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COORDINATION COMPLEXES OF THE *N*-OXIDES OF AROMATIC DIIMINES AND DIAZINES

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ABBREVIATIONS

For example, if the designation of the parent amine is am, the corresponding *N*-oxide is abbreviated as *N*-amO and the *N*,*N*-dioxide as *N*,*N*-amO$_2$. Abbreviations for the various amines are as follows

py: pyridine
bipy: 2,2′-bipyridine
phen: 1,10-phenanthroline

pyz:	pyrazine
pym:	pyrimidine
pdz:	pyridazine
qx:	quinoxaline
phz:	phenazine

dpoq is the abbreviation for 2,3-di(pyridine *N*-oxide)quinoxaline.

A. INTRODUCTION

The metal complexes of heterocyclic monoamine *N*-oxides (e.g., the *N*-oxides of pyridine, quinoline, acridine, piperidine, etc. and substituted derivatives) have been the subject of numerous studies in recent years [1—3]. In these complexes the *N*-oxide coordinates as a unidentate oxygen ("oxo") [4] ligand. The N—O oxygen also has the ability to coordinate as a bridging group between neighboring metal ions as in several bi- or poly-nuclear Cu(II) complexes which exhibit subnormal magnetic moments [2,3,5]. Some monoamine *N*-oxides involving substituents with coordinating ability may act as chelating (e.g., 2-amino- [6], 2-hydroxy- and 2-mercapto-pyridine *N*-oxides [7,8], 8-quinolinol *N*-oxide [9], and picolinate *N*-oxide [10]) or bridging, bidentate (e.g., nicotinate [11] and nicotinamide *N*-oxides [12]) ligands, depending on the ring position of the substituent.

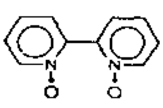
Until recently relatively little was known about the metal complexes of the *N*-oxides of aromatic amines involving two or more ring nitrogen atoms. The parent bases include some of the best known chelating agents (e.g., 2,2′-bipyridine(bipy) and 1,10-phenanthroline(phen)) [13—16] as well as several bridging, bidentate ligands (e.g., pyrazine(pyz), quinoxaline (qx), and phenazine(phz)) [17—23]. A number of metal complexes with the *N*-oxides of several of these bases were synthesized in the late 1950's and early 1960's [24—28]. A brief account of the developments in this field up to 1971 has been described in previous reviews on the coordination complexes of aromatic amine *N*-oxides [2,3]. Recently, numerous new metal complexes with ligands of these types have been prepared at these and other laboratories. The present review deals in some detail with the metal complexes of the *N*-oxides and *N*,*N*-dioxides of aromatic diimines and diazines. The metal complexes of *N*-oxides of related compounds (e.g., five membered ring heterocycles) are also briefly discussed.

B. THE LIGANDS

(i) Methods of preparation

Aromatic amine *N*-oxides are generally prepared in satisfactory yields by direct *N*-oxidation of the parent aromatic amine with an organic peracid, such as monoperphthalic acid or hydrogen peroxide in acetic acid [29—34]. Other preparative methods involve cyclization reactions of organic compounds with aliphatic chains [29—31,35,36]. Since the majority of ligands reviewed herein are the *N*-oxides of bipy, phen, pyz, qx and phz, the methods used for their preparation are briefly covered below.

Bipy and phen N-oxides. Bipy is converted quite easily to the *N,N*-dioxide-(*N,N*-bipyO_2, I) by oxidation with H_2O_2 and glacial acetic acid [27,37—39]. The corresponding mono-*N*-oxide (*N*-bipyO, II) can be isolated in the form of its picrate salt from the mother liquor after the removal of *N,N*-bipyO_2 has been effected [38]. In the case of phen, oxidation at 70—75°C in the presence of glacial acetic acid and H_2O_2 leads to the relatively facile isolation of the mono-*N*-oxide (*N*-phenO, III) [40,41]. The corresponding *N,N*-dioxide-(*N,N*-phenO_2) is rather difficult to isolate because of its extreme solubility in water [42]. The compound may be prepared by refluxing phen in glacial acetic acid in the presence of an excess of H_2O_2 and NaOH, extracting the crude precipitate with ethanol and isolation of the *N,N*-dioxide in the form of the picrate salt [42].



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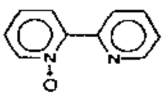

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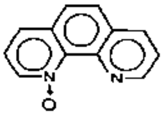

(III)

Pyz, qx and phz N-oxides. Pyrazine 1-oxide and 1,4-dioxide (*N*-pyzO, (IV) and N,N-pyzO_2) and the corresponding derivatives of pyrimidine (pym) and pyridazine (pdz) are prepared by treatment of the parent base with H_2O_2 and glacial acetic acid at 70—90°C. Performance of the *N*-oxidation in the presence of excess H_2O_2 and at higher temperatures (95°C) favors the formation of the dioxides [43—47]. Quinoxaline 1-oxide and 1,4-dioxide (*N*-qxO, (V) and *N,N*-qxO_2) and phenazine 5,10-dioxide (*N,N*-phzO_2) are also prepared by the same general methods used for the pyz derivatives [48—52]. Phenazine 5-oxide (*N*-phzO, (VI)), is obtained in good yields by a cyclization reaction involving condensation of nitrobenzene and aniline in the presence of an alkaline condensing agent in an inert diluent (e.g., KOH and benzene, respectively) [53,54]. It should be noted at this point that several derivatives of the pyz and qx *N*-oxides can also be obtained by cyclization reactions (e.g., 2-aminopyrazine *N*-oxides are prepared by reaction of α-aminonitriles with α-keto oximes) [31,55,56].

(ii) Properties and substituent effects

N-oxidation leads to significant alteration of the reactivity of the aromatic ring owing to a reversal in the electron density distribution about the ring when compared with that observed for the parent amine [57—60]. The N^+—

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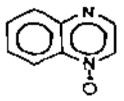

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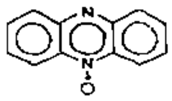
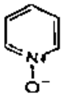


(VI)

O^- group is strongly polarizable in both directions and can act either as an electron-attracting or an electron-donating group thereby facilitating both electrophilic and nucleophilic substitutions [61]. In contrast electrophilic substitution is not facile for aromatic amines.

Before formation of the N—O bond, the nitrogen lone pair of electrons are in a sp^2 orbital. Thus, in aromatic amine *N*-oxides the N—O bond is in the same plane as the aromatic ring and the oxygen $2p\pi$ electrons interact directly with the π-electron system of the ring [29,31]. The unsubstituted pyridine *N*-oxide (*N*-pyO) involves nearly equal contributions [62] from canonical structures VII, VIII and IX. Electron-withdrawing substituents enhance the contributions of structural type VIII, while the contributions of canonical



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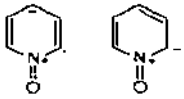

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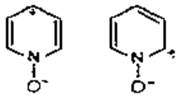
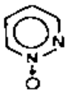


(IX)

forms like IX increase in the presence of electron-releasing ring substituents or with increasing size of the parent heterocycle [2,3,8,9,31,63]. The effects of ring substituents on the various properties of both free and complexed pyridine *N*-oxides, as well as successful correlations of the substituent σ (Hammett) constants to these properties have been discussed in previous reviews of aromatic amine *N*-oxide metal complexes [1—3] (see also refs. 64—71). The presence of electron-withdrawing substituents results in a shift of the ν_{N-O} mode of the free *N*-oxide to higher frequencies due to the increased double-bond character of the N—O bond in response to the larger contribution of canonical forms like VIII, while electron-releasing substituents have the opposite effect leading to a ν_{N-O} frequency decrease. For example, 4-nitro-, 4-methoxy- and unsubstituted pyridine *N*-oxides exhibit the ν_{N-O} band at 1279, 1212 and 1243 cm^{-1}, respectively [69,72,73]. The N—O bond order in aromatic amine *N*-oxides is ca. 1.5 [74,75]. The difference in dipole moments between the parent base and its *N*-oxide is generally smaller with increasing electron-withdrawing and larger with increasing electron-releasing character of the substituent, viz., μ in D(Debye units): pyridine, 2.22; *N*-pyO, 4.24; 4-nitro-pyridine, 1.65; 4-nitro-*N*-pyO, 0.69; 4-methoxy-pyridine, 2.96 and 4-methoxy-*N*-pyO, 5.08 [76].

The diazine mono-*N*-oxides differ from *N*-pyO in that an aza (=N—) group is also present as a member of the aromatic ring. The strong electron-withdrawing character of the aza-group [63,77] (σ constants equal to +1.0, +0.6 and +0.8, respectively, for 2-, 3- and 4-aza substituents on the ring [77]) leads to the following ν_{N-O} values: *N*-pdzO (X), 1342; *N*-pymO (XI), 1281 and *N*-pyzO, 1319 cm^{-1} [78,79]. The dipole moments of the parent bases and *N*-oxides also follow the expected trend, viz., μ in D units: pdz, 3.94, *N*-pdzO, 5.21; 4-methyl-pym, 2.42, 4-methyl-*N*-pymO, 3.72 and pyz, 0.0, *N*-pyzO, 1.61 [80—82]. The presence of the aza-group in *N*-pyzO leads to a significantly larger contribution of canonical form XII than that occurring with canonical forms VIII in *N*-pyO [82]. Similar trends are also observed when *N*-qxO and *N*-phzO are compared to the parent bases or the monoazine *N*-oxide analogs, quinoline and acridine *N*-oxides, respectively. Thus ν_{N-O} values are as follows (cm^{-1}): *N*—qxO, 1319—1325 [83—85] (1380 also reported [86]); quinoline *N*-oxide, 1229 [71]; *N*-phzO, 1349, 1257 [84,87], and acridine *N*-oxide, 1332 [88]. Comparison of some dipole moments yields (μ in D units): qx, 0.82, *N*-qxO, 1.87 [89]; 2-chloro-phz, 2.46, 2-chloro-*N*-phzO, 2.69, 2-chloro-*N*,*N*-phzO$_2$, 3.16 and 2-nitro-phz, 6.61, 2-nitro-*N*-phzO, 5.85 [90].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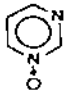
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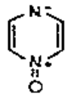
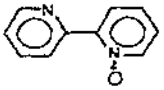

(XII)

For the diazine *N*,*N*-dioxides the N—O groups in the *para*-derivatives (*N*,*N*-pyzO$_2$, *N*,*N*-qxO$_2$ and *N*,*N*-phzO$_2$) are weaker electron-withdrawing substituents relative to the aza-group (σ values of 0.4 vs 0.8 [77]). In addition, there is the possibility of internal electron-release effects between the two N—O groups in view of the ambivalent nature of this substituent [58,59,61, 91—93]. Thus the overall effect on the ν_{N-O} frequency in these dioxides is much less pronounced than that observed with the aza-substituent (*N*,*N*-pyzO$_2$, 1259 [78]; *N*,*N*-qxO$_2$, 1287—1284 [83,84], also showing bands with N—O characteristics at 1346 and 1373 [83,86] and *N*,*N*-phzO$_2$, 1270, 1257 cm^{-1} [84,94,95]). Comparison with the ν_{N-O} frequencies in *N*-pyO, quinoline *N*-oxide and acridine *N*-oxide (vide supra) suggests that in *N*,*N*-pyzO$_2$ and *N*,*N*-qxO$_2$, the contribution of canonical forms similar to VIII is enhanced, but in *N*,*N*-phzO$_2$ the contribution of canonical forms similar to IX appears to be predominant. The fact that the N—O bond has more double bond character in diazine mono-*N*-oxides rather than the corresponding *N*,*N*-dioxides is also demonstrated by the results of the crystal structure determinations for *N*-phzO and *N*,*N*-phzO$_2$ [96—100]. In fact the N—O distance in *N*-phzO is 1.24 Å [96], while that of both *N*-oxide groups in *N*,*N*-phzO$_2$ is 1.264 Å [99].

In bipy and phen *N*-oxides and *N*,*N*-dioxides the inductive effects of the aza- or NO-substituent of the first pyridine ring on the NO group of the second pyridine ring are substantially less pronounced than those observed with the diazine oxides [93,101,102]. In fact, the ν_{N-O} bands in these ligands appear at frequencies very close to that of unsubstituted *N*-pyO, viz. (cm^{-1}): *N*-bipyO, 1250, 1232 [38,103–106]; *N*,*N*-bipyO$_2$, 1262, 1255 [28] and *N*-phenO, 1269, 1249 [105,107,108] (the IR spectrum of *N*,*N*-phenO$_2$ has not been reported in the pertinent literature) [42,109]. Bipy exists in the *trans*-form in the crystal [110,111], but assumes the bidentate, *cis*-configuration in its metal chelates [112,113]. The same behavior appears to characterize *N*-bipyO and *N*,*N*-bipyO$_2$ which have the *trans*-configuration (XIII and XIV, respectively) in the crystal [27,28,104], but convert to the *cis*-form (II and I, respectively) in the metal chelates [27,28,105,106]. Phen, however, is rigidly held in a *cis*-configuration and is almost always found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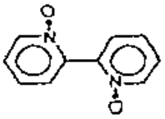

(XIV)

as a planar ligand [13,15,114]. Presumably, *N*-phenO and *N*,*N*-phenO$_2$ are in the *cis*-form in the crystal [107] and the metal chelates [105,108].

The vapor UV spectrum of *N*-pyO is characterized by a very intense band at 278 nm and a relatively less intense absorption at 341 nm. These bands are due to the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively. At higher energies two additional bands attributable to $\pi\rightarrow\pi^{**}$ and $n\rightarrow\pi^{**}$ transitions are observed [115]. On proceeding from *N*-pyO to quinoline *N*-oxide and finally to acridine *N*-oxide, the energies of the UV-visible bands decrease [29,116,117]. In the corresponding diazine mono-*N*-oxides, there is a tendency for an increase in energy for the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions relative to the spectra of the parent monoazine *N*-oxides as a result of the introduction of an aza-group into the pyridine ring [29,31,44,47,118–127]. In the case of diazine *N*,*N*-dioxides, the $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions are shifted toward lower energies relative to the spectra of the corresponding mono-*N*-oxides. This is due to the less pronounced inductive effect of the N—O substituent in comparison to the aza- group (vide supra) [29,31,44,47,118–127]. *N*-BipyO and *N*-phenO exhibit two or three $\pi\rightarrow\pi^*$ transition bands [128] at 200–281 nm and $n\rightarrow\pi^*$ transition bands [129] at higher wavelengths (295–325 nm) [105, 106,108].

