of the behavior of bis(*N*-methylsalicylaldimino)copper(II).[30]

The reaction of copper(II) acetate monohydrate with salicylaldehyde and *N*-(2-aminoethyl)aziridine in methanol has resulted in low yields (always 10% or less) of bis(salicylidene)ethylenediiminecopper(II), [Cu((sal)$_2$en)]. The low yield in this reaction supports the contention that the six-coordinate complex may be the intermediate as in the corresponding reaction with nickel(II). The concentration of six-coordinate copper(II) species is not likely to be large and perhaps the course of the reaction is different from that of the nickel(II) complex. As is true with nickel, the occurrence of a ring-opening reaction with [Cu(salAPA)$_2$] has not been detected.

Acknowledgment.—We acknowledge the contributions of Miss Patricia L. Dedert to this work and thank Professor Larry T. Taylor for his assistance in obtaining mass spectra.

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Cationic Nickel Nitrosyl Complexes with Two "Tripod-Like" Aliphatic Triphosphines[1]

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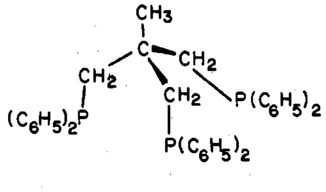
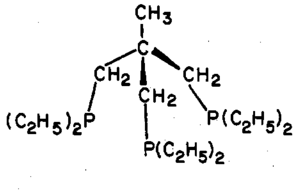
The deep red, diamagnetic, uni-univalent electrolytes [Ni(tpp)NO]X and [Ni(tep)NO]X (where X = Cl, Br, I, BF_4, $B(C_6H_5)_4$; tpp and tep = the "tripod-like" triphosphines $CH_3C(CH_2PPh_2)_3$ and $CH_3C(CH_2PEt_2)_3$, respectively) result from the reactions of nickel(II) halides, nitrite ion, and the triphosphine ligands in absolute ethanol. An X-ray structural determination of [Ni(tep)NO]BF_4 has shown that the nickel atom is surrounded in a pseudotetrahedral fashion by three phosphorus atoms and a linearly bonded nitrosyl group.

Introduction

During our investigations into the structures of five-coordinate nickel(II) complexes resulting from polyphosphines, we observed[2] that the "tripod-like" triphosphines tpp and tep react with nickel(II) halides in ethanol to form planar Ni(ligand)X_2 complexes in which the triphosphine functions only as a bidentate ligand. However, the same reagents in the presence of nitrite ion give intensely colored solutions from which deep red complexes of elemental composition [Ni(ligand)(NO)]X (X = Cl, Br, I) crystallize. The presence of the nitrosyl group is indicated by a strong infrared absorption at *ca.* 1760 cm^{-1}, which may be assigned to the N–O stretching frequency. This reaction appears to be analogous to Feltham's studies[3,4] in which the tetrahedral $Ni(PPh_3)_2X_2$ complexes were mixed with nitrite ion and the nitrosyl complexes $Ni(PPh_3)_2(NO)X$ were isolated. This paper reports the preparation and characterization of two series of Ni(triphosphine)(NO)X complexes (X = Cl, Br, I, BF_4, $B(C_6H_5)_4$) and discusses the data in terms of the ambiguities involved in assigning formal oxidation states to nickel and the nitrosyl group.


tpp


tep

Experimental Section

Reagents.—The nickel(II) salts, sodium tetraphenylborate, and absolute ethanol were reagent grade and were used without further purification. The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, tpp, was prepared according to the procedure of Hewertson and Watson[5] by Strem Chemicals, Inc., and by Orgmet, Inc., on a custom order basis. *Anal.* Calcd for $C_{41}H_{39}P_3$:[6] C, 78.85; H, 6.25; P, 14.90. Found: C, 78.90; H, 6.21; P, 15.04. The corresponding diethylphosphino ligand, tep, was prepared by a procedure analogous to that for tpp by Orgmet, Inc. The $CH_3C(CH_2PEt_2)_3$ ligand is a clear liquid that is extremely sensitive to oxidation; thus, all of the handling and syntheses involving the tep ligand were conducted in a dry, oxygen-free atmosphere (usually purified nitrogen or argon).

