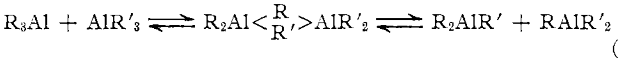
ing will occur upon complexing because of increased quadrupolar interaction of the aluminum nucleus with the molecular electric field gradients.[11]

Alkyl Interchange.—A rapid alkyl interchange on mixing two different aluminum alkyls has been postulated[12] and verified experimentally by Al^{27} nmr.[10] Such an exchange probably results because of the equilibria



$$R_3Al + AlR'_3 \rightleftharpoons R_2Al{<}{\overset{R}{\underset{R'}{}}}{>}AlR'_2 \rightleftharpoons R_2AlR' + RAlR'_2 \qquad (3)$$

It has been found that an equimolar mixture of TEA and TNBA added to NaF exhibits an Al^{27} nmr line width intermediate to the line widths of the NaF·2TEA and NaF·2TNBA complexes at a given temperature and at all power levels (see Table I). This would only be expected if an alkyl interchange took place upon mixing the TEA and TNBA resulting in a $NaF \cdot 2AlR_3$ complex containing mixed alkyl groups. A plot of the logarithm of the line width of the mixed complex as a function of the reciprocal of the absolute temperature shows that the data fit the relationship given by eq 1. From this relationship a ΔE value of 7.1 kcal/mole was determined, which is intermediate between the ΔE values determined for the NaF·2TEA and NaF·2TNBA complexes.

It has also been found that there is no alkyl interchange when two different $NaF \cdot 2AlR_3$ complexes are mixed. This has been shown by mixing 0.5 ml of NaF·2TEA with 2 ml of NaF·2TNBA, heating to 152°, and recording the Al^{27} nuclear magnetic resonance of the mixture. By successively lowering the modulation amplitude to 0.1 gauss, two fairly distinct resonances were obtained—a narrow line of 4 gauss which is due to NaF·2TEA and a broad line of 10 gauss which is due to the NaF·2TNBA complex.

Also, Al^{27} nmr was used to determine if any exchange takes place when TEA is mixed with NaF·2TNPA. At room temperature TEA forms a separate phase when added to NaF·2TNPA. Upon heating to 120° a single phase forms which exhibits two resonances—a narrow line due to TEA and a broad line corresponding to the NaF·2TNPA complex. Thus, there is very little, if any, exchange when TEA is mixed with NaF·2TNPA at 120° to form NaF·2TEA and TNPA.

All of the $NaF \cdot 2AlR_3$ complexes exhibited single, Lorentzian Al^{27} nmr line widths regardless of temperature. These results indicate that all of the aluminum nuclei are equivalent and support the proposed structure where an aluminum–fluorine–aluminum collinear bond exists[13] instead of the proposed structure, $Na^+[Al(C_2H_5)_3F]^- \cdot Al(C_2H_5)_3$, where the aluminum nuclei are not equivalent.[14] However, more refined techniques will have to be used to obtain conclusive proof of the structure of these liquid complexes.

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Chloride Ion Exchange with *trans*-Dichlorobis(pyridine)platinum(II) in Selected Solvents

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It has been shown[2] that in substitution reactions of square-planar platinum(II) complexes, nucleophilic reactions may be divided into two classes: (a) those that are first order in complex, zero order in nucleophile, and all of similar rate; (b) those that are first order in both complex and nucleophile and, in general, faster than those of class a. In the mechanism proposed for these reactions, it has been assumed that the solvent coordinates on the z axis above and below the primary ligand plane. In this fashion, the complex becomes six coordinate, with the magnitude of the solvent interaction assumed to be of great importance in determining the mechanistic route followed during substitution.

