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A Study of the Donor Properties of 4-Substituted Pyridine N-Oxides

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A series of complexes of the type $[Ni(4\text{-}Z\text{-}C_5H_4NO)_6]X_2$ (Z = H, Cl, NO_2, CH_3, OCH_3, $COCH_3$; X = ClO_4, BF_4) has been isolated, and various properties of the ligands and their complexes have been studied by means of infrared, electronic, and nuclear magnetic resonance spectroscopy. An ordering of donor strengths of the ligands toward the Lewis acid phenol is reported, along with spectrochemical parameters for the complexes $[Ni(Z\text{-}C_5H_4NO)_6]^{2+}$. Several correlations of properties of the ligands with their Hammett substituent constants, σ^+ and σ^-, are also reported.

Introduction

In recent years, there have appeared several detailed reports[2-6] concerning complexes of pyridine N-oxide with nickel(II) and cobalt(II). Infrared studies[6-8] and other data presented in the literature have shown that pyridine N-oxide forms hexakis-coordinated nickel(II) and/or cobalt(II) species, $[M(C_5H_5NO)_6]^{2+}$, not only in the presence of such poorly coordinating anions as perchlorate ion,[2,3,5] but also with better coordinating agents such as nitrate ion,[6] chloride ion,[2,9] bromide ion,[2,4,9] and iodide ion.[2,4] The ease of formation of hexakis-coordinated nickel(II) and cobalt(II) complexes with pyridine N-oxide is in marked contrast to the coordination tendencies of pyridine, which has been shown to form tetragonal nickel(II)[10,11] and cobalt(II)[12] complexes $[M(C_5H_5N)_4X_2]$ in the solid state and to form $[M(C_5H_5N)_6]^{2+}X^-_2$ (M = Co(II), Ni(II); X = ClO_4, BF_4) only in solution.[11,12]

Several attempts have been made to obtain the spectral data of and to assign the spectrochemical parameters to complexes containing pyridine N-oxide. Critical examination of the spectral data reported[3,5,6] for solutions of the pyridine N-oxide complexes of nickel(II) indicates at least partial replacement of the N-oxide moiety by the solvents acetonitrile,[3,6] N,N-dimethylformamide,[5] and methanol.[6] The *Dq* values obtained from the spectral data presented for $[Ni(C_5H_5NO)_6^2]^+$ vary from solvent to solvent and are all greater than the value we report, as would be expected from the average environment rule in view of the high *Dq* values of the solvents.[13-15] As a result of the above considerations, it may be assumed that the solution spectrochemical data reported in the literature for pyridine N-oxide with respect to nickel(II) or any other metal ion are incorrect. Definitive values are contained in this article.

The availability of many 4-substituted pyridine N-oxides[16] has prompted several attempts to correlate substituent constants for the various groups with observable properties of either the ligands themselves or their complexes. A correlation (which we consider to be unsuccessful) of the N–O stretching frequency with σ for a number of 4-substituted pyridine N-oxides in carbon disulfide and Nujol mulls has been attempted.[17] Shupack and Orchin[18] have plotted the N–O stretching frequency for both a series of 4-substituted pyridine N-oxides and their *trans*-$(C_2H_4)PtCl_2(4\text{-}Z\text{-}C_5H_4NO)$ complexes *vs.* σ, noting similarly shaped, nonlinear curves for both plots. They did, however, obobtain[18] a linear plot of $\nu_{C=C}$ for the coordinated ethylene *vs.* pK_a for the six 4-substituted pyridine N-oxides. In the nmr spectra[19] of these complexes, a downfield shift of the olefinic protons is observed as the electron-donating power of Z increases. In addition, Hatfield and co-workers have explained the magnetic properties[20,21] and singlet–triplet energy separations[20] of a series of complexes of the type $[Cu(4\text{-}Z\text{-}C_5H_4NO)X_2]_2$ (X = Cl, Br) by proposing that the energy separation is a function of σ_R, with $\sigma_R \equiv \sigma - \sigma_I$ (as defined by Taft).[22]

In view of the considerable interest in both the parent pyridine N-oxide and its many 4-substituted derivatives, we decided that a detailed investigation of their donor properties was in order. In previous work this order had to be assumed. The interaction of these pyridine N-oxides was observed with the Lewis acid phenol.[23] This study was undertaken to ascertain the donor order of the 4-substituted pyridine N-oxides, so

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(11) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).

(12) M. R. Rosenthal, Ph.D. Thesis, University of Illinois, 1965.

(13) *Dq*(acetonitrile) = 1040 cm^{-1}: A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

(14) *Dq*(N,N-dimethylformamide) = 850 cm^{-1}: R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *ibid.*, **2**, 124 (1963).

(15) *Dq*(methanol) = 843 cm^{-1}: V. I. Imhof and R. S. Drago, *ibid.*, **4**, 427 (1965).

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(19) P. D. Kaplan and M. Orchin, *Inorg. Chem.*, **4**, 1393 (1965).

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(21) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965).

(22) R. W. Taft, *J. Am. Chem. Soc.*, **79**, 1045 (1957).