Isolation of the Complexes.—All of the steps in the preparations of the complexes were executed in an oxygen-free atmosphere. For the tep complexes, the dissolved oxygen was removed from the solvents before the ligand was added. The solid complexes were collected in a closed filter funnel on a sintered-glass frit and were dried with a stream of nitrogen.

[Ni(tep)(NO)]I.—Anhydrous nickel(II) iodide was prepared, *in situ*, by adding 2,2-dimethoxypropane (5 ml) to the absolute ethanol solution that resulted from mixing sodium iodide (0.49 g, 3.28 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (0.48 g, 1.64 mmol) and filtering off the sodium nitrate. The tep ligand was added and the resulting solution was refluxed for 15 min. Then potassium nitrite (0.56 g, 6.56 mmol), which was partially dissolved in 20 ml of ethanol, was added to the solution. The mixture was stirred for 12 hr at room temperature; then the ethanol was evaporated and the compound was extracted from the solid with dichloromethane. A red-orange solid, which was recovered by evaporating the CH_2Cl_2, was recrystallized from CH_2Cl_2–*n*-C_5H_{12} (5 ml of each).

[Ni(tep)(NO)][B(C$_6$H$_5$)$_4$].—An ethanol solution of $NaB(C_6H_5)_4$ was added slowly to an ethanol solution of [Ni(tep)(NO)]I.

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[1] Abstracted in part from the Ph.D. dissertation of D. B. presented to the Graduate School of The Ohio State University in March 1969.

[2] D. Berglund, Ph.D. Dissertation, The Ohio State University, 1969.

[3] R. D. Feltham, *J. Inorg. Nucl. Chem.*, **14**, 307 (1960).

[4] R. D. Feltham, *Inorg. Chem.*, **3**, 116 (1964).

[5] W. Hewertson and H. R. Watson, *J. Chem. Soc.*, 1490 (1962).

[6] Analytical data given on the Orgmet sample, as it was the one used for these nitrosyl complexes.

TABLE I

CHARACTERIZATION DATA FOR THE NICKEL NITROSYL COMPLEXES OF THE TRIPHOSPHINES

	Elemental anal., %						Λ_M,[a] cm²/(ohm mol)	μ_{eff}, BM	N–O str freq,[b] cm⁻¹
	C		H		Other				
Complexes	Calcd	Found	Calcd	Found	Calcd	Found			
$[Ni(tep)(NO)]I$	36.96	37.44	7.07	7.18	(N) 2.54	2.49	84	0.49	1750
					(I) 23.01	22.40			
$[Ni(tep)(NO)][B(C_6H_5)_4]$	66.13	66.64	7.93	8.22	(N) 1.88	1.72	59		1760
$[Ni(tep)(NO)][BF_4]$	39.89	39.74	7.68	7.57	(N) 2.73	2.57	86	0.46	1750
$[Ni(tpp)(NO)]Cl$	65.76	62.28	5.25	5.04	(Cl) 4.74	4.29			1760
$[Ni(tpp)(NO)]Br$	62.08	62.23	4.95	5.14	(N) 1.76	1.60			1760
					(Br) 10.07	10.38			
$[Ni(tpp)(NO)]I$	58.61	60.64	4.68	5.01			65	0.29	1750
$[Ni(tpp)(NO)][B(C_6H_5)_4]$[c]	75.62	75.88	5.75	5.89	(N) 1.36	1.47	52	0.54	1770
					(P) 9.00	8.87			
$[Ni(tpp)(NO)][B(C_6H_5)_4]$[d]	75.62	75.56	5.75	5.89			52	0.62	1770
$[Ni(tpp)(NO)][B(C_6H_5)_4]$[e]	75.62	75.83	5.75	5.84			52	0.58	1765

[a] The conductance data were obtained on $\sim10^{-3}$ *M* nitromethane solutions. [b] The infrared spectra were obtained on Nujol mulls of the solid complexes. The N–O peaks were strong and sharp and are believed to be accurate to ±3 cm⁻¹. [c] Prepared from the chloride salt of the cation. [d] Prepared from the bromide salt of the cation. [e] Prepared from the iodide salt of the cation.

The resulting red-orange crystals were collected on a filter after 20 min, washed with ethanol, and dried with a stream of nitrogen.

