2.67 \cdot 10^4$ radian/sec gauss, $g(\mathrm{Ni(II)}) = 2.25$,[15] $\mu_B = 0.927 \cdot 10^{-20}$ erg/gauss and $S = 1$. Hyperfine coupling constants A_i and computed spin densities were converted into each other according to

$$A_i/h = \rho_i A_H \qquad (8)$$

where A_H is the proton hyperfine coupling constant, equal to 1420 MHz in a hydrogen atom. Because the electron density distribution on 1s orbitals of the hydrogens in salicylaldoxime is different from that in a hydrogen atom the coefficient A_H was considered as an adjustable parameter.

RESULTS AND DISCUSSION

Data on the temperature dependence of the magnetic susceptibility of $\mathrm{Ni(Saldox)_2}$ in pure DMSO solutions were analysed according to the model with $m = 2$ because the magnetic moment is controlled by the symmetry of the nearest environment of the $\mathrm{Ni^{2+}}$ ion and the formation of *bis* adducts was established for solutions in pyridine.[12] These data yielded upon optimisation of K(273), Q and μ_{para} an adequate description (the regression error of Δ being 0.0012 ppm) with $K(273) = 0.016 \pm 0.007\,\mathrm{M^{-2}}$, $\mu_{para} = (3.42 \pm 0.21)\mu_B$ and $\Delta H = -18.6 \pm 2.9$ kJ/mol. The entropy of solvation calculated from these estimates amounts to (-102.1 ± 9.2) J/mol K. The lowest limit of magnetic moment ($3.2\,\mu_B$) falls in the region of typical magnetic moments of octahedral complexes of Ni(II). A slightly higher than expected estimate of μ_{para} might be caused by a spin-crossover transition of the non-solvated $\mathrm{Ni(Saldox)_2}$ at higher temperatures but most probably is a result of a strong correlation between the estimates of parameters of the mathematical model. Actually, the description with the fixed value of

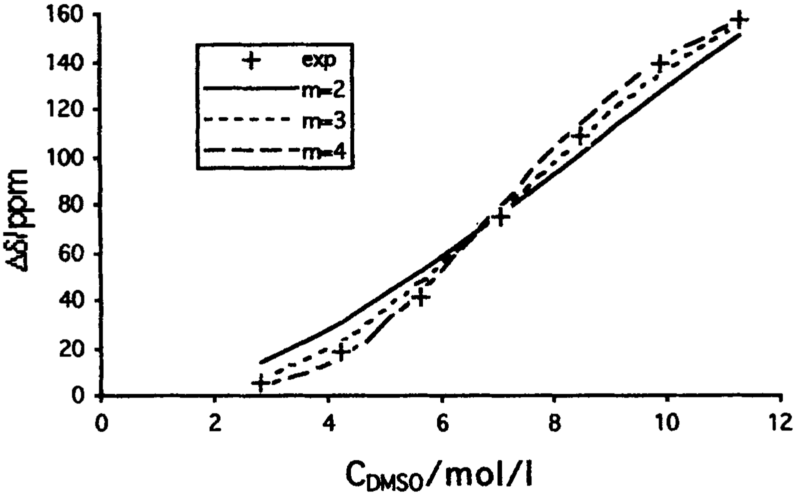


FIGURE 3 Dependence of contact shift of the HC=N proton on the concentration of DMSO assuming different numbers of DMSO molecules in a solvate (*m*).

$\mu_{\text{para}} = 3.2\,\mu_B$ might present more realistic estimates of thermodynamic parameters: $K(273) = 0.0279 \pm 0.0008\,M^{-3}$, $\Delta H = (-22.3 \pm 0.5)$ KJ/mol and $\Delta S = -110.9$ J/molK.

The data on chemical shifts when fitted to models with $m = 2$, 3 and 4 produce respectively the following regression errors: ±3.16, ±1.14 and ±1.98 ppm. Figure 3 represents part of these data corresponding to the HC=N proton at 298K.

According to Figure 3, the formation of a *bis* adduct cannot be chosen as a model for the description of the data. It is difficult to decide, based on the data shown, whether three or four molecules solvate the $Ni(Saldox)_2$ complex. Most probably an equilibrium exists between different species certainly containing more than two molecules of DMSO. The formation of $Ni(Saldox)_2 \cdot 4DMSO$ was postulated as a formal description in order to obtain estimates of thermodynamic parameters of solvation and hyperfine interaction constants. These estimates are shown in Table II.

Chemical shift data thus indicate an outer-sphere solvation of the $Ni(Saldox)_2$ complex. It proved to be possible to establish the mode of such solvation by analysis of the contact shifts (hyperfine coupling constants).

