

For the same ligand the ratio, square-planar/octahedral, increases from the perchlorate to the tetrafluoroborate, in agreement with the lower coordinating ability expected for the latter. The stereochemistry of the solid complexes varies with the basicity of the ligand following a trend similar to, though not quite so regular as, that observed in solution. Thus,  $\text{Ni}(3,5\text{-L})_4\text{X}_2$  ( $\text{X} = \text{ClO}_4, \text{BF}_4$ ) is octahedral in the solid state but square-planar in solution;  $\text{Ni}(4\text{-pic})_4\text{X}_2$  ( $\text{X} = \text{ClO}_4, \text{BF}_4$ ) is square-planar in the solid state but predominantly octahedral in solution; and  $\text{Ni}(3\text{-pic})_4\text{X}_2$  ( $\text{X} = \text{ClO}_4, \text{BF}_4$ ) gives, in the solid state, both octahedral and square-planar isomers, but the octahedral form is unstable in the solid state though predominant in solution. This points out that for crystalline compounds an intrinsically slightly less stable configuration may be favored because of lattice energy effects. It may be observed that for ligands with  $\text{p}K_A$  not included in, nor close to, the borderline region,  $\sim 5.5$  to  $\sim 6.1$ , the perchlorate and tetrafluoroborate complexes have the same structure both in the solid and in solution. As the basicity of the ligand increases, the solid complexes may have a square-planar configuration, even when X is a halide. The 3,4-lutidine forms a square-planar complex for  $\text{X} = \text{I}$ , and the more basic 4-aminopyridine gives a square-planar complex also for  $\text{X} = \text{Br}$  and even for  $\text{X} = \text{Cl}$ , although the latter is very unstable.

On the basis of this observed trend, it now appears possible to predict the stereochemistry of a complex of the type  $\text{NiL}_4\text{X}_2$ , where L is a nitrogen-donor aro-

matic heterocyclic ligand and X is an anion listed in Table II. The chloride complexes should be octahedral for ligands with a  $\text{p}K_A$  lower than about 9.0, the iodide complexes should be octahedral for ligands with  $\text{p}K_A$  lower than about 6.5, and for bromide complexes the change from octahedral to square-planar should take place at an intermediate  $\text{p}K_A$  value. The perchlorate and tetrafluoroborate complexes should be octahedral for ligands with  $\text{p}K_A$  lower than 5.5 and square-planar for ligands with  $\text{p}K_A$  higher than 6.2, and within this range either or both configurations may be expected. Although these predictions refer to complexes in solution, they may also be extended to solid complexes, if it is kept in mind that near the borderline regions lattice effects may determine the actual structure. In agreement with the above predictions we find that the perchlorate complex of 3-bromopyridine ( $\text{p}K_A = 2.84$ ) reported as octahedral in the solid state<sup>19</sup> is also octahedral in solution (with strong tetragonal distortion). Investigations are now in progress to establish the ligand  $\text{p}K_A$  values at which the change of structure from octahedral to square-planar occurs for the halide complexes.

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(19) L. E. Moore, R. B. Gayhart, and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, 896 (1964).

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## The Coordination of Substituted Pyridine N-Oxides with Oxovanadium(IV) Cations<sup>1</sup>

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Complexes of oxovanadium(IV) chloride, bromide, and perchlorate with various substituted pyridine N-oxide ligands have been prepared and characterized. The variation in stoichiometry with changes in the 4-substituent for a series of these N-oxides allowed a relative coordination stability for the ligands to be established. Activator substituted molecules ( $\text{CH}_3\text{O}$ - and  $\text{CH}_3$ -) as well as the parent gave only highly coordinated species of the type  $\text{VOL}_4^{2+}$  and  $\text{VOL}_5^{2+}$  ( $\text{L} = 4\text{-Z-C}_5\text{H}_4\text{NO}$ ). Deactivator substitution ( $\text{Cl}$ -,  $\text{Br}$ -, and  $\text{NO}_2$ -) gave species of the type  $\text{VOL}_2\text{X}_2\cdot\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ). In all cases only the higher coordination was observed for  $\text{X} = \text{ClO}_4$ .

### Introduction

The donor properties of pyridine N-oxide have been studied for many transition metal ions<sup>3-6</sup> including

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(3) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, H. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961), and references therein.

