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THE COORDINATION CHEMISTRY OF AROMATIC AMINE *N*-OXIDES

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CONTENTS

A. INTRODUCTION

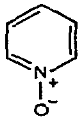
This review is concerned primarily with the coordination chemistry of aromatic amine *N*-oxides. The oxygen atom in the N-oxides is more polar than it is in other common oxo donors such as alcohols, ethers, and amides. This conclusion is supported by dipole moment[1-3] and thermodynamic studies[4]. In aromatic amine oxides the oxygen $2p\pi$ electrons are conjugated with the aromatic ring[1-3,5-8] whereas in the aliphatic amine oxides this cannot occur. The basicity of the aromatic *N*-oxides may, therefore, be systematically varied by appropriate substitution on the aromatic ring with a concomitant minimal change in steric interaction at the reaction site. These properties, plus the ready availability of an extended series of substituted pyridine 1-oxides[5], have greatly contributed to the abundance of coordination chemistry utilizing these ligands.

B. PYRIDINE 1-OXIDES

(i) *The ligand*

The organic chemistry of aromatic amine *N*-oxides has been reviewed extensively[5,9–12]. The formation of the N-oxide greatly alters the reactivity of the pyridine molecule. A reversal in the electron density distribution about the ring occurs relative to that found for pyridine itself[6,13–15]. Electrophilic substitution which takes place only with difficulty at the 3-position for pyridine occurs readily at the 4- and 2-positions of pyridine 1-oxide.

The reactivity of pyridine 1-oxides, as well as certain other characteristic physical properties, have been attributed to different electronic configurations of the molecule[5,16,17]. Nearly equal contributions from canonical structures I, II, and III have been suggested for the unsubstituted parent molecule[16,18]. Electron withdrawing ring substituents at the 2- or 4-position enhance contributions from structural type II. Electron donating groups, on the other hand, enhance contribution of structural types III.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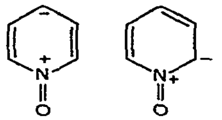
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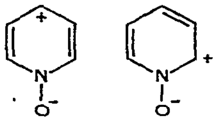
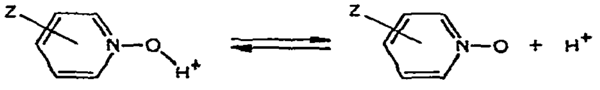

III

By considering that the oxygen $2p\pi$ electrons interact directly with the π electron system of the aromatic ring[1,2,5,18], it has been possible to calculate the spectra[19], dipole moments[7,8] and trends in ionization constants[19] of various pyridine 1-oxides. Linton[3] pointed out that the difference (2.02 D) in dipole moments of pyridine N-oxide (4.24 D) and pyridine (2.22 D) is far smaller than that (4.37 D) between trimethylamine N-oxide (5.02 D) and trimethylamine (0.65 D), and concluded that the contribution of a resonance form such as (II) is important in pyridine 1-oxide.

X-ray crystallographic data delineate a longer nitrogen-oxygen bond length for representative aliphatic amine N-oxides (1.424 Å for $(CH_3)_3$-NO · HCl)[20] compared[21,22] to 1.37 Å for PyNO · HCl. X-ray diffraction studies of substituted pyridine 1-oxides[23,24] indicate a foreshortening of the N–O bond. In 4-nitropyridine 1-oxide, for example, the distance[23] is 1.260 Å. This indicates a greater contribution of canonical form II when the *para* hydrogen is replaced by deactivating substituents.

(ii) Correlations and generalizations

When investigating the chemistry of functional groups associated with aromatic rings, it is often instructive to correlate observed properties *via* extrathermodynamic relationships[25]. Thus, the acid ionization constants for the reaction



(1)

were correlated with the Hammett sigma constants[26]. However, the best linearity was achieved using a hybrid set of substituent parameters[26–28]; σ^+ values[29] for strongly electron donating substituents, σ values[30] for weakly deactivating and weakly activating substituents, and σ^- values[10,30] for strongly electron withdrawing substituents were employed.

Many reasonable correlations between measured physical properties of a system containing substituted pyridine 1-oxides and a hybrid set of substituent parameters have been found[9,26,28,31–40]. Nevertheless, it is indeed unfortunate that one single set of substituent parameters has not been employed. As is now the practice, use of a hybrid set of substituent parameters makes comparison of the various properties of analogous systems very difficult. Anomalies of interaction are not easily recognized.

Nelson *et al.*[41] have suggested a return to the fundamental definition of substituent parameters. That is, to define an internally self-consistent set of values based upon the measured acid dissociation constants, $K_{BH_0}{}^+$, determined for pyridine 1-oxides according to reaction (1). The pyridine 1-oxide substituent constant, "σ_{PyNO}" is then defined according to the relationship

$$\sigma_{PyNO} = \frac{\Delta pK_{BH^+}}{\rho} \tag{2}$$

where $\Delta pK_{BH}{}^+$ represents the difference between the value of the conjugate acid ionization constant for the unsubstituted pyridine 1-oxide, $pK_{BH_0}{}^+$, and that for the substituted pyridine 1-oxide, $pK_{BH_z}{}^+$.

$$\Delta pK_{BH}{}^+ = pK_{BH_0}{}^+ - pK_{BHz}{}^+ \tag{3}$$

A value for ρ equal to 2.09 was chosen such that values of σ_{PyNO} most nearly conform to the existing sets of substituent constants. Values of σ_{PyNO}[41] are compared with the corresponding literature[42] values of σ^+, σ, σ^- and σR in Table 1.

All of the presently available data may be satisfactorily correlated with

σ_{PyNO}. There exists no example to our knowledge where adjusted σ_{PyNO} values are necessary. Therefore, in this review all the figures will be drawn using σ_{PyNO}.

Some of the correlations which have been made with the various sigma constants will now be discussed. Shindo[43] studied the hydrogen bonding ability of a series of substituted pyridine 1-oxides with methanol in chloroform. The O–H stretching frequency, v_{OH}, of methanol could be correlated with appropriate σ constants. Herlocker and coworkers[33] found that the shift in values of v_{OH} for phenol upon hydrogen bonding to 4-substituted pyridine 1-oxides in carbon tetrachloride solution were correlated rather well with the aforementioned hybrid set of substituent parameters.

TABLE 1

"SIGMA VALUES" FOR SUBSTITUTED PYRIDINE 1-OXIDES

Substituent	*Ligand* $\mathrm{p}K_{\mathrm{BH}^+}$	$\sigma^{-\,a}$	σ^{a}	$\sigma^{+\,b}$	$\sigma_{\mathrm{R}}{}^{c}$	$\sigma_{\mathrm{PYNO}}{}^{d}$
4 $(\mathrm{CH_3})_2\mathrm{N}$–	3.88[e]	—	−0.60	−1.49[f]	—	−1.48
4 $\mathrm{CH_3O}$–	2.05[e]	—	−0.268	−0.764[y]	−0.51	−0.603
4 HO–	2.36[g]	—	−0.357	−0.82[f]	−0.60	−0.751
4 $\mathrm{H_2N}$–	3.65[h]	—	−0.660	−1.33[f]	−0.76	−1.37
4 $\mathrm{C_6H_5O}$–	2.67[e]	—	−0.028	−0.63[f]	−0.41	−0.574
3 $\mathrm{H_2N}$–	1.47[g]	—	−0.161	—	—	−0.325
3 Cl–	1.34[i]	—	0.373	0.391	—	−0.263
4 $\mathrm{H_3C}$–	1.29[g]	—	−0.170	−0.306	−0.11	−0.240
3 $\mathrm{H_3C}$–	1.08[g]	—	−0.069	−0.065	—	−0.139
H–	0.79[g]	0	0	0	0	0
4 Cl–	0.36[j]	—	0.227	0.11	−0.24	0.206
3 HOOC–	0.09[k]	—	0.355	—	—	0.335
4 $\mathrm{H_3CO_2C}$–	−0.41[j]	0.64	0.32	—	−0.09	0.574
4 HOOC–	−0.48[k]	0.728	0.728	—	—	0.608
4 $\mathrm{O_2N}$–	−1.7[g]	1.27	0.778	—	0.65 (0.16)	1.19
4 CN–	−1.17[l]	—	0.63	—	—	0.94

[a] Refs. 6 and 30. [b] Ref. 29. [c] Ref. 42. [d] Ref. 41. [e] J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, (1957) 4375. [f] N. C. Deno and W. L. Evans, *J. Am. Chem. Soc.*, *79* (1957) 5804. [g] Ref. 26. [h] H. Hirama and T. Kubota, *J. Pharm. Soc., Japan*, *73* (1953) 140. [i] I. I. Grandberg, G. K. Faizova and A. N. Kost, *Khim. Geterotsikl Soedin*, (1966) 561. [j] Ref. 28. [k] Ref. 16. [l] R. G. Garvey and R. Scheele, unpublished results.

Infrared absorption curves of pyridine 1-oxides display a prominent[43–44] band between 1200–1300 cm^{-1}. The band often exceeds in intensity all other absorptions of the spectrum. Shindo[43] found that the band positions were affected in a systematic manner by changing substituents on the pyridine ring. The more activating the substituent, the lower the energy of this absorption. The nitrogen-oxygen stretching frequency, $v_{\mathrm{N-O}}$, is however, only moderately well correlated by σ^{+} values[9,28,33,39,46]. A detailed discussion of the infrared spectra and substituent constants has been given by Jaffe and Jones[9]. Upon coordination, v_{NO} for pyridine 1-oxides is decreased from values for the free ligands by 12 to 60 cm^{-1} [28,33–35,46–49].

This observation clearly suggests metal oxygen bond formation[28,49]. Formation of such a bond increases demand by the oxygen atom for electron density. The result is, therefore, tantamount to a reduced contribution of canonical structures II and concomitant increased contribution of I and III to the electronic configuration of the ligand. Correlations of v_{NO} values with substituent parameters for 4-substituted pyridine 1-oxides coordinated with nickel(II)[33,46], titanium(IV)[39] chromium(III)[46], iron(III)[46], cobalt(II)[46], copper(II)[46] and dioxouranium(VI)[47] have appeared. Values of metal-ligand oxygen stretching frequencies, v_{MO}, for nickel(II)[33] and titanium(IV)[39] compounds could also be correlated with σ_{PyNO} values. In Figure 1 are illustrated correlations of $v_{\mathrm{N-O}}$ free, $v_{\mathrm{N-O}}$ complexes and $v_{\mathrm{Ti-O}}$ with σ_{PyNO}[39,41].

