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Spectral Properties of Some 4-Substituted Pyridine N-Oxide Complexes with Iron Perchlorate

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Visible, infrared and Mössbauer spectra of 4-substituted pyridine N-oxide complexes of the formula $[Fe(4\text{-}ZC_5H_4NO)_6](ClO_4)_2$, *where* $Z = OCH_3$, CH_3, *H, Cl and* NO_2 *are reported. Spectral data indicate that the six coordinated complexes are of high-spin octahedral structure distorted from* O_h *symmetry. From infrared spectral measurements metal–oxygen stretching vibrations are found to be correlated with the* σ_{pyNO} *values of the ligand. Crystal field parameters are evaluated from diffuse reflectance spectra and the trend of parameter was discussed in terms of spectrochemical series.*

Introduction

In recent years, there have appeared several detailed reports concerning complexes of pyridine N-oxide with transition metals[1,2]. These investigations include the infrared and visible spectral properties of complexes with pyridine N-oxide derivatives. This paper reports the spectral properties of some 4-substituted pyridine N-oxide complexes with iron complexes that have been studied only a little so far. The availibility of many kinds of 4-substituted pyridine N-oxides has prompted several attempts to correlate substituent constants for the various groups with observable properties of either the ligands or their complexes. In our study a correlation of the N–O stretching frequency and other properties with σ_{pyNO} which parameter was reported by Nelson[3] has been attempted.

The ligands $4\text{-}ZC_5H_4NO$ ($Z = OCH_3$, CH_3, H, Cl, NO_2) were selected for their wide range of electron-donating and withdrawing powers and also for expected variation in the conjugative tendencies of the 4-substituent with the donor site.

Experimental

Pyridine N-oxide, 4-chloro, 4-methyl and 4-nitropyridine N-oxide were prepared by the method of Ochiai[4]. 4-methoxy derivative was prepared according to Tanaka's method[5]. All reagents were recrystallized from ethanol or acetone. The purity was checked by elemental analysis and measurement of melting point. The method of complex preparation was merely the one of mixing together degassed ethanolic solution containing 2,2-dimethoxypropanol of the ligand and of the haxaaquoiron(II) perchlorate prepared freshly in a nitrogen atmosphere. Precipitation occured within 1 min after mixing. The complexes were filtered after five minutes, washed with ethanol, ether and dried over phosphorus pentoxide *in vacuo.* Microanalyses for carbon, hydrogen and nitrogen were performed by Elemental Analysis Center, Kyushu University. The data are given in Table I. 4-methoxy compounds were more difficult to isolate as the complexes having the logical chemical composition and more unstable to

TABLE I. Analytical Data for $[Fe(4\text{-}ZpyO)_6](ClO_4)_2$.

Compounds	C(%)		H(%)		N(%)	
	Found	Calc.	Found	Calc.	Found	Calc.
$Fe(4\text{-}OCH_3pyO)_6(ClO_4)_2$	41.80	42.99	4.21	4.18	8.15	8.36
$Fe(4\text{-}CH_3pyO)_6(ClO_4)_2$	46.86	47.52	4.52	4.62	9.13	9.24
$Fe(pyO)_6(ClO_4)_2$	43.47	43.65	3.73	3.66	10.09	10.18
$Fe(4\text{-}ClpyO)_6(ClO_4)_2$	34.86	34.99	2.33	2.33	8.12	8.16
$Fe(4\text{-}NO_2pyO)_6(ClO_4)_2$	32.85	32.88	2.33	2.19	15.11	15.34

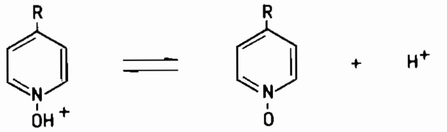
oxidation than other complexes. Good analytical data of 4-methoxy pyridine N-oxide complexes are attained when the complex is prepared in the solution containing two-fold excess ligand over that expected from chemical composition of the complexes.

Far infrared spectra in the region 200–700 cm^{-1} were recorded on a JASCO IR-F Spectrophotometer. The samples were measured as nujol mulls supported between vinyl film. Infrared spectra of the complexes in the potassium bromide region (650–4000 cm^{-1}) were obtained for the disk of the samples, using Hitachi Part NO 215–1351. Reflectance spectra in the region 5000–25000 cm^{-1} were taken with a Shimazu multipurpose recording spectrometer, with reflectance attachment. Mössbauer measurement were obtained with TMC constant acceleration spectrometer[6]. 5 mCi of ^{57}Co was doped in a palladium film. The spectrometer was calibrated by using sodium nitroprusside. Isomer shifts are quoted with respect to the centroid of the sodium nitroprusside spectrum.

