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).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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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

BY L. L. RUSNAK, J. E. LETTER, JR., AND R. B. JORDAN*

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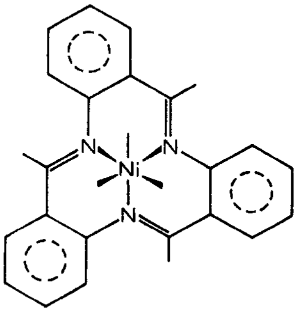
This note reports the results of a proton magnetic resonance study of the *N*,*N*-dimethylformamide-exchange rates of two nickel(II) Schiff base complexes, tribenzo[*b*,*f*,*g*][1,5,9]triazacyclododecinenickel(II), $NiTRI^{2+}$, and tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraazacyclohexadecinenickel(II), $NiTAAB^{2+}$. 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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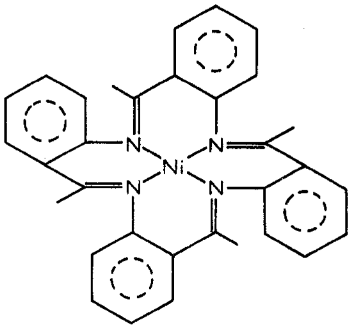

II

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 $NiTRI(H_2O)_3(ClO_4)_2$: 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).

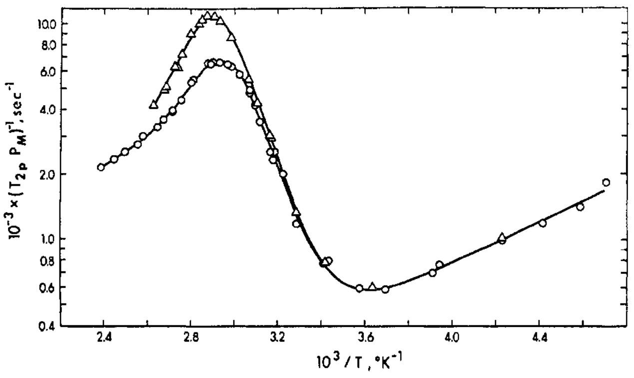

Figure 1.—Temperature dependence of $(T_{2P}P_M)^{-1}$ for the formyl proton in DMF solutions of NiTRI^{2+}: ○, 60 MHz; △, 100 MHz.

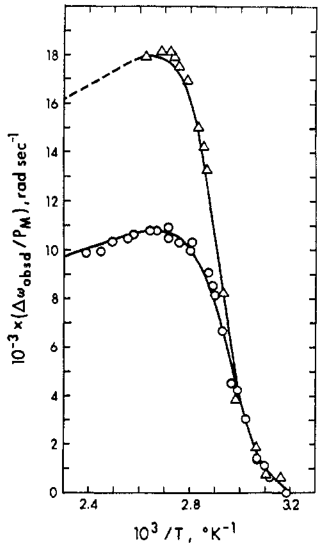

Figure 2.—Temperature dependence of $\Delta\omega_{obsd}/P_M$ for the formyl proton in DMF solutions of NiTRI^{2+}: ○, 60 MHz; △, 100 MHz.

ing and data from the nitrate salt were used only in the lower temperature region.

The solvent proton nmr line broadening caused by the paramagnetic species is expressed as

$$(T_{2P}P_M)^{-1} = \frac{\pi(\Delta\nu_{obsd} - \Delta\nu_{solv})}{P_M} \qquad (1)$$

where the terms have their usual meaning as described previously.[2] In calculating P_M, a solvation number of 3 has been used for NiTRI^{2+} and 2 for NiTAAB^{2+}.

The temperature dependence of $(T_{2P}P_M)^{-1}$ has been analyzed by a nonlinear least-squares fit of the data to the equation developed by Swift and Connick[4] with the inclusion of an outer-sphere line-broadening term, T_{2O}^{-1}, as given previously.[2] The temperature dependence of the solvent molecule lifetime in the coordination sphere of the metal ion is given by

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

The inner- and outer-sphere solvent proton transverse relaxation times are given by

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

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

The effective magnetic moment (μ_{eff}) is assumed to have a Curie law temperature dependence so that[5]

$$\Delta\omega_M = -\left(\frac{A}{\hbar}\right)\frac{\omega_O\mu_{eff}\beta\sqrt{S(S+1)}}{3kT} = \frac{-C_\omega}{T} \qquad (5)$$

The observed chemical shift ($\omega_{sample} - \omega_{solvent}$) is given by[4]

$$-\frac{\Delta\omega_{obsd}}{P_M} = \frac{\Delta\omega_M}{(\tau_M/T_{2M} + 1)^2 + (\tau_M\Delta\omega_M)^2} \qquad (6)$$

The temperature dependences of $(T_{2P}P_M)^{-1}$ and $\Delta\omega_{obsd}/P_M$ for NiTRI(ClO$_4$)$_2$ are shown in Figures 1 and 2, respectively. The parameters resulting from the least-squares fits of the line-broadening and shift data to the appropriate equations are given in Table I.