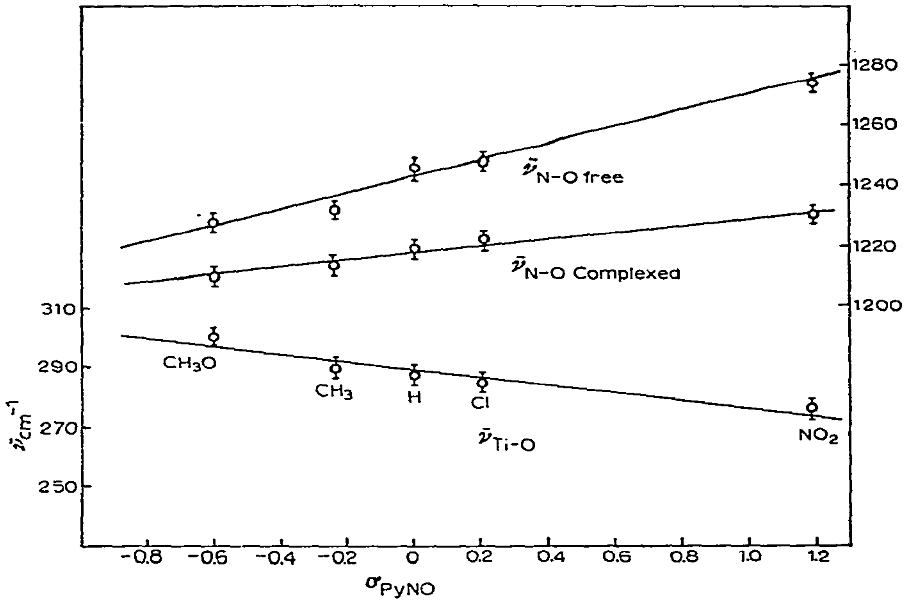


Fig. 1. Correlation of ν(Ti–O), ν(N–O), complexed and ν(N–O) free with σ_{PyNO} for titanium tetrafluoride complexes of 4-substituted pyridine 1-oxides.

Recently, it was pointed out that changes in $v_{\mathrm{N-O}}$ with changing substituents for coordinated 4-substituted pyridine 1-oxides often displayed a range of values similar to that for the free ligand[50]. However, for complexes of metal ions from earlier groups of the transition series, the range is much more restricted than is the case for the uncoordinated ligands or their complexes with metal ions from later groups. In Table 2 the $v_{\mathrm{N-O}}$ values for representative 4-substituted pyridine 1-oxide coordination complexes as well as for the corresponding noncoordinated ligands are listed.

It has been suggested that upon coordination the pyridine 1-oxide oxygen

TABLE 2

COMPARATIVE VALUES OF ν(N–O) cm^{-1} FOR COORDINATED PYRIDINE 1-OXIDES

Ligand, L	*Free Ligand*[33]	TiF_4L_2[39]	VOL_4X_2[33, 51]			VOL_2X_2[32, 51]										
			Cl	*Br*	*ClO₄*	*NCS*	*Cl*	*CrZ*[f]	*MnY*[g]	*FeY*	*FeZ*	*CoY*	*NiY*[33]	*CuY*[46]	*ZnY*	$C_2H_4LPtCl_2$[33]
$4CH_3OC_5H_4NO$	1228	1210	1205 1195			1212		1198[c]	1207[b]		1207[c]	1201[c]	1201		1209[c]	1190
$4CH_3C_5H_4NO$	1213	1213	1198 1196	1202	1205			1200[c]	1211[d]		1205[de]	1209[d]	1212	1200	1212[c]	1224
C_5H_5NO	1228	1212 1226	1202			1200	1195	1199[c]	1220[d]	1220[d]	1215[d]	1221[d]	1220	1232 1215	1225[d]	1235
$4ClC_5H_4NO$	1242	1222				1202	1202	1199[c]	1235[b]		1209[c]	1209[c]	1212 1220		1230[c]	1238
$4NO_2C_5H_4NO$	1274	1230					1205	1206[a]	1228[d]	1229[d]	1212[d]	1213[c] 1229[d]	1230		1262[c]	1250

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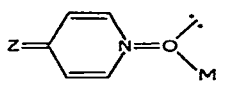
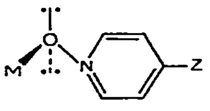
[a] R. G. Garvey and M. Urdaneta, unpublished results. [b] R. G. Garvey and M. A. Schaeffer, unpublished results. [c] R. G. Garvey and G. A. McCarty, unpublished results. [d] W. Byers, A. B. P. Lever and R.V. Parish, in press. [e] Ref. 46. [f] $Z = L_6(ClO_4)_3$. [g] $Y = L_6(ClO_4)_2$.

can function as either a donor or an acceptor of π-electron density[33,39,50]. Should the metal ion possess empy d orbitals of correct symmetry, donation of electron density from the highest filled π-molecular orbital of the ligand could occur. Changing substituents on the pyridine ring under these conditions increases only minimally the competition of the pyridine nitrogen atom for π-orbitals of the oxygen atom, thereby little affecting the nitrogen-oxygen bond order. On the other hand, metal ions with nearly filled d orbitals do not readily act as π-electron acceptors, and thus a metal to empty ligand π^* orbital back bonding interaction becomes preferred[33]. Nuclear magnetic resonance data[52] support a π-mechanism for spin delocalization from nickel to pyridine 1-oxide donors in bis(pyridine 1-oxide)bis(2,4-pentanedionato)nickel (II). However, the data did not answer the question of whether the spin was delocalized in the highest-filled molecular orbital of the ligand or in the lowest empty antibonding orbital. Comparison of the values of ν(N–O) for the titanium complexes in Table 2 with those of vanadium and chromium indicates that the above explanations do not strictly apply to the titanium tetrafluoride complexes. A possible explanation for this anomaly is that the titanium π bonding d orbitals are not readily available for bonding with the oxygen π orbitals, because the pyridine 1-oxides cannot compete effectively with fluorine for these orbitals.

Ligation of substituted pyridine 1-oxide molecules to transition metal ions evokes considerable stereochemical interest. If the metal–ligand bond has covalent character in addition to significant ionic character, the concepts of directed valence would predict a non-centrosymmetrical environment for the oxygen. Tetrahedral disposition (modified somewhat by multiple bonding to the pyridine nitrogen and electron pair repulsions) of oxygen lone electron pairs might be anticipated[53]. Trigonal planar sp^2 bonding would represent the other extreme for high nitrogen-oxygen double bond character. Thus, the M–O–N bond angle should lie somewhere between 108 and 120° as illustrated.



sp^2 M–O–N ∢ ~120°



sp^3 M–O–N ∢ ~108°

Nuclear magnetic resonance pseudocontact shifts observed for bis(substituted pyridine 1-oxide)bis(2,4-pentanedionato)cobalt(II) species in solution suggest a cobalt–oxygen–nitrogen bond[52] angle (Co–O–N) of 114 to 125°. Another indication for non-centrosymmetric metal-ligand bonding is found in X-ray structural data for pyridine 1-oxide hydrochloride[21,22] where a nitrogen-oxygen-chlorine bond angle of 110° is measured. This angle is calculated using the assumption that the O–H–Cl group is linear.

Effects due to changing substituents on coordinated aromatic donor molecules are often detectable in concomitant changes in properties of a second ligand coordinated to the central metal ion. The second, often structurally unrelated, ligand acts as an "indicator group." For example, the vanadium-vanadyl-oxygen bond of oxovanadium(IV) can serve as an indicator group. In tetragonal pyramidal bis(2,4-pentanedionato)oxovanadium(IV)[54,55] and related compounds coordination *trans* to the vanadyl oxygen, causes a shift to lower energies of the vanadium–vanadyl–oxygen stretching frequency, ν(V–O)[56–59]. The magnitude of the shift in $\nu_{\text{V–O}}$, with changing substituent upon adduct formation with 4-substituted pyridine 1-oxides was found to give a linear correlation[60] with σ_{PyNO}, as shown in Figure 2.

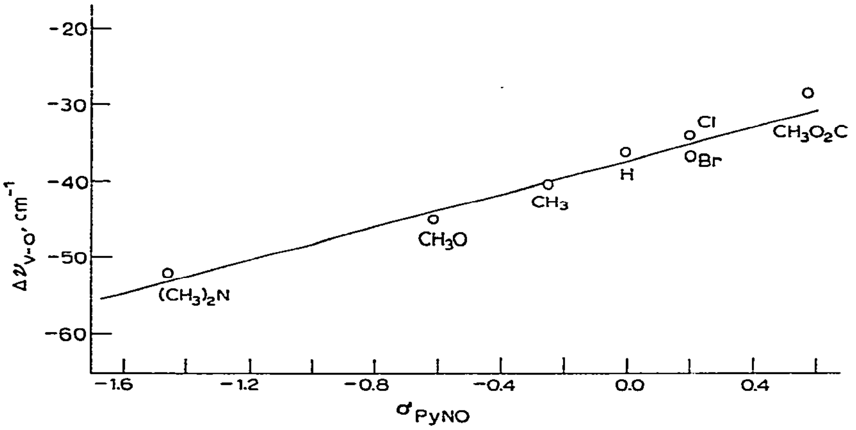


Fig. 2. Variation of $\Delta\nu$(V–O) with σ_{PyNO} values of 4-substituted pyridine 1-oxide adducts with bis(2,4-pentanedionato)oxovanadium(IV) in dichloromethane.

Another example of an indicator is obtained from the ^{19}F nmr chemical shift data for the three chemically different fluorines in tetrafluoro-*cis*-4-substituted pyridine 1-oxide-*N*,*N*-dimethylacetamidetitanium(IV)[31]. The chemical shifts for all three types of fluorine were found to correlate linearly with σ_{PyNO}[41] as illustrated in Figure 3. The fluorine *trans*, F_β', to the pyridine 1-oxide molecules displays the greatest range in chemical shift values. It is suggested[31] that the large perturbation produced by the changing substituents in the shielding of the fluorine at the site *trans* to the N-oxide is transmitted through the titanium-(IV) *d* orbitals by a π-mechanism. The progressive downfield shift in the spectra as the *para*-substituent becomes more electron withdrawing is brought about by an increase in the relative amount of fluorine π-donation to the titanium d orbitals. The more oxygen–nitrogen π-bonding that exists (contribution of canonical structure II), the less successfully can the oxygen compete with fluorine for the available metal d orbitals.

The electronic spectrum is another physical property which has been investigated[32,33,46]. A linear correlation of optical absorption band maxima (charge transfer and d-d electron transition) for substituted pyridine 1-oxide complexes of oxovanadium(IV) with appropriate sigma substituent constants has been found[32].

Quagliano *et al.*[48] reported abnormally low temperature dependent magnetic moments for copper(II) chloride complexes of pyridine 1-oxide. Subsequently, several investigators[37,61–64] have used substituted pyridine 1-oxides to probe characteristics of related complexes with copper(II) halides. Trends in magnetic susceptibility data for complexes of 4-substituted pyridine 1-oxides suggest that the spin–spin coupling occurs in these compounds *via* a super exchange mechanism operating through the orbitals of bridging oxygen atoms[37,65]. Refined X-ray structural data[65] favor a π-mechanism for the interaction.

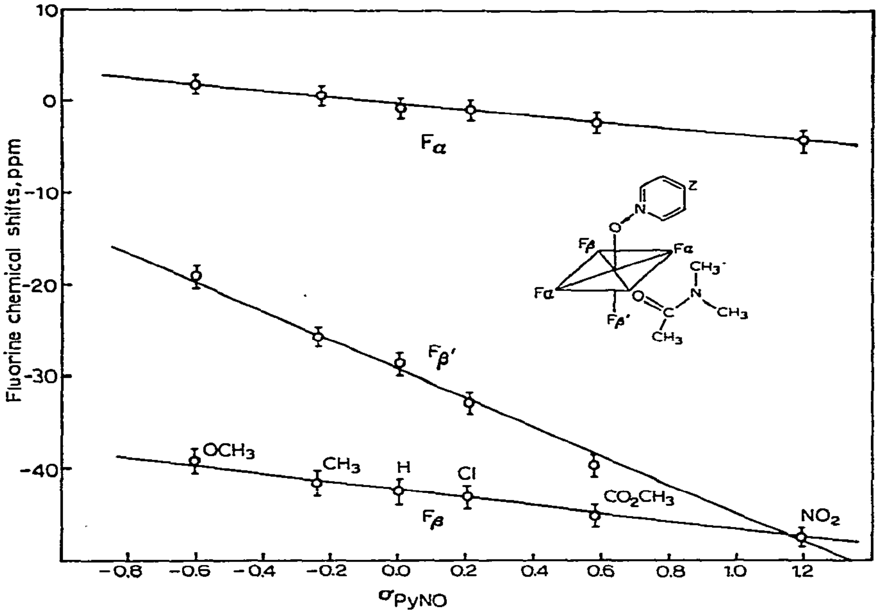


Fig. 3. Correlation plot of the chemical shifts for F_α, F_β, and F_β', versus σ_{PyNO} for $TiF_4(CH_3)_2NC(O)CH_3,4\text{-}ZC_5H_4NO$ complexes.