(23) See, for example, M. D. Joesten and R. S. Drago, *ibid.*, **84**, 3817 (1962).

an attempt could be made to correlate these properties with the substituent constants and with the spectrochemical parameters for the nickel(II) complexes of the pyridine N-oxides. The ligands (4-Z-C_5H_4NO) (Z = H, Cl, NO_2, CH_3, OCH_3, $COCH_3$) were selected for their breadth of electron-donating and -withdrawing powers and also for the expected variation in the conjugative tendencies of the 4-substituent with the donor site. The complexes of nickel(II) perchlorate with 4-methylpyridine N-oxide[24] and 4-acetylpyridine N-oxide[8] have been previously reported but have not been extensively characterized.

Experimental Section

Reagents.—Pyridine N-oxide (practical grade) was obtained from Aldrich Chemical Co. The 4-chloro, -methoxy, -methyl, and -nitro derivatives were obtained as reagent grade chemicals from City Chemical Co. The 4-acetyl derivative was obtained as the parent pyridine from Aldrich Chemical Co. and converted to the pyridine N-oxide by the method of Oachi.[16] Its purity was checked by elemental analysis. For use in the preparation of the complexes, no further purification of the 4-substituted pyridine N-oxides was found to be necessary, with the exception of the 4-chloro compound (sublimed at <2 mm pressure at ~100°). For spectral work all of the 4-substituted N-oxides but the 4-chloropyridine N-oxide (*vide supra*) were purified by recrystallization from ethanol–ether solutions. Pyridine N-oxide was purified by subliming it three times under a pressure of <2 mm at 110°. It was then stored in a dry-atmosphere box and handled there for all spectral work. Phenol was sublimed under vacuum (<2 mm at 70–80°) and stored in a desiccator when not in use.

The hexaaquonickel(II) perchlorate (G. F. Smith) and tetrafluoroborate (Alfa Inorganics) were used as obtained. Eastman Organics Spectrograde nitromethane and acetonitrile and Fisher Reagent carbon tetrachloride were stored over Linde 4-A Molecular Sieves. Mallinckrodt anhydrous ether, Fisher Analyzed ethyl acetate, and reagent grade methanol and ethanol were used as obtained. Nitrobenzene was distilled under reduced pressure from barium oxide and stored over Linde 4-A Molecular Sieves.

Synthesis.—With the exception of the 4-nitropyridine N-oxide complexes, the method of preparation was merely one of mixing together methanolic or ethanolic solutions of the ligand and the hexaaquonickel(II) perchlorate or tetrafluoroborate. Precipitation occurred within 1 min of mixing, if not immediately. The complexes were stirred for 0.5 hr, filtered in a drybox, washed with dry ether, and dried *in vacuo* overnight. If preliminary elemental analysis indicated the presence of excess ligand in the product, it was stirred with ethyl acetate (100 ml) for 1 hr and treated as before.

In the case of 4-nitropyridine N-oxide, which is only slightly soluble in ethanol and methanol, an ethanolic solution of the ligand was heated to ~60° on a heater–stirrer to induce partial dissolution of the ligand. To this mixture was then added an ethanolic solution of the metal compound, immediate precipitation of the complex resulting. The complexes were then treated as above. The analytical data for the complexes are shown in Table II. None of the complexes is appreciably hygroscopic.

Phenol Frequency Shifts.—The basic technique used for obtaining the shifts of the phenol O–H stretching frequency upon complexation of a 4-substituted pyridine N-oxide is similar to that previously reported.[23] Saturated solutions of ~0.05 *M* pyridine N-oxide and ~0.12 *M* phenol in carbon tetrachloride were run against the same concentration of phenol in carbon tetrachloride in the reference beam. The results are indicated in Table I and Figure 1.

The spectra of mixtures of phenol with nitrobenzene, pyridine N-oxide, and 4-nitropyridine N-oxide were studied in the 1100–1700-cm^{-1} range by a similar method.

TABLE I

FREQUENCY SHIFTS FOR C_6H_5OH–4-Z-C_5H_4NO INTERACTIONS IN CARBON TETRACHLORIDE

Z	$\nu_{OH(complexed)}$, cm^{-1} [a]	$\Delta\nu_{OH}$, cm^{-1}	$-\Delta H$, kcal/mole [b]
OCH_3	<3090	>530	>9.0
CH_3	3108 ± 10	512 ± 10	8.8 ± 0.2
H	3152 ± 10	468 ± 10	8.1 ± 0.2
Cl	3185 ± 10	435 ± 10	7.6 ± 0.2
CH_3CO	3220 ± 10	400 ± 10	7.0 ± 0.2
NO_2	3400 ± 25	220 ± 25	4.1 ± 0.2

[a] $\nu_{OH(free)}$ is assumed to be 3620 cm^{-1} in carbon tetrachloride. [b] Calculated from the expression $-\Delta H = 0.016\Delta\nu_{OH} + 0.63$.[23]

Solid-State Electronic Spectra.—The nickel(II) perchlorate complexes were mulled with Nujol to give a stiff paste and were run in the 350–1500 mμ region on a Cary 14M recording spectrophotometer on Whatman No. 1 filter paper against a reference consisting of a similar piece of filter paper soaked in Nujol.[25] A beam attenuator was at times needed to balance the sample and reference energies.