TABLE I

LEAST-SQUARES-FIT PARAMETERS FOR NiTRI(ClO$_4$)$_2$ IN *N,N*-DIMETHYLFORMAMIDE

	$(T_{2P}P_M)^{-1}$ data		$\Delta\omega_{obsd}/P_M$ data	
	60 MHz	100 MHz	60 MHz	100 MHz
$\Delta H^{\ddagger}$, kcal mol^{-1}	15.58	15.67	15.60	15.67[b]
$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}	6.28	6.66	6.37	6.56
$10^{-6}C_\omega$, radians sec^{-1} deg	4.13	7.15	4.20	7.00[c]
$E_M = E_O$, kcal mol^{-1}	2.14	2.14[a]	2.14[b]	2.14[a]
C_M, sec^{-1}	150.1	150.1[a]	150.1[b]	150.1[a]
C_O, sec^{-1}	10.6	10.6[a]	...	...

[a] The parameters defining T_{2M}^{-1} and T_{2O}^{-1} have been held constant as determined by the 60-MHz $(T_{2P}P_M)^{-1}$ fit. [b] Held constant at value given by the 100-MHz $(T_{2P}P_M)^{-1}$ fit. [c] Held constant at 60/100 of the value from the 60-MHz $\Delta\omega_{obsd}/P_M$ fit.

Excellent agreement is obtained for the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values from the different data sets. It seems reasonable to conclude that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 15.6 ± 0.25 kcal mol^{-1} and 6.5 ± 0.5 cal mol^{-1} deg^{-1}, respectively. The value of 4.2×10^6 radians sec^{-1} deg for C_ω may be used along with a μ_{eff} of 3.2 BM[3] in eq 5 to calculate a hyperfine coupling constant ($A/\hbar$) of 2.9×10^6 radians sec^{-1} for the C–H proton of DMF.

The line-broadening and chemical shift data for NiTAAB^{2+} are shown in Figures 3 and 4. The results are qualitatively similar to those for NiTRI^{2+}; however it was observed that the chemical shift decreased more rapidly above 90° ($10^3/T = 2.75$ deg^{-1}) than predicted by a T^{-1} dependence. Measurements of the solution magnetic susceptibility, using the method suggested by Evans,[6] have shown that the decreased chemical shift is due to the presence of a diamagnetic–paramagnetic equilibrium, with the diamagnetic species being formed at high temperature. The solvent proton chemical shift study indicates that nickel(II) is about 10% diamagnetic at the highest temperature studied (138°).[7]

Because of the complication outlined above only shift data for temperatures below 90° have been fitted to

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

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

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

[7] For the equilibrium written as diamagnetic species $\rightleftarrows$ paramagnetic species, the values $\Delta H° = -4.1$ kcal mol^{-1} and $\Delta S° = -5.6$ cal mol^{-1} deg^{-1} were calculated from the observed formyl proton chemical shift data (dashed lines) and the predicted chemical shifts (solid curve) of Figure 4. A least-squares fit of the molar magnetic susceptibilities gave $\Delta H° = -3.96$ kcal mol^{-1} and $\Delta S° = -7.4$ cal mol^{-1} deg^{-1}. These values are of limited accuracy because the equilibrium is displaced only ~10% toward the diamagnetic form.

TABLE II

LEAST-SQUARES BEST-FIT PARAMETERS FOR NiTAAB^{2+} IN *N,N*-DIMETHYLFORMAMIDE

	$(T_{2P}P_M)^{-1}$ data[a]						$\Delta\omega_{obsd}$ data	
	60 MHz		100 MHz				60 MHz	100 MHz
	A	B	C	D	E	F	G	H
$\Delta H^\ddagger$, kcal mol^{-1}	11.46	11.87	11.19	11.90	11.65	11.40	11.65[f]	11.46
$\Delta S^\ddagger$, cal mol^{-1} deg^{-1}	2.24	3.68	0.96	3.46	2.65	1.68	2.79	2.18
$10^{-6}C_\omega$,[a] radians sec^{-1} deg	3.21	3.21	5.35	5.35	5.35	5.35	3.22	5.35
E_M, kcal mol^{-1}	1.78	1.78	2.13	2.34[c]	2.18	1.78[d]	1.78[e]	1.78[e]
E_O, kcal mol^{-1}	2.85	2.34[b]	2.77	2.34[c]	2.34[b]	2.34[b]	...	...
C_M, sec^{-1}	312.5	308.4	189.0	137.8	173.1	312.9	308.4[e]	308.4[e]
C_O, sec^{-1}	2.30	7.63[b]	2.82	7.63	7.63[b]	7.63[b]	...	...

