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On the Sn–O Bond in Some Pyridine *N*-Oxide Complexes of Tin(IV)

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The stability constants of several pyridine *N*-oxide complexes of trimethyltin chloride and dimethyltin dichloride have been measured spectrophotometrically in acetonitrile. The values decrease with an increase in the electron-attracting power of the substituent on the pyridine ring. The infrared spectra of several pyridine *N*-oxide complexes of tin(IV) have been measured from 60 cm^{-1} to 5000 cm^{-1}. The Sn–O stretching vibration has been observed in the region of 300—400 cm^{-1}, and the frequency depends considerably on the substituents of the tin atom. The Sn–O stretching frequency in the pyridine *N*-oxide complexes of tin(IV) is rather lower than those in alkyltin alkoxides, which have a large covalent character in the Sn–O bond, but it is higher than those in trialkyltin carboxylates, which have an ionic character in the Sn–O bond. The Sn–O bond in the pyridine *N*-oxide complexes has been assumed to have a rather large ionic character, from the fact that the dependence of the stability constant on the substituent of the pyridine ring is similar to that of the pK_a of the ligand, and from the fact that the frequency of the Sn–O stretching vibration is rather close to that of the trialkyltin carboxylates.

Recently the preparation methods and the properties of many stable organotin complexes have been reported,[1–16] but quantitative data such as the stability constant of these complexes are relatively few.[17–19] We have, therefore, measured the stability constants of pyridine *N*-oxide complexes of trimethyltin chloride and dimethyltin dichloride spectrophotometrically in acetonitrile.

The infrared spectra of these complexes have also been studied in order to examine the stretching frequency of the Sn–O bond in the coordination compounds. The frequency of this band has been compared with the M–O stretching frequency in several pyridine *N*-oxide complexes of transition metals[20,21] and with several other Sn–O stretching frequencies in several organotin alkoxides[22] and acetylacetonato complexes of tin(IV).[23]

Experimental

Materials. Pyridine *N*-oxide and its derivatives were kindly supplied by the Shionogi Research Laboratory. Trimethyltin chloride was prepared by the disproportionation reaction of tetramethyltin with tin tetrachloride[24] and purified by distillation (mp 35—37°C). Dimethyltin dichloride was purified by sublimation. Methyltin tribromide was prepared by passing the dried HBr gas into methyltin oxide.[25] Triphenyltin chloride and diphenyltin dichloride were supplied by the Nitto Kasei Co., Ltd, and were purified by recrystallization.

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1) D. Blake, G. E. Coates and J. M. Tate, *J. Chem. Soc.*, **1961** 756.
2) D. L. Alleston and A. G. Davies, *ibid.*, **1962**, 2025.
3) I. R. Beattie and G. P. McQuillan, *ibid.*, **1963**, 1519.
4) R. Barbieri, C. Farglia, M. Giustiani and L. Roncucci, *J. Inorg. Nucl. Chem.*, **26**, 203 (1964).
5) L. Roncucci, G. Farglia and R. Barbieri, *J. Organometal Chem.*, **1**, 427 (1964).
6) G. Farglia, L. Roncucci and R. Barbieri, *Ric. Sci. Rend.*, **5**, 205 (1965).
7) T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, *J. Organometal Chem.*, **1**, 484 (1964).
8) Y. Kawasaki, T. Tanaka and R. Okawara, This Bulletin, **37**, 903 (1964).
9) W. H. Nelson and D. F. Martin, *J. Inorg. Nucl. Chem.*, **27**, 89 (1965).
10) A. H. Westlake and D. F. Martin, *ibid.*, **27**, 1579 (1965).
11) A. Cassol, R. Partanova and R. Barbieri, *ibid.*, **27**, 2275 (1965).
12) M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).
13) C. Mehrotra and V. D. Gupta, *J. Organometal Chem.*, **4**, 237 (1965).
14) R. Ueeda, Y. Kawasaki, T. Tanaka and R. Okawara, *ibid.*, **5**, 194 (1966).
15) H. G. Langer and A. H. Blut, *ibid.*, **5**, 291 (1966).
16) Y. Kawasaki, T. Tanaka and R. Okawara, *ibid.*, **6**, 95 (1966).
17) M. Yasuda and R. S. Tobias, *Inorg. Chem.*, **2**, 206 (1961).
18) M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Organometal Chem.*, **4**, 308 (1965).
19) G. Matsubayashi, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Inorg. Nucl. Chem.*, **28**, 2937 (1966).
20) S. Kida, J. V. Quagliano, J. A. Walmsley and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).
21) Y. Kakiuchi, S. Kida and J. V. Quagliano, *ibid.*, **19**, 201 (1963).
22) F. K. Buchev, W. Greeard, E. F. Mooney, R. G. Rees and H. A. Willis, *ibid.*, **20**, 51 (1964).
23) Y. Kawasaki, T. Tanaka and R. Okawara, *ibid.*, **22**, 1571 (1966).
23) L. G. A. Luijiten and G. J. M. van der Kerk, "Investigations in the Field of Organotin Research Institute," Grenford (1955).
25) M. P. Brown, R. Okawara and G. Rochow, *Spectrochim. Acta*, **16**, 595 (1960).

