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Temperature Dependence of Isotropic Shifts of Nickel Complexes

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Isotropic proton shifts of octahedral nickel(II) complexes with benzylamine, dimethylformamide, N,N,-dimethylacetamide, N-methylacetamide and n-propanol were determined as functions of the absolute temperature. Apparent non-Curie behavior was found for most of the isotropic shifts. Sources for this behavior were examined and the conclusions drawn are presented.

Introduction

Isotropic nmr shifts of paramagnetic transition metal complexes have been reported extensively and have frequently been assumed to be inversely proportional to the absolute temperature, *i.e.*, to show a Curie law dependence. However, non-Curie behavior, exhibited by a non-linear plot of isotropic shift versus 1/T, has been observed and attributed to structural interconversion equilibria,[2-5] conformational equilibria.[6-11] or coalescence of doublets due initially to hindered internal rotation.[12-14] A second kind of non-Curie behavior, exhibited by a linear plot of isotropic shift versus 1/T with a non-zero intercept, may arise from these same sources in certain circumstances or from temperature independent paramagnetism, hydrogen bonding,[15,16] solvent effects other than hydrogen bonding,[15] ion pair formation[17,18] or a pseudcontact shift.[19] In view of the importance of isotropic shifts in providing information on electron density and molecular structure, it is necessary to correctly identify as many contributions to the isotropic shift as possible. Here we report the temperature dependence of isotropic shifts of labile, octahedral complexes of nickel(II) with some monodentate, predominantly σ-bonding ligands in excess ligand as solvent at temperatures in the very rapid exchange region where the chemical exchange process does not contribute to the observed shift. These complexes have a non-degenerate ground state and exhibit negligible pseudocontact shift.

Experimental Section

Reagents and Solutions. Hydrated nickel(II) tetrafluoroborate (Alfa Inorganics), hydrated nickel(II) perchlorate (Alfa Inorganics), zinc tetrafluoroborate (Alfa Inorganics), anhydrous reagent grade diethyl ether (Mallinckrodt) (B and A), normal propyl alcohol (Baker Analyzed), spectroquality methanol (Matheson, Coleman, and Bell) were used without further purification. Benzylamine (Baker Analyzed) was distilled over barium oxide under reduced pressure. The constant boiling middle fraction was stored in a stoppered flask in a dessicator over P_2O_5. Eastman N,N-dimethylacetamide was stored over Linde 3A molecular sieves at least 24 hours before use. N-methylacetamide was recrystallized before use.

Solutions were prepared by weighing. Preparation of hygroscopic solutions was carried out in a nitrogen atmosphere.

Preparation of Complexes. The nickel(II) complexes with benzylamine, N, N-dimethylacetamide, N,N-dimethylformamide and N-methylacetamide, and the zinc complex with N,N-dimethylformamide were prepared by methods reported by Drago and co-workers.[20,21] The product was stored over P_2O_5 in a dessicator. All procedures were carired out in a nitrogen atmosphere, either in a glove bag or in a dry box.