The equilibrium constant obtained from chemical shift data can be considered as a product of the equilibrium constant of the formation of the *bis* adduct (reflected by susceptibility data) and of the outer-sphere solvation

TABLE II Estimates of the equilibrium constant and enthalpy of reaction (1), hyperfine coupling constants and spin densities on the protons of $Ni(Saldox)_2$

Parameter	*Estimates*	$\rho_{exp} = A_i/1420$	ρ*(closed)*	ρ*(open)*	ρ*(4DMSO)*
$K(273)/M^{-4}$	$(2.34 \pm 0.16)10^{-3}$				
$-\Delta H$/kJ/mol	56.6 ± 1.4				
$-\Delta S$/J/mol K	248.9 ± 5.0				
A_1/MHz	$-(0.0249 \pm 0.0077)$	-1.75×10^{-5}	-1.17×10^{-4}	-6.8×10^{-5}	-7.2×10^{-5}
A_2/MHz	0.172 ± 0.008	1.21×10^{-4}	$+2.16 \times 10^{-4}$	$+2.3 \times 10^{-4}$	$+2.16 \times 10^{-4}$
A_3/MHz	$-(0.0034 \pm 0.0077)$	-2.42×10^{-6}	-7.5×10^{-5}	-1.55×10^{-5}	-2.5×10^{-5}
A_4/MHz	0.0351 ± 0.0077	2.47×10^{-5}	$+8.6 \times 10^{-5}$	-9.5×10^{-6}	$+8.4 \times 10^{-6}$
A_5(HCN)/MHz	2.384 ± 0.014	1.67×10^{-3}	$+2.4 \times 10^{-3}$	$+1.2 \times 10^{-3}$	$+2.05 \times 10^{-3}$
A_6(NOH)/MHz	0.602 ± 0.008	4.24×10^{-4}	-1.36×10^{-3}	$+1.1 \times 10^{-3}$	$+6.8 \times 10^{-4}$

equilibrium

$$Ni(Saldox)_2 \cdot 2DMSO + 2DMSO \rightleftharpoons Ni(Saldox)_2 \cdot 4DMSO \qquad (9)$$

and

$$K_{cs} = 2.34 \cdot 10^{-3}\,(M^{-4}) = K_{os} {*} 1.64 \cdot 10^{-2}\,(M)^{-2} \qquad (10)$$

which yields $K_{os} = 0.142\,M^{-2}$ (or $K_{os} = 0.838\,M^{-2}$ for the model with fixed $\mu_{para} = 3.2\,\mu_B$). The enthalpy of outer-sphere solvation is accordingly the difference of the enthalpies obtained from chemical shift and susceptibility data, *i.e.*, 37.9 kJ/mol (or 34.34 kJ/mol for the model with fixed $\mu_{para} = 3.2\,\mu_B$). This result (although being a rough approximation neglecting the distribution of species with various *m*) shows that outer-sphere solvation of $Ni(Saldox)_2 \cdot 2DMSO$ might be even stronger than inner sphere solvation. This proceeds from a high contribution of electric dipole–dipole interactions of DMSO molecules both in bulk solvent and in solvate. The inner sphere solvation of $Ni(Saldox)_2$ implicitly includes a disruption of intermolecular interaction of DMSO molecules. The outer-sphere solvation, on the other hand, brings four molecules of DMSO into more or less close contact (see, Figure 5) thus compensating for interactions broken in bulk solvent.

Small equilibrium constants reflect highly negative entropies of both inner and outer-sphere solvation (−102.1 and −145.2 J/mol K, respectively). These most probably result from the disruption of self-association of DMSO molecules, but may also be due to the formation of species of low symmetry. The mode of outer-sphere solvation of $Ni(Saldox)_2$ is clearer after an analysis of spin-densities in $Ni(Saldox)_2 \cdot m$DMSO solvates.

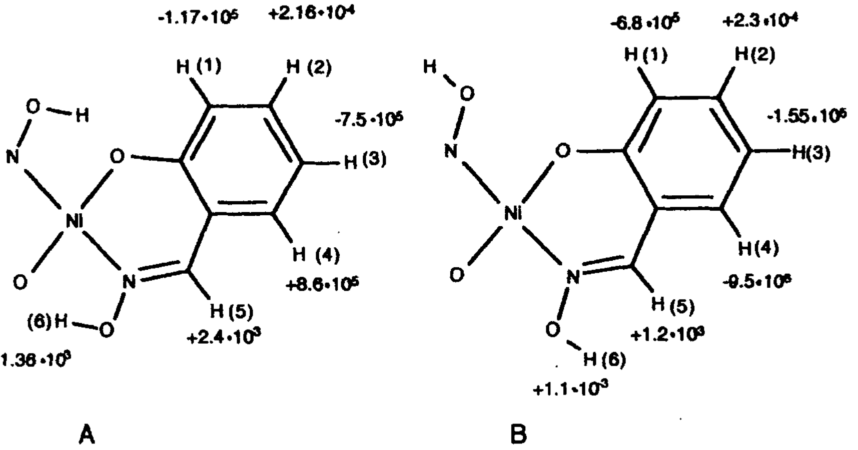


FIGURE 4 Spin density distributions in the 'closed' (A) and 'open' (B) configurations of the oxime group in $Ni(Saldox)_2\cdot2DMSO$ adducts.

