axial perturbation to a stronger axial perturbation. Energywise less and less CFSE is gained by electron pairing; therefore, the high-spin state becomes more favored. It should be easier for pyridine to unpair electrons for a weak in-plane field than for a strong in-plane field because Δ is smaller. Consequently, one might argue that (1) Ni(salen) is diamagnetic in pyridine because of the strong ligand field presented by salen, (2) Ni(salophen) is partially paramagnetic because salophen presents a weaker field arising from the lower coordinating ability of the imine nitrogen atoms which are in conjunction with the aromatic ring systems, and (3) Ni(Xsaldien) is fully paramagnetic and pseudooctahedral in pyridine since Xsaldien should present the weakest in-plane ligand field in that five atoms join the imine nitrogens. Alternatively the secondary nitrogen atom may present some small degree of axial perturbation, the degree being limited by the steric requirements of the ligands and the metal–ligand distance. For metal–donor atom distances of 2.3–2.5 Å, saldien has been shown to function as a planar pentadentate ligand with a stable noneclipsed conformation of its aliphatic chain.[22] This conformation is not anticipated for first-row transition ions since the metal to donor atom distance is approximately 2.0 Å. The extent of this perturbation is difficult to measure but it would seem that it becomes more pronounced if a donor occupies the other axial position. That the pyridine adduct of Ni(5-Br(saldien)) shows a sharp N–H stretch in the infrared spectrum supports the postulate.

The suggested weaker in-plane field for Ni(Xsaldien) lends credence to our contention that the anomalous magnetic moments in the solid state may arise from a thermal population of singlet and triplet states.

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[22] M. N. Akhtar, E. D. McKenzie, R. E. Paine, and A. J. Smith, *Inorg. Nucl. Chem. Lett.*, **5**, 673 (1969).

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An Investigation of the Diamagnetic–Paramagnetic Equilibrium of Two Nickel(II)–Schiff Base Complexes in Several Coordinating Solvents

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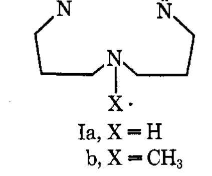
The temperature dependence of the diamagnetic–paramagnetic equilibrium of the Schiff base complex of nickel(II) with the quadridentate ligand 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene has been studied in water, methanol, *N,N*-dimethylformamide, dimethyl sulfoxide, and acetonitrile. Observations disclose that the diamagnetic form of the complex is thermodynamically favored at higher temperatures. The equilibrium was quantitatively characterized by studies of the magnetic susceptibility and chemical shift of the ligand azomethine methyl resonance. Equilibrium parameters are consistent with a square-planar–octahedral structural change accompanying the spin-state change. Similar measurements in water and *N,N*-dimethylformamide were performed on the analogous complex in which a methyl group replaces the secondary amine hydrogen in the macrocyclic ligand.

Introduction

This paper reports the results of a study of the diamagnetic–paramagnetic equilibrium for the solvated nickel(II) complex of 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene (Ia), henceforth referred to as $NiCR^{2+}$, and its methylated analog, Ib, $NiCRCH_3^{2+}$.



Ia, X = H
b, X = CH_3

The study of this equilibrium was necessary in order to interpret the solvent nmr line broadening properties of these nickel(II) complexes.[1] The diamagnetic–paramagnetic equilibrium has been studied as a function of temperature in water, methanol, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile. The changes in magnetic susceptibility and in ligand proton contact shift have been measured.

The presence of a diamagnetic–paramagnetic equilibrium in the $NiCR^{2+}$ system is not surprising in view of the observations of Busch and Karn[2–4] on these systems in the solid state. Similar results on complexes less closely related to those studied here have been reviewed recently by Barefield, Busch, and Nelson.[4]

Several types of reactions have been associated with the diamagnetic–paramagnetic change in nickel(II) complexes. In the solid state, where ligand movement is restricted, a simple equilibrium between electronic

[1] L. Rusnak and R. B. Jordan, in preparation.
[2] J. L. Karn and D. H. Busch, *Nature* (*London*), **211**, 160 (1966).
[3] D. H. Busch, *Advan. Chem. Ser.*, **No. 62**, 616 (1967).
[4] E. K. Barfield, D. H. Busch, and S. M. Nelson, *Quart. Rev., Chem. Soc.*, **22**, 457 (1968).

states exists. For tetragonally distorted nickel(II) this would take the form

$$\mathrm{NiA_4X_2(^1A_{1g})} \rightleftharpoons \mathrm{NiA_4X_2(^3B_{1g})} \qquad (1)$$

Such equilibria normally have small values for $\Delta H°$ ($\sim$1 kcal mol^{-1}) and $\Delta S°$ ($\sim$1 cal mol^{-1} deg^{-1}).

In solution a square-planar–octahedral interconversion may occur according to the reaction

$$\underset{S\,=\,0}{\mathrm{NiA_4}} + 2\mathrm{X} \rightleftharpoons \underset{S\,=\,1}{\mathrm{NiA_4X_2}} \qquad (2)$$

For Ni(CRH)$^{2+}$ in water with X = H_2O, the $\Delta H°$ and $\Delta S°$ values[3] for equilibrium 2 are -4.5 kcal mol^{-1} and -16 cal mol^{-1} deg^{-1}. Recently Kannan and Chakravorty[5] studied a series of 2-hydroxyacetophenimine complexes of nickel(II), with X = pyridine, and found $\Delta H°$ values of -4 to -11 kcal mol^{-1} and $\Delta S°$ values of -25 to -39 cal mol^{-1} deg^{-1}.