[a] C_ω has been held constant at the value determined by the 60-MHz shifts or at its corresponding 100-MHz value in all of the $(T_{2P}P_M)^{-1}$ fits. [b] T_{2O}^{-1} fixed as determined by fit D. [c] $E_M = E_O$ assumed. [d] E_M held constant at value indicated by fits A and B. [e] T_{2M}^{-1} parameters held constant as determined by fit B. [f] Held constant at value from fit E.

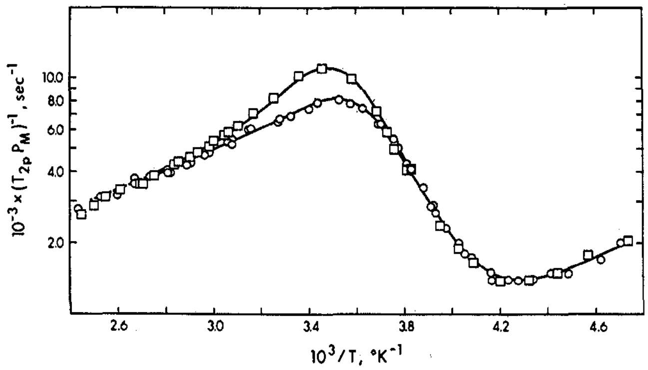

Figure 3.—Temperature dependence of $(T_{2P}P_M)^{-1}$ for the formyl proton in DMF solutions of NiTAAB^{2+}: ○, 60 MHz; □, 100 MHz.

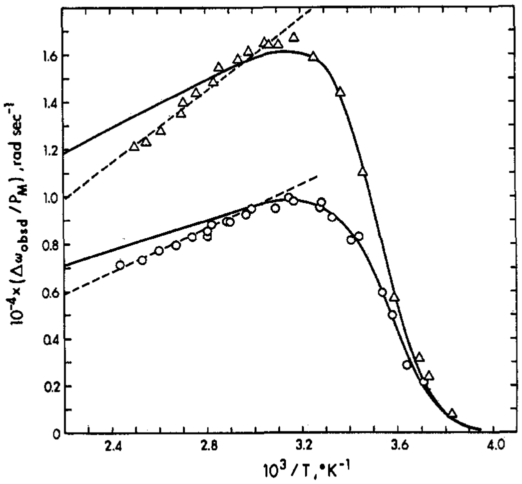

Figure 4.—Temperature dependence of $\Delta\omega_{obsd}/P_M$ for the formyl proton in DMF solutions of NiTAAB^{2+}: ○, 60 MHz; △, 100 MHz. The differences between the experimental (dashed) lines and the calculated (solid) curves were used to obtain $\Delta H°$ and $\Delta S°$ for the diamagnetic ⇄ paramagnetic equilibrium.

eq 6. It has also been necessary to fix C_ω at the value obtained from an analysis of the shift data when fitting the $(T_{2P}P_M)^{-1}$ results, because C_ω never makes a major contribution to the latter. The parameters from various least-squares fits are given in Table II. The differences between E_O and E_M at 60 and 100 MHz might be real but various fits show that $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are not greatly affected by changes in E_M or E_O.

The average values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ with their estimated uncertainties are 11.5 ± 0.5 kcal mol^{-1} and 2.5 ± 2 cal mol^{-1} deg^{-1}, respectively. With $C_\omega = 3.21 \times 10^6$ radians sec^{-1} deg at 60 MHz and $\mu_{eff} = 3.14$ BM,[8] the hyperfine coupling constant $(A/\hbar)$ of the CH proton is calculated to be 2.9×10^6 radians sec^{-1}.

