Carbonyl fluoride was condensed into a stainless steel reactor that contained CsF and thawed. Any unreacted COF_2 was then pumped off, and a fourfold excess of OF_2 was condensed into the reactor. The reactor was maintained at room temperature for 72 hr. The reaction mixture was then passed through a −160° bath (to trap the CF_3OOOCF_3) and a −183° bath (to trap the CF_3OOF), and then the excess OF_2 was condensed in a −196° trap. The products CF_3OOF and CF_3OOOCF_3 were found in approximately 75 and 25% yields, respectively, based on the stoichiometry given in eq 1–3.

C. Properties of Fluoroperoxytrifluoromethane.—The CF_3OOF was characterized by ^{19}F nmr spectral analysis and molecular weight determinations. The ^{19}F nmr spectrum agrees with that of Thompson[12] and contains the characteristic line (−291.5 ppm) due to the $OO^{19}F$ as well as the $C^{19}F_3$ line (69.2 ppm). The molecular weight was determined by gas density measurements (calcd, 120; obsd, 118, 121).

Fluoroperoxytrifluoromethane is a colorless liquid with a melting point below −196°. Room-temperature stability studies were made by confining a sample in an ir cell and monitoring spectral changes as a function of time. At 5 mm pressure, it required some 138 hr before most of the CF_3OOF decomposed; it has not been ascertained whether the decomposition is due to instability or reaction with its surroundings.

The infrared spectrum consisted of strong bands at 7.75 μ (1290 cm^{-1}), 7.90 μ (1266 cm^{-1}), and 8.55 μ (1170 cm^{-1}) which correspond closely to the infrared spectrum of bis(trifluoromethyl) trioxide. The difference appears to be the 10.5-μ (952-cm^{-1}) band for the CF_3OOF and the 11.15-μ (897-cm^{-1}) band for the CF_3OOOCF_3.

Acknowledgment.—Technical direction was provided by the Director of Engineering Sciences, SREP, Air Force Office of Scientific Research, Contract No. F44620-70-C-0027.

(12) P. J. Thompson, personal communication, 1967.

Contribution from the Department of Chemistry,
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Solvent-Exchange Rates from Manganese(III) Protoporphyrin IX Dimethyl Ester Studied by Nuclear Magnetic Resonance Line Broadening

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It has been found previously that a knowledge of the solvent-exchange rates from the first coordination sphere of a metal ion is useful in establishing the general lability and mechanism of complexation to the metal.[1,2] The exchange rates of the solvents methanol and *N,N*-dimethylformamide from manganese(III) protoporphyrin IX dimethyl ester (Mn(DMPrpor)$^+$) are reported here. The general reaction being studied is

$$\mathrm{Mn(DMPrpor)(S)_2^+ + S^* \rightleftharpoons Mn(DMPrpor)(S)(S^*)^+ + S}$$

where S* and S are initially free and coordinated solvent molecules, respectively. In a previous study[3] Fleischer did not observe any complexing with manganese(III) hematoporphyrin; therefore there is no information on the reaction rates of these high-spin d^4 systems. It was also of interest to extend earlier studies on iron(III) protoporphyrin IX[4] and cobalt(III) and iron(III) hematoprophyrin.[3]

Experimental Section

The chloride salt of manganese(III) protoporphyrin IX dimethyl ester Mn(DMPrpor)$^+$ was prepared and purified as described by Boucher.[5] *Anal.* Calcd for $C_{36}H_{36}O_4N_4MnCl \cdot H_2O$: C, 62.02; H, 5.49; N, 8.04. Found: C, 62.88; H, 5.45; N, 7.53.

The visible spectrum of Mn(DMPrpor)Cl·H_2O in methanol shows maxima (with molar extinction coefficients in parentheses) at 27,000 cm^{-1} (7.73×10^{-4} M^{-1} cm^{-1}), 21,600 cm^{-1} (5.90×10^4 M^{-1} cm^{-1}), and 18,200 cm^{-1} (1.1×10^4 M^{-1} cm^{-1}), with a further weak band at ~17,200 cm^{-1}. The band positions agree with those given by Boucher,[5] but the extinction coefficients seem to be slightly higher than those which can be read from Figure 5 of ref 5. It has also been found, in agreement with Boucher, that removal of chloride ion with silver perchlorate has no effect on the spectrum in methanol.