(4) R. L. Carlin, *ibid.*, **83**, 3773 (1961).

selected oxometal cations.<sup>6-8</sup> Diverse stoichiometries were often observed for a particular metal ion. Ap-

(5) (a) R. L. Carlin and M. J. Baker, *J. Chem. Soc.*, 5008 (1964); (b) R. L. Carlin, R. Roitman, M. Dankleff, and J. O. Edwards, *Inorg. Chem.*, **1**, 182 (1962); (c) K. Issleib and A. Kreibich, *Z. anorg. allgem. Chem.*, **313**, 338 (1961).

(6) The term *oxometal cation* is taken to mean those species in which strong metal-to-oxygen bonding persists in the general solution chemistry of the metal ion. See, for example, J. Selbin, *J. Chem. Educ.*, **41**, 86 (1964).

(7) S. Y. Tyree, S. M. Horner, and D. L. Venzky, *Inorg. Chem.*, **1**, 844 (1962).

(8) P. R. Murthy and C. C. Patel, *Can. J. Chem.*, **42**, 865 (1964).

parently, anion coordination is an important factor contributing to the ligational properties of the metal atom toward the N-oxides (or *vice versa*). Similar interactions are further indicated by the isolation of analogous compounds with other amine N-oxides,<sup>5c,9</sup> substituted phosphine and arsine oxides,<sup>3,7</sup> and dimethyl sulfoxide.<sup>7,10</sup> From such observations, the relative ligational strength of pyridine N-oxide might be expected to parallel that of the chloride ion.

To further this hypothesis, substituted pyridine N-oxide complexes of oxovanadium(IV) were studied. Of the various anions considered, the chloride, bromide, and perchlorate compounds are reported here in detail.

### Experimental

**Materials.**—Oxovanadium(IV) chloride was prepared in a manner similar to the procedure described for the preparation of oxovanadium(IV) sulfate.<sup>11</sup> A mixture of vanadium pentoxide, hydrochloric acid, and ethanol was heated until all the metal oxide had reacted. The resulting blue solution was filtered and concentrated to a syrupy liquid. Portions of this concentrate were employed as described below. By a similar procedure, oxovanadium(IV) bromide was also obtained as a syrupy blue solution.

Oxovanadium(IV) perchlorate was prepared from oxovanadium(IV) chloride by first precipitating the hydrated vanadium(IV) oxide with sodium hydroxide, washing the residue free of chloride, and redissolving the brown solid with perchloric acid. The resulting solution was concentrated prior to use. A second preparation was carried out using oxovanadium(IV) sulfate, precipitating barium sulfate from the solution by the addition of barium perchlorate.

Pyridine and 4-methylpyridine N-oxides were obtained from Distillation Products, Inc.; 4-nitro-, 2-methyl-, 2,6-dimethyl-, and 4-methoxypyridine N-oxides were obtained from Aldrich Chemical Co. Pyridine N-oxide was purified by vacuum sublimation. 4-Methoxypyridine N-oxide was purified by recrystallization from an acetone-ether solvent. The remaining amine oxides were used with no further purification.

4-Bromo- and 4-chloropyridine N-oxides were prepared from the 4-nitro compound using acetyl bromide and acetyl chloride, respectively, as outlined by Ochiai.<sup>12</sup>

**Preparation of Oxovanadium(IV)-Pyridine N-Oxide Complexes.**—Portions of the syrupy oxovanadium(IV) chloride concentrate were dissolved in acetone and warmed. These solutions were then added to warm, concentrated acetone solutions of the various substituted pyridine N-oxides. In several experiments, 10 to 20% 2,2'-dimethoxypropane was also added to remove excess water present in the reaction mixture. The addition of oxovanadium(IV) ion was continued until the N-oxide solution became slightly blue in color. Immediate precipitation was observed for bis(4-nitropyridine N-oxide) aquodichloro-oxovanadium(IV) [(4-NO<sub>2</sub>C<sub>5</sub>H<sub>4</sub>NO)<sub>2</sub>VOCl<sub>2</sub>·H<sub>2</sub>O] (see Table I) and the corresponding chloro- and bromo-substituted compounds. Precipitation of the tetrakis 4-substituted pyridine N-oxide compounds resulted after slow concentration of the appropriate N-oxide solution {(4-CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>NO)<sub>4</sub>VOCl<sub>2</sub>·4H<sub>2</sub>O and (4-CH<sub>3</sub>OC<sub>5</sub>H<sub>4</sub>-NO)<sub>4</sub>VOCl<sub>2</sub>·4H<sub>2</sub>O} or only after addition of anhydrous ethyl ether {(C<sub>2</sub>H<sub>5</sub>NO)<sub>4</sub>VOCl<sub>2</sub>·4H<sub>2</sub>O}.<sup>13</sup> The resulting solids were collected,

washed with anhydrous ether, and dried under reduced pressure over phosphorus pentoxide.