TABLE 1. MELTING POINTS AND ANALYTICAL DATA

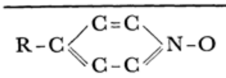
Compound	Mp °C	Sn% Found (Calcd)	C% Found (Calcd)	H% Found (Calcd)
$(CH_3)_3SnCl\cdot OPy$	86— 87*	40.05 (40.32)		
$(C_6H_5)_3SnCl\cdot OPy$	133—135*	24.23 (24.70)	57.39 (57.48)	4.27 (4.19)
$(CH_3)_2SnCl_2\cdot 2OPy$	135—136.5*	29.07 (28.96)	34.94 (35.16)	3.88 (3.93)
$(C_6H_5)_2SnCl_2\cdot 2Opy$	166—168*	22.15 (22.23)	49.70 (49.48)	3.66 (3.78)
$CH_3SnBr_3\cdot 2OPy$	138—142*	20.99 (21.06)	23.53 (23.44)	2.33 (2.32)
$SnI_4\cdot 2OPy$	138—143*	14.44 (14.54)	15.21 (14.70)	1.34 (1.24)
$SnBr_4\cdot 2OPy$	265.5—266.5*	18.86 (18.88)	19.31 (19.11)	1.56 (1.60)
$SnCl_4\cdot 2OPy$	233—240*	26.21 (26.33)	26.82 (26.65)	2.25 (2.24)

* Decompose.

Preparation of Complexes. All of the complexes were prepared by mixing pyridine *N*-oxide in benzene with benzene solution of the corresponding tin(IV) halides. Among the complexes, (bispyridine *N*-oxide)tin tetrahalides and methyl(bispyridine *N*-oxide)tin tribromide were obtained immediately after mixing the solutions; they are sparingly soluble in usual organic solvents. The compounds were washed with benzene and dried *in vacuo*. On the other hand, the pyridine *N*-oxide complexes of trimethyltin chloride and dimethyltin dichloride were obtained by letting them stand overnight after mixing the solutions. They were recrystallized from benzene and chloroform respectively. The analytical data and the melting points are shown in Table 1.

Infrared and Ultraviolet Spectra. The infrared spectra were measured in Nujol mulls using a Hitachi EPI-2G grating spectrometer for the 400—5000 cm^{-1} region. The spectra for 60—400 cm^{-1} region were measured in low melting solid paraffin using a Hitachi FIS-1 far Infrared spectrometer. The ultraviolet spectra were measured by a Hitachi EPU-2A spectrometer with 1 cm quartz cells. The absorption maxima, their ε values of some pyridine *N*-oxide and the magnitudes of the blue shifts of the absorption maxima with the complex formation are shown in Table 2.

