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METAL COMPLEXES OF AROMATIC AMINE N-OXIDES

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CONTENTS

ABBREVIATIONS

ANO	acridine *N*-oxide
$BiPO_2$	2, 2′-bipyridine *N, N*-dioxide
2, 4, 6-CNO	2, 4, 6-collidine *N*-oxide
CNPNO	cyanopyridine *N*-oxide
DBNO·	di-*tert*-butyl nitroxide
DPNOQ	2, 3-di(2-pyridine *N*-oxide) quinoxaline
4-EtOPNO	4-ethoxypyridine *N*-oxide
2-EtPNO	2-ethylpyridine *N*-oxide
IQNO	isoquinoline *N*-oxide
2, 6-LNO	2, 6-lutidine *N*-oxide
PicANO	picolinic acid *N*-oxide
PicNO	picoline *N*-oxide
PTNO	2-pyridinethiolate *N*-oxide

QNO	quinoline *N*-oxide
TENO	triethylamine *N*-oxide
TMNO	trimethylamine *N*-oxide
TMPNO	2, 2, 6, 6-tetramethylpiperidine nitroxide
TPNO	tripropylamine *N*-oxide

A INTRODUCTION

Amine *N*-oxides act as electron-pair donors, forming molecular adducts and complexes with a variety of acceptor molecules, such as metal salts and complexes[1,2], halogens[3], and organic compounds[4] Although complexes of pyridine *N*-oxides with HCl (ref 5), SO_3 (ref 6), BF_3 (ref 7), iron carbonyl[8], and uranium compounds[9], and a larger number of adducts between aliphatic amine *N*-oxides and various Lewis acids[10–15] were previously known, systematic synthetic and characterization studies of metal complexes of aromatic amine *N*-oxides were initiated[16–19] in 1961 During the last decade, a strong interest in the coordination chemistry of aromatic amine *N*-oxides was displayed by many research groups, and a large number of publications appeared in the literature. These studies were greatly encouraged by the ready availability of a variety of ligands of this type[20]. Two reviews[1,2] covering the subject appeared in this journal in 1968 Since then a significant number of important contributions has appeared in the literature The present review is mainly concerned with the progress in the field of the coordination compounds of aromatic amine *N*-oxides to date The metal complexes of aliphatic and non-aromatic heterocyclic amine *N*-oxides are also briefly covered.

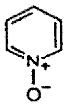
B AROMATIC AMINE *N*-OXIDES

(i) *Preparation and properties*

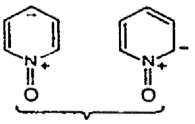
Aromatic amine *N*-oxides are generally prepared in good yields by direct *N*-oxidation of the corresponding aromatic amine with an organic peracid, such as monoperphthalic acid, or hydrogen peroxide and glacial acetic acid[5,20–23]. Other preparative methods involve cyclization reactions of compounds with aliphatic chains[20,21,24,25] *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, in comparison with that observed in the corresponding amine[26–29] The N^+-O^- group is strongly polarizable in both directions and can act either as an electron-attracting or as an electron-donating group, facilitating both electrophilic and nucleophilic substitutions[30] In contrast, electrophilic substitution is not facile in aromatic amines.

In aliphatic amine *N*-oxides the four atomic orbitals of the nitrogen atom are close to sp^3, and have an approximately regular tetrahedral structure[20,31]. In aromatic amine *N*-oxides, however, the lone-pair electrons of the nitrogen, before formation of the N–O bond, are on the sp^2 orbital, so that 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.

This leads to differences in the chemical properties of aliphatic and aromatic amine *N*-oxides[20]. The unsubstituted pyridine *N*-oxide involves nearly equal contributions[32] from canonical structures I, II and III.



I



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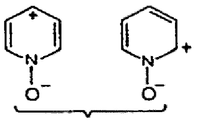


III

The contributions of structural type II are demonstrated by X-ray data and dipole moment determinations. Thus, the N–O bond is significantly shorter in pyridine *N*-oxide (1.37 Å)[33] than in trimethylamine *N*-oxide (1.388 Å)[31] or its hydrochloride (1.424 Å)[34]. Contributions of structural type II are enhanced when electron-withdrawing substituents occupy ring positions[1]. This is suggested by the increased double-bond character of N–O in compounds of this type (e.g. the N–O bond length in 4-nitropyridine *N*-oxide is 1.26 Å)[35]. On the other hand, the fact that the difference in dipole moment between pyridine (2.22 debye) and pyridine *N*-oxide (4.24 debye) is considerably smaller than that between trimethylamine (0.65 debye) and trimethylamine *N*-oxide (5.02 debye) has been also attributed to the importance of the contributions of canonical structure II in the aromatic oxide[36].

The organic chemistry of aromatic amine *N*-oxides has been repeatedly reviewed[20,21,30,37,38]. The vapor ultraviolet spectra of pyridine *N*-oxide are characterized by a very intense band at 35,960 cm^{-1} and a relatively less intense absorption at 29,291 cm^{-1}; these bands are, respectively due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions[39]. At higher energies two additional bands are observed, and attributed to $\pi \rightarrow \pi^{**}$ and $n \rightarrow \pi^{**}$ transitions[39]. Similar vapor UV spectra have been reported for substituted pyridine *N*-oxides[40]. In aprotic solvents, the $\pi \rightarrow \pi^*$ transition in aromatic amine *N*-oxides exhibits a red shift and a hyperchromic effect when compared to the same absorption in the corresponding aromatic amine. In hydroxylic solvents, on the other hand, the *N*-oxide $\pi \rightarrow \pi^*$ band shows a blue shift, which is mainly due to hydrogen bonding[41,42]. The infrared spectra of aromatic amine *N*-oxides have been studied extensively[43–46]. The bands of special interest to coordination chemists are: ν_{N-O}, occurring at 1300–1200 cm^{-1}, δ_{N-O}, occurring at 880–830 cm^{-1}, and CH out-of-plane deformations, which occur in the 900–650 cm^{-1} region[47,48]. These bands usually exhibit characteristic shifts upon metal complex formation[47,48] (vide infra). Proton NMR spectra of pyridine *N*-oxides in non-polar aprotic solvents exhibit chemical shifts in the order γ-H > β-H > α-H from the higher magnetic field[20,28,49]. The α- and γ-protons of the parent base undergo higher shifts than the β-protons upon *N*-oxidation[49]. This is due to an increase in the negativity of the nitrogen by *N*-oxidation, leading to a general decrease in the electron density of the aromatic ring; this decrease is most pronounced for the β-carbon atoms, which do not receive the electron-donating resonance contribution from the oxygen atom[20].

(ii) Substituent effects and correlations

As already mentioned, electron-withdrawing substituents enhance the contributions of structural type II, contributions of canonical forms like III increase in the presence of electron-releasing ring substituents or with increasing size of the parent heterocycle[1,20,38]. These effects are manifested by changes of various physical and chemical properties with variation of the substituent(s) on the aromatic ring. Many successful correlations of various properties of substituted aromatic *N*-oxides with the substituent Hammett sigma constants[50] or the hybrid set of parameters σ^+ (for strongly electron-releasing), σ^- (for strongly electron-withdrawing) and σ (for weakly electron-releasing or withdrawing substituents)[51] have been reported[1,38,50,52–54].

The ν_{N-O} frequencies of substituted aromatic *N*-oxides correlate moderately well with the Hammett σ constants[38,43]; correlations of ν_{N-O} with the σ^+, σ^- and σ hybrid set of parameters are more successful[38,53]. In 1967 Nelson et al. introduced the σ_{PyNO} constants (Table 1), which were derived from the acid dissociation constants of protonated substituted pyridine *N*-oxides[55]. Correlations of σ_{PyNO} with various properties of free and complexed (vide infra) substituted pyridine *N*-oxides are generally successful[1,55].

TABLE 1

σ_{PyNO} constants for substituted pyridine *N*-oxides[55]

Substituent	Ligand pK_{BH^+}	σ_{PyNO}
4-CH_3O–	2.05 [a]	–0.603
4-CH_3–	1.29 [b]	–0.240
3-CH_3–	1.08 [b]	–0.139
H	0.79 [b]	0
4-Cl–	0.36 [c]	0.206
3-Cl–	1.34 [d]	–0.263
4-O_2N–	–1.7 [b]	1.19
4-HO–	2.36 [b]	–0.751
4-H_2N–	3.65 [e]	–1.37
3-H_2N–	1.47 [b]	–0.325
4-HOOC–	–0.48 [f]	0.608
3-HOOC–	0.09 [f]	0.335
4-H_3COOC–	–0.41 [c]	0.574
3-H_9C_4OOC–	0.03 [b]	0.364
3,4-$(CH_3)_2$–	1.01 [b]	–0.105
4-$(CH_3)_2N$–	3.88 [a]	–1.48
4-C_6H_5O–	2.67 [a]	–0.574
4-CN–	–1.17 [g]	0.94

[a] J. N. Gardner and A. R. Katritzky, *J. Chem. Soc., London*, (1957) 4375.

[b] A. R. Katritzky and F. J. Swinbourne, *J. Chem. Soc., London*, (1965) 6707.

[c] Ref. 54.

[d] I. I. Grandberg, G. K. Faizova and A. N. Kost, *Khim. Geterotsikl. Soedin.*, 4 (1966) 561.

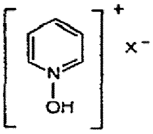
[e] H. Hirayama and T. Kubota, *Yakugaku Zasshi*, 73 (1953) 140.

[f] Ref. 32.

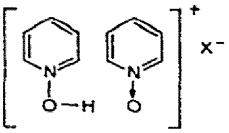
[g] R. G. Garvey and R. Scheele, results reported in ref. 55.

(iii) Donor properties

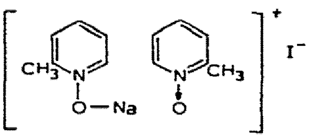
The oxygen in *N*-oxides is basic and hence susceptible to electrophilic addition by metal ions, Lewis acids, protons, halogens and organic electron-pair acceptors[20]. 1:1 and 2:1 adducts of aromatic amine *N*-oxides with hydrogen halides have been reported; 2:1 adducts are also obtained with other inorganic acids of the type HX (X = ClO_4^-, $SbCl_6^-$, PF_6^-, AsF_6^-, SbF_6^-, etc.)[56–58]. The 1:1 adducts are of the normal type IV, while the 2:1 adducts have been formulated as involving hydrogen bonding (V); in fact, their IR spectra do not exhibit absorptions characteristic of free hydroxyl groups[56–58]. An "abnormal" 1:2 NaI salt with 2-picoline *N*-oxide has also been prepared by Vozza[56] and assigned structure VI.



IV



V



VI

Amine *N*-oxides also form molecular adducts with alcohols and phenols through intermolecular hydrogen bonding. A number of 1:1, 2:1 and 1:2 adducts of various phenols with 4-nitropyridine *N*-oxide have been isolated in crystalline form[59]. The infrared spectra of adducts of this type provide a measure of the donor strength of the *N*-oxide. In fact, the negative shift of the ν_{OH} mode of the alcohol or phenol, observed during adduct formation with a neutral ligand, is a function of the bonding formation enthalpy[60,61]. Numerous studies of the properties of aprotic solvent (e.g. CCl_4) solutions containing mixtures of aromatic *N*-oxides and alcohols or phenols have been reported[43,53,55,62–65]. Successful $\Delta\nu_{OH}$ correlations with σ, σ^+ and σ^- or σ_{PyNO} demonstrate that the σ-donor strength of aromatic *N*-oxides increases with increasing contributions of canonical forms III, i.e. with increasing electron-releasing character of the substituent, as would be expected[43,53,55,62]. Figure 1 illustrates the $\Delta\nu_{OH}$ vs σ_{PyNO} plot for a series of adducts of substituted pyridine and quinoline *N*-oxides with phenols[53,55,62]. Linear ΔH^0 vs $\Delta\nu_{OH}$ plots were also reported for methanol adducts with pyridine *N*-oxides[65]. Studies of the adducts between aromatic *N*-oxides and iodine are also suggestive of an increase in the donor strength of the oxide with increasing electron-releasing ability of the substituent[3,66–68]. A linear log K_{eq} vs σ_{PyNO} plot, obtained for a series of 4-substituted pyridine *N*-oxides[67], is illustrated in Fig. 1. Recent studies of the molecular adducts between mono-*N*-oxides of aromatic diazines and iodine led to the conclusion that the N–O oxygen rather than the second ring nitrogen is the donor atom in these compounds[69].

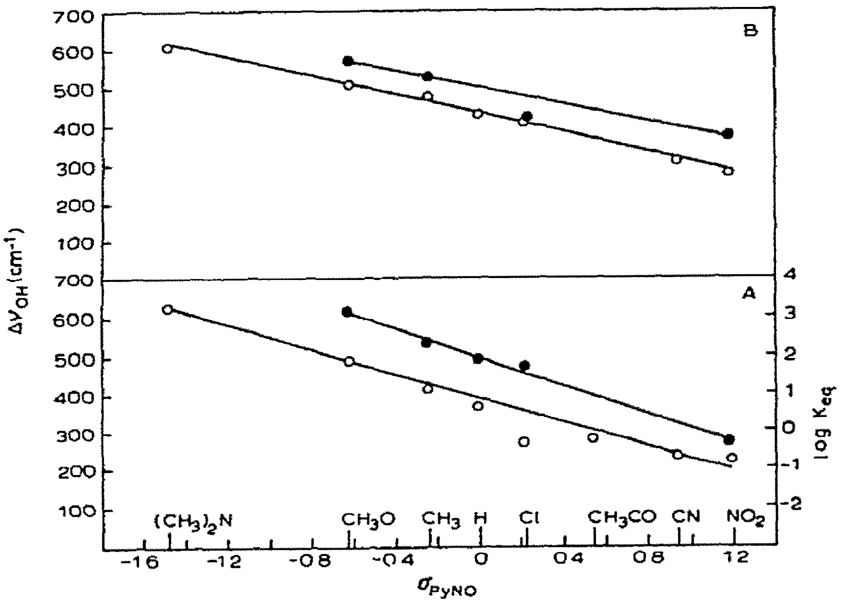


Fig 1 Correlations of σ_{PyNO} (ref 55) with (A), ○, $\Delta\nu_{OH}$ frequencies for the interactions of 4-substituted pyridine *N*-oxides with *p*-methylphenol[62], ●, log K_{eq} for the interactions of 4-substituted pyridine *N*-oxides with iodine[67], (B), ○ and ●, $\Delta\nu_{OH}$ frequencies for the interactions of 4- and 6- (respectively) substituted quinoline *N*-oxides with phenol[62] $\Delta\nu_{OH}$ for 6-substituted quinoline *N*-oxides gives more satisfactory plots when correlated with the Hammett σ constants[62]

C. METAL COMPLEXES OF MONO *N*-OXIDES OF AROMATIC AMINES

(i) Preparation of metal complexes and some reactions between N-*oxides and metallic compounds*

The majority of the metal complexes of aromatic amine *N*-oxides are decomposed by water The methods employed for their preparation involve, therefore, interactions between ligand and metallic compound in non-aqueous solvents[1] In certain cases, organic dehydrating agents, such as triethyl orthoformate[70] and 2,2-dimethoxypropane[71], have been utilized either for the dehydration of hydrated metal salts or even as interaction media Crystalline metal complexes with *N*-oxides are usually rather easily obtained and a large number of compounds of this type are stable in the atmosphere. Descriptions of the various synthetic methods employed for the preparation of *N*-oxide complexes are, thus, considered unnecessary, special synthetic procedures or handling precautions required for certain metal complexes will be mentioned in the appropriate sections

Synthetic procedures for mixed *N*-oxide–π-ligand Pt^{II} complexes of the general type (A)PtCl$_2$(L) (where A = alkene, alkyne, styrene, vinyl ester or CO and L = aromatic amine *N*-oxide)[72–79] were described in detail in a previous review[2] Analogous Pd^{II} complexes are more difficult to isolate, owing to their lower stability, nevertheless, a series of complexes of the type $[(C_2H_4)PdCl_2L]$ (L = C_5H_5NO and substituted derivatives) was obtained by interaction of $[(C_2H_4)PdCl_2]_2$ with an aromatic *N*-oxide in dichloromethane, under an ethylene blanket at low temperatures[80].

In certain cases, the aromatic *N*-oxides react with labile metallic compounds. Thus, when V^{III} salts interact with excess *N*-oxide, either in the presence of air or under inert conditions, part of the ligand[81–83] may oxidize V^{3+} to VO^{2+} Reactions of $V(ClO_4)_3$ with various pyridine *N*-oxides, under inert conditions, resulted in the formation of *N*-oxide complexes of the V^{III} salt, contaminated with major or minor amounts of $VO(ClO_4)_2$-*N*-oxide complexes[82] Pure $VO(ClO_4)_2 \cdot 5C_5H_5NO$ was prepared from VCl_3, C_5H_5NO and $LiClO_4$ in ethanol in the presence of atmospheric oxygen[81] On the other hand, $VO(NCS)_2 \cdot nC_5H_5NO$ ($n = 4, 5$) and $VO(NCS)_2 \cdot 4(4\text{-}CH_3C_5H_4NO)$ were obtained by reaction of $V(NCS)_3$ and aromatic *N*-oxide, under inert conditions[83] The following redox reaction was proposed for these interactions[83], where Z = H, CH_3

$$V(Z\text{-}C_5H_4NO)_n(NCS)_3 \rightarrow VO(Z\text{-}C_5H_4NO)_{n-1}(NCS)_2 + \{Z\text{-}C_5H_4N + SCN\} \qquad (1)$$

Redox reactions of the above type have been widely utilized for the deoxygenation of aromatic *N*-oxides, for synthetic purposes[20] Reactions of aromatic *N*-oxides with P^{III} halides in organic solvents lead to the formation of the corresponding amines and P^{V} oxohalides; the reactions most probably involve formation of a PX_3–*N*-oxide adduct as an intermediate[84]

$$C_5H_5NO + PCl_3 \rightarrow [C_5H_5NO \cdot PCl_3] \rightarrow C_5H_5N + POCl_3 \qquad (2)$$

Other reducing agents, reportedly deoxygenating *N*-oxides, are ferrous salts[85], sodium hydrosulfite or sulfite, $NaBH_4 + AlCl_3$ (ref 86), NO (ref. 59), Fe or Zn powder in acetic acid[87] or alkaline media[59]. sulfur (in liquid ammonia), sulfur compounds[88] (e g mercapto compounds, thiourea, S_2Cl_2, C_6H_5SCl), etc. Sulfur dioxide, which reportedly forms a 1 1 adduct with trimethylamine *N*-oxide[10, 13] can reduce aromatic *N*-oxides only under certain reaction conditions[89] Mixtures of triphenylphosphine and an aromatic amine *N*-oxide react at 230°C, yielding triphenylphosphine oxide and the corresponding aromatic amine[90] Neutral phosphite esters are not very effective deoxygenating agents for *N*-oxides[84], however, the reaction goes to completion when triethyl phosphite is used in combination with a peroxide and oxygen[91]. Reaction of aromatic *N*-oxides and *N,N*-dioxides with PCl_5, $POCl_3$ or KCN leads to deoxygenation of the amine oxide and simultaneous insertion of halogen or CN groups at the 2- or 4- ring position[92–94] Intermediates of the types $L \cdot PCl_5$ (ref. 92) and $(L)P(O)Cl_2$ (ref. 93) (L = amine *N*-oxide) have been proposed for *N*-oxide reactions with PCl_5 and $POCl_3$ respectively. Pyridine *N*-oxide reacts with C_6H_5MgBr in tetrahydrofuran to yield 1-hydroxy-2-phenyl-1,2-dihydropyridine, the quinoline analog can be obtained by a similar reaction at low temperatures, but at higher temperatures 2-phenylquinoline *N*-oxide derivatives are the main reaction products[95]

Aromatic amine *N*-oxides can generally displace π-ligands from their metal complexes. Thus, in addition to the displacement of ethylene in Pt^{II} (refs 2, 72–79) and Pd^{II} (ref. 80) complexes, reaction of pyridine *N*-oxide (PNO) with iron tetracarbonyl in benzene, leads to the formation of $[Fe(PNO)_6][Fe_4(CO)_{13}]$, iron is in the +2 oxidation state in the cationic PNO complex[8]. Substitution reactions of halopentacarbonylrhenium(I) complexes with PNO yield $Re(CO)_3(PNO)_2\ X$ (X = Cl, Br, I), while tricarbonyl(cycloheptatriene)molybdenum produces $Mo(CO)_3(PNO)_3$ when allowed to interact with PNO[96]. Finally, metallations of the aromatic ring of *N*-oxides have also been reported reaction of PNO with Hg^{II} acetate in glacial acetic acid yields[97] 4-$ClHgC_5H_4NO$, and reaction of 4-chloro-3-methylpyridine *N*-oxide with *n*-butyllithium results in the insertion of Li at the 6-position of the aromatic ring, via an *N*-oxide–Bu^nLi adduct intermediate[98].