Several systems[4,6] have been found to exhibit the equilibrium

$$\underset{S\,=\,0}{n\mathrm{NiA_4(monomer)}} \rightleftharpoons \underset{S\,=\,1}{\mathrm{(NiA_4)_{\mathit{n}}\ associated\ species}} \qquad (3)$$

Such equilibria are characterized by their concentration dependence and sensitivity to steric factors in the A_4 ligand(s).[7]

A final type of equilibrium (eq 4) involving a structural and spin change has been observed. The tetrahedral species can normally be detected from the characteristic electronic spectrum. Such an equilibrium seems unlikely with the fused-ring quadridendate ligands since it requires considerable ligand distortion. Therefore equilibrium 4 has not been considered further here.

$$\underset{S\,=\,0}{\mathrm{NiA_4(planar)}} \rightleftharpoons \underset{S\,=\,1}{\mathrm{NiA_4(tetrahedral)}} \qquad (4)$$

Experimental Section

Preparation and Characterization of Compounds.—$\mathrm{NiCRCl_2}$ was prepared from stoichiometric amounts of $\mathrm{NiCl_2 \cdot 6H_2O}$, diacetylpyridine, and 3,3′-diaminodipropylamine, using Curry's procedure, as described by Karn and Busch.[2] The product was recrystallized from warm water.

The hexafluorophosphate salt, which is much less water soluble than the chloride, was prepared by mixing saturated aqueous solutions of $\mathrm{NiCRCl_2}$ and $\mathrm{NaPF_6}$. The yellow product was recrystallized from aqueous solution.

The very water-soluble tetrafluoroborate salt was prepared by mixing saturated solutions of $\mathrm{AgBF_4}$[8] and $\mathrm{NiCRCl_2}$. The AgCl was removed by filtration and the resultant solution was evaporated under vacuum until crystallization commenced. The solution was cooled and the product was collected by filtration and then recrystallized twice from aqueous solution. Alternatively the tetrafluoroborate salt was prepared by using $\mathrm{Ni(BF_4)_2 \cdot 6H_2O}$ in place of $\mathrm{NiCl_2 \cdot 6H_2O}$ in the original condensation reaction. Some care is necessary in the latter method since overheating or prolonged reaction time results in a mixture of fluoride and tetrafluoroborate salts. The dried tetrafluoroborate salt was brick red.

$\mathrm{NiCR(ClO_4)_2}$ and $\mathrm{NiCR(NO_3)_2}$ were prepared as described by Karn and Busch.[2]

$\mathrm{NiCRCH_3Cl_2}$ was prepared by the same procedure as that used for $\mathrm{NiCRCl_2}$, except that the amine 3,3′-diamino-*N*-methyldipropylamine was used. The perchlorate and tetrafluoroborate salts were prepared by methods analogous to those described above.

All of the salts were dried under vacuum over P_4O_{10} until the resolved OH stretching bands at 3500–3600 cm^{-1}, in Nujol, had disappeared from the infrared spectrum. The compounds were characterized by carbon, hydrogen, and nitrogen analyses given in Table I and by their infrared, electronic, and nmr spectra.

TABLE I

MICROANALYTICAL RESULTS

Compound	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
$\mathrm{NiCR(PF_6)_2}$	29.70	29.67	3.65	3.90	9.23	9.19
$\mathrm{NiCR(BF_4)_2}$	36.71	36.57	4.52	4.55	11.41	11.71
$\mathrm{NiCR(ClO_4)_2}$	34.77	34.91	4.24	4.26	10.93	10.86
$\mathrm{NiCRCH_3(BF_4)_2}$	38.15	38.01	4.80	4.70	11.13	10.70
$\mathrm{NiCRCH_3(ClO_4)_2}$	35.26	35.86	4.56	4.51	10.58	10.70
$\mathrm{NiCR(DMF)_2(PF_6)_2}$	33.50	33.11	4.83	4.85	11.15	11.31

Infrared Measurements.—The infrared spectra of $\mathrm{NiCR(BF_4)_2}$, $\mathrm{NiCR(ClO_4)_2}$, and $\mathrm{NiCR(PF_6)_2}$ in Nujol mulls are identical except for bands characteristic of the anion. Band positions are in general agreement with those reported by Rich and Stucky[9] for $\mathrm{NiCR(ZnCl_4)}$. However, their spectra in KBr show a water absorption at 3380 cm^{-1} and fail to show the sharp N–H stretching absorption at 3230 cm^{-1} observed in the present work. The complex absorption due to C=N stretching and pyridine ring vibrations, in the 1575–1595-cm^{-1} region, has been observed in this and the previous work.

The infrared spectrum of $\mathrm{NiCRCH_3(BF_4)_2}$ was almost identical with that of $\mathrm{NiCR(BF_4)_2}$ except for the absence of the N–H stretching absorption at 3230 cm^{-1}, as expected since this is now an *N*-CH_3 group. There is an additional peak at 1245 cm^{-1}, consistent with a C–N stretching vibration, and two different sharp peaks at 850 and 780 cm^{-1}.