TABLE 2. THE ABSORPTION MAXIMA, THEIR ε VALUES OF SOME PYRIDINE *N*-OXIDE AND MAGNITUDES OF BLUE SHIFTS OF ABSORPTION MAXIMA WITH COMPLEX FORMATION

 R-C<C=C, C-C>N-O	λ_{max} mμ	ε_{max} $\times 10^{-4}$	$\Delta\nu$ $\times 10^{-3}$cm^{-1}*
R = $C_6H_5CH_2O$	283	2.02	2.42
C_2H_5	278	1.69	2.05
CH_3	278	1.69	2.20
H	289	1.50	1.80
Cl	284	1.83	1.20
C_2H_5OCO	302	1.91	0.9
NO_2	327	1.68	~1.0

* $\Delta\nu = \nu_{complex} - \nu_{free}$

Determination of the Stability Constant. An equilibrium (1) was assumed as the main portion for the trimethyltin chloride- and dimethyltin dichloride-pyridine *N*-oxide systems in acetonitrile, because the concentration of tin(IV) chloride is larger by tens to thousands of times than that of pyridine *N*-oxide. The *K* value of this equilibrium (1) was determined using Eq. (2)[18]:

$$Sn(IV) + PyO \overset{K}{\rightleftharpoons} Sn(IV)\cdot PyO \qquad (1)$$

$$\frac{1-(d_0/d)}{(A_0)} = -K + K(\varepsilon_{AD}/\varepsilon_D)(d_0/d) \qquad (2)$$

where ε_D and ε_{AD} are the molar extinction coefficients of pyridine *N*-oxide and its complexes respectively. d_0 and d are the absorbances of a solution containing only pyridine *N*-oxide and of a series of solutions containing a constant amount of pyridine *N*-oxide, but varying amounts of trimethyltin chloride or dimethyltin dichloride. A_0 is the total concentration of tin(IV)

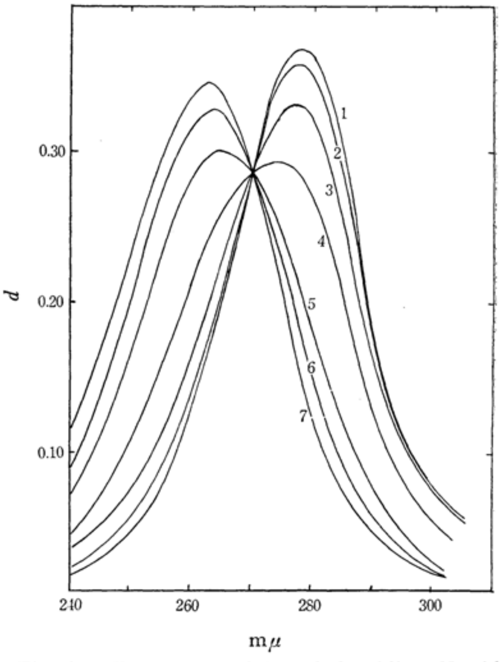


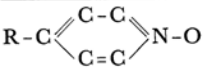
Fig. 1. The spectra of 4-methylpyridine *N*-oxide in acetonitrile (2.18×10^{-5} mol/l), containing varying amounts of trimethyltin chloride: (1) 0, (2) 2.64×10^{-4}, (3) 1.05×10^{-3}, (4) 2.64×10^{-3}, (5) 9.73×10^{-3}, (6) 3.29×10^{-2}, (6) 1.15×10^{-1} mol/l.

chloride. Equation (2) was derived on the assumption that the concentration of pyridine *N*-oxide is very small compared with that of trimethyltin chloride or of dimethyltin dichloride. Typical spectra obtained by changing the concentrations of trimethyltin chloride are shown in Fig. 1.

Results and Discussion

Stability Constant. The stability constants of some of the pyridine *N*-oxide complexes of trimethyltin chloride and dimethyltin dichloride obtained in this experiment are shown in Table 3. The pK_a values of ligands are added in this table for the sake of comparison. As is shown in Fig. 2, we have obtained a linear relationship between the stability constants of some pyridine *N*-oxide complexes of trimethyltin chloride and Hammett's constant, σ^p,[26] of the substituent on the 4 position of the pyridine ring. The stability constants decrease as the electron-attracting power of substituent on the pyridine ring becomes large. The effects of the substituent of the pyridine ring acting on the stability constants of these complexes are comparable with that on the pK_a of the pyridine *N*-oxide derivatives.[27,28] The results imply that the interaction between the tin atom and ligand oxygen in pyridine *N*-oxide complexes of tin(IV) is mainly an electrostatic and, therefore, a $d_\pi - p_\pi$ interaction is less important. This is consistent with the results obtained previously for the interaction between the tin atom and ligand nitrogen in 2, 2′-bipyridine complexes of tin(IV).[18]