(iii) Coordination complexes

One of the more notable aspects of the coordination chemistry of aromatic amine oxides is their ability to form complexes with transition elements from each of the major groups of the periodic table. Complexes of other elements have also been formed. The elements with which complexes have been formed are indicated in Figure 4. Perchlorate salts of the appropriate metal ions in ethanol or acetone solvents react with pyridine 1-oxides generally yielding compounds having maximum coordination number of the metal ion[32,33,46,48,51,64,66–68]. Often anions more basic than perchlorate are found along with the N-oxide ligands in the primary coordination sphere of the metal ion[32,37,47,48,51,61,64,69–73]. The diversity of compounds and compound types now reported in the literature makes it necessary for us to treat certain metal ions separately.

1. *Titanium group*

The first reported coordination compound of titanium with pyridine 1-oxide was apparently pentakis(pyridine 1-oxide)oxotitanium(IV), isolated as a slightly hygroscopic white solid[74]. Hexakis(pyridine 1-oxide) oxozirconium(IV) perchlorate has also been reported[75]. Coordination of pyridine 1-oxide to oxotitanium(IV), oxozirconium(IV), and thorium(IV) perchlorates[75] helps to stabilize the perchlorate salts. Stabilization is greater as one proceeds down the titanium group. Infrared data indicate noncoordinating perchlorate anions.

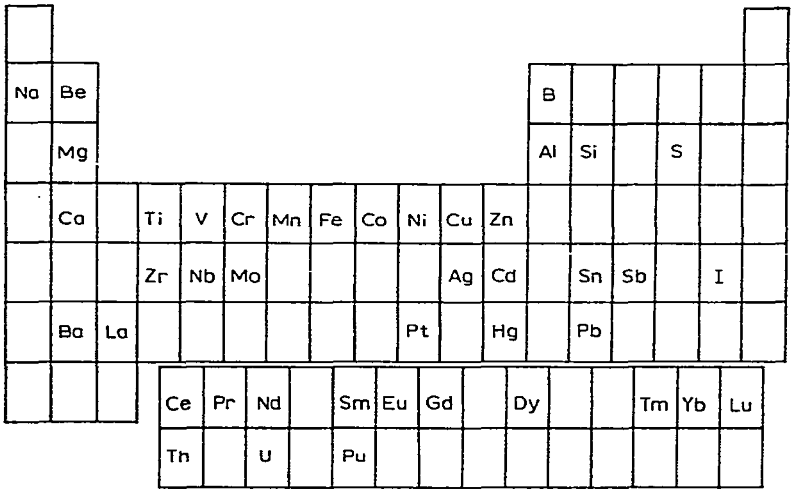


Fig. 4. Elements for which pyridine 1-oxide complexes have been reported.

Monofunctional donors coordinating through oxygen form octahedral complexes with titanium tetrafluoride[31,76,77]. Generally these complexes are of the type $TiF_4 \cdot 2D$ in which the "donor", D, molecules occupy *cis* positions[76,77]. Reaction of 4-substituted pyridine 1-oxides with titanium tetrafluoride in ethanol readily give compounds of the type $TiF_4(4\text{-}ZC_5H_4NO)_2$. Infrared spectral correlations[39] for these complexes have previously been mentioned and are illustrated in Figure 1. Reported examples of these complexes are listed in Table 3.

Mixed "donor" complexes of titanium tetrafluoride of the type $TiF_4(4\text{-}ZC_5H_4NO)$ (D) have also been reported for D = *N,N*-dimethylacetamide or tetramethylurea[31,78]. Fluorine-19 nuclear magnetic resonance investigations of these compounds and $TiF_4 \cdot 2D$ indicate that exchange processes occur readily in solution[31]. As a result most spectra are recorded from −30 to −60 °C so as to decrease the rate of exchange. Usually a *cis* configuration for the mixed donor ligands is obtained. Correlation of ^{19}F chemical shifts with σ_{PyNO} is shown in Figure 3. Examples of $TiF_4(4\text{-}ZC_5H_4NO)$ (D) compounds are indicated in Table 3.

Although the *cis* configuration for $TiF_4 \cdot 2D$ complexes in various solvents has been established[31,76–78], the occurrence of *cis-trans* isomerism is not precluded. In fact, low temperature ^{19}F nmr spectra of bis(2,6-dimethylpyridine 1-oxide)tetrafluorotitanium(IV) show a *trans* configuration for the N-oxide ligands[78,79]. At −40° in chloroacetonitrile only a single resonance line is observed, indicating equivalence of the four fluorine nuclei. Under similar conditions, resonance lines were observed for both *cis* and *trans* isomers of bis(2-methylpyridine 1-oxide)tetrafluorotitanium(IV). Only the *cis* isomer of the bis(pyridine 1-oxide) complex was found. Apparently the *trans* configuration is favored only when sufficient steric interaction exists to overcome symmetry effects and the tendency to maximize pπ-dπ bonding[79]. The bis(3,5-dimethylpyridine 1-oxide) tetrafluorotitanium(IV) complex has the *cis* configuration in solution[78], whereas detectable amounts of both *cis* and *trans* (*N,N*-dimethylacetamide-2,6-dimethylpyridine 1-oxide)tetrafluorotitanium(IV) are observed for solutions of the bis(*N,N*-dimethylacetamide)complex to which 2,6-dimethylpyridine 1-oxide is added[78].

TABLE 3

FLUOROTITANATE COMPLEXES OF SUBSTITUTED PYRIDINE 1-OXIDES[a]

Stoichiometry

Ligand (D)	$TiF_4 \cdot 2D$		$TiF_4 \cdot DMA \cdot D^b$		$TiF_4 \cdot TMU \cdot D^c$	$TIF_5 \cdot D^-$
C_5H_5NO	39	79	31	80	80	78
$4ClC_5H_4NO$	39		31	80	—	78
$4NO_2C_5H_4NO$	39		31		80	78
$4CH_3C_5H_4NO$	39	78	31	80	—	78
$2CH_3C_5H_4NO$	78	79	—	—	—	—
$2CH_3CH_2C_5H_4NO$	78		—	—	—	—
$2,6(CH_3)_2C_5H_3NO$	78	79	—	—	—	—
$2,4(CH_3)_2C_5H_3NO$	78		—	—	—	—
$3,5(CH_3)_2C_5H_3NO$	78		—	—	—	—
$4CH_3OC(O)C_5H_4NO$	—		31	80	—	78
$4CH_3OC_5H_4NO$	39		31	80	80	78
$4BrC_5H_4NO$	—		31		—	—

[a] Reference 39 is an infrared study. References 31, 78, 79, 80 are ^{19}F nmr studies. [b] DMA = *N,N*-Dimethylacetamide. [c] TMU = tetramethylurea.

In situ preparation of 4-substituted pyridine 1-oxide pentafluoro titanium(IV) and subsequent ^{19}F nmr studies have been affected[78]. As with the $TiF_4 \cdot (CH_3C(O)N(CH_3)_2(4\text{-}ZC_5H_4NO)$ complexes, correlations of the chemical shifts with σ_{PyNO} were obtained. The greatest change in chemical shift was found for the fluorine *trans* to the pyridine 1-oxide. This change was approximately five times that of the *cis* fluorines.

2. *Vanadium*

Reaction of dodeca-μ_2-chlorohexaniobium cation with oxygen donor ligands, including pyridine 1-oxide has been described[81]. By far the more abundant and diverse coordination chemistry of N-oxide donors with metal ions of this group is that of vanadium(IV)[32,51].

Two distinct groups of compounds are isolated from the direct reaction of substituted pyridine 1-oxides with oxovanadium(IV) ions. The first may be characterized as a "high N-oxide coordination series". This group is represented by pentakis- and tetrakis(substituted pyridine 1-oxide)oxovanadium(IV) molecular ions. The second grouping of compounds may, on the other hand, be described as a "low N-oxide coordination series". It is represented by bis(substituted pyridine 1-oxide)dianionooxovanadium(IV) complexes. These compounds are shown in Table 4.

TABLE 4

COMPLEXES OF OXOVANADIUM(IV) WITH PYRIDINE 1-OXIDES 32, 50, 51, 67

Stoichiometry

Ligand (L)	VOL_5X_2	$VOL_4X_2 \cdot H_2O$	$VOL_2X_2 \cdot H_2O$	VOL_2X_2
$4CH_3OC_5H_4NO$		Cl		NCS, Cl
$4CH_3C_5H_4NO$	Cl, Br	Br, ClO_4, BF_4, Cl	NCS	Cl, NCS
$2CH_3C_5H_4NO$	ClO_4	ClO_4. BF_4, Br		
$2,6\text{-}(CH_3)_2C_5H_3NO$		Br	Cl	NCS, Cl
C_5H_5NO	ClO_4, Br	Cl	Cl, NCS	Cl, NCS
$4ClC_5H_4NO$	ClO_4	ClO_4	NCS, Cl, Br	Cl, Br
$4BrC_5H_4NO$			Br, Cl	Cl, Br
$4NO_2C_5H_4NO$			Cl, Br	Cl

Each series of complexes could be further subdivided. The "high coordination" compounds express stoichiometries which may be designated as VOL_5X_2, $VOL_4X_2 \cdot H_2O$, and possibly as VOL_4X_2. The "low coordination" compounds are composed of complexes of the types $VOL_2X_2 \cdot H_2O$ and VOL_2X_2.

The complexes were usually prepared by direct reaction of oxovanadium(IV) salts in acetone solution (often extensively dehydrated with 2,2-dimethoxypropane) with substituted pyridine 1-oxides[32,51]. Anion coordination as well as incorporation of water molecules proved to be important factors influencing ligation of N-oxides in the primary coordination sphere about the metal ion. The disposition for or against aquo ligation in these compounds appears to be very sensitive to environmental conditions existing in the solution. This is exemplified by the isolation of both tetrakis(4-chloropyridine 1-oxide) aquooxovanadium(IV) perchlorate and pentakis(4-chloropyridine 1-oxide)oxovanadium(IV) perchlorate depending upon the degree of prior dehydration of the oxovanadium(IV) perchlorate solution.

Horner, Tyree and Venzeky[67] were apparently the first authors to report a pyridine 1-oxide complex of oxovanadium(IV). They were attempting to prepare hexakis(pyridine 1-oxide)vanadium(III) perchlorate. Air oxidation of the metal ion (probably aided by the presence of the N-oxide ligand) was said to have occurred in all cases leading to isolation of only the oxovanadium(IV) complex.