Pearson, Gray, and Basolo[3] have studied the rate of chloride ion exchange with *trans*-$[Pt(py)_2Cl_2]$ (py = pyridine) in a number of solvents. They proposed that the observed rates of chloride ion exchange in the various solvents are consistent with a mechanism based on strong interaction of the solvent with the metal complex in the rate-determining step. It was proposed that this strong interaction facilitates chloride ion displacement from the complex, enhancing the rate for the process that is zero order in chloride (*i.e.*, a slow ionization step followed by fast chloride attack). These authors again state that the reactions are first order in the platinum complex.

Previous work in this laboratory on the coordination model[4] treated anion displacement from metal ions by solvent. The thermodynamic cycle for this reaction contained an energy step for the gas phase reaction corresponding to the anion leaving the coordination sphere and the solvent entering. The enthalpy for this reaction is related to the difference in the donor strength of the anion and solvent. The difference in the ability of the solvent to solvate the products and starting materials (*i.e.*, without entering the coordination sphere) is related to the solvating ability of the solvent. The results of these studies for various nonaqueous solvents have led us to question whether the observed and proposed mechanisms could be attributed solely to solvent donor strength as reported[3] or could also be dependent on the solvating properties of the solvent media. By selecting solvents on the basis of both solvating properties and donor ability, a more

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[1] Abstracted in part from the Ph.D. Thesis of V. A. Mode, University of Illinois, 1965; National Science Foundation Graduate Fellowship, 1964–1965.

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complete assessment of the effect of solvent on the substitution mechanism can be made.

Experimental Section

Tetraethylammonium Chloride.—Radioactively labeled chlorine was introduced into the purified salt as previously described in the literature.[5]

trans-**Dichlorobis((pyridine)platinum(II).**—The synthesis of the platinum complex was essentially that described by Hedin.[6] After isolating and purifying $[Pt(py)_4]Cl_2$, the white salt was heated to 156° for approximately 30 min, producing the yellow *trans*-$[Pt(py)_2Cl_2]$, which was then washed with water and air dried. *Anal.* Calcd for $PtC_{10}H_{10}Cl_2N_2$: Pt, 45.99; C, 28.30; H, 2.47; N, 6.63. Found: Pt, 45.53; C, 28.35; H, 2.51; N, 6.60.

Dimethyl Sulfoxide.—Fisher reagent grade dimethyl sulfoxide was dried with 4-A molecular sieves, vacuum distilled, and stored in a desiccator prior to use.

Chloroform-*d*$_1$.—Deuterated chloroform was dried prior to use with 4-A molecular sieves. Gas chromatographic analysis indicated less than 10^{-4} *M* water and the concentration of low molecular weight chlorinated hydrocarbons to be minimal (less than 0.5% CCl_4).

1,2-Dichloroethane.—This solvent was purified as described in the literature.[7]

Pyridine.—Reagent grade pyridine was vacuum distilled prior to use.

Tetramethylene Sulfone (Sulfolane).—This reagent was purified according to a previously reported[8] procedure.

Nmr Study.—Samples for proton nmr analysis were prepared from stock solutions and diluted to the desired concentration. After addition of tetramethylsilane as an internal standard, the solutions were degassed by repeated freeze–melt cycles under reduced pressure. Once gas evolution ceased, the procedure was repeated for one additional cycle and the samples were sealed.

Proton nmr spectra were obtained on dilute solutions with a Varian HA-100 instrument and on more concentrated solutions with an A-60. Readout on the A-60 gave peak location to within ±0.5 cps; readout on the HA-100 gave peak location to within ±0.1 cps.

Exchange Study.—In order to make an accurate comparison with the work reported by Pearson, *et al.*,[3] the experimental procedure has been conducted essentially as they described. Details of the constant-temperature bath, counting equipment, and technique of radioactive-labeling introduction are contained in an earlier paper.[5] Standard samples show zero-time exchange to be less than 2% and the reproducibility of any one sample to be ±1%. The total rate of exchange of chloride between dichlorobis(pyridine)platinum(II) and ionic chloride ($(C_2H_5)_4NCl$) was determined from the fraction of exchange as a function of time.[9] Since the dissociation of tetraethylammonium chloride is not known in all of the solvents studied, the rate of exchange has been converted to a pseudo-first-order rate constant $k_1 = R/[Pt(py)_2Cl_2]$ for purposes of the present discussion.

