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Ligand Substitution Kinetics of Nickel(II) Ion in 2-Propanol and Isobutyronitrile as Solvents. Influence of Steric Crowding in the Inner Sphere and of Other Factors

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Rate constants and activation parameters are reported for the reactions of nickel(II) ion with 4-phenylpyridine, 2,2'-bipyridine, 1,10-phenanthroline, and 2,2',2''-terpyridine in 2-propanol and isobutyronitrile as solvents. For the first three ligands, rate constants have also been measured in 1-propanol as solvent. The results are compared with those obtained in all other solvents studied so far. Solvent properties involved in the ligand substitution kinetics of nickel(II) ion are indicated. The donor strength of the solvent appears to be of particular importance, not only in the dissociation but also in the formation of complexes.

As part of a systematic investigation with the objective to identify those solvent properties that influence the kinetics of ligand substitution reactions,¹ we report here results obtained in 2-propanol and isobutyronitrile, two solvents in which the inner-coordination spheres of metal ions are expected to be relatively crowded, and, for purposes of comparison, in 1-propanol as well. We also compare rate constants for the reactions of nickel(II) ion with pyridine-type ligands in all solvents studied so far.

Experimental Section

Solvent. Isobutyronitrile (Aldrich Chemical Co., 99%) was purified by shaking successively with silica gel (Baker analyzed reagent, 60–200 mesh) and neutral alumina (Fisher Certified Reagent, 80–200 mesh), followed by distilling, first from phosphorus pentoxide (Baker analyzed reagent) and then from calcium hydride (Fisher Purified grade), in a 4-ft Type C Stedman column at a reflux ratio of 8:1. 1-Propanol (Aldrich 99+%) and 2-propanol (Fisher Certified reagent) were distilled from magnesium turnings (Baker Purified grade) under nitrogen in a Stedman column at a reflux ratio of 9:1. The water content of the products, as determined with a Photovolt Aquatest II Karl Fischer titrator, was 8×10^{-3} M for isobutyronitrile, 1.9×10^{-2} M for 1-propanol, and 2.9×10^{-2} M for 2-propanol. The water contents could be decreased significantly with molecular sieves (Linde 4A dried in vacuo at 350 °C). In order to investigate the effect of water on reaction rates, kinetic runs were carried out on some systems both before and after addition of molecular sieves; differences were modest. Owing to the hygroscopic nature of the solvents, all solvents were handled in a glovebag.

Reagents. Nickel was introduced as $\text{Ni}(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$ ($n \approx 2$), prepared as described previously.¹ All other chemicals used were reagent quality.

Instrumentation and Experimental Procedure. Kinetic measurements were made with a Durrum Instrument Co. (Palo Alto, Calif.) Model D-110 stopped-flow spectrophotometer equipped with a Kel-F flow system under the same conditions as described elsewhere.¹ Typically, the total ligand concentration was held constant at 2.5×10^{-5} M (after mixing) and the total nickel concentration was varied through three or four values from 0.3 to 6.0 mM. Ionic strength effects were small; for example, addition of 0.1 M lithium perchlorate had little effect. Wavelengths at which reactions were monitored were the same as for propylene carbonate.¹

Results

Rate constants and activation parameters for ligand substitution at nickel(II) ion are reported in Table I for 2-propanol and 1-propanol as solvents. In Table II, corresponding data are listed for isobutyronitrile as solvent and compared with results previously obtained in acetonitrile. In Table III, rate constants for substitution by 4-phenylpyridine, 1,10-phenanthroline, 2,2'-bipyridine, and 2,2',2''-terpyridine are summarized for all solvents studied so far. Also included in Table III are comparisons of rate constants for ligand substitution ($k_{1,f}$) in a given solvent with that for solvent exchange (k_s), as well as of rate constants for ligand substitution by the

Table I. Rate Constants and Activation Parameters for Ligand Substitution at Nickel(II) Ion in 2-Propanol and Rate Constants in 1-Propanol