$[Ni(tep)(NO)]BF_4$.—This complex was prepared with $NaBF_4$ by a procedure analogous to the above tetraphenylborate complex.

$[Ni(tpp)(NO)]X$ Complexes (X = Cl, Br, I).[7]—The tpp ligand (2 mmol) and the appropriate sodium halide (4 mmol) were mixed with an absolute ethanol solution of $Ni(NO_3)_2\cdot6H_2O$ (0.58 g, 2 mmol). The resulting mixtures were refluxed 30 min, during which time yellow to orange precipitates (Cl^- to I^-) formed. Then powdered potassium nitrite (0.36 g, 4.2 mmol), ethanol (10 ml), and 2,2-dimethoxypropane (10 ml) were added to each flask. The heterogeneous mixtures were stirred at 40–50° for 24 hr, during which time most of the precipitates dissolved. The solvent was evaporated and the brick red compounds were extracted under nitrogen from the solid residues with dichloromethane. The solid samples of $[Ni(tpp)(NO)]X$ were obtained by evaporation of the dichloromethane.

$[Ni(tpp)(NO)][B(C_6H_5)_4]$.—An excess of sodium tetraphenylborate (0.51 g, 1.5 mmol) in 60 ml of ethanol was added to 1 mmol (dissolved in 10 ml of ethanol and 10 ml of dichloromethane) of each of the complexes $[Ni(tpp)(NO)]Cl$, $[Ni(tpp)(NO)]Br$, and $[Ni(tpp)(NO)]I$. Slow evaporation of the dichloromethane gave deep red crystals; these were collected and dried *in vacuo* at room temperature.

Characterization Measurements on the Complexes.—The elemental analyses were performed by M-H-W Laboratories, Garden City, Mich. The infrared and electronic spectra, conductivity, and magnetic susceptibility data were obtained as described previously.[8] The observed susceptibilities were corrected for the diamagnetism of the ligands;[9] the corrections for the tep and tpp ligands are 291 × 10⁻⁶ and 430 × 10⁻⁶ cgsu, respectively.

Results

The nickel(II) halide complexes $Ni(tep)X_2$ and $Ni(tpp)X_2$ can be isolated and used as reagents for the nitrite reactions, or they may be prepared *in situ* and used. These halide complexes are nonelectrolytes and are known on the basis of the magnetic and electronic spectral data to possess a planar structure;[2] thus, one phosphino group of the triphosphine ligands is apparently uncoordinated in the $Ni(tep)X_2$ and $Ni(tpp)X_2$ complexes. In the presence of nitrite ion, these planar nickel halide complexes give good yields (>60%) of the nitrosyl complexes Ni(triphosphine)(NO)X (X = Cl, Br, I). Using the preparative conditions described in the Experimental Section, no nitrite complex (*i.e.*, $Ni(triphosphine)(NO_2)_2$) was detected.

The resultant Ni(tep)(NO)X and Ni(tpp)(NO)X complexes are deep red and possess a strong, sharp N–O infrared stretching frequency at ~1760 cm⁻¹. Both series of complexes are uni-univalent electrolytes in nitromethane and their electronic spectra are invariant with respect to X, proving that the anion is not coordinated to the metal in solution. Furthermore, the electronic absorption maxima are identical in solution and in the solid state, showing that structural changes do not occur on dissolving the Ni(ligand)(NO)X complexes. The crystalline compounds are all diamagnetic, and molecular weight determinations indicate a monomeric formulation in solution. To provide additional support for the ionic nature of the halide and the identity of the $[Ni(tpp)NO]^+$ cation in the different Ni(tpp)(NO)X compounds, a metathetical replacement of the halides with the BF_4^- and $B(C_6H_5)_4^-$ anions was accomplished according to

$$Ni(tpp)(NO)X + NaB(C_6H_5)_4 \xrightarrow{C_2H_5OH} [Ni(tpp)(NO)]B(C_6H_5)_4 + NaX \quad (1)$$

As can be seen from Tables I and II, the spectra of the resultant tetraphenylborate complexes are very similar to those of the original halides.

The 2000–400-cm⁻¹ range of the infrared spectrum of $[Ni(tep)NO]BF_4$ (Nujol mull) is shown in Figure 1. The dominant features of the spectrum are the strong N–O peak at ~1760 cm⁻¹, the characteristic peaks of the BF_4^- ion and the triphosphine ligand, and the absence of NO_3^- or NO_2^- absorptions in the 900–1400-cm⁻¹ region.