(ii) Generalities

Monodentate "oxo-ligands"[99] of the general type R_nZO (where Z is a Group VA element N, P, As, etc) coordinate invariably through the oxygen to metal ions[16–18,47,48,100–102] Only in the case of metal complexes of organonitroxide free radicals has the possibility of interaction of an unoccupied orbital of the metallic compound with the three π-electron fragments N O been advanced[103], however, infrared evidence is generally in favor of coordination of the latter ligands through the N–O oxygen[104–107] The nitrogen atom in tertiary amine *N*-oxides is devoid of a lone pair, in fact, the lone electron pair of nitrogen in tertiary amines is used for bonding to the oxygen atom during *N*-oxidation, i e


(3)

Hence, the only site available for coordination in tertiary amine *N*-oxides is the oxygen atom

The aromatic rings of PNO, quinoline *N*-oxide (QNO) and isoquinoline *N*-oxide (IQNO) do not introduce severe steric hindrance during formation of cationic metal complexes[16–18,53,81,82,108–121] Thus, complexes of the types $[ML_6]^{n+}$ (n = 2 or 3) (refs 16–18, 53, 82, 108, 110–112, 117–120) and $[MOL_5]^{2+}$ (refs 81, 114, 115) are formed during interactions of these ligands with most 3*d* metal perchlorates, tetrafluoroborates and, in certain cases in the presence of excess ligand, nitrates Copper(II) generally forms $[CuL_4]^{2+}$ cationic complexes with aromatic *N*-oxides, and only in the cases of PNO and 4-methylpyridine *N*-oxide were $[CuL_6]^{2+}$ complexes also isolated[17,122]. Although the maximum possible coordination numbers for complexes of 3*d* metal ions with monodentate ligands are usually attained in cationic 3*d* metal complexes with PNO, QNO or IQNO, the effective symmetries of these $[ML_6]^{n+}$ and $[CuL_4]^{2+}$ complexes are lower than O_h or D_{4h}, respectively[123] (vide infra) This is due to the non-linearity of the N–O–M bond sequence, a necessary requirement of the electronic distribution about the oxygen atom[123] Examination of the two extreme cases of tetrahedral sp^3 (for a purely single N–O bond)[1,124] and trigonal planar sp^2 (for a double N–O bond) disposition of oxygen lone pairs in the metal complexes of aromatic amine *N*-oxides, shows[1] that the M–O–N bond angle should lie somewhere between 108° and 120° X-ray crystal structure determinations of various cationic and neutral aromatic amine *N*-oxide metal complexes has established[125–134] that the M–O–N bond angle lies between 108° and 134°. Comparison of the cationic 3*d* metal complexes of unsubstituted pyridine and quinoline *N*-oxides with those reported for R_3ZO (R = alkyl, aryl, dialkylamino group, Z = Group VA element)[100,102,135–140] clearly shows the greater steric hindrance introduced during coordination of the latter ligands In fact, R_3ZO ligands usually form 4 1 complexes with divalent 3*d* metal perchlorates[100,102,135–139], complexes of the type $[M(R_3ZO)_5]^{2+}$ have been reported[140] for R = CH_3 and Z = P The highest possible coordination numbers are, nevertheless, not always attained in PNO metal complexes, for instance, Y^{III} and Ln^{III} ions form $[M(PNO)_8]^{3+}$ cationic complexes[113] Higher coordination numbers have been reported for several cationic complexes of these metal ions with other monodentate ligands (e g certain sulfoxides yield $[YL_9]^{3+}$ and $[LnL_9]^{3+}$ complexes[141])

The presence of 3- or 4-substituents in the aromatic ring of PNO and 4- or 6-substituents in that of QNO does not introduce steric interference at the coordination site, thus, $[ML_6]^{n+}$ complexes of ligands of these types with a variety of 3*d* metal ions have been reported[48,53,82,108 117–119] 4-Ethoxypyridine *N*-oxide (4-EtOPNO) forms $[M(4\text{-}EtOPNO)_5]^{2+}$ with certain metal (Mn, Co, Ni, Zn) perchlorates[142], but $[M(4\text{-}EtOPNO)_6]^{2+}$ complexes were obtained during interactions of an excess of this ligand with Co^{II} and Ni^{II} nitrates[143] Steric effects become obvious in 2-substituted and 2,6-disubstituted pyridine *N*-oxides 2-Picoline *N*-oxide (2-PicNO) forms $[Co(2\text{-}PicNO)_5](ClO_4)_2$, involving a trigonal bipyramidal complex cation[123,133], and 4 1 complexes with Ni^{II} nitrate and perchlorate[144] However, the 2-ethylpyridine *N*-oxide (2-EtPNO) yields a hexacoordinated cationic Ni^{II} complex, under the same experimental conditions[144], QNO, which corresponds to a 2,3-disubstituted pyridine *N*-oxide, behaves in a similar way, as already mentioned 2,6-Lutidine *N*-oxide (2,6-LNO) forms 4 1 complexes with divalent 3*d* metal perchlorates (M = Mn to Zn)[145] These ligands (2-PicNO, 2-EtPNO, 2,6-LNO) were, on the other hand, also found to yield 6 1 complexes with the same 3*d* metal perchlorates, when different synthetic procedures were employed[146]. The $[Co(2,6\text{-}LNO)_5]^{2+}$ cation has been shown to exist in solutions of $[Co(2,6\text{-}LNO)_4](ClO_4)_2$, containing excess ligand[145,147] and in nitromethane solutions[146] of $[Co(2,6\text{-}LNO)_6](ClO_4)_2 \cdot 2H_2O$. 2-, 3- and 4-cyanopyridine *N*-oxides generally form[148] 6 1 complexes with Co^{II} and Ni^{II} perchlorates and 2 1 complexes with $AgClO_4$ The above examples suggest that substituents at the 2- and 6- positions of the PNO ring, although introducing sufficient steric interference as to cause the stabilization of lower than hexacoordinated cationic complexes with 3*d* metal ions, do not provide a severe enough steric hindrance to impede the formation of the corresponding 6 1 complexes, the stoichiometry of the complexes obtained with these ligands depends on the synthetic method utilized. Finally, acridine *N*-oxide (ANO), corresponding to a 2,3,5,6-tetrasubstituted pyridine *N*-oxide, forms complexes of the type $[M(ANO)_4(OH_2)_2](ClO_4)_2 \cdot xH_2O$ (M = Co, Ni, Zn)[149] Trivalent 3*d* metal ions (i e Cr^{3+}, Fe^{3+}) yield $[ML_6]^{3+}$ complexes with 2- and 2,6-substituted pyridine *N*-oxides and ANO[145,146,149].

The steric effects of substituents on the aromatic ring of *N*-oxides are also evidenced by the influence they exert on various properties of mixed *N*-oxide–anionic or neutral ligand metal complexes Thus, adducts of the type $TiF_4 \cdot 2L$ (or, more generally, $MX_4 \cdot 2L$, X = halide ion) with non-bulky or sterically hindered ligands, such as pyridine *N*-oxides, are normally *cis*-octahedral[150–153] The *trans*-octahedral isomers are stabilized only when there is sufficient steric interaction to overcome symmetry effects and the tendency to maximize F-to-Ti p_π–d_π bonding, ^{19}F NMR studies of adducts of this type with various pyridine *N*-oxides suggest that the *cis* isomer is the predominant species when L = PNO, 2-PicNO, 2-EtPNO, 2,4-LNO and 3,5-LNO, however, in the case of $TiF_4 \cdot 2(2,6\text{-LNO})$, stabilization of the *cis* isomer is sterically hindered, and the *trans* complex is formed exclusively[153].

Bis-(β-ketoenolato) Co^{II}, Ni^{II} and Cu^{II} chelates form isolable 1:2 and/or 1:1 adducts with aromatic amine *N*-oxides[154–157]. Proton NMR contact and pseudocontact shift studies of these adducts in solution have established many cases of steric interference of the ring substituents of aromatic amine *N*-oxides. Thus, the *meta*-substituent in 3-PicNO interferes with the $Co(2,4\text{-pentanedionato})_2$ ($Co(AA)_2$) ring system (but, presumably not with the corresponding $Ni(AA)_2$ system), restricting the rotation of the pyridine ring[154]. The steric influence of the methyl substituents of 2,6-LNO in adducts with $M(AA)_2$ is suggested by the fact that no proton is allowed to spend much of its time at apogee or perigee (in a rotamer, having the plane of the pyridine ring perpendicular to that of the β-ketoenolato ring, the protons at apogee and perigee with respect to the metal were, respectively, defined as at 0° and 180° internal rotation), similar effects were not observed for the corresponding adducts of any of the less sterically hindered picoline *N*-oxides, moreover, 2,6-LNO apparently forms only the 1:1 adduct with $M(AA)_2$ (M = Co, Ni)[154]. QNO, corresponding to a 2,3-disubstituted pyridine *N*-oxide, also forms only 1:1 adducts with $M(AA)_2$, whereas IQNO, a 3,4-analog, forms 2:1 adducts with these metal chelates[155].

Steric effects may also influence the mode of coordination of polyanions with coordinating ability in aromatic amine *N*-oxide metal complexes. Thus, divalent 3*d* metal nitrates generally form neutral 1:2 complexes with these ligands when stoichiometric amounts of salt and ligand are allowed to interact[16, 18, 110, 143, 144, 158, 159]. Complexes of this type (the exception being the Cu^{II} compound) with PNO and 4-substituted derivatives are hexacoordinated, involving two chelating nitrato groups, as indicated by spectral and magnetic evidence[16, 18, 110, 143, 144]. $[Co(2,6\text{-LNO})_2(NO_3)_2]$ and its 2,4,6-collidine *N*-oxide (2,4,6-CNO) analog were assigned similar structures[158]. However, more recent studies of $[M(2,6\text{-LNO})_2(NO_3)_2]$ (M = Mn, Co, Ni, Zn) complexes led to the conclusion that these compounds are pentacoordinated, involving one mono- and one bidentate nitrato ligand[159]. In fact, the electronic spectra and magnetic moments of these complexes are suggestive[159] of pentacoordinated configurations[123, 142, 145, 146, 160]. On the other hand, the presence of two types of coordinated nitrate (mono- and bi-dentate) is demonstrated by the occurrence[159] of four bands (combination vibrational modes of the nitrato groups[161, 162]) at 1800–1700 cm^{-1}, compounds involving one type of coordinated nitrate exhibit only two bands in this region[161, 162]. Formation of complexes of this type with 2,6-LNO is apparently due to steric interference between the methyl ring substituents and the nitrato ligands[159].

In a series of papers Muto et al. discussed the effects of aromatic ring substituents on the properties of 1:1 complexes between *N*-oxides and Cu^{II} halides[163–166]. Compounds of this type are binuclear, *N*-oxide-bridged, and exhibit subnormal and temperature-dependent paramagnetism[167], they have been the subject of extensive studies, which will be discussed in a later section. Spin–spin coupling in compounds of this type primarily occurs by means of a super-exchange interaction between the Cu^{II} ions of the dimer, through the bridging oxygen atoms of the *N*-oxide ligands[168–170]. Primarily, Muto et al. found the following. Although substituent Hammett σ constants do not correlate with the observed (*d*–*d*) band positions or magnetic moments in the complexes, a fairly linear plot of the $\bar{\nu}_{max}$ (kK) of the (d–d) band vs μ_{eff} is obtained. Increasing spin–spin interaction and occurrence of the Cu^{2+} (d–d) transition at higher energies are generally observed with increasing steric hindrance of the N-oxide ligand. Thus for example, μ_{eff} and the wavelengths of the (d–d) band maximum increase along the series 2,6-LNO < 2-PicNO < 3-PicNO < 4-PicNO. These trends, which are illustrated in Table 2, suggest that in Cu^{II}–N-oxide binuclear complexes, the steric factor is more important in determining the extent of the magnetic interaction, or the (d–d) transition energy, than the electronic effect[163–166]. The importance of the substituent(s) electronic effects is evident in monomeric N-oxide–metal complexes, in complexes of this type a variety of successful correlations of substituent sigma constants to various physicochemical properties (including linear $\bar{\nu}_{max}$ of the (d–d) band in $[CuL_4](ClO_4)_2$ vs σ plots[166]) have been reported, and will be detailed in the next section.

Mixed N-oxide–anionic or neutral ligand metal complexes can be obtained in a variety of metal to N-oxide ratios. Specifically, studies of equilibria in the system $Cr(ClO_4)_3$–$HClO_4$–H_2O–PNO revealed that the complete series of species, typically $[Cr(OH_2)_{6-n}\cdot(PNO)_n]^{3+}$, where n = 0–6 inclusive, are formed[171]. For n = 2, 3 or 4 both *cis* and *trans* isomers were obtained with separation achieved by ion-exchange techniques[171]. The widest variety of metal to N-oxide ratios has been reported for metal halide complexes. The stoichiometries of the complexes obtained with these salts depend on the synthetic procedure utilized, complexes involving high metal to N-oxide ratios have also been ob-

TABLE 2

Effects of substituents on the aromatic ring on the magnetic moments and the (d–d) transition maxima in 1:1 $CuCl_2$–aromatic amine N-oxide complexes[163–166]

Ligand	λ_{max} (nm)	μ_{eff} (25°C) (B.M.)
3-ClPNO	820	0.46
3-HOOCPNO	885	0.54
$3\text{-}H_5C_2OOCPNO$	825	0.48
$4\text{-}H_5C_2OOCPNO$	830	0.50
$3\text{-}CH_3COPNO$	900	0.57
$4\text{-}NO_2PNO$	1100	1.20
4-CNPNO	805	0.96
3-HOPNO	795	0.37
4-HOPNO	[a]	0.33
2-EtPNO	763	0.32
3-EtPNO	810	0.46
4-EtPNO	820	0.59
2,4-LNO	765	0.37
$2\text{-}CH_2OH\cdot PNO$	800	0.39
$3\text{-}CH_2OH\cdot PNO$	813	0.50
$4\text{-}CH_2OH\cdot PNO$	818	0.53
QNO	733	0.33
4-MeQNO	750	0.40
IQNO	810	0.51

[a] Not reported

tained[172,173] by thermal elimination of *N*-oxide or aquo groups from richer (in *N*-oxide ligands) or hydrated metal halide complexes A few illustrate examples of certain metal halide–aromatic amine *N*-oxide (L) complexes of various stoichiometries are cited here (X = halide ligand) $MCl_4 \cdot nL$ (n = 1, M = Te (ref 174), n = 2, M = Hf, Th, Te, Sn (refs. 174–176); n = 3, M = Zr, Pt (ref 175)), MCl_3 nL (n = 2, M = Fe (refs 177, 178), n = 3, M = Fe, Ru (refs. 177, 179), n = 5, M = Rh (ref 179)), $MX_2 \cdot nL$ ($n = \frac{1}{2}$, M = Mn, Ni (ref. 172), n = 1, M = Mn, Co, Ni, Cu, Zn, Cd, Hg, Sn (refs 16, 167, 172, 173, 180–183), n = 2, M = Mn, Co, Ni, Pd, Cu, Zn, Cd, Sn (refs 16, 18, 142, 167, 172, 173, 180, 183, 184), n = 3, M = Co (ref 16), n = 4, M = Ni, Cu (refs 18, 185), n = 5, M = Ni (ref 172), n = 6, M = Ni (refs 18, 172)), $M_3X_6L_2$ (M = Cu, Cd) (refs 180, 186), $M_4X_8L_2$ (M = Cu, Cd) (refs 180, 186) It should be noted that, in addition to the two latter types of complex, many of the $MX_2 \cdot nL$ compounds involving high M to L ratios are bi- or polynuclear

(iii) Infrared spectra

Coordination of aromatic amine *N*-oxides through the N–O oxygen is manifested by characteristic shifts of various ligand IR bands In metal complexes of pyridine *N*-oxide and its substituted derivatives, ν_{N-O} generally occurs at lower frequency than in the free ligand[47,48]. Coordination of pyridine *N*-oxides with metal ions results in a drain of electron density from the oxygen to the metal, this leads to an increase of the energy mismatch between the oxygen and nitrogen *p* orbitals and, consequently, a decrease of the contribution of the oxygen orbitals in the π system of the aromatic ring[53]. The N–O bond is thus weakened to some extent, this effect gives rise to negative ν_{N-O} frequency shifts[48,53,111] On the other hand, kinematic coupling[111] and, in the case of transition metal ions, metal-to-ligand d_π–p_π back-bonding would tend to produce positive ν_{N-O} frequency shifts In metal complexes with pyridine *N*-oxides the former effect obviously overrides the latter effects, since negative ν_{N-O} shifts are invariably observed. Metal complexes of isoquinoline and acridine *N*-oxides also exhibit negative ν_{N-O} shifts[117,149]. However, in 3*d* metal complexes with quinoline *N*-oxides and 4-substituted derivatives, ν_{N-O} is found either at the same frequency as in the free ligand or even slightly shifted towards higher frequencies[117,119]. This is mainly due to the "impurity" of ν_{N-O} in quinoline *N*-oxides[119], in fact, ν_{N-O} is coupled with vibrations of the quinoline ring in these compounds[187]. Nevertheless, extensive metal-to-ligand π-bonding may also be contributing to this effect[117], in fact, metal ions with no *d* electrons available for d_π–p_π back-donation (e g TiO^{2+}, ZrO^{2+}, Th^{4+}), form QNO complexes, exhibiting large negative ν_{N-O} shifts[121] Transition metal complexes of 6-substituted quinoline *N*-oxides show negative shifts[118] of the bands assigned as ν_{N-O}. Typical examples, illustrating the shifts of ν_{N-O} and other IR bands of aromatic amine *N*-oxide metal complexes, are given in Table 3. ν_{N-O} splittings in $[ML_6]^{n+}$ and $[CuL_4]^{2+}$ complexes with pyridine *N*-oxides have been interpreted in terms of ligand-field symmetries lower than O_h and D_{4h}, respectively[123] (cf Sect C(*vii*))

Other ligand IR bands, undergoing shifts upon metal complex formation, are δ_{N-O} and the CH out-of-plane deformation modes[47,48,176] (Table 3). The δ_{N-O} mode occurring at 880–830 cm^{-1} in the free ligands shows small negative or positive frequency shifts in PNO metal complexes[47,48]; larger and invariably positive δ_{N-O} shifts are observed in

TABLE 3

Regions of ν_{N-O}, δ_{N-O}, γ_{CH} and ν_{M-O} (cm^{-1}) vibrations in cationic aromatic amine *N*-oxide metal complexes (Nujol mull spectra)

Compound	M	ν_{N-O}	δ_{N-O}	γ_{CH}	ν_{M-O}	Ref.
PNO		1243	842	922, 777 [a]		47
$[M(PNO)_6](ClO_4)_3$	Al, Cr, Fe	1224–1206	849–839	936–932 776–774	442–385 402–325	47,48
$[M(PNO)_6](ClO_4)_2$	Mn, Fe, Co, Ni, Cu, Zn	1226–1217	839–836	924–919 778–776	368–311	47,48
2-PicNO		1242	850	757 [b]		123
$Ni(2\text{-}PicNO)_4(ClO_4)_2$		1194	*c*	762	380, 359	144, 193
$[Co(2\text{-}PicNO)_5](ClO_4)_2$		1208, 1196	*c*	780	365	123, 193
$[Cu(2\text{-}PicNO)_4](ClO_4)_2$		1202	*c*	*c*	420	146
2,6-LNO		1245	844	762 [b]		145
$[Cr(2,6\text{-}LNO)_6](ClO_4)_3$		1188	*c*	770	485	145, 193
$[Mn(2,6\text{-}LNO)_4(OClO_3)](ClO_4)$		1203	*c*	772	338	145, 193
$[M(2,6\text{-}LNO)_4](ClO_4)_2$ (tetracoordinated)	Fe, Co, Ni, Cu, Zn	1212–1190 [d]	*c*	781–765	456–372 [d]	145, 193
$Ni(2,6\text{-}LNO)_4(ClO_4)_2$ (pentacoordinated)		1186	*c*	775	407, 390, 370	146, 193
QNO		1229	788	*c*		117–119
$[Fe(QNO)_6](ClO_4)_3$		1230	*c*	*c*	363	119
$[M(QNO)_6](ClO_4)_2$	Mn, Co, Ni, Zn	1230–1224	804–797	*c*	388–349	117, 119
IQNO		1182	818	*c*		117
$[M(IQNO)_6](ClO_4)_2$	Co, Ni	1160–1159	834–829	*c*	*c*	117
ANO		1332	*c*	*c*		149
$M(ANO)_4(ClO_4)_2 \cdot xH_2O$ [e]	Co, Ni, Zn	1326–1323	*c*	*c*	368–366	149

[a] ν_{10b} and ν_{11} modes (KBr spectra), these bands occur at 877 and 758 cm^{-1}, respectively, in CS_2 solution[47,48] Other γ_{CH} PNO bands ν_5, 965, ν_{17a}, 944, ν_{10a}, 816 cm^{-1} (in CS_2)[48]

[b] ν_{11} (ref 43).

[c] Not reported

[d] One or two bands.