Ligand	$\log k_{1,f}^a$			ΔH^\ddagger ^b	ΔS^\ddagger ^c
	10 °C	25 °C	40 °C		
4-Phenylpyridine	4.8, ^d	5.1 ₇ (4.1 ₆ ^e)	5.2 ₇	4. ₉	-19
Phenanthroline	5.5 ₈ ^f	5.9 ₂ (5.1 ₂ ^e)		8	~-4
Bipyridine	4.7 ₉	5.0 ₄ (4.0 ₂ ^e)	5.3 ₂	6. ₆	-13
Terpyridine	4.0 ₈ ^g	4.4 ₀	4.7 ₁	8. ₂	-11

^a Units: $\text{l. mol}^{-1} \text{s}^{-1}$. Solvent is 2-propanol except where noted otherwise. ^b Units: kcal mol^{-1} (1 cal = 4.18 J). ^c Units: $\text{cal K}^{-1} \text{mol}^{-1}$. ^d Actual temperature 10.7 °C. ^e Solvent is 1-propanol. ^f Additional value: 5.68 at 15 °C. ^g Actual temperature 10.4 °C.

Table II. Comparison of Rate Constants^a for Ligand Substitution at Nickel(II) Ion in Isobutyronitrile and Acetonitrile as Solvents

Ligand	Isobutyronitrile ^b	Acetonitrile ^c
4-Phenylpyridine	3.5 ₉ (10 °C)	
	3.8 ₈ (25 °C)	2.9 ₉
	4.2 ₂ (40 °C)	
Phenanthroline	>5	4.7
Bipyridine	3.7	3.6
Terpyridine	3.6	3.3

^a Values listed are those of $\log k_{1,f}$ and are for 25 °C, except where noted otherwise. ^b For L = 4-phenylpyridine: $\Delta H^\ddagger = 8 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -14 \text{ cal K}^{-1} \text{mol}^{-1}$. ^c For L = 4-phenylpyridine: $\Delta H^\ddagger = 11 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -7 \text{ cal K}^{-1} \text{mol}^{-1}$.

multidentate ligands, with that for substitution by 4-phenylpyridine as reference ligand. The earlier data in Table III come from a variety of sources, principally the work of Wilkins in water, Smith in ethanol, and Bennetto and Caldin, as well as Coetzee et al., in a variety of solvents. Most of the earlier work is referred to in ref 2 and is reviewed in ref 3. Donor numbers are from ref 4. Solvent-exchange data are summarized in ref 3.

Discussion

The principal features of the results in Table III are the following. (1) Rate constants for ligand substitution vary by six powers of 10 in the range of solvents studied. The solvent effects dealt with here are not merely minor perturbations. (2) It was shown in the preceding paper¹ that, if an I_d mechanism applies, the ratio R_1 of eq 8 should have a value near unity. Keeping in mind the indicated limitations of this diagnostic approach,² it may be concluded that, in all solvents, 4-phenylpyridine or pyridine reacts via a normal I_d mechanism. The same conclusion was reached by Hoffmann⁵ for a variety of simple anionic unidentate ligands, such as thiocyanate ion, in dimethyl sulfoxide, methanol, and acetonitrile. On the basis of the expected straightforward behavior of 4-phenylpyridine

Table III. Comparison of Rate Constants for Substitution by Phenanthroline, Bipyridine, and Terpyridine at Nickel(II) Ion with Rate Constants for Solvent Exchange and for Substitution by 4-Phenylpyridine^a