Electronic Spectral Measurements.—The peak maxima and molar extinction coefficients for $\mathrm{NiCR(BF_4)_2}$ and $\mathrm{NiCR(PF_6)_2}$ in water are given in Table II. The results for $\mathrm{NiCR(BF_4)_2}$ are in good agreement with those given by Rich and Stucky,[9] except that the latter workers did not observe the band at 720 nm. Measurements on the perchlorate and nitrate salts at 396 nm gave extinction coefficients of 127 and 122 M^{-1} cm^{-1}, respectively, in agreement with the value for the BF_4^- salt.

TABLE II

ELECTRONIC SPECTRUM OF $\mathrm{NiCR^{2+}}$ IN AQUEOUS SOLUTION (25°)

Band position, nm	Extinction coeff, M^{-1} cm^{-1} $\mathrm{NiCR(BF_4)_2}$	Extinction coeff, M^{-1} cm^{-1} $\mathrm{NiCR(PF_6)_2}$
720	25.0	. . .[a]
396	124	148
300 sh	2.26×10^3	2.32×10^3
266	5.14×10^3	5.20×10^3
230	1.54×10^4	1.56×10^3

[a] The salt is too insoluble for this extinction coefficient to be measured.

It should be noted however that the extinction coefficient of the PF_6^- salt at 396 nm is significantly greater than that of the BF_4^- salt. Recrystallization of the PF_6^- salt and addition of F^- or PF_6^- to solutions of the BF_4^- salt failed to affect the extinction coefficient. Since both salts were derived from the same $\mathrm{NiCRCl_2}$ source and since the extinction coefficients agree at other wavelengths, an impurity seems unlikely. No adequate explanation has been found for this phenomenon, but both the ClO_4^- and PF_6^- salts gave identical nmr results in DMF. Also the results of the nmr study on the BF_4^- and ClO_4^- salts in water were in agreement.

The spectrum of the $\mathrm{NiCRCH_3(BF_4)_2}$ in water at 25° is similar to that of $\mathrm{NiCR(BF_4)_2}$. There are maxima at 750 and 396 nm with extinction coefficients of 12.7 and 595 M^{-1} cm^{-1}, respectively. The same values were obtained for $\mathrm{NiCRCH_3(ClO_4)_2}$ in water. The large difference in extinction coefficients at 396 nm between $\mathrm{NiCR^{2+}}$ and $\mathrm{NiCRCH_3^{2+}}$ is mainly due to the greater percentage of diamagnetic species present in the latter system at 25°.

The nmr and magnetic susceptibility studies show that only the diamagnetic form of the complexes is present in trifluoroethanol. In this solvent the visible spectra of $\mathrm{NiCR(BF_4)_2}$,

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(5) T. S. Kannan and A. Chakravorty, *Inorg. Chem.*, **9**, 1153 (1970).

(6) R. H. Holm, *J. Amer. Chem. Soc.*, **83**, 4683 (1961).

(7) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962).

(8) The $AgBF_4$ solution was prepared by addition of 25% HBF_4 to silver carbonate until neutralization was complete.

(9) L. R. Rich and G. L. Stucky, *Inorg. Nucl. Chem. Lett.*, **1**, 61 (1965).

$NiCR(ClO_4)_2$, and $NiCR(PF_6)_2$ show a maximum at 390 nm with extinction coefficients of 1.40×10^3, 1.32×10^3, and 1.44×10^3 M^{-1} cm^{-1}, respectively. Under the same conditions $NiCRCH_3(ClO_4)_2$ and $NiCRCH_3(BF_4)_2$ also show a maximum at 390 nm with extinction coefficients of 1.36×10^3 and 1.30×10^3 M^{-1} cm^{-1}, respectively.

It is clear from these results that the absorbance at 396 nm in aqueous solutions is strongly affected by the diamagnetic species. The temperature variations of the visible spectra, to be discussed later, are consistent with this assignment.

Pmr Measurements.—When either $NiCR(BF_4)_2$ or $NiCRCH_3(BF_4)_2$ is dissolved in trifluoroacetic acid, nitromethane-d_3, or trifluoroethanol, the macrocyclic ligand pmr spectrum of the diamagnetic complex is observed. The spectra are shown in Figure 1. The A_2B multiplet centered at $\tau \sim 2$ is due to the pyridine ring protons and the peak at τ 7.46 is readily assigned to the two equivalent CH_3 groups. The amine CH_3 in $NiCRCH_3^{2+}$ is observed at τ 6.85. The integrated intensities of the peaks are completely consistent with this assignment. These chemical shifts are assigned to the pure diamagnetic form since they are independent of the noncoordinating solvent used and also temperature independent over the range −42 to +82° in trifluoroethanol.