The effective magnetic moment of Mn(DMPrpor)$^+$ in methanol has been determined between −60 and +40°, using the nmr shift method suggested by Evans.[6] The sample was prepared under vacuum by treating Mn(DMPrpor)Cl·H_2O with $AgClO_4$ and molecular sieves. Cyclopentane was used as an internal standard. A Curie law temperature dependence, with an effective magnetic moment of 5.01 (after correction for diamagnetism of the porphyrin), was found. This result is in agreement with values of 4.86–4.97 determined by Boucher[5] on various solid salts.

All solutions for nmr analysis were prepared on a vacuum line using standard techniques. All samples were treated with $AgClO_4$ and molecular sieves to remove chloride and water, respectively, from Mn(DMPrpor)Cl·H_2O. The metal complex concentration was determined from the weight of solvent and complex used. In several cases this concentration was checked spectrophotometrically, and agreement with the expected value was always better than 5%.

In methanol the Mn(DMPrpor)$^+$ concentrations used were 9.65×10^{-2}, 9.81×10^{-3}, and 2.38×10^{-2} *m*, in order to obtain line broadenings in the range of 5–50 Hz and shifts of 1–12 Hz. The shifts and broadenings were found to be directly dependent on the Mn(DMPrpor)$^+$ concentration and in a separate study this dependence was confirmed, at 40°, up to 8.25×10^{-2} *m*, the maximum concentration studied.

In DMF, complex concentrations of 6.88×10^{-3}, 1.23×10^{-2}, and 2.39×10^{-2} *m* were used to give broadenings and shifts in the same range as those observed in methanol. The methyl proton broadenings were determined by a least-squares fit of the two overlapping methyl resonances to the sum of two Lorentzian curves. Only the data for the higher field methyl resonance are given here, since the other methyl resonance shows essentially the same behavior.

The solvents were purified by double vacuum distillation from molecular sieves, the middle fraction of each distillation being used. Solvents were stored under vacuum over molecular sieves.

The nmr measurements were made on a Varian Associates A-56/60 spectrometer equipped with a Varian Model V-4343 temperature controller. Temperatures were determined from the peak separation in pure methanol or ethylene glycol.

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(1) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965).

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(4) N. S. Angerman, B. B. Hasinoff, H. B. Dunford, and R. B. Jordan, *Can. J. Chem.*, **47**, 3217 (1969).

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

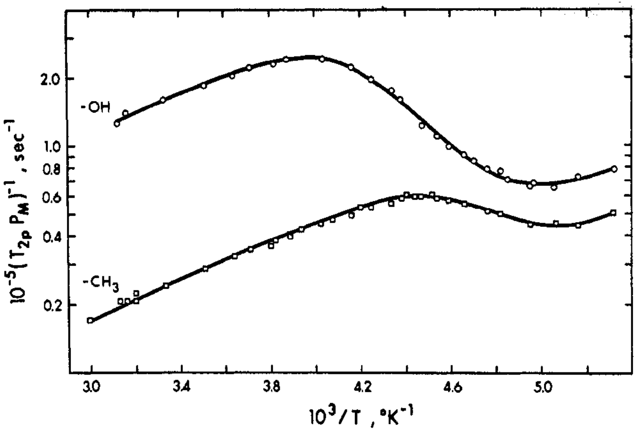

Figure 1.—Temperature dependence of $(T_{2M}P_M)^{-1}$ for solutions of Mn(DMPrpor)$^+$ in methanol. Smooth curves are calculated from fits B and E (Table I) for the OH and CH$_3$ protons, respectively.