Following a similar procedure, oxovanadium(IV) bromide and oxovanadium(IV) perchlorate complexes were prepared. Unlike the chloride complexes, precipitates were readily obtained, making addition of ether completely unnecessary to induce crystallization. The resulting solids were likewise collected and dried under reduced pressure over phosphorus pentoxide.

**Visible and Ultraviolet Spectra.**—Visible and ultraviolet spectra were recorded using a Cary Model 14 recording spectrophotometer. Solution spectra, when possible, were recorded using a 10-cm. path length. Mull spectra were recorded for all compounds using the technique recently described by Kleinberg, *et al.*<sup>14</sup>

**Infrared Spectra.**—Infrared spectra were recorded on a Beckman IR-4 spectrophotometer equipped with sodium chloride optics. Most samples were run both as potassium bromide disks and as Nujol mulls. Comparable results were obtained in each case.

**Chemical Analyses.**—Carbon, nitrogen, hydrogen, and halogen analyses were performed by Geller Laboratories, Charleston, W. Va., and by Alfred Bernhardt Microanalytical Laboratories, Mulheim, Germany.

Metal analyses were carried out by permanganate oxidation of oxovanadium(IV) in aqueous acid.<sup>15</sup> Weighed solid samples were treated with a 10% sulfuric acid solution and heated until dissolution was effected. Titrimetric end points were observed potentiometrically using a platinum *vs.* standard calomel electrode system. The absence of detectable amounts of oxovanadium(V) species was confirmed by titration of freshly prepared solutions of the various complexes with standardized ferrous solutions.<sup>15</sup>

### Results

The oxovanadium(IV) compounds containing bromo-, chloro-, and nitro-substituted pyridine N-oxides (Table I) appeared to be quite stable (although all the complex species were rapidly hydrolyzed in water) and displayed relatively limited hygroscopic tendencies. In contradistinction, the hydrogen-, methyl-, and methoxy-substituted compounds showed significant hygroscopic action. This is best illustrated for (CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>NO)<sub>4</sub>VOCl<sub>2</sub>·4H<sub>2</sub>O. When this compound was prepared in the presence of 2,2'-dimethoxypropane, a green solid was obtained which became blue upon standing in the atmosphere for several hours. That the color change was not due to reaction of the oxovanadium(IV) ion, in the classical sense (no change in metal oxidation state was found), was demonstrated by the reversible return of the initial green color after extended drying of the solid under reduced pressure over phosphorus pentoxide. Infrared spectra clearly indicated the presence of strong water bands for the blue species. These bands are greatly reduced in intensity for the green compound.

Solution spectra should be of immeasurable value in a discussion of the bonding in these complexes of oxovanadium. In general though, the compounds of Table I were found to be insoluble or to dissolve with significant spectral variations depending upon the sol-

(9) J. T. Summers and J. V. Quagliano, *Inorg. Chem.*, **3**, 1767 (1964).

(10) J. Selbin and L. H. Holmes, Jr., *J. Inorg. Nucl. Chem.*, **24**, 111 (1962).

(11) R. A. Rowe and M. M. Jones, *Inorg. Syn.*, **5**, 114 (1957).

(12) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

(13) This stoichiometry is based upon the chloride-to-nitrogen ratio. The anomalies observed for carbon and hydrogen analyses are explicable in terms of solvation effects. Both water and organic solvent molecules may be present in the crystal structure. Some support for this is offered by the decomposition temperature data of Table I. Metal analyses were not sufficient to allow unequivocal assignment to be made.

(14) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).

(15) H. R. Grady in "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Ed., Part II, Vol. 8, Interscience Publishers, New York, N. Y., 1962, p. 222 ff.