(iii) Donor properties and some reactions

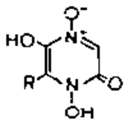
The oxygen in *N*-oxides is basic and hence susceptible to electrophilic addition by metal ions, Lewis acids, protons, halogens and organic electron-pair acceptors [1–3,29]. The diimine and diazine mono *N*-oxides contain, in addition to the *N*-oxide oxygen, a ring nitrogen with the ability to function as an electron-pair donor. Several adducts of the ligands under study with mineral acids, halogens and phenols or alcohols have been reported. Thus, *N*-bipyO [104], *N*-phenO [107] and *N,N*-bipyO$_2$ [130] form crystalline salts (1 : 1 adducts) with HCl, HBr, HI, HClO$_4$, HBF$_4$ and HSbCl$_6$ in addition to the deutero acids. The IR spectra of these salts suggest that hydrogen bonding occurs and is of the type N—H· ·O in the former two cases [104,107] and O—H· · ·O in the latter case [130]. Adducts of *N*-phzO with HClO$_4$ (probably at a 2 : 1 molar ratio) have been co-precipitated with the Cr(III), Co(II) or Ni(II) perchlorate complexes [84,87] (vide infra). In the case of *N*-pyzO, *N*-pymO and *N*-pdzO, adducts with iodine [79,131] and phenol [132] have been studied. The three diazine mono-*N*-oxides coordinate through the oxygen atom to iodine [79,131]. Infrared and thermodynamic data suggest that the donor ability toward iodine decreases along the series *N*-pyO > *N*-pymO > *N*-pyzO > *N*-pdzO [79,131]. Whether oxygen or nitrogen is the donor site, it is not surprising that the diazine mono-*N*-oxides are weaker donors than both *N*-pyO and pyridine, since both the aza- and N—O groups are base weakening substituents [63,77,131]. For hydrogen bond formation with phenol, the donor strength was found to decrease along the series *N*-pyO > *N*-pymO > *N*-pdzO > *N*-pyzO [132]. Thus, the donor ability toward I$_2$ appears to be determined by the π-electron density at the oxygen atom [81,131], whereas the hydrogen bond strength (adduct formation with phenol) is determined to a large extent by dipole—dipole forces [132]. It should be mentioned that since a larger σ constant is found for the aza- than for the N—O substituent in 4-substituted aromatic compounds, one might expect nitrogen to be the donor site in the *N*-pyzO adduct with I$_2$ (in 2- or 3-substituted derivatives $\sigma_{=N-} < \sigma_{N-O}$ [77]) [131]. The fact that oxygen is the donor site in this case was discussed as follows [131], "It may be that steric as well as electronic factors govern the choice of the donor site. Steric repulsion between the hydrogens α to nitrogen and the large iodine molecule could cause oxygen to be the donor site even if the electronic factors are not completely favorable for it to do so. Gardner and Ragsdale suggested that such steric repulsions were important in order to explain why the association constants of pyridine and pyridine *N*-oxide iodine complexes were so close, while their pK_a values differed by 4.5 pK_a units [133]".

Examination of the donor properties of the simplest six-membered aromatic ring amine and amine *N*-oxide (pyridine and *N*-pyO, respectively) show that the nitrogen in pyridine is a better donor than the oxygen in *N*-pyO [79,131] toward both the hydrogen ion [64,134] and a Lewis acid such as I$_2$ [133,135,136]. It is obvious from the above discussion that the *N,N*-dioxides under study should function as weaker ligands than the corresponding diazines or diimines. For α,α-diimine mono-*N*-oxides which generally act as bidentate, chelating N,O-ligands [105—107], it follows that the donor strength is intermediate between that of the corresponding diimine and *N,N*-dioxide. However, in the case of *N*-pyzO, *N*-qxO, *N*-phzO and related compounds, it is not certain which of the two available lone pairs of electrons will participate in coordination [79,131]. As may be seen later in the text, compounds of this type can coordinate either as unidentate O- or N-bonding or as bidentate, bridging (O,N-bonding) ligands. It should be mentioned at this point that when *N*-pyzO acts as an O-bonding ligand, it is a weaker base [63,77] or electron-pair donor [79,131,132] than *N*-pyO. Nevertheless, pyrazine exhibits a pronounced tendency for metal-to-ligand π-bonding in its transition metal complexes [18] and gives rise to a crystal field having comparable strength to that of pyridine [18,137]. Hence, the nitrogen in *N*-pyzO might be expected to exhibit donor ability comparable to that of pyridine or pyrazine.

The organic chemistry of aromatic amine *N*-oxides has been reviewed [29—31,61,63,138]. Metal complexation is the subject of this and previous reviews [1—3]. At this point some reactions between *N*-oxides and labile inorganic or organometallic compounds should briefly be mentioned. Several reducing agents cause the deoxygenation of *N*-oxides, e.g., PCl_3 [139], $TiCl_3$ [140], Fe or Zn powder in acetic acid [141] or alkaline media [142], ferrous salts [143], stannous chloride in HCl [144] and $NaBH_4$ + $AlCl_3$ [135]. Redox reactions of this type also have been observed during attempts at complex formation between aromatic amine *N*-oxides with V^{3+} salts [146—148]. Usually, part of the ligand oxidizes V^{3+} to VO^{2+} and vanadyl salt *N*-oxide complexes are precipiated [146,147]. Under strictly inert conditions V^{3+} salt-*N*-oxide complexes contaminated with various amounts of VO^{2+} derivatives have been isolated [148]. Reaction of aromatic amine *N*-oxides with PCl_5. $POCl_3$ or KCN leads to deoxygenation of the *N*-oxide with simultaneous insertion of halogen or CN groups at the 2- or 4-ring position [46,149,150]. Reactions of *N*-pdzO with phenylmagnesium or phenyllithium derivatives result in deoxygenation and introduction of phenyl substituents on various ring carbons [151,152].

Aromatic amine *N*-oxides can generally displace π-ligands from their metal complexes. Thus, they displace ethylene in Pt(II) [1] and Pd(II) [153] olefin complexes and carbonyl groups from iron, rhenium, molybdenum and other metal carbonyls [154,155]. Metallation of the *N*-oxide aromatic ring has also been reported. Reaction of *N*-pyO with Hg(II) acetate in glacial acetic acid yields $4\text{-}ClHgC_5H_4NO$ [156], while reaction of 4-chloro-3-methylpyridine *N*-oxide with *n*-BuLi results in the insertion of Li at the 6-position of the aromatic ring, via an *N*-oxide—*n*-BuLi adduct intermediate [157].

It should be mentioned at this point that a number of the ligands which are the subject of this review are biologically important compounds. Thus, iodinin, a potent antibiotic from *Chromobacterium iodinum* has been identified as 1,6-dihydroxyphenazine 5,10-dioxide [52], while the antibiotic aspergillic acid, isolated from the mold *Aspergillus flavus* is 1-hydroxy-2-pyrazinone [158]. Other closely related compounds with antibiotic activity have also been isolated from microbial sources: 1,6-dihydroxyphenazine 5-oxide [159]; myxin, which is the 6-methoxy derivative of iodinin [160]; hydroxy-, muta- and neo-aspergillic acids [161]; pullcheriminic acid (XV) [162]; mycellianamide (XVI) [163] and enimycin (XVII) [164]. In addition, some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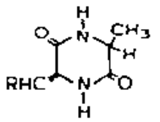
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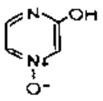

(XVII)

of the parent bases are biologically important (e.g., purines and pyrimidines). The interesting chemistry of the *N*-oxides under review lies in the ability of diimine *N*-oxides and *N,N*-dioxides to act as bidentate chelating agents, forming six and seven-membered rings, respectively, while the diazine analogs can act either as unidentate ligands or bidentate, bridging ligands. In the case of unidentate diazine mono-*N*-oxide ligands, coordination through N- or through O- has been observed in various complexes. Finally, several transition metal complexes with the above ligands have been found to exhibit subnormal magnetic properties for high spin compounds, arising from either magnetic exchange in the case of bi- or poly-nuclear complexes, or the presence of spin-free—spin-paired equilibria or a half-quenched spin in the case of iron complexes (vide infra).

C. METAL CHELATES WITH 2,2'-BIPYRIDINE- AND 1,10-PHENANTHROLINE-*N*-OXIDES

(i) Generalities

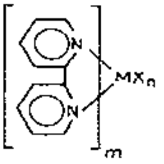
Bipy and phen are members of a class of organic compounds which contain the aromatic diimine (=N—C—C—N=) group. The strong chelating ability of these ligands is considered to result from $d_\pi—p_\pi$ bonding between the metal ion and the ligand which imparts some aromatic character to the five-membered chelate ring (XVIII) [165,166]. The metal chelates of bipy and phen have been extensively reviewed [13—16]. In bipy metal chelates the ligand is generally non-planar, involving twisting of the two aromatic rings about the 2,2'-bond [112,113,128,167,168]. Phen, on the other hand, is almost invariably found as a planar ligand [13,15,114] as previously mentioned. The $\pi \to \pi^*$ transition bands in the UV spectrum of bipy exhibit larger shifts and splittings upon metal chelate formation than the corresponding bands in phen [13—16, 112—114,128,165]. This is predominantly due to the fact that for the former ligand a *trans—cis* rearrangement is necessary for chelation (see structures (I), (II), (XIII), (XIV)), while phen is in the *cis*-form in both the crystal and its chelates. Ferrous chelates with bipy, phen and related ligands are intensely colored. The absorption responsible for this color results from a Laporte-allowed transition of the $t_{2g} \to \pi^*$ (metal-to-ligand) type occurring in the 500 nm region [165,166,169—174]. Metal-to-ligand electron-transfer processes are considerably more important for Fe(II)-bipy or -phen than for the complexes of these ligands with other 3*d* metal ions [170]. *N*-PyO 3*d* metal complexes also show intense metal-to-ligand electron-transfer bands ($t_{2g} \to \pi^*$

in hexacoordinated Fe(II), Co(II) and Ni(II) complexes, and $e_g \rightarrow \pi^*$ in the corresponding Mn(II) and Cu(II) complexes) [175,176].

Bipy and phen give rise to fields of sufficient strength to induce spin-pairing in ferrous and ferric chelates. For example, crystal field splitting (Dq) values obtained for Fe(II); bipy, at least 1330—1400 [171,177] and most probably in the 1650—1900 cm^{-1} range [171]; phen, 1311 cm^{-1} [178]. Cationic chelates of the type $[FeL_3]^{n+}$ (L = bipy, phen; n = 2, 3) exhibit low-spin electronic configurations [171,177,179]. Mixed-ligand ferrous complexes of the type $[FeL_2X_2]$ (L = bipy, phen) exhibit dramatic differences in magnetic behavior with variation of the X groups [14]. Both high-spin (X = Cl, Br, I, N_3) and low-spin (X = CN, NCO, NO_2) compounds have been reported in addition to compounds exhibiting intermediate-spin attributable to spin-free—spin-paired equilibria (X = NCS, NCSe) or a half-quenched spin (X = F, $\frac{1}{2}$ oxalate, $\frac{1}{2}$ malonate) [14,180—185]. Pyridine *N*-oxides give rise to considerably weaker ligand fields and their 3*d* metal complexes are usually of the high-spin type [1—3]. Several binuclear Cu(II) chloride complexes with unidentate aromatic amine *N*-oxides with the general formula $[Cl_2CuL_2CuCl_2]$ have been reported to involve subnormal magnetic moments. Spin—spin coupling between neighboring Cu^{2+} ions has been shown to occur via a superexchange mechanism operating through the orbitals of the bridging oxygen atoms [5, 186,187]. Magnetic moments intermediate to those corresponding to high- and low-spin configurations have been reported for a number of iron complexes with 2,6-lutidine *N*-oxide (L), viz: $[FeL_4](ClO_4)_2$, square-planar involving a half-quenched spin [188]; $[FeL_6](NO_3)_3$, appearing to involve spin-free—spin-paired equilibria [189] and a number of mixed ligand (2,6-lutidine *N*-oxide—acetic anhydride) Fe(III) complexes, which are thought to involve partial spin-pairing [190].

Chelation of bipy or phen through the two nitrogen atoms results in small, but observable frequency shifts of the ring vibrational modes (ν_{CC} and ν_{CN}, 1600—1000 cm^{-1} region) [191—195]. Several other ligand bands also undergo characteristic shifts (e.g., the γ_{CH} mode at ca. 760 cm^{-1} in the free ligands) [194,195]. In the case of *N*-pyO and derivatives, metal complex formation results almost invariably in substantial negative frequency shifts of the ν_{N-O} mode, which occurs in the range 1350—1200 cm^{-1} for the majority of the free ligands [1—3,196,197]. Other ligand bands in the 1000—600 cm^{-1} region undergoing characteristic shifts upon complex formation are the δ_{N-O} (ca. 880—830 cm^{-1}) and γ_{CH} modes [196,197]. The lower frequency IR spectra of bipy and phen metal chelates have been the subject of several publications [191,192,194,198—202]. The most reliable ν_{M-N} assignments were obtained using the metal-isotope technique [200—202]. The same technique also has been used for a number of aromatic amine *N*-oxide metal complexes [203]; thus confirming previous ν_{M-O} band assignments [68—71,196,197,204—207].