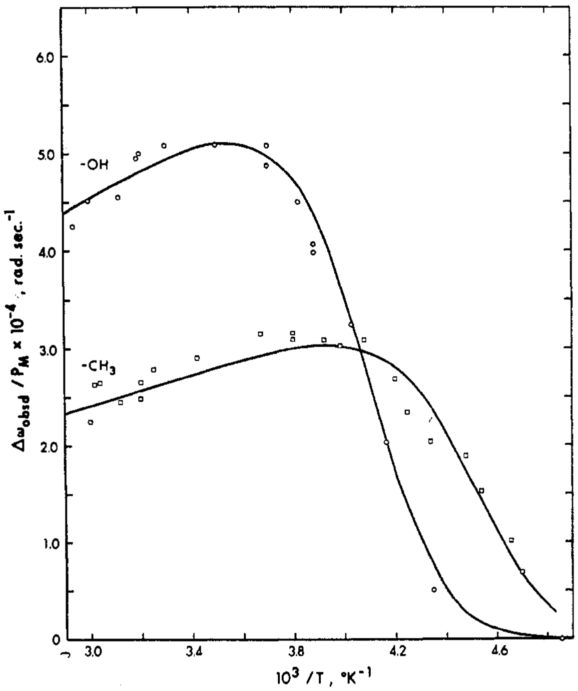

Figure 2.—Temperature dependence of $\Delta\omega_{obsd}/P_M$ for solutions of Mn(DMPrpor)$^+$ in methanol. Smooth curves are calculated with parameters fixed from fits B and E (Table I) for the OH and CH$_3$ protons, respectively, and $C_{\omega(OH)} = 1.52 \times 10^7$ radians sec^{-1} deg and $C_{\omega(CH_3)} = 8.04 \times 10^6$ radians sec^{-1} deg.

Results

The temperature dependence of the line broadenings and chemical shift caused by Mn(DMPrpor)$^+$ in methanol are shown in Figures 1 and 2, respectively. The effective relaxation time T_{2P}, chemical shift $\Delta\omega_{obsd}$, and concentration ratio P_M have been defined previously.[7] A solvation number of 2 has been assumed.[8]

The temperature dependence of $(T_{2P}P_M)^{-1}$ for this system can be described by the equation

$$(T_{2P}P_M)^{-1} = \frac{1}{\tau_M}\left\{\frac{(1/T_{2M})^2 + 1/T_{2M}\tau_M}{(1/T_{2M} + 1/\tau_M)^2}\right\} + T_{2O}^{-1} \tag{1}$$

This equation results from the general expression developed by Swift and Connick,[9] if the $\Delta\omega_M^2$ terms are small, except for the addition of the outer-sphere relaxation term T_{2O}^{-1}.

The solvent lifetime in the coordination sphere of the metal ion, τ_M, is assumed to have the temperature dependence predicted by transition-state theory

$$\tau_M^{-1} = \frac{kT}{h}\exp\left(\frac{-\Delta H^{\ddagger} + T\Delta S^{\ddagger}}{RT}\right) \tag{2}$$

The solvent proton transverse relaxation times in the first coordination sphere, T_{2M}, and in the outer spheres, T_{2O}, are assumed to have a simple exponential temperature dependence

$$T_{2M}^{-1} = C_M \exp(E_M/RT) \tag{3}$$

$$T_{2O}^{-1} = C_O \exp(E_O/RT) \tag{4}$$

Substitution from eq 2–4 into eq 1 gives an equation with six parameters which can be determined in principle from a nonlinear least-squares fit of the variation of $(T_{2P}P_M)^{-1}$ with temperature. Some discretion must be used in evaluating the resulting parameters and it is of value to fix certain of them and examine the effect on the others.

A summary of the best-fit parameters in methanol is given in Table I. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from fit D are not considered to be realistic because τ_M^{-1} is never a major contribution to $(T_{2P}P_M)^{-1}$ for the CH$_3$ protons as can be seen from Figure 1. Aside from fit D all the fits in Table I show general agreement of the various parameters, and it seems reasonable to conclude that $\Delta H^{\ddagger}$ is 8.0 ± 0.3 kcal mol^{-1} and $\Delta S^{\ddagger}$ is 1.3 ± 1.5 cal mol^{-1} deg^{-1}.