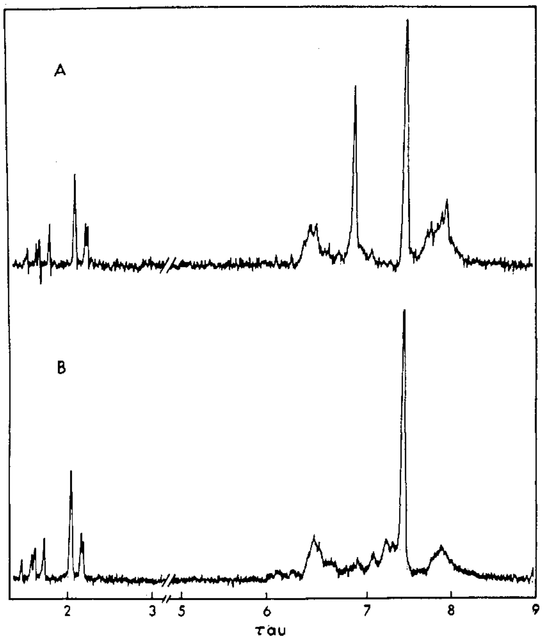

Figure 1.—The nmr spectra, at 60 MHz, of (A) $NiCRCH_3(BF_4)_2$ and (B) $NiCR(BF_4)_2$ in trifluoroacetic acid.

When the complexes were dissolved in the various coordinating solvents used in this study, it was found that the macrocyclic ligand proton chemical shift became very temperature dependent, indicating a temperature-dependent diamagnetic–paramagnetic equilibrium. For a solution of $NiCR(PF_6)_2$ in DMF at 60° the pyridyl proton resonances appeared downfield, while the azomethine methyl protons and two types of CH_2 from the dipropylamine portion of the molecule were shifted upfield, the latter more than the former, relative to their positions in the diamagnetic species. Measurements of the temperature dependence of the shift of the sharpest resonance, due to the azomethine methyl protons, were used to determine the position of the equilibrium. The chemical shift in trifluoroacetic acid was taken as that of the pure diamagnetic form. All shifts were found to be independent of concentration at least in the range 0.3–0.8 m studied. The accuracy of the shift measurements was generally controlled by the line width and is estimated to vary from ±2 Hz at the higher temperatures to ±10 Hz at lower temperatures.

Magnetic Susceptibility Measurements.—These were performed by Evans' nmr method,[10,11] using precision-made coaxial tubes (Wilmad Glass Co.). Cyclopentane was used as an internal standard in methanol and N,N-dimethylformamide, while TMS was used in acetonitrile and dimethyl sulfoxide. For aqueous solutions t-butyl alcohol or DSS (sodium 3-trimethylsilyl-1-propanesulfonate) served as the internal standard. The internal standard was at a concentration of approximately 5% by volume. In this range the measurements were found to be independent of internal standard concentration. The concentration of the nickel complex was chosen so that shifts of 25–75 Hz were observed, and at least two different concentrations were used in all cases. No concentration dependence of the normalized molal shifts was observed when the concentration was varied by approximately a factor of 2.

Molar susceptibilities were calculated from eq 2 of ref 10, which can be rewritten in the form

$$\chi_M = \left(\frac{3\Delta f}{2\pi f_0 m M \rho_t \times 10^{-3}} + \chi_0\right) M \qquad (5)$$

where Δf is the susceptibility shift in hertz, f_0 is the spectrometer operating frequency (60 MHz), m is the solute molality, ρ_t is the solution density at t°C, M is the solute molecular weight, and χ_0 is the solvent diamagnetic susceptibility in cgs units. The value of χ_0 was estimated from Pascal constants when measured values were not available. The χ_M values were corrected for the macrocyclic ligand diamagnetic susceptibility (-162.7×10^{-6} cgs unit).

Sample Preparation.—Nonaqueous solvents were purified by double distillation from molecular sieves and then stored over molecular sieves.

Samples were prepared and sealed off under vacuum using standard techniques. $NiCR(PF_6)_2$ was used in DMF, DMSO, and acetonitrile, but because of solubility limitations, $NiCR(BF_4)_2$ was used in methanol and water. In the case of $NiCRCH_3^{2+}$ the tetrafluoroborate salt was used in water, and the perchlorate salt, in DMF. All of the salts of $NiCRCH_3^{2+}$ which were prepared proved to be too insoluble in methanol to permit a study in this solvent.

Instrumentation.—Electronic spectra were measured on a Cary 14 spectrometer. The nmr spectra were recorded on a Varian A56/60 spectrometer equipped with a Model 4343 temperature controller. Temperatures were determined from the peak to peak separation of methanol or ethylene glycol and calibration charts provided by Varian Associates.

Results

Preliminary studies on the $NiCR^{2+}$ system in water indicated that the visible spectrum was highly temperature dependent. For example, the extinction coefficient at 396 nm undergoes a reversible change from 76 M^{-1} cm^{-1} at 5° to 272 M^{-1} cm^{-1} at 59.5°. This type of observation indicates that an equilibrium exists in the system but is of little help in defining the type of change which is occurring. Therefore, studies of the temperature dependence of the magnetic susceptibility and of the ligand proton chemical shifts were undertaken. These studies show unambiguously that a diamagnetic–paramagnetic equilibrium exists, with the diamagnetic form being favored at higher temperatures. The equilibrium constants have been determined from both the shift and susceptibility measurements. The accuracy of this determination is limited primarily by the inability to obtain the shift or susceptibility of the pure paramagnetic form.

