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.

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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

		Kcal/mol	
Solvent	Base (number)	$-\Delta H^a$	$-\Delta H^b$
CCl_4	Ethyl acetate (1)	15.5 ± 0.2	
$C_2H_4Cl_2$	Ethyl acetate (1)	16.6 ± 0.3	17.1
CCl_4	Benzonitrile (2)	12.7 ± 0.2	
$C_2H_4Cl_2$	Benzonitrile (2)	13.0 ± 0.2	11.9
$C_2H_4Cl_2$	Acetonitrile (3)	14.6 ± 0.1	14.1
$C_2H_4Cl_2$	*p*-Methylpyridine *N*-oxide (4)	36.3 + 0.4	
CCl_4	Monochloroacetonitrile (5)	9.6 ± 0.3[c]	
$C_2H_4Cl_2$	*N*,*N*-Dimethylacetamide (6)	...	27.8
$C_2H_4Cl_2$	*N*-*N*-Dimethylformamide (7)	...	26.6
$C_2H_4Cl_2$	Dimethyl sulfoxide (8)	...	29.8
$C_2H_4Cl_2$	Pyridine (9)	34.0 ± 0.4	33.1
$C_2H_4Cl_2$	Diethyl ether (10)		19.2
$C_2H_4Cl_2$	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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[1] Abstracted in part from the Ph.D. Thesis of Y. Y. Lim, University of Illinois, Urbana, Ill., 1971.

[2] G. Olafsson, *Acta Chem. Scand.*, **22**, 377 (1968), and references therein.

[3] V. Gutmann in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, New York, N. Y., 1968, Chapter 4, p 67, and references therein.

[4] R. S. Drago, G. C. Vogel, and T. Needham, *J. Amer. Chem. Soc.*, **92**, (1971).

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[7] T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5770 (1967).

[8] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," 1st ed, Pergamon Press, Elmsford, N. Y., 1966.

[9] J. C. Hill, Ph.D. Thesis, University of Illinois, 1968.

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

With the exception of the weak base, monochloroacetonitrile, it was found that the interaction of $SbCl_5$ with various bases goes nearly to completion in the solvents carbon tetrachloride and 1,2-dichloroethane. Under these conditions, the enthalpy of reaction is obtained by dividing the measured heat evolved by the number of moles of base which was the limiting reagent. In several of the systems reported[3] where the enthalpies are low, the heats reported are not enthalpies of adduct formation because the authors failed to determine K. Adducts of acetonitrile, pyridine, and p-methylpyridine N-oxide are insoluble in carbon tetrachloride and calorimetric measurements were carried out in 1,2-dichloroethane where they are soluble.

We were interested in incorporating $SbCl_5$ into our E and C correlation[4]

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

It has previously been reported[3] that $SbCl_5$ does not obey this relation. If this is the case, we become confronted with a very strange bit of scientific logic as applied to the concept of donor numbers. Since a very large number of Lewis acids (about 25 in all) do obey this equation, if $SbCl_5$ does not, how can $SbCl_5$ be used as a model compound to predict enthalpies of interaction for other acids which do obey the E and C equation? Obviously, it could not. Consequently, we were interested in thoroughly analyzing the experimental data for this acid.

As reported,[3] a satisfactory fit of the data reported in the literature to the E and C equation (1) could not be obtained by us. A potential cause of breakdown for an E and C correlation of the data is the existence of steric effects.[4] In order to eliminate this possibility, the data considered were limited to a series of donors in which the donor atom has only one other atom bonded to it and in which we felt steric effects were minimal. These bases are numbered 1 to 8 in Table I. Again, a satisfactory fit to eq 1 was not obtained.

Our next concern was with the magnitude of the solvation energy contribution that could arise from using 1,2-dichloroethane as solvent.[11] We found two systems that could be studied in both CCl_4 and 1,2-dichloroethane solvents. We made many attempts to find adducts of stronger donors that had CCl_4 or cyclohexane solubility without success. The results are reported in Table II.

