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Titanium Complexes of *para*-Substituted Pyridine N-Oxides. I. Effect of Substituent on the Nitrogen-Oxygen and Titanium-Oxygen Stretching Vibrations

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para-Substituted pyridine N-oxides and their titanium tetrafluoride complexes have been studied in the infrared in the region 4000–33 cm^{-1}. Particular attention has been paid to shifts occurring in both the N–O and Ti–O stretching mode as a function of *para* substituent. Correlation of both of these vibrational modes with the substituent constant, σ^+, reveals that little, if any, back bonding occurs between the titanium atom and the ligands.

Introduction

In the past several years much interest has been generated in metal complexes of pyridine N-oxides. Of particular interest was the recent publication of Herlocker, *et al.*,[2] in which the electronic nature of *para*-substituted pyridine N-oxides was elucidated through a comprehensive study of the nickel complexes. Use was made of infrared and ultraviolet spectroscopy to define the effect of the *para* (4) substituent on the electron density in the N–O and metal–oxygen (M–O) bonds. Our interest in this subject has been a result of a more general study in the far-infrared region (400–33 cm^{-1}) of the titanium complexes of similar molecules, a work soon to be published. An obvious extension, therefore, was to compare the studies of the nickel complexes with complexes of titanium.

Experimental Section

Complexes of 4-nitro-, 4-chloro-, 4-methyl-, 4-methoxy-, and pyridine N-oxide (4-H) were prepared by adding saturated solutions of recrystallized 4-substituted ligands in methylene chloride to saturated solutions of titanium tetrafluoride in methylene chloride. In most cases, immediate precipitation of the complexes occurred. It was found that *p*-dioxane could also be used as a solvent in this preparation. The precipitates in each case were washed in cold carbon tetrachloride, recrystallized from suitable solvents ($CHCl_3$, CH_2Cl_2, etc.), and dried in a vacuum oven at 80°

Except for the 4-chloro derivative, all starting materials were procured from commercial suppliers. The 4-chloro derivative was prepared in <90% yield from 4-nitropyridine N-oxide by the method of Ochiai.[3] Structure of the resulting 4-chloropyridine N-oxide was confirmed by elemental analysis as well as infrared and nmr spectra. In all cases, repurification of the commercially procured starting materials was required. It should be noted that repurification of the 4-methoxypyridine N-oxide proved to be a rather difficult task due to at least four impurities, one of which very closely resembled the *para* derivative. Purification was finally achieved by vacuum sublimation and the structure was confirmed by elemental analysis and nmr and infrared spectra.

Complex formation was confirmed in each case by elemental analysis, as well as characteristic infrared frequencies. In each case, analysis revealed 2 moles of ligand/mole of TiF_4. This observation is consistent with those of Dyer, *et al.*,[4] who have shown the complex structure in the case of the pyridine N-oxide to be a regular octahedron with the ligands occupying sites in the adjacent *cis* positions and the titanium atom in the center.

Infrared spectra of all materials studied were obtained on Beckman IR-9 and IR-11 infrared spectrophotometers over the 4000–33-cm^{-1} region. Samples were prepared as Nujol mulls with KBr and high-density polyethylene being used as window material in the mid- and far-infrared regions, respectively. Nmr spectra pertinent to the determination of purity were obtained on a Varian A-60 spectrometer in chloroform-*d* with tetramethylsilane as an internal reference.

Results

Infrared frequencies for the N–O stretching mode in both the complexed and uncomplexed molecules are given in Table I along with the frequencies observed by Herlocker, *et al.*, for the nickel complexes. In almost all cases, excellent agreement is obtained showing that the nature of the metal apparently has little effect on the change in N–O frequency on complexing. The disagreement which exists between our value and the value reported by Herlocker for the 4-methoxy frequency may be explained on the basis of the several impurities which we have observed and previously mentioned. In addition, it is felt that the two frequencies observed for the pyridine N-oxide complex represent a splitting due to mixing with other frequencies. Figure 1 shows a plot of the N–O frequencies *vs.* σ^+, the substituent constant.[5,6] Excellent correlation is obtained if the average of the two pyridine N-oxide complex frequencies is used, further substantiating our suspicion.