The values of T_{2M} and T_{2O} can be well accounted for in terms of the dipolar and scalar contributions to T_{2M}[9] and only dipolar contributions to T_{2O}.[10] For NiTRI(DMF)$_3^{2+}$ an inner-sphere interaction distance (r_i) of 3.29 Å, a rotational correlation time (τ_R) of 1.2×10^{-10} sec,[11] and an electron spin relaxation time ($T_{1e} = T_{2e}$) of 2.9×10^{-11} sec give dipolar and scalar contributions of 5.41×10^3 and 1.67×10^2 sec^{-1} at 25°, respectively. The observed T_{2M}^{-1} at 25° is 5.58×10^3 sec^{-1} obtained from Table I. An outer-sphere interaction distance (d_o) of 5.75 Å is predicted from the observed outer-sphere broadening of 3.94×10^2 sec^{-1} at 25° for NiTRI(DMF)$_3^{2+}$ using the above values for τ_R and $T_{1e} = T_{2e}$.

Similarly for NiTAAB(DMF)$_2^{2+}$ the observed value of 6.22×10^3 sec^{-1} for T_{2M}^{-1}, from fit B of Table II is consistent with $r_i = 3.02$ Å, $\tau_R = 1.2 \times 10^{-10}$ sec, and $T_{1e} = T_{2e} = 1.85 \times 10^{-11}$ sec. The outer-sphere relaxation time of 3.98×10^2 sec^{-1} is consistent with $d_o = 5.75$ Å, the same value as found for NiTRI(DMF)$_3^{2+}$. All of the interaction distances and relaxation times appear to be consistent with expected values for nickel(II) complexes.

Discussion

In Table III are summarized the kinetic results from this work and some related systems studied previously. The NiTRI(DMF)$_3^{2+}$ and Ni(DMF)$_6^{2+}$ complexes are even more similar than the aquo systems. This confirms the previous conclusion[2] that the rigid tridendate

TABLE III

KINETIC PARAMETERS FOR *N,N*-DIMETHYLFORMAMIDE EXCHANGE ON SOME NICKEL(II) COMPLEXES

Complex	k(25°), sec^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal mol^{-1} deg^{-1}
NiTRI(DMF)$_3^{2+}$ [a]	5.9×10^2	15.6	6.5
Ni(DMF)$_6^{2+}$ [b]	3.8×10^3	15.0	8.0
NiTAAB(DMF)$_2^{2+}$ [a]	7.3×10^4	11.5	2.5
NiCR(DMF)$_2^{2+}$ [c]	1.9×10^6	9.5	2.2
NiCRCH$_3$(DMF)$_2^{2+}$ [c]	2.8×10^6	7.8	−2.9

[a] This work. [b] N. A. Matwiyoff, *Inorg. Chem.*, **5**, 788 (1966). [c] L. Rusnak and R. B. Jordan, *ibid.*, **10**, 2686 (1971).

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(8) The limiting value of μ_{eff} determined from the solution magnetic susceptibility study.

(9) D. Fiat and R. E. Connick, *J. Chem. Phys.*, **44**, 4103 (1966).

(10) Z. Luz and S. Meiboom, *ibid.*, **40**, 1066 (1964).

(11) N. S. Angerman and R. B. Jordan, *ibid.*, **54**, 837 (1971).

chelate does not greatly affect the solvent-exchange kinetics.

These observations also indicate that the TRI ligand is not particularly more or less electron donating than the DMF ligands. Therefore the lower $\Delta H^{\ddagger}$ for NiTAAB(DMF)$_2^{2+}$ cannot be attributed to greater electron donation from the macrocyclic ligand. Models indicate that steric interactions should not be important in NiTAAB(DMF)$_2^{2+}$. It can only be concluded that the lower $\Delta H^{\ddagger}$ may lie in the rather indeterminate solvation and crystal field effects.[12]

The kinetic parameters for NiTAAB(DMF)$_2^{2+}$ also show that exchange involving tetragonally distorted nickel(II) complexes is not necessarily unusually rapid. Therefore the low $\Delta H^{\ddagger}$ and large exchange rates for NiCR(DMF)$_2^{2+}$ and NiCRCH$_3$(DMF)$_2^{2+}$ may be due to steric interactions or to coupling to the diamagnetic paramagnetic equilibrium as noted previously.[1]

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.

[12] N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 2579 (1969).