Results and Discussion

Infrared Spectra

Nitrogen-oxygen frequencies are observed in the region of 1200–1300 cm^{-1}. These hexakis-complexes show all multiple bands near 1200 cm^{-1}. N–O frequency of free ligand agreed well with the results reported previously[7]. The listed values for the perchlorate complexes in Table II are given to the center of the splits (about 10 cm^{-1}). A study of the infrared spectra of these pyridine N-oxide metal complexes suggests that the frequencies of N–O atoms can be correlated with σ_{pyNO} and with the degree of π bonding in the N–O bond. The pyridine N-oxide substituent constants σ_{pyNO} are defined by Nelson *et al.* in the literature,



which constant is determined from the ionization constants of the reaction as follows.

The customary decrease in $\nu_{N\text{–}O}$ value upon coordination is observed in all complexes. The values of the nitrogen–oxygen stretching mode lie in the order R = $OCH_3 < CH_3 < H < Cl < NO_2$. The trend correlates quite well with the σ_{pyNO} values of the substituents in the 4-substituted position on the aromatic ring. Whyman *et al.* have already dealt with the infrared spectra of the 4-substituted pyridine oxide complexes of cobalt (II), nickel(II) and iron(III)[8]. Comparing with their results, the strength of the coordinative metal–oxygen bond is found to be greater for higher oxidation number metal. Because of the electropositivity of iron atom, 2*p* electron density of oxygen atom of the ligand is induced more strongly toward the iron atom. From infrared spectral measurement, it is shown that the increase of $\nu_{N\text{–}O}$ results in the increase of N–O bonding because the energy match of the nitrogen and oxygen *p* orbitals improves and thus leads to a greater contribution of 2*p* electron of oxygen atom into the system of the aromatic ring. The trend of the frequencies of N–O atom for iron(II) compounds agreed with those for cobalt and nickel complexes. The data presented in Table II vary linearly with σ_{pyNO}. The plots for the complexed N–O stretching frequencies are shown as a function of σ_{pyNO} in Figure 1.

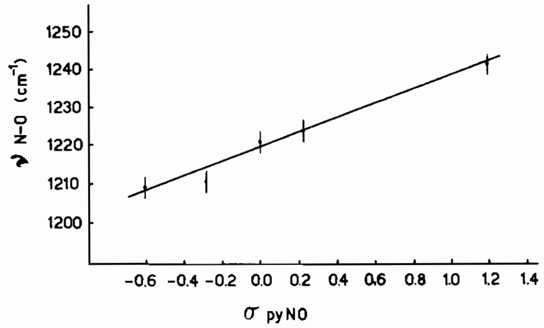


Figure 1. Nitrogen–Oxygen Stretching Frequencies, $\nu_{N\text{–}O}$, as a Function of σ_{pyNO}.

TABLE II. Hammet Functions and Infrared Frequencies of 4-Substituted Pyridine N-Oxides and Their $[Fe(4\text{-}Z\ pyO)_6](ClO_4)_2$ Complexes.

Complexes (Z)	σ_{pyNO}	$\nu_{N\text{–}O\ ligand}$ (cm^{-1})	$\nu_{N\text{–}O\ complex}$ (cm^{-1})	$\Delta\nu_{N\text{–}O}$ (cm^{-1})	$\nu_{Fe\text{–}O}$ (cm^{-1})
4-OCH_3	−0.603	1213 ± 3	1209 ± 3	4	280
4-CH_3	−0.240	1228	1210	18	375
4-H	0.000	1242	1221	21	318
4-Cl	0.206	1248	1222	26	365, 345
4-NO_2	1.190	1273	1240	33	343

Far-infrared Spectra

The value of M–O stretching vibration is determined from the consideration of the customary decrease Fe(II) < CO(II) < Ni(II)[9] in the complexes with the same ligand.

The value of metal–oxygen stretching frequencies of methoxy compounds, however, cannot be determined with certainty. The value of metal–oxygen stretching frequency for the compound having trivalent metal ion, customarily, should be higher than for those of divalent oxidation states. The frequency of iron(III) compound having the same ligand is observed at 311 cm^{-1} in Whyman's paper. We assigned a peak of medium intensity at 280 cm^{-1} to this mode of vibration although sample of $Fe(4\text{-}OCH_3pyO)_6(ClO_4)_2$ has also an absorption at 315 cm^{-1}.

If we take these assignments for the metal–oxygen stretching vibration, we cannot find that the correlation with σ_{pyNO} extends to the metal-oxygen stretching frequencies.