Molecular orbital calculations on the hydrogen bonded or "closed" structure of $Ni(Saldox)_2\cdot2DMSO$, generally assumed for oxime complexes of transition metals, (Table II, Figure 4A) show that the spin densities on NOH and HCN protons (corresponding to the most shifted lines in PMR spectra) must be of opposite signs (-1.36×10^{-3} on NOH and $+2.4\times10^{-3}$ on HC=N). This contradicts the observed positive contact shifts of both these protons. On the other hand, in a non-bonded or "open" structure, Figure 4B, calculated spin densities on both these protons are positive and practically equal ($+1.1\times10^{-3}$ on NOH and $+1.2\times10^{-3}$ on HCN; Figure 4, Table II).

The experimental hyperfine coupling constants for these protons differ significantly (2.34 and 0.602 MHz) and therefore the 'open' structure does not fit the experimental data *quantitatively*. These facts might indicate an equilibrium between open and closed configurations of $Ni(Saldox)_2$ in DMSO adducts in solution. In fact, the experimental data can be described as resulting from a linear combination of spin densities in 'open' and 'closed' structures with a regression error of ±0.103 MHz and estimates of $A_H = 1522\pm6.5$ MHz and fraction of the open structure $0.71\pm.03$. However, the same accuracy of regression (0.098 MHz) can be achieved with the spin densities in the adduct containing four DMSO molecules, two of them ligating the Ni^{2+} ion and another two hydrogen bonded to the oxime group (last column in the Table II, Figure 5). The estimate of A_H obtained with these spin densities is 1129 ± 45 MHz, which is a reasonable value, slightly lower (as it should be) than A_H in a hydrogen atom.

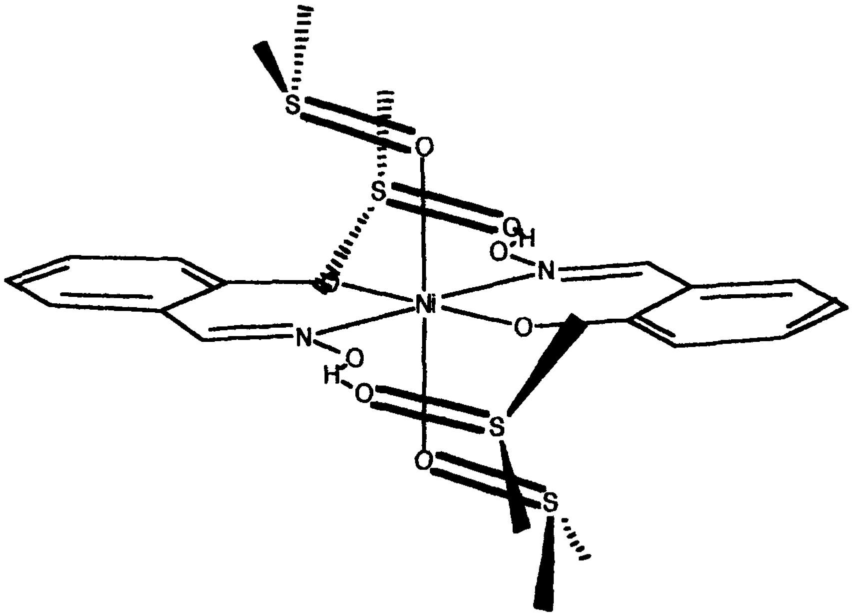


FIGURE 5 Optimised structure of the Ni(Saldox)$_2$·4DMSO complex.

In the structure of Ni(Saldox)$_2$·4DMSO obtained by HyperChem ZINDO/1 geometry optimisation shown in the Figure 5, hydrogen bonding of the NOH proton with DMSO stabilises the 'open' conformation of the oxime group. In the absence of strong donors (in non-polar solvents) this group forms intramolecular H-bonds which stabilise the square-planar structure of diamagnetic Ni(Saldox)$_2$. A peculiar characteristic of the DMSO solvate of Ni(Saldox)$_2$ is that S–O bonds of four DMSO molecules are oriented pairwise and anti-parallel (see Figure 5) which indicates the importance of electric dipole–dipole interactions in this system.

Acknowledgements

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