[e] $x = 3$ or 6

QNO and IQNO metal complexes[117,118] The CH out-of-plane deformation bands (γ_{CH}) are generally shifted towards higher frequencies upon metal complex formation[47,48,176]. These positive shifts are due[188] to a decrease in the electron density of the ring, resulting from the coordination of the ligand to a metal ion[48]. Absorptions attributable to characteristic vibrations of substituents on the aromatic ring may also be shifted in *N*-oxide metal complexes Thus, $\nu_{C=O}$ in 3- and 4-acetyl-substituted pyridine *N*-oxides is shifted towards higher frequencies in the metal complexes of these ligands[48]. These shifts are larger for the 4- than for the 3-substituted ligand, this is consistent with the much greater influence of the increased (through coordination to metal ions) electron-attracting property of the NO group on the electron density at the 4- (and 2-) ring position relative to the 3-position, in fact, complex formation results in an inhibition of resonance structures II of the ligand[48]

Metal–ligand (ν_{M-O}) vibrational modes occur[47,48,53,108,111,119,146,180–182,189–193] in the low-frequency IR region, at 500–200 cm^{-1} ν_{M-O} for a given metal ion and *N*-oxide ligand decreases with increasing coordination number (e g ν_{M-O} occurs[108] at 366 cm^{-1} in $[Cu(PNO)_6]^{2+}$ and as a doublet at 417 and 385 cm^{-1} in $[Cu(PNO)_4]^{2+}$) (cf. Table 3) Metal halide complexes exhibit the metal–halogen stretching vibrations in the same frequency region, these bands are generally diagnostic of the stereochemistry of these complexes (see, for example, ref 194). Conclusions concerning the nature of the bridging ligand in bi- or polynuclear *N*-oxide metal halide complexes can be drawn from the splitting of the ν_{M-O} or ν_{M-X} bands[180–182,189,195,196]. Raman spectra lead, of course, to more decisive conclusions[197], especially when the nature of the bridging ligand (i e. *N*-oxide or halogen) cannot be unambiguously established from IR spectra alone. For instance, dimeric *N*-oxide complexes of the type $HgLX_2$, for which both *N*-oxide oxygen-[181] and halogen-[180,195]bridged structures were proposed by different groups on the basis of low-frequency IR spectra, have been recently assigned a halogen-bridged structure on the basis of a combined IR–Raman study[197]) Finally, *N*-oxide metal complexes involving coordinated polyanions show bands attributable to the metal–polyanion stretching vibrations in the low-frequency IR region (e g ν_{M-O} (perchlorato[193], nitrato or sulfato[159,198]), ν_{M-N} or ν_{M-S} (thiocyanato[159,199]) etc), splittings of the fundamental vibrational modes of the ionic polyanions are also observed in the IR spectra of complexes of this type

The frequencies of various IR bands of free and coordinated aromatic amine *N*-oxides are influenced by the inductive effects of substituents on the aromatic ring ν_{N-O} vs σ plots are linear for 4-substituted pyridine *N*-oxides[53,55,108], as already mentioned Successful correlations of ν_{N-O} with σ constants have also been reported for the complexes of 4-substituted pyridine *N*-oxides with several metal ions[53,108,190,191,200,201] Metal ions reportedly showing linear ν_{N-O} vs. σ plots for their 4-substituted pyridine *N*-oxide complexes are Mn^{II} to Zn^{II} (refs 53, 108), Ti^{IV} (ref. 190), Zr^{IV} (ref. 191), UO_2^{2+} (ref. 200), and organo-tin(IV) and -lead(IV) ions[201]. Characteristic plots of this type are illustrated in Fig. 2 and Table 4. Nevertheless, in pyridine *N*-oxide complexes with other metal ions, ν_{N-O} was found insensitive to substituent variations[82,108,202–205], (Table 4), metal ions showing this trend are: vanadium ions (V^{III}, V^{IV}, VO^{2+}) (refs 82, 202, 203), Cr^{III}, Fe^{III} (refs 108, 205), Sn^{4+} (refs. 203, 204) ν_{N-O} is also rather insensitive to substituent variations in $TiCl_4$ complexes with pyridine *N*-oxides[203], but the corresponding

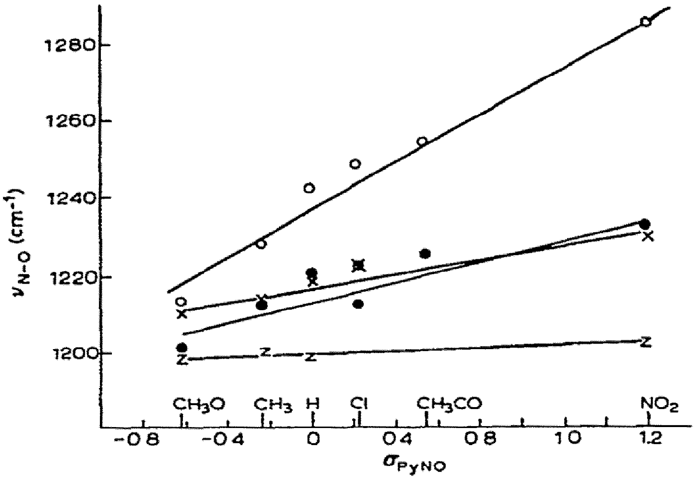


Fig 2 Correlations of σ_{PyNO} (ref 55) with ν_{N-O} frequencies of 4-substituted pyridine *N*-oxides and their metal complexes. o, free 4-Z-PNO (ref 53), •, $[Ni(4\text{-}Z\text{-}PNO)_6](ClO_4)_2$ (ref 53), ×, $Ti(4\text{-}Z\text{-}PNO)_2F_4$ (ref 190), Z, $V(4\text{-}Z\text{-}PNO)_2F_4$ (ref 192)

TiF_4 complexes produced a linear ν_{N-O} vs σ plot[190]. In (A)$PtCl_2$(L) (A = alkene or CO, L = PNO and derivatives) complexes, ν_{N-O} is sensitive to the inductive effects of substituents on the aromatic ring[2,77]. The $\nu_{C=C}$ or $\nu_{C=O}$ modes of the π-ligand are virtually insensitive to these effects[2, 73, 79] Trans-axial coordination (relative to the vanadyl oxygen) of one aromatic amine *N*-oxide ligand to the V^{IV} ion in bis-(β-ketoenolato)oxovanadium(IV) chelates results in negative shifts of the V=O stretching vibrational mode[206–208] $\Delta\nu_{V=O}$ (i e $\nu_{V=O}$ (in the original pentacoordinated chelate) minus $\nu_{V=O}$ (in the hexacoordinated *N*-oxide adduct)) was quite successfully correlated to 4-substituent σ_{PyNO} constants, in addition, linear plots of $\Delta\nu_{V=O}$ vs $-\Delta H$ (reaction enthalpy) and $-\Delta H$ vs. σ_{PyNO} were reported[206–208]. In analogous uranyl complexes the U–O (uranyl or β-ketoenolato) vibrations are insensitive to the effects of 4-substituents on the pyridine ring[209], but ν_{N-O} in UO_2^{2+} complexes with aromatic *N*-oxides is, generally, sensitive to these effects[209, 210] For cationic complexes of the unsubstituted pyridine *N*-oxide with 3*d* metal ions a linear ν_{N-O} vs. ν_{M-O} plot was reported, for divalent $3d^{5-10}$ metal ions (Mn^{II} to Zn^{II}) the order of increase of ν_{N-O} (or ν_{M-O}) follows the usual pattern of increasing ligand-field stabilities for this series[111] In the quinoline *N*-oxide series, no correlations of ν_{N-O} to σ constants or other parameters have been generally attempted, in view of the "impurity" of this IR band (vide supra)[187].

ν_{M-O} bands in aromatic amine *N*-oxide metal complexes are generally sensitive to the inductive effects of ring substituents, furthermore, they are inherently more sensitive than ν_{N-O} to metal-to-ligand (or ligand-to-metal) π-bonding[192] Linear ν_{M-O} vs σ plots for 4-substituted pyridine *N*-oxide complexes with metal ions with no *d* electrons available for back-donation (i e Ti^{4+}, Zr^{4+}) or d^1 systems (V^{4+}) were reported[190–192]; ν_{M-O} in complexes of this type increases with increasing electron-releasing property of the substituent[190–192] (Fig 3) No correlation was, however, found in similar plots of the cor-

TABLE 4

Effects of substituents on the ν_{N-O} and ν_{M-O} frequencies (cm^{-1}) of some substituted aromatic amine *N*-oxide metal complexes

Ligand	Z	$[CrL_6](ClO_4)_3$ ^{a}		$[CoL_6](ClO_4)_2$ ^{a}		$[NiL_6](ClO_4)_2$ ^{a}	
		ν_{N-O}	ν_{Cr-O}	ν_{N-O}	ν_{Co-O}	ν_{N-O}	ν_{Ni-O}
4-Z-PNO	CH_3O	1198	340	1201	282 422–410^{b}	1201	299^{c} 422–410^{b}
	CH_3	1200	445	1207 1227, 1205^{b}	392, 384	1206 1212 1222, 1212, 1205^{b}	393 325^{c}
	H	1199 1215, 1200^{b}	428, 405	1217 1220, 1215, 1200^{b}	340, 330	1218 1220 1210^{b}	340, 328 337^{c}
	Cl	1199	481, 460	1220	362, 355	1220 1222–1212	367, 355 374^{c}
	NO_2			1237 1220^{b}	367, 354	1239 1230±3	370, 360 374^{c}
4-Z-QNO	CH_3O	1294	441^{b}	1289^{e}	416^{b}	1287^{e}	403^{b}
	CH_3	1217	443^{b}	1206^{e}	385^{b}	1206^{e}	382^{b}
	H			1229^{e}	349^{b}	1229^{e}	350^{b}
	Cl	1304, 1263	456^{b}	1302^{e}, 1251^{e}	389^{b}	1302, 1251^{e}	387^{b}
	NO_2	1302	450^{b}	1300^{e}	375, 355^{b}	1300^{e}	368^{b}
6-Z QNO	CH_3O					1213, 1180^{f}	
	CH_3					1205, 1170^{f}	
	Cl					1267, 1223^{f}	
	NO_3					1300, 1265^{f}	

[a] Data from ref 108 unless otherwise indicated [b] Ref 119 [c] Ref. 53 [d] Ref 123 [e] Ref. 117 [f] Ref 118

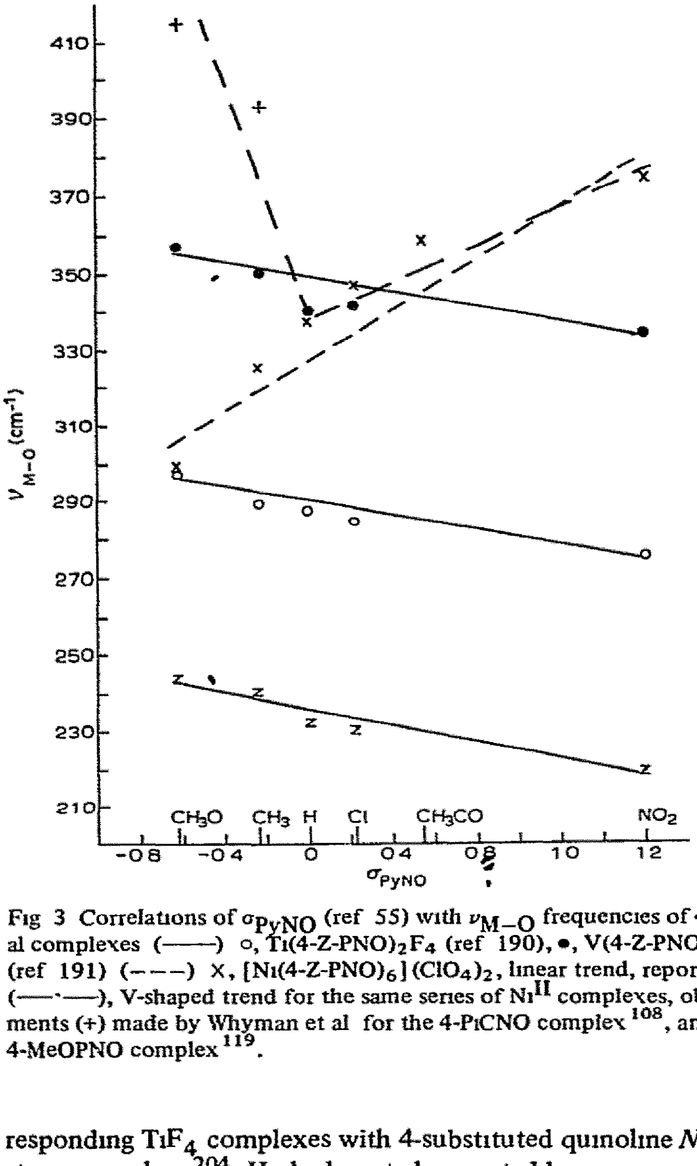


Fig 3 Correlations of σ_{PyNO} (ref 55) with ν_{M-O} frequencies of 4-substituted pyridine *N*-oxide metal complexes (——) o, Ti(4-Z-PNO)$_2$F$_4$ (ref 190), •, V(4-Z-PNO)$_2$F$_4$ (ref 192), Z, Zr(4-Z-PNO)$_2$F$_4$ (ref 191) (– – –) X, [Ni(4-Z-PNO)$_6$](ClO$_4$)$_2$, linear trend, reported by Herlocker et al [53] (—·—), V-shaped trend for the same series of Ni^{II} complexes, obtained by using the ν_{M-O} assignments (+) made by Whyman et al for the 4-PicNO complex[108], and by Nathan and Ragsdale for the 4-MeOPNO complex[119].

responding TiF$_4$ complexes with 4-substituted quinoline *N*-oxides; this was attributed to strong coupling[204]. Herlocker et al. reported linear ν_{Ni-O} vs σ plots for [NiL$_6$](ClO$_4$)$_2$ complexes with 4-substituted pyridine *N*-oxides[53] (Fig 3) In these complexes ν_{Ni-O} increases with increasing electron-withdrawing ability of the substituent, owing to Ni-to-ligand back-donation. This was attributed to an increase in the energy of the ligand π^* orbital with decreasing electron-withdrawing character of the substituent. Thus, although the σ-bond initially formed between nickel ion and ligand becomes stronger with 4-substituent variation along the series NO$_2$ < COCH$_3$ < Cl < H < CH$_3$ < OCH$_3$, the overall strength of the Ni–O bond increases in the reverse order, owing to increased nickel-to-

-ligand π-bonding with decreasing energy of the π* orbital[53]. Whyman et al. found similar linear trends in ν_{M-O} vs. σ plots for the corresponding Cr^{III}, Fe^{III} and Co^{II} complexes; however, the ν_{M-O} values for the 4-methyl-substituted ligand were always high[108]. More recently, Nathan and Ragsdale obtained V-shaped ν_{M-O} vs. σ plots for Cr^{III}, Mn^{II}, Fe^{III} and Zn^{II} perchlorate complexes with 4-substituted quinoline *N*-oxides[119]. A reexamination of the low-frequency IR spectra of 4-methoxypyridine *N*-oxide-Co^{II}, -Ni^{II} and -Zn^{II} perchlorate complexes revealed that two bands having all the characteristics of ν_{M-O} occur at 300–280 and 422–410 cm^{-1} (ref. 119). The lower frequency bands have been assigned as ν_{M-O} during earlier studies[53, 108], assignment of ν_{M-O} at 422–410 cm^{-1} would lead to V-shaped plots[119] (Fig. 3). V-shaped trends of this type were interpreted in terms of combination of two competing effects, i.e. for electron-releasing substituents, the basicity of the ligand is the factor determining the M–O bond strength, while for electron-withdrawing substituents the π-bonding effect is predominant[119]. More recently similar V-shaped trends were reported for $FeCl_3$ and $Fe(ClO_4)_3$ complexes with 4-substituted pyridine *N*-oxides, moreover, the assignment of ν_{Fe-O} in the $FeCl_3 \cdot 2L$ complex with 4-methoxypyridine *N*-oxide at 440 cm^{-1} appears to be unambiguous, as no band with the characteristics of ν_{Fe-O} was observed at 350–290 cm^{-1} in this complex[205]. Also, ν_{M-O} vs. σ correlations could not be made for $SnF_4 \cdot 2L$ complexes with 4-substituted pyridine and quinoline *N*-oxides, as well as $TiF_4 \cdot 2L$ complexes with the quinoline *N*-oxide series[204]. In the case of SnF_4 complexes, the change of ν_{Sn-O} with substituent variation was attributed to back-donation from Sn^{IV} to ligand, increasing with the increase of the electron-withdrawing ability of the substituent, and counterbalancing the sigma interaction to reduce the ν_{Sn-O} range[204]. Thus, both Zn^{II} (ref. 119) and Sn^{IV} (ref. 204), which have filled outer *d*-shells, appear to be non inert to metal-to-ligand back-bonding. Michelson et al. comment also on the possible ambiguity of *cis* or *trans* stereochemical assignments on the basis of IR evidence alone[204] (see also ref. 211). A characteristic example for aromatic amine *N*-oxide complexes is provided by the case of $(CH_3)_2SnX_2(PNO)_2$ (X = halogen) complexes. IR evidence seems to point to *cis* configurations[212], but the crystal structure determination of $(CH_3)_2SnCl_2(PNO)_2$ established the location of all pairs of identical ligands in *trans* positions[131].

(iv) Electronic spectra

Hexacoordinated first-row transition metal complexes with PNO and substituted derivatives exhibit electronic spectra, which may be conveniently divided into three regions[213]: (1) 45,000–29,000 cm^{-1}, (2) 29,000–21,000 cm^{-1}, and (3) 21,000–5,000 cm^{-1}. Region 1 contains the π–π* and n–π* transitions of the ligand (vide supra). High-spin PNO complexes with 3*d* metal ions exhibit the π–π* transition at lower energies than in the free ligand (Table 5)[213]. 4-Nitropyridine *N*-oxide analogs show a shift of the π–π* band towards higher energies[213]. These trends concern solid-state spectra, in acetonitrile solution the UV spectra of these complexes were identical to those of the free ligand, with the exception of Cr^{III} complexes, in the latter case the kinetic stability of the d^3 chromium ion precludes dissociation during the course of the measurement[213]. The dissociation of aromatic amine *N*-oxide metal complexes in various solvents (acetonitrile, nitromethane etc.) has also been pointed out by Herlocker et al.[53]. Acetonitrile solution spectra

TABLE 5

Diffuse reflectance spectra of pyridine *N*-oxides and their metal complexes in the ultraviolet region[213]

Compound	ν[a] (kK)
PNO	39.4, 30.3[b]
$[Cr(PNO)_6](ClO_4)_3$	38.6
$[Fe(PNO)_6](ClO_4)_3$	38.5 (29.15)
$[Fe(PNO)_6](ClO_4)_2$	38.3
$[Co(PNO)_6](ClO_4)_2$	38.3 (29.75)
$[Cu(PNO)_6](ClO_4)_2$	38.9
$[Zn(PNO)_6](ClO_4)_2$	38.5 (32.25)
$[Ni(4\text{-}PicNO)_6](ClO_4)_2$	38.8 (31.25)
$4\text{-}NO_2PNO$	42.4, 30.5[c]
$[Fe(4\text{-}NO_2PNO)_6](ClO_4)_2$	43.7, 30.85[c]
$[Ni(4\text{-}NO_2PNO)_6](ClO_4)_2$	44.25, 31.0[c]
$[Cu(4\text{-}NO_2PNO)_4](ClO_4)_2$	42.4, 31.05[c]

[a] Shoulders in parentheses

[b] $n \to \pi^*$ transition

[c] The band at 30–31 kK is associated with the nitro group

of PNO and QNO complexes with TiO^{2+}, ZrO^{2+}, Th^{4+} and UO_2^{2+} perchlorates exhibit $\pi \to \pi^*$ transition shifts towards higher energies[114,116,121]. The ligand $n \to \pi^*$ transition is not observed in the UV spectra of aromatic *N*-oxide metal complexes[114,116,121,213]; bands observed in certain 3*d* metal complexes with PNO at 33,000–29,000 cm^{-1} (Table 5) are unlikely to be due to this transition, which should be of high energy in metal complexes[213].

Region 2 in octahedral 3*d* metal ion complexes contains low-lying charge-transfer bands and, for certain metal ions (e.g. Cr^{3+}, Ni^{2+}), higher energy (*d*–*d*) bands[213]. Carlin, in one of the earlier studies of transition metal perchlorate complexes with PNO, pointed out the unusual yellow color of the Mn^{II} complex and ascribed it to the presence of a low-lying charge-transfer band[17]. The onset of the charge transfer for the series of $[ML_6]^{n+}$ (M = Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}) and $[CuL_4]^{2+}$ complexes was observed[17] at 3875–5000 Å. Lever and co-workers discussed the charge-transfer spectra of divalent 3*d* metal complexes with pyridine *N*-oxides in detail[213,214]. With PNO the charge-transfer band moves to higher energy in the sequence $Mn^{II} < Ni^{II} \sim Fe^{II} \approx Co^{II} < Cu^{II}$; the fact that the species most difficult to oxidize (Cu^{II}) lies at highest energy suggests that the charge transfer is from metal to ligand[213]. Introduction of electron-withdrawing substituents ($-NO_2$, $-COO$ etc.) at the 2- or 4- ring positions results in considerable shifts of the charge-transfer bands towards lower energies; thus, an increase in the acceptor ability of the ligand leads to a decrease in the energy of the charge-transfer band, as would be expected for metal-to-ligand charge transfer[213]. In picolinic acid *N*-oxide divalent 3*d* metal chelates the energy of the charge-transfer band increases[215] along the series $Fe^{II} < Co^{II} < Ni^{II} < Mn^{II} < Cu^{II}$. In the cases of Cr^{III} and Fe^{III} complexes, shoulders observed on the rising absorption of the UV band were not assigned by Lever and co-workers[213]. In high-spin complexes, the lowest energy metal-to-ligand charge transfer was assigned as follows: $t_{2g} \to \pi^*$ for d^1–d^3 and d^6–d^8 systems; and $e_g \to \pi^*$ for d^4, d^5 and d^9 systems[213]. Rationalization of the data was made by using, for the first time, the optical electronegativity approach for the elucidation of metal-to-ligand charge-transfer spectra[213]. This method had been successfully used by Jørgensen et al. for the explanation of the ligand-to-metal electron-transfer spectra of metal hexa- and tetra-halides[216]. Selected optical electronegativity data for divalent 3*d* metal complexes with aromatic amine *N*-oxides are shown in Table 6. The energy of the metal-to-ligand charge-transfer band, corrected for changes in spin-pairing energy is given by

$$\nu^*_{\mathrm{CT}} = 30{,}000\,(\chi_{\mathrm{opt}}(\mathrm{M}) - \chi_{\mathrm{opt}}(\mathrm{L})) \tag{4}$$

and

$$\nu^*_{\mathrm{CT}} = \nu_{\mathrm{CT}} - \Delta\mathrm{SPE} + nDq \tag{5}$$

where $\chi_{\mathrm{opt}}(\mathrm{M})$ and $\chi_{\mathrm{opt}}(\mathrm{L})$ are the optical electronegativities of the metal ion (in the stereochemical environment of interest) and the ligand, respectively, ΔSPE is the change in spin-pairing energy from the ground state to the excited state; $n = 6$ for $e_g \to \pi^*$ transitions and $n = -4$ for $t_{2g} \to \pi^*$ transitions, and Dq is the ligand-field parameter[213]. The charge-transfer bands in aromatic amine *N*-oxide metal complexes were, therefore, assigned as $t_{2g} \to \pi^*$ transitions for $\mathrm{Fe^{II}}$, $\mathrm{Co^{II}}$ and $\mathrm{Ni^{II}}$ and as $e_g \to \pi^*$ transitions for $\mathrm{Mn^{II}}$ and $\mathrm{Cu^{II}}$ complexes[213]. (cf. Table 6). It should be noted that a pure O_h symmetry was assumed for the hexacoordinated *N*-oxide complexes for the purposes of these studies[213], although these compounds are not octahedral[123] (vide infra).