Solution Electronic Spectra.—Solution spectra were run in the 380–1500-mμ region on a Cary 14M recording spectrophotometer. Since all spectra listed in Table III were obtained in nitromethane solutions containing excess ligand to prevent dissociation, the nitromethane reference solutions contained an equal amount of dissolved ligand. Matched quartz cells of path length 0.1–5 cm were used. The spectral data are tabulated in Tables III and IV.

Nuclear Magnetic Resonance Spectra.—Nuclear magnetic resonance spectra of nitromethane solutions of the 4-substituted pyridine N-oxides and their nickel(II) complexes (with added ligand) were obtained on a Varian A-60 recording spectrometer, using tetramethylsilane as an internal standard. All samples were run at 32 ± 2°. The low solubilities of the nickel perchlorate complexes of the unsubstituted and 4-nitropyridine N-oxides necessitated the use of the nickel tetrafluoroborate complex for these studies. A typical plot is given in Figure 2.

Infrared Spectra.—Infrared spectra of the ligands and their nickel(II) perchlorate complexes in the sodium chloride region (650–4000 cm^{-1}) and the cesium bromide region (250–1600 cm^{-1}) were obtained for Nujol mulls of the samples, using a Perkin-Elmer Model 521 or a Beckman IR5A recording spectrophotometer. The spectra were calibrated with known frequency bands of polystyrene and indene. For studying the metal–oxygen stretching frequencies, the instruments were flushed with either dry air or dry nitrogen for 20 min prior to use. Calibration on the IR5A was achieved by comparison with bands of known frequency taken from the spectra obtained from the calibrated Perkin-Elmer 521. The data obtained are listed in Table V and shown graphically in Figure 3.

Results

The frequency shift of phenol upon complexation to the series of 4-substituted pyridine N-oxides is reported in Table I. Although the phenol–4-substituted pyridine N-oxide solutions studied in the infrared region 2800–3600 cm^{-1} (Table I) were prepared with equal amounts of phenol present in both the sample and reference solutions, it was found that upon complexation the extinction coefficients of the C–H stretching frequencies in the phenol increased, thus causing an imbalance in the absorptions and leading to net absorptions in the 3000–3100-cm^{-1} region. This factor, along with the large frequency shifts for most of the N-oxides, gave an asymmetric peak with excess absorption

(24) R. L. Carlin, J. Roitman, M. Dankleff, and J. O. Edwards, *Inorg. Chem.*, **1**, 182 (1962).

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TABLE II

ANALYTICAL DATA FOR THE $[Ni(4\text{-}Z\text{-}C_5H_4NO)_6]X_2$ COMPLEXES

Z	X	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
H	ClO_4	43.48	43.76	3.62	3.61	10.14	9.92
H	BF_4	44.83	44.43	3.74	3.73	10.41	10.07
NO_2	ClO_4	32.80	32.54	2.19	2.25	15.39	14.98
NO_2	BF_4	33.55	33.57	2.24	2.42	15.66	15.35
OCH_3	ClO_4	42.80	43.06	4.17	4.18	8.35	8.25
OCH_3	BF_4	43.94	43.86	4.27	4.20	8.54	8.16
CH_3	ClO_4	47.40	47.60	4.61	4.62	9.21	9.16
CH_3	BF_4	48.70	48.41	4.73	4.84	9.47	9.14
Cl	ClO_4	34.78	34.73	2.31	2.60	8.11	7.67
Cl	BF_4	35.64	35.56	2.37	2.56	8.32	7.92
$COCH_3$	ClO_4	46.66	46.96	3.88	4.04	7.77	7.35
$COCH_3$	BF_4	47.77	47.53	3.98	4.16	7.96	7.56

TABLE III

BAND ASSIGNMENTS IN THE ELECTRONIC SPECTRA OF $Ni(4\text{-}Z\text{-}C_5H_4NO)_6X_2$ COMPLEXES

Z	X	Solvent	c, M	λ_{max}, mμ	ν_{max}, cm^{-1}	ϵ_{max}[a]	Assignment
NO_2	BF_4	0.0628 *M*	8.02×10^{-3}	410[b]	...	...	...
		$NO_2C_5H_4NO$		695	14,388	17.3	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		765 sh[c]	...	...	$\rightarrow {}^1E_g$
				1205	8,299	16.6	$\rightarrow {}^3T_{2g}$
OCH_3	ClO_4	0.0796 *M*	0.0101	385	25,974	450	$\rightarrow {}^3T_{1g}(P)$
		$CH_3OC_5H_4NO$		712	14,045	13.9	$\rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		780	12,820	12.5	$\rightarrow {}^1E_g$
				1250	8,000	12.2	$\rightarrow {}^3T_{2g}$
CH_3	ClO_4	0.1612 *M*	0.0236	391	25,575	460	$\rightarrow {}^3T_{1g}(P)$
		$CH_3C_5H_4NO$		712	14,045	11.7	$\rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		770	12,987	10.6	$\rightarrow {}^1E_g$
				1260	7,936	11.2	$\rightarrow {}^3T_{2g}$
H	BF_4[d]	0.1024 *M*	0.0101	388	25,773	419	$\rightarrow {}^3T_{1g}(P)$
		C_5H_5NO in		705	14,184	13.7	$\rightarrow {}^3T_{1g}(F)$
		CH_3NO_2		770	12,986	11.7	$\rightarrow {}^1E_g$
				1260	7,936	11.0	$\rightarrow {}^3T_{2g}$
Cl	BF_4	0.0295 *M*	5.75×10^{-3}	401	24,938	431	$\rightarrow {}^3T_{1g}(P)$
		ClC_5H_4NO		728	13,736	14.5	$\rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		775	12,903	13.4	$\rightarrow {}^1E_g$
				1272	7,862	12.5	$\rightarrow {}^3T_{2g}$
$COCH_3$	ClO_4	0.1290 *M*	0.0211	424	23,585	727	$\rightarrow {}^3T_{1g}(P)$
		$CH_3C(O)C_5H_4NO$		712	14,045	16.0	$\rightarrow {}^3T_{1g}(F)$
		in CH_3NO_2		765	13,072	13.9	$\rightarrow {}^1E_g$
				1275	7,842	15.4	$\rightarrow {}^3T_{2g}$