Results

The pyridine proton nmr spectrum was resolved into eight resonance peaks—a doublet and two sets of triplets. The observed peak positions are reported as δ in Table I for free and complexed pyridine in three solvents. No attempt was made to analyze the AB_2C_2 spectrum.

The results of our exchange studies are summarized in Table II. Exchange, zero order in chloride, is observed in dimethyl sulfoxide and tetramethylene sulfone, while a chloride ion dependent order is observed in pyridine and deuteriochloroform.

Discussion

Nmr Study.—The nmr spectrum of the platinum–pyridine complex in dimethyl sulfoxide (DMSO) is easily distinguished from that of the complex in deuteriochloroform (see Table I). In a solvent composed of 10% DMSO in deuteriochloroform (by volume), the platinum complex was observed to have a spectrum identical with that in neat DMSO (Table I). On the

TABLE I

COMPLEXED PYRIDINE NMR PEAKS IN DIFFERENT SOLVENTS[a]

		δ							
		α		β			γ		
Solvent	Pyridine								
$CDCl_3$	Free	8.53	8.60	7.13	7.23	7.33	7.53	7.63	*b*
	Complexed	8.90	8.96	7.25	7.30	7.36	7.70	7.76	7.85
$(CH_3)_2SO$	Free	8.50	8.56	7.26	7.36	7.46	7.70	7.80	*b*
	Complexed	8.61	8.68	7.33	7.40	7.46	7.80	7.86	7.96
Mixed[c]	Free	8.53	8.60	7.30	7.36	*b*	7.53	7.70	*b*
	Complexed	...	...	7.34	7.41	7.45	*b*	7.85	7.96

[a] In ppm relative to internal TMS. Spectra of dilute solutions of the complex were obtained on an HA-100. Splittings of the α proton by the γ proton are then resolved leading to peaks at 897.5, 895.8, 890.6, and 889.1 cm^{-1}. [b] Peak identified but too obscure to determine accurate location. [c] A 1:9 volume ratio of $(CH_3)_2SO:CDCl_3$.

TABLE II

RATE OF CHLORIDE EXCHANGE AT 25°

Solvent	Molarity of *trans*-$[Pt(py)_2Cl_2]$ × 10^3	Molarity of $(C_2H_5)_4NCl$ × 10^3	10^8R, *M* sec^{-1}	10^8k_{obsd}, sec^{-1} [a]
$(CH_3)_2SO$	0.93	0.98	38.5	41.3
	0.93	4.90	40.0	43.0
	0.93	9.79	39.2	42.2
	1.0[b]	2.53[b]		38[b]
$CDCl_3$	0.92	0.61	0.6	0.6[c]
	0.92	1.22	0.8	0.8[c]
Mixed[d]	0.93	1.15	1.3	1.4
	0.93	5.72	3.0	3.0
	0.93	11.45	3.7	4.0
$(CH_2)_4SO_2$	0.93	1.02	9.1	9.8
	0.93	1.79	9.7	10.3
	0.93	3.51	9.0	9.7
C_5H_5N	0.93	0.51	0.08	0.08[c]
	0.93	1.73	0.2	0.2[c]
	0.93	3.84	0.33	0.3[c]

[a] Calculated using $R = k[Pt(py)Cl_2]$; this value may be compared with k_{obsd} in ref 3. [b] From ref 3. [c] Data scatter makes reporting of more significant figures inappropriate. [d] DMSO: $CDCl_3$ is 1:9 (by volume).

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basis of these data, it is proposed that the species present in the mixed solvent is a platinum complex of DMSO. It is assumed that the coordination positions above and below the ligand plane are occupied by molecules of dimethyl sulfoxide in a manner similar to that in neat dimethyl sulfoxide and that the platinum species is similar in both systems.