Region 3 contains exclusively crystal-field (*d*–*d*) bands. Earlier reports on electronic spectra of cationic 3*d* metal complexes with aromatic *N*-oxides and determinations of ligand-field parameters[17, 110, 217, 218] were based on solution spectra. However, aromatic amine *N*-oxide metal complexes are dissociated in solution[53, 213], as already mentioned; thus, reliable data can be obtained by spectral measurements either in the solid state (reflectance or mull spectra) or in solutions containing excess *N*-oxide ligand. Room-temperature solid-state electronic spectra of $[\mathrm{ML_6}]^{n+}$ complexes with aromatic *N*-oxides exhibit, in certain cases, splitting of the (*d*–*d*) bands[108], at low temperatures (−196°) this splitting is resolved in two distinct peaks, in addition, other (*d*–*d*) bands are split in the low-temperature spectra[123] (Table 7). This splitting is indicative of the presence of lower symmetry components in the ligand field[123] (cf. Sect. C(*vii*)). Table 7 shows the electronic spectra of a number of hexa-, penta- and tetracoordinated complexes of 3*d* metal perchlorates with aromatic amine *N*-oxides. Band assignment and calculations of ligand-field parameters given in Table 8 for hexacoordinated complexes of this type were generally based on the assumption that these cationic complexes are purely O_h. Caution must be exercised in assigning the higher energy (*d*–*d*) bands, since they may overlap with the charge-transfer band in this region.

Reedijk[111] calculated the ligand-field parameters for hexakis-PNO cationic 3*d* metal complexes from low-energy (*d*–*d*) bands (see ref. 219). Comparison of the *Dq* values of PNO with those of H_2O and dimethyl sulfoxide (DMSO) towards octahedral divalent 3*d*

TABLE 6

Optical electronegativity data for some octahedral aromatic amine *N*-oxide metal complexes (metal-to-ligand charge transfer)[213]

Complex	B^a (cm^{-1})	ΔSPE^b (cm^{-1})	Dq (cm^{-1})	CFSE^c (cm^{-1})	ν_{CT} (cm^{-1})	ν^*_{CT} (cm^{-1})	$\chi_{opt}(L)$	$\chi_{opt}(M)$
$Mn(PicANO)_2 \cdot 2H_2O$	835	15,590	850	−5100	24,700	14,220	0.8	1.3
$[Mn(PNO)_6](ClO_4)_2$	835	15,590	850	−5100	24,330	13,840	0.8	1.3
					22,570sh	12,080	0.8	1.2
$Mn(4\text{-}NO_2PNO)_2Cl_2$ [d]	835	15,590	850	−5100	21,800	11,810	0.9	1.3
					19,800sh	9,310	0.9	1.2
$Fe(PicANO)_2 \cdot 2H_2O$	800	−14,930	1020	4080	21,000	31,850	0.8	1.9
$[Fe(PNO)_6](ClO_4)_2$	800	−14,930	890	3560	25,250	36,620	0.8	2.0
					22,620sh	33,990	0.85	1.95
$Co(PicANO)_2 \cdot 2H_2O$	770	−10,780	1030	4120	23,800	30,460	0.8	1.8
$[Co(PNO)_6](ClO_4)_2$	750	−10,500	910	3640	25,450	32,310	0.8	1.9
					22,900sh	29,760	0.85	1.85
$Co(PNO)_2(NO_3)_2$ [d]	750	−10,500	910	3640	27,700	34,560	0.7	1.9
$Ni(PicANO)_2 \cdot 2H_2O$	900	−8,400	935	3740	24,400	29,060	0.8	1.8
$[Ni(PNO)_6](ClO_4)_2$	960	−8,960	810	3240	25,200	30,920	0.77	1.8
					22,800sh	28,520	0.85	1.8
$Cu(PicANO)_2 \cdot 2H_2O$	1000	−4,670	1200	−7200	26,600	38,470	0.8	2.1
$[Cu(PNO)_6](ClO_4)_2$	1000	−4,670	1250	−7500	27,400	39,570	0.8	2.1
$[Cu(PNO)_4](ClO_4)_2$ [e]	1000	−4,670	1470	−8820	26,700	40,180	0.8	2.1
					22,950sh	36,430	0.8	2.0

[a] Racah parameter of interelectronic repulsion

[b] ΔSPE values are as follows Mn^{II}, $+\frac{8}{3}D$, Fe^{II}, $-\frac{8}{3}D$, Co^{II}, $-2D$, Ni^{II}, $-\frac{4}{3}D$, Cu^{II}, $-\frac{2}{3}D$ (D is the spin-pairing energy parameter, which is approximately equal to $7B$ for d electrons).

[c] CFSE values are $+6\,Dq$ for Mn^{II} and Cu^{II}, and $-4Dq$ for Fe^{II}, Co^{II} and Ni^{II}

[d] Bridging *N*-oxide ligand

[e] Square planar.

TABLE 7

Electronic spectra of some 3*d* metal perchlorate complexes with aromatic amine N-oxides[a]

Complex	Coordination number	ν_{max} (band assignments[b]) (kK)	Ref.
$[V(4\text{-}ClPNO)_6](ClO_4)_3$	6	15.6 ($^3T_{1g}(F) \to {}^3T_{2g}(F)$), 23.25 ($^3T_{1g}(F) \to {}^3T_{1g}(P)$)	52
$[Cr(PNO)_6](ClO_4)_3$	6	15.15 ($^4A_{2g}(F) \to {}^4T_{2g}(F)$), 16.9sh, 22.7 ($^4A_{2g}(F) \to {}^4T_{1g}(F)$)	108
		[15.4, 17.65, 22.2, 23.25][c]	123
$[Mn(QNO)_6](ClO_4)_2$	6	18.2 ($^6A_{1g} \to {}^4T_{1g}(G)$), 19.7, 20.5, 22.0 ($^6A_{1g} \to {}^4T_{2g}(G)$), 24.4 ($^6A_{1g} \to {}^4E_g, {}^4A_{1g}(G)$), 27.6 ($^6A_{1g} \to {}^4T_{2g}(D)$), 29.2 ($^6A_{1g} \to {}^4E_g(D)$)	119
$[Fe(4\text{-}NO_2PNO)_6](ClO_4)_2$	6	9.1 ($^5T_{2g} \to {}^5E_g$)	123
$[Fe(QNO)_6](ClO_4)_3$	6	12.0 ($^6A_{1g} \to {}^4T_{1g}(G)$), 18.7 ($^6A_{1g} \to {}^4T_{2g}(G)$), 20.0 22.7 ($^6A_{1g} \to {}^4E_g, {}^4A_{1g}(G)$) 25.2 ($^6A_{1g} \to {}^4E_g(D)$)	119
$[Co(PNO)_6](ClO_4)_2$	6	8.3 ($^4T_{1g}(F) \to {}^4T_{2g}(F)$), 15.15, 17.9 ($^4T_{1g}(F) \to {}^4A_{2g}(F)$), 20.0 ($^4T_{1g}(F) \to {}^4T_{1g}(P)$), 25.0	108
		[7.3, 8.3, 17.95, 18.9, 20.0][c]	123
$[Ni(4\text{-}PicNO)_6](ClO_4)_2$	6	8.3 ($^3A_{2g}(F) \to {}^3T_{2g}(F)$), 12.35 ($^3A_{2g}(F) \to {}^1E_g(D)$) 14.3 ($^3A_{2g}(F) \to {}^3T_{1g}(F)$), 19.6, 25.3 ($^3A_{2g}(F) \to {}^3T_{1g}(P)$)	108
		[7.3, 8.1, 9.0, 12.35, 13.8, 14.5][c]	123
$[Cu(PNO)_6](ClO_4)_2$	6	9.6, 12.2 ($^2E_g \to {}^2T_{2g}$), 26.7	108
		[10.15, 12.9][c]	123
$[Co(2\text{-}PicNO)_5](ClO_4)_2$	5	11.5, 12.8, 15.4, 18.6, 26.7	123
$Ni(2,6\text{-}LNO)_4(ClO_4)_2$	5	9.0, 13.0, 19.5, 23.2	123
$[Ni(2,6\text{-}LNO)_4](ClO_4)_2$	4	14.25, 18.15, 28.7	145
$[Fe(2,6\text{-}LNO)_4](ClO_4)_2$	4	10.4, 27.7	145
$[Co(2,6\text{-}LNO)_4](ClO_4)_2$	4	7.2, 8.5, 15.0, 19.4, 27.9	145
$[Cu(2,6\text{-}LNO)_4](ClO_4)_2$	4	15.5, 25.5, ~28.0	145
$[Cu(PNO)_4](ClO_4)_2$	4	13.7, 14.7, 26.3	108

[a] Solid state (reflectance or Nujol mull) spectra, at room temperature, unless otherwise stated.

[b] (*d*–*d*) transition assignments for hexacoordinated complexes were made by assuming a pure O_h symmetry for the complex cations.

[c] At −196°C.

TABLE 8

Ligand-field parameters for $[ML_6](ClO_4)_n$ complexes with aromatic amine *N*-oxides

Metal ion	Ligand	*Dq* (cm^{-1})	β^a	Ref.
Cr^{3+}	4-MeOPNO	1613	0.76	108
	4-PicNO	1600	0.75	108
	PNO	1587	0.77	108
	4-ClPNO	1575	0.71	108
	2,6-LNO	1686		145
	4-MeOQNO	1600	0.73	119
	4-MeQNO	1558	0.72	119
	QNO	1618	0.83	119
	4-ClQNO	1562	0.80	119
	4-NO$_2$QNO	1575		119
	ANO	1590		149
Mn^{2+}	4-MeOQNO	710	0.76	119
	4-MeQNO	747	0.78	119
	QNO	703	0.77	119
	4-ClQNO	690	0.78	119
Fe^{2+}	PNO	930		111
Fe^{3+}	QNO	1373		119
Co^{2+}	4-MeOPNO	950	0.88	108
	2-PicNO	657	0.96	146
	3-PicNO	898.5	0.82	146
	4-PicNO	950	0.88	108
		906	0.85	146
	2-EtPNO	657	0.955	146
	PNO	950	0.88	108
		890	0.80	111
	4-ClPNO	950	0.88	108
	4-NO$_2$PNO	940	0.89	108
	2-CNPNO	996	0.80	148
	3-CNPNO	1010	0.94	148
	4-CNPNO	986	0.80	148
	4-MeOQNO	835	0.94	117
	4-MeQNO	971	0.94	117
	QNO	976	0.97	117
	IQNO	979	0.94	117
	4-ClQNO	955	0.93	117
	4-NO$_2$QNO	965	0.98	117
Ni^{2+}	4-MeOPNO	800	0.98	53
	2-PicNO	780	0.935	146
	3-PicNO	800	0.91	146
	4-PicNO	794	0.96	53
		833	0.90	108
	PNO	794	0.97	53
		826	0.91	108
		820	0.81	111

TABLE 8 (continued)

Metal ion	Ligand	Dq ($\mathrm{cm^{-1}}$)	β[a]	Ref
$\mathrm{Ni^{2+}}$	2-EtPNO	780	0.935	146
	4-ClPNO	786	0.92	53
		823	0.93	108
	4-$\mathrm{NO_2}$PNO	830		53
		823	0.95	108
	4-$\mathrm{CH_3CO}$PNO	784	0.83	53
	2-CNPNO	808	0.87	148
	3-CNPNO	826	0.89	148
	4-CNPNO	813	0.82	148
	4-MeOQNO	835	0.94	117
	6-MeOQNO	813	0.88	118
	4-MeQNO	826	0.79	117
	6-MeQNO	809	0.88	118
	QNO	790	0.84	117
	IQNO	805	0.83	117
	4-ClQNO	842	0.89	117
	6-ClQNO[b]	785	0.84	118
	6-BrQNO	811	0.79	118
	4-$\mathrm{NO_2}$QNO	874	0.78	117
	6-$\mathrm{NO_2}$QNO	824	0.87	118
$\mathrm{Cu^{2+}}$	PNO	1220		111

[a] $\beta = B$ (complex)$/B$ (gaseous ion)

[b] Tetrafluoroborate complex

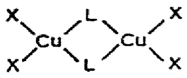
metal ions produces the spectrochemical series[111,127] DMSO < PNO < $\mathrm{H_2O}$, although $\nu_{\mathrm{M-O}}$ values indicate that DMSO is a generally stronger ligand than PNO[220]. Dq values towards octahedral $\mathrm{Cr^{III}}$ are suggestive of the spectrochemical series[108,221] DMSO $\simeq$ PNO < $\mathrm{H_2O}$. The nephelauxetic series for $\mathrm{Co^{II}}$ and $\mathrm{Ni^{II}}$ has the sequence[111] PNO < DMSO < $\mathrm{H_2O}$. Unsubstituted aromatic amine *N*-oxides compare as follows[53,108,111,117–119,149] in the spectrochemical series towards O_h $\mathrm{Cr^{III}}$ PNO $\simeq$ ANO < QNO, towards O_h $\mathrm{Co^{II}}$ PNO < QNO < IQNO, and towards O_h $\mathrm{Ni^{II}}$ PNO $\simeq$ QNO < IQNO. 4-Substituted pyridine *N*-oxides exhibit a trend of decrease of Dq towards O_h $\mathrm{Cr^{III}}$, $\mathrm{Co^{II}}$ or $\mathrm{Ni^{II}}$ with decreasing σ-donor strength of the ligand (i.e. increasing electron-withdrawing ability of the substituent)[53,108]. However, 4-$\mathrm{NO_2}$-PNO shows the highest Dq value[53] towards $\mathrm{Ni^{II}}$. In the quinoline *N*-oxide series, introduction of 4- or 6-substituents in the aromatic ring results in generally higher Dq values towards O_h $\mathrm{Co^{II}}$ and $\mathrm{Ni^{II}}$ relative to those reported for the corresponding 4-substituted pyridine *N*-oxides[117,118]. One explanation advanced involves consideration of a lowering of the quinoline *N*-oxide's π^* orbitals relative to those in pyridine *N*-oxides, so that there would be more metal-to-ligand back-bonding in the complexes of the former ligands[117]. Dq (for O_h $\mathrm{Ni^{II}}$) vs σ plots for 4- and 6-substituted quinoline *N*-oxides show a V-shaped trend[117,118], however, the 4-chloro- and 4-nitroquinoline *N*-oxides exhibit lower Dq values towards O_h $\mathrm{Co^{II}}$ than QNO[117], while Dq towards O_h $\mathrm{Cr^{III}}$ for 4-substituted quinoline *N*-oxides increases along the series[119] 4-$\mathrm{CH_3}$ < 4-Cl < 4-$\mathrm{NO_2}$

$< 4\text{-}CH_3O < 4\text{-}H$. The effects of the same substituent at different ring positions have been reported for cyano-substituted pyridine *N*-oxides: Dq towards O_h Co^{II} or Ni^{II} and ν_{Co-O} or ν_{Ni-O} are generally highest for the 3-cyano derivative, increasing in the order $4\text{-}CN < 2\text{-}CN < 3\text{-}CN$ with the exception of the Dq towards O_h Ni^{II}, which gives the series[148] $2\text{-}CN < 4\text{-}CN < 3\text{-}CN$. Analogous data for 2-, 3- and 4-alkyl-substituted pyridine *N*-oxides are not available. 2,6-LNO exhibits a higher Dq value towards O_h Cr^{III} than any monodentate pyridine *N*-oxide ligand studied thus far[145]; this value is lower than those reported for trimethylamine *N*-oxide (TMNO)[100] and the chelating agent picolinic acid *N*-oxide (PicANO)[215]. The spectrochemical series towards O_h Cr^{III} for the latter two ligands and a number of aromatic amine *N*-oxides is: $4\text{-}CH_3\text{-}QNO < 4\text{-}Cl\text{-}QNO < 4\text{-}NO_2\text{-}QNO \simeq 4\text{-}Cl\text{-}PNO < PNO < ANO < 4\text{-}CH_3O\text{-}QNO \simeq 4\text{-}CH_3\text{-}PNO < 4\text{-}CH_3OPNO < QNO < 2,6\text{-}LNO < TMNO$ ($Dq = 1740\ cm^{-1}$) $<$ PicANO ($Dq = 1755\ cm^{-1}$)[100, 108, 119, 145, 149, 215].

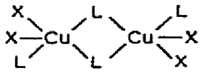
Electronic spectra have also been reported for a variety of other hexa-, penta- and tetracoordinated neutral and cationic complexes with aromatic amine *N*-oxides (L), e.g. $VCl_4 \cdot 2L$ (ref. 222), $VOX_2 \cdot nL$ ($X = Cl, Br, NCS, ClO_4$; $n = 4$ or 5)[223], $FeCl_3 \cdot nL$ ($n = 2, 3$)[177], $[Co(4\text{-}PicNO)_6](ClO_4)_2$ (octahedral, mull and solution spectra)[224], $[Co(2\text{-}PicNO)_5](ClO_4)_2$ (trigonal bipyramidal)[123], $CoCl_2 \cdot 2L$ (tetrahedral)[184], $CoCl_2 \cdot 3L$ (ref. 225), $Co(NO_2)_2 \cdot 2L$ (ref. 226), $[Ni(2,6\text{-}LNO)_4](ClO_4)_2$ (square-planar, diamagnetic[145] and its paramagnetic isomer)[146, 193], $CuX_2 \cdot L$ and $CuX_2 \cdot 2L$ (X = halogen)[163–166, 227]. In dimeric $CuX_2 \cdot L$ complexes the position of the (d–d) band depends on the steric effect of substituents on the aromatic ring[163–166], as already mentioned (cf. Table 2).

(v) Magnetic properties

Cupric halide complexes with aromatic amine *N*-oxides have been the subject of extensive magnetic and structural studies, which were recently summarized by Watson[167] (cf. Table 9 for examples). Binuclear complexes of the types $[CuLX_2]_2$ and $[CuL_2X_2]_2$ (L = aromatic amine *N*-oxide, $X = Cl, Br$) almost invariably exhibit subnormal and temperature-dependent magnetic moments. $[Cu_3Cl_6(2\text{-}PicNO)_2(OH_2)_2]_n$ also shows subnormal paramagnetism. These compounds normally contain bridging *N*-oxide ligands and their demagnetization has been generally attributed to spin–spin coupling occurring via a superexchange mechanism operating through the orbitals of the bridging oxygen atoms (refs. 129, 163–170, 186, 228–239). Refined X-ray structural data favor a π mechanism for this interaction[125]. The magnetic susceptibility of the Cu^{II} ions in these bi- or polynuclear complexes can be fitted to an equation which is derived from a simple scalar interaction of the form $-2J_{ij}S_i \cdot S_j$. For a binuclear complex the exchange energy J is the separation between the singlet and triplet states generated by the scalar interaction. The interaction is usually antiferromagnetic and the ground state is the singlet[237]. The temperature dependence of the paramagnetism of complexes of these types was established during a number of studies[169, 186, 229, 230, 236, 237]; μ_{eff} is generally subnormal in the 80–450°K region, for example[230], μ_{eff} (B.M.) for $[Cu(PNO)Cl_2]_2$: 0.16 at 140°K, 0.62 at 293°K, 1.01 at 448°K, and for $[Cu(PNO)_2Cl_2]_2$: 0.32 at 263°K, 0.52 at 307°K, 0.82 at 395°K. The triplet state was found to be appreciably populated at temperatures below 195°K, in most cases[169]. The magnetic properties of these Cu^{II} complexes were suggestive of bi- or polynuclear structures, involving bridging *N*-oxide ligands; a series of crystal structure determinations established that this is indeed the case[125,127,129,240–243]. Structures VII and VIII (L = aromatic amine *N*-oxide; X = halogen)



VII



VIII

have been respectively established for binuclear 1:1 and 1:2 cupric halide complexes with aromatic amine *N*-oxides[125,129,241–243]. A more recent refinement of the crystal structure of $[Cu(PNO)Cl_2]_2$ led to the conclusion that the complex consists of oxygen-bridged dimers VII held together by weak chloride bridges[240]. However, ^{35}Cl NQR studies of this complex suggest that chloride bridging between adjacent dimers does not occur[244,245]. It should also be noted that Hyde et al. obtained a better fit of magnetic susceptibility and EPR data for this complex by assuming the presence of small amounts of the monomeric $Cu(PNO)Cl_2$ species in their samples[235]. $[Cu_3Cl_6(2\text{-PicNO})_2(OH_2)_2]_n$ consists of an infinite chain of 1:1 dimers (structure VII) joined by chloride bridges to Cu^{II} ions with distorted octahedral geometry[127].

The majority of $CuX_2 \cdot L$ complexes with aromatic *N*-oxides (X = halide ion), as well as their 1:1 adducts with other ligands (e.g. H_2O, DMSO, *N,N*-dimethyl formamide) are magnetically subnormal[163–167,228,229,234]. A number of chloro- or nitro-substituted quinoline and methylquinoline *N*-oxides form magnetically normal 1:1 complexes with Cu^{II} halides[186,233,246,247] (e.g. $[Cu(4\text{-}NO_2\text{-}QNO)Cl_2]_2$ with μ_{eff} (B.M.) = 1.98 at 4.2°K, and 2.08 at 299°K (ref. 247)), however. The magnetic behavior of the latter complexes was attributed to halide-bridged dimeric structures by Hatfield and co-workers[186], while Muto and Jonassen assumed oxygen-bridged structures for these complexes and interpreted their normal paramagnetism in terms of the electron-withdrawing effect of the nitro or chloro substituent on the bridging oxygens[233].