In addition to infrared bands attributable to vibrational modes of the respective coordinated ligands, spectra of oxovanadium(IV) complexes display a prominent absorption band near 1000 cm^{-1}. This band is associated with the vanadium-vanadyl oxygen stretching mode[82,83]. Upon coordination of a donor ligand *trans* to the vanadyl oxygen atom, a significant shift occurs in values of the vanadium-vanadyl oxygen stretching frequency, ν(V–O) (Figure 5). Such band displacements are much greater than can conveniently be accounted for by simple mass effects[56,82]. Adducts of pyridine 1-oxide and its derivatives with bis(2,4-pentanedionato)oxovanadium(IV) and certain other bis(*beta*-diketonato)oxovanadium(IV) complexes are of this type[60]. It has previously been shown[59,84] that bis(2,4-pentanedionato)-oxovanadium(IV) could be employed as a reference acid for various pyridine bases. By forming adducts with pyridine 1-oxides this reference acid is used to establish a quantitative ordering of the N-oxides in terms of the parameter $\Delta\nu$(V–O). These results are depicted in Figure 2.

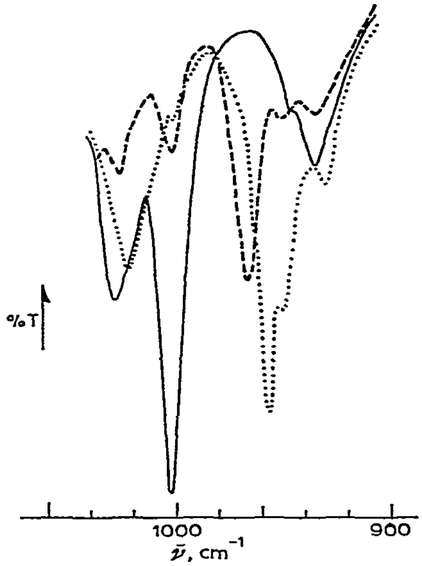


Fig. 5. Infrared curves in the region of ν(V–O) for bis(2,4-pentanedionato)oxovanadium(IV) in dichloromethane (———) illustrating the effect of adding approximately equimolar amounts of 4-methyl (..........) and 4-chloropyridine 1-oxide (– – – – –).

Although detailed optical absorption spectra have been recorded for pyridine 1-oxide complexes of oxovanadium(IV)[32,51,67], attempts to rationalize the optical spectra of these compounds have been less than satisfactory. Nevertheless, systematic substituent effects on particular optical band energies with changing ligand substitution are evinced by several series of complexes[32]. Theoretical interpretation of these results currently awaits magnetic susceptibility measurements and electron spin resonance studies now in progress[85,86]. Ambiguity in proper assignment of optical absorption maxima for oxovanadium(IV) complexes in general also complicates interpretation of electron configurations in the N-oxide complexes[82,83].

3. *Chromium*

Of the chromium group elements, complexes have only been reported with chromium(III). Methanolic solutions of hexaaquochromium(III) perchlorate react with methanolic solutions of pyridine 1-oxide[87] and several of its derivatives[87] to give blue white or faintly purple crystalline materials. However, if hexaaquochromium(III) chloride is reacted with pyridine 1-oxides in the presence of excess lithium perchlorate, or if hexaaquochromium(III) perchlorate is first dehydrated by treating it with 2,2-dimethoxypropropane, green powders or oils result[46,66,87]. Elemental analyses suggest both the blue-white and the green compounds are of the type involving hexakis(pyridine 1-oxide)chromium(III) ions[87]. Complexes with the substituents $4CH_3O$, $4CH_3$, 4Cl and $4NO_2$, have been obtained.

Optical absorption spectra of hexakis($4\text{-}ZC_5H_4NO$)chromium(III) ions in acetone or acetonitrile have yielded D_q values[46] in the range 1575–1613 cm^{-1}. These values are somewhat lower than that of 1740 cm^{-1} reported for the hexaaquochromium(III) ion[88], thus suggesting that the N-oxides are slightly below water in the spectrochemical series. The nitrogen-oxygen stretching frequency is relatively insensitive to substituent effects as indicated by the data in Table 2. The magnetic moments range from 3.82 to 3.88 Bohr magnetons which is typical of high spin complexes.

4. *Manganese*

Bright yellow crystals of hexakis(pyridine 1-oxide)manganese(II)perchlorate form readily upon combination of alcoholic solutions of hexaaquomanganese(II) perchlorate and the N-oxide[49,66]. In view of the usual pink color of manganese(II) ions coordinated with simple oxygen donors, the bright yellow to orange coloration of pyridine 1-oxide complexes is rather striking. Magnetic susceptibility measurements yield values of ~5.80 Bohr magnetons[66], commensurate with the supposed A_1 ground state for the metal ion. It would, therefore, appear that the yellow coloration results from a strong charge transfer band centered at 3834 Å for the complex with pyridine 1-oxide[66], and in this general vicinity for complexes of substituted pyridine 1-oxides[89]. Charge transfer seemingly induces a degree of instability to these manganese(II) complexes, but a much greater instability is reported for the related complexes with 2,2′-bipyridine-1,1-dioxide[90]. A predominant charge transfer band is also noted for pyridine 1-oxide complexes of manganese(II) nitrate[69]. Complexes having both ionic and bidentate nitrato anions are suggested, in analogy to similar complex types known for cobalt(II), copper(II) and nickel(II).

5. *Iron*

Both iron(II) and iron(III) ions react with pyridine 1-oxides giving the corresponding hexakis(pyridine 1-oxide) complexes[46,48,66,89]. Values of ν(N–O) for the coordinated N-oxide shift to lower frequencies with increased charge on the metal ion[49,89,91]. These results are shown in Table 2. As with Cr^{III} the range for the N–O stretching frequency is rather limited (1205 to 1215 cm^{-1}). Magnetic data indicate, as one would expect, that both Fe^{II} and Fe^{III} form high spin complexes. The Fe^{II} complexes have magnetic moments around 5.4 and Fe^{III} around 5.9 Bohr magnetons.

6. *Cobalt*

The reactions of pyridine 1-oxides with cobalt(II) ions have been studied quite extensively. Cobalt(II) salts containing anions having little basic tendency yield products which tend to express maximal coordination of pyridine 1-oxide ligands[48,66]. In the presence of more basic anions, such as chloride, bromide, or even nitrate, coordination of the anion, and/or water molecules in the primary coordination sphere is observed[48,69,71,72,92]. To our knowledge, however, no coordination complex of cobalt(III) containing a pyridine 1-oxide donor has yet been reported. The cobalt(II) complexes which have been prepared to date are given in Table 5.

The diversity of pyridine 1-oxide coordination with cobalt(II) ions is illustrated by the formation of compounds of the general type $Co(C_5H_5NO)_nCl_2$ where n is 2 or 3. $Co(C_5H_5NO)_3Cl_2$, for example, has been shown[92] to be the compound $Co(C_5H_5NO)_6CoCl_4$, with a similar structure for the bromide salt. Compounds of the type CoL_2X_2, where L represents a substituted pyridine 1-oxide, and X is Cl^-, Br^-, NCS^-, or NO_3^-, appear to have ligands distributed tetrahedrally about the metal ion[71,72]. Ready conversion of tetrahedrally coordinated CoL_2X_2 (X = halide ion) to an octahedral configuration is suggested by spectral changes associated with dissolution[72]. Spectra recorded for solutions of the complex in a variety of solvents are similar to those recorded for solutions of hexakis(pyridine 1-oxide)cobalt(II) and clearly different from those recorded for solid samples[95].

Pyridine 1-oxide complexes containing both noncoordinated and bidentate nitrate anions have been reported. Bis(pyridine 1-oxide)dinitratocobalt(II) represents possibly the first essentially octahedral nitrato complex of cobalt(II) which exhibits a magnetic moment consistent with its geometry. Similarity of optical absorption spectra for the bis- and hexakis(pyridine 1-oxide) complexes $CoL_2(NO_3)_2$ and $CoL_6(NO_3)_2$, suggest that pyridine 1-oxide and the nitrato group must be very close together in the spectrochemical series[69].

Complexes of the type $CoL_2(NO_2)_2$, where L represents 2,4-, 2,6-dimethyl or 2,4,6-trimethyl pyridine 1-oxide were prepared and studied[94]. Infrared and electronic spectra have shown that the complexes are six-coordinate with chelating nitrite groups. Steric effects as well as basic strength of the ligands appear to be factors which lead to chelation of the nitrite groups. Lower magnetic moments were obtained for these complexes[94] than for bis(pyridine 1-oxide)dinitratocobalt(II)[69].

Pyridine 1-oxide and its monomethyl derivatives form a series of isolable 2:1 complexes with cobalt(II) acetylacetonates[52], whose pseudocontact nmr shifts were discussed in section (ii) above.

The infrared nitrogen-oxygen stretching frequency ν(N–O) has been correlated with σ for a series of hexakis(pyridine 1-oxide)cobalt(II) complexes[46].

7. *Nickel group*

Nickel(II) perchlorate reacts readily with 4-substituted pyridine 1-oxides to give yellow colored hexakis(substituted pyridine 1-oxide)nickel(II) perchlora-

TABLE 5

COMPLEXES OF COBALT(II) WITH PYRIDINE *N*-OXIDES

Complex	*Dq*	*ν(N–O)cm⁻¹*	*μ_{eff}BM*	*Reference*
$Co(4CH_3C_5H_4NO)_6(ClO_4)_2$	950	1209	4.63	68, 89, 46
$Co(3CH_3C_5H_4NO)_6(ClO_4)_2$			4.72	89
$Co(2CH_3C_5H_4NO)_6(ClO_4)_2$		1208	4.58	89
		1196		
$Co(2CH_3C_5H_4NO)_2Br_2$		1205	4.52	89
$Co(C_5H_5NO)_6(ClO_4)_2$	950	1219	4.69	48, 66, 46
$Co(C_5H_5NO)_6(NO_3)_2$			4.77	48, 69
$Co(C_5H_5NO)_6I_2$		1220	4.75	89
$Co(C_5H_5NO)_6CoI_4$		1221	4.51, 4.61	89
$Co(C_5H_5NO)_6CoBr_4$		1221	4.67	89
$Co(C_5H_5NO)_6CoCl_4$		1220	4.75	48, 70, 92, 89
$Co(C_5H_5NO)_6CdBr_4$				92
$Co(C_5H_5NO)\ (H_2O)Cl_2$		1220	4.75	48
$Co(4NO_2C_5H_4NO)_6(ClO_4)_2$	940	1229	4.62	89, 46
$Co(C_5H_5NO)_2(NO_3)_2$		1195	4.92	69, 89
$Co(2,4(CH_3)_2C_5H_3NO)_2Cl_2$		1200	4.50	71
$Co(2,6(CH_3)_2C_5H_3NO)_2Cl_2$		1205	4.59	72, 89
$Co(2,6(CH_3)_2C_5H_3NO)_2Br_2$		1200	4.61	72
$Co(2,6(CH_3)_2C_5H_3NO)_2(NO_3)_2$		1200	4.41	72
$Co(2,6(CH_3)_2C_5H_3NO)_2(NCS)_2$		1195	4.75	72
$Co(2,4,6(CH_3)_3C_5H_2NO)_2Cl_2$		1200	4.54	71, 72
$Co(2,4,6(CH_3)_3C_5H_2NO)_2Br_2$		1200	4.68	72
$Co(2,4,6(CH_3)_3C_5H_2NO)_2(NCS)_2$		1195	4.74	72
$Co(2,4,6(CH_3)_3C_5H_2NO)_2(NO_3)_2$		1200	4.40	72
$Co(4CH_3OC_5H_4NO)_6(ClO_4)_2$	950	1201	4.79	46
$Co(4ClC_5H_4NO)_6(ClO_4)_2$	950	1220	4.82	46
$Co(2,4\text{-}(CH_3)_2C_5H_3NO)_2(NO_2)_2$			4.63	94
$Co(2,6\text{-}(CH_3)_2C_5H_3NO)_2(NO_2)_2$			4.67	94
$Co(2,4,6\text{-}(CH_3)_3C_5H_2NO)_2(NO_2)_2$			4.36	94

tes[33,46]. Correlations of spectral properties recorded for these compounds with substitutent parameters for the changing ligands have been discussed[33] and are illustrated in Figure 6. Nickel(II) nitrate, like cobalt(II) nitrate, forms complexes in which the nitrate anion is non-coordinating or acts as a bidentate ligand. In the presence of other basic anions, less than maximal coordination of pyridine 1-oxide is reported[48].