TABLE II

COMPARISON OF ENTHALPIES OF $SbCl_5$ ADDUCT FORMATION MEASURED IN CCl_4 AND $C_2H_4Cl_2$ AS SOLVENTS

	$-\Delta H$, kcal mol^{-1}		
Base	CCl_4 solvent	$C_2H_4Cl_2$ solvent	Difference
$CH_3COOC_2H_5$	15.5 ± 0.2	16.6 ± 0.3	1.1
C_6H_5CN	12.7 ± 0.2	13.0 ± 0.4	0.3

In a recent report from this laboratory,[11] we have been able to show some cases where a series of bases interacting with a given acid give rise to a constant difference in solvation energy of any adduct minus that of the corresponding base in a given solvent when specific interactions are absent.[11,12] If this were true for the data in Table II, the difference in solvation should have been the same for the two adducts. The large experimental error in the difference precludes drawing a definite conclusion. For the moment, we shall proceed, assuming a constant difference in enthalpy measured in the two solvents of 0.7 kcal mol^{-1}, *i.e.*, the average of the two values in Table II. Using the data in Table I for bases 1 to 8 and correcting it as described still did not produce a decent fit of the data to eq 1. We were able to obtain an excellent fit for the corrected acetonitrile and 4-methylpyridine N-oxide enthalpies and the CCl_4 data for chloroacetonitrile and ethyl acetate. The results are illustrated in Table III. This fit gave C_A and E_A values for $SbCl_5$ of 5.20 and 7.52, respectively. These results are very close to those obtained by using only the enthalpy data from the two systems measured in CCl_4 for which C_A and E_A values of 5.0 and 7.6 were obtained. Using these values, enthalpies of adduct formation of 23.0, 21.9, and 24.0 kcal mol^{-1} are predicted for DMA, DMF, and DMSO in CCl_4. When the 0.7 kcal mol^{-1} correction is applied to convert the enthalpies to those in 1,2-dichloroethane solvent, the results are seen to be in poor agreement with the experimental values in Table I.

TABLE III

CALCULATED AND EXPERIMENTAL ENTHALPIES OF ADDUCT FORMATION OF $SbCl_5$ WITH VARIOUS BASES

Base	$-\Delta H$ (calcd)[a]	$-\Delta H$ (measd)
$ClCH_2CN$	9.7	9.6
CH_3CN	13.5	13.9[b]
4-Methylpyridine N-oxide	35.4	35.6[b]
Ethyl acetate	15.9	15.5

[a] Calculated with eq 1 using a newly reported set of E_B and C_B values.[4] [b] Corrected for 0.7 kcal mol^{-1} solvation.

Since there is a considerable amount of data reported on $SbCl_5$ as an acid in 1,2-dichloroethane, it would be advantageous to convert it to useful form for predicting donor–acceptor interactions free of solvent effects. The model we tried next assumed that the enthalpy of solvation was directly proportional to the enthalpy of adduct formation. The rationale for this involves assuming that the stronger the base–antimony interaction, the more negative charge on the chlorine and the greater the solvation by the 1,2-dichloroethane (either *via* hydrogen bonding or dipole–dipole interaction). To test such a model, we plotted the enthalpy of adduct formation from eq 1 *vs.* the difference in the experimental and calculated enthalpy, *i.e.*, we are attributing this difference to solvation. Also included on the plot are the data from Table II. The results, illustrated in Figure 1, indicate that such a model works well for all systems considered except pyridine N-oxide. Either extensive solvation of the base or less extensive solvation of this adduct could be the cause of this discrepancy; the former being favored in view of the greater basicity (when the C_A number is important) for this donor. We do not recommend this as a procedure for correcting enthalpies on this system, but have pursued this discussion merely to show that the existence of substantial solvation effects is plausible.

Even if the solvation of the adduct were proportional to the heat of formation of the adduct in most

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(11) M. Nozari and R. S. Drago, submitted for publication.

(12) M. Nozari and R. S. Drago, *J. Amer. Chem. Soc.*, in press.

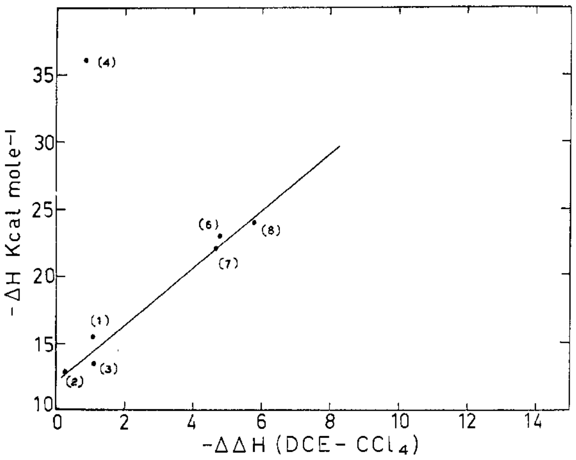

Figure 1.—Scatter in the $-\Delta H$ of the adduct formation *vs.* $-\Delta\Delta H$ of solvent transfer.