Solvent	<i>D</i> ^b	log <i>k</i> _s ^c	4-Ph(py)	phen	bpy	terpy
Ethylene glycol		3.6			1.5, -1.7, ...	1.0, -2.2, ...
Dimethyl sulfoxide	30	3.9	3.2, -0.5	2.6, -1.1, -0.6	1.8, -1.9, -1.4	1.4, -2.3, -1.8
Dimethyl methylphosphonate		4.4			2.3, -2.0, ...	
Dimethylformamide	27	3.9			2.7, -1.1, ...	
Water	33?	4.5	3.6, ^d -0.3	3.5, -0.4, -0.1	3.2, -0.7, -0.4	3.1, -0.8, -0.5
Methanol	19	3.0	2.1, -0.5	2.8, +0.2, +0.7	2.0, -0.6, -0.1	1.6, -1.0, -0.5
Ethanol		4.0	3.8, ^d -0.1	4.5, +0.6, +0.7	3.8, -0.1, 0	
1-Propanol			4.2, ...	5.1, ..., +0.9	4.0, ..., -0.2	
2-Propanol			5.2, ...	5.9, ..., +0.7	5.0, ..., -0.2	4.4, ..., -0.8
Acetonitrile	14	3.4	3.0, -0.3	4.7, +1.4, +1.7	3.6, +0.3, +0.6	3.3, 0.0, +0.3
Isobutyronitrile			3.9, ...	>5, ..., >1	3.7, ..., -0.2	3.6, ..., -0.3
Propylene carbonate	15		5.3, ...	7, ..., 2	5.4, ..., +0.1	5.3, ..., 0

^a For each ligand-solvent combination, the first entry represents log *k*_{1,t}, the second log *R*₁, and the third log *R*₂, where *R*₁ = (4/3)*k*_{1,t}/*K*₁*k*_s and *R*₂ = (*k*_{1,t})_L/(*k*_{1,t})_{L'} with L' representing 4-phenylpyridine as reference ligand. *T* = 25 °C. ^b Donor number; see text. ^c Refers to solvent exchange. ^d Ligand is pyridine.

in those solvents for which NMR data for solvent exchange are not yet available, we estimate for 1-propanol, 2-propanol, isobutyronitrile, and propylene carbonate approximate values of log *k*_s at 25 °C of 4.5, 5.5, 4.3, and 5.7 and for the last three solvents values of Δ*H*[‡] near 5, 8, and 8 kcal mol⁻¹, respectively. (3) In dimethyl sulfoxide, the multidentate ligands react significantly more slowly than the norm established by 4-phenylpyridine and other unidentate ligands.⁶⁻⁸ It seems clear that the cause is steric inhibition of coordination, but it is not yet certain whether this involves first-bond formation, ring closure, or both, and to what extent the sheetlike structure of dimethyl sulfoxide contributes to the steric barrier.³ (4) In acetonitrile, the behavior of the multidentate ligands is diametrically opposed to that in dimethyl sulfoxide. Here they react significantly faster than the norm. This rate enhancement is particularly marked for phenanthroline, and we have attributed it to exceptional outer-sphere stabilization caused by electrostatic and/or π-orbital interaction of phenanthroline present in the outer sphere with the polarized acetonitrile molecules of the inner sphere.⁹ The new results presented in Table III now show that this rate enhancement is not limited to acetonitrile but occurs in all solvents listed except dimethyl sulfoxide and water and also that it is most pronounced in those solvents expected to be the weakest donors toward nickel(II) ion. We therefore generalize our explanation of the outer-sphere stabilization of ligands such as phenanthroline by attributing it mainly to two types of electrostatic interaction: a dipole-dipole interaction between the ligand and the polarized solvent molecules of the inner sphere and also a direct ion-dipole interaction between the ligand and the effective positive charge of nickel(II) ion. Both types of interaction would be most pronounced with phenanthroline because this rigid molecule has two nitrogen atoms in fixed positions which can assume a favorable orientation in the outer sphere. The type of outer-sphere stabilization visualized here must have something in common with the interesting "stacking" interactions described by Margerum¹⁰ for aqueous solutions, even though, in our case, the component due to hydrophobic bonding is absent. A contributing factor to the direct ion-dipole interaction proposed here must be the openness of the inner sphere which will influence the interaction distance between nickel(II) ion and the ligand. An illustration of such an effect may be provided by the values of *R*₂ for bipyridine and terpyridine in acetonitrile relative to those in isobutyronitrile. In acetonitrile, the inner sphere is particularly open and outer-sphere complexes are therefore expected to be more stable than in isobutyronitrile. (5) In methanol, ethanol, and 1-propanol, the reaction rate of 4-phenylpyridine increases in going up the homologous series. When additional steric crowding is introduced into the inner sphere by going from 1-propanol to 2-propanol, the rate in-