Discussion

These two series of nickel nitrosyl complexes are classic examples of the ambiguities involved in assigning formal oxidation states to the metal and the coordinated nitrosyl group. Either of the two models below are consistent with the characterization data,

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(7) Although the observed magnetic moments of the $[Ni(tpp)(NO)]Cl$ and $[Ni(tpp)(NO)]Br$ complexes were variable and somewhat high for diamagnetic complexes, these values probably result from small amounts of the strongly paramagnetic, tetrahedral nickel(II) complexes that arise from coordination of the corresponding triphosphine trioxide ligands.[2] The latter arise owing to the oxygen sensitivity of the triphosphine ligands. In fact, in several syntheses, small quantities of green crystals were observed microscopically to be mixed with the red-violet crystals of $[Ni(tpp)NO]X$. Also, the infrared spectra indicated that varying small amounts of the P=O group were present, depending on the isolation and recrystallization procedures. To ascertain that these somewhat paramagnetic Ni(tpp)(NO)X (X = Br, Cl) compounds contained mainly the diamagnetic $[Ni(tpp)(NO)]X$ materials, the diamagnetic tetraphenylborate salts were isolated in ~80% yield directly from $[Ni(tpp)(NO)]X$ (X = Br, Cl).

(8) T. D. DuBois and D. W. Meek, *Inorg. Chem.*, **6**, 1395 (1967).

(9) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, p 403.

TABLE II

ELECTRONIC ABSORPTION SPECTRA OF THE $[Ni(triphosphine)NO]^+$ COMPOUNDS

	E_{max}, cm^{-1}	
Complex	Solid state (Nujol mull at ~300°K)	Soln (CH_2Cl_2)
[Ni(tep)NO]I	20,620 sh[a]	20,620 sh[a] (689)[b]
	23,750	23,980 (1500)
	29,940	29,410 (740)
$[Ni(tep)NO]BF_4$	20,620 sh	20,620 sh (703)
	23,700	23,980 (1490)
	29,410	28,740 (685)
[Ni(tpp)NO]Cl	20,200 sh	20,200 sh (517)
	23,200	23,040 (709)
	29,410 sh	29,070 (847)
[Ni(tpp)NO]Br	20,200 sh	20,240 sh (622)
	23,260	23,090 (793)
	29,410 sh	29,250 (890)
[Ni(tpp)(NO)]I	19,880 sh	19,840 sh (609)
	23,530	23,310 (984)
	29,150 sh	28,570 (855)
$[Ni(tpp)NO]B(C_6H_5)_4$[c]	19,800 sh	19,920 sh (840)
	23,880	23,260 (1260)
	29,450 sh	28,490 (1000)

[a] sh = shoulder on a more intense absorption. [b] Molar absorptivity values (ϵ) are in parentheses. [c] The spectrum of the compound at 77°K in a Nujol mull has well-resolved maxima at 19,620, 24,300, and 29,350 cm^{-1}.

which strongly suggest the presence of a four-coordinate, monomeric, deep red, diamagnetic cation containing a coordinated nitrosyl group and three phosphine donors from a single triphosphine ligand.

(1) The $[Ni(ligand)(NO)]^+$ cations could be formulated as *planar* nickel(II) complexes containing a coordinated nitrosyl (NO^-) anion. In such a structure, the "tripod-like" nature of these triphosphine ligands would force the apex carbon atom very close to the nickel ion; thus, the ligands would favor a tetrahedral or distorted planar structure when all three phosphino groups are bonded in a four-coordinate complex. A tetrahedral geometry for the Ni(II) and NO^- formulation may be discounted on the basis that there are no tetrahedral, diamagnetic Ni(II) complexes known to date. However, the electronic spectra of the $[Ni(ligand)NO]^+$ complexes do not appear to be consistent with known planar Ni(II) complexes.

(2) The $[Ni(ligand)(NO)]^+$ cations could be formulated as Ni(0) complexes containing a coordinated nitrosyl (NO^+) cation. In this case, the four-coordinate complex would be expected to have tetrahedral geometry as a result of the d^{10} electronic configuration of the metal. With this formulation, the deep red color of the cations would be attributed to a charge-transfer band.