[a] The extinction coefficient, ε, is calculated from $\epsilon = A/bc$, with *A* being the absorbance of the sample, *c* the concentration of the sample in moles per liter, and *b* the path length (in centimeters) of the cell. [b] This band is obscured by a solvent transition. [c] sh = shoulder. [d] $[Ni(C_5H_5NO)_6](ClO_4)_2$ is insoluble in nitromethane.

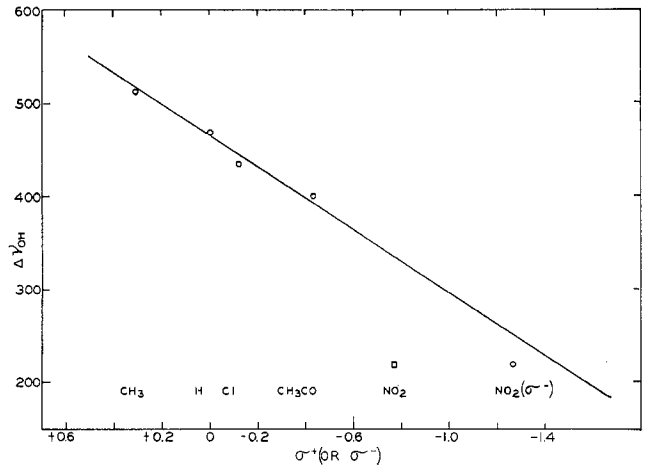

Figure 1.—The observed shifts in the O–H stretching frequency ($\Delta\nu_{OH}$) of phenol upon complexation with various 4-substituted pyridine N-oxides as a function of σ^+ (σ^- for 4-nitropyridine N-oxide).

on the low-frequency side. The reported shifts were determined by: (1) picking frequencies at which there were no absorptions for free phenol in carbon tetrachloride and assuming that in the spectrum of the complexed phenol the absorptions at these frequencies were due only to the O–H stretching frequency of the adduct; (2) constructing a symmetrical curve for the $\nu_{OH(complexed)}$ absorption, utilizing as much of the unperturbed curve as possible, along with points determined as described above for the lower energy side of the curve; (3) determining the center of $\nu_{OH(complexed)}$ and $\Delta\nu_{OH}$ as previously reported.[23] The correlation of σ^+ *vs.* $\Delta\nu_{OH}$ is illustrated in Figure 1. The center of the peak for the 4-methoxypyridine N-oxide is located at <3090 cm^{-1}, and only a poorly defined curve was constructed for this absorption. Thus $\Delta\nu_{OH}$ can be reported only as being >530 cm^{-1}.

The data from Table II indicate that the complexes prepared may be formulated as $[NiL_6](ClO_4)_2$ and [Ni-

TABLE IV
LIGAND FIELD PARAMETERS FOR
$[Ni(4\text{-}Z\text{-}C_5H_4NO)_6]X_2$ COMPLEXES

Z	Dq, cm^{-1}	β	ν_2, cm^{-1} Calcd	ν_2, cm^{-1} Obsd	% diff
NO_2	830	...	...[a]	...	...
OCH_3	800	0.98	13,515	14,045	3.9
CH_3	794	0.96	13,398	14,045	4.8
H	794	0.97	13,423	14,184	5.7
Cl	786	0.92	13,230	13,736	3.8
$COCH_3$	784	0.83	13,405	14,045	4.8

[a] Since the highest energy d–d transition in $[Ni(4\text{-}NO_2\text{-}C_5H_4NO)_6](BF_4)$ was obscured by some type of solvent charge-transfer peak, ν_2 could not be calculated.

