account in treating the kinetic data. Studies have not been made on hypophosphite ion as a "bridging" ligand in electron-transfer reactions; the rate of Cr(II)–Cr(III) exchange in $CrH_2PO_2^{2+}$ + $^*Cr^{2+}$ should provide very useful information on this point. This reaction may be of especial interest, in view of the important role of phosphate ions in biochemical oxidation–reduction processes. Hypophosphorous acid is itself a reducing agent with some unusual kinetic properties, which have been previously summarized.[2] The question of the mechanism of oxidation of coordinated hypophosphite ion merits attention. Preliminary experiments have shown that this ligand can be oxidized while remaining coordinated to chromium(III). For example, the net reaction with iodine solutions is

$$CrH_2PO_2^{2+} + I_3^- + H_2O = CrH_2PO_3^{2+} + 3I^- + 2H^+$$

The mechanism of this reaction has not yet been investigated in detail, but probably differs substantially from that for the free acid.

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Kinetics of *trans*-Dichlorobis(piperidine)platinum(II) in Different Solvents

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Rate data of monohalide displacements on *trans*-dichlorobis(piperidine)platinum(II) with several entering groups in five structurally different dipolar aprotic solvents are reported. The entering group reactivity order parallels the polarizability order in all the solvents and the reactivity does not vary strongly as the hydrogen-bonding capacity changes from protic to aprotic solvents. The kinetic data are discussed in terms of solvation of the reagent entering group.

Introduction

Rate data concerning the solvent effect in substitution reactions of some Pt(II) phosphine complexes have recently been reported.[1] The objectives of investigations on this subject are to offer, first, some evidence concerning the mechanism of nucleophilic displacement in the reactions of d^8 complexes and, second, to determine the factors which promote strong interactions between the reaction center and the entering group at the transition state.

This paper reports a kinetic study of *trans*-$[Pt(pip)_2Cl_2]$ (pip = piperidine) with several entering groups in a variety of structurally different dipolar aprotic solvents. The effect of the solvent on the rates of these reactions is investigated and a comparison between the rate data of the piperidine and of the analogous phosphine complex is presented.

Experimental Section

Materials.—Platinum(II) compounds were prepared following the methods reported in the literature.[2] All the compounds were characterized by analysis.

Acetone was dried with potassium carbonate and distilled, bp 56.5°; dimethyl sulfoxide was distilled under reduced pressure in nitrogen atmosphere; nitromethane was washed with aqueous sodium hydrogen carbonate, dried with calcium chloride, and fractionated, bp 101°; dimethylformamide was dried with calcium oxide and distilled, bp 153°; acetonitrile was dried with potassium carbonate and fractionated, bp 81°. Other materials used were reagent grade.

Kinetics.—The reactions of isotopic exchange were followed by the same procedure as previously reported.[1a]

Other reactions were followed by measuring changes in optical density of the reaction mixture in the ultraviolet region by means of 1-cm quartz cells in the thermostat-controlled cell compartment of a Beckman DK-2A, a Beckman DU, and an Optica CF-4 spectrophotometer. The reactions in nitromethane were carried out in 0.1-cm quartz cells. The reference cell in each case contained the reagent blank. In the case of relatively fast reactions, an Optica CF-4 was used and the chart drive on the attached recorder was started at the moment of mixing. The absorbance at a selected wavelength was recorded against time, starting a few seconds after mixing. The solution of entering group was added with a syringe. All solutions were kept at 25° prior to mixing. At the experimental temperature, 25 ± 0.1°, there was no evidence to suggest a *cis–trans* isomerization. In the range of the experimental concentrations, Beer's law was obeyed for both reactants and products in all the solvents examined.

The kinetics were performed with a 10–100-fold excess of the entering group in order to provide pseudo-first-order conditions and to force the reactions to go to completion. The complex concentration was changed in the range 10^{-4}–10^{-3} *M*. Tetrabutylammonium salts were used. Except in a few cases, at least four concentrations of entering group were examined, in the range 5×10^{-3} to 5×10^{-2} *M*. The ionic-strength effects were not important, as found for the reactions in methanol.[3] No attempt was made therefore to keep a constant electrolyte concentration.