TABLE I  
 COMPLEXES OF OXOVANADIUM(IV) WITH VARIOUS SUBSTITUTED PYRIDINE N-OXIDES<sup>a</sup>

Empirical formula	Dec. pt., °C.	C, %		H, %		N, %		Cl, %		Br, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
(CH <sub>3</sub> OC <sub>5</sub> H <sub>4</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·4H <sub>2</sub> O	127-129	40.57	41.45	5.08	5.18	7.89	8.14	9.99	9.12		
(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·4H <sub>2</sub> O	~70 <sup>b</sup>	44.60	44.78	5.58	5.67	8.67	9.37	10.98	12.07		
(C <sub>5</sub> H <sub>5</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·4H <sub>2</sub> O <sup>d</sup>	<i>c</i>	40.69	46.47	4.75	5.08	9.49	7.25	12.02	9.85		
(BrC <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> VOCl <sub>2</sub> ·H <sub>2</sub> O	200-201	23.83	24.14	1.99	1.96	5.56	5.73	14.08	14.29	31.73	31.66
(ClC <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> VOCl <sub>2</sub> ·H <sub>2</sub> O	205-257	28.94	29.74	1.95	1.97	6.82	6.99	34.19	34.05		
(NO <sub>2</sub> C <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> VOCl <sub>2</sub> ·H <sub>2</sub> O	212-213	26.98	27.08	2.47	2.42	12.59	11.95	15.94	16.15		
(2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>5</sub> H <sub>3</sub> NO) <sub>2</sub> VOCl <sub>2</sub> · <sup>1</sup> / <sub>2</sub> H <sub>2</sub> O		42.77	43.55	4.84	4.87	7.13	7.02	18.48	18.11		
(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> NO) <sub>4</sub> VO(ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	166	38.95	39.24	4.33	4.24	7.57	7.43	9.73	9.49		
(C <sub>5</sub> H <sub>5</sub> NO) <sub>5</sub> VO(ClO <sub>4</sub> ) <sub>2</sub> <sup>e</sup>	181	40.41	40.28	3.37	3.43	9.43	9.26	9.68	9.39		
(ClC <sub>5</sub> H <sub>4</sub> NO) <sub>5</sub> VO(ClO <sub>4</sub> ) <sub>2</sub>	139	32.90	32.88	2.19	2.14	7.67	7.55	26.95	26.86		
(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> NO) <sub>5</sub> VOBr <sub>2</sub> ·H <sub>2</sub> O	146-148	45.59	45.48	4.67	4.79	8.86	8.79			20.23	20.05
(C <sub>5</sub> H <sub>5</sub> NO) <sub>5</sub> VOBr <sub>2</sub> ·2H <sub>2</sub> O	175-178	40.76	41.33	3.93	4.02	9.49	9.30			21.66	21.48
(2-CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> NO) <sub>4</sub> VOBr <sub>2</sub> ·H <sub>2</sub> O	191	42.30	42.14	4.41	4.53	8.23	8.16			23.48	23.57
(ClC <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> VOBr <sub>2</sub> ·H <sub>2</sub> O	190	23.41	24.82	2.15	1.79	5.46	5.34	13.81	13.89	31.19	31.24
(NO <sub>2</sub> C <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> VOBr <sub>2</sub> ·H <sub>2</sub> O	200-202	22.86	22.72	1.96	1.75	10.67	10.63			30.46	30.27

<sup>a</sup> 4-Substituted pyridine N-oxides unless otherwise noted. <sup>b</sup> Liquid forms in this temperature range. <sup>c</sup> Liquid forms upon first application of heat. <sup>d</sup> See ref. 13. Excess C<sub>7.4</sub>H<sub>8</sub>O over proposed stoichiometry. <sup>e</sup> Reported by Tyree, *et al.*<sup>7</sup>

 TABLE II  
 ABSORPTION BANDS IN THE VISIBLE AND ULTRAVIOLET REGIONS  
 FOR THE SOLUTION SPECTRA OF SELECTED *para*-SUBSTITUTED  
 PYRIDINE N-OXIDE-OXOVANADIUM COMPLEXES