creases by one order of magnitude. When additional information becomes available, it may well turn out that this behavior is general for homologous series of solvents and that a major factor contributing to relative substitution rates in different homologues is the relative activities (free energies of solvation) of the metal ion. Variations in the activity of the metal ion in such homologous series of solvents will be determined by variations in the energetics of the specific coordination reactions of the metal ion with the solvent (about which little is known at present) and also variations in the Born free energy determined by the bulk dielectric constant of the solvent (values for methanol, ethanol, 1-propanol, 2-propanol, acetonitrile, and isobutyronitrile are 32.7, 24.6, 20.3, 19.9, 36.0, and 20, respectively). For such solvents as 2-propanol and isobutyronitrile, lateral solvent-solvent repulsion significantly increases the activity of the metal ion. It would be highly desirable to evaluate the enthalpies and entropies of transfer of nickel(II) ion from one solvent to another. The donor numbers listed in Table III cannot be expected and are not intended to serve as more than a rough guide for this particular purpose. They represent the -Δ*H*^o values (in kcal mol⁻¹) for the reactions of the donors with antimony pentachloride in 1,2-dichloroethane as solvent. Consequently, they will not necessarily apply to such acceptors as nickel(II) ion. For example, the electronic spectra of nickel(II) ion in acetonitrile-propylene carbonate mixtures show that the former solvent is a much better donor toward nickel than the latter, which is the opposite order of that of the donor numbers. Furthermore, the donor numbers cannot be expected to apply in solvents possessing extensive order, and, as pointed out by Gutmann and Schmid,⁴ steric factors often will be important in solvent exchange as well as in substitution by other ligands. Consequently, the correlations previously found between rate constants for dissociation of complexes and donor numbers of solvents⁵ are not likely to be general. For all of these reasons, we have started to measure the enthalpies of transfer of anhydrous nickel salts from one solvent to another and intend to split the numbers obtained by employing the extra-thermodynamic assumption that the enthalpies of transfer of tetraphenylarsonium and tetraphenylborate ions are equal.¹¹

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Registry No. Ni²⁺, 14701-22-5; 4-phenylpyridine, 939-23-1; phenanthroline, 66-71-7; bipyridine, 366-18-7; terpyridine, 1148-79-4.

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Lewis Acid Adducts of *trans*-PtHCN(P(C₂H₅)₃)₂

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The reactions of several Lewis acids with *trans*-PtHL₂CN [where L = P(C₂H₅)₃] gave stable adducts with the Lewis acid coordinated to the lone pair of electrons of the nitrogen atom. Variations in the coupling constant, ¹J(Pt-H), with the Lewis acid are used to establish a series of relative strengths of the Lewis acids. The acidity decreases roughly in the order AlCl₃ > BAr₃ > BR₃ ~ CoCl₂ > AlAr₃ > ZnCl₂ > B(OAr)₃ > AlR₃ > AlR₂(OR). The reaction between 1 molar equiv each of PtHL₂CN, PtHL₂Cl, and AgPF₆ gives the complex [PtHL₂CNPtHL₂](PF₆) which contains a cyanide bridging two PtHL₂⁺ units.

Introduction

Lewis acids are very important cocatalysts for many industrial and laboratory reactions, a few of which are olefin polymerizations and dismutations, Friedel-Crafts alkylations, hydrogenations, and isomerizations. A study of the nature of the interaction between transition metals and Lewis acids is important in understanding the mechanisms of these processes.

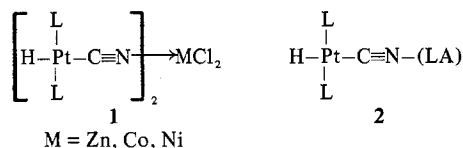
Kristoff and Shriver¹ examined the infrared spectra of a series of Lewis acid adducts of (C₅H₅)Fe(CO)₂CN in which the acid was coordinated to the nitrogen lone pair of the cyanide. Because of the sensitivity of ν_{CO} to the nature of the group attached to the cyanide and because of negligible kinematic coupling of the CO stretching mode with other vibrations, they were able to arrange the Lewis acids according to their relative electron pair acceptor strengths.