The reactions proceed by a slow, rate-determining step, followed by a rapid second step

$$trans\text{-}[Pt(pip)_2Cl_2] + Y^- \xrightarrow{k_{obsd}} trans\text{-}[Pt(pip)_2YCl] + Cl^-$$

$$trans\text{-}[Pt(pip)_2YCl] + Y^- \xrightarrow{\text{fast}} trans\text{-}[Pt(pip)_2Y_2] + Cl^-$$

Except in acetone, good linearity was obtained for the plots of k_{obsd} *vs.* the initial reagent concentrations with nonzero intercepts in all the solvents.

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[1] (a) U. Belluco, M. Martelli, and A. Orio, *Inorg. Chem.*, **5**, 582 (1966); (b) U. Belluco, P. Rigo, M. Graziani, and R. Ettorre, *ibid.*, **5**, 1125 (1966).

[2] J. Chatt, L. A. Ducanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955).

[3] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Am. Chem. Soc.*, **87**, 241 (1965).

TABLE I[a]

SECOND-ORDER RATE CONSTANTS OF FREE IONS, 10^3k_2 (M^{-1} SEC^{-1}), FOR THE REACTIONS

$trans\text{-}[Pt(pip)_2Cl] + Y^- \xrightarrow{k_2} trans\text{-}[Pt(pip)_2ClY] + Cl^-$ IN VARIOUS SOLVENTS AT 25°

Nucleophile, Y^-	$n°_{Pt}$[d]	CH_3OH[c]	$(CH_3)_2CO$	$(CH_3)_2SO$	$HCON(CH_3)_2$	CH_3CN	CH_3NO_2
Solvent[b]	0[e]	1.2×10^{-5}	8×10^{-5}	7×10^{-4}	4×10^{-5}	3×10^{-5}	2.5×10^{-5}
Cl^-	3.04	0.9	3.5	1.0	0.56	1.1	1.5
N_3^-	3.58	5.3	...	...	...	...	...
Br^-	4.18	6.16	80	5.2	6.7	12.8	15
I^-	5.42	...	165	18	27	86	78
SCN^-	5.65	400	375	15	...	...	...
$SeCN^-$	7.10	...	...	...	...	910	710
Thiourea	7.17	3500	10,600	480	780	...	...

[a] Supplementary material (specific kinetic data used to estimate values in this table) has been deposited as Document No. 8885 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks payable to: Chief, Photoduplication Service, Library of Congress. [b] Values of k_1, in sec^{-1}. [c] Values at 30° from ref 3. [d] Reactivity constants at 30° (ref 6). [e] Value for methanol.

This is in accordance with the dissociation of the salts used in these solvents.[4] For example, a straight line is obtained by plotting k_{obsd} *vs.* reagent concentration for the reaction of *trans*-[Pt(pip)$_2$Cl$_2$] with various entering groups in dimethyl sulfoxide (Figure 1).

Thus, the rate data obtained in the solvents examined do fit the rate law usually found for square-planar complexes: $k_{obsd} = k_1 + k_2[Y^-]$. Rate constant k_1 (the intercept) is for the solvent path and k_2 (slope of the plots) is for the direct reagent path.[5]

In some kinetic runs in which an equilibrium was reached (*e.g.*, with bromide salts), the value of the absorbance at infinite time (A_∞) used to calculate k_{obsd} was that of the spectra of the expected reaction product. Thus, the usual first-order plots were made but only the initial points were used to give an initial observed rate constant.

For the reactions in acetone, the plots of k_{obsd} *vs.* the concentration of entering group indicate that the apparent second-order rate constants decrease by increasing the initial reagent concentration. However, good linearity is obtained by plotting k_{obsd} *vs.* the concentration of the *free* ion, as calculated by using the dissociation constants in acetone at 25°.[6] The reactivity of the ion pairs is practically negligible in comparison to that of the *free* ion.