Solvent	Compound	—Wave length, Å.—		
		III	II	I
CH <sub>2</sub> Cl <sub>2</sub>	(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> NO) <sub>4</sub> VO(ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	3680	5610	6220
CH <sub>2</sub> Cl <sub>2</sub>	(C <sub>5</sub> H <sub>5</sub> NO) <sub>5</sub> VO(ClO <sub>4</sub> ) <sub>2</sub> <sup>a</sup>	3650	5700	6220
CH <sub>2</sub> Cl <sub>2</sub>	(CH <sub>3</sub> OC <sub>5</sub> H <sub>4</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·4H <sub>2</sub> O	3780		6730
CH <sub>2</sub> Cl <sub>2</sub>	(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·4H <sub>2</sub> O	3610		6730
C <sub>2</sub> H <sub>5</sub> OH	(CH <sub>3</sub> OC <sub>5</sub> H <sub>4</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·4H <sub>2</sub> O	3820	6770	7750
C <sub>2</sub> H <sub>5</sub> OH	(CH <sub>3</sub> C <sub>5</sub> H <sub>4</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·4H <sub>2</sub> O	3630	6940	7800
C <sub>2</sub> H <sub>5</sub> OH	(ClC <sub>5</sub> H <sub>4</sub> NO) <sub>2</sub> VOCl <sub>2</sub> ·H <sub>2</sub> O	3810	7050	7750

<sup>a</sup> Also reported by Tyree, *et al.*,<sup>7</sup>  $\lambda = 625, 555, 360 \text{ m}\mu$ .

vent employed.<sup>16</sup> This is demonstrated, for those few compounds showing some solubility, by the data of Table II. A typical solution spectrum is shown in Figure 1.

To circumvent this difficulty somewhat, comparative mull spectra were recorded. Table III lists the band maxima<sup>17</sup> for the respective compounds of Table I.

Table IV lists the vanadium–vanadyl oxygen stretching frequencies for the various compounds. In general infrared spectra were recorded from the same mulls used to obtain the visible bands of Table III.

### Discussion

The analytical data of Table I clearly indicate two series of compounds can be isolated when substituted pyridine N-oxides are allowed to interact with oxovanadium(IV) bromide and chloride solutions. The transition from higher coordination (pentakis and tetra-kis N-oxide species) to lower coordination (bis in all

(16) An interested referee quite rightly pointed out that although these spectral shifts might come about as a result of ligand dissociation, nondissociate solvent–solute interactions may be occurring. In this connection it is interesting to note that the solution spectra are remarkably similar to those for various pentacoordinated oxovanadium(IV) ions. See, for example, J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

(17) No attempt has been made to indicate extinction coefficients for the various mull bands as their value for absorption data on granular suspensions may be questionable. Crystal lattice perturbation, sample crystallite size, etc., all become important variables over which one has only limited control under ideal conditions. In general peak height distributions were very similar to that shown in Figure 1.

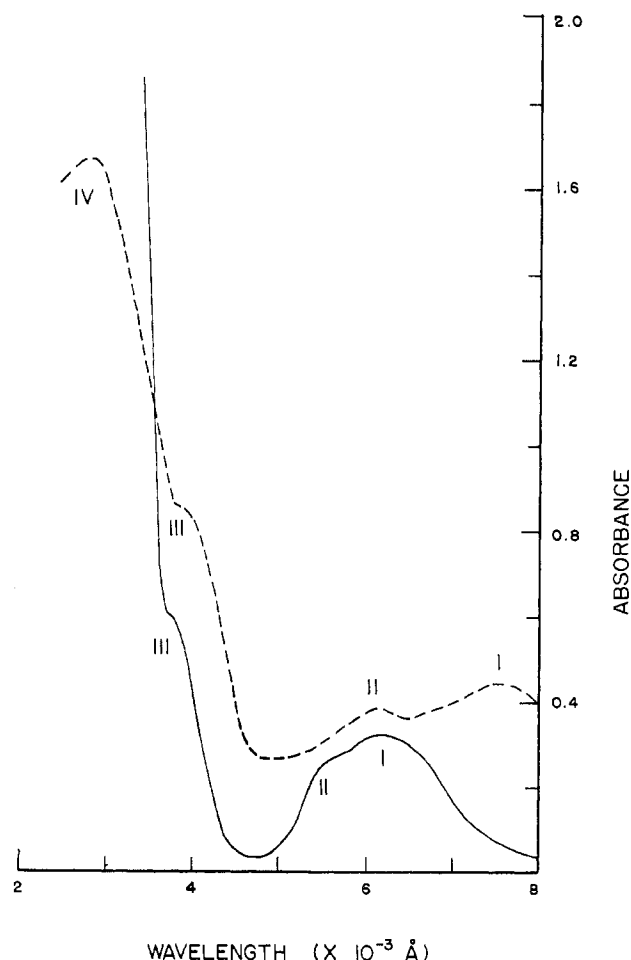


Figure 1.—Solution (CH<sub>2</sub>Cl<sub>2</sub> —) and mull (-----) spectra for pentakis(pyridine N-oxide)oxovanadium(IV) perchlorate.