While bipy and phen form five-membered metal chelate rings (e.g., XVIII), the corresponding mono-*N*-oxides and *N*,*N*-dioxides form, respectively, six- (e.g., XIX) and seven- (e.g., XX) membered chelate rings.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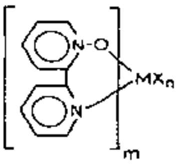
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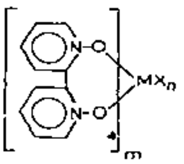

(XX)

(ii) Metal chelates of 2,2′-bipyridine- and 1,10-phenanthroline-mono-N-oxides

Thus far only first row transition metal ion complexes with *N*-bipyO and *N*-phenO have been prepared and characterized. Complex formation between *N*-bipyO and Fe^{3+} was described in 1956 [38], while *N*-phenO chelates with $CoCl_2$, $NiCl_2$ and $CuCl_2$ were prepared in 1965 but not fully characterized [41]. More recently, a series of 3*d* metal (M = Cr through Zn) chloride, perchlorate and nitrate chelates with both *N*-bipyO and *N*-phenO were synthesized and characterized [105,106,108,208—215]. The $CuBr_2$ chelate with *N*-phenO was also reported [215]. Table 1 is a compilation of the various complexes which have been prepared. Characterization has been based on spectral (IR-electronic), magnetic, conductance, X-ray powder diffraction, and in the case of iron chelates, Mössbauer studies [105,106,108,208—215]. *N*-bipyO and *N*-phenO appear to function invariably as bidentate, O,N-chelating agents forming chelate rings of the type shown in (XIX).

The chelates listed in Table 1 were generally prepared via the ligand and metal salt solutions in a mixture of absolute ethanol and triethylorthoformate (a dehydrating agent [216]) [105,106,108,208—215]. Co(II), Ni(II) and Cu(II) halide complexes with *N*-phenO also have been prepared by using absolute ethanol as the reaction medium [41,215]. Coordination of the ligands through the N—O oxygen was established by negative frequency shifts of the ν_{N-O} bands which occur in the 1265—1232 cm^{-1} region in the free ligands [38, 103—108] (cf. Section B(ii)). The magnitude of the negative shift for each of the two ligand ν_{N-O} doublets ranges between 15—50 cm^{-1}. Coordination of *N*-bipyO and *N*-phenO through nitrogen is demonstrated by characteristic frequency shifts of several IR bands attributable to the pyridine fragment of the ligands [104,107] (e.g., $\nu_{CC} + \nu_{CN}$ modes at 1650—1400 and γ_{CH} modes at 860—700 cm^{-1}) [105,106,108,208—215]. Metal—ligand stretching vibrational modes were tentatively identified at the following wavenumber (cm^{-1}) regions, ν_{M-O}: 450—360 for hexacoordinated M(III) chelates (M = Cr, Fe) [105,208,209,211,213], 430—360, 400—375 and 390—340 for tetra-, penta- and hexa-coordinated, respectively, M(II) chelates, (M = Mn, Fe, Co, Ni, Cu, Zn) [105,106,108,208,210—212]; and ν_{M-N}: 390—340 for hexacoordinated M(III) chelates, 350—250 for M(II) chelates [105,106,108,208—214]. It is of interest to note that most of the Fe(II) complexes with *N*-bipyO and *N*-phenO which are of the high-spin type exhibit the ν_{Fe-N} mode at substantially lower frequencies than observed for the bipy and phen low-spin

TABLE 1

3*d* metal chelates with *N*-bipyO(L) and *N*-phenO(L′)

Chelate	Coordination number	μ_{eff} (B.M.) [a]	Ref.
$[CrL_3](ClO_4)_3 \cdot 2 H_2O$	6	3.73	209
$[MnL_3](ClO_4)_2$	6	5.73	106
$[FeL_3](ClO_4)_2$	6	5.45	106
$[FeL_3](ClO_4)_3 \cdot 2 H_2O$	6	3.66	209
$[CoL_3](ClO_4)_2$	6	4.86	106
$[NiL_3](ClO_4)_2$	6	3.36	106
$[CuL_2](ClO_4)_2$	4 [b]	1.83	106
$[ZnL_3](ClO_4)_2$	6		106
$[CrL'_3](ClO_4)_3$	6	3.79	209
$[MnL'_3](ClO_4)_2$	6	5.76	108
$[FeL'_3](ClO_4)_2$	6	5.47	108
$[FeL'_3](ClO_4)_3$	6	2.51	209
$[CoL'_3](ClO_4)_2$	6	4.89	108
$[NiL'_3](ClO_4)_2 \cdot 2 H_2O$	6	3.21	108
$[CuL'_2](ClO_4)_2$	4 [b]	2.19	108
$[ZnL'_3](ClO_4)_2$	6		108
$[CrL(O_2NO)_2](NO_3)$	6	3.89	213
$[FeL_3](NO_3)_3$	6	2.91	213
$[FeL_2(ONO_2)_2](NO_3)$	6	5.74	213
$[CoL_2(O_2NO)](NO_3)$	6	4.64	210
$[NiL_3](NO_3)_2 \cdot H_2O$	6	3.36	210
$[CuL_2(O_2NO)](NO_3)$	6	2.24	210
$[ZnL_2(O_2NO)](NO_3)$	6		210
$[CrL'_2(O_2NO)](NO_3)_2 \cdot 2 C_2H_5OH$	6	3.78	213
$[FeL'_3](NO_3)_3$	6	3.88	213
$[FeL'_2(O_2NO)](NO_3)_2$	6	6.12	213
$[CoL'_3](NO_3)_2$	6	4.54	210
$[CoL'_2(ONO_2)_2]$	6	4.73	210
$[NiL'_3](NO_3)_2$	6	3.22	210
$[NiL'_2(O_2NO)](NO_3)$	6	3.32	210
$[CuL'_2](NO_3)_2$	4 [b]	2.18	210
$[ZnL'_3](NO_3)_2$	6		210
$[CrL_2Cl_2]Cl \cdot 4 H_2O$	6	3.88	211
$[MnLCl_2] \cdot C_2H_5OH$	4 [c]	6.08	211
$[FeLCl_2] \cdot C_2H_5OH$	4 [b]	3.46	211
$[FeL_2Cl_2][FeCl_4]$	6 and 4 [c]	5.76	211
$[CoLCl_2] \cdot C_2H_5OH$	4 [c]	4.67	211
$[NiL_2Cl_2] \cdot H_2O$	6	3.34	211
$[CuLCl_2]_x$	6 [d]	1.99	211
$[ZnLCl_2]$	4 [c]		211
$[CrL'_2Cl_2]Cl \cdot H_2O$	6	3.81	212
$[MnL'_2Cl_2]$	6	5.60	212
$[ClL'MnCl_2MnL'Cl] \cdot 2 H_2O$	5	5.75	212
$[FeL'Cl_2]_x$	4 or 5 [e]	5.45	212
$[FeL'_2Cl_2]Cl$	6	5.79	212
CoL'_2Cl_2	(*f*)	(*f*)	41

Chelate	Coordination number	μ_{eff} (B.M.) [a]	Ref.
$[CoL'_2Cl_2]\cdot H_2O$	6	4.92	212
$[CoL'Cl_2]\cdot H_2O$	4 [c]	4.47	212
$NiL'_2Cl_2\cdot 0.5\,H_2O$	([f])	([f])	41
$[NiL'_2Cl_2]\cdot 2\,H_2O$	6	2.97	212
$CuL'_2Cl_2\cdot 2\,H_2O$	([g])	2.17	41, 212
$CuL'Cl_2\cdot H_2O$	([h])	2.00	215
$[CuL'Br_2]_2$	5 [i]	1.90	215
$[ZnL'_3][ZnCl_4]\cdot 2\,H_2O$	6 and 4 [c]		212

[a] Room temperature (290—300 K). [b] Square planar. [c] Tetrahedral. [d] Polynuclear, Cl-bridged. [e] Monomeric, involving a distorted square planar symmetry, or binuclear, Cl-bridged, pentacoordinated. [f] Not characterized. [g] Coordination no. 5 ($[CuL'_2Cl]Cl\cdot 2\,H_2O$) or 6 ($[CuL'_2Cl_2]\cdot 2\,H_2O$). [h] Coordination no. 4 or 5 (depending on whether H_2O is coordinated). [i] Binuclear, Br-bridged.

analogs [105,106,108,208,212], as may be expected [198—202,217]. Several of the *N*-bipyO and *N*-phenO complexes (Table 1) contain water or ethanol of crystallization. Infrared spectra in the ν_{OH} region (3600—3100 cm^{-1}) generally consist of very broad absorption bands indicative of the presence of several maxima [105,108,208—214]. The lack of a relatively sharp single absorption maximum in the IR was interpreted as being indicative of the presence of lattice water or ethanol [218], rather than coordinated aquo [219] or ethanol [220] ligands. The lattice ethanol is easily removed by treatment at 65° C and 60 mmHg vacuum for 24 h. However, only part of the water of crystallization is removed under the same conditions [211,213]. Strong association of lattice water is also common in metal chelates of the parent diimines [221—225], the water molecules residing in "pockets" formed by the chelate rings [221].

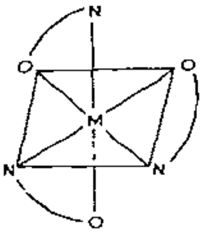
With respect to the anionic groups present in the *N*-bipyO and *N*-phenO metal chelates, the perchlorate group has been found to be exclusively ionic, as suggested by the single character of the ν_3 and ν_4 fundamental vibrational modes of the ClO_4 group [105,106,108,209,226]. Thus, the perchlorate containing compounds of *N*-bipyO and *N*-phenO are characterized by complex cations of the type $[ML_3]^{n+}$ (M = Cr, Fe; $n = 3$ and M = Mn, Fe, Co, Ni, Zn; $n = 2$) and $[CuL_2]^{2+}$ (Table 1). In the case of the metal nitrate chelates of these ligands a number of the same complex cations are formed, viz. $[ML_3]^{n+}$ (M = Fe; $n = 3$ and M = Co, Ni, Zn; $n = 2$) and $[CuL_2]^{2+}$ involving ionic nitrate (Table 1). In addition a number of complexes containing coordinated nitrate ligands have been isolated, viz. $[Cr($*N*-bipyO$)(O_2NO)_2](NO_3)$, $[Cr($N-phenO$)_2(O_2NO)](NO_3)_2\cdot 2\,C_2H_5OH$, $[Fe($*N*-bipyO$)_2(ONO_2)_2](NO_3)$, $[Fe($N-phenO$)_2(O_2NO)](NO_3)_2$, $[M($*N*-bipyO$)_2(O_2NO)](NO_3)$ (M = Co, Cu, Zn), $[Co($*N*-phenO$)_2(ONO_2)_2]$ and $[Ni($*N*-phenO$)_2(O_2NO)]$-

(NO_3) [105,210,213]. Distinction between ionic and various modes of nitrato coordination was based [105,210,213] on the number and frequency of occurrence of the fundamental and combination vibrational modes of the nitrate group [227—230]. Uni- and bi-dentate nitrato coordination was assigned, based on the frequency difference between the combination bands due to ($\nu_1 + \nu_4$) in the 1800—1700 cm^{-1} region, since bidentate nitrato ligands exhibit larger ($\nu_1 + \nu_4$) splittings than unidentate coordinated nitrate [230]. Infrared bands attributable to the ν_{M-O} (nitrato) mode [231,232] were tentatively assigned in the spectra of the chelates involving coordinated nitrato ligands [105,210,213].

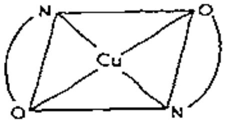
The metal chloride and Cu(II) bromide chelates (Table 1) invariably contain coordinated Cl or Br ligands [105,208,211,212,215]. In two cases, the presence of tetrachlorometallate anions [205,208,211,212] is suggested by IR evidence [233—235] and the compounds were formulated as $[Fe(N\text{-bipyO})_2Cl_2][FeCl_4]$ and $[Zn(N\text{-phenO})_3][ZnCl_4] \cdot 2\,H_2O$. A number of compounds were found to involve both coordinated and ionic chloride groups (e.g., $[CrL_2Cl_2]Cl \cdot nH_2O$; L = *N*-bipyO or *N*-phenO) [105,208,211, 212], while others exhibited bi- or poly-nuclear halogen bridged configurations (e.g., $[Cl(N\text{-phenO})MnCl_2Mn(N\text{-phenO})Cl] \cdot 2\,H_2O$ [212] and $[Br(N\text{-phenO})CuBr_2Cu(N\text{-phenO})Br]$ [215]). Assignments of ν_{MCl} modes were based [105, 208,211,212] on literature assignments for terminal and bridging chloride ligands and tetrachlorometallate anions [19,20,233—239].

The molar conductivities [240] of the solutions of the metal perchlorate chelates in various polar solvents are in agreement with the formulations shown in Table 1 [105,106,108,209]. In the case of a number of metal nitrate or chloride chelates, the Λ_M values in solvents with coordinating ability (e.g., *N,N'*-dimethylformamide, nitromethane) do not agree with the formulations derived from IR evidence [105,108,210—213] (Table 1). Similar behavior has previously been observed in metal nitrate complexes with other aromatic amine *N*-oxides [189,241,242] and metal chloride complexes with bipy [243]. Higher than anticipated Λ_M values are usually due to displacement of nitrato or chloro ligands by solvent molecules [189,241—243], while in the case of metal nitrate complexes low Λ_M values have been attributed to displacement of the *N*-oxide ligand by NO_3 groups which are ionic in the crystal [189,241, 242]. Λ_M determinations for complexes sufficiently soluble in solvents with low coordinating ability, such as nitrobenzene, are generally in agreement with the formulations in Table 1 [105,208,210—213].

The ligand UV bands of *N*-bipyO generally were found to undergo larger shifts and greater splittings than those of *N*-phenO upon metal complex formation. Thus both these ligands appear to behave in a manner similar to the parent bases [13—16,112—114,128,165], i.e., *N*-bipyO undergoes a *trans—cis* rearrangement necessary for chelation, whereas *N*-phenO is in the *cis*-form in the crystal and maintains this configuration in its metal chelates [104—108, 208—214]. Metal-to-ligand electron-transfer bands are generally observed in all the paramagnetic metal chelates with *N*-bipyO and *N*-phenO [105,106,108, 208—214] as is also the case with the parent bases [165,166,169—174] or pyridine *N*-oxides [175,176]. Room temperature μ_{eff} values (Table 1) are normal for high-spin compounds of 3*d* metal ions [244] with the exception of a number of iron complexes. In most cases the high-spin metal chelates exhibit magnetic moments within the limits predicted or observed for tetra-, penta- or hexa-coordinated complexes of 3*d* metal ions [244]. Nevertheless, some hexacoordinated Co(II) and Ni(II) chelates exhibit magnetic moments somewhat below or above (respectively) the "octahedral" region for Co^{2+} or Ni^{2+} [244]. This is not unusual in Co(II) and Ni(II) complexes for which the overall symmetry is lower than O_h [245]. It should be mentioned in this connection that the highest possible symmetry for $[ML_3]^{n+}$ cationic complexes with *N*-bipyO or *N*-phenO is C_3 (XXI) and that for $[CuL_2]^{2+}$ species C_{2h} (XXII) [246]. Several geometrical and optical isomers for the complex cations are possible [246—248]. In addition diastereoisomers of the *N*-bipyO chelates would be expected to be in a *cisoid*-form involving some twisting of the aromatic rings about the 2,2′-bond as is also the case with the bipy ligand [112,113,246—248]. Thus far, no attempts at the resolution of such isomers have been reported.