Results and Discussion

Rate data for the reaction of *trans*-[Pt(pip)$_2$Cl$_2$] with a variety of entering groups are presented in Table I. For a quantitative comparison, the discrimination factors of the piperidine and phosphine complexes in different solvents are reported in Table II. These factors have been calculated for each complex as the slopes of the best straight lines of log k_2, plotted against the reactivity constants, $n°_{Pt}$. The $n°_{Pt}$ are relative rate constants for the substitution reactions of *trans*-[Pt(py)$_2$Cl$_2$] (selected as a standard) with various ligands Y^- in methanol at 30°.[3,7]

TABLE II

DISCRIMINATION FACTORS OF *trans*-[PtL$_2$Cl$_2$] IN DIFFERENT SOLVENTS AT 25°

Solvent	*trans*-[Pt(pip)$_2$Cl$_2$]	*trans*-[Pt(P(C$_2$H$_5$)$_3$)$_2$Cl$_2$]
CH_3OH[a]	0.91	1.43
$(CH_3)_2CO$	0.78	1.04
$(CH_3)_2SO$	0.61	1.06
$HCON(CH_3)_2$	0.74	...
CH_3CN	0.70	...
CH_3NO_2	0.64	...

[a] Values at 30°.

It is evident from a comparison of data in Tables I and II that in monohalide displacements on *trans*-[PtL$_2$Cl$_2$] (L = piperidine or P(C$_2$H$_5$)$_3$) the reactivity order parallels the polarizability order of the entering groups in both classes of solvent. Moreover, the entering group order as well as the reactivity are hardly affected by a change of the solvent.

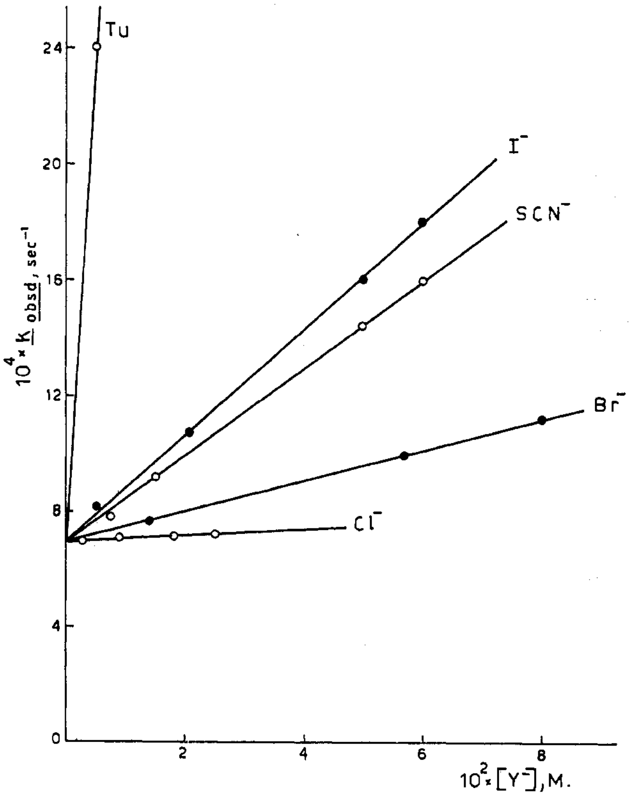

Figure 1.—Dependence of k_{obsd} on concentration of Y^- in dimethyl sulfoxide at 25°.

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(6) S. Winstein, L. G. Savedoff, S. Smith, J. D. R. Stevens, and J. G. Gall, *Tetrahedron Letters*, **9**, 24 (1960), and references therein; M. B. Reynolds and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 1709 (1948).

(7) U. Belluco, "Coordination Chemistry Review," Elsevier Publishing Co., New York, N. Y., 1966.

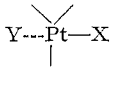
Substitution reactions of the halide complexes *trans*-$[Pt(P(C_2H_5)_3)_2X(m\text{-}FC_6H_4)]$[1b] and [Pt(diethylenetriamine)X]$^+$[8] in different solvents indicate that the solvation of the leaving group is not a kinetically significant step. Furthermore, no leaving-group effect was found in protic or in dipolar aprotic solvents, despite the fact that bond strengths of platinum halides are different.[5] These results can be interpreted in terms of a five-coordinated intermediate mechanism in which the bond formation step is the driving force of the reaction.[5b]

Data in Table II show that the discrimination factors change approximately to the same extent in both classes of solvent, suggesting that the phosphine and piperidine complexes are equally susceptible to the solvent variation, as far as the displacement is concerned. The absence of any significant differentiation in the kinetic behavior of the two complexes provides evidence that in these substrates the metal–solvent interaction is kinetically unimportant. It would be expected, in fact, that if any interaction is operative, a differentiation would be exhibited. Thus, in the case of the *trans*-$[Pt(P(C_2H_5)_3)_2Cl_2]$ the two strong π-bonding ligands can reduce the π interaction from the metal ion to the solvents having empty or potentially empty orbitals by withdrawing d-electron density from the platinum. Such a metal–solvent interaction is unaffected by the neutral ligands in the case of the piperidine complex. Of course, the same activated complex structure is assumed for these complexes in the solvents examined.