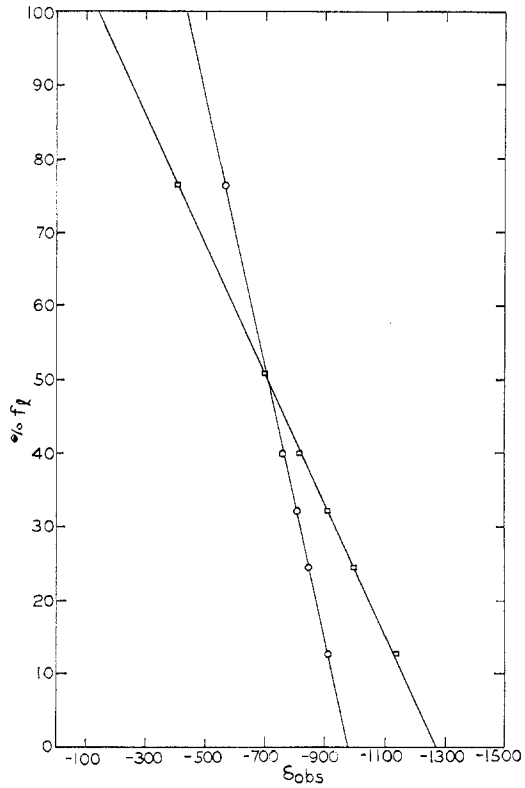

Figure 2.—The observed chemical shift (δ_{obsd}) of β protons O and 4-methyl protons □ in $[Ni(CH_3C_5H_4NO)_6](ClO_4)_2$ as a function of f_1, the mole percentage of free $CH_3C_5H_4NO$.

$L_6](BF_4)_2$, with L corresponding to the different pyridine N-oxides.

Table III contains the solution spectral data for the complexes. Since it was desirable to obtain solution spectra of the various complexes in approximately the same concentrations as those used for nmr studies (which will be described shortly), approximately 0.01 M solutions of the nickel tetrafluoroborate complexes of the unsubstituted and 4-nitropyridine N-oxides were studied. In the case of the 4-chloropyridine N-oxide, the tetrafluoroborate complex is more soluble than that of the perchlorate. Solid-state mull spectra indicated no gross differences from the solution spectra, although the bands were much broader than those in solution and their positions somewhat shifted. Table IV contains a summary of the spectrochemical parameters for the complexes. The values for β and ν_2 were obtained by the standard procedure.[5] Although there has been

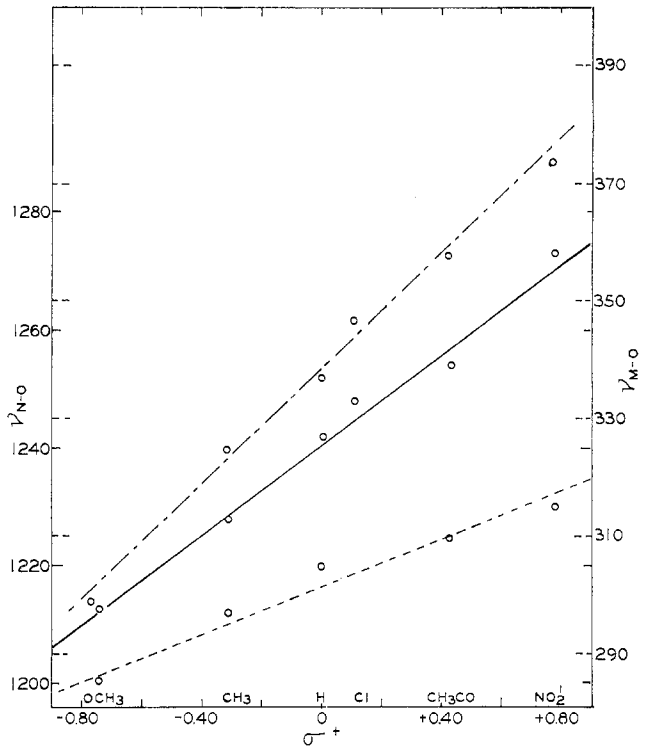

Figure 3.—The changes in the N-oxide stretching frequencies of both free and complexed 4-substituted pyridine N-oxides and the metal–oxygen stretching frequencies of their nickel(II) complexes as a function of σ^+: ———, free N-oxide stretching frequencies; – – – –, complexed N-oxide stretching frequencies in the complexes; and — – —, metal–oxygen stretching frequencies.

disagreement[26,27] over the assignment of the shoulder in the middle band of the electronic spectra of octahedral nickel(II), following Dunn[28] we assign the shoulder to the $^3A_{2g} \rightarrow {}^1E_g$ transition and the more intense peak to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition. The agreement between the calculated and observed values of ν_2 for several of the complexes is good.

The nmr spectra of solutions of the complexes in nitromethane containing excess ligand were investigated to obtain additional evidence to support the contention that six pyridine N-oxides are coordinated to the nickel ion in solution. Since the coordinated and free ligands undergo rapid exchange leading to the observance of only a single peak, the observed frequency, δ_{obsd}, is given in the rapid exchange approximation by

$$\delta_{obsd} = \delta_1 f_1 + \delta_c f_c \quad (1)$$

in which δ_c is the chemical shift of the coordinated ligand, δ_1 that of the "free" ligand, and f_1 and f_c the mole fractions of free and complexed ligands, respectively. The quantity of complexed ligand is n, the coordination number, times the concentration of the metal ion.

If δ_{obsd} is plotted as a function of f_1, one should obtain a linear plot, with intercepts δ_1 and δ_c, providing that the species in solution remains the same over the concen

(26) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955), and later papers.
(27) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).
(28) T. M. Dunn, *Pure Appl. Chem.*, **6**, 1 (1963).