(XXI)



(XXII)

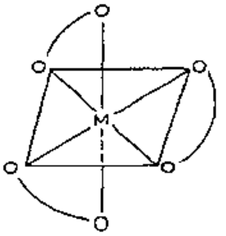
As far as the Fe(II) and Fe(III) chelates with the ligands under discussion are concerned, the tris-Fe(II) complex cations are magnetically normal high-spin compounds while the corresponding tris-Fe(III) complex cations exhibit μ_{eff} values intermediate to those corresponding to high- and to low-spin Fe(III) compounds [105,106,108,209,213]. Determination of *Dq* values from the (*d*—*d*) transition spectra yielded the following values toward hexacoordinated Fe(II): *N*-bipyO, 1160 and *N*-phenO, 1032 cm^{-1}. The fact that these compounds are of the high-spin type in contrast to the bipy and phen analogs (vide supra) is due to ligand—field strengths insufficient [249] to induce spin-pairing in Fe^{2+} [105,106,108]. Spectrochemical parameters for the other hexacoordinated 3*d* metal ions have been published and are as follows: for *N*-bipyO, Cr(III), Dq = 1800—1900 cm^{-1}; Co(II), Dq = 1113 cm^{-1}, β = 0.60; Ni(II), Dq = 1029 cm^{-1}; and for *N*-phenO, Cr(III), Dq = 1919 cm^{-1}; Co(II), Dq = 1144 cm^{-1}, β = 0.66; Ni(II), Dq = 1036 cm^{-1}. *N*-bipyO and *N*-phenO occupy the following relative positions in the spectrochemical series; phen > bipy > *N*-phenO > *N*-bipyO > *N,N*-bipyO$_2$ [105,106,108,209,210,213, 250,251]. In several cases (e.g., for hexacoordinated Fe(II)) *N*-bipyO generates a stronger ligand—field than *N*-phenO.

The ligand—field strength of the mono-*N*-oxides under discussion is sufficient to cause spin-free—spin-paired equilibria in compounds of the type $[FeL_3]X_3$ ($X = ClO_4$ or NO_3) [105,209,213]. As previously mentioned, bipy and phen chelates of this type are low-spin compounds [171,177,179], whereas the *N,N*-bipyO_2 analog is a magnetically normal high-spin complex [27,28]. It should be noted that several weaker ligands than *N*-bipyO or *N*-phenO have been shown to give rise to spin-free—spin-paired equilibria (e.g., *N,N*-diethyldithiocarbamate and 2,6-lutidine *N*-oxide, which show Dq values of 1560 [252] and 1686 [188] cm^{-1}, respectively, toward O_h Cr(III)). That the strength of the ligand—field causes the reported equilibria in $[FeL_3]X_3$ complexes with *N*-bipyO and *N*-phenO is also supported by the fact that ferric chelates involving mixed ligands in the complex cation (i.e., *N*-bipyO or *N*-phenO and the considerably weaker nitrato- or chloro-ligands) are magnetically normal high-spin compounds [105,209,213]. Temperature-dependence studies of the magnetic susceptibilities of $[FeL_3]X_3$ chelates are in favor of the presence of $S = \frac{5}{2} \rightarrow S = \frac{1}{2}$ equilibria, rather than a half-quenched spin ($S = \frac{3}{2}$). In fact μ_{eff} increases (0.4—0.75 B.M.) for these chelates over the temperature range 80—315 K [209,213,214]. Fe(III) complexes involving spin-free—spin-paired equilibria reportedly show an increase in μ_{eff} ranging from 0.5—4.5 B.M. over the same temperature range [253—255]. On the other hand, magnetic moments of ferric complexes with an $S = \frac{3}{2}$ spin state are relatively insensitive to temperature variations, i.e., increases of 0.05—0.15 B.M. at 80—315 K [190,256,257]. Furthermore, a severely distorted structure is required for partially spin-paired hexacoordinated Fe(III) complexes [190], since ligand—field theory excludes a half-quenched spin for octahedral d^5 configurations [258]. Mössbauer parameters for the $[FeL_3]X_3$ chelates with *N*-bipyO and *N*-phenO suggest [214] that the low-spin isomer is present in significantly higher amounts than the high-spin isomer based on chemical isomer shifts (δ) and quadrupole splittings (ΔE_Q) [255,259]. In fact, the δ and ΔE_Q values determined are similar to those reported for ferric complexes exhibiting a $^6A_1$—$^2T_2$ crossover and containing a higher quantity of low-spin isomer [259]. The ΔE_Q values (1.27—1.39 $mm.sec^{-1}$) for the $[FeL_3]X_3$ chelates [214] are substantially lower than those observed for Fe(III) compounds involving a $S = \frac{3}{2}$ spin-state (2.4—3.0 $mm.sec^{-1}$) [260, 261].

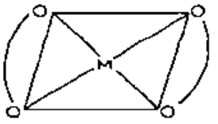
Finally, $[Fe(N\text{-bipyO})Cl_2] \cdot C_2H_5OH$ also has been reported to exhibit a subnormal room temperature magnetic moment [211] (Table 1). In this case the stereochemistry of the complex rather than the ligand—field strength is responsible for the partial spin-pairing ($S = 1$) [211,214], since the tris-chelate *N*-bipyO with Fe(II) is high-spin (vide supra). A square planar configuration was assigned [211] to this complex on the basis of electronic and IR spectral evidence, in addition to the fact that a square planar configuration reportedly [188,262—264] favors partial spin-pairing. The existence of a $S = 1$ ground state rather than a spin-free ($S = 2$)—spin-paired ($S = 0$) equilibrium is supported by temperature-dependence studies of the magnetic susceptibility and Mössbauer effect for the compound [214]. The magnetic moment increases by 0.27 B.M. over the range 86—302 K [214]. This increase is within the range of values reported for other Fe(II) complexes exhibiting a half-quenched spin [180,181,263,264]. This may be compared with compounds exhibiting (S = 2)—(S = 0) equilibria which generally show substantially higher μ_{eff} increases of the order of 2—4.5 B.M. [182,183,185]. Similarly, the ΔE_Q values reported for [Fe(N-bipyO)Cl_2] · C_2H_5OH (1.08 and 1.32 $mm.sec^{-1}$ at 295 and 81 K, respectively) [214] are also within the range of values reported for Fe(II) compounds with a S = 1 ground state [180,181,265], and do not exhibit the variation with temperature associated with a magnetic crossover situation [182, 183,266—269].

(iii) Metal chelates of 2,2′-bipyridine- and 1,10-phenanthroline-N,N-dioxides

Of all the ligands reported here, the coordination ability of N,N'-bipyO_2 has been studied to the greatest extent [2,3]. This is in marked contrast to N,N-phenO_2 for which only one coordination compound has been reported [109]. The paucity of information on the latter ligand may be due to the difficulties encountered in the preparation of this compound [40,42] (vide supra). In the case of the tris- and bis-metal chelates with these dioxide-type ligands (XXIII and XXIV, respectively), higher symmetries are possible when compared to the mono-N-oxide analogs (D_3 for XXIII and D_{2h} for XXIV). N,N-bipyO_2 and N,N-phenO_2 act, in most cases, as bidentate



(XXIII)



(XXIV)

O,O-chelating agents forming seven-membered chelate rings (XX). Complexes of N,N-bipyO_2 (the only N,N-phenO_2 complex reported is [V(N,N'-phenO_2)-Cl_4] [109]) with 3d metal perchlorates, halides, nitrates, persulfates, thiocyanates, hexafluorophosphates and tetrachloroplatinates(II) [26—28,109, 215,251,270—273] are shown in Table 2, while Table 3 lists N,N-bipyO_2 complexes with other metal ions (4d, 5d, lanthanide, actinide and main group) [27,28,155,251,270,273—283]. The synthetic procedures for the preparation of these complexes primarily encompassed the interaction of ligand and metal salt in either water or alcohol solutions. Other reaction media have been used on certain occasions (e.g., dichloromethane for VCl_4 complexes [109] and

TABLE 2

3*d* metal complexes with *N,N*-bipyO_2(L) and *N,N*-phenO_2

Complex	Coordination number	μ_{eff} (B.M.)[a]	Ref.
$[ScL_3](ClO_4)_3$	6		271
$[VLCl_4]$	6	1.50	109
$[V(N,N\text{-phen}O_2)Cl_4]$	6	1.60	109
$[VOL_2](ClO_4)_2$	5	1.63	270
$[CrL_3](ClO_4)_3 \cdot 2\,H_2O$	6	[b]	27, 251
$[CrL_2Cl_2](ClO_4) \cdot H_2O$	6	[b]	27
$[CrL_2Cl_2](PtCl_4)$	6	[b]	27
$[CrL_3](NO_3)_3$	6	3.70	251
$[MnL_3](ClO_4)_2 \cdot H_2O$	6	[b]	27, 251
$[MnL_3](PtCl_4)$	6	6.34	27
$[MnL_3]Br_2 \cdot 2\,H_2O$	6	6.20	251
$[MnL_3]I_2 \cdot H_2O$	6	5.40	251
$[MnL_3](ClO_4)_3 \cdot 3\,H_2O$	6	4.97	26
$[MnL_3]_2(S_2O_8)_3 \cdot 8\,H_2O$	6	5.00	26
$[FeL_3](ClO_4)_3 \cdot 3\,H_2O$	6	6.13	27
$[FeL_3]_2(PtCl_4)_3$	6	[b]	27
$[FeL_3](ClO_4)_3 \cdot L$	6	6.40	251
$[CoL_3](ClO_4)_2 \cdot 2\,H_2O$	6	4.72	27, 251
$[CoL_3](PtCl_4)$	6	[b]	27
$[CoL_3](PF_6)_2$	6	[b]	272
$[CoL_2Cl_2]$	6	4.90	251
$[CoL_3]Br_2 \cdot 4\,H_2O$	6	4.70	251
$[CoL_3]I_2 \cdot 2\,H_2O$	6	4.80	251
$[CoL_3](NO_3)_2 \cdot H_2O$	6	4.60	251
$[CoL_2(NCS)_2]$	6	4.70	273
$[NiL_3](ClO_4)_2 \cdot 2\,H_2O$	6	3.24	27, 251
$[NiL_3](PtCl_4)$	6	[b]	27
$[NiL_3]I_2 \cdot H_2O$	6	3.30	251
$[NiL_3](NO_3)_2 \cdot H_2O$	6	3.30	251
$[NiL_3](PF_6)_2$	6	[b]	272
$[NiL_2(NCS)_2]$	6	3.20	273
$[CuL_3](ClO_4)_2 \cdot 2\,H_2O$	6	2.10	27, 251
$[CuL_2](PtCl_4)$	4	1.90	27
$[CuL_2(OH_2)_2](PtCl_4)$	6	1.98	27
$[CuL_2(OH_2)_2](PtCl_4) \cdot 2\,H_2O$	6	1.99	27
$[CuLCl_2]_2$	5[c]	2.00, 2.20	215, 251
$[CuLBr_2]_x$	5[d]	0.70	215
$CuL(NO_3)_2 \cdot 1.5\,H_2O$	6[e]	2.00	215
$[ZnL_3](ClO_4)_2 \cdot 2\,H_2O$	6		27, 251
$[ZnL_3](PtCl_4)$	6		27, 251
$[ZnL_3](NO_3)_2 \cdot 2\,H_2O$	6		251
$[ZnL_2(NCS)_2]$	6		273

[a] Room temperature (290—300 K). [b] Not reported. [c] Binuclear Cl-bridged. [d] Bi- or polynuclear L-bridged (see text). [e] Possible structural types: $[CuL_2(ONO_2)_2] \cdot 1.5\,H_2O$ or $[CuL_2(O_2NO)](NO_3) \cdot 1.5\,H_2O$.