cases, the enthalpies for the formation of the diethyl ether, tetrahydrofuran, and pyridine adducts cause additional difficulties. The predicted enthalpies are 23.9, 28.9, and 41.8 compared to measured values of 19.2, 20.0, and 33.3. These differences are in the opposite direction of the expected solvent effect and may be due to the fact that steric effects outweigh any solvation effects. The larger discrepancy in the calculated and experimental heats for THF than for diethyl ether indicate that this is not the whole story and that complications from solvation are again present.

In addition to these complications, an additional problem was encountered with diethyl sulfide and the free radical base 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TMPN).[13] It was found that in $C_2H_4Cl_2$ the adducts ionize. TMPN gives a molar conductance of 24 ohm^{-1} mol^{-1} cm^2 at 1.2×10^{-3} *M* concentration at 25° and diethyl sulfide gives one of 23 ohm^{-1} mol^{-1} cm^2 at 2×10^{-3} *M* and 25°. The conductance of many 1:1 electrolytes is of the order of magnitude of 100 ohm^{-1} cm^2 mol^{-1} (± 25). The ionization process occurring in 1,2-dichloroethane could be attributed to the equilibrium

$$2SbCl_5 \cdot B \rightleftarrows SbCl_4(B)_2^+ + SbCl_6^-$$

Ionization is favored by a high dielectric constant solvent and a high donor strength (apparently large *C* number) of the base. Such an ionization process greatly complicates the interpretation of any heat measurement. The conductances of all of the other adducts reported here were minimal in 1,2-dichloroethane, but the results of similar measurements on many of the other systems reported in the literature[3] have not been published.

In conclusion and contrary to what we have been led to believe,[3] $SbCl_5$ investigated in the solvent 1,2-dichloroethane is a very poor reference acid for the quantitative determination of donor strength. Many of the applications in the literature of these donor number data are probably correct because these applications are very qualitative. Steric effects also influence the magnitude of the metal–ligand interaction in many of the transition metal ions to which these studies have been applied, so again such an effect would be in the same direction if the donor number were used, but we cannot expect the steric interaction in the transition metal ion complex to be quantitatively reproduced in $SbCl_5$. For all of the reasons described above, donor numbers clearly do not provide us with quantitative, fundamental information about the donor properties of bases. Complications arising from steric effects and the unusual solvating properties of 1,2-dichloroethane[12] give rise to significant and unpredictable contributions to the measured enthalpy. The *E* and *C* numbers reported here should enable us to predict enthalpies (in the absence of steric and appreciable solvent effects) to within 1 kcal mol^{-1}. As can be seen from Figure 1, we have not been able to find a reliable procedure that could be employed to correct the donor numbers for solvation effects.

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(13) Y. Y. Lim and R. S. Drago, *J. Amer. Chem. Soc.*, **93**, 891 (1971).

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Complexes of Iron(II), Nickel(II), and Tin(IV) Chlorides with Hydrazine Derivatives[1]

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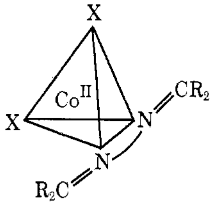
The complexes of cobalt(II) halides with azines have been reported recently[2] wherein compounds of the type $R_2C{=}N{-}N{=}CR_2Co^{II}X_2$ were found to be tetrahedral complexes (I) which could be obtained by direct reaction of cobalt(II) halides with ketazines and aldazines or by condensation of bis hydrazine complexes of $Co^{II}X_2$ with ketones or aldehydes. The present work relates to the preparation of similar addition compounds of hydrazine derivatives with iron(II) and nickel(II) dichlorides as well as tin(IV) tetrachloride. The infrared and electronic spectra of the complexes of the transition metal halides were used to determine their probable structure, and resonance absorption of low energy γ radiation (Mössbauer effect) has proved to be a very useful tool for the tentative elucidation of the structure of the tin(IV) compounds.[3]



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(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., 1971, Abstract No. INOR-151.

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