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(1)Abstracted from the Ph.D. thesis of Joyce E. Jentoft, University of Minnesota, December, 1971.
(2) A. Chakravorty, V.P. Fennessey, and R.H. Holm, *Inorg. Chem.*, *4*, 26 (1965).
(3) G.N. LaMar and L. Sacconi, *J. Amer. Chem. Soc.*, *89*, 2282 (1967).
(4) J.D. Thwaites, I. Bertini, and L. Sacconi, *Inorg. Chem.*, *5*, 1036 (1966).
(5) W. DeW. Horrocks, Jr., *J. Amer. Chem. Soc.*, *87*, 3779 (1965).
(6) F.F.-L. Ho and C.N. Reilley, *Anal. Chem.*, *42*, 600 (1970).
(7) F.F.-L. Ho, L.E. Erickson, S.R. Watkins, and C.N. Reilley, *Inorg. Chem.*, *9*, 1139 (1970).
(8) C.R. Powers and G.W. Everett, Jr., *J. Amer. Chem. Soc.*, *91*, 3468 (1969).
(9) G.W. Everett, Jr., and C.R. Powers, *Inorg. Chem.*, *9*, 521 (1970).
(10) R.F. Evilia, D.C. Young, and C.N. Reilley, *Inorg. Chem.*, *10*, 433 (1971).
(11) F.F.-L. Ho and C.N. Reilley, *Anal. Chem.*, *41*, 1835 (1969).
(12) H.S. Gutowsky and C.H. Holm, *J. Chem. Phys.*, *25*, 1228 (1956).
(13) M. Rogers and J.C. Woodbrey, *J. Phys., Chem.*, *66*, 540 (1962).
(14) C. Looney, W.D. Phillips, and E.L. Reilley, *J. Amer. Chem. Soc.*, *79*, 6136 (1957).
(15) J.C. Davis and K.K. Deb in Advances in Magnetic Resonance, Academic Press, New Yark, 1970. J.S. Waugh, Ed., pp. 207-9.
(16) W.D. Perry and R.S. Drago, *J. Aemr. Chem. Soc.*, *93*, 2183 (1971).
(17) I. Walker and R.S. Drago, *J. Amer. Chem. Soc.*, *90*, 6951 (1968).
(18) W. DeW. Horrocks, Jr., R.H. Fischer, J.R. Hutchison, and G.N. LaMar, *J. Amer. Chem. Soc.*, *88*, 2436 (1966).
(19) J. Reuben and D. Fiat, *J. Chem. Phys.*, *47*, 5440 (1967).
(20) R.J. Fitzgerald and R.S. Drago, *J. Amer. Chem. Soc.*, *89*, 2879 (1967).
(21) B. Wayland, R.S. Drago, and H.F. Henneicke, *J. Amer. Chem. Soc.*, *88*, 2455 (1966).

Table I. Results of Elemental Analyses.

Compound	% Ni Found	% Ni Calc.	% C Found	% C Calc.	% H Found	% H Calc.	% N Found	% N Calc.
**$Ni(C_6H_5CH_2NH_2)_5(BF_4)_2$	—	—	53.26	54.2	5.87	5.80	—	—
**$Ni(C_6H_5CH_2NH_2)_5(ClO_4)_2$	7.93	7.40	53.62	52.99	6.21	5.72	—	—
*$Ni(DMF)_6(BF_4)_2$	8.52	8.75	32.42	32.23	6.39	6.31	—	—
*$Ni(DMA)_6(BF_4)_2$	—	—	37.92	38.1	7.31	7.2	10.94	11.1
*$Ni(NMA)_6(BF_4)_2$	—	—	31.96	32.1	6.16	6.26	12.37	12.5
*$Zn(DMF)_6(BF_4)_2$	—	—	30.45	29.8	5.84	5.8	11.73	11.6

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Attempts to prepare a nickel(II) complex with propanol by the above method and any other method were unsuccessful. The nickel-propanol solutions used in nmr work were prepared by dissolving a weighed amount of $Ni(CH_3OH)_6(BF_4)_2$ in propanol, evaporating and adding propanol several times. Finally the solution was diluted to 25.0 ml in a volumetric flask. This solution was used as a stock solution for preparing solutions of varying concentrations for nmr studies. All the nickel was assumed to be in the form $Ni(CH_3CH_2CH_2OH)_6(BF_4)_2$ for purposes of calculating concentrations.

Results of elemental analyses of complexes studied are found in Table I.

Apparatus and Techniques. All nuclear magnetic resonance spectra were obtained using a Varian A-60D. The temperature was adjusted by means of a Varian 6040 Variable Temperature Controller. Sidebands, used in calibrating peak positions relative to TMS, were generated by a Hewlett-Packard 5210 electronic counter. Frequencies were measured to the nearest 0.1 Hz unless indicated otherwise. Temperatures were recorded with an iron-constantan thermocouple and a Honeywell model 2725-3 potentiometer equipped with a direct temperature read-out. All chemical shifts were measured relative to tetramethylsilane (TMS) as an internal standard.