TABLE 3

N,N-bipyO_2(L) complexes with 4*d*, 5*d*, 4*f*, 5*f* and main group metal ions

Complex	Coordination number	Ref.
$[YL_4](ClO_4)_3$	8	276
$[LnL_4](ClO_4)_3$ (Ln = La — Yb)	8	276, 277
$[CeL_3(NO_3)_2](ClO_4)_2$	[a]	279
$[CeL_4]X_4$ (X = Cl, ClO_4, NO_3)	8	283
$[HL_2]_2(CeCl_6)$	6	283
$[ThL_4](ClO_4)_4$	8	270
$[UO_2L_2](ClO_4)_2$	6	270
$[UO_2L(O_2NO)]$	8	280
$[UO_2L_2(ONO_2)_2]$	8	274
$[UO_2L(O_2SO_2)]$	6	280
$[UO_2L_2(SCN)_2]$	8	280
$UO_2L_{1.5}Cl_2$	[b]	280
$PuO_2Cl_2(L \cdot HCl)_2$	[b]	274
$[ZrOL_3](ClO_4)_2 \cdot 2\,H_2O$	7	270
$[Nb_6Cl_{12}L_2]Cl_2$	[c]	278
$[Mo_2O_4Cl_2L_2] \cdot 2\,H_2O$ [d]	6	270
$[Mo_2O_3Cl_4L_2] \cdot 2\,H_2O$ [e]	6	270
$Mo(NO)_2LCl_2$	[b]	275
$[Re(CO)_3LX]$ (X = Cl, Br, I)	6	155
$[AgL_2](ClO_4) \cdot 3\,H_2O$	2	251
$[CdL_3](ClO_4)_2 \cdot H_2O$	6	27, 251
$[CdL_2Cl_2]$	6	27
$[CdL(SCN)_2]$	4	273
$[HgL_3](ClO_4)_2$	6	251
$[HgLCl_2]$	4	282
$[HgLBr_2]$	4	282
$[HgL(SCN)_2]$	4	273, 282
$Hg_2L(CN)_4$	[f]	282
$[AlL_3](ClO_4)_3 \cdot 2\,H_2O$	6	251
$[(C_6H_5)_3SnCl]_2L$	5	281
$[(C_6H_5)_3Sn(NCS)]_2L$	5	281
$[(CH_3)_2SnLCl_2]$	6	281
$[(CH_3)_2SnL(NCS)_2]$	6	281
$[(CH_3)_3SnL][B(C_6H_5)_4]$	5	281
$[(CH_3)_2SnL_2][B(C_6H_5)_4]_2$	6	281
$[(C_6H_5)_2SnL_2][B(C_6H_5)_4]_2$	6	281
$[(C_6H_5)_2PbLCl_2]$	6	281
$[PbL_2](ClO_4)_2$	4	251

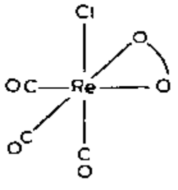
[a] Coordination number (C.N.) may vary from 8 to 10 depending on the uni- or bi-dentate nature of the nitrato ligands. [b] Not reported. [c] Nb cluster compound (see text). The niobium ions involving coordinated *N,N*-bipyO_2 have C.N. 9, and the other Nb ions C.N. 8. [d] μ_{eff} = 1.23 B.M. [e] μ_{eff} = 1.48 B.M. [f] Polymeric cyano-bridged complex.

1 M HCl aqueous solution tor the PuO_2Cl_2 complex [274]). The uncoordinated *N,N*-bipyO_2 molecule exists in a staggered (*gauche*) conformation in the solid state as suggested by the occurrence of two ν_{N-O} bands at 1262 and 1255 cm^{-1} [28]. Metal chelate formation results in negative frequency shifts and splittings of the ν_{N-O} bands (two to four ν_{N-O} bands appear in the IR spectra of the *N,N*-bipyO_2 metal chelates) [28,281]. The ν_{M-O} (*N,N*-bipyO_2) modes have been identified in the 450—250 cm^{-1} region depending on the metal ion, its oxidation state and coordination number [28,215,271,273,280,282]. As was the case with *N*-bipyO, a *trans—cis* rearrangement is necessary for the chelation of *N,N*-bipyO_2. However, chelate ring formation through the two oxygen donor atoms does not result in coplanarity of the two phenyl rings. The resulting non-planarity of the chelate rings may give rise to both *d* and *l* ligand diastereoisomers for the tris-(*N,N*-bipyO_2) metal chelate compounds. Combination of these diastereoisomer arrangements with the Δ and Λ possibilities for tris-pseudooctahedral complexes results in a total of eight possible optical isomers [246—248,272]. Proton NMR data for the $[M(N,N\text{-bipy}O_2)_3](PF_6)_2$ (M = Co, Ni) chelates (contact and dipolar shifts and the corresponding geometrical factors) were best interpreted by assuming an M—O distance of 2.20 Å and an O—M—O angle of 85°. The geometrical factors obtained in this manner correspond to a staggered configuration for the chelated *N,N*-bipyO_2 ligand involving an angle of 67° between the planes of the two aromatic rings and an M—O—N angle of 115° [272]. The NMR studies also revealed that two of the eight possible optical isomers are present in appreciable amounts in the above complexes; these are the Δ*ddd* (≡ Λ*lll*) and Δ*lll* (≡ Λ*ddd*) isomers [272].

The perchlorate groups are exclusively ionic in all the complexes shown in Tables 2 and 3 based on IR [226] and conductance [240] measurements [26—28,251,270,271,276,277,279,283]. In addiction to $[ML_n]^{m+}(ClO_4)_m$ compounds a number of perchlorate complexes, involving mixed-ligand (*N,N*-bipyO_2 and chloro or nitrato) cationic complexes have been reported [27,279]. The H_2O present in metal perchlorate—*N,N*-bipyO_2 complexes appears to be exclusively lattice water [27,251] as was also the case with the *N*-bipyO analogs (vide supra). However, Cu(II) tetrachloroplatinate(II) analogs are characterized as involving $[CuL_2(OH_2)_2]^{2+}$ complex cations [27]. This was established [27] by the presence of IR bands in the OH_2-bending and -rocking region [219,284—287] in the spectra of the $CuPtCl_4$ complexes characteristic of aquo ligands. No absorptions of this type are present in the spectra of $[CuL_2](PtCl_4)$ or $[CuL_2](PtCl_4) \cdot 4\,D_2O$ [27]. The tetrachloroplatinate (II) [27], persulfate [26], hexafluorophosphate [272] and tetraphenylborate [281] groups are exclusively ionic in the complexes of Tables 2 and 3. The nitrate and halide groups function as either ionic or coordinating ligands [27, 109,155,251,270,274,275,278—281,283]. The uranyl sulfate complex (Table 3) appears to contain a bidentate sulfato ligand [280] on the basis of IR evidence [287], while the IR data for metal thiocyanate complexes point to the presence [288,289] of isothiocyanato ligands (M—NCS) for M = Co^{2+},

Ni^{2+}, Zn^{2+}, Sn^{4+} and thiocyanato ligands (M—SCN) for M = Cd^{2+}, Hg^{2+}, UO_2^{2+} [273,280—282]. The IR spectrum of Hg_2 (*N,N*-bipyO_2)$(CN)_4$ suggests [290] that this compound is polynuclear, involving bridging cyano ligands [282].

As described previously, *N,N*-bipyO_2 functions as a bidentate chelating agent in the majority of its metal complexes (Tables 2 and 3) forming a seven-membered chelate ring (XX). In mixed-ligand complexes the ligand occupies, of necessity, coordination sites lying at positions *cis* to one another (e.g. [$Re(CO)_3$(*N,N*-bipyO_2)Cl] (XXV) [155] and VCl_4L (XXVI) (L = *N,N*-bipyO_2 or *N,N*-phenO_2) [109]). Formation of an eight-membered chelate ring by coordination of each *N,N*-bipyO_2 oxygen to a different metal ion (XXVII) occurs in (Nb_6Cl_{12}(*N,N*-bipyO_2)$_2$]Cl_2 [278]. In fact, the structure of the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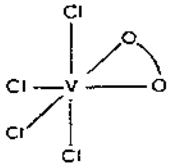
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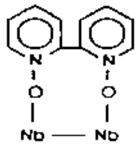
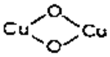
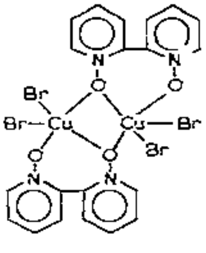

(XXVII)

$[Nb_6Cl_{12}]^{2+}$ cations consists of an octahedral cluster of six low-valent niobium ions with bridging chlorine groups situated above each edge of the octahedron such that each Nb atom is in the environment of four adjacent Nb atoms and four adjacent chlorine atoms. One additional ligand can be added to each Nb atom in a "centrifugal" position such that the niobium—ligand bond points radially outward from the center of the octahedral cluster [278,291]. The function of *N,N*-bipyO_2 as a bridging, bidentate ligand has been proposed for complexes of the type $[(C_6H_5)_3SnX]_2L$ (X = Cl or NCS) [281] on the basis of established analogs with other bridging ligands [292] and $[CuLBr_2]_x$ [215] on the basis of its anomalously low magnetic moment, which is suggestive of the presence of  groupings [5,186,187]. For the latter complex two possible structural formulae (XXVIII and XXIX) involving, respectively, a *cis*- and a *trans*-arrangement of the ligands were considered as possible [278]. In $[AgL_2](ClO_4) \cdot 3\,H_2O$ the function of *N,N*-bipyO_2 as a unidentate ligand coordinating through only one of its oxygens was considered as probable [251] in view of the tendency of Ag(I) to exhibit linear two-fold coordination [293]. For the remaining metal complexes of Tables 2 and 3, *N,N*-bipyO_2 coordinates as shown in (XX).

The complexes with metal oxo cations (VO^{2+}, ZrO^{2+}, UO_2^{2+}, PuO_2^{2+}, $Mo_2O_3^{4+}$ and $Mo_2O_4^{2+}$) generally exhibit [270,274,280] $\nu_{M=O}$ bands in the 1000—900 cm^{-1} region [294]. The two Mo^{5+} complexes also show $\nu_{-Mo-O-Mo-}$ bands at 740—710 cm^{-1} [270]. These complexes were assigned the binuclear structures (XXX) and (XXXI) [270]. The other metal oxocation complexes



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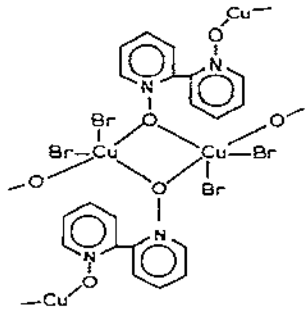

(XXIX)

appear to be devoid of M—O—M groupings and are monomeric as shown in Tables 2 and 3. In the PuO_2Cl_2 complex the ligand is probably in the form of its hydrochloric acid salt [274], while a 4 : 1 *N,N*-bipyO_2 adduct with the

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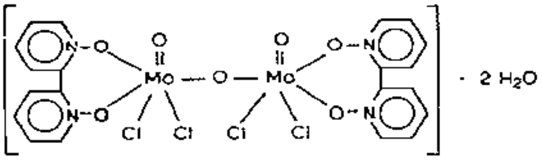

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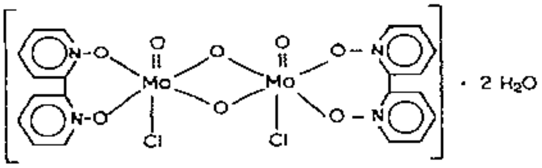


hexachloroceric acid was prepared during the study of several Ce(IV) chelates of this ligand [283].

Spectrochemical parameter calculations for *N,N*-bipyO_2 in various $[ML_3]^{2,3+}$ chelates with 3*d* metal ions show that it is a substantially weaker ligand than *N*-bipyO or *N*-phenO (vide supra), viz.: *Dq* towards hexacoordinated Cr(III), 1495—1585 cm^{-1} and Ni(II), 857 cm^{-1} [251]. Thus, the strength of the *N,N*-bipyO_2 ligand is insufficient to induce spin-pairing in any of its complexes with 3*d* metal ions [26—28,109,215,251,270—273]. The subnormal μ_{eff} value measured for $[Cu(N,N\text{-bipyO}_2)Br_2]_x$ (μ_{eff} = 0.70 B.M.) is due to spin—spin coupling between adjacent Cu^{2+} ions via the oxygen bridges of structure (XXVIII) or (XXIX) [5,186,187,215]. The (*d*—*d*) transition spectra of the paramagnetic chelates in Tables 2 and 3 are generally consistent with the coordination numbers listed. Among the $[LnL_4](ClO_4)_3$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) [276] complexes, the Eu(III) and Tb(III) chelates fluoresce in both the solid state and nitromethane solution. Fluorescence spectra and band assignments ($^5D_0 \rightarrow {}^7F_0, {}^7F_1, {}^7F_2, {}^7F_3$

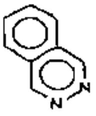
transitions for the Eu^{3+} ion at 579—670 nm and $^5D_4 \rightarrow {}^7F_6$ and $^5F_5$ transitions for the Tb^{3+} ion at 480—490 and 544 nm, respectively) were reported for these compounds [277]. UV spectra of the *N,N*-bipyO_2 complexes have been reported only in the case of organotin derivatives, i.e., (nm): free *N,N*-bipyO_2, 207s, 216sh, 251.2vw, 257.5vw, 261.8vw, 263.7vw and 267.6vw; $[(C_6H_5)_3SnCl]_2L$, 217.5vs, 268s; and $[(CH_3)_2SnLCl_2]$, 222.5s, 245.6wb, 270s,b [281]. The former complex involves bridging *N,N*-bipyO_2, probably in the *trans*-form, while in $[(CH_3)_2SnLCl_2]$, the ligand is chelated and has presumably assumed the *cis*-conformation.

A final point of interest is that from the shifts [295] of the $\nu_{U=O}$ and $\nu_{Pu=O}$ (asymmetric) modes in uranyl and plutonyl complexes with various ligands, it appears that the order of complexing ability of these ligands with the UO_2^{2+} ion is dimethyl sulfoxide > pyridine > *N,N*-bipyO_2 > phen > bipy and with the PuO_2^{2+} ion this order is *N,N*-bipyO_2 > phen > bipy [274]. It may be mentioned that from a historic point of view, *N,N*-bipyO_2 metal chelates were first prepared in 1959 by Simpson [296]; these studies were later expanded and appear in refs. 27 and 28.