2:1 *N*-oxide–cupric halide complexes are, in most cases, monomeric and magnetically normal (Table 9). However, the PNO complexes of this type are binuclear (structure VIII)[241,243], while for the 4-PicNO analogs, two isomers have been isolated: a yellow oxygen-bridged dimer, VIII[242], and a green *trans* monomer[167]. The magnetic moments of the above binuclear complexes are subnormal (Table 9). The PNO and QNO 2:1 complexes with Cu^{II} nitrate are also binuclear, with a structure similar to VIII (X = $-ONO_2$ in this case), involving a tetragonal pyramidal symmetry[126]. These complexes are, nevertheless, magnetically normal[16,168,230] (Table 9). Recent magnetic susceptibility and EPR studies of $[Cu(PNO)_2(ONO_2)_2]_2$ suggest that this compound represents the first authenticated example of exchange-coupled Cu^{II} ions with a triplet ground state[248]. The exchange coupling is a σ-orbital mechanism which is transmitted through the orbitals of the bridging oxygen atoms by electron transfer plus intraatomic direct exchange[248] (see also ref. 249). Finally, EPR studies of mixed metal ion dimeric complexes of structural types VII and VIII (where the one metal ion is Cu^{II} and the other is Zn^{II}, Ni^{II}, Cd^{II}, Pb^{II} or Ba^{II}) have also been reported[250,251].

The magnetic properties of aromatic amine *N*-oxide complexes with the halides of other 3*d* metal ions are generally normal for high-spin configurations and the stereochem-

TABLE 9

Types of copper(II) halide complexes with aromatic amine *N*-oxides [a]

Compound	μ_{eff} (B.M.)	Ref.
1:1 complexes		
$[Cu(PNO)Cl_2]_2$	0.59–1.06	16, 167, 168, 228
$[Cu(QNO)Cl_2]_2$	0–0.36	168, 228, 230
$[Cu(4\text{-}NO_2PNO)Br_2]_2$	0.45–1.77	129, 164
$[Cu(3\text{-}NO_2\text{-}6MeQNO)Br_2]_2$	1.72	186
Adducts of 1:1 complexes		
$[Cu(PNO)(DMF)Cl_2]_2$ [b]	0.53	228
$[Cu(PNO)(DMSO)Br_2]_2$ [b]	1.12	228
2:1 dimeric complexes		
$[Cu(PNO)_2Cl_2]_2$	0.46–0.63	129, 230
$[Cu(4\text{-}PicNO)_2Br_2]_2$	1.33	229
Trans 2:1 monomers		
$[Cu(2\text{-}PicNO)_2Cl_2]$	1.95	167
$[Cu(2,6\text{-}LNO)_2Cl_2]$	1.90	129
$[Cu(QNO)_2Cl_2]$	1.88	230
Distorted cis 2:1 monomers		
$[Cu(2,6\text{-}LNO)_2Cl_2]$	1.91	186
2:1 CuBr₂ monomers		
$[Cu(2,6\text{-}LNO)_2Br_2]$	2.04	129
$[Cu(QNO)_2Br_2]$	1.96	230
Adducts of 2:1 monomers		
$[Cu(4\text{-}NO_2PNO)_2(OH_2)_2Cl_2]$	1.96	230
Polynuclear complexes		
$[Cu_3Cl_6(2\text{-}PicNO)_2(OH_2)_2]_n$	1.22	167
$[Cu_3Cl_6(4\text{-}ClQNO)_2]$	2.07	186
$[Cu_4Cl_8(3\text{-}NO_2\text{-}6\text{-}MeQNO)_3]$	1.91	186

[a] See ref. 167 for a complete Table.
[b] DMF = *N,N*-dimethyl formamide, DMSO = dimethylsulfoxide

istry of each complex. However, a number of Mn^{II} complexes of the type $MnLCl_2$ show low μ_{eff} (5.40–5.60 B.M.) for this metal ion, these compounds are bi- or polynuclear and, most probably, chlorine-bridged[182]. $[CoL_6]^{2+}$ cationic complexes with *N*-oxides show magnetic moments[123] of 4.70–4.80 B.M. These moments are low for purely O_h configurations and suggest a loss in orbital degeneracy of the ground state ($^4T_{1g}$), caused by lower-symmetry components in the ligand field[123]. Ni^{II} analogs exhibit moments of 3.30 B.M. or slightly higher, these are also indicative of the presence of distortion from an octahedral environment[123]. The paramagnetism of complexes involving $[ML_6]^{n+}$ ($M = Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}$) or $[CuL_4]^{2+}$ cations is normal for high-spin configurations. $[Co(2\text{-}PicNO)_5](ClO_4)_2$ shows a moment (4.58 B.M. at 20°C) consistent with a high-spin trigonal bipyramidal configuration[123]. The violet $[Ni(2,6\text{-}LNO)_4](ClO_4)_2$ complex is spin-paired (diamagnetic) and isomorphous with its Cu^{II} analog, both these compounds involve square planar MO_4 moieties[145]. The corresponding Co^{II} and Fe^{II} complexes also appear to involve square planar MO_4 moieties[145,193], the Fe^{II} complex exhibits a half-quenched spin ($S = 1$, μ_{eff} = 3.88 B.M.), while the Co^{II} compound is of the spin-free (μ_{eff} = 4.73 B.M.) type[145]. High-spin, square planar Co^{II} complexes are unusual, in addition to the above compound high-spin Co^{II} complexes with 1,2-bis(mercapto)-*o*-carborane[252] and *o*-hydroxyaryl aldehydes or ketones[253] were also characterized as square-planar in recent years. Furthermore, it has been pointed out that a donor set of four oxygens might produce a ligand field of intensity insufficient to induce spin-pairing in planar Co^{II} compounds[254], orbital contributions leading to moments higher than 4.70 B.M. can be explained if the energy order $d_{xz}, d_{yz} > d_{z^2}$, which gives a ^4E_g ground state is assumed[254]. Paramagnetic yellow or green complexes of the type $NiL_4(ClO_4)_2$ (L = 2-PicNO or 2,6-LNO, μ_{eff} = 3.16 and 2.83 B.M., respectively[144,146]) are penta- (ref. 193) or hexa- (refs. 144, 146) coordinated, a monomeric structure, involving coordinated perchlorato ligands[146], and bi- or polynuclear structures, involving *N*-oxide-bridged complex polycations[144,193] have both been proposed for compounds of this type.

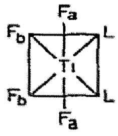
(vi) Other properties

(a) Conductances

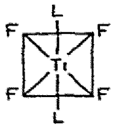
Conductivity measurements in suitable solvents (e.g. nitromethane, nitrobenzene, acetonitrile) are, in most cases, in agreement with structures suggested by other data. Thus, many metal halide - *N*-oxide complexes in high metal-to-ligand ratios appear from their other properties to be neutral, and behave, in fact, as non-electrolytes in solution[16,18]. In the case of Fe^{III} complexes, $FeCl_3 \cdot 2PNO$ exhibits low-frequency IR and Raman bands typical of the tetrachloroferrate(III) anion, and was formulated as $[Fe(PNO)_4Cl_2][FeCl_4]$, this complex behaves as a 1:1 electrolyte in solution[177]. $FeCl_3 \cdot 3PNO$, on the other hand, is a non-electrolyte in solution, does not exhibit bands attributable to the presence of $[FeCl_4]^-$ and was formulated[177] as $[Fe(PNO)_3Cl_3]$. Cationic complexes of the type $[ML_n][X]_m$ ($X = ClO_4, BF_4$, n = 4, 5 or 6, m = 2, 3) show conductances consistent with their formulations[16-18,123,145]. $[Mn(2,6\text{-}LNO)(OClO_3)](ClO_4)$ behaves as a 1:2 electrolyte in nitromethane, however, although the presence of coordinated perchlorato groups is quite obvious from IR studies, the conductance of this complex is suggestive of dissociation in solution[145]. On the other hand, certain metal nitrate complexes of the type $[ML_6](NO_3)_n$ ($M = Ni^{II}, Cr^{III}, Fe^{III}$), showing IR evidence favoring the exclusive presence of ionic nitrate, behave as 1:1 electrolytes in nitromethane[144,159], this behavior has been interpreted in terms of displacement of *N*-oxide by nitrato ligands in solution[144].

(b) NMR spectra

^{19}F NMR studies have been used extensively for characterization of $TiF_4 \cdot 2L$ and $TiF_4(L)(L')$ (L = aromatic amine *N*-oxide, L′ = dimethylacetamide or tetramethylurea) complexes[150,152,153,204,255–259]. These studies were covered in a previous review[1]. Distinction between the *cis*-IX and *trans*-X isomers



IX



X

in complexes of this type can be based on ^{19}F NMR spectra[153,258,259] Satisfactory correlations of σ_{PyNO} with the chemical shifts of F_a and F_b were reported for a series of *cis*-$TiF_4 \cdot 2L$ complexes with 4-substituted pyridine *N*-oxides[152] Chemical shifts for F_a fluorines are much less sensitive to 4-substituent variation than those for F_b fluorines[258] In $SnF_4 \cdot 2L$ analogs with 4-substituted pyridine and quinoline *N*-oxides, the ^{19}F NMR chemical shifts do not appear to be sensitive to substituent variation[204]

Proton NMR spectroscopy has also been employed in various studies of *N*-oxide complexes Kluiber, Horrocks et al (see also Sect C(*ii*)) interpreted the contact shifts of the ligand protons, in mixed *N*-oxide-β-ketoenolato complexes of paramagnetic metal ions (Co^{II}, Ni^{II}, Cu^{II}), in terms of spin delocalization from metal to *N*-oxide via a π mechanism[154–156,260]. For complexes with pyridine *N*-oxides it was impossible to distinguish whether the spin was delocalized in the highest filled π-bonding or the lowest empty π-antibonding orbital of the *N*-oxide, because of the spin distribution similarity in these two orbitals[154] In the case of the quinoline *N*-oxide complexes, correlations of experimental data and spin density distribution suggest that the spin is delocalized in the highest filled π-bonding molecular orbital[155] Recently, Perry et al reported ^{1}H NMR contact shift studies in $[M(4\text{-PicNO})_6](ClO_4)_2$ (M = Co, Ni) complexes[224]. Although the general pattern of the observed contact shifts has the gross features of spin delocalization via a π-mechanism, Perry et al concluded that ^{1}H contact shifts alone do not provide sufficient information for an unambiguous distinction between a π or σ mechanism for spin delocalization in paramagnetic metal complexes, especially in the absence of MO calculations[224] In addition the ratios of the proton shifts for Co^{II}, with unpaired electrons in both the e_g and t_{2g} sets, and Ni^{II}, with unpaired electrons only in the e_g set, are identical, contrary to what one might have expected. Thus, Perry et al. suggested that the contact shifts of atoms other than the protons (^{13}C or ^{14}N) should be determined before conclusions concerning the importance of spin density delocalized in σ or π molecular orbitals of the aromatic *N*-oxide ligands are reached[224]. Recent ^{1}H NMR studies of $[M(PNO)_6](BF_4)_2$ complexes (M = Fe, Co, Ni) established that the contact shift ratios of the pyridine *N*-oxide protons are identical for these three metal ions[261] INDO spin density calculations on $Ni(AA)_2L_2$ complexes (L = PNO and derivatives, QNO, IQNO) suggest that the direction of spin transfer is from ligand to metal[262,263]. Metal orbitals were neglected in these calculations, which considered only the ligand fragment; metal-to-ligand spin transfer was considered as relatively unimportant, since the metal atom is separated by an oxygen atom from the antibonding π orbitals of the ring system[262,263] The results of INDO calculations were in better agreement with NMR and EPR data than those made by other methods of calculation[262] (e g Huckel method; cf ref 264) Contact shift data for the above Ni^{II} complexes demonstrate that 2,6-LNO, containing two electron-releasing *ortho* substituents, is a considerably stronger ligand than PNO and mono-substituted derivatives[262], this is in agreement with *Dq* values[145] (vide supra) and ν_{M-O} data[193] reported for these ligands

Ligand exchange kinetics in *N*-oxide paramagnetic metal complexes have also been studied by ^1H NMR spectroscopy[147,157,265] For complexes of the type $[M(AA)_2(4\text{-PicNO})_2]$ it was found that the rates of *N*-oxide exchange are faster in Co^{II} than in Ni^{II} complexes; this order of lability for hexacoordinated Co^{II} and Ni^{II} complexes has been observed in many other cases and is in agreement with ligand-field stabilization arguments[157]. $[Co(2,6\text{-LNO})_4](ClO_4)_2$ yields $[Co(2,6\text{-LNO})_5](ClO_4)_2$ when dissolved in the presence of excess ligand[145], the latter complex is quite stable over a wide range of conditions in $CD_3NO_2/(CD_3)_2CO$ (1 1) solutions[147], proton NMR studies indicate that this trigonal bipyramidal cationic complex exhibits a first-order exchange rate law, suggesting that the exchange mechanism may be dissociatively controlled[147] Studies of $[Ni(3\text{-PicNO})_6][BF_4]_2$ in the same solvent mixture, involving variation of the free ligand concentration, demonstrated that the exchange rate is independent of this concentration[265].

Proton NMR spectroscopy has been utilized in several studies of diamagnetic metal ion complexes with *N*-oxides NMR shifts of the *N*-oxide ring α-protons in 4-substituted pyridine *N*-oxide-UO_2Cl_2 complexes were correlated[210] with ν_{N-O}, in mixed-ligand, 4-Z-PNO-β-ketoenolato-uranyl complexes, the chemical shifts of the *N*-oxide α-protons vary linearly with the σ constant of the substituent; however, the chemical shifts of the β-protons in these complexes are reasonably constant[209], except when Z = NO_2 In $(CH_3)_3MX \cdot (4\text{-Z-PNO})$ complexes (M = Sn, Pb, X = Cl, Br) the β-protons of the *N*-oxide are sensitive to substituent effects, whereas the resonance of the α-protons appears static or even suffers modest high-field shifts on complexation, the latter effect was attributed to a shielding, having its origin in the magnetic influence of the bulky tin or lead atoms, and specifically affecting the *ortho* regions[201] A more sensitive response was observed for the *N*-oxide protons in complexes of the type $(CH_3)_2SnCl_2 \cdot 2(4\text{-Z-PNO})$, since a greater range in *J* is theoretically and actually possible in these complexes[266]. Studies of analogous 2,4-LNO complexes with $(CH_3)_3MX$ show a marked movement of the resonance of the α-proton to high field, as well as indications of a steric congestion in the region of the 2-methyl group, which, because of its bulk displaces the metal atom towards the unsubstituted 2-position[201]. This effect is less pronounced in $(CH_3)_2SnCl_2 \cdot 2(2,4\text{-LNO})$, since the inductive deshielding effect is greatest in this case, and tends to nullify the shielding effect[201] In 2,4,6-collidine *N*-oxide complexes with $(CH_3)_3MX$, a rather severe steric inhibition of approach of the metal to form a strong bond with oxygen is suggested by the ^1H NMR data $(CH_3)_2SnCl_2$ forms a 1 1 pentacoordinated complex with this ligand, formation of the 2 1 complex is obviously sterically hindered[201].

Finally, the NMR chemical shifts in $(A)PtCl_2(L)$ (A = olefin or CO) of the pyridine ring and olefinic ligand protons[267,268] have been rather extensively discussed in a previous review[2].

(c) NQR spectra

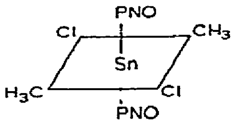
^{35}Cl and ^{79}Br nuclear quadrupole resonance (NQR) studies of binuclear complexes of the types $[Cu(L)X_2]_2$, $[Cu(L)X_2(DMSO)]_2$ and $[Cu(L)_2X_2]_2$ (L = *N*-oxide, X = Cl or Br) are generally suggestive of the exclusive presence of terminal halide ligands[244, 245]. Similar studies (^{35}Cl, ^{81}Br, ^{127}I) on $Hg(L)X_2$ complexes suggest that tetrahedral mercury is unlikely in these compounds[269]. A recent X-ray study of the 3,5-dibromopyridine *N*-oxide – $HgCl_2$ complex of this type shows that this lattice is made up of infinite chains of $HgCl_2$ molecules; thus, with the coordination of the *N*-oxide ligand mercury attains very distorted pentacoordination[270]. All the chlorine atoms in the lattice bridge to some extent[270].

(d) EPR spectra

In addition to EPR data obtained for aromatic amine *N*-oxide complexes with cupric halides and 3*d* metal β-ketoenolates (vide supra), EPR studies have been reported during several other studies. Thus, X-band EPR spectra of $[Fe(PNO)_6]X_2$ (X = ClO_4 or NO_3) complexes are clearly indicative of a severe distortion from pure O_h symmetry[177]. $[Mn(PNO)_6](ClO_4)_2$ has a *g* value of 2.00 ± 0.01, and a band width of about 250 gauss. Nuclear hyperfine splitting was observed when this complex was diluted in the isomorphous Zn^{II} analog[111]. No X-band EPR spectrum has been observed for $[Ni(PNO)_6](ClO_4)_2$; this was attributed to a zero-field splitting of the ground state larger than the energy of radiation; measurements at higher frequencies would be expected to give a resonance signal[111]. $[Cu(PNO_6](ClO_4)_2$ shows a single band at $g = 2.15 \pm 0.01$ (width 60 gauss). The first derivative of this band is symmetrical even below room temperature, the EPR signal becomes asymmetric at −40 to −60°C. In view of the isomorphism of this complex and the Ni^{II} analog, and the fact that $[Cu(PNO)_6]^{2+}$ complexes exhibit split ν_{N-O} bands, the above data were attributed to a possible dynamic Jahn–Teller distortion, which becomes static at lower temperatures[111].

(e) Mossbauer spectra

The ^{57}Fe Mossbauer spectrum of $[Fe(PNO)_6](ClO_4)_2$ exhibits normal chemical shift and quadrupole splitting for hexacoordinated, high-spin Fe^{II} compounds[111]. $Fe(PTNO)_3$ (PTNO = 2-pyridinethiolate 1-oxide ligand) shows Mossbauer chemical shifts at 300 and 77°K suggesting that little, if any, additional covalency due to sulfur exists in comparison with the spectra of Fe^{III} complexes with bidentate *O,O*-ligands[271]. Quadrupole splittings for $Fe(PTNO)_3$ are smaller than those of *O,O*-ligand analogs[271]. ^{119}Sn Mossbauer spectra have also been reported on Sn^{II} adducts of the type $SnX_2 \cdot L$ (X = Cl, Br, NCS) the following order of decreasing donor strength for several ligands was derived from Mossbauer chemical shifts: triphenylarsine oxide > triphenyl phosphine oxide > pyridine > thiourea > PNO > diglyme > urea > water[272]. The largest decrease in chemical shift occurs upon 1:1 complex formation for SnX_2 compounds. The addition of a second ligand molecule results in a smaller drop in chemical shift, possible explanations for this further drop in shift are that either the second ligand is weakly bonded to the tin *d*-orbitals or that it is not bonded to the tin atom, but the structure of the complex is such that the original bond between the Sn atom and the first ligand is strengthened[272]. The Mossbauer spectrum of $(CH_3)_2SnCl_2(PNO)_2$, in which each set of identical ligands (i.e. CH_3, Cl or PNO) are *trans* to one another (structure XI)[131]



XI

shows a positive sign for the quadrupolar interaction and a negative V_{zz} (ref 273) In complexes of the types $R_2Sn(PTNO)_2$, the R groups are *cis* to each other for R = phenyl and *trans* to each other for R = n-C_4H_9, as suggested by Mossbauer quadrupole splittings[274] Mossbauer data and the occurrence of a band attributable to ν_{Sn-O} at 355 cm^{-1}, led to the conclusion[274] that Sn^{IV} is octacoordinated in $Sn(PTNO)_4$ Finally, complexes of the type $RSnX(PTNO)_2$ (R = C_4H_9, C_6H_5; X = Cl, NCS) were characterized as involving R and X groups *cis* to each other, on the basis of Mossbauer, IR and electric dipole moment studies[275].

(f) Luminescent metal complexes

Fluorescent Eu^{III} complexes with aromatic amine *N*-oxides of various types have been prepared and characterized on the basis of fluorescence emission spectral studies[276–281]. Assignments of $^5D_0 \rightarrow {}^7F_{0-3}$ and $^5D_1 \rightarrow {}^7F_{0-2}$ transitions led to the following conclusions regarding the stereochemistries of these compounds In $[Eu(PNO)_8]X_3$ complexes (X = Cl, Br, I, ClO_4, PF_6) the Eu^{III} ion is in a site with D_{4d} symmetry, slightly distorted to D_{2d}, the stereochemistry of the complex cation is square antiprismatic[279,281] 1:2 adducts between tris(-β-ketoenolato)Eu^{III} and aromatic amine *N*-oxides[276–278,280] have a face-centred trigonal prismatic structure, and the point symmetry[278] at the rare earth site is C_{2v} 1 1 analogs[276,280] are most probably heptacoordinated Finally, $Eu(PNO)_3Cl_3$ and analogous complexes are obviously hexacoordinated[276].