Magnetic susceptibility measurements were made by nmr on solutions using the method of Evans[22] and on solid $Ni(benzylamine)_5(BF_4)_2$ at 25°C using the Guoy balance. The measured susceptibilities were corrected for diamagnetism by use of literature values when available, otherwise by use of Pascal's constants.

Absorption spectra were recorded on a Cary 14 spectrophotometer, using matched one centimeter quartz cells.

A Universtiy Computer Center library program, ORTHON, was used for least squares calculations. Computer programs were run on the University of Minnesota's CDC 6600 digital computer.

Results and Discussion

For most systems, the solutions for nmr studies were prepared using the ligand as the solvent; these systems were studied over a temperature range in which the ligand exchanged very rapidly between the bulk solvent and the nickel(II) coordination sphere. In this exchange region, the isotropic shift, $\Delta\nu_M$, is given by equation (1)

$$\Delta\nu_{obs} = \nu_{obs} - \nu_o = P_M \Delta\nu_M \qquad (1)$$

where ν_{obs} is the observed proton resonance frequency relative to a standard, ν_o is the resonance frequency of the same proton in the absence of nickel(II), $\Delta\nu_M$ is the isotropic shift, and P_M is the fraction of coordinated ligand in the solution. Equation (1) was used to determine isotropic shifts from the least squares slope of the plot of ν_{obs} versus P_M. The values of $\Delta\nu_M$ for each magnetically different proton of a given system were then plotted versus 1/T. If the plot was linear with a zero (or very small) intercept it was concluded that the system showed Curie behavior. If the plot was linear with a large non-zero intercept it was concluded that the system showed non-Curie behavior.

Benzylamine System. All calculations were made assuming $Ni(C_6H_5CH_2NH_2)_6^{2+}$ to be the species[20] in solution since the ligand was present in very large excess. As a representative example of the kind of data obtained the observed shifts for the amine and methylene protons of a series of solutions are given in Table II. The resulting $\Delta\nu_M$ values for the amine and methylene protons are given in Table III and plotted versus 1/T in Figure 1. The temperature dependence of the $\Delta\nu_M$ values of the methylene and amine protons are given by

$$\Delta\nu_M = (-1180 \pm 135) - \frac{(39.6 \pm 4.1) \times 10^4}{T} \text{Hz}$$

and

$$\Delta\nu_M = (-2263 \pm 636) + \frac{(305 \pm 20) \times 10^4}{T} \text{Hz}$$

respectively. The dependence of line width on temperature for both kinds of proton showed that chemical exchange was: contribute to the shift; the enthalpy of activation for the change of line width was approximately −1.9 kcal.mole^{-1}.

The nickel-benzylamine solutions were observed to change hue from blue to blue-green upon heating to about 100°C and back to blue upon cooling. Some solutions which were heated to this temperature for a period of roughly 20 minutes and then cooled to room temperature gave observed shifts which were different from the observed shifts obtained from the

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(22) D.F. Evans, *J. Chem. Soc.*, 2003 (1959).

Table II. Concentration Dependence at Various Temperatures of the Coalesced Resonance Positions for Methylene and Amine Protons of $Ni(BzNH_2)_6^{2+}$ in Benzylamine.