The usual approach to explaining the structural features of the coordinated nitrogen(II) oxide group starts with a consideration of the valence-bond resonance forms of the nitrosyl (NO^+) cation.[10,11] Linearly N-bonded NO^+ groups have been considered to arise *via* σ donation of the lone pair of electrons on nitrogen to a suitable metal. In the few cases where the M-N-O angle is approximately 120°, it was suggested that the NO^+ cation could function as a Lewis acid and accept a pair of electrons from certain transition metals, producing sp^2 hybridization on nitrogen.[12,13] For the cases where the M-N-O angle is bent significantly from 180°, any explanation of oxidation states and bonding depends somewhat on the investigator's viewpoint, as the complexes can be formulated either as $M^{(n+2)+}$ and NO^- cases[14,15] or as M^{n+} and NO^+ examples.[12,13]

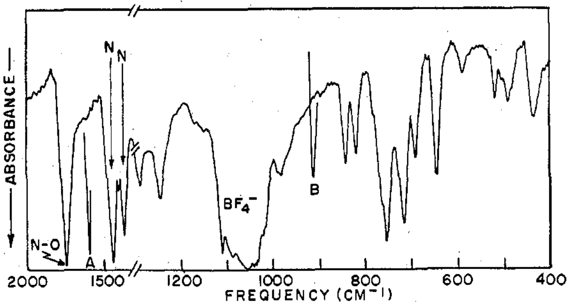

Figure 1.—The 2000–400 cm^{-1} range of the infrared spectrum (Nujol mull) of $[Ni(tep)(NO)]BF_4$. The A and B designated peaks are the 1601 cm^{-1} and 907 cm^{-1} peaks of polystyrene used for calibration, and the strong Nujol peaks at ~1450 and ~1375 cm^{-1} are designated N.

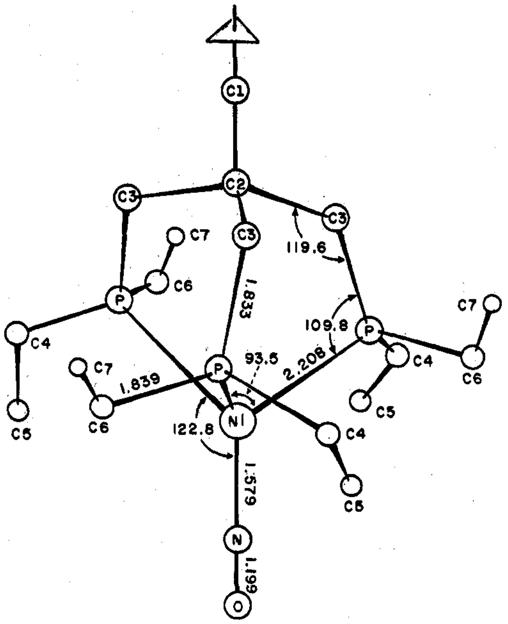

Figure 2.—View of the structure of $[Ni(tep)NO]^+$ in $[Ni(tep)NO]BF_4$ perpendicular to the threefold axis. The carbon atoms are numbered arbitrarily as in the crystallography report of ref 21.

The position of the N-O stretching frequency does not appear to be a useful criterion of bond type in the metal nitrosyl complexes, as overlapping wide ranges have been cited[10,16] (and disputed[11]) previously for complexes that were assumed to contain the coordinated NO^+, $NO\cdot$, or NO^- groups. For example, Ibers and coworkers have shown that the $[Ir(PPh_3)_2Cl(CO)NO]BF_4$,[17] $[Ir(PPh_3)_2I(CO)NO]BF_4 \cdot C_6H_6$,[13] and

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[16] R. J. Irving, *Rec. Chem. Progr.*, **26**, 115 (1965).

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$[Ir(PPh_3)_2(NO)_2]$[18] complexes have Ir–N–O angles of 124, 125, and 164°; yet these iridium compounds have N–O infrared absorptions at 1680, 1720, and 1715–1760 cm^{-1},[19] respectively. Also, Enemark[20] recently found that the Ni–N–O angle and the N–O infrared peak in $Ni(PPh_3)_2(NO)N_3$, which was prepared from Feltham's $Ni(PPh_3)_2(NO)Cl$,[4] are 153° and 1710 cm^{-1}, respectively.