More recently Cohen and Hoffman² recorded the ESR spectra of the complexes formed between the free radicals di-*tert*-butyl nitroxide or 2,2,6,6-tetramethylpiperidine-*N*-oxyl and group 4A Lewis acids. Variations in the nitroxide ¹⁴N hyperfine coupling constants upon complexation were used to measure relative acceptor strengths of the Lewis acids.

In this paper we report a convenient method for measuring relative Lewis acidities toward a hydridoplatinum-cyano group using NMR spectroscopy.³

Results

a. Preparation of the Complexes. The cyanide in *trans*-PtHCNL₂⁴ [L = P(C₂H₅)₃] possesses a lone pair of electrons and reacts rapidly with NiCl₂·6H₂O, CoCl₂·6H₂O, and ZnCl₂ in acetonitrile to give 2:1 adducts, **1**. The nickel and cobalt



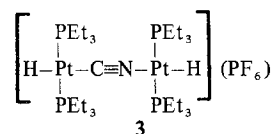
complexes are stable indefinitely in the solid state but decompose slowly in solution. Trialkyl- and arylboron and -aluminum compounds react rapidly with PtHCNL₂ to form 1:1 adducts, **2**. These complexes were obtained as air-stable, white, crystalline solids.

The NMR spectra of the diamagnetic complexes are very similar. The phosphine ethyl resonances are complex and absorb downfield from tetramethylsilane. The platinum hydride resonance appears as a triplet due to coupling with

the two equivalent ³¹P nuclei (*I* = 1/2, 100% natural abundance). The value of ²J(H-Pt-P) is 15 Hz and does not vary from one complex to another. Each resonance is flanked by ¹⁹⁵Pt satellites (*I* = 1/2, 33.8% natural abundance) and the magnitude of ¹J(Pt-H) varies with the Lewis acid. The NMR data obtained at 220 MHz are listed in Table I in order of decreasing ¹J(Pt-H).

The infrared spectra of the complexes show a very weak Pt-H stretching vibration around 2070 cm⁻¹ and a strong C≡N vibration in the range 2050-2060 cm⁻¹. It is likely that these vibrations are strongly coupled to each other and are not pure.

The addition of AgPF₆ to an equimolar amount of *trans*-PtHClL₂ and *trans*-PtHCNL₂ in methanol gives a precipitate of AgCl and a clear colorless solution. Removal of the solvent gives a white crystalline complex. The NMR spectrum of the complex shows two nonequivalent platinum hydride resonances. The magnitudes of the Pt-H coupling constants (840 and 1100 Hz) are consistent with a hydride trans to C and N, respectively,⁵ and support structure **3**.



The electronic spectrum of [PtHL₂CN]₂NiCl₂ in benzene shows two bands in the visible region at 535 and 590 nm with molar extinction coefficients of 122 and 142 cm⁻¹ m⁻¹. Similar spectra have been previously observed for tetrahedral nickel(II) complexes.⁶ Generally they show a multiple band of approximately 10² cm⁻¹ m⁻¹ intensity which has been assigned to the ³T₁(P) ← ³T₁(ν₃) transition. The magnetic moment which was determined in benzene by the Evans technique⁷ gave an effective magnetic moment, μ³⁰³_{eff}, of 3.4 μ_B. This moment also is consistent with a tetrahedral d⁸ configuration.⁸ We were unable to observe an ESR spectrum above liquid helium temperature suggesting a rapid electron spin relaxation. The NMR spectrum although slightly broadened gave chemical shifts comparable to those of the diamagnetic ZnCl₂ complex. We were unable to locate the hydride resonance. The NMR spectrum of [PtHL₂CN]₂CoCl₂ showed broadened phosphine ethyl resonances. A search upfield of tetramethylsilane did not reveal any hydride resonance; however, this resonance was located at 15.53 ppm downfield from TMS. Assuming that