One can also realize that the solvent effects are similar for the reactions of *trans*-$[Pt(pip)_2Cl_2]$ in a number of structurally different dipolar aprotic solvents.[9] This suggests that it is not a reactive substrate–solvent adduct which is reacting in the bimolecular process. On the basis of these considerations, the observed decrease of the discrimination factors and the difference of reactivity in going from protic to dipolar aprotic solvents can be ascribed to the variation in the entering group solvation, which depends on the nature of the solvent.[10]

Generally speaking, as far as solvent effects are concerned, substitution reactions of Pt(II) complexes are rather different from SN2 processes of saturated carbon and SN processes of aromatic carbon.[11] In these systems, in fact, the rate constants k_2 increase by a factor greater than 10^4 as the hydrogen-bonding capacity of the solvents decreases from CH_3OH to dimethylformamide.

As reported above, the relative unimportance of the solvent in Pt(II) reactions should be in favor of a five-coordinated mechanism, in which an unstable intermediate of the type



is formed, regardless of the role played by the solvent.

The alternative one-step mechanism in which bond-making and bond-breaking steps are of comparable importance and the transition-state configuration is close to that of the reactants is actually not preferable to the intermediate mechanism since it is not compatible with the widely accepted *trans*-effect theory[12] proposed independently by Chatt, *et al.*, and by Orgel. In this theory, in fact, the activated complex is assumed to have a trigonal-bipyramid structure with entering group, leaving group, and *trans* group in the trigonal plane. This theory correctly predicts that the reaction proceeds with retention of configuration and that the properties of the *trans* group already coordinated and of the entering group will influence the rate of the reaction in a similar way. Following this picture, one must expect that a good *trans* group is also a good entering group (as is, indeed, found experimentally) and a poor leaving group. This is not, however, found for the leaving groups. Thus, nitrite and azide ions are generally poor entering groups toward Pt(II) (small values of $n°_{Pt}$), but they are also poor leaving groups.[13]

It is interesting to remark, furthermore, that in this theory the five-coordinated species also may be an unstable intermediate.[5]

In terms of reaction mechanism, the evidence reported above strongly suggests the statement that the substitution reactions of Pt(II) complexes proceed *via* a two-step mechanism involving two transition states and an unstable intermediate. In the cases in which halide ions are the leaving groups, bond formation, *i.e.*, the first step, is rate determining. Thus, the Pt(II) reaction mechanism resembles that of many aromatic nucleophilic substitutions. In SNAr processes, however, alternative mechanisms may be possible, depending on the activating groups present, the nucleophile, and the nature of the leaving group.[14] Moreover, the greater effect of solvent changes on SNAr processes[15] in comparison with the reactions at soft Pt(II) centers may be rationalized in terms of the different extent of bond formation realized at the transition state which is related to the different electrophilic character of the two reaction centers.

Finally, it is of interest to note that five-coordinated stable complexes of spin-paired d^8 configurations have been found frequently.[16]

The occurrence and the stereochemistry of five-coordinated $(n-1)dnsnp^3$ complexes have been discussed in terms of over-all energy separation between the filled $(n-1)d_{z^2}$ orbital and the empty np_z orbital.

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The extent to which the empty p_z orbital can be utilized for higher coordination depends upon a number of factors, most of which are controlled by the effective nuclear charge.[17]

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Some (L-Aminoacido)triethylenetetraminecobalt(III) Iodides[1]

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The preparation of seven stable crystalline complex compounds of the type $[\mathrm{Co(trien)(L\text{-}aminoacido)}]\mathrm{I_2 \cdot H_2O}$ is reported. The cations of these complexes are assumed to be α forms, although conclusive evidence is lacking. Existence of diastereoisomers is demonstrated and separation of some pairs of isomers is achieved simply by successive fractionations. The equilibration of optical isomers with activated charcoal and the effect of coordination on the optical activity of the L-amino acid are discussed. Infrared and electronic spectra are also presented.