(g) Crystal structure determinations

The literature is rich in X-ray crystal structure determinations of *N*-oxide metal complexes of various types[125–134,167,240–243,268,270,282–286]. The data are presented in appropriate sections, during the discussion of these metal complexes or their properties. Unfortunately, no X-ray data have been as yet published on *N*-oxide complexes involving cations of the type $[ML_6]^{n+}$. The stereochemical aspects of these complexes are discussed below

(vii) Stereochemical aspects of cationic metal complexes

(a) $[ML_6]^{n+}$

Byers et al [123] interpreted the combined evidence provided by ν_{N-O}, ν_{M-O} and (d–d) transition splittings and the magnetic behavior (vide supra) of hexakis-(*N*-oxide) cationic metal complexes in terms of a ligand-field symmetry lower than O_h. The MO_6 moieties may be O_h, but the nonlinear M—O—N groupings and arrangement of the aromatic rings in space introduce lower symmetry components[123], so that the true (local or effective) symmetry influencing the metal ion is lower than O_h. The splittings of the $(d-d)$ transitions in the electronic spectra are generally consistent with a symmetry lowering to S_6 or D_{3d} symmetry, however, in the case of $\mathrm{Ni^{II}}$ complexes, where the spin–orbit coupling coefficient is moderately large and the splitting moderately small, the possibility of attributing the components of the spectrum to spin–orbit structure cannot be entirely excluded[123]. On the other hand, a molecule of S_6 symmetry would be expected to give rise to two active $\nu_{\mathrm{N-O}}$ and two active $\nu_{\mathrm{M-O}}$ bands of classification[123] $A_u + E_u$. The magnetic data were discussed in Sect. C(v). Although these observations provide little information when viewed individually, their combination provides definitive evidence[123] in favor of an interaction between the metal d orbitals and the ligand orbitals such that the effective symmetry of the species is lower than O_h.

Reedijk observed single $\nu_{\mathrm{N-O}}$ and $\nu_{\mathrm{M-O}}$ bands in most of the $[\mathrm{M(PNO)_6}]^{n+}$ complexes; $\nu_{\mathrm{N-O}}$ splittings were observed only in the case of $[\mathrm{Cu(PNO)_6}]^{2+}$, and attributed to the Jahn–Teller effect[111]. In the low-frequency region additional bands that might possibly be attributed to a splitting of $\nu_{\mathrm{M-O}}$ have been observed for $\mathrm{Cr^{III}}$, $\mathrm{Fe^{III}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$ and $\mathrm{Al^{III}}$ complexes of this type[48, 108]. However, Reedijk, in view of the absence of split $\nu_{\mathrm{M-O}}$ bands in $[\mathrm{M(PNO)_6}]^{2+}$ (M = Mn, Cu, Zn, Cd) and the isomorphism between $[\mathrm{M(PNO)_6}]^{2+}$ (M = Mn to Zn, Cd), concluded that it is unlikely that deviations from O_h symmetry, if present, are responsible for these additional bands[111]. In the near IR spectrum of $[\mathrm{Zn(PNO)_6}]^{2+}$ an IR overtone was identified[111] at ca. 7300 $\mathrm{cm^{-1}}$. Reedijk[111] pointed out that splittings of the lower energy $(d-d)$ bands reported by Byers et al.[123] for $\mathrm{Co^{II}}$ and $\mathrm{Ni^{II}}$ involve one band in this region (7280 $\mathrm{cm^{-1}}$), and thus, no conclusions regarding possible distortion of the octahedron may be derived from these splittings. It should be noted, however, that $[\mathrm{Ni(4\text{-}PicNO)_6}]^{2+}$ exhibits three bands in this region (7280, 8060, 9000 $\mathrm{cm^{-1}}$)[123]; these probably account for both a splitting of the $(d-d)$ transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and the IR overtone mentioned above. Reedijk concluded that the general information obtained from IR and electronic spectra, magnetic properties and X-ray powder diagrams suggests that the $\mathrm{MO_6}^{n+}$ octahedral groups in PNO complexes are hardly distorted, and only the relatively low μ_{eff} recorded for $[\mathrm{Co(PNO)_6}]^{2+}$ complexes may be an indication[111] for a symmetry lower than O_h.

A crystal structure determination of a representative $[\mathrm{ML_6}]^{n+}$ complex would be most desirable at this point. It may be stated, nevertheless, that the overall evidence and stereochemical considerations presented by Byers et al.[123] in combination with the established invariable presence of bent M–O–N groupings in aromatic amine N-oxide metal complexes[125–134, 167, 240–243, 268, 270, 281–285], the EPR spectrum of $[\mathrm{Fe(PNO)_6}](\mathrm{ClO_4})_3$ (ref. 177), and the fact that the spin delocalization patterns in $[\mathrm{M(4\text{-}PicNO)_6}](\mathrm{ClO_4})_2$ (M = Co, Ni) suggest that M–O–N is also nonlinear in these complexes[224], are definitely in favor of an effective symmetry lower than O_h in the complexes under discussion. Furthermore, similar assignments were made for analogous $[\mathrm{ML_6}]^{n+}$ complexes with DMSO[220] and tetramethylene sulfoxide[287], on the basis of stereochemical considerations (the M–O–S groupings are also nonlinear) and from detailed theoretical and experimental vibrational spectral studies.

(b) $[ML_5]^{2+}$

The crystal structure determination[133] of $[Co(2\text{-}PicNO)_5](ClO_4)_2$ revealed that the CoO_5 chromophore has a slightly distorted trigonal bipyramidal structure; the average Co—O axial bond length is 2.098 Å and the average Co—O equatorial bond length is 1.975 Å. The Co—O—N angles for the three equatorial and one of the axial Co—O bonds are 121—124°, but that corresponding to the other axial Co—O bond is 134°. The perchlorate groups are ionic[133].

(c) $[ML_4]^{2+}$

Stereochemical considerations by Byers et al. indicate that $[ML_4]^{2+}$ complexes (M = mainly Cu^{2+}; L = PNO and derivatives) have a D_{4h} (square planar) symmetry if only the MO_4 moiety is examined; however, interaction of the copper *d*-orbital wave functions with the ligand wave functions via the nonlinear M—O—N bonds will lead to a lowering of the effective symmetry[123]. There are a number of possible orientations of the pyridine *N*-oxide about the copper atom which would minimize steric interaction between adjacent ligand molecules. The most symmetric of these structures have C_{4h}, D_{2d} and C_{4v} symmetry[123]. Unequivocal IR evidence in support of these predictions was not obtained[123], but the crystal structure determinations of $[Cu(PNO)_4]X_2$ ($X = ClO_4$, BF_4) established[128, 282, 2 that the complex cation has indeed an effective symmetry close to C_{4h}; the CuO_4 chromophore has a square planar arrangement (Cu—O bond lengths = 1.92—1.93 Å) and the arrangement of the four PNO molecules around the Cu^{II} ion is a "swastika"-like configuration, the nitrogen atoms lying approximately in the copper—oxygen plane and the benzenoid rings lying approximately perpendicular to this plane (Cu—O—N angles 116.7—118.6°). The polyanions occupy approximately octahedral positions, but are not involved in any coordination[128, 282, 283], since the closest Cu—O (or F) approach is 3.34—3.38 Å. The isomorphous $[M(2,6\text{-}LNO)_4](ClO_4)_2$ complexes (M = Ni, Cu) have[145], most probably, stereochemistries similar to $[Cu(PNO)_4]^{2+}$; Fe^{II} and Co^{II}—2,6-LNO analogs are not isomorphous with the above complexes and may involve greater distortion from pure D_{4h} symmetry[145]. Finally, for paramagnetic $NiL_4(ClO_4)_2$ complexes (L = 2-PicNO, 2,6-LNO), a crystal structure determination would be desirable in order to establish whether these complexes are bi- or polynuclear *N*-oxide-bridged cations[144, 193], or monomeric involving coordinated perchlorate[146] (vide supra). The latter possibility might appear as rather remote, as no IR bands attributable to coordinated perchlorate were observed in these complexes[144, 193]; however, for similar pentacoordinated divalent 3*d* metal complexes with phosphine oxides not exhibiting splittings of the ionic perchlorate IR bands, the overall evidence was interpreted as pointing to the presence of $[ML_4(OClO_3)]^+$ cations by certain groups[136, 140, 288]; while other groups believe that the presence of $[L_3ML_2ML_3]^{4+}$ cations is more probable[138, 289].

(d) $[ML_2]^+$, $[ML_3]^+$ *and* $[M_2L_4]^{2+}$

Complexes of aromatic *N*-oxides with Ag^I perchlorate, of the types $[AgL_2](ClO_4)_2$, have been characterized as involving either a linear, mononuclear $[AgL_2]^+$ cation[290] or a binuclear, *N*-oxide-bridged $[LAgL_2AgL]^{2+}$ cation[148], by different groups of workers. Hg^I analogs were formulated[291] as involving four ligand groups per Hg_2^{2+} ion (i.e. $[Hg_2L_4](ClO_4)_2$). 3:1 *N*-oxide—$AgClO_4$ complexes are believed[290] to be of the type

$[AgL_2](ClO_4)\cdot L$, the formulation $[AgL_3](ClO_4)$ cannot be ruled out, however.

(viii) Metal complexes of monodentate mono-N-oxide ligands

(a) Complexes with 3d metal ions

Several Sc^{III} complexes with aromatic amine *N*-oxides have been reported, i.e. $ScL_3\cdot(NCS)_3$ (L = PNO, 2-, 3- and 4-PicNO, 2,6-LNO)[292], complexes of this type are neutral and of low symmetry, as demonstrated by ν_{N-O} and $\nu_{C\equiv N}$ splittings (Table 10), the NCS ion is N-bonded[292]. Sc^{III} perchlorate forms cationic $[ScL_6]^{3+}$ complexes with PNO[120,293] and the picoline *N*-oxides[120]. These complex cations are also distorted octahedral, as shown by splittings of the ν_{N-O} and ν_{Sc-O} modes[120] (Table 10). The titanium complexes with *N*-oxides isolated in crystalline state involve the Ti^{4+} and TiO^{2+} ions, however, complexes of Ti^{3+} and, possibly, Ti^{2+} with monodentate aromatic amine *N*-oxide ligands are most probably present in Ziegler- Natta catalysts for olefin polymerization ($TiCl_3$–Al

TABLE 10

Scandium, titanium and vanadium complexes with aromatic amine *N*-oxides[a]

Complex	Ref.
$[Sc(PNO)_6](ClO_4)_3$	120
$Sc(PNO)_3(NCS)_3$	120, 292
$Ti(PNO)_2F_4$	190
$Ti(PNO)(DMA)F_4$ [b]	153, 257
$Ti(PNO)(TMU)F_4$	257
$TiO(PNO)_5(ClO_4)_2$	114
$[TiF_5(PNO)]$	259
$Ti(PNO)_2[C_6H_4(O^-)_2]_2$	295
$[V(4\text{-}MeOPNO)_6](ClO_4)_3$	82
$V(PNO)_2F_4$	192
$V(PNO)_2Cl_4$	222
$VO(PNO)_5(ClO_4)_2$	81, 115, 223
$VO(4\text{-}PicNO)_4(ClO_4)_2\cdot H_2O$	115, 223
$VO(4\text{-}CNPNO)F_2\cdot HF\cdot H_2O$	297
$VO(PNO)_4Cl_2\cdot H_2O$	115, 223
$VO(4\text{-}BrPNO)_2Cl_2\cdot H_2O$	115, 223
$VO(2,6\text{-}LNO)_2Cl_2$	115, 223
$VO(PNO)_5Br_2\cdot 2H_2O$	115, 223
$VO(4\text{-}ClPNO)_2Br_2\cdot H_2O$	115, 223
$VO(4\text{-}PicNO)_4(BF_4)_2\cdot H_2O$	115, 223
$VO(PNO)_5(NCS)_2$	83
$VO(PNO)_4(NCS)_2$	83
$VO(4\text{-}PicNO)_2(NCS)_2$	83
$VO(PNO)(AA)_2$ [c]	207
VO^{3+}–PNO–pyrocatechol and VO_2^{+}–PNO–pyrocatechol systems	300

[a] Representative examples

[b] DMA – N,N-dimethylacetamide, TMU = tetramethylurea

[c] AA – acetylacetonato ligand

alkyl combinations), modified by various pyridine *N*-oxides[294]. $TiF_4 \cdot 2L$ adducts with a variety of aromatic *N*-oxides have been reported[142,152,153,190,192,203,204,257–259], and their properties were discussed in some detail in Sects. C(*ii*), (*iii*) and (*vi*). As already mentioned the *cis* octahedral complexes of this type are normally stabilized, and only sterically hindered *N*-oxides (2,6-LNO) favor the formation of the *trans* isomer. Mixed *N*-oxide–*N*,*N*-dimethylacetamide or tetramethylurea complexes with TiF_4 (i.e. $TiF_4 \cdot L \cdot L'$) where also synthesized[1] (vide supra). Anionic complexes $[TiF_5 \cdot L]^-$ with PNO and 4-substituted derivatives (methoxy-, methyl-, chloro-, acetyl-, nitro-) have been prepared in situ and studied by ^{19}F NMR spectroscopy[259]. PNO and QNO form 5:1 complexes[114,121] with $TiO(ClO_4)_2$. The ν_3 and ν_4 modes of ionic ClO_4^- are not split in the IR spectra of these compounds, which were formulated as $[TiOL_5](ClO_4)_2$, involving a hexacoordinated cationic Ti^{4+} complex[114,121]. Finally, PNO–Ti^{4+}–pyrocatechol systems form a complex[295] of the type $Ti(PNO)_2[C_6H_4(O^-)_2]_2$ at pH 2–3. Typical examples of Ti^{IV} complexes with *N*-oxides are shown in Table 10.

VO^{2+} complexes with *N*-oxide ligands have been extensively studied[1,81–83,115,146,202,206–208,223,296–298]. Oxovanadium(IV) salts form complexes of various stoichiometries, i.e. VOL_5X_2 (X = Cl, Br, ClO_4, NCS), VOL_4X_2 (X = Cl, Br, ClO_4, BF_4, NCS), VOL_2X_2 (X = Cl, Br, NCS), aquo adducts of complexes of the above types, $VOLF_2 \cdot HF \cdot H_2O$, and $VOL_4Br(OH)$ (see also Table 10)[1,81,83,115,146,202,223,297,298]. Anion coordination and incorporation of water molecules are important factors influencing the ligation of the *N*-oxides in the first coordination sphere of the metal ion. Environmental conditions (interaction medium, degree of dehydration of the oxovanadium(IV) salt, etc.) influence the stoichiometry of the complex stabilized[1]. Thus, for example, both tetrakis- and pentakis-(4-chloropyridine *N*-oxide)oxovanadium (IV) perchlorate complexes can be isolated, depending on the degree of prior dehydration of the oxovanadium(IV) perchlorate solution[1]. In most cases oxovanadium(IV) salts were utilized as starting materials for the syntheses of the above complexes[115,146,202,223,297,298], when V^{III} salts are used instead, V^{III}, VO^{2+} or mixed V^{III}–VO^{2+} complexes may be obtained (vide supra, Sect. C(*i*))[81–83]. Thus $V(NCS)_3$, under inert conditions, interacts with *N*-oxides yielding $VO(NCS)_2$ complexes ($\mu_{eff} \simeq 1.70$ B.M.)[83]. $V(ClO_4)_3$ forms $VO(ClO_4)_2$–*N*-oxide complexes, when the interaction takes place in the atmosphere[81], whereas, under inert conditions, $[VL_6](ClO_4)_3$ compounds are obtained (for L = 4-MeOPNO or 4-ClPNO, fairly pure V^{III} complexes were isolated, showing a μ_{eff} of 2.54–2.71 B.M., the PNO, 4-PicNO and $4\text{-}NO_2PNO$ analogs were contaminated with oxovanadium(IV) products, clearly showing IR $\nu_{V=O}$ bands)[82]. Oxovanadium(IV) β-ketoenolates form 1:1 adducts with pyridine and quinoline *N*-oxides (Table 10)[206–208,296]. The *N*-oxide ligand coordinates at the *trans* position, relative to the vanadyl oxygen, in these compounds[206–208,296]. $VO(AA)_2$ has been used successfully as a reference acid for aromatic *N*-oxides, in fact, a linear relation exists between the $VO(AA)_2$–*N*-oxide adduct formation enthalpy and the $\nu_{V=O}$ shift upon formation of this adduct[149,207,208]. The presence or absence of *trans*-axial *N*-oxide ligands in VO^{2+} complexes can be generally deduced from the position of $\nu_{V=O}$, thus, hexacoordinated compounds involving one *trans*-axial *N*-oxide ligand exhibit this mode at 960–950 cm^{-1}, whereas pentacoordinated complexes, not involving ligation of this type, show[115,149,206–208,22] $\nu_{V=O}$ at 1000–990 cm^{-1}. For the electronic spectral bands of oxovanadium(IV) complexes with *N*-oxides, various assignments have been made by different groups[83,146,297]

Thus, for example, for the spectra of oxovanadium(IV) perchlorate with alkyl-substituted pyridine *N*-oxides, Schmauss and Specker[146] made the following assignments: $b_2 \to b_1^*$ at 10.6–12.5 kK, $b_2 \to e_\pi^*$ at 12.5–16.3 kK, $b_2 \to a_1^*$ at 14.6–15.0 kK, and a charge-transfer band at 25.6–27.5 kK. Band assignments for V^{III} complexes were given in Table 7. $VCl_4 \cdot 2L$ (L = PNO, 4-NO_2-, 4-Cl-, or 4-MeO-PNO, 2- and 4-PicNO, 2,6-LNO) and $VCl_4 \cdot L$ (L = 4-benzyloxy-PNO) complexes were prepared by Bridgland and McGregor under inert conditions, as exposure of these compounds to moist air leads to their conversion to the corresponding $VOCl_2$ complexes[222]. These complexes exhibit magnetic moments of 1.65–1.78 B.M., and their electronic spectral bands were assigned as follows[222]: $^2B_{2g} \to {}^2B_{1g}$ at 14.6–17.0 kK, $^2B_{2g} \to {}^2A_{1g}$ at 20.0–22.0 kK. $VF_4 \cdot 2L$ complexes with PNO and 4-substituted derivatives were also prepared[299], and their IR spectra were studied[192]; ν_{N-O} was found insensitive to 4-substituent effects in this series of complexes[192]. V^V–pyrocatechol–PNO systems form a variety of colored products at different pH regions; the composition of the species formed in this system was found by the equilibrium displacement method; the formation of violet 1:1:1 and 1:1:2 complexes involving the VO_2^+ ion, and green 1:2:2, 1:1:1 and 1:2:1 complexes of the VO^{3+} ion was proposed[300] (Table 10).

The complexes of the remaining 3*d* metal ions (Cr to Zn) are discussed together. As already mentioned (vide supra, Sects. C(*ii*)–(*vii*), Tables 3–8, Figs. 2, 3), non-sterically hindered aromatic amine *N*-oxides form $[ML_6]X_n$ (M = Cr^{III}, Mn^{II}, Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, $n = 2, 3$; X = ClO_4, BF_4 and, with the exception of Cu^{II}, NO_3) and $[CuL_4]X_2$ (X = ClO_4, BF_4, NO_3) complexes[16–18,48,53,108–112,117–119,122,123,128,142–144,146–148,177,205,213,217,218,224,261,265,282,283,301]. For Cr^{III}, the complete series of $[Cr(OH_2)_{6-n}(PNO)_n](ClO_4)_3$ ($n = 0$–6, inclusive) was identified in solution[171]. A 7:1 PNO:$Fe(ClO_4)_3$ complex isolated by Carlin[17] was formulated as $[Fe(PNO)_6](ClO_4)_3 \cdot PNO$. The properties of the cationic metal complexes were described above. Sterically hindered aromatic amine *N*-oxides do not influence the stoichiometries[145,146,149,159] of Cr^{III} or Fe^{III} cationic complexes, which are also of the type $[ML_6]^{3+}$. In the case of divalent 3*d* metal ions, however, $[ML_n]^{2+}$ ($n < 6$) complexes with ligands of this type may be stabilized[123,133,144,145,147,149,193] (vide supra, Sect. C(*ii*)–(*vii*)). Ligands behaving in this manner are 2-substituted and 2,6-disubstituted pyridine *N*-oxides and acridine *N*-oxide. The environmental conditions are of key importance as far as the nature of the complexes precipitated is concerned. Thus, for instance, $[Co(2\text{-}PicNO)_5](ClO_4)_2$ was synthesized[123] by dissolving equal weights of ligand and salt in a small amount of hot alcohol with prolonged cooling of the resulting mixture at 0°C, while $[Mn(2,6\text{-}LNO)_4(OClO_3)](ClO_4)$ and $[M(2,6\text{-}LNO)_4](ClO_4)_2$ (M = Fe, Co, Ni, Cu, Zn) (square-planar complexes) were precipitated by mixing triethyl orthoformate–acetone solutions of ligand and salt[145]. On the other hand, complexes of the following stoichiometries were obtained when 7:1 ligand:hydrated salt methanolic or ethanolic solutions were allowed to cool at −30°C: $[MnL_6](ClO_4)_2$ (L = 2-PicNO, 2-EtPNO), $[Co(2\text{-}PicNO)_6](ClO_4)_2$, $[Co(2,6\text{-}LNO)_6](ClO_4)_2 \cdot 2H_2O$, $[Co(2,6\text{-}LNO)_4(OH_2)_2](ClO_4)_2$, $[NiL_6](ClO_4)_2 \cdot H_2O$ (L = 2-PicNO, 2-EtPNO), $[Ni(2,6\text{-}LNO)_6](ClO_4)_2 \cdot 3H_2O$, $Ni(2,6\text{-}LNO)_4(ClO_4)_2$ (green, paramagnetic)[146]. It is noteworthy that complexes of the types $[M(2,6\text{-}LNO)_6](ClO_4)_2 \cdot 3H_2O$ (M = Co, Ni) and $[M(2,6\text{-}LNO)_6](ClO_4)_3 \cdot (2,6\text{-}LNO)$ (M = Cr, Fe) are colorless; the Cr^{III} complex of this type exhibits unusually weak (ϵ = 0.5–0.6 in nitromethane) (d–d) bands[146]. $[Cr(2,6\text{-}LNO)_6](ClO_4)_3$, on the other hand, shows (d–d) bands with normal extinction coefficients in nitromethane ($\epsilon = 58.6$ for the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition)[145] The green, paramagnetic Ni(2,6-LNO)$_4$(ClO$_4$)$_2$ complex is converted to the violet diamagnetic [Ni(2,6-LNO)$_4$](ClO$_4$)$_2$ during prolonged (several months) desiccation[302] over P_2O_5; the nature of this reaction is currently under study. It should also be noted that even when the same synthetic procedure is employed, *N*-oxides with similar steric features may form complexes of different stoichiometries. e.g. 2-PicNO yields NiL$_4$(ClO$_4$)$_2$, while the more severely sterically hindered 2-EtPNO forms [NiL$_6$](ClO$_4$)$_2 \cdot 2H_2O$, under the same conditions[144]; and 4-EtOPNO forms [ML$_5$](ClO$_4$)$_2$ and [ML$_6$](NO$_3$)$_2$ (M = Co, Ni) complexes[142, 143] The structural aspects of [ML$_5$]$^{2+}$ and [ML$_4$]$^{2+}$ complexes with *N*-oxides were discussed in Sect C(*vii*).