Magnetic Susceptibility.—If the diamagnetic–paramagnetic equilibrium is represented by

$$\mathrm{D}\ (S = 0) \rightleftharpoons \mathrm{P}\ (S = 1) \qquad (6)$$

then the equilibrium constant is given by

$$K = \frac{[\mathrm{P}]}{[\mathrm{D}]} = \exp\left(\frac{-\Delta H^\circ + T\Delta S^\circ}{RT}\right) \qquad (7)$$

The molar magnetic susceptibility can be expressed as

$$\chi_M = \frac{\mu_\infty^2 N}{3k(T + \Theta)\{1 + \exp[(\Delta H^\circ - T\Delta S^\circ)/RT]\}} \qquad (8)$$

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[10] D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

[11] H. P. Fritz and K. E. Schwarzhans, *J. Organometal. Chem.*, **1**, 208 (1964).

TABLE III

LEAST-SQUARES BEST FIT PARAMETERS OF THE MAGNETIC SUSCEPTIBILITY DATA

		Fit A[a]			Fit B[b]			Fit C[c]		
Complex	Solvent	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} deg^{-1}	μ_∞, BM	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} deg^{-1}	Θ, °K	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal mol^{-1} deg^{-1}	Θ, °K
$NiCR(BF_4)_2$	Water	−7.29	−19.1	2.28	−6.97	−18.3	35.3	−6.81	−17.7	35.3
$NiCR(BF_4)_2$	Methanol	−4.63	−12.6	2.91	−4.26	−11.5	11.0	−5.00	−13.1	34.7
$NiCR(PF_6)_2$	Acetonitrile	−4.28	−11.1	2.99	−4.28	−11.0	2.3	−4.90	−11.8	25.1
$NiCR(PF_6)_2$	DMF	−3.53	−6.8	3.00	−3.50	−6.7	0.4	−4.20	−7.1	15.9
$NiCR(PF_6)_2$	DMSO	−4.71	−9.3	2.95	−4.60	−9.2	9.7	−6.00	−11.1	16.8
$NiCRCH_3(BF_4)_2$	Water	−5.31	−17.0	2.62	−4.58	−15.3	35.3[d]	−4.58	−15.3	35.3[d]
$NiCRCH_3(ClO_4)_2$	DMF	−4.47	−10.0	2.91	−4.06	−9.1	12.4	−6.40	−14.0	18.0

[a] Fitted to eq 8 with $\Theta = 0$. [b] Fitted to eq 8 with $\mu_\infty = 3.00$ BM for each system. The data do not permit an independent determination of Θ and μ_∞. [c] Fitted as in B but with a density correction taken from the pure solvent included. [d] Θ fixed at 35.3°, as obtained from $NiCR(BF_4)_2$ in water, since the three-parameter fit gave an unreasonable value of $\Theta = 78.5$°K, with $\Delta H° = -5.32$ kcal mol^{-1} and $\Delta S° = -17.2$ cal mol^{-1} deg^{-1}.

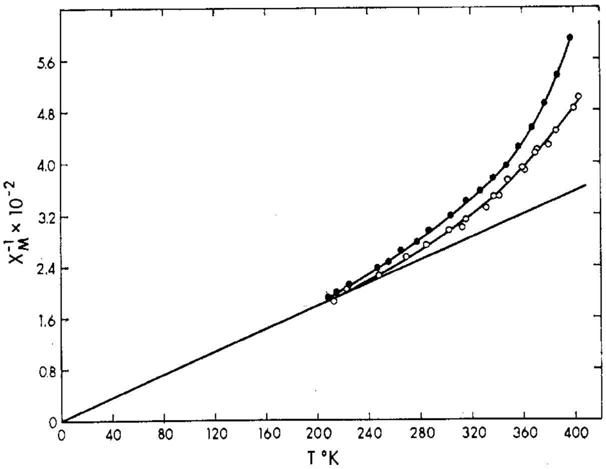

Figure 2.—Variation of the reciprocal of the magnetic susceptibility with temperature, in DMF, for 8.05 × 10^{-2} *m* $NiCRCH_3(ClO_4)_2$ (●) and 6.55 × 10^{-2} and 1.67 × 10^{-1} *m* $NiCR(PF_6)_2$ (O). The straight line represents the limiting paramagnetic susceptibility, assuming a Curie law dependence with $\mu_\infty = 3.00$ BM.

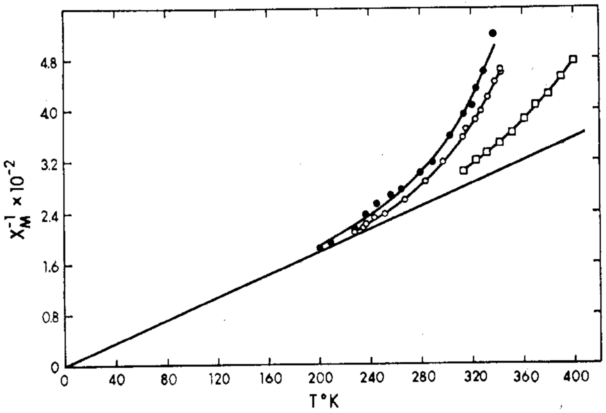

Figure 3.—Variation of the reciprocal of the magnetic susceptibility with temperature for 9.52 × 10^{-2} and 1.06 × 10^{-1} *m* $NiCR(BF_4)_2$ in methanol (●), for 1.03 × 10^{-1} and 1.23 × 10^{-1} *m* $NiCR(PF_6)_2$ in acetonitrile (O), and for 1.24 × 10^{-1} *m* $NiCR(PF_6)_2$ in DMSO (□). The straight line is the same as in Figure 1.

where μ_∞ is the magnetic moment of the paramagnetic species, *N* is Avogadro's number, and Θ is the Weiss constant. A Curie–Weiss temperature dependence is assumed for μ_∞ since previous work[2,4] provides some guidelines as to likely Θ values. Alternatively, a temperature-independent term may be added to eq 8 with $\Theta = 0$; however the two procedures are equivalent from the point of view of fitting the data, as long as $T \gg \Theta$.