Dickson *et al.*[39], found that for complexes of titanium(IV) (a d° case) the

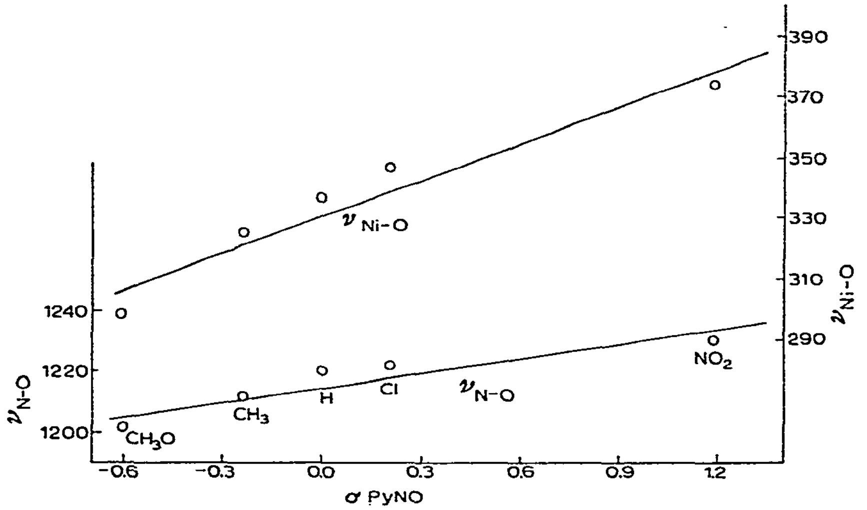


Fig. 6. Correlation of ν(N–O) and ν(Ni–O) for nickel(II) complexes with pyridine 1-oxides and σ_{PyNO} values.

TABLE 6

COMPLEXES OF NICKEL(II)

Complex	*Dq*	*ν(N–O)cm^{-1}*	*ν(M–O)*	*BMμ_{eff}*	*Ref.*
$Ni(4CH_3OC_5H_4NO)_6(ClO_4)_2$	800	1201	299		33
$Ni(4CH_3C_5H_4NO)_6(ClO_4)_2$	794, 833	1212, 1206	325, 393	3.32	33, 46
$Ni(C_5H_5NO)_6(ClO_4)_2$	794, 826	1220, 1218	337, 340	3.32	33, 46, 48
$Ni(C_5H_5NO)_6(BF_4)_2$	794	1220	337		33
$Ni(4ClC_5H_4NO)_6(ClO_4)_2$	786, 823	1212, 1222	347, 367	3.34	33, 46
$Ni(4ClC_5H_4NO)_6(BF_4)_2$	786	1212, 1222	347		33
$Ni(4CH_3C(O)C_5H_4NO)_6(ClO_4)_2$	784	1225	358		33
$Ni(4NO_2C_5H_4NO)_6(ClO_4)_2$	830, 823	1230, 1239	374, 370	3.30	33, 46
$Ni(C_5H_5NO)_6(NO_3)_2$					69
$Ni(C_5H_5NO)_2(NO_3)_2$				3.12	69
$Ni(C_5H_5NO)_6I_2$					48
$Ni(C_5H_5NO)_4I_2$					48
$Ni(C_5H_5NO)_6Br_2$				3.28	48
$Ni(C_5H_5NO)(H_2O)Cl_2$				3.21	48
$Ni(C_5H_5NO)(H_2O)Br_2$				3.16	48
$Ni(4NO_2C_5H_4NO)_6Cl_2$		1229			89
$Ni(4NO_2C_5H_4NO)_2Br_2$		1210			89

metal-oxygen stretching frequency, ν(M–O), increased with increasing electron donating ability of the *para* substituent, while Herlocker *et al.*[33], found an opposite relation, *i.e.*, ν(M–O) decreased for nickel(II) complexes (a d^8 case). This has been interpreted as indicating π bonding from ligand to metal in the case of titanium and π back bonding from metal to oxygen π* orbitals with nickel. The nickel(II) compounds, like those previously discussed, are typical high spin complexes. It is interesting to note that two different series of D_q values have been reported for the nickel(II) complexes[33,46]. One series[46] is constant while the other correlates roughly with the sigma constants[33].

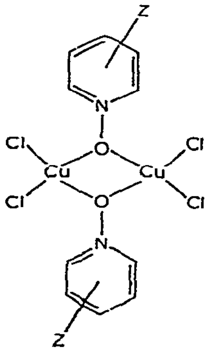
Bis(2,4-pentanedionato)nickel(II), like bis(2,4-pentanedionato)cobalt(II), forms adducts with pyridine 1-oxides. Illustrative examples of nickel(II) complexes are given in Table 6.

Orchin and coworkers[28,40,96–99] have published extensively on the properties of 1-(substituted pyridine 1-oxide)-3-olefin-2,4-dichloroplatinum(II) complexes. Not only have substituents on the N-oxide moiety been modified, but also a variety of olefins including 3- and 4-substituted styrenes have been incorporated. These and other studies will be reviewed by Orchin and Smith[100].

8. *Copper*

Pyridine 1-oxide reacts with copper(II) perchlorate to give either a yellow-green hexakis- or a blue-green tetrakis(pyridine 1-oxide)copper(II) salt[64,66]. Often the tetrakis compound is deposited initially from solutions of the appropriate mole ratio of ligand to metal ion, but when allowed to stand in the presence of excess ligand, the initially precipitated blue-green solid becomes more yellow in color. Copper(II) salts of anions more basic than perchlorate react with pyridine 1-oxide and many of its derivatives giving two series of compounds. These are characterized by the general formula CuL_2X_2 or $CuLX_2$, where $X = Cl^-$ or Br^- and L = pyridine 1-oxide. Typical copper(II) complexes are listed in Table 7.

On the basis of low magnetic moments observed at room temperature and a marked temperature dependence of the magnetic susceptibility[61,64], the $CuLX_2$ type compounds were assigned a bi-or polynuclear structure of the type



Complete X-ray examination of single crystals[65,101] confirm the proposed structure for the complex with pyridine 1-oxide. The magnetic data reflect considerable spin–spin interaction between unpaired electrons on adjacent copper ions in the binuclear complexes[37,48,61–64,69,102–105]. A super-exchange mechanism operating through the bridging N-oxide oxygen atom has been suggested to account for the low magnetic moments[37].

Copper(II) complexes of the type CuL_2X_2, on the other hand, generally display a near normal magnetic moment. Greater distance between metal ions and probable asymmetric ligand bridging between metal ions is suggested by the molecular structure of bis(pyridine 1-oxide)-dinitratocopper(II)[106]. A molecular unit composed of the two centrosymmetrically related complex monomers is defined by the formula, $[Cu(C_5H_5NO)_2(NO_3)_2]_2$. In the structure, the copper atom has a distorted tetragonal pyramidal environment of five oxygen atoms.

Preliminary electron spin resonance data indicate that there is a significant concentration of spin density on the N-oxide ligand for bis(2,6-dimethylpyridine 1-oxide)dichlorocopper(II) diluted in bis(2,6-dimethylpyridine 1-oxide)dichloro zinc(II). Electron paramagnetic and proton nuclear magnetic resonance spectra have been described for the 4-methylpyridine 1-oxide adduct of bis(1,1,1-trifluoro-2,4-pentanedionato)copper(II)[107]. Under conditions of rapid ligand exchange, isotropic chemical shifts were calculated using as diamagnetic positions those found for the free ligand, which were approximately those for the corresponding adduct with bis(1,1,1-trifluoro-2,4-pentanedionato)zinc(II). The isotropic shifts for 4-methylpyridine 1-oxide protons complexed with copper(II) were observed to be temperature dependent, but unlike normal isotropic shifts which follow a Curie (T^{-1}) relationship, those observed for the 3-ring and the 4-methyl protons increase with increasing temperature. It is therefore suggested that at elevated temperatures electrons are delocalized into the π orbitals of the N-oxide. At lower temperatures very little spin is delocalized onto the ring of 4-methylpyridine 1-oxide. This data coupled with the Curie behavior of the magnetic susceptibility indicates the existence of an equilibrium between at least two paramagnetic species having approximately the same magnetic moments.

Several coordination complexes of silver(I) perchlorate with substituted pyridine 1-oxides have been reported[118]. Not only is the expected *bis* coordination exhibited by the metal ion, but also several of the salts resulting from reaction of $AgClO_4$ with the N-oxides in acetone, methanol and ethanol solvents contain one, or more additional moles of ligand. Representative examples of these compounds are listed in Table 8.

9. *Zinc group*

Hexaaquozinc(II) perchlorate or nitrate react with pyridine 1-oxide in ethanolic solution to give white crystals of hexakis(pyridine 1-oxide)zinc(II) perchlorate