TABLE V

HAMMETT FUNCTIONS AND INFRARED FREQUENCIES OF 4-SUBSTITUTED PYRIDINE N-OXIDES AND THEIR $Ni(4\text{-}Z\text{-}C_5H_4NO)_6(ClO_4)_2$ COMPLEXES

Z	σ[a]	σ^+[b]	$\nu_{N-O(ligand)}$, cm^{-1}	$\nu_{N-O(complex)}$, cm^{-1}	$\Delta\nu_{N-O}$, cm^{-1}	$\nu_{Ni-O(complex)}$, cm^{-1}
NO_2	+0.79	+0.78	1273 ± 3	1230 ± 3	43	374
CH_3CO	+0.43	+0.43[c]	1254	1225	29	358
Cl	+0.23	+0.11	1248	1212–1222[d]	...	347
H	0	0	1242	1220	22	337
CH_3	−0.16	−0.31	1228	1212	16	325
OCH_3	−0.26	−0.76	1213	1201	12	299

[a] R. W. Taft, N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 292 (1958). [b] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957). [c] This value is assumed on the basis of findings of H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958), who find little change in σ and σ^+ for those substituents which are incapable of resonance-electron donation. [d] A doublet (due to overlap of two individual peaks) is obtained with maxima at 1212 and 1222 cm^{-1}; regardless of which peak is assigned as the N–O stretching frequency, the exact center of the N–O peak cannot be obtained accurately.

tration range studied. Measuring δ_{obsd} over a wide range of excess ligand concentration provides a useful but not rigorous criterion for the existence of the fully coordinated species in solution. The conclusion that the single species giving straight-line behavior is the fully coordinated species would be in error if some other complex, *e.g.*, $[Ni(C_5H_5NO)_5CH_3NO_2]^{2+}$, were the only stable species over the entire range of concentration studied. This situation is considered unlikely in these systems where there is such a large excess of ligand in solution and the solvent is a poor ligand. A typical plot is shown in Figure 2. A further check on this method can be utilized in the cases of the 4-acetyl-, 4-methoxyl-, and 4-methylpyridine N-oxide complexes. Since the methyl groups in these ligands are not coupled to the ring proton system, the extrapolations to 100% free ligand concentration should yield frequencies identical with those measured in the free ligands. For example, in the case of the 4-methylpyridine N-oxide (whose methyl contact shift is −1117 cps), extrapolation to 100% free ligand concentration yields a frequency of −142 ± 2 cps from tetramethylsilane, while the measured frequency in the free ligand is −141 ± 1 cps from tetramethylsilane.

A similar method for determining the diamagnetic resonances for protons in pyridine N-oxide and several methyl-substituted pyridine N-oxides has been reported,[29] yielding values for pyridine N-oxide and 4-methylpyridine N-oxide within 3% of our values.

The values of the infrared stretching frequencies for the ligands presented in Table V are consistent with those results reported previously.[2,7,8,17,30,31] Although the data presented in Table V do not vary linearly with σ, a linear fit is obtained with σ^+. The σ^+ values are chosen because the 4-substituents in the pyridine N-oxides are conjugated with the N–O portion of the compounds.[32] The effect of this conjugation interaction on electron-donating groups causes σ^+ to be quite different from σ (see Table V), while the effect for those groups which are capable only of electron withdrawal is negligible.[33] The plots for both the "free" and "complexed" N–O stretching frequencies are shown as a function of σ^+ in Figure 3 along with a plot of the metal–oxygen stretching frequencies.

Although coupling of the above modes with other vibrational modes in these systems most certainly exists, the correlations obtained would seem to indicate that these effects are either small, relatively constant, or vary in the same direction as the substituent effect in this series of compounds.

Discussion

Donor Strength toward Phenol.—The change in O–H stretching frequency of phenol, $\Delta\nu_{OH}$, has been correlated with the enthalpy of adduct formation of phenol with many donors[23] (for thermodynamic data obtained in CCl_4). The data reported in Table I indicate decreasing donor strength of the 4-substituted pyridine N-oxide with the increasing electron-withdrawing ability of the substituent. The correlation of σ^+ with $\Delta\nu_{OH}$ is illustrated in Figure 1. The value obtained for the interaction of phenol and 4-nitropyridine N-oxide falls far below the line. A somewhat better fit is obtained if one uses the value of σ^- (1.27)[34] for the nitro substituent. Use of both types of constants in this correlation has precedent in that a combination of σ^+ values for electron-donating groups and σ^- values for strongly electron-withdrawing groups was used to correlate the basicities of a series of 3- and 4-substituted pyridine N-oxides.[34,35] Since Shupack and Orchin[18] correlated the change in $\nu_{C=C}$ in their olefin complexes with pK_a, these results would also correlate with a combination of σ^+ and σ^- values.