T(°C)	$P_M \times 10^2$	Methylene Protons ν_{obs} (Hz)	Amine Protons ν_{obs} (Hz)
—12	0.783	—230.7	—43.5
	2.141	—260.7	
	2.459	—271.6	+107
	3.371	—292.0	
	3.672	—306.0	
	3.963	—311.8	
	4.770		+127
—1	0.521	—223.6	—48.4
	0.783	—234.2	
	2.141	—268.4	+104.1
	2.459	—272.0	+123.4
	3.963	—316.1	+244.7
	4.770	—337.1	+346.6
	5.454	—354.1	+413.9
	6.240		+478
13.4	0.000	—215.5	—74.4
	0.521	—225.3	—38.6
	0.783	—234.2	
	2.141	—268.2	+108.1
	2.459	—274.7	+127.0
	3.371	—299.5	+209.0
	4.065	—316.7	+277.3
	4.770	—339.6	+330.8
	5.454	—355.8	+391.8
	6.240		+453.6
26.8	0.875	—235.8	
	1.831	—259.9	+81.2
	2.451	—275.1	+123.9
	3.060	—290.5	+176.7
	4.297	—319.1	+269.4
	4.965	—338.5	+332.7
29.5	0.875	—238.5	
	1.831	—261.2	+77.1
	2.451	—277.5	+122.4
	3.060	—289.7	+172.0
	4.297	—318.1	+264.0
	4.965	—337.1	+323.3
	6.111	—366.6	+417.3
44.0	0.000	—212.3	
	0.521	—226.5	—39.1
	0.783	—234.9	—16.2
	1.531	—253.2	+43.0
	2.459	—274.6	+106.2
	3.371	—298.9	+178.3
	4.036	—315.2	+227.2
	4.770	—335.7	+279.7
	5.454	—351.1	+341.1
	6.240	—368.5	+396.2
57.5	0.875	—236.3	—9.5
	1.831	—260.2	+63.5
	2.451	—273.5	+102.3
	3.060	—288.2	+144.3
	4.297	—315.6	+226.1
	4.965	—332.7	+278.6
	6.111	—361.1	+361.0
96.6	0.875	—236.3	—11.5
	1.831	—259.9	+57.6
	2.451	—273.3	+93.8
	3.060	—287.3	+133.5
	4.297	—315.2	+211.1
	6.111	—360.2	+338.4
80.3	0.875	—236.3	—13.0
	1.831	—259.1	+53.1
	2.451	—272.7	+87.4
	3.060	—286.9	+126.5
	4.297	—313.9	+200.8
	6.111	—358.2	+322.0
92.2	0.875	—236.5	—14.8
	1.831	—259.4	+47.9
	2.451	—271.7	+80.6
	3.060	—285.7	+118.1
	4.297	—312.3	+190.4
	6.111	—355.8	+305.5

Table III. Isotropic Shifts of Bound Methylene and Amine Protons for $Ni(BzNH_2)_6^{2+}$ in Benzyamine.

T(°C)	Methylene Protons $\Delta\nu_M$ (Hz)	Amine Protons $\Delta\nu_M$ (Hz)
—12	—2691±86	
—1	—2622±25	+8644±368
13.4	—2630±20	+8662±52
26.8	—2474±15	+7988±94
29.5	—2430±25	+7952±49
44.0	—2490±11	+7107±201
57.5	—2357±12	+6996±40
69.6	—2344±13	+6604±44
80.3	—2311±14	+6335±37
92.2	—2257±14	+6064±32

Table IV. Magnetic Susceptibility Data for $Ni(BzNH_2)_6^{2+}$.

T(°C)	$\chi_M^{corr} \times 10^4$	μ_{eff} B.M.
—7.2	44.1	3.04
11.0	41.9	3.16
26.8	38.9	3.04
33.0	37.8	3.06
50.5	37.9	3.14
67.3	36.1	3.15
83.8	34.8	3.17