cases reported) must occur at the parent compound, pyridine N-oxide. A closer inspection of the spectral data for the series of oxovanadium(IV) chloride complexes suggests that both the bis and higher coordinated species are present for the pyridine N-oxide oxovanadium(IV) chloride compound (*i.e.*,  $\lambda = 3120$  and  $4500 \text{ Å}$ . for the bis and  $\lambda = 3600 \text{ Å}$ . for the higher co-

TABLE III

ABSORPTION BANDS IN THE VISIBLE AND ULTRAVIOLET REGIONS FOR THE MULL SPECTRA OF VARIOUS SUBSTITUTED PYRIDINE N-OXIDE-OXOVANADIUM COMPLEXES

Compound	Wave length, Å.			
	IV	III	II	I
(CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NO) <sub>4</sub> VO(ClO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	2550	3600	5720	6850
(C <sub>6</sub> H <sub>4</sub> NO) <sub>5</sub> VO(ClO <sub>4</sub> ) <sub>2</sub>	2630	3650	6200	7470
(ClC <sub>6</sub> H <sub>4</sub> NO) <sub>5</sub> VO(ClO <sub>4</sub> ) <sub>2</sub>	2540	4030	6030	7350
(CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·4H <sub>2</sub> O	2680	3600		5770, 7350 <sup>a</sup>
(CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·4H <sub>2</sub> O	2670	3600		6430, 7200 <sup>a</sup>
(C <sub>6</sub> H <sub>5</sub> NO) <sub>4</sub> VOCl <sub>2</sub> ·xH <sub>2</sub> O	2600	3120, <sup>b</sup> 3600, 4500		7200
(2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NO) <sub>2</sub> VOCl <sub>2</sub> ·1/2H <sub>2</sub> O	2660	3980		6390
(BrC <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub> VOCl <sub>2</sub> ·H <sub>2</sub> O	2750	2100, <sup>b</sup> 4000		6430
(ClC <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub> VOCl <sub>2</sub> ·H <sub>2</sub> O	2630	3200, <sup>b</sup> 3800		6360
(NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub> VOCl <sub>2</sub> ·H <sub>2</sub> O	3050	3500, 4300		6630
(CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NO) <sub>5</sub> VOBr <sub>2</sub> ·H <sub>2</sub> O	2700	3700	6500	8000
(C <sub>6</sub> H <sub>4</sub> NO) <sub>5</sub> VOBr <sub>2</sub> ·2H <sub>2</sub> O	2600	3800	6400	7900
(2-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NO) <sub>4</sub> VOBr <sub>2</sub> ·H <sub>2</sub> O	2850	3500	5560, 6080	
(ClC <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub> VOBr <sub>2</sub> ·H <sub>2</sub> O	2800	3200, <sup>b</sup> 3960	6470	7740
(NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO) <sub>2</sub> VOBr <sub>2</sub> ·H <sub>2</sub> O	2420	3910, 4500	6660	7920

<sup>a</sup> Wave lengths noted for bands in this region only when maximum was unequivocally identified. The presence of this band was inferred for several other spectra, but exact location is difficult. <sup>b</sup> Appear as weak shoulders on the charge-transfer band.

TABLE IV

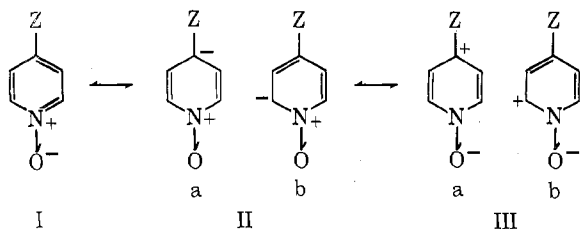
VANADIUM-VANADYL OXYGEN STRETCHING FREQUENCIES FOR OXOVANADIUM(IV) PYRIDINE N-OXIDE COMPLEXES<sup>a</sup>

Substituent	VOCl <sub>2</sub>	VO(ClO <sub>4</sub> ) <sub>2</sub>	VOBr <sub>2</sub>
4-CH <sub>3</sub> O	1017	...	...
4-CH <sub>3</sub>	989	978	956
4-H	1017	948	944
4-Br	1000	...	...
4-Cl	1005	976	1003
4-NO <sub>2</sub>	997	...	999
2-CH <sub>3</sub>	...	...	991
2,6-(CH <sub>3</sub> ) <sub>2</sub>	998	...	...