The results of the susceptibility measurements are shown in Figures 2–4. A nonlinear least-squares fit[12] of the χ_M data to eq 8 would not give reasonable values for all the parameters—μ_∞, Θ, $\Delta H°$, and $\Delta S°$. However, fits to within the estimated experimental error of the χ_M values could be obtained using the assumptions summarized in Table III.

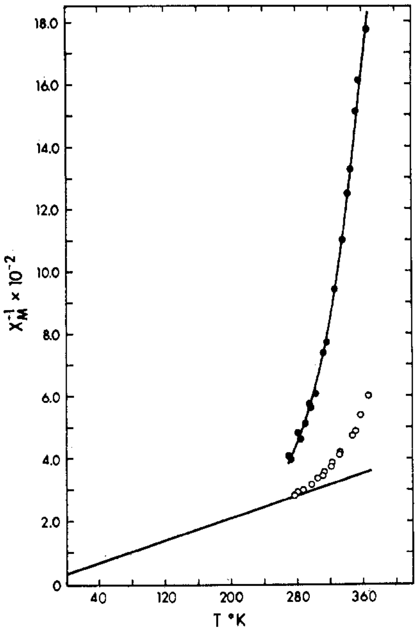

Figure 4.—Variation of the reciprocal of the magnetic susceptibility with temperature, in water, for 0.151 and 0.173 *m* $NiCR(BF_4)_2$ (O) and 0.162 and 0.232 *m* $NiCRCH_3(BF_4)_2$ (●). The straight line is calculated assuming a Curie–Weiss temperature dependence with $\Theta = 35.3$°.

In fit C of Table III an attempt was made to account for the changing solution density (eq 5) with temperature. Temperature–density functions of the pure solvents were used. The resulting $\Delta H°$ and $\Delta S°$ values do not agree with those from the chemical shift study. It would appear that the use of pure solvent densities for solutions containing from ~0.05 to ~0.2 *M* complex and ~5% of internal standard is not at all justified.

Ligand Proton Chemical Shifts.—The temperature dependence of the chemical shift of the azomethine

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(12) IBM Share Library Program, SDA 3094, 1964.

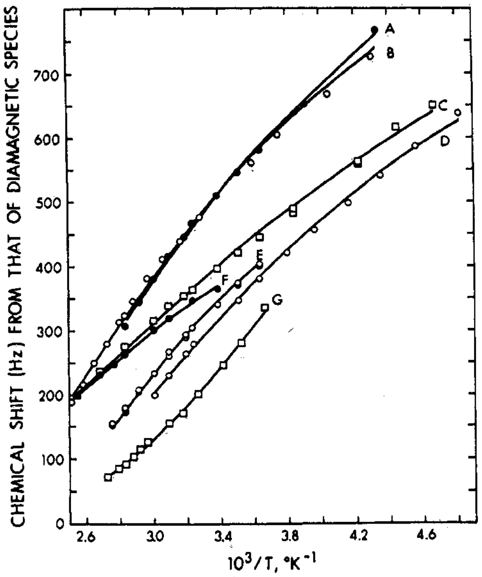

Figure 5.—Temperature dependence of the chemical shifts of the azomethine methyl protons for $NiCR^{2+}$ in CH_3CN (A), $NiCRCH_3^{2+}$ in DMF (B), $NiCR^{2+}$ in DMF (C), $NiCR^{2+}$ in CH_3OH (D), $NiCR^{2+}$ in H_2O (E), $NiCR^{2+}$ in DMSO (F), and $NiCRCH_3^{2+}$ in H_2O (G). The smooth curves are calculated from parameters in Table IV.

methyl protons (Figure 5) also has been used to measure the equilibrium constant for eq 6. If only the Fermi contact contribution to the shift is considered,[13] then eq 40 of ref 14 can be used to obtain

$$\Delta\omega_p = \frac{A}{\hbar}\left(\frac{\bar{g}\beta(S)(S+1)\omega_0}{3kT\gamma_I}\right)\left(\frac{T-\Delta}{T}\right) \times \left(1 + \exp\left(\frac{\Delta H^\circ - T\Delta S^\circ}{RT}\right)\right)^{-1} \qquad (9)$$

where $\Delta\omega_p$ is the measured chemical shift relative to that in the diamagnetic form, $A/\hbar$ is the coupling constant in radians per second, ω_0 is the operating frequency of the nmr spectrometer, and γ_I is the magnetogyric ratio of the proton. The third quantity in eq 9 is obtained by rearrangement of the expression given by Kurland and McGarvey,[14] with $\Delta = ((g_{\parallel} - g_{\perp})D/9\bar{g}k)$, where D is the zero-field splitting energy and $\bar{g} = {}^1/_3(g_{\parallel} + 2g_{\perp})$. When $\Delta = 0$, eq 9 reduces to the form normally used to fit contact shifts.[15]

The results of the nonlinear least-squares fits for the different systems are summarized in Table IV. The ΔH° and ΔS° values are in good agreement with those of fit B of Table III but not in such good agreement with fit C of Table III. This would tend to indicate that the density corrections applied in fit C are incorrect, for reasons outlined at the end of the previous section.