If one assumes that a concurrent decrease in σ bonding in the M–O bond will occur (precluding any back bonding) as the π-bond character of the N–O bond increases, then one would expect a similar but inverse correlation with σ^+ to be obtained using the M–O stretching frequencies. Assigning the proper frequency in the region 400–33 cm^{-1} to the M–O stretching mode is by no means unambiguous. Many authors,[2,7,8] however, have assigned complexed M–O and M–N stretching vibrations (where M = Ni, Co, Mn, Cu, Fe,

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[2] D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 11 (1966).

[3] E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

[4] (a) D. S. Dyer and R. O. Ragsdale, *Chem. Commun.*, **17**, 601 (1966); (b) D. S. Dyer and R. O. Ragsdale, *Inorg. Chem.*, **6**, 8 (1967).

[5] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957).

[6] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 89.

[7] Y. Kakiati, S. Kida, and J. V. Quagliano, *Spectrochim. Acta*, **19**, 201 (1963).

[8] C. W. Frank, Ph.D. Thesis, Purdue University, 1965; University Microfilms, Inc., Ann Arbor, Mich., No. 66-2261.

Table I

N–O Stretching Frequencies of *para*-Substituted Pyridine N-Oxides and Their TiF_4 Complexes

		ν_{N-O}, cm^{-1}			
		Ligand		Complex	
Substituent	σ^+	This work	Herlocker[a]	This work	Herlocker[a]
NO_2	+0.79	1274	1273	1230	1230
Cl	+0.11	1248	1248	1222	1212–1222
H	0	1246	1242	(1219)[b]	1220
CH	−0.31	1232	1228	1213	1212
OCH_3	−0.76	1228	1213	1210	1201

[a] Note that these frequencies are for Ni complexes of the substituted pyridine N-oxide. [b] This value represents an average of a doublet at 1212 and 1226.

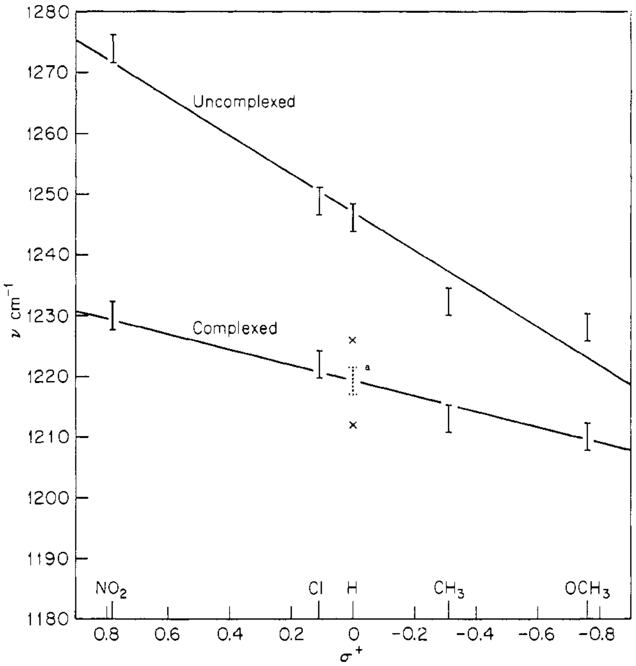

Figure 1.—Frequency (ν, cm^{-1}) *vs.* σ^+ for the N-O stretching vibration in several 4-substituted pyridine N-oxides and their TiF_4 complexes. Point a indicates the average value of a doublet.