TABLE 7

COMPLEXES OF COPPER(II) WITH PYRIDINE *N*-OXIDES

Compound	*ν(N–O)cm⁻¹*	μ_{eff}*BM*	*T °K*	*Reference*
$Cu(C_5H_5NO)_6(ClO_4)_2$	1232	1.94		64, 66, 89
	1215			
$Cu(C_5H_5NO)_6(NO_3)_2$				69
$Cu(4CH_3C_5H_4NO)_4(ClO_4)_2$	1200	1.92		89
$Cu(2CH_3C_5H_4NO)_4(ClO_4)_2$	1205	1.91		89
$Cu(4NO_2C_5H_4NO)_4(ClO_4)_2$		1.92		89
$Cu(2,6(CH_3)_2C_5H_3NO)_4(ClO_4)_3$	1205	1.92		89
$Cu(2,4,6(CH_3)_3C_5H_2NO)_4(ClO_4)_2$	1204	1.90		89
$Cu(C_5H_5NO)_4(ClO_4)_2$	1215	2.09[64]		48, 64, 66
	1205	1.62[48]		
$Cu(C_5H_5NO)_2(NO_3)_2$	1205	1.90	297	48, 69
$Cu(C_5H_5NO)_2Cl_2$	1223	0.63	298	48, 66
	1206			
$Cu(C_5H_5NO)_2Br_2$	1211	1.46	293	61, 62
	1201			
$Cu(4CH_3C_5H_4NO)_2Cl_2$		1.99	273	102
$Cu(4CH_3C_5H_4NO)_2Br_2$	1209	1.33	297	61, 62
$Cu(3CH_3C_5H_4NO)_2Cl_2$				102
$Cu(2CH_3C_5H_4NO)_4(ClO_4)_2$		1.87	273	102
$Cu(4ClC_5H_4NO)_2Cl_2$	1209	1.75	298	61, 62
	1195			
$Cu(4NO_2C_5H_4NO)_2Cl_2$				62
$Cu(4NO_2C_5H_4NO)_2Br_2$	1208	1.74	292	61,
$Cu(2,6(CH_3)_2C_5H_3NO)_4(ClO_4)_2$	1205	1.92		89
$Cu(2,6(CH_3)_2C_5H_3NO)_2Cl_2$		1.90	298	63
Yellow				102
Green		1.50	273	
$Cu(2,6(CH_3)_2C_5H_3NO)_2Br_2$	1203	1.80	289	61
$Cu(2,4,6(CH_3)_3C_5H_2NO)_2Cl_2$	1208	2.20	298	61
		1.91	298	63
$Cu(2,4,6(CH_3)_3C_5H_2NO)_2Br_2$	1205	1.85	298	63
$Cu(C_5H_5NO)\ ((CH_3)_2NC(O)H)Cl_2$	1203			62
$Cu(C_5H_5NO)\ ((CH_3)_2SO)Cl_2$	1203			62
$Cu(C_5H_5NO)\ ((CH_3)_2NC(O)H)Br_2$	1202			62
$Cu(C_5H_5NO)\ ((CH_3)_2SO)Br_2$	1211	0.97	298	64
$[Cu(C_5H_5NO)Cl_2]_2$	1202	1.06	299	48, 64, 62, 102
$[Cu(C_5H_5NO)Br_2]_2$	1200	0.65	298	61, 64
$[Cu(4CH_3C_5H_4NO)Cl_2]_2$	1200	0.52	298	61, 102, 62
	1203			
$[Cu(3COOHC_5H_4NO)Cl_2]_2$		0.53	294	103
$[Cu(3COOHC_2H_4C_5H_4NO)Cl_2]_2$		0.48	297	103
$[Cu(3COOHC_2H_4C_5H_4NO)Br_2]_2$		0.39	297	103
$[Cu(4COOHC_2H_4C_5H_4NO)Cl_2]_2$		0.50	297	103
$[Cu(4COOHC_3H_4C_5H_4NO)Br_2]_2$		0.28	297	103
$[Cu(4CNC_5H_4NO)Br_2]_2$		0.79	297	103
$[Cu(4CNC_5H_4NO)Cl_2]_2$		0.95	297	103
$[Cu(4CH_3C_5H_4NO)Br_2]_2$	1203	0.26	298	48, 62
$[Cu(3CH_3C_5H_4NO)Cl_2]_2$	1248	0.55	297	61, 63, 102
$[Cu(3CH_3C_5H_4NO)Br_2]_2$	1244	0.48	291	61, 63
$[Cu(4ClC_5H_4NO)Cl_2]_2$	1208	0.49	296	61, 62
	1195			

TABLE 7 *(continued)*

Compound	*ν(N–O)cm*$^{-1}$	μ_{eff}*BM*	*T °K*	*Reference*
$[Cu(3ClC_5H_4NO)Cl_2]_2$		0.46	297	103
$[Cu(4ClC_5H_4NO)Br_2]_2$	1199	0.23	298	61, 62
$[Cu(3ClC_5H_4NO)Br_2]_2$		0.25	291	103
$[Cu(NO_2C_5H_4NO)Cl_2]_2$	1238 1225	1.94	298	62
$[Cu(4NO_2C_5H_4NO)Br_2]_2$		0.45	298	103
$[Cu(4HOC_5H_4NO)Cl_2]_2$	1210	0.23	298	62
$[Cu(2,6(CH_3)_2C_5H_3NO)Cl_2]_2$	1199	0.22	298	61, 63, 102
$[Cu(2,6(CH_3)_2C_5H_3NO)Br_2]_2$	1195	0.30	298	61, 63
$[Cu(2,4,6(CH_3)_3C_5H_2NO)Cl_2]_2$	1199	0.63	295	61, 63
$[Cu(2,4,6(CH_3)_3C_5H_2NO)Br_2]_2$	1202	0.60	295	61, 63

TABLE 8

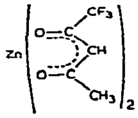
COMPLEXES OF SILVER(I) WITH PYRIDINE 1-OXIDES[110]

Compounds	*ν(N–O)cm*$^{-1}$
$Ag(C_5H_5NO)_2ClO_4 \cdot C_5H_5NO$	1210, 1238 cm^{-1}
$Ag(2CH_3C_5H_4NO)_2ClO_4 \cdot 2CH_3C_5H_4NO$	1202
$Ag(3CH_3C_5H_4NO)_2ClO_4 \cdot 3CH_3C_5H_4NO$	1228, 1260
$Ag(4CH_3C_5H_4NO)_2ClO_4$	1200
$Ag(2C_2H_5C_5H_4NO)_2ClO_4$	1197
$Ag(2C_3H_7C_5H_4NO)_2ClO_4 \cdot 2C_3H_7C_5H_4NO$	1202

or nitrate, respectively[48]. Even for a ligand to metal ion ratio of 4 to 1, the hexakis N-oxide complex was isolated. Anions more basic than perchlorate or nitrate, on the other hand, may be coordinated, leading to four coordinate complexes[48,102] of the type ZnL_2X_2. Physical data for several zinc(II) complexes with pyridine 1-oxides have resulted from studies directed toward isolation of compounds to serve as inert diluents for corresponding copper(II) complexes. Some examples of these coordination complexes are listed in Table 9.

TABLE 9

COMPLEXES OF ZINC(II) WITH PYRIDINE 1-OXIDES

Compound	*ν(N–O)cm*$^{-1}$	*Density*	*Reference*
$Zn(C_5H_5NO)_6(ClO_4)_2$	1221		48
$Zn(C_5H_5NO)_6(NO_3)_2$	1224		48
$Zn(C_5H_5NO)_2Cl_2$	1209	1.72 g/ml	48, 102
$Zn(2CH_3C_5H_4NO)_2Cl_2$		1.61	102
$Zn(3CH_3C_5H_4NO)_2Cl_2$		1.55	102
$Zn(4CH_3C_5H_4NO)_2Cl_2$		1.55	102
$Zn(2,6(CH_3)_2C_5H_3NO)_2Cl_2$		1.50	102
 $\cdot\ 4CH_3C_5H_4NO$			107

The low stability of highly coordinated mercury(II) ions is well known. In addition, most oxygen donors coordinate only weakly with this ion. Yet pyridine 1-oxide readily forms the white compound, hexakis(pyridine 1-oxide)mercury(II) perchlorate[66,68]. Except for minor, but expected variation in line intensity, X-ray diffraction powder patterns of the salt are said to be similar to those for hexakis-(pyridine 1-oxide)nickel(II) and cobalt(II) perchlorates. Thus, an octahedral coordination for the mercury(II) ion appears most likely.

Mercury(I) also reacts to form complexes with pyridine 1-oxide[109]. These compounds are of the type $Hg_2(C_5H_5NO)_4(ClO_4)_2$ and $Hg_2(C_5H_5NO)_5SiF_6$. The properties of the latter compound suggest that the fifth ligand may be more loosely bound than the other four. However, the preparation of these compounds is difficult since a large amount of impure material is first precipitated from solution. The infrared stretching frequency ν(N–O) (for $Hg_2(C_5H_5NO)_4(ClO_4)_2$, = 1208 cm.$^{-1}$ and for $Hg_2(C_5H_5NO)_5SiF_6$ = 1218 and 1200 cm^{-1}) suggests coordination of the N-oxide, through the oxygen atom, and the presence of two types of ligand in the latter compound.

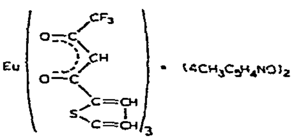
Recently the preparation of fifty two coordination complexes with pyridine 1-oxide and its 2-methyl, 3-methyl, 4-methyl, 2-ethyl, 2-*n*-propyl, 2,6-dimethyl, and 4-methoxy derivatives containing zinc(II), cadmium(II) and mercury(II) cations has been reported[117]. Infrared data suggest the relative order of the metal oxygen bond strengths, Zn > Cd > Hg. The nuclear magnetic resonance data for the series of 4-methylpyridine 1-oxide complexes confirm this order. Compounds of the types ML_2X_2 (M = Zn, Cd; (X = Cl^-, Br^-, I^-); $[MLX_2(H_2O)]_n$ (M = Cd); ML_2X_4 (M = Cd, Hg); $M_3L_2X_6$ (M = Cd), and $M_4L_2X_8$ (M = Cd) are reported[110].

10. *Rare earth group*

Ethanolic solutions of pyridine 1-oxides react with the lanthanide perchlorates[111] yielding compounds acting as 1:3 electrolytes. In Table 10 are listed representative examples. Dissociation of the complex in water, but not in non-aqueous dipolar solvents is indicated by molecular weight measurements. All complexes of lanthanum perchlorate have the usual coordination number of eight. Seemingly anions more basic than perchlorate can effectively compete for coordination sites about the metal cation. Thus europium(III) chloride reacts with 4-methylpyridine 1-oxide to form a crystalline compound corresponding to a composition[73] formulated as $Eu(4CH_3C_5H_4NO)_3Cl_3$. The iodide, perchlorate, and hexafluorophosphate salts, on the other hand, yield *octakis*(4-methylpyridine 1-oxide)europium(III) complexes which all display similar optical spectra, readily distinguishable from that of the *tris*(4-methylpyridine 1-oxide) complex of europium(III) chloride. Compounds of the type *tris*(*beta*-diketonato)-*bis*(4-methylpyridine 1-oxide)europium(III) have also been reported[73]. These compounds are noted to strongly fluoresce as solids and in organic solvents.

TABLE 10

COMPLEXES OF THE LANTHANONS WITH PYRIDINE 1-OXIDES

Compound	*ν(N–O)cm^{-1}*	*Reference*
$Eu(4CH_3C_5H_4NO)_3Cl_3$		73
$Eu(4CH_3C_5H_4NO)_8(ClO_4)_3$		73
$Eu(4CH_3C_5H_4NO)_8I_2$		73
$Eu(4CH_3C_5H_4NO)_8(PF_6)_3$		73
		73
$Ln(4CH_3C_5H_4NO)_8(ClO_4)_3$	1224	111
$Ce(4CH_3C_5H_4NO)_8(ClO_4)_3$	1224	111
$Pr(4CH_3C_5H_4NO)_8(ClO_4)_3$	1223	111
$Nd(4CH_3C_5H_4NO)_8(ClO_4)_3$	1224	111
$Sm(4CH_3C_5H_4NO)_8(ClO_4)_3$	1224	111

Thorium(IV) perchlorate, like the lanthanons, reacts with pyridine 1-oxides to give octakis(pyridine 1-oxide)thorium(IV) perchlorate[75]. Of the remaining members of the actinides, complexes of uranium(VI) have been reported[47,75]. These are listed in Table 11.