The large error reported for the phenol frequency shift upon complexation to 4-nitropyridine N-oxide is due to a large amount of asymmetry in the curve. This asymmetry is believed to result from the occurrence of overlapping bands, arising from coordination of both the nitro group and the N-oxide group of the donor molecule with phenol, causing two types of 1:1 complexed species to exist in solution. To support this assumption, infrared spectra of 4-nitropyridine N-oxide, nitrobenzene, and pyridine N-oxide were studied

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(31) G. Costa and P. Blasina, *Z. Physik. Chem.* (Frankfurt), **4**, 24 (1955).
(32) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 89.
(33) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).
(34) H. H. Jaffé and G. O. Doak, *ibid.*, **77**, 4441 (1955).
(35) H. H. Jaffé, *J. Org. Chem.*, **23**, 1790 (1958).

in the 1100–1700-cm^{-1} region both with and without added phenol. Shifts of the N-oxide, symmetric nitro, and asymmetric nitro stretching frequencies in 4-nitropyridine N-oxide were observed upon addition of phenol. The shifts were assigned by comparison of shifts of the analogous absorptions in nitrobenzene[36] and pyridine N-oxide. As would be expected by comparison with the analogous carboxylate vibrations,[37] the frequency of the symmetric stretch of the nitro group decreases upon coordination and that of the asymmetric stretch increases. These results indicate competition between the nitro group and the N-oxide group as donor sites in this molecule in solution. Extension of the π system over the entire molecule would tend to make the nitro group in 4-nitropyridine N-oxide a better donor than the nitro group in nitrobenzene, and, as indicated by the phenol shift, the amine oxide a poorer donor site than that in pyridine N-oxide.

Nickel(II) Complexes.—The electronic spectral data in Table III are typical of octahedral nickel(II), indicating that the species in both the solid and solution phases are of the form $[Ni(4\text{-}Z\text{-}C_5H_4NO)_6]^{2+}$. For all solution spectra an excess of ligand was present as a precaution to prevent dissociation of the complexes in nitromethane. Spectral data attributed to the octahedral species $[Ni(C_5H_5NO)_6]^{2+}$ in earlier work[3,5,6] were incorrect because dissociation had occurred in solution. The extinction coefficients for the ν_3 band are, however, some 20–40 times larger than those normally seen for Laporte-forbidden d–d transitions in octahedral nickel(II). These absorptions are believed to be[3] in reality d–d transitions located on the tail of a charge-transfer peak which extends into the visible region, giving yellowish casts to the solid complexes and their nitromethane solutions.

The existence of six-coordinate substituted pyridine N-oxide complexes in solution and the validity of their spectrochemical parameters (Table IV) are supported by the nmr data graphed in Figure 2 and the general agreement of the mull and solution spectra. Solutions of $[Ni(CH_3COC_5H_4NO)_6](ClO_4)_2$ dissolved in acetonitrile, a situation in which dissociation occurs, do not give a linear plot of δ_{obsd} *vs.* f_1.

The Dq values reported (Table IV) are in the main consistent with the idea that, as more electron density is transmitted onto the N-oxide group, a stronger ligand field splitting occurs. The accuracy of the measurement (the ν_1 bands are quite broad) does not permit detailed comparison of the Dq values obtained for compounds with fairly close σ^+ values.

The β values are quite high, suggesting little covalency in the metal–oxygen bond. The β values for the 4-methoxy, 4-methyl, and unsubstituted pyridine N-oxides are the highest yet reported, the previous high being $\beta = 0.95$ for nickel(II) in an alkali sulfate melt at 700°.[38]

From a consideration of the basicity of 4-nitropyridine N-oxide[34,35] and the strongly electron-withdrawing nature of the nitro group, along with the phenol data presented, one would expect the Dq for $[Ni(4\text{-}NO_2\text{-}C_5H_4NO)_6]^{2+}$ to be less than those in the other complexes studied. From the data given in Table IV, it is seen, however, that the opposite case is in fact true. The nmr spectrum for protons in the complex of 4-nitropyridine N-oxide with Ni(II) as a function of concentration of excess ligand is similar to that plotted in Figure 2, suggesting that the same species (presumably the six-coordinate N-oxide complex) is present. The possibility of 4-nitro coordination in solution (similar to the situation with phenol) is unlikely in view of the nmr results. Examination of the infrared spectrum of solid $[Ni(4\text{-}NO_2\text{-}C_5H_4NO)_6](ClO_4)_2$ shows no band which can be assigned to a free N-oxide stretching frequency. The infrared spectrum of the complex cannot be studied in solution in the absence of added ligand (needed to prevent dissociation). In addition, if the high Dq is to be explained by consideration of coordination of nitro groups on the 4-nitropyridine N-oxide, invoking of the average environment rule for the observed Dq requires a very high value for the Dq of the nitro groups toward nickel(II). Assuming a Dq for the N-oxide group of 775 cm^{-1} (*vide infra*) and 20% coordination by the nitro groups requires a Dq for the nitro group of over 1000 cm^{-1}. Assuming a smaller percentage of coordination by the nitro group raises this value. Thus, we believe the high Dq cannot be due to coordination of the nitro group in this complex.