Inorganic complexes of the quadridentate ligand triethylenetetramine have recently been prepared and their geometrical isomers identified.[4–7] The present paper reports the preparation and properties of seven complexes of the type $[\mathrm{Co(trien)(L\text{-}AA)}]\mathrm{I_2 \cdot H_2O}$, in which L-AA refers to an L-amino acid anion.

Experimental Section

Reagents.—*cis*-Dichlorotriethylenetetraminecobalt(III) chloride was prepared by the methods of Basolo[4] and Bailar.[5] Both methods yielded products with identical infrared and visible–ultraviolet spectra. The amino acids were purchased from Nutritional Biochemicals Corp., Cleveland, Ohio, and used as received.

Preparation of Complexes.—L-Amino acid (0.03 mole) was dissolved in 50 ml of water containing NaOH (0.03 mole) at 60° by magnetic stirring, after which solid *cis*-α-$[\mathrm{Co(trien)Cl_2}]\mathrm{Cl}$ (0.03 mole) was added. The solution was filtered while warm, and an excess of solid sodium iodide (0.1 mole) was added. The solution was cooled in an ice bath for a few minutes after which crystallization was induced by scratching with a glass rod, and the beaker was stored in a refrigerator for several hours. The crystals were collected and washed with ethanol and acetone. Purification of the product was accomplished by recrystallization from aqueous sodium iodide solutions. The purified compound was dried in a heated vacuum desiccator at 40° overnight.

In the preparation of L-methioninato, L-tyrosinato, and L-phenylalaninato complexes, slight modifications of the procedure were made. In preparing the L-methioninato complex, after treatment with sodium iodide, the resulting solution crystallized slowly on standing at room temperature for 4 hr. Chilling was avoided because this led to the formation of a rubberlike precipitate. In the case of the other two complexes, a saturated solution of sodium iodide was added slowly with stirring to effect precipitation. Addition of solid sodium iodide in this case led to the formation of a rubberlike precipitate.

Fractionation of the Complexes.—The procedure was essentially the same as described in the preparation of the complexes, except in the manner in which the sodium iodide was added. The first precipitate was obtained by adding 0.02 mole of solid sodium iodide and allowing the solution to stand overnight. To the first filtrate was then added 0.02 mole of sodium iodide to obtain a second precipitate. The third precipitate likewise was obtained from the second filtrate. All isolated fractions were recrystallized and washed with ethanol and acetone and dried in a heated vacuum desiccator before measurement of optical rotation.

Equilibration of the Diastereoisomers.—A 0.1% aqueous solution (400 ml) was prepared from each of the fractionated products. Each solution was divided into four equal portions. Activated charcoal (0.05 g) was added to two portions, one of which was shaken at room temperature. A charcoal-free portion was also shaken at room temperature. Likewise, two portions, one containing charcoal, were loosely stoppered and warmed on steam baths. Optical rotations were measured after 20, 60 min, etc.

Optical Rotations.—Optical activities of the complexes were measured on aqueous solutions in a 1-dm tube with a Rudolph 80 precision polarimeter equipped with a mercury-vapor lamp and green filter. Each rotation reported was based on an average of ten readings. A determination of water blank was made before each measurement.

Infrared Spectra.—Spectra for the range 2.5–16 μ were obtained using a Perkin-Elmer Model 237 grating infrared spectrophotometer. Both Nujol-mull and KBr-disk tenchniques were used. Nujol mull spectra for the range 15–35 μ were obtained using a Perkin-Elmer Model 21 recording spectrophotometer with cesium bromide optics.

Electronic Spectra.—Visible and ultraviolet spectra were recorded by Beckman DK-1 and Hitachi Perkin-Elmer Model 139 spectrophotometers. Samples were prepared as aqueous solutions.

Results and Discussion

Preparation of the Complexes.—Analytical data of the (L-aminoacido)triethylenetetraminecobalt(III) iodides are summarized in Table I. The yields ranged from 25 to 60%. The crystalline complexes had characteristic colors of orange-red to brick-red similar to

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[1] The letters D and L refer to the configuration of the amino acid, whereas *d*, *l*, +, and − refer to the optical rotation. Trien refers to triethylenetetramine; en refers to ethylenediamine.

[2] Deceased, March 10, 1965.

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