TABLE I

LEAST-SQUARES BEST-FIT PARAMETERS FOR Mn(DMPrpor)$^+$ IN METHANOL

Proton	fit	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	C_M, sec^{-1}	E_M, kcal mol^{-1}	C_O, sec^{-1}	E_O, kcal mol^{-1}	Std error[a]
OH	A	8.26	2.25	5200	1.99	603	1.81	0.030
	B	7.72	−0.14	4950	2.04[b]	323	2.04[b]	0.036
	C	7.94	0.81	5098	2.02	313	2.05[c]	0.030
CH$_3$	D	10.53[d]	7.07[d]	908	1.78	201	2.05	0.024
	E	8.15	2.04	578	2.04[e]	196	2.04[e]	0.032
	F	7.72[f]	−0.46	586	2.04[e]	191	2.04[e]	0.032

[a] Normalized standard error $= \Sigma_n((Y_o - Y_p)/Y_o)^2/(n - k)$, where Y_o and Y_p are the observed and predicted values of $(T_{2P}P_M)^{-1}$, n is the number of observed values, and k is the number of variable parameters used in the fit. [b] Constrained by setting $E_M = E_O$. [c] Held constant at value given by fit D. [d] These values are not considered significant for reasons given in the text. [e] Held constant at value given by fit B. [f] Held constant at value given by fit B.

Under the same conditions as apply to eq 1, it can be shown that the observed chemical shift is given by

$$\Delta\omega_{obsd} = -\frac{P_M\Delta\omega_M}{(\tau_M T_{2M} + 1)^2} \tag{5}$$

The chemical shift of the solvent protons in the first coordination sphere of the metal ion, $\Delta\omega_M$, is given by[10]

$$\Delta\omega_M = -(A/\hbar)\frac{\omega_O\mu_{eff}\beta\sqrt{S(S+1)}}{3kT\gamma_I} = -\frac{C_\omega}{T} \tag{6}$$

where the symbols have their usual meanings.[7]

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[7] J. E. Letter, Jr., and R. B. Jordan, *J. Amer. Chem. Soc.*, **93**, 864 (1971).

[8] If the solvation number is 1, then the exchange rates and coupling constants increase by a factor of 2, and $\Delta S^{\ddagger}$ increases by 1.4 cal mol^{-1} deg^{-1}.

[9] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[10] N. Bloembergen, *ibid.*, **27**, 595 (1957).

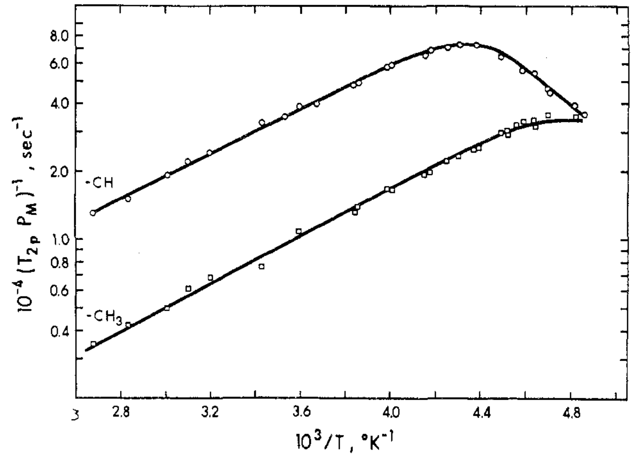

Figure 3.—Temperature dependence of $(T_{2M}P_M)^{-1}$ for solutions of Mn(DMPrpor)$^+$ in *N,N*-dimethylformamide. Smooth curves are calculated from fits A and H (Table II) for the CH and high-field CH$_3$ protons, respectively.

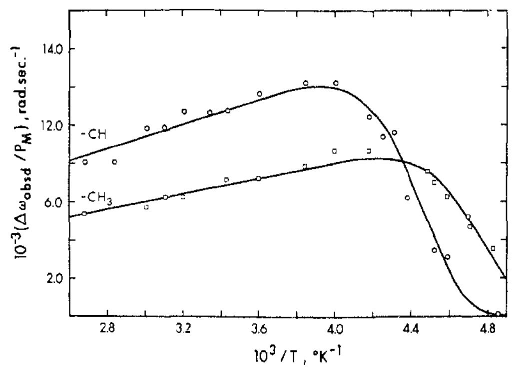

Figure 4.—Temperature dependence of $\Delta\omega_{obsd}/P_M$ for solutions of Mn(DMPrpor)$^+$ in *N,N*-dimethylformamide. Smooth curves are calculated with parameters fixed from fits A and H (Table II) for the CH and high-field CH$_3$ protons, respectively, and $C_{\omega(CH)} = 3.16 \times 10^6$ radians sec^{-1} deg and $C_{\omega(CH_3)} = 2.02 \times 10^6$ radians sec^{-1} deg.