<sup>a</sup> Band energy in cm.<sup>-1</sup>.

ordinated forms). No such indications were observed for the corresponding oxovanadium(IV) bromide complexes.

Pyridine N-oxide and its substituted derivatives form a series of ligands with continuously variable donor strengths while at the same time providing an essentially unchanged molecular environment about a coordinated central metal atom. This is commensurate with the structure and unique electronic configuration of pyridine N-oxides<sup>18</sup> which is often represented in terms of the resonance forms



For electron-releasing groups in the 4-position ( $Z = \text{methyl}$ ) enhancement of structural contributions such as IIIa would be expected, while for electron-withdrawing groups ( $Z = \text{nitro}$ ) the opposite effect would be expected to enhance contributions from structures such as IIa. For the parent compound ( $Z = \text{H}$ ) all three structures are claimed to make about equal contributions.<sup>18</sup>

(18) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 381-383, and references therein.

Therefore, the isolation of two different series of compounds derived from oxovanadium(IV) chloride and bromide (Table I) is understandable. The ligational strengths of the various 4-substituted pyridine N-oxides have been found to depend directly upon the nature of the substituent.<sup>19</sup> This then suggests that in the case of oxovanadium(IV) ions, activator substituted N-oxides preferentially enter the primary coordination sphere. Only those water (or possibly solvent) molecules are retained which are necessary to stabilize the crystalline lattice of the resulting solids. On the other hand, the lower ligational powers for deactivator substituted N-oxides allow chloride and bromide ions to be retained in the primary coordination sites (or to compete successfully when aquo displacement is the controlling factor), leading to the observed bis-type complex.

The parent N-oxide appears to be very similar in coordination ability to the chloride ion, being more readily coordinated than bromide. But, as Selbin has recently pointed out,<sup>20</sup> it is generally observed that chloride is not a strong ligand toward oxovanadium(IV). It is only when there are other ligands also coordinated that chloride seems to be bound strongly at all.

Relatively long bonds result when coordination to oxovanadium(IV) cations occurs *trans* to the vanadyl oxygen.<sup>21,22</sup> Water molecules often occupy this position, possibly due to a greater packing symmetry in the solid state as opposed to an increased stability inherent to formation of a coordination bond. Based on such observations, the lack of pentakis N-oxide coordination in all the "high coordination" cases might have been predicted. No pentakis coordination was found for chloride anions, probably as a result of the smaller size of the anion. The coordination found in the presence of the larger (and also less strongly competing)

(19) M. Orchin and S. I. Shupack, *J. Am. Chem. Soc.*, **85**, 902 (1963).

(20) J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

(21) A. C. Hazell, *J. Chem. Soc.*, 5745 (1963).

(22) M. B. Palma, M. U. Palma, D. Palumbo, and F. Sgarlata, *Nuovo Cimento*, **3**, 718 (1956).

bromide and noncoordinating perchlorate anions was somewhat erratic, indicating again that lattice forces may be rather important in determining the final product isolated in the solid state.

The variation in stoichiometry among the complexes prepared in the presence of bromide and chloride ions was not totally unexpected. Although Tyree, *et al.*,<sup>7</sup> report the preparation of  $\text{VOL}_5(\text{ClO}_4)_2$  ( $\text{L} = \text{C}_5\text{H}_5\text{NO}$ ), the compound  $\text{VOL}_2\text{Cl}_2$  [ $\text{L} = \text{dimethyl sulfoxide (DMSO)}$ ] was also noted. Selbin, *et al.*,<sup>10</sup> record preparation of  $\text{VOL}_5(\text{ClO}_4)_2$ ,  $\text{VOL}_5\text{Br}_2$ ,  $\text{VOL}_3\text{Cl}_2$ , and  $\text{VOL}_3\text{SO}_4$  ( $\text{L} = \text{DMSO}$ ), for which conductometric data indicate 3, 2, 0, and 0 ions, respectively. As DMSO exhibits a ligational strength similar to that of pyridine N-oxide,<sup>23</sup> the complex stoichiometry for the various pyridine N-oxide compounds should, and apparently does, follow. Chloride ions and at times bromide and nitrate ions have also been shown to compete successfully with various amine N-oxides for coordination sites about a wide variety of central metal atoms of diverse oxidation states.<sup>10,24</sup>

(23) Unpublished results.