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Lewis Acidity of Antimony Pentachloride

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Antimony pentachloride is a strong Lewis acid and the thermodynamic data for the interaction of this Lewis acid with a number of bases have been reported.[2,3] The claim has been made that enthalpies of interaction toward this acid, called *donor numbers*, can be used as a fundamental measure of the donor properties of molecules commonly used as nonaqueous solvents toward various solutes. Recently, it has been shown[4] that such an approach is basically a one term ordering of interactions and cannot possibly provide a general ordering of solvent donor strengths. It will provide a reliable ordering only when the solute has similar E and C numbers[4,5] to those of SbCl$_5$ or when both the E and C number of a given solvent are larger than those of another solvent. Thus, in place of the donor number, we advise as originally suggested[6] in our formulation of the coordination model that the enthalpy of interaction of a given donor be determined toward phenol and iodine so its E and C numbers can be evaluated to provide a quantitative measure of the donor strength. The application of this information toward understanding the behavior of solutes in nonaqueous solvents is still qualitative[6] because the E and C numbers of most solutes are not known, the reactions are not simple 1:1 adduct formation as in the case of SbCl$_5$ or systems incorporated into the E and C correlation, steric effects are often important when several bases are coordinated to a single Lewis acid solute, and solvating properties of the solvent are important. In this article, we report some additional limitations on the use of antimony pentachloride as a Lewis acid capable of providing information about the donor strength of bases.

Experimental Section

Purification of Chemicals.—Antimony pentachloride (Allied Chemical reagent grade) was purified by distillation under reduced pressure at 50°. Great precaution was taken to prevent it from coming in contact with air. It was stoppered and stored in an anhydrous calcium chloride desiccator in the dark. An approximately 0.03 M solution of SbCl$_5$ in dried 1,2-dichloroethane was found to have a negligible equivalent conductance ($\simeq$0.01–0.02 ohm^{-1} cm^2 equiv^{-1}).

Ethyl acetate (reagent grade), acetonitrile (reagent grade), chloroacetonitrile (Eastman Organic Chemical), pyridine[7] (reagent grade), benzonitrile (Eastman Organic Chemical),[8] and *p*-methylpyridine *N*-oxide (City Chemical)[9] were all purified as previously described.

Reagent grade carbon tetrachloride was stored over Linde 4A Molecular Sieves for several days prior to use. 1,2-Dichloroethane (Fisher Certified ACS grade) was stored over Linde 4A Molecular Sieves for at least 24 hr and used without further purification.

Calorimetric Measurement.—The calorimeter used has been described previously.[7,10] The solutions containing SbCl$_5$ were transferred to the dewar flask in a nitrogen-filled dry glove bag. A stream of dry nitrogen was passed over the Teflon top of the flask during the time of measurement. The resulting enthalpies of interaction and equilibrium constants were calculated simultaneously from the calorimetric data by a reported procedure.[7]

Results and Discussion

The enthalpies measured in this work are summarized in Table I. They are compared with those reported by Gutmann[3] and Olafsson,[2] and it is seen that good agreement is generally obtained.

TABLE I
ENTHALPIES OF ADDUCT FORMATION OF ANTIMONY PENTACHLORIDE AND VARIOUS BASES

Solvent	Base (number)	Kcal/mol $-\Delta H^a$	 $-\Delta H^b$
CCl$_4$	Ethyl acetate (1)	15.5 ± 0.2	
C$_2$H$_4$Cl$_2$	Ethyl acetate (1)	16.6 ± 0.3	17.1
CCl$_4$	Benzonitrile (2)	12.7 ± 0.2	
C$_2$H$_4$Cl$_2$	Benzonitrile (2)	13.0 ± 0.2	11.9
C$_2$H$_4$Cl$_2$	Acetonitrile (3)	14.6 ± 0.1	14.1
C$_2$H$_4$Cl$_2$	*p*-Methylpyridine *N*-oxide (4)	36.3 + 0.4	
CCl$_4$	Monochloroacetonitrile (5)	9.6 ± 0.3[c]	
C$_2$H$_4$Cl$_2$	*N*,*N*-Dimethylacetamide (6)	. . .	27.8
C$_2$H$_4$Cl$_2$	*N*-*N*-Dimethylformamide (7)	. . .	26.6
C$_2$H$_4$Cl$_2$	Dimethyl sulfoxide (8)	. . .	29.8
C$_2$H$_4$Cl$_2$	Pyridine (9)	34.0 ± 0.4	33.1
C$_2$H$_4$Cl$_2$	Diethyl ether (10)		19.2
C$_2$H$_4$Cl$_2$	Tetrahydrofuran (11)		20.0

[a] Measured in this laboratory, error limits indicate precision (ref 7). [b] Ref 2 and 3. [c] K(equilibrium constant) = 128 ± 11 (25°).

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[10] R. S. Drago, N. O'Bryan, and G. C. Vogel, *J. Amer. Chem. Soc.*, **92**, 3924 (1970).