The measured chemical shifts were not considered to be sufficiently accurate to warrant an independent fit to obtain $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Therefore the latter have been held constant along with C_M and E_M at the values given by fit C, and only C_ω was allowed to vary. The least-squares best-fit values at 60 MHz are $C_{\omega(OH)} = (1.5 \pm 0.18) \times 10^7$ radians sec^{-1} deg and $C_{\omega(CH_3)} = (8.04 \pm 0.33) \times 10^6$ radians sec^{-1} deg. If μ_{eff} is 5.01, then from eq 6, $(A/\hbar)_{OH} = 3.96 \times 10^6$ radians sec^{-1} and $(A/\hbar)_{CH_3} = 2.09 \times 10^6$ radians sec^{-1}. The smooth curves in Figure 2 have been calculated using these parameters.

Essentially similar results have been obtained for Mn(DMPrpor)$^+$ in DMF, as shown in Figures 3 and 4. One significant difference between the DMF and methanol systems is that no well-defined outer-sphere broadening is observed in the former. It may also be noted that the CH$_3$ proton results show practically no effect due to chemical exchange controlled line broadening.

The results of various least-squares fits of the data to eq 1 are summarized in Table II. Fits A–E show the sensitivity of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ to various assumptions about the outer-sphere contribution for the CH proton. All of the fits except E and I provide calculated $(T_{2P}P_M)^{-1}$ values which are within the experimental error of the observed results. Fits F and G are anomalous in that the C_O for the CH$_3$ proton is larger than that of the CH proton from fit D. Therefore the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values from fit A appear to give a more reasonable fit of the CH$_3$ proton results.

TABLE II

LEAST-SQUARES BEST-FIT PARAMETERS FOR Mn(DMPrpor)$^+$ IN *N,N*-DIMETHYLFORMAMIDE

Proton fit		$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	C_M, sec^{-1}	E_M, kcal mol^{-1}	C_O, sec^{-1}	E_O, kcal mol^{-1}	Std error[a]
CH	A	10.50	12.40	509	2.30	92.3	2.25	0.026
	B	10.01	10.23	516	2.30[b]	74.8	2.30[b]	0.027
	C	6.36	−5.72	513	2.40	0[c]	. . .	0.035
	D	7.96	1.30	502	2.37[b]	33.6[d]	2.37[b]	0.029
	E	7.96	0.74	605	2.22[b]	93.5[e]	2.22[b]	0.057
CH$_3$	F	7.96[f]	1.30[f]	57.2	2.37[f]	83.5	2.37[f]	0.045
	G	7.96[f]	1.30[f]	66.9[g]	2.37[f]	66.9[g]	2.37[f]	0.044
	H	10.50[h]	12.40[h]	63.4[g]	2.43[b]	63.4[g]	2.43[b]	0.051
	I	10.50[h]	12.40[h]	72.1[i]	2.53[b]	36.1[i]	2.53[b]	0.081
	J	10.50[h]	12.40[h]	82.3[g]	2.30[h]	82.3[g]	2.30[h]	0.063

[a] Calculated as described in footnote *a* of Table I. [b] Constrained by setting $E_M = E_O$. [c] Fixed at zero to give no outer-sphere contribution. [d] Calculated value held constant. [e] Value held constant. [f] Held constant at value given by fit D. [g] Constrained by setting $C_M = C_O$. [h] Held constant at value given by fit A. [i] Constrained by setting $C_M = 2C_O$.

The chemical shift results in Figure 4 were fitted to eq 5, using parameters from fits A and H for the CH and CH$_3$ protons, respectively, and allowing only C_ω to vary. The least-squares fit gave $C_\omega = 3.16 \pm 0.10) \times 10^6$ and $(2.02 \pm 0.08) \times 10^6$ radians sec^{-1} deg for the CH and CH$_3$ protons, respectively. If μ_{eff} is taken as 5.01, then $(A/\hbar)_{CH} = 8.11 \times 10^5$ radians sec^{-1} and $(A/\hbar)_{CH_3} = 5.25 \times 10^5$ radians sec^{-1}.