(24) C. M. Harris, I. Kokot, S. L. Lenzer, and T. N. Lockyer, *Chem. Ind. (London)*, 651 (1962); J. T. Summers and J. V. Quagliano, *Inorg. Chem.*, **3**, 1767 (1964); L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **86**, 5117 (1964), are recent examples.

The coordination stereochemistry is quite obvious for compounds of the type  $\text{VOL}_5\text{X}_2$  ( $\text{L} = \text{substituted pyridine N-oxide}$ ). Four ligands occupy the equatorial positions while the fifth ligand coordinates *trans* to the vanadyl oxygen. From the previous discussion one would predict for  $\text{VOL}_4\text{X}_2 \cdot \text{H}_2\text{O}$  that the *trans* axial ligand would be a water molecule (the remaining N-oxide ligands again being arranged in the equatorial plane), although the presence of X at this site cannot as yet be completely ruled out. The general absence of a pyridine N-oxide molecule in the *trans* axial position follows from a consideration of the spectral data for band I (Table III). This band is greatly displaced to longer wave lengths for such N-oxide coordination as is illustrated in the case of the perchlorate complexes. Here the shift in band position is 500 to 600 Å. in going from *trans* axial water coordination to coordination of  $\text{C}_5\text{H}_5\text{NO}$  and  $\text{C}_5\text{H}_3\text{NO}$ , respectively. The main band (I) for the tetrakis compounds is evidently that expected for *trans* axial aquo (or possible anion) coordination. Yet a longer wave length shoulder for several of the tetrakis(substituted pyridine N-oxide)-oxovanadium(IV) chloride complexes suggests that perhaps some of the metal ions may be penta N-oxide coordinated.

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## Copper(II) Complexes of Unsaturated Acids

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Copper(II) salts of acrylic, vinylacetic, and allylacetic acids, and some adducts with nitrogen or phosphorus donor ligands, of formula  $\text{Cu}(\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CO}_2)_2\text{L}_x$  ( $n = 0, 1, \text{ and } 2$ ;  $x = 1 \text{ and } 2$ ) are reported. Magnetic, spectrophotometric, molecular weight, and conductivity data indicate that the simple salts, and the adducts with one donor ligand per copper atom, are binuclear both in the solid state and in solution. The complexes with two donor ligands per copper atom are polynuclear in the solid but tend to form dimers with loss of donor ligand, in solution. On the basis of infrared spectra it is tentatively suggested that the double bond coordinates to the copper(II) atom in the simple salts. The electronic spectra support the  $\delta$  model for the metal-metal bond.

Many copper compounds have been observed to have subnormal magnetic moments<sup>1</sup> since Lifschitz and Rosenbohm<sup>2</sup> first observed in 1915 that the molar susceptibility of cupric acetate monohydrate was much less than the value of approximately 1600 c.g.s. usually observed with copper salts. Cupric acetate monohydrate exists as a binuclear molecule  $\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$ , in which the two copper atoms are bridged by the four acetate groups.<sup>3</sup> The structure of the pyridine adduct is similar.<sup>4</sup> These compounds exhibit anomalous paramagnetic behavior; their magnetic mo-

ments vary with temperature due to exchange interaction between the pairs of adjacent copper atoms. This leads to the formation of a lower diamagnetic singlet state and an excited paramagnetic triplet state.<sup>5-9</sup> Many copper carboxylate derivatives show similar behavior. The magnetic interaction depends upon the nature of the attached ligands. There has been considerable interest in investigating the effect of varying the acid and of altering the donor ligand.

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(6) R. L. Martin and A. Whitley, *ibid.*, 1394 (1958).

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(8) E. Kokot and R. L. Martin, *Inorg. Chem.*, **3**, 1306 (1964).

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