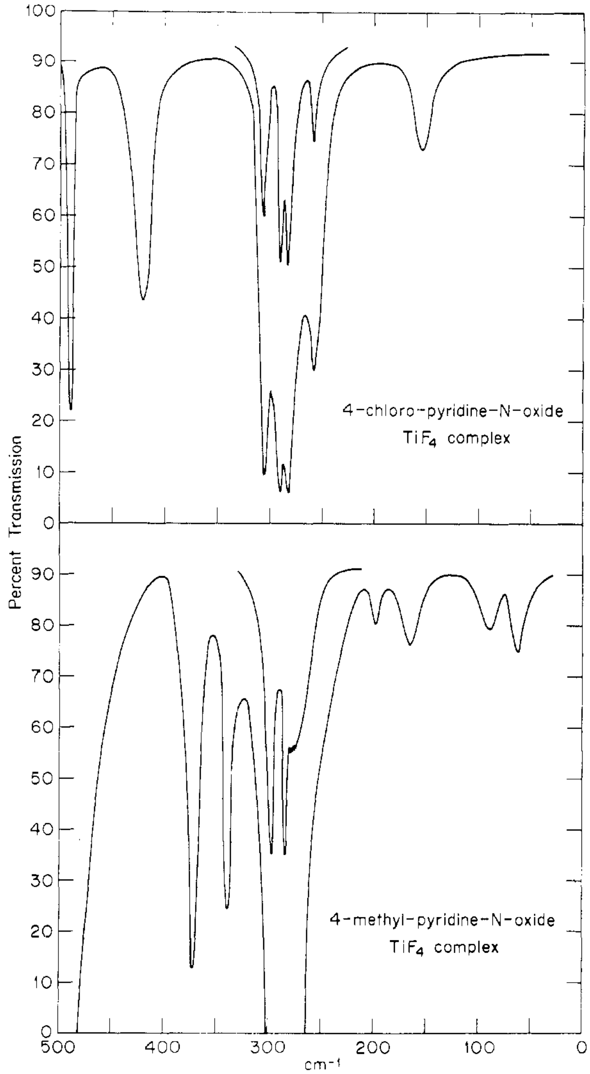

Figure 2.—Far-infrared spectra of TiF_4 complexes of 4-chloro- and 4-methylpyridine N-oxide.

Zn, Al) in the 200–400 cm^{-1} region. It is not unlikely, therefore, that the complexed Ti–O stretch should also appear in this region. Our far-infrared spectra (Figure 2—spectra redrawn) reveal many absorptions in the 400–33-cm^{-1} region the strongest of which, however, occurs between 200 and 400 cm^{-1}. We feel that the following analysis offers evidence for the tentative assignment of the Ti–O stretch.

With the assumption, as mentioned above, that a similar but inverse relation of the M–O frequencies to the N–O frequencies exists, then a correlation of M–O frequencies *vs.* σ^+ with a slope opposite in sign to that of the N–O plot ought to exist. By using all of the far-infrared frequencies of the pyridine N-oxide complex ($\sigma^+ = 0$) as *y* intercepts, calculating the slope of the N–O plot, and reversing the sign, one can calculate frequencies, using the equation for a straight line, for the other 4-substituted complexes in the region 400–33 cm^{-1}.

Comparison of the observed frequencies with those calculated ought to reveal matching frequencies for the M–O stretching mode if such a correlation exists. Naturally, a similar series of calculations using a positive slope was also made. The spectra revealed that *only two* bands in the infrared spectrum of each complex matched the calculated frequencies, and the separation in each case was 14 cm^{-1} or less. The correlations using the positive slope revealed no matching frequencies whatsoever. Calculated and observed frequencies which we have tentatively assigned to the Ti–O stretching mode are given in Table II and a plot of the average of the two observed frequencies *vs.* σ^+ is given in Figure 3. In each case, the assignment of either of the doublet bands represents the strongest absorption below 400 cm^{-1}. It is seen that ν_{M-O} decreases with increasing withdrawing power of the 4 substituent, an opposite result to that obtained by Herlocker, *et al.* The splitting of the M–O band is apparently the result of the C_{2v} symmetry of the *cis* complex and may represent both the symmetric and antisymmetric stretching modes.

Discussion

As pointed out by several workers,[3,9] pyridine N-oxide most probably exists in a resonance state, in

(9) S. Kida, J. V. Quagliano, J. V. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).