Exchange Study.—The kinetic data for chloride ion exchange with the platinum complex in neat DMSO are zero order in chloride and are consistent with the mechanism proposed[3] in which the displacement of chloride from the complex is the rate-controlling step. However, if it is mainly the donor strength of the DMSO which facilitates chloride ion displacement,[3] then the complex $[Pt(py)_2Cl_2(DMSO)_2]$ should undergo reaction by a similar mechanism in the solvent $CDCl_3$. Examination of the data in Table II shows that in the mixed solvent the chloride-dependent path (possibly in addition to some chloride-independent mechanism) is occurring. This result is in direct contradiction to the above prediction based on the reported[3] role of the solvent in this reaction. It appears in this instance as though the ability of the medium to facilitate charge separation (*i.e.*, the solvating ability of the solvent) is a more important parameter than the magnitude of the metal ion–solvent interaction. In order to test this proposal further, the exchange was investigated in pyridine and sulfolane. The former is a strong donor but poor solvating solvent,[4] and the latter is a poor donor solvent[10] but a good solvating solvent.[4] Again, the solvating properties dominate, and the reaction mechanism is found to be zero order in chloride in sulfolane and very much dependent on chloride ion concentration in pyridine.

For the solvents used in this study, the donor strength is in the order[4] pyridine > DMSO > sulfolane >> $CDCl_3$ and the solvating ability is in the order[4] DMSO $\sim$ sulfolane >> pyridine > $CDCl_3$.

Although the exchanges described above have been found to correlate with the solvating ability of the solvent, it would be naïve to attempt to account for the mechanism of this reaction in a series of solvents solely on the basis of solvating ability. For very good solvating solvents,[4] safe predictions for this reaction can be made. For example, a chloride-independent path would be predicted in N-methylformamide and N-methylacetamide, but an *a priori* prediction of the experimentally observed[3] chloride-dependent path in N,N-dimethylformamide could not have been anticipated. For borderline solvents, one must consider, in addition to donor strengths, how the change in solvent affects the relative rates of the two processes, *i.e.*, the chloride-dependent and chloride-independent paths. In this connection, many unknown parameters are introduced when the solvent is varied (*e.g.*, entropies and enthalpies of activation of the two mechanistic routes will change, and variations in the free energies and enthalpies of solvation of the chloride ion will occur in the different solvents).

In spite of the lack of complete understanding, studies in nonaqueous solvents can show when solvating properties are important. This approach is considerably better than ignoring solvation completely as has so often been done on studies carried out in water. The importance of solvation has been clearly demonstrated in this study and should cast doubt on many of the conclusions drawn from studies where solvation is neglected.

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[10] It might be argued that sulfolane is "biphilic".[3] However, the donor strength of sulfolane toward iodine is low[8] and iodine should make use of the biphilic character of the donor. A very large interaction of iodine with donors containing empty d orbitals, *e.g.*, $(C_2H_5)_2S$, is found to occur. It appears that an assignment of biphilic character to $(CH_3)_2SO$ and CH_3NO_2 is not warranted on the basis of the reported[3] data. This biphilic concept (and possibly other concepts derived from reaction rates and orders in polar solvents) disappears in this system when solvent effects are considered.

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Hydrolysis of the Aquo Ions R_3Sn^+ and R_2Sn^{2+}: Steric Effects on the Dissociation of Aquo Acids[1]

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Recently, there has been some interest in the solution chemistry of the dialkyltin(IV) and trialkyltin(IV) moieties from the standpoint of complexation reactions in aqueous solution,[2–8] complex formation in nonaqueous solution,[9] assignment of Raman spectra of these moieties in solutions,[10–12] and the interpretation of changes in the indirect tin-117 and tin-119 proton spin–spin coupling constants in aqueous solutions.[13–17]

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