D. METAL COMPLEXES WITH DIAZINE *N*-OXIDES

(i) Generalities

The aromatic diazines are characterized by the presence of two nitrogen atoms in the same six-membered ring. Their ligand properties have been the subject of numerous studies [17—23,297—316]. Pyz, pym and pdz have been shown to coordinate either through one of the two nitrogens, as a terminal ligand, or through both nitrogen atoms. In the latter case the ligands appear to function invariably as bridging groups, even for pym which has, a priori, the potential to act as a chelating agent [18—20,297—307,315,316]. Shifts of fundamental vibrational modes of the diazine ring occur upon metal complex formation [18—20,297,302,303]. The best IR criteria for distinguishing between bridging and terminal diazine ligands are that ν_{M-N} (bridging) occurs at higher frequencies than ν_{M-N} (terminal) and that in complexes involving exclusively bridging ligands, no Raman—IR coincidences of the internal ring fundamentals are observed. A large number of Raman—IR coincidences are observed in the spectra of complexes with terminal diazine [303]. Nevertheless, interpretations of the IR spectra of 3*d* metal halide complexes with these ligands by several investigators have led to the proposal of different structures, i.e., halogen-bridged [18,19,302], diazine-bridged [18,20,303] or both halogen- and diazine-bridged [19,302]. Qx [21,23,308—310,312,313], phthalazine (XXXII) and benzocinnoline (XXXIII) [316] have also been found to coordinate either as unidentate or as bidentate bridging ligands. In the case of qx, several ligand fundamental vibrational modes were found to undergo frequency shifts and splittings upon metal complex formation [312]. Phz has been shown to act both as a σ-ligand, coordinating through nitrogen [311,314] and as a π-ligand [22]; in the latter case one of the benzene rings is involved in π-coordination to the metal, e.g., in Fe(0) complexes of the type [$Fe(CO)_3$(phz)] [22]. Chelating ligands containing diazine rings have also been reported, e.g., bipyrazinyl (XXIV) [317] and 2-mercaptopyrimidine (XXXV) derivatives [318]. Bipyrazinyl acts in the same way as bipy, forming $[ML_3]^{n+}$ complex cations, in which chelation occurs through the 1- and 1′-nitrogens of the two pyrazine rings. However, complexes with two or three metal ions per bipyrazinyl ligand, obviously involving participation of additional nitrogens of the ligand, which function as chelating and bridging sites, have been isolated [317]. In the case of 2-mercaptopyrimidines, coordination through sulfur and one ring nitrogen leads to the formation of a four-membered chelate ring [318].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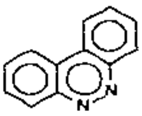
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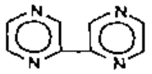
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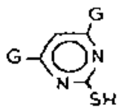

(G = NH_2 or OH)

(XXXV)

The electronic spectra of 3*d* metal complexes with pyz and qx are characterized by metal-to-ligand charge transfer bands [18,310] (as is also the case with aromatic amine *N*-oxide 3*d* metal complexes [176]). In the case of phz the (*d*—*d*) transition spectra are complicated by a ligand band at 360—370 nm [311]. The 3*d* metal complexes with aromatic diazines are, in most cases, magnetically normal. A number of polynuclear Fe(II) halide complexes with pyz exhibit somewhat low μ_{eff} values (4.4—4.7 B.M.), probably due to spin—spin coupling operating via a superexchange mechanism [19]. $[Cu(pyz)(O_2NO)_2]_x$ is polymeric involving bridging pyz and also exhibits spin—spin coupling [301]. However, Cu(II) halide complexes with pyz, pym, pdz or qx are magnetically normal [19,310]. $[Cu(qx)(CH_3COO)_2]_x$ exhibits a μ_{eff} of 1.41 B.M., which is thought to be due to the presence of acetato bridging groups [187] rather than the qx ligands [310]. Temperature-dependence studies of the magnetic susceptibilities of 1 : 1 Cu(II) complexes with aromatic diazines reveal that these compounds are polymeric with considerable interaction between chains. The magnetic interactions in these complexes are antiferromagnetic in nature and the magnitude of the exchange energy, *J*, generally reflects the nature of the chain linkages. These chain linkages are highly dependent on the type and number of substituents on the aromatic ring [23,307,308].

The donor properties of diazine *N*-oxides have been discussed in B(iii). It should be added at this point that ESR investigations of the cation radicals of *N,N*-pyzO_2, *N,N*-qxO_2 and *N,N*-phzO_2 (electrochemically generated) show that spin densities in these radicals are very large for the *N*-oxide oxygen atom but small for the nitrogen atom and increase along the series *N,N*-phzO_2 < *N,N*-qxO_2 < *N,N*-pyzO_2 [319].

(ii) Metal complexes of diazine mono-N-oxides

From the discussion in sections B(iii) and D(i) it is obvious that diazine N-oxides can coordinate as unidentate N-bonded (L_N) or O-bonded (L_O) ligands or as bridging N,O-bonded (${}_{N}L_{O}$) ligands.

Among the mono-heterocyclic aromatic diazine mono-*N*-oxides, the ligating properties of only *N*-pyzO (IV) have been studied to date. *N*-pyzO forms complexes with 3*d* metal perchlorates [119,320], chlorides [321] and nitra-

TABLE 4

Metal complexes with *N*-pyzO(L) [a] and some substituted pyrazine mono-*N*-oxides (L′)

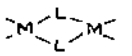
Complex	Coordination number	μ_{eff} (B.M.) [b]	Ref.
$[Cr(L_O)_n({}_{N}L_O)_{4-n}(C_2H_5OH)]_x(ClO_4)_{3x}$	6	3.75	119
$[Mn(L_O)_n({}_{N}L_O)_{4-n}]_x(ClO_4)_{2x}$	5 or 6 [d]	6.02	119
$[Fe(L_O)_n({}_{N}L_O)_{3-n}]_x(ClO_4)_{2x}$	4 or 5 [d]	5.34	119
$[Fe(L_O)_n({}_{N}L_O)_{3-n}(OH_2)(OClO_3)]_x(ClO_4)_x$	6	5.29	119
$[Fe(L_O)_6](ClO_4)_3$	6	6.13	119
$[Co(L_O)_n({}_{N}L_O)_{3-n}(OH_2)(OClO_3)]_x(ClO_4)_x$	6	4.79	119
$[Ni(L_O)_n({}_{N}L_O)_{3-n}(OH_2)_2]_x(ClO_4)_{2x}$	6	3.16	119
$[Cu(L_N)_4(OH_2)(OClO_3)](ClO_4)$	6	2.13	119
$[Zn(L_N)_n(L_O)_{4-n}(OH_2)(OClO_3)](ClO_4)$	6		119
$[Cr(L_N)_3Cl_3]$	6	3.85	321
$[Mn({}_{N}L_O)Cl_2]_x$ [e]	5	5.63	321
$[Fe({}_{N}L_O)Cl_2]_x$ [e]	5	5.34	321
$[Co_2(L_N)_n({}_{N}L_O)_{3-n}Cl_4]_x$ [e]	5	4.94	321
$[Ni(L_N)_n({}_{N}L_O)_{3-n}Cl_2]_x$ [f]	6	3.40	321
$[Cu(L_N)({}_{N}L_O)Cl_2]_x$ [e]	6	1.73	321
$[Co(L_O)(L_N)(O_2NO)_2]$	6	4.57	322
$[Ni(L_O)_n(L_N)_{4-n}(ONO_2)_2]$	6	3.12	322
$[Cu(L_O)_n(L_N)_{4-n}(ONO_2)_2]$	6	1.74	322
$[Y(L_O)_8](ClO_4)_3$	8		323
$[La(L_O)_7(OH_2)_2](ClO_4)_3$	9		323
$[Pr(L_O)_8](ClO_4)_3$	8	[c]	323
$[Eu(L_O)_8](ClO_4)_3$	8	[c]	323
$[Er(L_O)_8](ClO_4)_3$	8	[c]	323
$Ag(L_N)_2(NO_3)$	[g]		324
$Ag({}_{N}L'_O)(NO_3)$ [h]	[g]		324

[a] The designations L_O, L_N, ${}_{N}L_O$ indicate, respectively, unidentate O-bonded, N-bonded and bidentate, bridging N,O-bonded, *N*-pyzO. [b] Room temperature (290—300 K) values. [c] Not reported. [d] Coordination numbers for bi- or poly-nuclear complex cations. [e] Presence of both terminal and bridging chloride groups. [f] Exclusive presence of terminal chloride. [g] Coordination number may be 2, if the NO_3 group is ionic (no IR evidence on the NO_3 vibrations was presented), i.e., $[Ag(L_N)_2](NO_3)$ and $[Ag({}_{N}L'_O)]_x(NO_3)_x$. [h] L′ = 2-methyl-, 2,5-dimethyl-, 3,5-dimethyl-, 2-chloro-3-methyl-pyrazine-1-oxide and 2-chloro-3-methyl-pyrazine-4-oxide.

tes [322]; rare earth perchlorates [323] and silver(I) nitrate [324]. Table 4 gives a compilation of the complexes, as well as a number of $AgNO_3$ complexes with substituted pyrazine mono-*N*-oxides. The synthetic procedures followed for the isolation of these complexes involved interaction of ethanol—triethyl orthoformate solutions of ligand and salt for the 3*d* metal complexes [119,321,322] or an ethanol solution of the ligand with an aqueous solution of $AgNO_3$ [324]; in the case of the rare earth perchlorate complexes [323] ethanolic solutions of ligand and salt were allowed to interact and the crystalline complexes were precipitated by addition of 2,2-dimethoxypropane, a dehydrating agent [325].

Evidence regarding the coordination site(s) of *N*-pyzO was based predominantly on the changes of the ν_{N-O} mode in each metal complex, the tentative identification of ν_{M-O} and ν_{M-N} bands and the sensitivity of the ν_{C-N} band at 1585 cm^{-1} to complex formation [119,320—324]. Complexes involving exclusively unidentate, O-bonded *N*-pyzO were found to show negative ν_{N-O} frequency shifts (ν_{N-O} in free *N*-pyzO occurs at 1309 cm^{-1}) [119,320—323], while the frequency of the ν_{C-N} band remains unchanged [323]. Coordination of this type is observed in the ferric and trivalent rare earth perchlorate complexes [119,320,323]. On the other hand, the presence of exclusively N-bonded *N*-pyzO ligands resulted either in positive ν_{N-O} frequency shifts ($CrCl_3$ and $Cu(ClO_4)_2$ complex) [119,320,321] or in no shift of the ν_{N-O} band ($AgClO_4$ complex) [324]. In many cases (Table 4) the presence of both O- and N-bonded *N*-pyzO was concluded from the occurrence of ν_{N-O} bands at both higher and lower frequencies when compared to ν_{N-O} of free *N*-pyzO or its substituted derivatives [119,320—322, 324]. Structural assignments were based on the frequencies and number of ν_{N-O} and ν_{M-N} modes (ν_{M-N} (bridging) occurs at higher frequencies than ν_{M-N} (terminal) [303], as already mentioned, but ν_{M-O} (bridging) occurs at lower frequencies than ν_{M-O} (terminal) [326]). On the basis of this evidence, structures involving all possible modes of *N*-pyzO coordination, i.e., both terminal and bridging ligands, only terminal ligands (O-bonded or N-bonded), or exclusively bridging *N*-pyzO, have been proposed as shown in Table 4. Thus, *N*-pyzO appears to exhibit the same trends as the parent base, i.e., it can act either as a uni- or as a bi-(bridging) dentate ligand.

The 3*d* metal nitrate complexes with *N*-pyzO are characterized by the absence of ionic nitrate groups, as suggested [227—230] by splittings of the fundamental and combination vibrational modes of the NO_3 group. In the case of the metal perchlorate complexes, distinction between compounds involving exclusively ionic [119,323] or both ionic and coordinated [119] ClO_4 groups was based on the absence or presence of splittings in the ν_3 and ν_4 (ClO_4) fundamentals [226,327—329] and the tentative identification of ν_{M-O} (perchlorato) [231,330] bands [119,323]. It is of interest to note at this point that only mull (hexachlorobutadiene and Nujol) IR spectra can provide reliable solid-state information regarding the nature of the *N*-pyzO metal complexes. When 3*d* metal perchlorate or nitrate complexes with this ligand are pressed in a KBr die, dramatic differences, relative to the corresponding mull spectra, are observed in the ν_{N-O} region as well as the regions of the fundamental vibrations of the polyanion [119,320,322]. These changes were interpreted in terms of rearrangement of the coordination site of the *N*-pyzO ligands, displacement of *N*-pyzO by perchlorato ligands and displacement of nitrato by bromide ligands under the effect of pressure [331] and in the presence of KBr [119,320,322]. In the 3*d* metal chloride complexes, ν_{M-Cl} (terminal) and (bridging) band assignments [19,20,233—239] led to the formulations shown in Table 4 [321].

The *N*-pyzO 3*d* metal complexes are generally magnetically normal high-spin compounds. Their electronic spectra are characterized by shifts and occasional splittings of the $\pi \rightarrow \pi^*$ transition bands of the free ligand and strong metal to ligand charge-transfer bands originating in the UV and trailing off into the visible region. The (*d*—*d*) transition spectra are generally consistent with the coordination numbers given in Table 4 [119,320—322]. Finally, it should be noted that in the case of *N*-pyzO (as well as qx and phz *N*-oxide or *N*,*N*-dioxide) polymeric metal complexes with bidentate, bridging ligand groups exclusively involve single —M—L—M— bridges, since double bridges of the type 
may be ruled out in view of the steric interactions between the two bridging ligands [119,321,322].

N-qxO and *N*-phzO complexes with 3*d* metal salts were recently synthesized and characterized [83—85,87] (Table 5). The complexes of these ligands, as well as the corresponding *N*,*N*-dioxides, are usually dissociated in the presence of polar organic solvents including alcohols. Thus, only Cu(II) complexes with *N*-qxO, *N*,*N*-qxO_2, and substituted derivatives have been isolated by reaction of ligand and salt in absolute ethanol [83]. Interaction of these ligands with other 3*d* metal salts in ethanol, triethyl orthoformate or 2,2-dimethoxypropane does not lead to the formation of solid precipitates [322] (triethyl orthoformate and 2,2-dimethoxypropane form ethanol and methanol, respectively, during their hydrolysis [261,325]). It was found that interaction of ligand solution in chloroform with 3*d* metal chloride solution in acetone or 3*d* metal perchlorate solution in ethyl acetate leads to the precipitation of solid crystalline complexes [332]. However, these products are characterized by high water content. The amount of water coprecipitated with the metal complexes can be substantially reduced or even completely eliminated if the ligand and salt solutions are treated with molecular sieve zeolite 4A prior to their interaction [332].