In addition to the cationic complexes described above, divalent 3*d* metal nitrates also form neutral complexes, involving coordinated mono- or bidentate nitrato groups. The complexes usually obtained[16, 18, 110, 126, 143, 144, 158, 159, 248, 303] are of the type [ML$_2$(NO$_3$)$_2$] The Mn^{II}, Co^{II}, Ni^{II} and Zn^{II} complexes of this type are in most cases hexacoordinated involving two coordinated bidentate nitrato groups, however, [M(2,6-LNO)$_2$(NO$_3$)$_2$] (M = Mn, Co, Ni, Zn) complexes exhibit IR and electronic spectra favoring pentacoordinated configurations, involving one mono- and one bidentate nitrato ligand[159] (cf Sect C(*ii*)) [CuL$_2$(NO$_3$)$_2$] complexes contain monodentate nitrate exclusively The PNO complex of this type is a pentacoordinated, PNO-bridged dimer[126]. This compound involves bent M—O—N (nitrato) groupings[126], thus, the coordinated monodentate nitrate has a C_s local symmetry, in complexes of this type, while the bidentate nitrato group in analogous [ML$_2$(O$_2$NO)$_2$] compounds is of C_{2v} local symmetry (see refs 304, 305) In fact, distinct differences were reported for the fundamental vibrational modes of coordinated NO$_3$ of 4-EtOPNO complexes involving mono- ([CuL$_2$(NO$_3$)$_2$], [CoL$_3$(NO$_3$)$_2$]) and bi- (ML$_2$(NO$_3$)$_2$], M = Co, Ni, Zn) dentate nitrato ligands[143] Co^{II} and Cu^{II} nitrate—PNO complexes have found application as semiconductors for thermistors[306]. Neutral 3*d* metal nitrate complexes involving ligand-to-metal ratios higher than 2 have also been reported, viz . [Co(4-EtOPNO)$_3$(ONO$_2$)$_2$] (ref 143), Ni(QNO)$_3$(NO$_3$)$_2 \cdot \frac{1}{2}H_2O$, NiL$_4$(NO$_3$)$_2$ (L = 2-EtPNO, 2,4-LNO)[144] Co^{II} nitrite complexes of the type [CoL$_2$(NO$_2$)$_2$] (L = 2,4- and 2,6-LNO, 2,4,6-CNO, 2- and 4-MeQNO) are hexacoordinated, containing two chelating bidentate nitrito ligands[226]. A few 3*d* metal sulfate[159, 198] and trihaloacetate[307] complexes with aromatic amine *N*-oxides were also reported· [ZnLSO$_4$] complexes (L = PNO, 4-PicNO), with polynuclear structures involving coordination of all four oxygen atoms of the SO$_4$ group were proposed, the fundamental vibrations of the $SO_4{}^{2-}$ anion do not exhibit any splittings; however, both the ν_1 and ν_2 mode of this group are IR-active, while ν_{Zn-O}(sulfato) was identified at 261–260 cm^{-1} Thus it was concluded that the SO$_4$ groups retain an essentially T_d symmetry during coordination of their four oxygens to neighboring Zn^{II} ions[198]. A number of 3*d* metal sulfate complexes with 2,6-LNO, recently reported, were formulated as follows [Co(2,6-LNO)(OH$_2$)$_5$](SO$_4$), [(2,6-LNO)(O$_2$SO$_2$)Ni(2,6-LNO)$_2$Ni(O$_2$SO$_2$)(2,6-LNO)], binuclear pentacoordinated, 2,6-LNO-bridged, with chelating bidentate sulfato ligands; [(2,6-LNO)$_2$Cu(SO$_4$)$_2$—Cu(2,6-LNO)$_2$], binuclear, tetracoordinated, involving bridging bidentate sulfato groups, and [O$_2$SO$_2$)Fe(2,6-LNO)$_2$Fe(O$_2$SO$_2$)], binuclear, tetracoordinated, with bridging 2,6-LNO and chelating bidentate sulfato ligands[159]. These formulations were based on spectral (IR, electronic) and magnetic evidence[159]. Metal trihaloacetates form[307] form the following complexes: $[MLX_2]$ (M = Mn, Co, Ni, Zn; L = PNO, 4-PicNO; X = CF_3COO^-, CCl_3COO^-) and $[CuL_2X_2]$. The properties of these complexes suggest that the trihaloacetato ligand is coordinated, through one or both oxygens of the COO group[307]. A series of 2:1 complexes of Cu^{II} benzoate with *N*-oxides (PNO, the PicNO's, 2,6-CNO, 2,4,6-LNO, QNO, 2- and 4-MeQNO) were recently prepared; these complexes exhibit subnormal magnetic moments (1.38–1.42 B.M.)[308]. Cu^{II} acetate[230] and salicylate analogs are also magnetically subnormal, while bis-(salicylato) bis(PNO)–Cu^{II} shows a μ_{eff} of 1.95 B.M. (ref. 309).

3*d* metal halides form a wide variety of complexes with aromatic *N*-oxides (see also Sect. C(*ii*)). Some details on Cu^{II} halide complexes with *N*-oxides have already been presented in Sect. C(*ii*), C(*v*) and Tables 2 and 9. Magnetically normal 2:1 *N*-oxide–Cu^{II} halide complexes may be obtained in two crystalline modifications (a third modification is the dimeric, *N*-oxide-bridged structure)[167]. Green monomeric $[CuL_2X_2]$ complexes (e.g. L = 4-PicNO, X = Cl) have a *trans* square planar geometry[284], while yellow isomers (e.g. L = 2,6-LNO, X = Cl) have a distorted geometry, which is intermediate between *cis* square planar and tetrahedral[285]. As is the case with 1:1 analogs (vide supra), monomeric 2:1 *N*-oxide–Cu^{II} halide complexes may form adducts with neutral ligands; these adducts are magnetically normal[167] (Table 9); a monomeric adduct of this type, $[Cu(4\text{-}NO_2PNO)_2Cl_2(OH_2)_2]$, consists of *trans* square planar $CuCl_2(OH_2)_2$ groups having the amine-oxide oxygen atoms of the $4\text{-}NO_2PNO$ molecules loosely bonded to the copper ion at the axial positions; the geometry of the complex is distorted tetragonal bipyramidal[134]. Although the polymeric $[Cu_3Cl_6(2\text{-PicNO})_2(OH_2)_2]_n$ complex exhibits low magnetic moments[127,167] (vide supra), several $Cu_3Cl_6L_2$ (L = 4-ClQNO, 4-Cl-6-MeQNO) and $Cu_4Cl_8L_3$ (L = $3\text{-}NO_2$-6-MeQNO) complexes are magnetically normal[186]. These compounds are most probably characterized by chlorine, rather than *N*-oxide, bridges[167]. A number of $Cu_4OX_6L_4$ (X = Cl, Br; L = PNO and other neutral ligands) complexes were also reported[310]. These compounds exhibit an IR band, characteristic of the Cu_4O group, at 600–500 cm^{-1} (583 cm^{-1} for the PNO complex); the four Cu atoms lie in a tetrahedral arrangement around the Cu_4O oxygen; the halogen atoms are invariably bridging (each halogen is shared by two Cu atoms); while the four neutral ligands are terminal[310]. Finally, $Cu(PNO)_4Br_2$ was among the first *N*-oxide complexes to be reported[18].

Complexes of various stoichiometries may be formed during interactions between *N*-oxides and other 3*d* metal halides (Table 11). $Ni(PNO)_6X_2$ (X = Br, I) complexes obviously involve[18,172,185] the $[Ni(PNO)_6]^{2+}$ cation. NiL_5I_2 (L = 2- or 4-PicNO) complexes were reported but not characterized[172]. The red complex $Ni(PNO)_4I_2$ was obtained[185] by heating the yellow $[Ni(PNO)_6]I_2$ at 100°C. Its magnetic moment (3.26 B.M.) is indicative[185] of a hexacoordinated structure of the type $[Ni(PNO)_4I_2]$. 3:1 complexes have been reported for Fe^{III} and Co^{II} halides[16,18,177,225]. $[Fe(PNO)_3Cl_3]$ is neutral and probably *cis* octahedral[177]. Co^{II} complexes of this stoichiometry were formulated as $[Co(PNO)_3X]X$ (X = Cl, Br, I), on the basis of characterization studies (mol. wt., conductances, μ_{eff} of 4.67 B.M. for the bromide complex)[18]. More recent studies of these chloride and bromide complexes led to the conclusion that they are of the type $[Co(PNO)_6][CoX_4]$; in fact, the electronic spectra of these complexes are very similar to those of tetrahalocobaltate(II) compounds, while the $CoBr_2$ complex is isomorphous with the tetrabromocadmate(II) analog ($[Co(PNO)_6][CdBr_4]$), which was also reported[225]. 2:1 and 1:1 *N*-oxide 3*d* metal halide complexes are numerous and involve, in many cases, additional neutral

TABLE 11

3*d* Metal halide (Mn to Zn) complexes with aromatic amine *N*-oxides[a]

Complex	Coordination number	μ_{eff} (B.M.)	Ref.
Mn(PNO)$_{1/2}$Cl$_2$	6 (polynuclear)	*b*	172
Mn(PNO)Cl$_2$ · H$_2$O	6 (polynuclear)	5.77	172
Mn(PNO)Cl$_2$	6 (polynuclear)	5.60	182
Mn(4-PicNO)$_2$Br$_2$	6	5.82	172
[Fe(PNO)$_4$Cl$_2$][FeCl$_4$]	6	5.83	205
[Fe(PNO)$_3$Cl$_3$]	6	*b*	177
Co(PNO)Cl$_2$ · xH$_2$O ($x < 1$)	4 (tetrahedral)	*b*	182
Co(PNO)Cl$_2$ · H$_2$O	Probably 6	4.70, 4.75	16, 172
Co(4-PicNO)$_2$Cl$_2$	Probably 6	4.80	172
Co(2,4-LNO)$_2$Cl$_2$	4 (tetrahedral)	4.50	184
Co(PNO)$_3$Cl$_2$	Structure proposed: [Co(PNO)$_6$][CoCl$_4$]	4.75	16, 225
[Co(PNO)$_6$][CdBr$_4$]	6		225
Co(PNO)$_3$X$_3$ (X = Br, I)	Structures proposed: [Co(PNO)$_3$X]X and [Co(PNO)$_6$][CoX$_4$]	4.67, 4.58	18, 225
Ni(PNO)$_{1/2}$Cl$_2$	6 (polynuclear)	*b*	172
Ni(PNO)Cl$_2$	6 (polynuclear)	3.49	182
Ni(IQNO)Cl$_2$ · ½H$_2$O	6 (polynuclear)	*b*	144
Ni(PNO)Cl$_2$ · H$_2$O	6 (polynuclear)	3.21, 3.30	16, 172
Ni(QNO)Cl$_2$ · 2H$_2$O	6 (polynuclear)	3.23	144
Ni(2,6-LNO)$_2$Br$_2$	6 (polynuclear)	3.10	172
Ni(PNO)$_4$I$_2$	6	3.26	185
Ni(2-PicNO)$_5$I$_2$	*b*	*b*	172
[Ni(PNO)$_6$]I$_2$	6	3.28	185
Zn(PNO)Cl$_2$	6 (polynuclear)		172
Zn(2,6-LNO)$_2$Cl$_2$	4 (tetrahedral)		130, 180

[a] Representative examples (Cu^{II} halide complexes are given in Table 9).
[b] Not reported.

ligands (Table 11). FeX$_3$ · 2L complexes (X = Cl, Br; L = PNO, 4-substituted derivatives, 2-PicNO, 2,6-LNO) are invariably[177–179,205] of the type [FeL$_4$X$_2$][FeX$_4$]; a complex of the type [Fe(PNO)$_4$Cl$_2$](ClO$_4$)· H$_2$O was also prepared[177]. ML$_2$X$_2$ (M = Mn, Co, Ni, Zn) complexes with various aromatic amine *N*-oxides have been reported[16,18,130,142,158,172,173,180,184,297,311,312]. Certain complexes of this type are obtained in the form of hydrates, or alcoholates, e.g. Ni(3-PicNO)$_2$Cl$_2$ · H$_2$O, Ni(4-PicNO)$_2$Cl$_2$ · (C$_2$H$_5$OH) (ref. 172), Ni(4-CNPNO)$_2$Cl$_2$ · 3H$_2$O (ref. 297). Magnetic (μ_{eff} = 4.50–4.54 B.M.) and spectral properties are in favor of tetrahedral structures for CoL$_2$X$_2$ complexes[158,172,174]. The Zn^{II} analogs are also monomeric tetrahedral[130,172,180,311,312]; the crystal structure determination of [Zn(2,6-LNO)$_2$Cl$_2$] revealed that the Zn atoms lie on two-fold symmetry axes and are tetrahedrally coordinated to two chlorine atoms and two oxygen atoms from the 2,6-LNO groups; the tetrahedral geometry is slightly distorted, owing to differences in atomic size[130]. ML$_2$X$_2$ (M = Mn, Ni) complexes exhibit electronic spectra and magnetic moments (μ_{eff} = 3.10 B.M. for $\mathrm{Ni(2,6\text{-}LNO)_2Br_2}$; 5.82 B.M. for $\mathrm{Mn(4\text{-}PicNO)_2Br_2}$) suggestive of hexacoordinated, polynuclear structures[172]. 1:1 complexes of *N*-oxides with $\mathrm{Mn^{II}}$, $\mathrm{Co^{II}}$ and $\mathrm{Ni^{II}}$ halides are usually obtained in the form of hydrates[16,144,172,173,182,297]. Anhydrous $\mathrm{MLX_2}$ complexes with these metal ions may be obtained either by utilizing triethyl orthoformate as the reaction medium[142 182] or by heat treatment of $\mathrm{ML_2X_2}$ (ref. 172) or $\mathrm{MLX_2 \cdot \mathit{n}H_2O}$ (ref. 173) complexes. Complexes of aromatic amine *N*-oxides with metal halides, involving low M to L ratios, decompose at elevated temperatures yielding complexes with higher metal to ligand ratios[172]. Similar, although not identical, behavior has been observed in 3*d* metal halide–pyridine complexes[313]. Some typical examples of reactions of these types are[167,172,173,185]:

$$\mathrm{Mn(PNO)_2Br_2 \xrightarrow{240°} Mn(PNO)_{1/2}Br_2} \tag{6}$$

$$\mathrm{Mn(2\text{-}PicNO)Cl_2 \cdot H_2O \xrightarrow{160°} Mn(2\text{-}PicNO)Cl_2 \xrightarrow{240°} Mn(2\text{-}PicNO)_{1/2}Cl_2} \tag{7}$$

$$\mathrm{Co(3\text{-}PicNO)_3I_2 \xrightarrow{120°} Co(3\text{-}PicNO)_2I_2 \longrightarrow Co(3\text{-}PicNO)Cl_2} \tag{8}$$

$$\mathrm{Co(PNO)Cl_2 \cdot H_2O \xrightarrow{170°} Co(PNO)Cl_2} \tag{9}$$

$$\mathrm{Ni(PNO)_6I_2 \xrightarrow{100°} Ni(PNO)_4I_2} \tag{10}$$

$$\mathrm{Ni(PNO)_6I_2 \xrightarrow{210°} Ni(PNO)I_2} \tag{11}$$

$$\mathrm{Ni(4\text{-}PicNO)_5I_2 \xrightarrow{120°} Ni(4\text{-}PicNO)_2I_2} \tag{12}$$

$$\mathrm{Ni(PNO)Cl_2 \cdot H_2O \xrightarrow{180°} Ni(PNO)Cl_2 \xrightarrow{300°} Ni(PNO)_{1/2}Cl_2} \tag{13}$$

$$\mathrm{Ni(4\text{-}PicNO)_2Cl_2 \cdot (C_2H_5OH) \xrightarrow{120°} Ni(4\text{-}PicNO)_2Cl_2 \xrightarrow{220°} Ni(4\text{-}PicNO)Cl_2} \tag{14}$$

$$\mathrm{Zn(2\text{-}PicNO)_2Cl_2 \xrightarrow{250°} Zn(2\text{-}PicNO)Cl_2} \tag{15}$$

$$\mathrm{CuL_2Cl_2 \longrightarrow CuLCl_2} \tag{16}$$

$\mathrm{ZnLX_2}$ and $\mathrm{M(L)_{1/2}X_2}$ (M = Mn, Ni) complexes can be obtained only by thermal decomposition of analogous complexes with higher *N*-oxide content[172]. 1:1 and 0.5:1 *N*-oxide–$\mathrm{Mn^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$ or $\mathrm{Zn^{II}}$ halide complexes appear to be bi- or polynuclear in general[172,173,182] The corresponding hydrated complexes are also polynuclear in most cases (e.g. $\mathrm{Co(PNO)Cl_2 \cdot H_2O}$, $\mathrm{Ni(PNO)Cl_2 \cdot H_2O}$, $\mathrm{Co(4\text{-}PicNO)Cl_2}$ exhibit electronic and low-frequency IR spectra suggestive of octahedral ligand-field symmetries[172]; a lower hydrate of the type $\mathrm{Co(PNO)Cl_2 \cdot \mathit{x}H_2O}$, where $x < 1$, is tetrahedral and probably binuclear[182]). The low-frequency IR spectra of $\mathrm{MLCl_2}$ (M = Mn, Ni) complexes favor the presence of chlorine, rather than *N*-oxide, bridges in these bi- or polynuclear complexes[182]. For hydrated analogs, three possibilities exist, viz. chlorine, *N*-oxide or aquo bridges[144].

$\mathrm{Fe(NCS)_3}$ forms neutral complexes of the general type $\mathrm{[Fe(NCS)_3L_3]}$ (L = PNO, 2-, 3-, 4-PicNO, 2,6-LNO, 2-EtPNO and 2-isopentyl-PNO), involving N-bonded isothiocyanato ligands[177,314]. $\mathrm{[CoL_2(NCS)_2]}$ complexes (L = 2,6-LNO, 2,4,6-CNO) were characterized as polynuclear octahedral, containing NCS bridges[158]. Recent evidence for $\mathrm{[M(2,6\text{-}LNO)_2(NCS)_2]}$ (M = Co, Ni) complexes is suggestive of penta- rather than hexacoordinated configurations (similarity of the electronic spectrum of the $\mathrm{Co^{II}}$ complex[123] to that of $\mathrm{[Co(2\text{-}PicNO)_5](ClO_4)_2}$, occurrence of ν_{M-O} at ca. 380 $\mathrm{cm^{-1}}$, as is also the case with other pentacoordinated 2,6-LNO–$\mathrm{Co^{II}}$ and $\mathrm{Ni^{II}}$ complexes[193], μ_{eff} of 4.73 (Co) and 3.38

(Ni) B.M., appearance of split $\nu_{C\equiv N}$ bands, occurring at both the "bridging" and "N-bonded, terminal" regions for the NCS group[315], etc.)[159]. These compounds were, therefore, formulated as $[(2,6\text{-LNO})_2(\text{SCN})\text{M-(NCS)}_2\text{-M(NCS)}(2,6\text{-LNO})_2]$, i.e. binuclear, involving both bridging and N-bonded (terminal) NCS ligands[159]. $[\text{Cu(PNO)}_2(\text{NCS})_2]$ shows a normal magnetic moment (1.88 B.M.)[230]; the 2,6-LNO analog has a μ_{eff} of 1.53 B.M., and was assigned a hexacoordinated polynuclear structure, exclusively involving bridging thiocyanato ligands (a coordination number of six in this compound is suggested by the occurrence of ν_{Cu-O} at 330 cm^{-1} and the (*d–d*) transition maximum at 11.5 kK)[159].

A number of adducts of *N*-oxides with 3*d* metal chelates have also been reported. Bis-(β-ketoenolato)M^{II} complexes (M = Co, Ni, Cu, Zn) reportedly form adducts with a variety of pyridine and quinoline *N*-oxides[132, 154–157, 316]. (vide supra, Sects. C(*ii*), (*vii*)). Cu^{II} β-ketoenolates form square pyramidal 1:1 complexes with *N*-oxides and similar ligands[156, 316]. Co^{II} and Ni^{II} β-ketoenolates tend to form 1:2 pseudo-octahedral adducts with *N*-oxides, unless the steric features of the *N*-oxide favor the stabilization of 1:1 adducts (e.g. 2,6-LNO, QNO)[154, 155, 157, 316]. The crystal structure determination of $[\text{Ni(AA)}_2(\text{PNO})_2]$ shows that the six oxygen atoms coordinated to the nickel are in a nearly regular octahedral disposition; the PNO molecules are *cis* to one another[132] (Ni–O–N angle: 121°). A number of Co^{III} complexes of the type *trans*-$[\text{CoX(DH)}_2\text{L}]$ and *trans*-$[\text{Co(DH)}_2\text{L}_2]\text{X}\cdot\text{H}_2\text{O}$ (X = Cl, Br, I or NO_2; DH = dimethylglyoximato ligand; L = PNO or 4-NO_2PNO) were prepared by treating the corresponding aquo or methanolo (L = H_2O, CH_3OH) complexes with *N*-oxide[317]. An octahedral 2:1 adduct (μ_{eff} = 3.09 B.M.) of PNO with the square planar Ni^{II} ethylxanthate has also been prepared[318]. Finally, reaction of PNO with iron pentacarbonyl leads to the formation[8] of $[\text{Fe(PNO)}_6][\text{Fe}_4(\text{CO})_{13}]$.