However, the discrepancy is not too surprising in view of the obvious complexity of the vibration in a system of this sort. It is said that the substitution of 4-position on the ring has no great effect on the M–O bonding.

Reflectance Spectra

The spectra of all of the complexes have asymmetric bands in the near-infrared region assignable as a *d–d* transition which is typical of octahedral iron(II). The numerical results are given in Table III. The results show that in the compounds studied the ^5E_g level is appreciably split and that, in most cases, the ligand fields depart markedly from O_h symmetry. The $^5T_{2g}$ ground level will also be split but this should not affect the observed band splitting. The value summarized in Table III can be considered to be equal to $10D_q$ which is determined as the value at the maximum absorption. The value of $10D_q$ of pyridine N-oxide is smaller than one of H_2O, 10400[10]. We found linear correlation of the D_q values obtained for compounds with fairly close σ_{pyNO} although the result of $[Fe(4\text{-}ClpyO)_6](ClO_4)_2$ is not in the orderly correlation.

TABLE III. Ligand Field Parameters for $Fe(4\text{-}Z\,pyO)_6(ClO_4)_2$ Complexes.

Complexes (Z)	*d–d* Band (cm^{-1})	$D_q(cm^{-1})$
$4\text{-}OCH_3$	9350, 8700sh[a]	935
$4\text{-}CH_3$	9300, 8000sh[a]	930
4-H	9010	901
4-Cl	10000, 8700sh	1000
$4\text{-}NO_2$	8300	830

[a] sh = shoulder.

The D_q of chloro-substituted complexes is abnormally large. The band is not an overtone of stretching vibration band because of its broad shape.

Mössbauer Spectra

^{57}Fe Mössbauer spectra were recorded in order to detect the effects of substitution and bonding character of pyridine N-oxide complexes. The results are given in Table IV. The complexes studied here all exhibited normal chemical shift and quadrupole splitting for hexa-coordinate, high-spin ferrous compounds. Isomer shift measured is related to the electron density at the iron nucleus. The isomer shift of the complexes all agreed within the experimental error and the influence of the substitution of 4-site of the pyridine ring has not been observed, although nitrogen–oxygen stretching frequencies increase with the increasing electron withdrawing power. This result aggrees with the fact that the influence of the substitution is not observed in the M–O vibration.

Correlation of Pyridine N-oxide with the Other Oxygen Coordinated Ligands

The D_q value and Mössbauer data for the same compounds oxygen coordinated to metal are also given in Table V. The D_q values for Fe(II) complexes produce the spectrochemical series $H_2O < DMSO \sim DPSO < TMSO < pyO$. The D_q values of the pyO are smaller than those of the sulfoxides for Fe(II) in contrast with those for Co(II) and Ni(II). A stronger polarizing effect of Fe(II) may explain why the pyO, having larger

TABLE IV. Mössbauer Data of $[Fe(4\text{-}ZpyO)_6](ClO_4)_2$ Complexes.

Complexes (Z)	Room Temp.			Liq. Nitrogen Temp.		
	ΔE_a mm/sec	σ_N mm/sec	Abs. %	ΔE_a mm/sec	σ_N mm/sec	Abs. %
$4\text{-}OCH_3$	2.23	1.44	0.8	2.92	1.52	2.2
$4\text{-}CH_3$	2.55	1.44	1.1	3.05	1.53	5.0
4-H	1.63	1.42	2.0	1.71	1.50	4.0
4-Cl	2.74	1.41	0.9	3.28	1.60	3.0
$4\text{-}NO_2$	2.49	1.46	2.0	3.01	1.56	4.5

TABLE V. D_q Values and Mössbauer Data for Oxygen-coordinated Metal Complexes.

Complexes	D_q (cm^{-1})	ΔE_Q (mms^{-1})[a]	σ_N (mms^{-1})
$Fe(pyO)_6(ClO_4)_2$	901	1.63	1.42
$Fe(TMSO)_6(ClO_4)_2$	910	1.87	1.48
$Fe(DPSO)_6(ClO_4)_2$	975	2.55	1.43
$Fe(DMSO)_6(ClO_4)_2$	975	2.61	1.45

[a] Measured at room temperature.

net dipole than sulfoxide, has smaller D_q. The effect of covalency is to delocalize the 3*d* electron distribution over the entire complex. Such effect would bring about the smaller isomer shift. However, the isomer shift of the complexes shown in Table V is the same within experimental error. The covalency effect may be too small for a decrease of the isomer shift to be observed. The value of isomer shift, 1.5 ~ 1.6 mm/sec at room temperature, corresponds to the most ionic bonding.

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