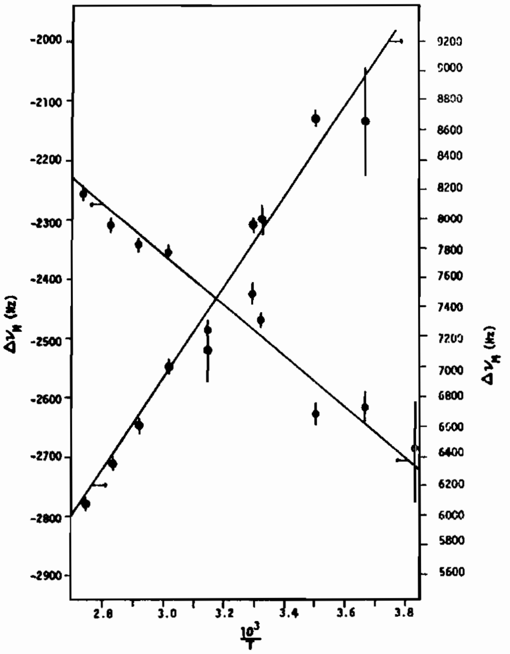

Figure 1. Temperature dependence of the isotropic shifts of the methylene (ϕ) and amine (♦) protons of $Ni(BzNH_2)_6^{2+}$.

same solutions at room temperature before heating. Shift data reported here were obtained from solutions whose room temperature shifts were monitored; solutions which showed a change of shift after cooling were discarded. A comparison was made of the spectra of room temperature and heated samples of the same solution of the nickel-benzylamine complex in benzylamine. Only slight changes in band position and in intensity were found from temperature dependent changes in solvent structure; there was no indication that new bands were appearing in positions which could be attributed to a species of some other coordination number.

The molar susceptibility, χ_M, and the effective magnetic moment, μ_{eff}, were determined by the method of Evans[22] from −7 to 84°C. The magnetic data are displayed in Table IV. The molar susceptibility varied linearly with inverse temperature and the magnetic moment was equal to 3.11±0.15 B.M. over the entire temperature region. The magnetic moment of the solid compound was checked by the Guoy method at room temperature and found to be equal to 3.16 B.M., the same value as obtained by the nmr method within experimental error. It is therefore concluded from the spectral and magnetic data that the non-Curie behavior observed for the isotropic shift was not due to a change in coordination number of nickel(II).

Dimethylformamide System. The ligand exchange rate of $Ni(DMF)_6(ClO_4)_2$ in DMF has been shown to be in the very fast exchange region above 50° by Matwiyoff.[23]

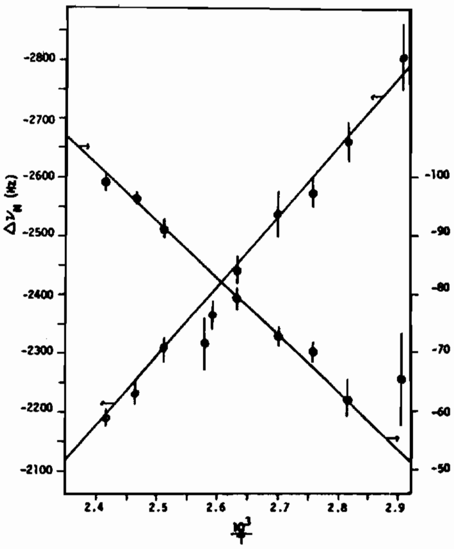

Figure 2. Temperature dependence of the isotropic shifts of the formyl (ϕ) and methyl (♦) protons of $Ni(DMF)_6^{2+}$ in dimethylformamide.

The nmr spectrum of DMF in the absence of a paramagnetic ion contains a single peak for the formyl proton and a doublet with a splitting of about 8 Hz for the methyl protons. This doublet has been attributed to hindered rotation about the N-C axis, caused by partial double bond character in this bond.[13] The doublet character is preserved in the presence of a paramagnetic ion until the temperature reaches about 110°C. Since the midpoint of the methyl doublet is not affected by the presence or absence of rotation only the temperature dependence of this midpoint is reported here for the methyl protons. All data were obtained between 70° and 140°. The resulting $\Delta\nu_M$ values for the formyl and methyl protons are plotted versus 1/T in Figure 2. The temperature dependence of the $\Delta\nu_M$ values for the formyl and methyl proton is given by

$$\Delta\nu_M = (804\pm90) - \frac{(123\pm3.4)\times10^4}{T}\,\text{Hz}$$

and

$$\Delta\nu_M = (-220\pm26) + \frac{(5.41\pm0.99)\times10^4}{T}\,\text{Hz}$$

respectively. Both kinds of protons show significant non-Curie behavior.