The bonding site or sites of *N*-qxO and *N*-phzO were deduced from the IR evidence [83—85,87] (variation of the ν_{N-O}, $\nu_{CC} + \nu_{CN}$ modes, and presence or absence of ν_{M-O} and ν_{M-N} bands) as was also the case with *N*-pyzO complexes. In addition to *N*-qxO and *N*-phzO functioning as unidentate, O- or N-bonding ligand and as a bidentate bridging, O,N-bonding ligand, a number of bi- or poly-nuclear metal complexes with these ligands were found to involve bridging unidentate O-bonded *N*-qxO or *N*-phzO [84,85,87] (Table 5). This assignment was based mainly on IR evidence and, occasionally, low magnetic susceptibility values [84,85,87] (Table 5). Binuclear Cu(II) *N*-oxide-bridged complexes with aromatic amine *N*-oxides are in most cases magneti-

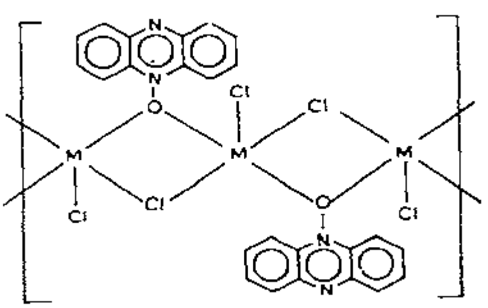
TABLE 5

3*d* metal complexes with *N*-qxO(L), *N*-phzO(L′) and some substituted quinoxaline 1-oxides (L″)

Complex	Coordination number	μ_{eff} (B.M.) [a]	Ref.
$[Cr(L_O)_n(L_N)_{4-n}(OClO_3)]_2(ClO_4)_4 \cdot 24\,H_2O$ [b]	6	3.53	84, 85
$[Mn(L_O)_n(L_N)_{4-n}(OClO_3)]_2(ClO_4)_2 \cdot 4\,L \cdot 12\,H_2O$ [b]	6	5.60	84, 85
$[Fe(L_O)_4(OClO_3)(OH_2)](ClO_4) \cdot 7\,H_2O$	6	5.31	84, 85
$[Fe(L_O)_n(L_N)_{3-n}(OClO_3)_2(OH_2)](ClO_4) \cdot H_2O$	6	2.61	84, 85
$[Co(L_O)_4(OClO_3)(OH_2)](ClO_4) \cdot 2\,H_2O$	6	4.49	84, 85
$[Ni(L_O)_4(OClO_3)(OH_2)](ClO_4) \cdot 7\,H_2O$	6	2.77	84, 85
$[Cu(L_O)_n(L_N)_{4-n}(OClO_3)]_x(ClO_4)_x \cdot xH_2O$ [b]	6	0.99	84, 85
$[Cu(L_O)(L_N)(OClO_3)(OH_2)_2](ClO_4) \cdot H_2O$	5	1.78	84, 85
$[Zn(L_O)_2({}_NL_O)(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 8\,H_2O$	6		84, 85
$[Cr_2(L_O)_3Cl_5(OH_2)_2]Cl \cdot 10\,H_2O$ [b,c]	6	3.66	84, 85
$[Mn(L_O)_2Cl_2]_2$ [c]	5	6.40	84, 85
$[Fe_2(L_O)_3Cl_5(OH_2)_2]Cl$ [b,c]	6	3.71	84, 85
$[Co(L_O)_2({}_NL_O)Cl_2]_x \cdot 5xH_2O$	6	4.80	84, 85
$[Ni(L_N)_2Cl_2]_x$ [c]	6	2.95	84, 85
$[Cu(L_N)_2Cl_2]_x \cdot xH_2O$ [c]	6	1.96	83, 84, 85
$[Cu(L_N)Br_2]_x$	6	*d*	83
$[Cu(L''_N)_2Cl_2]_x$ [c,e]	6	*d*	83
$[Cu(L''_N)_2Cl_2]$ [f]	4	*d*	83
$[Cu(L''_O)_2Cl_2]_x$ [c,g]	6	*d*	83
$[Zn({}_NL_O)Cl_2]_x$	4		84, 85
$[ML'_x(ClO_4)_n]_m[HL'_2ClO_4]_z \cdot yH_2O$ [h]	6		84, 87
$[Mn(L'_O)_5(OClO_3)] \cdot L' \cdot 3\,H_2O$	6	5.44	84, 87
$[FeL'({}_NL'_O)(O_2ClO_2)(OH_2)]_2(ClO_4)_2 \cdot H_2O$	6	5.44	84, 87
$[Cu(L'_O)_n(L'_N)_{4-n}](ClO_4)_2 \cdot 5\,H_2O$	4	1.87	84, 87
$[ZnL'({}_NL'_O)(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 6\,H_2O$	6		84, 87
$[Cr_3(L'_O)({}_NL'_O)Cl_9(OH_2)_4] \cdot 14\,H_2O$	6	3.62	84, 87
$[Mn_3(L'_O)_2Cl_6]_x \cdot xH_2O$ [b,c]	5	5.93	84, 87
$[Fe({}_NL'_O)Cl_3]_x \cdot 2xH_2O$	5	6.15	84, 87
$[Co(L'_O)_n(L'_N)_{3-n}Cl]_2Cl_2 \cdot 12\,H_2O$ [c]	5	4.69	84, 87
$[Cu_3(L'_O)_2Cl_6]_x \cdot 2xH_2O$ [b,c]	5	0.90	84, 87
$[Cu(L'_O)_2({}_NL'_O)Cl_2]_x \cdot xH_2O$ [b]	5	0.80	84, 87
$[Zn(L'_O)(L'_N)Cl_2(OH_2)]$	5		84, 87

[a] Room temperature values. [b] Complex involves unidentate (O-bonded), bridging ligand groups. [c] Halide-bridged complex. [d] Not reported. [e] L″ = 2- and 3-methyl-quinoxaline 1-oxide. [f] L″ = 2-phenylquinoxaline 1-oxide. [g] L″ = 3-phenylquinoxaline 1-oxide. [h] M = Cr^{3+}, Co^{2+}, Ni^{2+}, n = 2 or 3.

cally subnormal, as already mentioned, owing to spin—spin coupling via a superexchange mechanism operating through the oxygen bridges [2,3,5,186,187]. Magnetically subnormal, ligand-bridged, bi- or poly-nuclear complexes with other paramagnetic 3*d* metal ions are less common, but several examples have been reported in the literature [333—337]. Thus, bridging of this type was considered as likely for both magnetically normal and subnormal metal complexes with *N*-qxO and *N*-phzO [84,85,87]. Only in the case of Fe(III) complexes with low μ_{eff} values was the existence of spin-free—spin-paired equilibria assumed [84, 85,87] by analogy with the *N*-bipyO and *N*-phenO analogs [209,213]. An example of such a structural assignment is given in (XXXVI) for $(MCl_2)_3 \cdot (N\text{-phzO})_2 \cdot xH_2O$ complexes, M = Mn or Cu [84,87]. The presence of terminal, bridging or both terminal and bridging chloride or bromide groups also was based on IR data [83—85,87].



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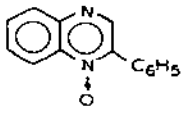

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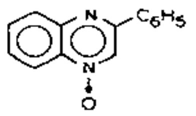

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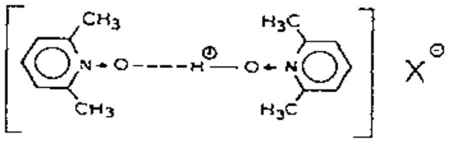
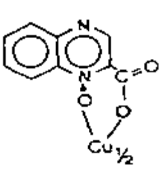


(XXXIX)

The steric effects exerted by the presence of bulky substituents at ring positions adjacent to the =N— or ⩾N—O groups of these ligands are clearly demonstrated by the coordination of 2-phenylquinoxaline 1-oxide (XXXVII) through nitrogen and the 3-phenyl analog (XXXVIII) through oxygen in the complexes with $CuCl_2$ [83]. The 3*d* metal perchlorate complexes are characterized in most cases by the presence of both ionic and coordinated perchlorate, as suggested [226,327—330] by IR evidence [84,85,87]. In the case of interaction between *N*-phzO and Cr(III), Co(II) or Ni(II) perchlorates, mixtures of the true metal complexes with the perchloric acid salt of *N*-phzO were obtained [84,87]. The precipitation of mineral acid salts, instead of the metal complex, during some reactions of *N*- or *P*-oxide ligands with metal salts, has been reported in the literature [338,339]; the 2 : 1 adducts of 2,6-lutidine *N*-oxide with perchloric, nitric or tetrafluoroboric acid are of the type shown in (XXXIX) (X = ClO_4, NO_3, BF_4) [338,340]. Coprecipitation of the perchloric acid salt in addition to the metal complex is not unprecedented. In fact, a number of colorless products of the interaction of 2,6-lutidine *N*-oxide with Cr(III), Co(II) and Ni(II) perchlorates, originally characterized as hydrated metal complexes [206], are now believed to be mixtures of the perchloric acid salt and the metal perchlorate complex of this ligand [338]. The $[M(N\text{-phzO})_x(ClO_4)_n]_m \cdot [H(N\text{-phzO})_2ClO_4]_z \cdot yH_2O$ products appear to contain substantially higher amounts of the salt relative to the metal complex; the perchlorate associated with the salt is ionic while the metal complex contains both ionic and coordinated ClO_4 [84,87].

In most cases, the *N*-qxO and *N*-phzO metal complexes involve lattice water, and in certain cases coordinated aquo ligands [84,85,87]. Far-IR studies (down to 33 cm^{-1}) including assignments of the γ_{N-O} mode of the ligand [341] and translational lattice modes of the perchlorate ion [342] were also reported for these complexes [84,85,87]. The electronic spectra are characterized by the usual shifts and splittings of the ligand bands, as well as metal to ligand charge-transfer absorptions. The latter bands, and in the case of *N*-phzO the visible bands of the ligands, overlap with a number of the higher energy (*d*—*d*) transitions [84,85,87].

The ligand properties of several *N*-qxO derivatives with potential chelating ability have also been investigated [343,344]. Thus, 2-quinoxalinecarboxylic acid 1- and 4-oxide form Cu(II) chelates of the type $CuL_2 \cdot 2\,H_2O$ and CuL_2, respectively [343]. The chelate of the 1-oxide derivative involves coordination through the N—O oxygen (XL) and that with the 4-oxide compound through the amine group nitrogen (XLI), as would be anticipated. The five-membered chelate ring in XLI appears to be more stable than the six-membered chelate ring in XL as indicated by the occurrence of ν_{Cu-O} (carboxyl) at a higher frequency in the 4-oxide as compared to the 1-oxide chelate [343]. Mn^{2+} and Zn^{2+} complexes with 2-mercaptoquinoxaline 1-oxide (XLII) and the corresponding disulfide (XLIII) have been reported in the patent literature [344].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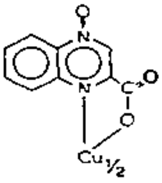
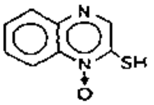
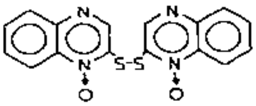
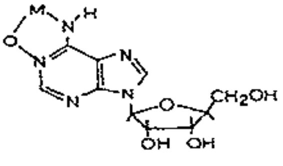

(XLI)


(XLII)


(XLIII)

Metal complexes with the *N*-oxides of some biologically important purine derivatives, have also been described in the literature [25,345—347]. Thus, adenosine 1-oxide was found to form in alkaline media 1 : 1 metal chelates of type (XLIV), involving coordination of the *N*-oxide oxygen of the pyrimidine ring with dipositive 3*d* metal ions (M = Mn through Zn) [25]. However, adenine 1-oxide forms chelates with the same metal ions involving coordination of the nitrogen of the amine group and one nitrogen of the imidazole ring (in position 7) (XLV) [25]. The latter ligand (LH) was found to act both as a neutral ligand in complexes of the type $Cu(LH)_nX$ (n = 1 or 2; X = SO_4, Cl_2, $(ClO_4)_2$) and as an anionic ligand in $CuL_2 \cdot 8\,H_2O$ [347]. Adenosine-5′-monophosphate-1-oxide forms Cu(II) chelates involving coordination of the NO oxygen (XLVI); with other M(II) ions (Mg, Ca, Ba, Mn, Co, Ni, Zn) the same type of coordination occurs in solution at a high pH, while at neutral or weakly acid pH this ligand coordinates exclusively through the phosphate group to



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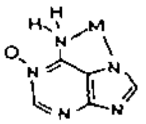
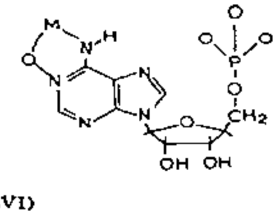
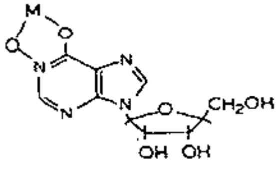


(XLV)



(XLVI)

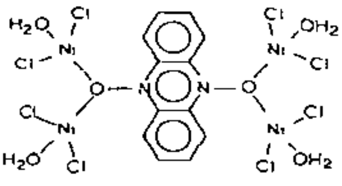


(XLVII)

these metal ions [345]. Similar studies with inosine 1-oxide and its 5′-monophosphate derivative established that these ligands coordinate through the N—O and hydroxy oxygens to divalent 3*d* metal ions (Mn, Co, Ni, Cu, Zn) (XLVII), whereas in the case of alkaline earth (Mg, Ca, Ba) divalent metal ions, an equilibrium between NO- and phosphato-bonded species exists in solution [346].

(*iii*) *Metal complexes of diazine N,N-dioxides*

N,N-pyzO_2 metal complexes have not been reported thus far. A 1 : 1 silver(I) nitrate complex with 2,6-dimethylpyrazine 1,4-dioxide is of the same type as the mono-*N*-oxide analogs, i.e., it probably involves bridging bidentate (O,O-bonded) ligand groups [324]. Recently 3*d* metal halide and perchlorate complexes with *N,N*-qxO_2 and *N,N*-phzO_2 were synthesized and characterized [83,84,95,348] (Table 6). Characterization studies of the complexes led to the conclusion that both these ligands have a pronounced tendency to act as either unidentate or as bidentate (O- and O,O-bonded, respectively) bridging ligands [84,95]. In two cases ($CrCl_3$ and $NiCl_2$ complexes with *N,N*-phzO_2) both types of bridging were postulated (structure XLVIII was assigned to $[Ni_4(N,N\text{-phz}O_2)Cl_8(OH_2)_4]$; this complex is tetrahedral) [84,95]. The Cu(II) complexes with *N,N*-qxO_2 and substituted derivatives can be isolated from ethanolic solutions [83], but the remainder of the metal chloride and per-



(XLVIII)

chlorate complexes are sensitive to the presence of alcohols and were prepared in the same manner as the *N*-qxO and *N*-phzO analogs (vide supra) [84,85,87, 95]. During synthetic studies with the metal perchlorate—*N,N*-phzO_2 complexes [332], it was found that M(II) perchlorates (M = Mn through Zn) yield products involving less water and higher ligand to metal ratios, if the ligand and salt solutions are pretreated with molecular sieve 4A. However, in the case of Cr(III) and Fe(III) perchlorates such a treatment led to heavily hydrated products; the Cr(III) and Fe(III) perchlorate—*N,N*-phzO_2 complexes shown in Table 6 were prepared without the use of the molecular sieves [84,95]. The intercalation product between TiS_2 and *N,N*-qxO_2 was obtained by interaction of this ligand with the hydrazine complex of TiS_2 and storage for five days at 25° C [348].