TABLE 11

COMPLEXES OF DIOXOURANIUM(VI) WITH SUBSTITUTED PYRIDINE 1-OXIDES

Compound	*ν(N–O)cm^{-1}*
$UO_2(C_5H_5NO)_3Cl_2$	1216 cm^{-1}
$UO_2(4CH_3OC_5H_4NO)_2Cl_2$	1205
$UO_2(4CH_3C_5H_4NO)_2Cl_2$	1210
$UO_2(4ClC_5H_4NO)_4Cl_2$	1212
$UO_2(4NO_2C_5H_4NO)_2Cl_2$	1235

11. *Non-transition elements*

Several non-transition elements serve as acceptor sites for pyridine 1-oxide donors. Relatively strong interaction is noted for adducts with tetrahalotin(IV)[48], sulfur trioxide[112], antimony pentachloride[113], boron trihalides[114] and silicon tetrahalides[115]. The reaction of tin(II)chloride in tetrahydrofuran with pyridine 1-oxide has been reported[108]. Both 1:1 and 1:2 adducts were prepared. In section B(ii) the reactions of the pyridine 1-oxides with hydrogen ion and phenol were discussed.

The interaction with molecular iodine has also been investigated[4,116]. Equilibrium constants and ΔH values of pyridine 1-oxide-iodine complexes are much greater than those for other oxo donor-iodine complexes. A parallel relationship between donor group $pK_{BH}{}^+$ and iodine complexing ability[4,116] is found (Figure 7). This observation implies a similarity of mechanism between hydrogen bond formation and iodine complexing for the N-oxide donor. Clearly the charge transfer effect plays a more important role in the latter case than in the former. However, detailed theoretical interpretation must await more precise information concerning the exact geometrical configuration present in the bimolecular N-oxide-iodine adducts. Complexes such as those illustrated in Table 12 have been found with the non-transition elements.

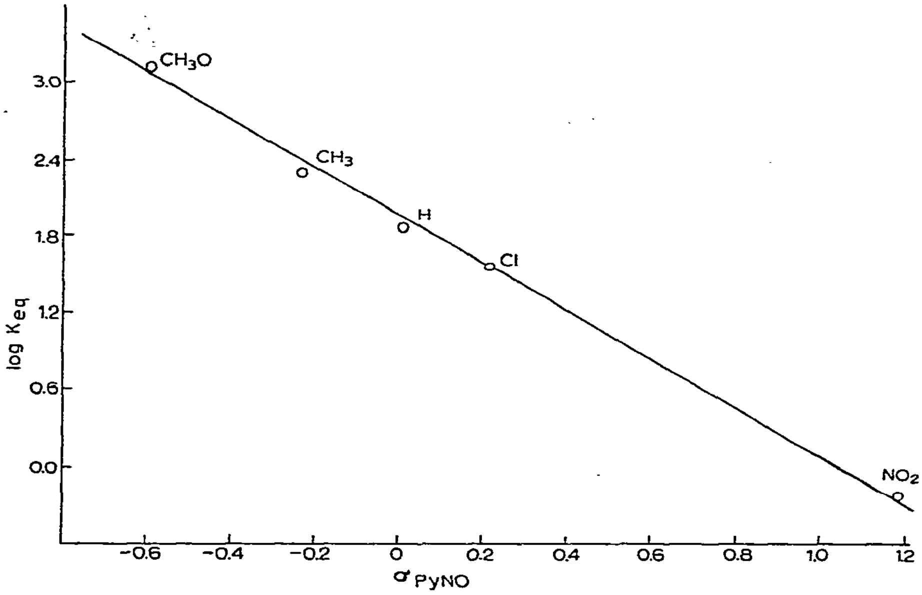


Fig. 7. Correlation of ΔH values with σ_{PyNO} for iodine-pyridine 1-oxide charge tranfer complexes.

TABLE 12

COMPLEX COMPOUNDS OF NON-TRANSITION ELEMENTS WITH PYRIDINE 1-OXIDE

Compound	*ν(N–O)cm⁻¹*	*Reference*
$SnBr_4(C_5H_5NO)_2$	1192	48
$SnCl_2(C_5H_5NO)$	1195	108
$SnCl_2(C_5H_5NO)_2$	1205, 1208	108
$BF_3(C_5H_5NO)$	1217	114
$BF_3(4CH_3C_5H_4NO)$	1127	114
$BCl_3(C_5H_5NO)$	1198	114
$BH_3(C_5H_5NO)$	1224	114
$BH_3(4CH_3C_5H_4NO)$	1121	114
$SO_3(C_5H_5NO)$		112
$SbCl_5(C_5H_5NO)$		113
$SiF_4(C_5H_5NO)_2$		115
$SiCl_4(C_5H_5NO)_2$		115
$SiBr_4(C_5H_5NO)_2$		115

C. OTHER N-OXIDE DONORS

Steric factors involved in N-oxide coordination have been probed to some degree using 2- and 2,6-substituted pyridine 1-oxides. In addition, the effects of an attached aromatic ring on the coordination properties of the pyridine 1-oxide system have been considered using substituted quinoline 1-oxides[118–121]. Quinoline 1-oxide complexes of copper(II) halides (Table 13) display magnetic behavior similar to that found for complexes of pyridine 1-oxides[119]. Seemingly for the bimolecular copper(II) chloride complexes, ligands with relatively low donor strengths (more negative pK_{BH^+} values) give rise to chloride bridged species. Ligands with higher donor strengths afford the characteristic oxygen bridged species. For ligands of intermediate donor strengths, a third class of compound is formed. Members of this series display a high magnetic moment and possess polymeric, halogen bridged structures. Both copper(II) chloride and bromide complexes with two molecules of substituted quinoline 1-oxides are isolable. These compounds exhibit normal magnetic moments which are virtually independent of temperature.

TABLE 13

COORDINATION COMPLEXES OF QUINOLINE OXIDES[119]

Compound	*Ligand* pK_{BH^+}	μ_{eff}[a] *(BM)*
$[Cu(4CH_3C_9H_6NO)Cl_2]_2$	1.44	0.56
$[Cu(4CH_3C_9H_6NO)Br_2]_2$		0.40
$[Cu(6CH_3C_9H_6NO)Cl_2]_2$	1.01	0.41
$[Cu(6CH_3C_9H_6NO)Br_2]_2$		0.60
$[Cu(C_9H_7NO)Cl_2]_2$[b]	0.86	0.37
$[Cu(C_9H_7NO)Br_2]_2$[b]		0.36
$[(CuCl_3)_3(4Cl\text{-}6CH_3C_9H_5NO)_2]$	0.61	1.69
$[Cu(4Cl\text{-}6CH_3C_9H_5NO)Br_2]_2$		0.38
$Cu(4Cl\text{-}6CH_3C_9H_5NO)_2Cl_3$		1.97
$Cu(4Cl\text{-}6CH_3C_9H_5NO)_2Br_2$		1.82
$(CuCl_3)_3(4ClC_9H_6NO)_2$	0.47	2.07
$[Cu(4ClC_9H_6NO)Br_2]_2$		0.39
$Cu(4ClC_9H_6NO)_2Cl_2$		1.88
$(CuCl_2)_4(3NO_2\text{-}6CH_3C_9H_5NO)_3$	—0.69	1.91
$[Cu(3NO_2\text{-}6CH_3C_9H_5NO)Br_2]_2$		1.72
$Cu(3NO_2\text{-}6CH_3C_9H_5NO)_2Cl_2$		1.81
$Cu(3NO_2\text{-}6CH_3C_9H_5NO)_2Br_2$		1.98
$[Cu(4NO_2\text{-}6CH_3C_9H_5NO)Cl_2]$	−1.20	1.92
$Cu(4NO_2\text{-}6CH_3C_9H_5NO)_2Cl_2$		1.87
$Cu(4NO_2\text{-}6CH_3C_9H_5NO)_2Br_2$		1.85
$[Cu(4NO_2C_9H_6NO)Cl_2]_2$	−1.39	2.13
$Cu(4NO_2C_9H_6NO)_2Cl_2$		1.86
$Cu(4NO_3C_9H_6NO)_2Br_2$		1.83
$Cu(C_9H_7NO)_4(ClO_4)_2$		1.89
$Cu(C_9H_7NO)_2(NO_3)_2$		1.91
$Co(2CH_3C_9H_6NO)_2(NO_2)_2$[c]		4.52
$Co(4CH_3C_9H_6NO)_2(NO_2)_2$[c]		4.62

[a] All magnetic moments recorded at 300 °K. [b] Also reference 64. [c] Reference 94.

It appears that there must be a critical relationship between such factors as the donor properties and steric requirements of the ligands and the lattice energies of the various compounds in favoring the formation of one species over another.

Complexes of cobalt(II) with 2-methyl and 4-methylquinoline 1-oxide having the general formula $Co(CH_3C_9H_5NO)_2(NO_2)_2$ have been prepared and have been shown to be octahedral with chelating nitrite groups[94].

Quinoline N-oxide forms a tetrahedral cobalt chloride complex in the solid state, but gives very labile nitrite complexes. The mauve solution turned brown upon concentration by solvent evaporation, probably owing to solvolysis. The insertion of a methyl group in the 2 or 4 position of quinoline N-oxide increases its basic strength and helps to yield stable nitrite complexes.

Proton magnetic resonance studies of isolable quinoline 1-oxide and isoquinoline 2-oxide complexes with bis(2,4-pentanedionato)cobalt(II) and nickel(II) have been reported[120]. Unpaired electron spin delocalization from the paramagnetic metal ion to ligand orbitals occurs through a π mechanism probably involving the highest filled bonding ligand molecular orbitals. Pseudo contact shifts derived for the adduct between bis(2,4-pentanedionato)cobalt(II) and isoquinoline 2-oxide, like that for corresponding pyridine 1-oxide adducts[52], are in qualitative agreement with restricted rotation about the metal oxygen bond and support a Co–O–N bond angle of 115–130°.

1,10-Phenanthroline 1-oxide readily forms coordination complexes of the type ML_2Cl_2 with copper(II), nickel(II) and cobalt(II)[122]. The compounds dissociate in water to regenerate the N-oxide and hydrated metal ions. The rigidity of the 1,10-phenanthroline system, relative to that of 2,2′-bipyridine 1-oxide suggests that there would be significant differences in complex stability and/or metal ion selectivity.

The di(N-oxide) of 2,2′-bipyridine functions as a novel bidentate oxodonor forming coordination compounds of the transition metal ions[123–126]. Seven membered chelate rings with a staggered (gauche) configuration of the pyridine rings are suggested from considerations of steric interactions and analysis of the infrared spectra of the complexes[124]. Metal oxygen stretching frequencies of complexes with divalent metal ions appear in the same order as that predicted by the Irving-Williams[124] series: $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ and $Zn^{2+} > Cd^{2+}$.

As expected, infrared absorption spectra for complexes of 2,2′-bipyridine 1,1′-dioxide become more complex than those of the pyridine 1-oxides. Splitting of bands associated with the N–O, C–H, and hetero-aromatic ring vibrational modes makes precise band assignments difficult. Table 14 lists these compounds, many of which were isolated from water solution.