The formyl proton has a large positive intercept; the negative intercept found by extrapolation[15] of Matwiyoff's data results from an error.[23] By comparison there was no shift of the formyl proton for the zinc(II)-DMF complex in methylene chloride at either 33° or 3°C and shifts of only 8 and 10 Hz downfield, respectively, for the methyl protons as compared to the free ligand. Hence the large positive intercept observed for the formyl proton in the nickel(II) complex did not result simply from an unusually large diamagnetic shift.

Since the nickel(II)-DMF complex was found to be soluble in both chloroform and methylene chloride and since chloroform has been established as a fairly strong hydrogen bonding solvent while methylene chloride has not, an attempt was made to ascertain the effects of a hydrogen-bonding solvent on the formyl proton intercept. Unfortunately the formyl proton resonance was so broad in these solvents that the maximum was uncertain by approximately 200 Hz and no conclusions could be made concerning hydrogen bonding effects.

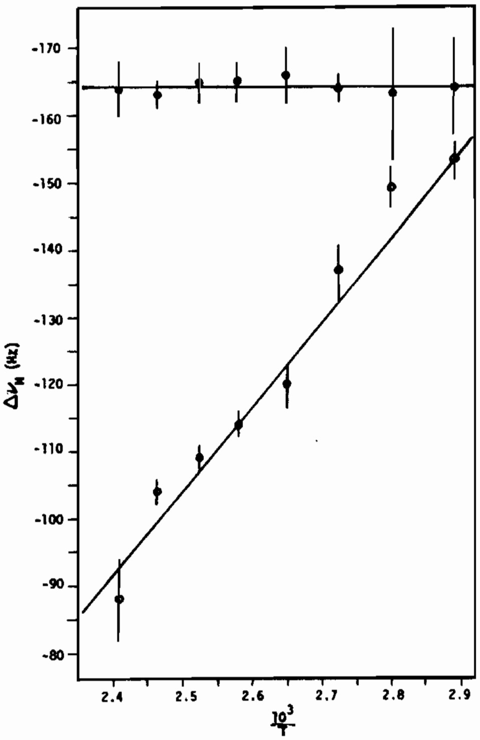

Figure 3. Temperature dependence of the isotropic shifts of the N-methyl (ϕ) and amide methyl (♦) protons of $Ni(DMA)_6^{2+}$ in dimethylacetamide.

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(23) N.A. Matwiyoff, *Inog. Chem.*, 5, 788 (1966).

Table V: Spectral Parameters for Octahedral Nickel(II) Complexes.

Complex	$^3A_{2g}\rightarrow{}^3T_{2g}$ [a]	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$ [a]	$^3A_{2g}\rightarrow{}^3T_{1g}(P)$ [a]	Ref.
$Ni(H_2O)_6^{2+}$	8500	13,500	25,300	25
$Ni(MeOH)_6^{2+}$	8431	14,226	25,000	26
$Ni(EtOH)_6^{2+}$	8180	13,404	24,795	26
$Ni(PrOH)_6^{2+}$	8220	13,508	24,888	This work

[a] All spectral parameters have units of cm^{-1}.

Dimethylacetamide System. The N-methyl proton peak is a doublet caused by the partial double bond character of the N–C bond. For reasons stated for the nickel(II)–DMF system only the average position of the N-methyl proton resonance was reported. The $\Delta\nu_M$ values for the N-methyl and amide methyl protons are plotted versus 1/T in Figure 3. The intercepts were -166 ± 15 Hz and -207 ± 23 Hz and the slopes were $(6\pm20)\times10^2$ and $(+12.4\pm0.9)\times10^4$ HzK for the N-methyl and amide methyl protons, respectively. There is significant non-Curie behavior and the isotropic shift for the N-methyl protons is essentially independent of temperature. In methylene chloride the value of $\Delta\nu_M$ appeared to be dependent on the concentration of the nickel complex so the effect of an inert solvent could not be studied.