Discussion

It is very difficult to assess the uncertainties in the kinetic parameters obtained here because of the large number of interdependent variables. The methanol system is least subject to uncertainty and it is concluded that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are 8.0 ± 0.3 kcal mol^{-1} and 1.3 ± 1.5 cal mol^{-1} deg^{-1} and that the rate constant for methanol exchange at 25° is $(1.5 \pm 0.3) \times 10^7$ sec^{-1}. The most internally consistent values for the DMF system are $\Delta H^{\ddagger} = 10.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 12.4$ cal mol^{-1} deg^{-1}, but the uncertainty in these is strongly dependent on the assumptions made about the outer-sphere contributions to the observed line broadening. These values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ predict a rate constant for solvent exchange of 6.4×10^7 sec^{-1} at 25°. The rate constant, at 25°, calculated from all of the fits, except C in which no outer-sphere contribution was allowed, range from 1.7×10^7 to 6.4×10^7 sec^{-1}.

Fleischer[3] has observed that hematoporphyrin seems to enhance the rate of ligand substitution by $\sim 10^6$ in the more inert cobalt(III) and low-spin iron(III) systems. For high-spin iron the solvent-exchange rates indicate that protoporphyrin IX increases the rate by $\sim 10^4$. The latter factor also seems consistent when solvent-exchange rates[2] on the isoelectronic solvated manganese(II)–iron(III) porphyrin and solvated chromium(II)–manganese(III) porphyrin systems are considered.

Comparison of exchange rates for DMF, methanol, and water in systems in which all three have been studied indicates the water exchange is ~ 10 to 10^2 times faster at 25°. Therefore the rate constant for water exchange on Mn(DMPrpor)$^+$ is probably 10^8 to 10^9 sec^{-1} and relaxation techniques similar to those used for copper(II)[11] will be necessary to measure ligand-substitution rates.

Acknowledgment.—Support for this research by the National Research Council of Canada is gratefully acknowledged. L. R. wishes to thank the National Research Council for support through a postgraduate scholarship.

[11] R. L. Karpel, K. Kustin, A. Kowalak, and R. F. Pasternack, *J. Amer. Chem. Soc.*, **93**, 1085 (1971).

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Nuclear Magnetic Resonance Line-Broadening Study of Two Schiff Base Complexes of Nickel(II), Tribenzo[*b,f,g*][1,5,9]triazacyclododecinenickel(II) and Tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecinenickel(II), in *N,N*-Dimethylformamide

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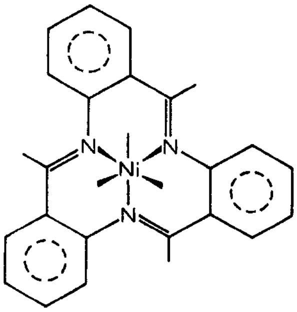
This note reports the results of a proton magnetic resonance study of the *N,N*-dimethylformamide-exchange rates of two nickel(II) Schiff base complexes, tribenzo[*b,f,g*][1,5,9]triazacyclododecinenickel(II), NiTRI^{2+}, and tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecinenickel(II), NiTAAB^{2+}. The complexes are shown in structures I and II, respectively. This work was carried out in order to compare the effects of the two macrocyclic ligands on the solvent-exchange rates and to compare NiTAAB^{2+} to the previously studied[1] NiCR^{2+} and NiCRCH$_3$$^{2+}$ complexes. The latter two compounds have quite high solvent-exchange rates and the question arises as to whether this is always true for tetragonally distorted nickel(II) complexes or if specific electronic or steric effects are operative in the NiCR^{2+} and NiCRCH$_3$$^{2+}$ systems. It was also of interest to determine if the similarity in the water-exchange rates for Ni(OH$_2$)$_6$$^{2+}$ and NiTRI(OH$_2$)$_3$$^{2+}$ [2] also extends to the DMF system.