TABLE II

CALCULATED AND OBSERVED FAR-INFRARED FREQUENCIES OF THE M–L STRETCHING MODE

para substituent	σ^+	ν(calcd), cm^{-1}	$\Delta\nu$ separation, cm^{-1}	ν(obsd), cm^{-1}	$\Delta\nu$ separation, cm^{-1}	$\Delta\nu$, obsd − calcd, cm^{-1}
NO_2	+0.79	283		280		3
			14		10	
		269		720		1
Cl	+0.11	292		288		4
			14		7	
		278		281		3
H	0	294		294		0
			14		14	
		280		280		0
CH_3	−0.31	299		296		3
			14		14	
		285		282		3
OCH_3	−0.76	310		306		4
			14		12	
		296		294		2

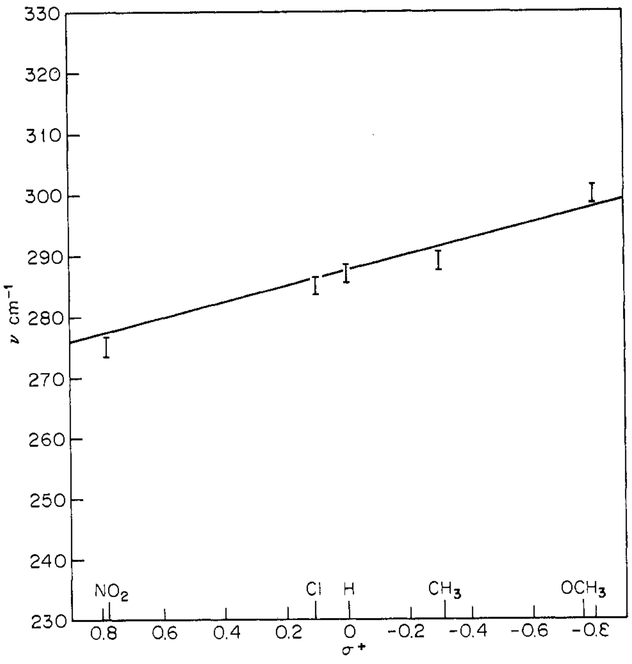

Figure 3.—Frequency (ν, cm^{-1}) *vs.* σ^+ for the Ti–O stretching vibration. Values of the frequencies are the average of two observed frequencies given in Table II.

which the electron densities are enhanced in the 2, 4, and 6 positions. Hence, an electron-donating or withdrawing substituent in these positions would have a marked influence on the nitrogen–oxygen bond. For example, an electron-withdrawing *para* substituent would effectively increase the electronegativity of the nitrogen atom and thus increase the bonding between the nitrogen and oxygen atoms. The opposite is true for electron-donating groups. This theory has been substantiated both in this study and in previous work.

The explanation of the bond character in the M–O bond in a complexed pyridine N-oxide is somewhat more ambiguous. Herlocker, *et al.*, have observed infrared absorptions in the region 375–290 cm^{-1} for each *para*-substituted species which they have assigned to the nickel–oxygen stretching mode of the complex. A correlation of these frequencies with σ^+ substituent constants for each *para* complex studied revealed a linear relation, the *p*-nitro substituent ($\sigma^+ = +0.78$) having the highest frequency, and the *p*-methoxy ($\sigma^+ = -0.76$), the lowest. Herlocker, *et al.*, explain this behavior as being due to back donation by the nickel atom. The reduction in the M–O σ bond order is compensated by the increase in M–O π bonding between the metal d orbitals and the N–O π^* orbitals. It would seem that back bonding in this case might tend to keep the electron density in the M–O bond roughly constant regardless of the substituent in the *para* position. In cases where back bonding did not or could not occur due to lack of available d electrons or a large energy difference between the π^* antibonding orbitals of the N–O and the metal d orbitals,[10] one would expect an inverse relation between σ^+ and the M–O stretching frequency. This behavior would be due to the decrease in σ-bond character of the M–O bond as σ^+ of the *para* substituent decreases. This is the case for our Ti^{4+} complexes.

Conclusions

The above data offer strong evidence for the tentative assignment of the Ti–O bond and its electronic behavior in the titanium tetrafluoride complexes as we have described it. The differences which exist between our data and that of Herlocker, *et al.*, are most likely due to the lack of available d electrons for back bonding purposes, in Ti^{4+} complexes, whereas these electrons are available in the Ni^{2+} complexes. Our interest in the near future will be directed toward a similar study of TiF_3 complexes. It is our belief that these systems ought to reveal back donation owing to the increase in availability of titanium d electrons and to the reduction of the energy difference between the N–O π^*-antibonding orbital and the titanium 4d orbitals.

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(10) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, N. Y., 1964, p 38.