One possible explanation for the unusual result for the 4-nitro-substituted compound involves considering a lowering of the N-oxide π^* orbitals relative to those on the other 4-substituted compounds, so that there would be more metal-to-ligand back-bonding in this nickel(II) complex, thus raising the value of Dq from the value of $\sim$775 cm^{-1} (expected from consideration of the other values on the basis of the substituent constant of the 4-NO_2 group) to the observed value of 830 cm^{-1}. The low-frequency shift toward phenol with the 4-nitro substituent indicates a poor donor strength (Figure 1) and is consistent with extensive nitrogen–oxygen π bonding in the nickel(II) complex.

Infrared Studies.—In view of the complexity of the vibrational problem (coupling of the vibrational modes, etc.), some surprisingly good correlations for the changes in frequency of the N-oxide stretching vibration (Table V) with the σ^+ value of the 4-substituents are found in both the free ligands and the complexes (Figure 3). These changes are in the order expected. Electron-withdrawing substituents increase the formal charge on nitrogen, in effect increasing its electronegativity. As nitrogen becomes more electronegative, the energy match of the nitrogen and oxygen p orbitals improves and thus facilitates a greater contribution of oxygen or-

(36) The symmetric and asymmetric nitro stretching frequencies in nitrobenzene were assigned from an infrared and Raman study by J. H. S. Green, W. Kynaston, and A. S. Lindsey, *Spectrochim. Acta*, **17**, 486 (1961).

(37) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 5262 (1962).

(38) D. S. Erley, *Anal. Chem.*, **29**, 1564 (1957).

bitals into the π system of the aromatic ring. This interaction therefore increases the π-bond order in the nitrogen–oxygen bond, thus raising the frequency of the N-oxide stretching mode. This trend appears to be the dominant one governing the change in both the free and complexed N-oxide stretching frequencies. The decrease in the N-oxide stretching frequency upon complexation is caused by the drain of electron density from the oxygen to the metal. This drain causes the oxygen to become more electronegative, increasing the energy mismatch between the oxygen and nitrogen p orbitals, decreasing the contribution of the oxygen orbitals in the π system, and thereby reducing the frequency of the N-oxide stretching vibration. However, if one examines the change in frequency on coordination, $\Delta\nu_{N-O}$, for the various 4-substituted compounds, a different result than expected is obtained. The magnitude of the shift is greatest for those substituents which give rise to the smallest *Dq* toward nickel(II) (which the exception of the 4-nitro compound) and exhibit the weakest donor strength toward phenol. Furthermore, the N-oxides that undergo the largest frequency shift have the free N-oxide stretching frequency at highest energy.

This result could be interpreted in terms of our model. The energies of the empty π^* orbital of the ligand would increase in the order $NO_2 < COCH_3 < Cl < H < CH_3 < OCH_3$. One would thus expect a decrease in the extent of metal-to-ligand back-bonding with increasing energy of the π^* orbital. This proposal is supported by the trend in metal–oxygen stretching frequencies (Figure 3), which increase in reverse order to that expected either on the basis of the σ^+ substituent values or donor strengths toward phenol. The increase in metal–oxygen stretching frequency follows the proposed order for increased back-bonding. Although both the change in N-oxide and the metal–oxygen stretching frequencies follow the back-bonding order, the spectrochemical parameter *Dq* appears to be dominated by the σ-donor strength (as manifested toward phenol) except for 4-nitropyridine N-oxide. Back-bonding would lower the energy of the t_{2g} orbitals relative to that of the e_g orbitals, thus raising *Dq*. If, as suggested by the infrared studies, back-bonding increases in the order $OCH_3 < CH_3 < H < Cl < COCH_3 < NO_2$, its effect must be to diminish the difference caused by changes in the σ-donor strength as a function of the substituents, giving rise to smaller differences in *Dq* than would be expected for this series in the absence of this effect. The increase in the extent of back-bonding in going from the 4-$COCH_3$ to the 4-NO_2 substituent must be so large that this effect dominates, and consequently *Dq* also increases.

An alternative explanation that accounts for all of the data except the high *Dq* for 4-nitropyridine N-oxide should be mentioned. This explanation involves assuming the absence of back-bonding, a σ-donor strength order toward nickel(II) as is manifested toward phenol, and coupling of the N-oxide and metal–oxygen stretching frequencies. Coupling would be greatest in the complex of the 4-OCH_3-substituted compound and least for the 4-NO_2 compound, since the energies of the two uncoupled vibrations would be closer in the former. Consequently, in the 4-OCH_3 compound the coupled N=O vibration would occur at a higher frequency than expected, $\Delta\nu_{N=O}$ would not be as great, and the metal–oxygen vibration would occur at a lower frequency than expected. Since these effects are not present to as great an extent as the metal–oxygen bond becomes weaker and the force constant for this vibration lower, the observed trend is rationalized.

Evidence against coupling dominating the observed order is found in reported values of $\Delta\nu_{N-O}$ in the adducts $BX_3 \cdot 4\text{-}Z\text{-}C_5H_4NO$ (X = F, H; Z = H, CH_3).[39] In these compounds, where the interaction of the oxygen with the boron involves essentially σ-electron pair donation, the observed order is $\Delta\nu_{N-O(CH_3)} > \Delta\nu_{N-O(H)}$. The same order of frequency shift is observed toward phenol, another Lewis acid in which back-bonding would not exist. Consequently we feel that the back-bonding argument best explains the observed trends in the infrared data of the nickel(II) complexes.

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