TABLE 3. VALUES OF STABILITY CONSTANTS OF SOME PYRIDINE *N*-OXIDE COMPLEXES OF TRIMETHYLTIN CHLORIDE AND DIMETHLYTIN DICHLORIDE

	log *K*	°K	pK_a
R = $C_6H_5CH_2O$	2.57 ± 0.02	288	2.05*,a)
C_2H_5	2.42 ± 0.02	289	
CH_3	2.40 ± 0.02	290	1.29b)
H	1.53 ± 0.02	290	0.79b)
Cl	1.08 ± 0.02	290	0.36a)
C_2H_5OCO	0.46 ± 0.02	289	−0.41**,b)
NO_2	-0.19 ± 0.02	290	−1.7a)
$(CH_3)_2SnCl_2$ C_5H_5NO system	2.28 ± 0.03	293	

a) Ref. 28.
b) Ref. 27.
* Value of 4-methoxy pyridine *N*-oxide.
** Value of 4-methylcarboxy pyridine *N*-oxide.

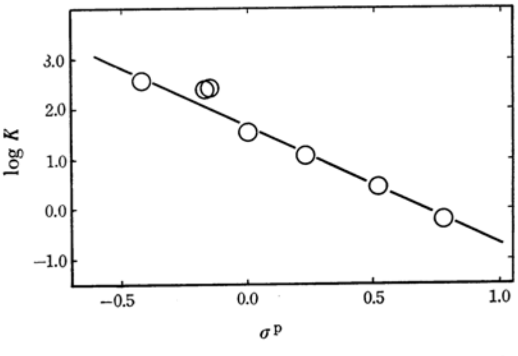


Fig. 2. Stability constants of pyridine *N*-oxide complexes of trimethyltin chloride *versus* Hammett's constant σ^p.

Infrared Spectra. The frequencies of the infrared absorption bands of several pyridine *N*-oxide complexes of tin(IV) from 60 cm^{-1} to 1250 cm^{-1} and the tentative assignment, which is based mainly on the results obtained for some pyridine *N*-oxide complexes of transition metals,[20,21] are shown in Table 4. The infrared spectra of tin(IV) complexes from 60 cm^{-1} to 400 cm^{-1} are shown in Fig. 3. As is shown in Table 4, the N-O stretching band shifts to a lower wave number when the electron-attracting power of the substituents on the tin atom becomes large. This may be due to the reduction of the double-bond character in the N-O bond with the complex formation in the resonance hybrids. The magnitude

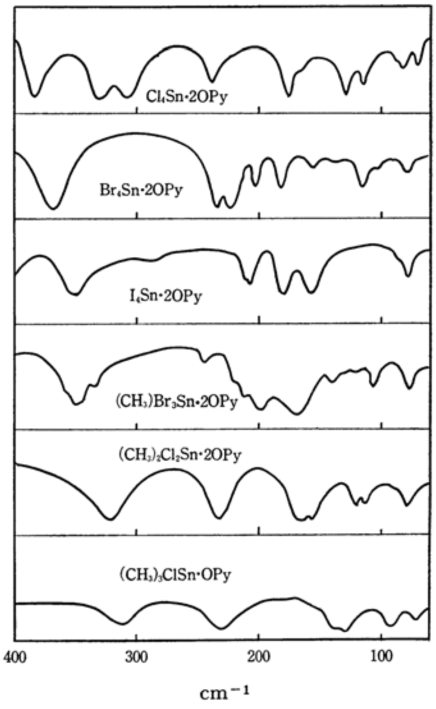


Fig. 3. Far infrared spectra of pyridine *N*-oxide complexes of tin(IV).

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[26] M. S. Newman (Editor), "Steric Effects in Organic Chemistry," John Wiley, New York (1956).

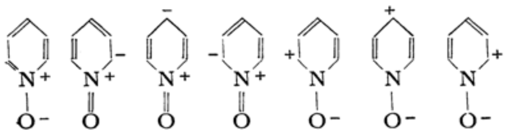
[27] H. H. Jaffé and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 4441 (1955).

[28] S. I. Shupack and M. Orchin, *ibid.*, **86**, 586 (1964).