Since the infrared and electronic spectra and the magnetism on the $[Ni(triphosphine)(NO)]^+$ cations did not provide a definitive interpretation about the nature of these complexes, Eller and Corfield[21] determined the structure of $[Ni(tep)(NO)]BF_4$. The cation, shown in Figure 2, has a C_3 axis, and the nickel atom is surrounded in a pseudotetrahedral fashion by three phosphorus atoms and a linearly bonded nitrosyl group. The Ni–N distance, 1.58 (1) Å, is very short as compared to other M–N distances involving first transition series metal nitrosyls, which usually have M–N distances in the range 1.70–1.80 Å.[17,22] The short Ni–N bond in $[Ni(tep)(NO)]^+$ signifies a large amount of multiple-bond character in the Ni–NO linkage and is much more consistent with NO^+ than with a NO^- group.[10,23] The pseudotetrahedral geometry around nickel, the short Ni–N bond, and the diamagnetism of the complex all favor a formulation of the metal as Ni(0) and the nitrosyl group as NO^+.

The $[Ni(tpp)NO]^+$ and $[Ni(tep)NO]^+$ cations are isoelectronic with $Ni[P(OC_2H_5)_3]_4$,[24] $Ni(CO)_4$, and $Co(CO)_3NO$.[16] The two nickel(0) complexes are colorless, whereas $Co(CO)_3NO$ is red, similar to the $[Ni(triphosphine)NO]^+$ compounds. As the $[Ni(tpp)NO]^+$, $[Ni(tep)NO]^+$, and $Co(CO)_3NO$ complexes all contain a d^{10} electronic configuration, the deep red colors exhibited by these complexes must arise from an M → NO charge transfer or from an $n \rightarrow \pi^*$ transition within the NO group.[25]

Acknowledgments.—The authors are grateful to the National Science Foundation for financial support of the research, to P. G. Eller and Professor P. W. R. Corfield for the X-ray determination and structural information on $[Ni(tep)(NO)]BF_4$,[21] and to Professor J. Enemark for a preprint about the structure determination of $Ni(PPh_3)_2(NO)N_3$.[20]

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Solvent Effects in Coordination Kinetics. II. Outer-Sphere Effects in Solvent–Ammonia Exchange on Nickel(II) in Methanol–Water Mixtures[1]

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The temperature-jump relaxation method has been used to study the kinetics of solvent–ammonia exchange on Ni(II) as a function of methanol–water solvent composition. In this study inner-sphere effects have been minimized by complexing the nickel ion with a quinquedentate ligand leaving only one coordination site available for exchange. As studied at 25°, $\mu = 0.3\ M$, both the anation and solvation rate constants are observed to increase with increasing methanol content of the solvent, the increases being particularly dramatic as anhydrous methanol is approached. The results do not correlate to previously proposed structural properties of the bulk solvent but can be accounted for by changes in the inner- and outer-sphere composition. The simplest interpretation which accounts for the formation (anation) rate constant trend indicates that this rate constant is directly related to the distribution of the two species containing either water or methanol at the sixth coordination site with methanol being 10–20 times more labile than water as a leaving group. To explain the trend in the dissociation (solvation) rate constant, however, it is concluded that significant solvent matrix effects exist. The observed behavior is shown to be consistent with a model in which the outer-sphere solvation shell is preferentially occupied by water molecules while methanol exerts a stronger influence than water in assisting the dissociation of the nickel–ammonia bond. Either a "pull" mechanism or a "push" mechanism may be used to explain the observed phenomena with some preference being given to the former process.

Introduction

A decade ago Eigen first demonstrated that ligand substitution reactions on octahedrally solvated metal ions proceed by a dissociative mechanism.[2] In the intervening years much additional evidence has been gathered to support the hypothesis that the rupture of a metal–solvent bond represents the rate-determining step in nearly all such reaction processes.[3,4]

Despite the broad implications of the dissociative mechanism for any ligand–solvent exchange process involving octahedral metal ions, the vast majority of definitive kinetic studies have been carried out in aqueous solution.[3,4] More recently several related studies have been carried out in other coordinating solvents

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