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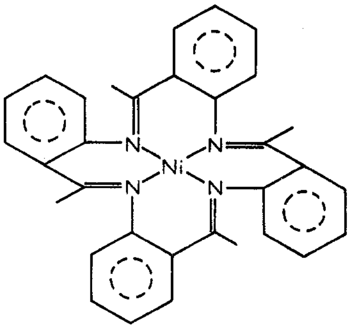

II

Experimental Section

The nitrate salts of NiTRI^{2+} and NiTAAB^{2+} were prepared as described by Melson and Busch.[3] The perchlorate salts were prepared by the addition of an aqueous solution of sodium perchlorate to solutions of the appropriate nitrate salt. All salts except the perchlorate salt of NiTAAB^{2+} were air-dried, the latter being dried under vacuum over P_4O_{10}. *Anal.* Calcd for NiTRI(H$_2$O)$_3$(ClO$_4$)$_2$: C, 40.61; N, 6.77; H, 3.41. Found: C, 40.20; N, 6.97; H, 4.14. Calcd for NiTAAB(ClO$_4$)$_2$: C, 50.19; N, 8.36; H, 3.01. Found: C, 50.20; N, 8.40; H, 3.02. Calcd for NiTAAB(OH$_2$)$_2$(NO$_3$)$_2$: C, 53.28; N, 13.31; H, 3.83. Found: C, 53.11; N, 13.05; H, 3.70.

The complexes were further characterized by comparison of the infrared spectra to those given by Melson and Busch.[3] These results were in agreement with the previous work and further confirmed that NiTAAB(ClO$_4$)$_2$ was anhydrous since no O–H stretching absorption was observed.

The samples for nmr analysis were prepared under vacuum using standard techniques. The concentration of paramagnetic ion was determined from the known weight of solvent and metal complex. Cyclopentane was used as an internal standard for the shift measurements. The DMF solutions of NiTRI(OH$_2$)$_3$(ClO$_4$)$_2$, NiTRI(OH$_2$)$_2$(NO$_3$)$_2$, and NiTAAB(OH$_2$)$_2$(NO$_3$)$_2$ were stored under vacuum over molecular sieves for at least 3 hr, in order to remove the water, before being transferred to an nmr tube.

Three samples of NiTRI(ClO$_4$)$_2$ with concentrations of 0.0235, 0.0553, and 0.0995 *m* were studied. Two samples of NiTAAB(ClO$_4$)$_2$ with concentrations of 0.0299 and 0.0538 *m* and three samples of NiTAAB(NO$_3$)$_2$ with concentrations of 0.0311, 0.0371, and 0.0511 *m* were used.

The solvent *N,N*-dimethylformamide was doubly distilled under vacuum from molecular sieves and then stored over molecular sieves.

The nmr spectra of the solvent C–H proton were recorded on Varian Associates A-56/60 and HA-100 spectrometers equipped with standard temperature-control units. Temperatures were obtained by comparison of the chemical shifts of pure methanol or ethylene glycol to calibration charts provided by Varian Associates.

Results

During the initial nmr work it was observed that the line broadenings were significantly but not markedly different for NiTRI(NO$_3$)$_2$ and NiTRI(ClO$_4$)$_2$. However, the chemical shifts from the nitrate salt were much smaller than those from the perchlorate. These differences have been attributed to nitrate complexing in DMF and only the results from the perchlorate salt are given here.

In the case of NiTAAB^{2+} the nitrate and perchlorate salts gave the same results, within experimental error, up to about −10° ($10^3/T \approx 3.4$ deg^{-1}). Above this temperature smaller broadenings and shifts were observed for the nitrate salt, and the shifts decreased more rapidly with increasing temperature for this salt. This effect is assumed to be associated with nitrate complex-

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[1] L. Rusnak and R. B. Jordan, *Inorg. Chem.*, **10**, 2686 (1971).

[2] J. E. Letter, Jr., and R. B. Jordan, *J. Amer. Chem. Soc.*, **93**, 864 (1971).

[3] (a) G. A. Melson and D. H. Busch, *ibid.*, **86**, 4834 (1964); (b) G. A. Melson and D. H. Busch, *ibid.*, **87**, 1706 (1965).