The ν_{N-O} mode of the ligand (1287 cm^{-1} for *N,N*-qxO_2 and 1257 cm^{-1} for *N,N*-phzO_2) undergoes a splitting into two or three bands upon metal complex formation. One of the resulting bands occurs at about the same or higher frequency than ν_{N-O} in the free ligands, while the other band(s) is shifted towards lower frequencies. Assignments concerning the presence of terminal unidentate ligand groups were based mainly on the number and frequencies of the ν_{M-O} modes [84—95]. The metal perchlorate complexes are invariably characterized by the presence of both ionic and coordinated ClO_4 groups, as suggested [226,327—330] by the IR data [84,95]. ν_{M-Cl} band assignments were used for differentiation between monomeric versus bi- or poly-nuclear structures of the metal chloride complexes [83,84,95]. Far-IR spectra (down to 33 cm^{-1}) were also reported for the metal chloride and perchlorate complexes with both ligands [84,95]. Distinction between coordinated and lattice water was based [218,219] on IR evidence [84,95].

Several *N,N*-qxO_2 and *N,N*-phzO_2 *3d* metal complexes are characterized by subnormal [244] magnetic moments for high-spin configurations (Table 6). These were interpreted in terms of bi- or poly-nuclear structures, involving unidentate, bridging *N,N*-qxO_2 or *N,N*-phzO_2 ligands (M—O—M bridges) in most cases. Only in the case of Fe(III) was the presence of spin-free—spin-paired equilibria assumed [84,95] (vide supra). The (*d*—*d*) transition spectra of the complexes of Table 6 are generally in agreement with the coordination numbers and stereochemistries suggested by the IR-evidence. Characteristic ligand band shifts and the appearance of intense metal-to-ligand charge-transfer absorptions are observed in the electronic spectra of the complexes. Overlaps between these bands and higher energy (*d*—*d*) transitions are also observed [83,84,95].

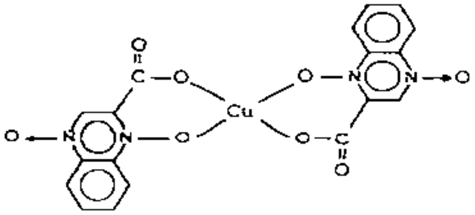
A number of copper(II) chelates with substituted quinoxaline 1,4- and phenazine 5,10-dioxides also have been described in the literature [24,343, 349]. These compounds are of the type [CuL_2] or [CuL]$^+$ [24,343,349]. 2-Quinoxaline carboxylic acid 1,4-dioxide and 1-hydroxyphenazine 5,10-dioxide form chelates of types (XLIX) and (L), respectively [24,343], whereas in the case of 1,6-dihydroxyphenazine 5,10-dioxide (iodinin), bridging of the type shown in (LI) was considered as possible [349].

TABLE 6

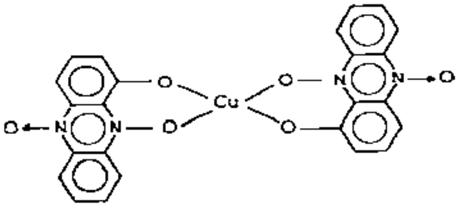
3*d* metal complexes with *N,N*-qxO_2(L), *N,N*-phzO_2(L′) and some substituted quinoxaline 1,4-dioxides(L″)

Complex	Coordination number	μ_{eff} (B.M.) [a]	Ref.
TiS_2—L [b]	([c])		348
$[CrL_2(OClO_3)_2(OH_2)]_2(ClO_4)_2 \cdot 6\,H_2O$ [d]	6	2.54	84
$[MnL_3(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 10\,H_2O$ [d]	6	5.70	84
$[FeL_3(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 10\,H_2O$ [d]	6	5.47	84
$[FeL_3(OClO_3)(OH_2)]_2(ClO_4)_4 \cdot 8\,H_2O$ [d]	6	2.50	84
$[CoL_3(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 10\,H_2O$ [d]	6	4.41	84
$[NiL_3(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 10\,H_2O$ [d]	6	2.57	84
$[CuL_3(OClO_3)]_2(ClO_4)_2$ [d]	5	1.55	84
$[Cu_2L_3(OClO_3)_2(OH_2)_4](ClO_4)_2 \cdot 6\,H_2O$ [d]	5	1.09	84
$[ZnL_3(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 10\,H_2O$ [d]	6		84
$[CrLCl_3(OH_2)_2] \cdot H_2O$	6	4.04	84
$[MnL_2Cl_2]_x$ [e,f]	6	5.92	84
$[FeL_2Cl_3(OH_2)] \cdot 6\,H_2O$	6	5.45	84
$[Co_2L_4Cl_4(OH_2)] \cdot 7\,H_2O$ [d]	5	4.12	84
$[NiL_2Cl_2(OH_2)]_2$ [f]	6	3.40	84
$[Cu_2L_3Cl_4] \cdot 2\,H_2O$ [d,f]	4	1.04	84
$[CuLX_2]_2$ [d] (X = Cl, Br)	4	[c]	83
$[CuL''_2X_2]$ [g] (X = Cl, Br)	4	[c]	83
$[CuL''_2X_2]_2$ [d,h] (X = Cl, Br)	5	[c]	83
$[CuL''X_2]_2$ [f,i] (X = Cl, Br)	4	[c]	83
$[ZnL_2Cl_2]_x \cdot xH_2O$	6		84
$[Cr_2L'_3(OClO_3)_4(OH_2)_4](ClO_4)_2 \cdot 8\,H_2O$ [d]	6	3.30	84
$[MnL'_3(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot H_2O$ [d]	6	5.71	84
$[FeL'_3(OClO_3)(OH_2)]_2(ClO_4)_2$ [d]	6	5.14	84
$[FeL'_3(OClO_3)(OH_2)_2](ClO_4)_2 \cdot 10\,H_2O$	6	3.95	84
$[CoL'_3(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 4\,H_2O$ [d]	6	4.97	84
$[NiL'_3(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 4\,H_2O$ [d]	6	1.99	84
$[CuL'_3(OClO_3)](ClO_4) \cdot H_2O$	4	2.02	84
$[ZnL'_3(OClO_3)(OH_2)]_2(ClO_4)_2 \cdot 3\,H_2O$ [d]	6		84
$[Cr_3L'Cl_9(OH_2)_6]$ [j]	6	3.54	84, 95
$[MnL'Cl_2]_x$ [f]	5	6.11	84, 95
$[FeL'_2Cl_3]_2$ [f]	6	6.08	84, 95
$[Co_2L'_3Cl_4] \cdot 6\,H_2O$ [d,f]	5	4.21	84, 95
$[Ni_4L'Cl_8(OH_2)_4]$ [j]	4	3.43	84, 95
$[Cu_4L'_3Cl_8]_x$ [d,f]	5	0.73	84, 95
$[ZnL'Cl_2(OH_2)]$	4		84, 95

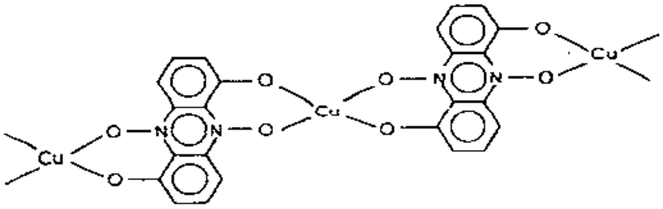
[a] Room temperature values. [b] Intercalation product between TiS_2 and *N,N*-qxO_2. [c] Not reported. [d] Complexes involving bridging unidentate *N,N*-dioxide ligands (M—O—M bridged). [e] Complexes involving bridging bidentate (O,O-bonded) *N,N*-dioxide ligands. [f] Halogen-bridged complexes. [g] L″ = 2-methyl-, 2,3-dimethyl-, 2-methyl-3-ethyl-, 2-methyl-3-isopropyl-, 2-phenyl-quinoxaline 1,4-dioxide; the complex with the 2-phenyl-substituted ligand appears to be *cis*-square planar, and those with the remainder of these ligands *trans*-square planar, based on IR evidence (ν_{Cu-Cl} or ν_{Cu-Br} bands). [h] L″ = 6-methylquinoxaline 1,4-dioxide; the complex is a dimer characterized by Cu—O—Cu bridges. [i] L″ = 2-methyl-3-phenylquinoxaline 1,4-dioxide; the complex is a halogen-bridged dimer. [j] Complexes appear to involve both types of bridging, i.e., *M*—O—*M* and  see structure XLVIII.



(XLIX)



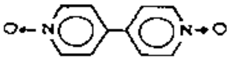
(L)



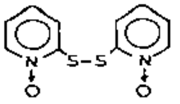
(LI)

E. METAL COMPLEXES WITH RELATED LIGANDS

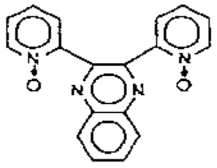
The present section briefly covers the metal complexes with ligands of the same general type as the diimine and diazine *N*-oxides. No complexes with substituted bipy- or phen-*N*-oxides have been reported thus far, although the literature is rich in examples of metal chelates of substituted derivatives of the parent bases [13—16]. 4,4′-Bipyridine *N*,*N*-dioxide (LII) was found to readily form crystalline complexes with transition metal perchlorates by these reviewers [350]. Characterization of these compounds is in progress; from their insolubility in organic media it appears that they are highly polymeric, ligand-bridged products [350], as is also the case with the metal complexes of the parent base [351—353]. Stannous chloride complexes with bis(2-pyridyl-1-oxide) disulfide (LIII) also have been prepared [354].



(LII)



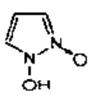
(LIII)

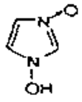


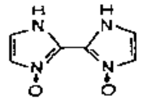
(LIV)

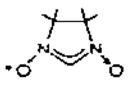
A quinoxaline derivative not involving *N*-oxidation of the diazine ring nitrogens is 2,3-di(pyridine *N*-oxide)quinoxaline (dpoq; LIV) [355]. This ligand was found to act as a O,N-chelating agent and in several instances, as a bridging ligand forming chelate rings with both bridged metal ions (each chelate ring is formed with each O,N-donor set). The following dpoq = (L) complexes have been reported: $CoLX_2 \cdot nH_2O$ (X = Cl, Br, I; n = 1, 1.5), $CuLX_2$ (X = Cl, Br), $NiL_2X_2 \cdot H_2O$ (X = Br, I), $Ni_3L_4Cl_6 \cdot 4\,H_2O$ and $Ni_5L_4Cl_{10} \cdot 4\,H_2O$ [355].

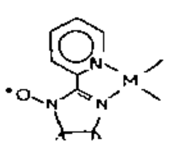
As far as the *N*-oxides of diazoles and their derivatives are concerned, a number of metal complexes have been reported. These include the Na(I) salt and the Co(II) and Cu(II) chelates of 1-hydroxypyrazole 2-oxide (LV) and derivatives [356], along with the alkali metal (Li, Na, K) salts of 1-hydroxyimidazole 3-oxide (LVI) and derivatives [357]. Copper(II) chelates and Na(I) salts with 2,2′-diimidazyl 3,3′-dioxide (LVII) [358], as well as the 3,3′-dioxides of indigo (2,2′-dibenzimidazyl) [358] and 4,4-dihydroxy- (or dinitro-)glycosine have been synthesized [359], in addition to metal complexes (Ag(I), Zn(II), Cd(II), Hg(II), Pb(II)) with the imidazolin-1-oxyl and the imidazolin-1-oxyl-3-oxide (LVIII) free radicals [360]. Metal chelates (LIX) (M = Cu(I), Ag(I), Rh(III), Pt(IV), Co(III), Hg(II), Pb(II)) with the pyridyl imidazoline 1-oxyl free radical [361] and a paramagnetic (μ_{eff} = 1.75 B.M.) $PdCl_2$ complex with the porphyrexide radical (LX) [362] have been prepared, however, the N—O oxygen does not appear to be involved in coordination in either case (LIX, LX).

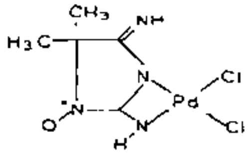

(LV)


(LVI)


(LVII)


(LVIII)


(LIX)


(LX)

NOTE ADDED IN PROOF

Most recent contributions in the field under review are: Binuclear, mixed valence Mn(III,IV) cationic complexes with *N*-bipyO and *N*-phenO of the type $[L_2MnO_2MnL_2]^{3+}(X^-)_3$ (X = ClO_4, 1/2 S_2O_8) [363]. Palladium complexes with the 4-oximinomethyl-2,2,5,5-tetramethyl-Δ^3-imidazoline-1-oxyl free radical [364]. And rare earth complexes with *N*-pyzO and *N*,*N*-pyzO_2, of the following types: M(*N*-pyzO)$_8$(PF_6)$_3$, M(*N*,*N*-pyzO_2)$_4$(ClO_4)$_3$ (M = Y, La, Pr, Eu, Er), $LaCl_3 \cdot 2$(*N*-pyzO), $MCl_3 \cdot 2 \cdot 5$(*N*-pyzO) (M = Pr, Eu), and $MCl_3 \cdot 3$(*N*-pyzO) (M = Y, Er) [365].

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