TABLE 4. INFRARED SPECTRA OF PYRIDINE *N*-OXIDE COMPLEXES OF TIN(IV) (cm^{-1})

PyO[a]	$SnCl_4$ 2PyO	$SnBr_4$ 2PyO	SnI_4 2PyO	CH_3SnBr_3 2PyO	$(CH_3)_2SnCl_2$ 2PyO	$(CH_3)_3SnCl$ PyO	Assignment
	1256 m	1255 m	1252 m	1250 m	1248 m	1242 m	
1265 vs		1205 sh	1202 vs	1206 vs	1209 vs	1211 vs	N–O str.
	1195 vs	1193 vs	1193 sh	1195 sh	1198 sh		
1188 w						1184 s	
1166 s	1175 s	1174 s	1171 s	1175 m	1178 vs	1174 sh	CH in-plane def.
	1154 m	1152 m	1151 m	1154 w	1162 w	1149 sh	
	1095 m	1093 m	1090 w	1092 m	1096 m	1098 w	
1068 m	1079 m	1070 m	1071 w	1070 m br	1074 m	1070 s	
	1049 m	1053 w	1050 w	1045 w	1050 vw		
1014 s	1029 m	1023 m	1024 m	1024 m	1023 s	1022 s	ring breath.
	1014 w				1002 m	969 sh	
887 m	935 m	932 m	927 m	926 w	927 m	939 m	CH out-of-plane def. and ring skeletal[b]
			920 sh			927 m	
840 s	832 vs	836 s	832 s	832 s	828 vs	833 s	
		830 vs	825 vs	826 vs	812 m	823 vs	
758 vs	777 vs	773 vs	796 vs	783 vs	777 vs	779 vs	
		768 vs	762 vs	769 vs			
				678 s	673 vs	697 sh	
667 vs	672 vs	670 vs	669 vs	667 vs		679 vs	
						676 vs	
634 w	640 w	642 w	640 w		640 w	640 w	
	600 w						
					572 s	557 vs	Sn–C asym. str.
541 s	570 vs	563 vs	568 vs	567 s	550 vs	532 s	ring skeletal[c]
			560 vs	560 sh			
518 s	536 m	534 m	527 m	521 m	527 sh	526 s	
463 vs	440 vs	448 vs	450 s	456 s br	462 vs br	457 s br	NO bend.
		442 vs br	436 s				
	384 vs	374 vs	355 vs	365 sh	325 s br	311 s br	Sn–O str.
				351 s			
				334 s			
	336 vs	239 vs	211 vs	244 sh			Sn–X str.
	308 vs	223 vs	176 vs	210 sh			
	240 vs	183 vs	156 vs	197 vs	234 vs	232 s	
233 m	178 vs	203 vs	207 s	220 sh	234 vs	232 s	NO out-of-plane def.
					164 vs	144 s	C–Sn–C def.
					152 vs		C–Sn–X def.
	168 sh	153 s	120 w	141 m	140 m		X–Sn–X def.
		142 m					
	128 s	121 s		106 m	118 s		
	115 m						
	85 m	80 m	80 m	80 m	84 m	98 m	
	77 m				77 sh	72 m	

a) Ref. 20.
b) Rocking vibrational bands of the methyl groups attached to the tin atom are overlaid.
c) Sn–C symmetric stretching vibrational band is overlaid.
vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.



of the frequency shift of this band in the pyridine *N*-oxide complexes of tin(IV) is somewhat larger than that in the transition metal complexes. On the other hand, the position of the C–H out-of-plane deformation vibration (at about 930 cm^{-1}) shifts to a higher wave number with the complex formation. This may be due to the reduction of the electron density on the aromatic ring.[20,21,29,30] These results indicate that the tin atom has a rather strong electron-acceptor property.

In the 300—400 cm^{-1} region, there is a characteristic strong band which is very sensitive to the substituents on the tin atom. The frequency of this band is comparable with the M-O stretching frequency observed in the pyridine *N*-oxide complexes of transition metals.[20,21] This band has, therefore, been identified as the Sn-O stretching vibration. As is shown in Fig. 4, a linear relationship has been obtained between the frequencies of this band and the sum of the Hammett's constant, σ^*, of the substituents[26] on the tin atom.