To this point in our discussion detailed consideration has been given only to those heterocyclic aromatic amine N-oxides having only N-oxide donor groups. Substituents of certain functional groups which could also serve as donor sites might lead to the formation of chelate complexes containing the structural entity

TABLE 14

COMPLEXES OF 2,2′-BIPYRIDINE-1,1′-DIOXIDE

Compound	μ_{eff}[a] *(BM)*	*ν(N–O)cm*$^{-1}$	*Reference*
$VO(C_{10}H_8N_2O_2)_2(ClO_4)_2$	1.63	1264, 1246	126
$Cr(C_{10}H_8N_2O_2)_3(ClO_4)_3 \cdot 2H_2O$		1215, 1210, 1199	123, 124
$Cr(C_{10}H_8N_2O_2)_3(NO_3)_3$	3.7		125
$Cr(C_{10}H_8N_2O_2)_2Cl_2(ClO_4) \cdot H_2O$		1207, 1195	123, 124
$[Cr(C_{10}H_8N_2O_2)_2Cl_2]_2PtCl_4$		1213, 1200	123, 124
$Mn(C_{10}H_8N_2O_2)_3(ClO_4)_3 \cdot 2H_2O$	4.97		123, 124, 125
$Mn(C_{10}H_8N_2O_2)_3(ClO_4)_2 \cdot H_2O$			123
$Mn(C_{10}H_8N_2O_2)_3(PtCl_4)$		1235, 1225, 1210	123, 124
$Mn(C_{10}H_8N_2O_2)_3Br_2 \cdot 2H_2O$	6.2		125
$Mn(C_{10}H_8N_2O_2)_3I_2 \cdot H_2O$	5.4		125
$Fe(C_{10}H_8N_2O_2)_3(ClO_4)_3 \cdot 3H_2O$	6.13	1225, 1213, 1200	123, 124
$[Fe(C_{10}H_8N_2O_2)_3]_2(PtCl_4)_3$		1228, 1206, 1200	123, 124
$Fe(C_{10}H_8N_2O_2)_3(ClO_4)_3 \cdot C_{10}H_8N_2O_2$	6.4		125
$Co(C_{10}H_8N_2O_2)_3(ClO_4)_2 \cdot 2H_2O$	4.72	1220, 1202	123, 124
$Co(C_{10}H_8N_2O_2)_3(PtCl_4)$		1215, 1198	125
$Co(C_{10}H_8N_2O_2)_2Cl_2$	4.9		125
$Co(C_{10}H_8N_2O_2)_3Br_2 \cdot 4H_2O$	4.7		125
$Co(C_{10}H_8N_2O_2)_3I_2 \cdot H_2O$	4.8		125
$Ni(C_{10}H_8N_2O_2)_3(ClO_4)_2 \cdot 2H_2O$		1220, 1209	123, 124
$Ni(C_{10}H_8N_2O_2)_3(PtCl_4)$		1212, 1200	123, 124
$Ni(C_{10}H_8N_2O_2)_3(NO_3)_2 \cdot 2H_2O$	3.3		125
$Ni(C_{10}H_8N_2O_2)_3I_2 \cdot H_2O$	3.3		125
$Cu(C_{10}H_8N_2O_2)_3(ClO_4)_2 \cdot 2H_2O$	2.10	1250, 1235, 1210	123–125
$Cu(C_{10}H_8N_2O_2)_2(PtCl_4) \cdot 4H_2O$	1.99	1210, 1203	123, 124
$Cu(C_{10}H_8N_2O_2)Cl_2$	2.2		125
$Zn(C_{10}H_8N_2O_2)_3(ClO_4)_2 \cdot 2H_2O$		1230, 1211	123, 124
$Zn(C_{10}H_8N_2O_2)_3(PtCl_4)$		1225, 1211	123, 124
$Zn(C_{10}H_8N_2O_2)_3(NO_3)_2 \cdot H_2O$			125
$Cd(C_{10}H_8N_2O_2)_3(ClO_4)_2 \cdot H_2O$		1230, 1211	123, 124
$Cd(C_{10}H_8N_2O_2)Cl_2$		1227, 1215, 1205	123, 124
$Ag(C_{10}H_8N_2O_2)_2ClO_4 \cdot 3H_2O$			125
$Hg(C_{10}H_8N_2O_2)_3(ClO_4)_2$			125
$Pb(C_{10}H_8N_2O_2)_2(ClO_4)_2$			125
$ZrO(C_{10}H_8N_2O_2)_3(ClO_4)_2 \cdot 2H_2O$		1261, 1225	126
$Mo_2O_4(C_{10}H_8N_2O_2)_2Cl_2 \cdot 2H_2O$	1.23	1261, 1230	126
$Mo_2O_3(C_{10}H_8N_2O_2)_2Cl_2 \cdot 2H_2O$	1.48	1260, 1223	126
$UO_2(C_{10}H_8N_2O_2)_2(ClO_4)_2$		1260, 1218	126
$Th(C_{10}H_8N_2O_2)_4(ClO_4)_4$		1267, 1232	126
$C_{10}H_8N_2O_2$		1264, 1256 1262, 1255	125

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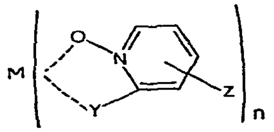
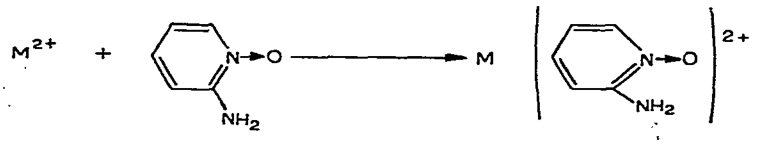
[a] Magnetic susceptibility measurements at room temperature.



where M = an acidic site, generally a metal ion, and Y = groups such as $-NH_2$, $-NH^-$, $-O^-$, S^-, $-CO_2^-$.

The formation of metal ion complexes of 2-aminopyridine 1-oxide has been investigated potentiometrically by titration in water-dioxane solutions[127], for the reaction



in which changes in degree of metal ion and ligand hydration have been neglected. The equilibrium data are given in Table 15. For comparison $pK_{f1} = -0.69$ for the analogous reaction of copper(II) with pyridine 1-oxide. In methanol solution, the metal ion perchlorates react with 2-aminopyridine 1-oxide (L) to give complexes of the types $ML_6(ClO_4)_2$- (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}), $ML_6(ClO_4)_3$ (M = Fe^{3+}), and $ML_4(ClO_4)_2$ (M = Cu^{2+} Ba^{2+}). Clearly the ligand acts in a monodentate fashion under these conditions[127].

In contrast 2-hydroxy and 2-mercaptopyridine 1-oxides readily form complexes with transition metal ions in which the donor acts as a bidentate ligand[128]. This is in accord with the relative acidity of hydroxo and mercapto protons ($pK_{AH} = 5.8$ and 4.5 respectively, in water)[128] relative to that of the amino proton ($pK_{AH} = 12$)[127]. Formation constants for the 1:1 metal chelates are indicated in Table 15.

TABLE 15

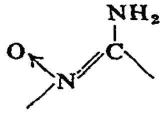
FORMATION CONSTANTS FOR COMPLEXES OF VARIOUS 2 SUBSTITUTED PYRIDINE 1-OXIDES

Metal ion	$2NH_2C_5H_4NO$[127]	$2HOC_5H_4NO$[128]		$2HSC_5H_4NO$[128]	$2HO_2CC_5H_4NO$[129]
	pK_{f1}	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_1$
Ba^{2+}	0.09[a]				
Ca^{2+}	0.01				
Mg^{3+}	−0.06				
Mn^{2+}	0.75	4.45[b]	3.9[c]	3.1[c]	
Co^{2+}	0.93	5.2	4.9	4.8	
Ni^{2+}	1.03	5.35	5.1	5.1	
Zn^{2+}	0.17	5.3	3.1	5.3	
Cu^{2+}			7.3	>8.5	
La^{3+}					2.53[d]
Ce^{3+}					2.71
Pr^{3+}					2.75
Nd^{3+}					2.91
Eu^{3+}					2.94
Gd^{3+}					2.93
Dy^{3+}					3.00
Tm^{3+}					3.16
Yb^{3+}					3.15
Lu^{3+}					3.48

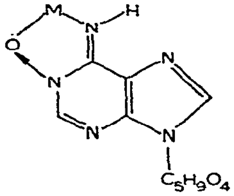
[a] Values for 1:1 dioxane-water solvent.
[b] Values determined potentiometrically in water at 0.005 M ionic strength.
[c] Values determined spectrophotometrically in water at 0.1 M ionic strength.
[d] Values determined potentiometrically in water at 2.0 M ionic strength.

2-Carboxypyridine 1-oxide was found to act as a bidentate ligand, based upon the variation in stability constants with increasing atomic number for a series of complexes with the lanthanons[129]. This is inferred from the similarity of the stability constant variations to those of known chelate systems[130–132] in which the constants increase from La to Lu. Comparative values are listed in Table 15. Other examples of coordination with 2-carboxypyridine 1-oxide have been reported[133,134].

From the fact that 2-aminopyridine 1-oxide acts as a monodentate ligand, it would appear that conjugation of the amino substituent to the pyridine nucleus does not overcome the stability of the free amino group in the presence of coordinated metal ions[127]. The analogous donor structure,



present in adenosine 1-oxide coordinates with ions of the first transition series only in basic solution[135]. The following structure is proposed for these complexes:



However, adenine 1-oxide did not coordinate through the N-oxide but in the following manner:

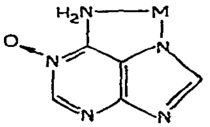


TABLE 16

STABILITY CONSTANTS FOR 1:1 COORDINATION COMPLEXES OF ADENINE 1-OXIDE AND ADENOSINE 1-OXIDE[135]

Metal ion	*Adenine 1-oxide* *log K_1*	*Adenosine 1-oxide* *log K_1*
Mn^{2+}	2.13	5.37
Fe^{2+}	2.80	6.58
Co^{2+}	3.13	7.01
Ni^{2+}	3.52	7.52
Cu^{2+}	7.10	11.32
Zn^{2+}	3.47	7.50

Stability of the resulting complexes is in the order adenosine 1-oxide > adenine 1-oxide > 2 aminopyridine 1-oxide. Both series of complexes fit the Irving-Williams series, Mn < Fe < Co < Ni < Cu > Zn.

D. SUMMARY

It is interesting to note that even though *Dq* values for pyridine N-oxides are larger than those for anions such as chloride or nitrate, or the water molecule, in most cases, the N-oxides will not replace these anions or water from the primary coordination sphere of transition metal ions. With most transition metal perchlorates maximal coordination is achieved regardless of the ligand to metal ratio used in the preparation; however, with anions of greater coordinating ability than perchlorate, various stoichiometries are formed.

Many correlations have been obtained with various properties of pyridine 1-oxide complexes and sigma constants. Considering the variety of linear free energy correlations which have been made one can expect many additional correlations to be made. The reasons for the wide-spread correlations involving this system are the ready availability of a large number of substituted pyridine 1-oxides and the wide range of basicities with a concomitant minimal change in steric interaction at the reaction site. These properties are also present in other heterocyclic N-oxides, *e.g.*, acridine and quinoline N-oxides. The investigation of the chemistry of these two systems will probably give rise to several more correlations.

It should be noted however, that the six coordinate complexes are octahedral if only the MO_6 moiety is considered. If the entire ligand is considered the symmetry of the complex is lower than octahedral[136]. Further examination of the exact symmetry of these complexes is necessary.

Although much work has been done, there is still a considerable amount remaining. The nature of the metal-oxygen bond and the geometry of the complex is still not well understood. Questions such as these and others remain unanswered.

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Corrigenda

Coordin. Chem. Rev., Vol. 3, No. 1, page 103, line 4 below the Table for distortion read distribution.

Vol. 3, No. 2, page 144, line 11, Ru(NO)dtc$_2$ does not exist and should therefore be deleted. Reference 13 refers to Fe(NO)dtc$_2$.

p. 166, delete present reference 13, replace by:

13 M. COLAPIETRO, A. DOMENICANO, L. SCARAMUZZA, A. VACIAGO AND L. ZAMBONELLI, *Chem. Comm.*, (1967) 583.