The effect of a non-Curie temperature dependence of the magnetic susceptibilities may be tested using the expression for the magnetic susceptibility of an $S = 1$ system, given by Kurland and McGarvey[16] to be

$$\bar{\chi} = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}) = \frac{2\bar{g}^2\beta^2}{3kT}\left(\frac{T - \Delta'}{T}\right) \qquad (10)$$

where $\bar{g}^2 = {}^1/_3(g_{\parallel}{}^2 + 2g_{\perp}{}^2)$ and $\Delta' = (g_{\parallel}{}^2 - g_{\perp}{}^2)D/k\bar{g}^2$. The Curie–Weiss law for the susceptibility may be written as

$$\chi = \frac{C}{T(1 + (\Theta/T))} \approx \frac{C}{T}(1 - (\Theta/T))$$

and then

$$\chi \approx \frac{C}{T}\left(\frac{T - \Theta}{T}\right) \qquad (11)$$

therefore the Weiss constant Θ can be identified with Δ'. In the absence of the g values, a relationship for Δ in terms of Θ cannot be obtained, but it can be shown that

$$\frac{\Delta'}{\Delta} = \frac{\Theta}{\Delta} = 1 + 3\left(\frac{g_{\parallel}}{g_{\perp}} + \frac{2g_{\perp}}{g_{\parallel}}\right)^{-1} \qquad (12)$$

In the limit of a completely isotropic case $\Delta = 0.5\Theta$ and it seems very unlikely that $\Delta > 0.67\Theta$. The data for the water systems which have the largest Θ values were refitted to eq 9 assuming $\Delta = 0.67\Theta$. The results for $NiCR^{2+}$ are $\Delta H^\circ = -5.92$ kcal mol^{-1} and $\Delta S^\circ = -16.7$ cal mol^{-1} deg^{-1}, and for $NiCRCH_3^{2+}$ $\Delta H^\circ = -4.61$ kcal mol^{-1} and $\Delta S^\circ = -15.2$ cal mol^{-1} deg^{-1}. These values for $NiCR^{2+}$ are in poorer agreement with those from fit C, and the $NiCRCH_3^{2+}$ values are essentially unaffected. The overall fit was not significantly improved. Therefore it appears that inclusion of Δ in eq 9 will not significantly affect the results or improve the agreement with the results of fit C.

TABLE IV

LEAST-SQUARES BEST FIT PARAMETERS OF THE CHEMICAL SHIFT DATA[a]

Complex	Solvent	ΔH°, kcal mol^{-1}	ΔS°, cal mol^{-1} deg^{-1}	$10^{-5}A/\hbar$,[b] radians sec^{-1}
$NiCR(BF_4)_2$	Water	−6.39	−17.9	−5.49
$NiCR(BF_4)_2$	Methanol	−4.09	−12.2	−6.20
$NiCR(PF_6)_2$	Acetonitrile	−4.16	−10.8	−8.26
$NiCR(PF_6)_2$	DMF	−3.27	−7.7	−6.57
$NiCR(PF_6)_2$	DMSO	−4.47	−10.0	−5.49
$NiCRCH_3(BF_4)_2$	Water	−4.60	−15.1	−5.91
$NiCRCH_3(ClO_4)_2$	DMF	−4.85	−12.6	−8.07

[a] Fitted to eq 9 with $\Delta = 0$. [b] Calculated assuming $\bar{g}\sqrt{S(S+1)} = 3.00$ in eq 9.

It is somewhat difficult to estimate the likely errors in ΔH° and ΔS° because of the various approximations required and the number of parameters needed to fit the data. The ligand chemical shift results are least subject to these problems and experience with the fitting indicates an error of ±0.5 kcal mol^{-1} on ΔH° and ±1 cal mol^{-1} deg^{-1} on ΔS°. These errors are also consistent when the results of the susceptibility and shift studies are compared.

Discussion

The values of ΔH° and ΔS° obtained for the diamagnetic–paramagnetic equilibrium are generally similar to those found previously[3–5] for a square-planar–octahedral[17] equilibrium as indicated by eq 2. The lack of any concentration dependence for the equilibrium indi-

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[13] It has been argued, in ref 14 for example, that the pseudocontact contribution should be small. The pseudocontact shift has mainly a $1/T$ temperature dependence with only a small $1/T^2$ term.[14] Therefore the omission of the pseudocontact contribution should not affect values of ΔH° and ΔS° but would affect the $A/\hbar$ values.

(14) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

(15) R. H. Holm, *Accounts. Chem. Res.*, **2**, 307 (1969).

(16) B. Kurland (private communication) has pointed out that eq 10 neglects any rhombic distortion and uses an approximate relationship between the g-tensor anisotropy and the zero-field splitting constant.

(17) It is possible that the paramagnetic form is only five-coordinate; however the isolation of $NiCR(DMF)_2(PF_6)_2$ (Table I) provides some indirect evidence for the octahedral formulation in addition to visible spectral evidence.

cates that association as shown by eq 3 is not occurring. Furthermore, the absence of temperature-dependent shifts of the ligand proton resonances in inert solvents argues against the formation of associated species in coordinating solvents.