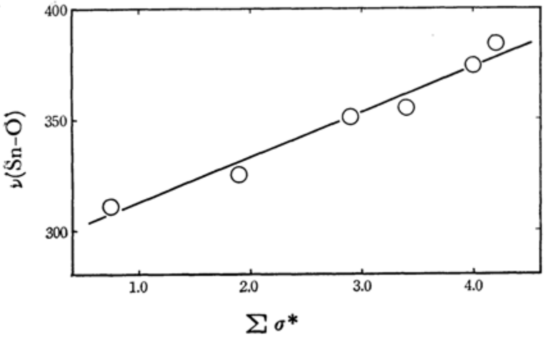


Fig. 4. Sn-O stretching frequencies of pyridine *N*-oxide complexes of tin(IV) *versus* Hammett's constant σ^*.

Some of the Sn-O stretching frequencies in several tin(IV) compounds are summarized in Table 5. The frequency of the Sn-O coordination bond in pyridine *N*-oxide complexes of tin(IV) is rather close to that of the Sn-O ionic bond in trialkyltin carboxylates,[31] but not to the Sn-O bond, which has a covalent character as in alkyltin alkoxides.[22] Considering these facts, the Sn-O bond in the pyridine *N*-oxide complexes of tin(IV) may be rather ionic. This result is consistent with that obtained from the study of the stability constants of trimethyltin chloride complexes of pyridine *N*-oxide and its 4-substituted derivatives.

TABLE 5. RANGE OF THE INFRARED ABSORPTION FREQUENCIES OF SEVERAL Sn-O BONDS IN SOME TIN(IV) COMPOUNDS

Compound	Frequency range cm^{-1}	Character of Sn-O bond	Ref.
$(R_3Sn)_2O$	780—740	cov.	a, b, c
$R_2Sn(OR')_2$	680—600 620—530	cov.	22
XYSn(Ox)$_2$*,**	540—510	cov. having ion.	7
XYSn(acac)$_2$***	460—400	ion. having cov.	23
Pyridine *N*-oxide complexes of tin	390—310	ion. having cov.	d, e
$R_3SnOOCH$	300	ion.	31

a) N. N. Vyshinskii and N. K. Rudnevskii, *Optics and Spectro.*, **10**, 421 (1961).
b) H. Kriegsman, H. Hoffman and S. Pischtochan, *Z. anorg. u. allgem. Chem.*, **315**, 283 (1962).
c) M. Ishii, I. Nakagawa, T. Shimanouchi and K. Kyogoku, Sym. Organometal Compound, Nagoya, Oct., 1963.
d) Present work.
e) C. J. Wilkins and H. M. Haendler, *J. Chem. Soc.*, **1965**; 3174; J. P. Clark and C. J. Wilkins, *ibid.*, **1966**, 871.
* X and Y represent alkyl, aryl and/or halogen.
** Ox represents 8-hydroxyquinoline.
*** acac represents acetylacetone.

Since the ligand in pyridine *N*-oxide complexes of tin(IV) shows two strong bands in the 520—570 cm^{-1} region, the assignment for the Sn-C stretching vibrations has not been made unambiguously. Even in this case, the positions of these bands seem not to move very much with the complex formation. On the other hand, the Sn-Cl stretching vibrational bands shift considerably to a lower frequency with the complex formation: in the trimethyltin chloride complex, for example, the Sn-Cl stretching vibration (232 cm^{-1}) appears at a position lower by about 110 cm^{-1} than that of trimethyltin chloride in cyclohexane (343 cm^{-1}).[32] This suggests that the polar Sn-Cl bond may be polarized largely by ligand oxygen, which coordinates to the tin atom from the trans-position of the chlorine atom.

We would like to thank Dr. Toshio Tanaka of Osaka University for his kind discussion of the assignment of the infrared vibrational bands and Mr. Masumi Yamakawa of the Shionogi Research Laboratory for supplying the pyridine *N*-oxide and its derivatives.

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[29] M. Margoshes and V. A. Fassel, *Spectrochim. Acta*, **7**, 14 (1955).
[30] R. D. Kross, V. A. Fassel and M. Margoshes, *J. Am. Chem. Soc.*, **78**, 1322 (1956).
[31] R. Okawara and M. Ohara, *J. Organometal Chem.*, **1**, 360 (1964).
[32] P. Taimsalu and J. L. Wood, *Spectrochim. Acta*, **20**, 1357 (1964).