The solutions of the nickel(II)-DMF complex in DMA were noticeably thermochromic above room temperature. Spectra of identical solutions were taken at room temperature and at approximately 80°C. Comparison of the spectra showed shifts of 5-10 nm, or less, in the maxima and slight changes in absorbances but no new bonds appeared to be forming .

N-Methylacetamide System. The solid compound $[Ni(NMA)_6](BF_4)_2$ was successfully isolated in the work reported here although earlier efforts[24] were unsuccessful. The compound was not very soluble in NMA and this is the source of the large errors reported for the intercepts and slopes. From determinations of $\Delta\nu_M$ over a range of nickel(II) concentrations at each temperature and over a range of 8 temperatures from 25° to 100°C, the dependence of $\Delta\nu_M$ upon the inverse temperature was found to be:

$$\Delta\nu_M=(-167\pm62)+\frac{(10.5\pm2.0)\times10^4}{T}\,\text{Hz} \quad \text{for the amide methyl protons,}$$

$$\Delta\nu_M=(797\pm455)-\frac{(93.3+15.0)\times10^4}{T}\,\text{Hz} \quad \text{for the N-H proton,}$$

and for the N-methyl protons:

$$\Delta\nu_M=(-27\pm38)-\frac{(2.8+1.7)\times10^4}{T}\,\text{Hz}$$

$$\Delta\nu_M=(40\pm63)-\frac{(2.8+1.7)\times10^4}{T}\,\text{Hz}$$

Contrary to the DMA system, there is no significant non-Curie behavior for the N-methyl protons although there may be non-Curie behavior for the N-H and amide methyl protons.

n-Propanol System. For purposes of calculating isotropic shifts $Ni(PrOH)_6^{2+}$ was assumed to be the species in solution. This assumption was supported by the spectral parameters reported in Table V which are typical of similar octahedral complexes.

Of the four magneticallv different protons in n-propanol only the methyl and β-methylene proton signals were in the very fast exchange region where the shift was not dependent on the exchange rate. Determination of $\Delta\nu_M$ values at various nickel(II) concentrations over the range $0\leqslant P_M\leqslant0.12$ at each temperature for 12 temperatures between −1° and 90°C gave the following temperature dependencies:

$$\Delta\nu_M=(-233\pm31)-\frac{(3.02+0.97)\times10^4}{T}\,\text{Hz} \quad \text{for the β-methylene protons,}$$

and

$$\Delta\nu_M=(2\pm25)-\frac{(1.91+0.79)\times10^4}{T}\,\text{Hz} \quad \text{for the methyl protons.}$$

The β-methylene shifts show significant non-Curie behavior while the methyl protons do not. It is appropriate to note that if the coordination number of nickel(II) is incorrect, the $\Delta\nu_M$ values would all be incorrect by a constant factor; however, a temperature-independent contribution to the isotropic shift would still have been observed.

Conclusions

Reuben and Fiat[19] have suggested that pseudocontact shifts might be the source of non-Curie behavior in aqueous solutions of some rare earth ions for which plots of the isotropic proton shifts versus 1/T gave apparent linear plots with non-zero intercepts over the temperature range sudied. This source of non-Curie behavior has been eliminated here because octahedral nickel(II) complexes with six identical ligands do not show significant pseudocontact shifts. Likewise, the choice of nickel(II) complexes eliminates the source of anomalous temperature dependence noted by LaMar and Van Hecke[25] for unsymmetrically substituted tris(o-phenanthroline) complexes of Cr^{II} and Co^{II}.

Ion pairing can probably be eliminated as a source of the apparent non-Curie behavior reported here

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(24) R.S. Drago, D.W. Meek, J.D. Joesten, and L. LaRoche, *Inorg. Chem.*, 2, 124 (1963).