It would be expected that solvating power, steric effects, and solvent $10Dq$ might be contributing factors to the $\Delta H°$ values. However, except for $NiCR^{2+}$ in water and DMF the $\Delta H°$ and $\Delta S°$ values are quite similar, being about 4.4 ± 0.4 kcal mol^{-1} and 12 ± 3 cal mol^{-1} deg^{-1}, respectively. Therefore it seems probable that a number of compensating factors may be at work and a qualitative analysis of the $\Delta H°$ values would be futile.

The $\Delta H°$ value for $NiCR^{2+}$ in water is the most negative, consistent with the recent proposal by Busch[8] that solvent structure breaking is an important factor. However $NiCRCH_3^{2+}$ in water has a rather normal $\Delta H°$ and it seems unlikely that introduction of a methyl group on the Schiff base would have a significant effect on the solvent structure.

The hyperfine coupling constants ($A/\hbar$) in Table IV have all been calculated with the assumption that $\mu_\infty = \bar{g}\sqrt{S(S+1)} = 3.00$ BM. It would seem likely that this assumption is good to within at least ±5% and therefore the variations in $A/\hbar$ for different systems are real. The nature of the axial ligand, solvation of the octahedral complex, and minor changes in geometry of the macrocyclic ligand are likely to affect $A/\hbar$. Therefore the observed variations are not considered to be unusual.

Finally it should be noted that the equilibrium constant parameters were determined for use in a study of the bulk solvent nmr in these systems. The values reported here have served adequately to correct both the solvent proton chemical shifts and line broadenings. The results of the latter study will be reported in a subsequent paper.[1]

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Monohalo Tridentate Nickel(II) Complexes

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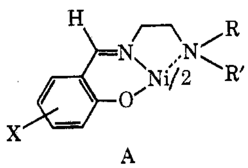
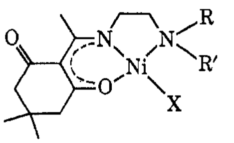
Neutral monohalo tridentate nickel(II) complexes have been synthesized and their magnetic and spectral properties described in which the halo (or pseudohalo) group is Cl, Br, or NCS and the tridentate ligand is an *N*-β-R,R′-aminoethyl-2-acetiminodimedonato or -2-formyldimedonato anion with R = R′ = alkyl or R = H, R′ = alkyl. According to the magnetic moment values, the ligand field, and pmr spectra, intermolecular interaction occurs for some of the complexes in the solid state and in chloroform solution, the amount of association decreasing in the order Br > Cl > NCS; formyl > acetyl; and, for the *N*-β-R,R′ substituent, $N(CH_3)_2 > N(H)CH_3 \geq N(H)C_2H_5 > N(C_2H_5)_2$. The R = H derivatives form 1:1 adducts with chloroform which have properties characteristic of high-spin, five-coordinate nickel(II) complexes. As this is the first report of neutral monohalo tridentate nickel(II) compounds, factors conducive to the formation of such nickel(II) complexes are considered.

Introduction

Numerous bis(*N*-β-R,R′-aminoethyl-X-salicylaldiminato)nickel(II) compounds, abbreviated Ni[X-Sal-en-N(R)R′]$_2$, structure A, have been investigated by Sacconi, *et al.*[1,2] We have found that the coordination of nickel(II) ions to bidentate ligands of N-substituted 2-acetiminodimedone differs significantly from that in nickel(II) chelates of N-substituted salicylaldimines;[3] therefore, we have studied nickel(II) chelates containing *N*-β-R,R′-aminoethyl-2-acetiminodimedone, abbreviated ac-Dim-en-N(R)R′ (where dimedone is 5,5-dimethyl-1,3-cyclohexanedione), the tridentate ligand in structure B.



A



B

The Ni[X-Sal-en-N(R)R′]$_2$ complexes are prepared by allowing bis(salicylaldehydato)nickel(II) dihydrate to react with the appropriate ethylenediamine. This is not applicable to the dimedone system due to the low solubility of bis(2-acetyldimedonato)nickel(II). Instead the Schiff base adduct of 2-acetyldimedone and an N-substituted ethylenediamine was prepared, and then it was treated with bis(tetraethylammonium)-tetrabromonickelate(II) in a procedure similar to the preparation of the bis(N-substituted 2-acetiminodimedonato)nickel(II) complexes.[3] The reaction yielded not only the anticipated Ni[ac-Dim-en-N(R)R′]$_2$ but also NiBr[ac-Dim-en-N(R)R′].

The latter monohalo tridentate Schiff base complexes of nickel(II) ions are novel, there being no reports of comparable NiBr[X-Sal-en-N(R)R′] compounds. Cationic species, such as $NiCl[(C_2H_5)_2NCH_2CH_2N(H)CH_2CH_2N(C_2H_5)_2]^+$, containing a nickel(II) ion bonded to a halide ion and a neutral tridentate ligand are known,[4] but we present here the first report of a neutral monohalo tridentate nickel system.

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(1) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965).

(2) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965).

(3) S. Y. Shaw and E. P. Dudek, *ibid.*, **8**, 1360 (1969).

(4) (a) Z. Dori and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 1394 (1966); (b) M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, **5**, 45 (1966).