(25) G.N. LaMar and G.R. Van Hecke, *J. Amer. Chem. Soc.*, 92, 3021 (1970).

because the octahedral nickel(II) complexes with six identical ligands will not form an ion pair with an anion preferentially on one face of the octahedron. If, during ion pairing, there exists no definite relative orientation so that the cation and anion can adopt all possible relative orientations, then the pseudocontact shifts aevrage to zero[26] and the isotropic shifts cannot show non-Curie behavior according to the suggestion of Reuben and Fiat.[19] If there was some ion pairing giving rise to some distortion of the nickel(II) complex its effect would be greatly diminished by the rapid exchange of the ligands.[27] Furthermore, except for $[Ni(DMA)_6](BF_4)_2$ in methylene chloride, none of the isotropic shifts were dependent on the concentration of the nickel(II) salt. If ion pairing was the source of the apparent non-Curie behavior noted in the ionizing solvents used, it is likely that a concentration dependence for the shifts would have been observed in more systems.

Hydrogen bonding may cause the apparent non-Curie behavior of some of the shifts but it probably is not the cause for the non-Curie behavior of the methylene and methyl proton shifts since these protons are not involved in hydrogen bonding. Unfortunately, attempts to study the shifts in several solvents were unsuccessful either because the solvent was too coordinating, because the nickel(II) compound was too insoluble, or because the resonances were too broad or concentration dependent.

Hindered rotation was not the cause of the apparent non-Curie behavior of the N-methyl prtoons in DMF or DMA because the midpoints of the doublet were used in the plots.

Because the magnetic moment of the benzylamide complex was constant within a small experimental error over a 90° temperature range a postulate of a changing value for the magnetic moment cannot explain the very marked apparent non-Curie behavior of this complex over this temperature range.

The apparent non-Curie behavior does not appear to result simply from a diamagnetic shift because, first, the zinc(II)-DMF complex did not show this behavior whereas the nickel(II) complex did and, second, the nickel(II) complexes of DMF and DMA showed this behavior for the N-methyl protons whereas the complex of NMA showed Curie behavior for the same protons.

Structural interconversion as a source of apparent non-Curie behavior cannot be eliminated definitely. However, in the two systems where thermochromic behavior was noted (benzylamine and DMA) the spectra did not reveal significant formation of complexes of a lower coordination number over temperature ranges of 50-60°.

Temperature independent paramagnetism (TIP) was suggested[26] as the cause of the temperature independent contribution to the isotropic shifts observed for the methyl protons in acetonitrile solutions of nickel(II) tetrafluoroborate. However, more rigorous calculation[27] of the shifts expected from this source do not agree with the observed temperature independent contributions. The observed temperature independent contributions did not show the necessary dependence upon R, the average distance between the nickel(II) ion and the proton, when there were two or more magnetically different protons in a ligand. Furthermore, the temperature independent contributions for the formyl proton of DMF and the N-H proton of NMA were large and positive, rather than negative as predicted by the theory. Although the temperature independent contributions to the N-methyl shifts of DMF and DMA (–220 and –207 Hz, respectively) were approximately equal to the theoretical value, the contribution for NMA was essentially zero whereas the theory would predict the same value as for DMF and DMA. These results show that TIP cannot be the dominant cause of the temperature independent contribution. It must be concluded that, although some sources of non-Curie behavior have been eliminated for the complexes studied, the source of the behavior is as yet uncertain.

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(26) H.M. McConnell and R.E. Robertson, *J. Chem. Phys.*, *29*, 1361 (1958).
(27) M. Wicholas and R.S. Drago, *J. Amer. Chem. Soc.*, *91*, 5963 (1969).

(26) J.F. O'Brien, Ph.D. Thesis, University of Minnesota, 1968.
(27) Yoyce E. Jentoft, Ph.D. Thesis, University of Minnesota, 1971.