(b) Complexes with 4d and 5d metal ions

The complexes of Y^{III} are discussed in the next section, together with the lanthanide ion complexes. A series of 2:1 *N*-oxide (PNO, and 4-MeO-, 4-Me-, 4-Cl-, and 4-NO_2-PNO)–ZrF_4 complexes were prepared (Table 12) and studied by IR spectroscopy[191]. Interaction of $ZrCl_4$ and $HfCl_4$ with 2,6-LNO leads to the formation[175] of $\text{ZrCl}_4\cdot3(2,6\text{-LNO})$ and $\text{HfCl}_4\cdot2(2,6\text{-LNO})$. Both these complexes are neutral, the former being heptacoordinated and the latter hexacoordinated, probably involving *cis* coordination of the two *N*-oxide ligands[175]. $\text{ZrO(ClO}_4)_2$ forms complexes of the types $[\text{ZrOL}_6](\text{ClO}_4)_2$ (L = PNO, QNO), involving heptacoordinated Zr^{4+} ions[116, 121]. Coordination of perchlorate does not occur in these compounds; the ν_3 and ν_4 IR modes of ClO_4^- appear either as single bands or show small splittings, which have been attributed to crystal-field effects rather than coordination of the polyanion[116, 121]. A complex of the type $\text{ZrOCl}_2\cdot2\text{QNO}$ was also reported[298].

Interaction of dodeca-μ_2-chlorohexaniobium dichloride ($[\text{Nb}_6\text{Cl}_{12}]\text{Cl}_2$) with aromatic amine *N*-oxides (PNO, 4-Me-, 4-(Me)$_2$N-, 4-Cl-, 4-NO_2-PNO) leads to the formation[319, 320] of $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2\text{L}_4]$ (Table 12). These complexes consist of a central $(\text{Nb}_6\text{Cl}_{12})^{2+}$ core, involving an octahedral cluster of six Nb ions of low formal oxidation state and twelve bridging chlorine atoms; an additional chlorine or *N*-oxide ligand is coordinated to each Nb atom in a "centrifugal" position such that the metal–ligand bond points radially outward from the center of the octahedral cluster[319, 320]. Mo^{II} chloride, which also involves a Mo_6 octahedral cluster and is of the type $[\text{Mo}_6\text{Cl}_8]\text{Cl}_4$, behaves in a similar manner, forming

TABLE 12

Aromatic amine *N*-oxide complexes with *4d* and *5d* metal ions [a]

Complex	Ref.	Complex	Ref.
$Zr(PNO)_2F_4$	191	$(CO)Pt(PNO)Cl_2$	74, 79, 328
$Zr(2,6\text{-}LNO)_3Cl_4$	175	$Pt(2,6\text{-}LNO)_3Cl_4$	175
$Hf(2,6\text{-}LNO)_2Cl_4$	175	$[Ag(PNO)_2]ClO_4 \cdot PNO$	111, 290
$ZrO(PNO)_6(ClO_4)_2$	121	$[Ag(4\text{-}CNPNO)_2](ClO_4)$	148
$ZrO(QNO)_2Cl_2$	298	$AgNO_3 \cdot PNO$	333
$(Nb_6Cl_{12})(PNO)_4Cl_2$	319, 320	$[Ag(PNO)][C(NO_2)_3]$	334
$(Mo_6Cl_8)(PNO)_2Cl_4$	320, 321	$[Cd(PNO)_6](ClO_4)_2$	111
$Mo(NO)_2(PNO)_2Cl_2$	323	$[Hg(PNO)_6](ClO_4)_2$	109, 111, 181
$MoO_2Cl_2 \cdot 2PNO$	322	$[Hg(PNO)_6]X_2$ [d]	181
$[Mo(O_2)_2O](PNO)(OH_2)$	324	$HgX_2 \cdot 2(PNO)$ [e]	181
$[M(O_2)_2O](4\text{-}PicNO)_2$ (M = Mo, W)	324	$[Cd(PNO)Br_2]_n$	180
$Re(CO)_3(PNO)_2Cl$	96	$Cd_3(PNO)_2Cl_6$	180
$Ru(CO)_3(PNO)Br_2$	325	$[Cd_2(3\text{-}PicNO)Cl_4]_n$	180
$Ru(2,6\text{-}LNO)_3Cl_3$	179	$[Hg(PNO)Cl_2]_2$	180
$[Rh(2,6\text{-}LNO)_5Cl]Cl_2$	179	$[Cd(PNO)(NCS)_2]_2$	199
$(C_2H_4)Pd(4\text{-}PicNO)Cl_2$	80	$[Hg(PNO)(SCN)_2]_2$	181
$Pd(4\text{-}EtOPNO)_2Cl_2$	142	$[Cd(2,6\text{-}LNO)_4(ONO_2)_2]$	159
$(C_2H_4)Pt(PNO)Cl_2$	77, 327	$(CF_3)_2Hg \cdot n$PNO (n = 1, 2, 3)	338, 339
$(RCH{=}CH_2)Pt(PNO)Cl_2$ [b]	2, 72, 73, 75–78	$Hg_2(PNO)_4(ClO_4)_2$	291
$(RC{\equiv}CR')Pt(PNO)Cl_2$ [c]	75	$Hg_2(PNO)_5(SiF_6)$	291

[a] Representative examples.

[b] R = CH_3, C_2H_5, $C_{10}H_{21}$, C_6H_5, C_6H_4-X (X = organic substituent), Y-CO_2 (Y = CH_3, C_2H_5, n-C_3H_7).

[c] R = $(CH_3)_3C$, $(CH_3)_2C(OH)$; R' = CH_3, $(CH_3)_2C(OH)$.

[d] X = BF_4, PF_6, AsF_6, SbF_6.

[e] X = NO_3, CN, CF_3COO, CCl_3COO.

$[(Mo_6Cl_8)Cl_4L_2]$ complexes with the same *N*-oxides[320,321] (Table 12). Linear ν_{Mo-O} vs. σ_{PyNO} plots for these complexes show a trend of decrease of the ν_{Mo-O} frequency with increasing electron-withdrawing character of the substituent; ν_{Nb-O} and ν_{M-Cl} (M = Nb, Mo) are relatively insensitive to the effects of 4-substituents[320]. Linear plots were also obtained[320] when the electronic spectral bands of the Nb complexes were plotted vs. σ_{PyNO}. The Nb compounds are slightly paramagnetic[319] (μ_{eff} = 0.45–0.65 B.M.). Other Mo and W complexes reported are (cf. Table 12): $MoO_2Cl_2 \cdot 2PNO$ (ref. 322), $Mo(NO)_2Cl_2(PNO)_2$ (ref. 323), $[Mo(O_2)_2O](PNO)(OH_2)$, and $[M(O_2)_2O](4\text{-}PicNO)$ (M = Mo, W) (ref. 324). Re^{I} complexes of the type $Re(CO)_3(PNO)_2X$ (X = Cl, Br, I) are obtained by interaction[96] between PNO and $Re(CO)_5X$. 2-*n*-Nonylpyridine *N*-oxide has been utilized for the extraction of rhenium compounds from aqueous solutions[325]. $RuX_2(CO)_3(PNO)$ complexes (X = Br, I) were prepared[326] by reaction between $Ru(CO)_4X_2$ and PNO. Interaction between 2,6-LNO and Ru^{III}, Rh^{III} or Ir^{III} chlorides in acetone–ethanol leads to the immediate precipitation of crystalline products; the Ru and Rh complexes are of the types $[Ru(2,6\text{-}LNO)_3Cl_3]$ and $[Rh(2,6\text{-}LNO)_5Cl]Cl_2$, respectively; the Ir complex is very unstable and has not been characterized as yet[179].

(A)$PtCl_2$(L) (A = alkene, alkyne, styrene, vinyl ester or CO; L = *N*-oxide) complexes[19, 72–79, 267, 268, 327, 328] were reviewed in detail by Orchin and Schmidt[2] (see also Sects.

C(*i*), (*iii*) and (*vi*) of the present review and Table 12). The crystal structure determination of (CO)$PtCl_2$(4-MeOPNO) revealed that the $PtCCl_2O$ moiety is square planar and the *N*-oxide and carbonyl ligands are *trans* to one another[2,268]. The Pt—O—N angle is 120°, while the Pt—C—O grouping is almost linear[2,268] (178°). The Pt—O bond is essentially a sigma bond with very little, if any, back-bonding[2] (Pt—O bond length[268] 1.99 Å). ν_{Pt-O} is insensitive to the effects of substituents on the aromatic ring of the *N*-oxide[2,327]. Olefin—olefin exchange studies in Pt^{II}—olefin complexes[329], and their derivatives with pyridines[330] and pyridine *N*-oxides[72] have been reported[2]. Exchange between different *N*-oxides in (A)$PtCl_2$(*N*-oxide) complexes also occurs in solutions[76,331], e.g.

$$(4\text{-}NO_2PNO)PtCl_2(C_6H_5CH{=}CH_2) + PNO \rightleftharpoons (PNO)PtCl_2(C_6H_5CH{=}CH_2) + 4\text{-}NO_2PNO \quad (17)$$

Pyridine and pyridine *N*-oxide ligands may be displaced from complexes of the above type by various solvent molecules (e.g. acetone, chloroform, acetonitrile)[328,330,332]; the *trans*-labilizing ability of the unsaturated ligand decreases along the series[330,332] ethylene ≫ *trans*-2-butene > *cis*-2-butene > CO. It should be noted, however, that caution is generally recommended in the interpretation of any type of exchange reaction with Pt^{II} complexes[2]; in fact, complexes of the above types can be quite labile even in the absence of any added free ligand[330], while the possibility of ready oxidation of Pt^{2+} to Pt^{4+} introduces an additional complication[2]. Pd^{II} analogs of the above complexes are considerably less stable and difficult to isolate; however, a number of $(C_2H_4)PdCl_2$(*N*-oxide) complexes have been prepared[80] (Table 12). Other palladium and platinum *N*-oxide complexes reported are: $[Pd(4\text{-}EtOPNO)_2Cl_2]$ (ref. 142) and $[Pt(2,6\text{-}LNO)_3Cl_3]Cl$ (ref. 175).

$AgClO_4$ forms complexes of the type $AgClO_4 \cdot nL$ (n = 2 or 3) with *N*-oxides (PNO, 2, 3- and 4-PicNO, 2,6-LNO, 2-, 3- and 4-CNPNO, and 2-ethyl, 2-*n*-propyl- and 2-isopentylpyridine *N*-oxides[111,142,148,290]. The 2:1 complexes involve either a mono- or a binuclear (*N*-oxide-bridged) complex cation (vide supra)[148,290], while the 3:1 analogs were formulated as $[AgL_2](ClO_4)\cdot L$, on the basis of the occurrence of ν_{N-O} as a doublet (suggestive of the presence of two chemically inequivalent sets of ligands) and the tendency of Ag^I to exhibit linear two-fold coordination[290] (Table 12). In $Ag(2\text{-}CNPNO)_2(ClO_4)$ the ligand appears either to contain bridging *N*-oxide groups or to involve coordination of both the *N*-oxide oxygen and the nitrile group[148]. $AgNO_3 \cdot PNO$ (ref. 333) and $[Ag(PNO)]^+$-$[C(NO_2)_3]^-$ (ref. 334) complexes were also reported.

Cd^{II} and Hg^{II} perchlorates and tetrafluoroborates yield $[ML_6]^{2+}$ hexacoordinated cationic complexes with *N*-oxides[109,111,142,173,181]. $[Hg(PNO)_6]X_2$ ($X = PF_6$, AsF_6, SbF_6) have also been prepared[181]. Cd^{II} and Hg^{II} halides form complexes of the following types (L = *N*-oxide); X = Cl, Br, I): $[CdLX_2]_2$, $CdLX_2(OH_2)$, CdL_2I_2, $Cd_3L_2Cl_6$, $Cd_4L_2Cl_8$ (refs. 180, 297, 311, 335) and $[HgLX_2]_2$ (refs. 173, 180, 181, 195, 197, 269, 311, 336) (Table 12). Although the possibility of *N*-oxide bridging in the binuclear 1:1 complexes was discussed[181], the overall spectroscopic evidence is in favor of halogen-bridged structures. Crystal structure determinations of $[HgLCl_2]$ complexes (L = 3,5-Br_2PNO, QNO) established that these compounds are chlorine-bridged[270,337]. Other Cd^{II} complexes reported are: $[CdL(NCS)_2]_n$ (L = PNO, 2-, 3- and 4-PicNO, 2,6-LNO), $[Cd(4\text{-}CNPNO)_2(NCS)_2]_n$, involving bridging thiocyanato ligands[199], and $[Cd(2,6\text{-}LNO)_4(ONO_2)_2]$, with monodentate nitrato ligands[159]. $[Hg(PNO)_2X_2]$ complexes ($X = NO_3$,

CF_3COO, CCl_3COO) involve coordinated polyanions, acting, most probably, as bidentate ligands; hence, Hg^{II} is probably hexacoordinated in these compounds[181]. Analogous compounds with X = CN, CF_3, C_2F_5, $CF_3 \cdot CHF$, $CF_3 \cdot CH_2$, C_6H_5, *o*-, *m*- and *p*-$CF_3 \cdot C_6H_4$ are probably tetrahedral[181,338,339]. Fluoro-alkyl and fluoro-aryl mercurials may form 1:1, 1:2 and 1:3 complexes[338,339] with PNO. [$HgL(SCN)_2$] complexes (L = PNO, 2,6-LNO) appear to be binuclear, *N*-oxide-bridged, with S-bonded terminal thiocyanato ligands[159,181]. For Hg^I the complexes $Hg_2(PNO)_4(ClO_4)_2$ and $Hg_2SiF_6 \cdot 5PNO$ were reported[291].

(c) Complexes with lanthanide and actinide ions

Y^{III} and Ln^{III} perchlorates form complexes[113,340] of the type $[ML_8](ClO_4)_3$ with PNO. The complex cations are square antiprismatic[279,281,340]; comparisons with analogous complexes of other ligands show that the stability order of $[LnL_8]^{3+}$ decreases along the series antipyrine > DMSO > PNO > *N,N*-dimethylformamide[340]. 4-PicNO also forms $[LnL_8]^{3+}$ complexes (Ln = Pr, Nd, Sm, Eu, Gd, Dy)[341]; hydrated complexes of the types $[Sm(4\text{-}PicNO)_7(OH_2)]^{3+}$, $[Eu(4\text{-}PicNO)_6(OH_2)_2]^{3+}$ and $[Er(4\text{-}PicNO)_7(OH_2)]^{3+}$ were also isolated[341]. QNO forms 7:1 cationic complexes with Y^{III} and Ln^{III} ions (Ln = La to Yb); a series of $[M(QNO)_7][Cr(NCS)_6]$ complexes with these metal ions has been prepared[342]. $[M(PNO)_4(NO_3)]X_2$ (X = NO_3, ClO_4, $B(C_6H_5)_4$) with Y^{III} and Ln^{III} ions most probably involve hexacoordinated complex cations with coordinated bidentate nitrate[343]. $LnCl_3$ salts form the following complexes[344] with QNO: $Ln(QNO)_3Cl_3 \cdot H_2O$ (M = Nd, Sm) and $Ln(QNO)_4Cl_3 \cdot H_2O$ (Ln = Eu, Gd, Tb, Dy, Ho, Yb). The 3:1 complexes are more thermally stable than the 4:1 complexes. The latter compounds lose two molecules of HCl at 50–100°C, forming complexes of the corresponding Ln oxychlorides[344] ($LnOCl(QNO)_4$). Eu^{III} complexes of the above types, as well as adducts of *N*-oxides with Eu^{III} β-ketoenolato complexes are fluorescent[276–281] (vide supra; Sect. C(*vi*)).

Th^{IV} and UO_2^{2+} perchlorates form the following complexes[116,121]: $Th(PNO)_8(ClO_4)_4$, $Th(QNO)_6(ClO_4)_4$ and $UO_2(PNO)_5(ClO_4)_2$. The shifts of the antisymmetric stretching frequency of the UO_2^{2+} ionic group, occurring upon interaction of equimolar amounts of uranyl compounds and a number of neutral or ionic ligands are as follows[345] (in cm^{-1}): bidentate oxalate, 65; bidentate sulfate, 63; bidentate nitrate, 37; pyridine, 34; antipyrine, 29; PNO, 29; bidentate perchlorate, 29; *N,N*-dimethylformamide, 27: tri-*n*-butylphosphate, 25; monodentate perchlorate, 22; di-*n*-butyl ether, 21; camphor, 19; H_2O, 19; CH_3CN, 16; nitromethane, 11. The trend observed in the case of the above shifts is that a ligand with a given $\Delta\nu_{UO_2}$ (*as*) shift will generally replace all ligands inducing lower $\Delta\nu_{UO_2}$ (*as*) shifts[345]. Th^{IV} chloride and nitrate complexes reported are: $ThCl_4 \cdot 2(2,6\text{-}LNO)$ (ref. 175), $ThCl_4 \cdot 2QNO \cdot 2H_2O$ and $Th(OH)_2(NO_3)_2 \cdot 2QNO$ (ref. 298). $UO_2(NO_3)_2$ forms 1:2 complexes with a variety of aromatic *N*-oxides[298,346]. Th^{IV} and uranyl nitrates can be precipitated from aqueous solutions in the form of their *N*-oxide (e.g. 3-*tert*.-butyl-2,4,6-trimethylpyridine *N*-oxide) complexes[347]. UO_2Cl_2 yields complexes[200,210,298,346] of various stoichiometries with *N*-oxides, i.e. $UO_2Cl_2 \cdot 2L$ (L = PNO, 2- and 4-PicNO, 4-MeOPNO, 4-NO_2PNO, QNO), $UO_2Cl_2 \cdot 3PNO$, $UO_2Cl_2 \cdot 4(4\text{-}ClPNO)$. 2:1 *N*-oxide complexes with UO_2Br_2 and UO_2SO_4 have also been reported[298,346]. UO_2^{2+} β-ketoenolato complexes of the type $UO_2(L)_2$ (L = bidentate β-ketoenolato ligand) form 1:1 adducts with PNO and 4-substituted derivatives[209]. Quite recently, adducts of bis-(dithiolato)UO_2

complexes with PNO and other neutral ligands were reported[348]. Finally, conductivity measurements of $UO_2Cl_2 \cdot 2L$ (L = QNO, IQNO) in methanol are considerably higher than those observed for anhydrous UO_2Cl_2 or $UO_2Cl_2 \cdot H_2O$ in the same medium[349]. The higher degree of dissociation in the *N*-oxide complexes has been attributed to weaker U–Cl bonds, resulting from the presence of the large QNO or IQNO molecules in the first coordination sphere of the U^{VI} ion[349].

(d) Complexes with compounds of other elements

The following PNO complexes have been reported[47,48,111] for the perchlorates of metal ions belonging to Groups IA, IIA and IIIA of the Periodic Table: $M(PNO)_4ClO_4$ (M = Li, Na), $M(PNO)_6(ClO_4)_2$ (M = Mg, Ca, Sr), $Ba(PNO)_4(ClO_4)_2$, $Al(PNO)_6(ClO_4)_3$, $Tl(PNO)_8(ClO_4)_3$. $NaI \cdot 2(2\text{-PicNO})$ (vide supra; structure VI) has also been reported[56]. 4-EtOPNO forms a 4:1 complex[142] with $Ca(ClO_4)_2$; $Mg(NCS)_2 \cdot 2(2,6\text{-LNO})$ has been formulated as $[(2,6\text{-LNO})(SCN)_2Mg(2,6\text{-LNO})_2Mg(NCS)_2(2,6\text{-LNO})]$, i.e. dimeric, *N*-oxide-bridged, involving *N*-bonded isothiocyanato groups[159]. B^{III} compounds generally form complexes of the type $BX_3 \cdot L$ (X = H, F, Cl; L = PNO, 4-PicNO, QNO)[7,350]. It is noteworthy that ν_{N-O} shifts of 18–44 cm^{-1} were observed[350] in PNO complexes of this type, whereas with the corresponding 4-PicNO compounds the shifts of this band were 111–117 cm^{-1}. A number of cationic complexes of the type $[(CH_3)_3NBH_2(L)]^+ PF_6^-$ (L = PNO and other neutral oxygen ligands) were also reported[351]. Indium trichloride forms a complex[352] of the type $In(PNO)_3Cl_3$. Examples of *N*-oxide reactions with Grignard reagents (e.g. refs. 20, 95, 353) and lithium insertion at the aromatic ring positions, via an *N*-oxide-Bu^nLi adduct intermediate[98], have already been discussed in Sect. C(*i*).

Si^{IV} halides form 1:4 complexes[354] with PNO, i.e. $SiX_4 \cdot 4PNO$ (X = Cl, Br). $SnX_2 \cdot PNO$ (X = Cl, Br) and $SnCl_2 \cdot 2PNO$ adducts have been reported[182,183,272]. For the former complex a monomeric structure[183], involving tricoordinated Sn^{II}, and a binuclear, chlorine-bridged structure[182] have been proposed by different groups. The splitting of ν_{N-O} in $SnCl_2 \cdot 2PNO$ may suggest that one PNO group is outside the coordination sphere, but does not preclude a tetracoordinated system[183,272]. *N*-Oxide complexes with Sn^{IV} halides[16,176,203,204,355,356] and organo-Sn^{IV} and -Pb^{IV} salts[131,201,212,266,273,357] have been studied to some extent (Table 13); SnX_4 (X = F, Cl, Br, I) forms 1:2 adducts with aromatic amine *N*-oxides[16,176,203,204,355,356] (vide supra, Sects. C(*iii*), (*vi*)). $R_3MX \cdot L$ complexes (R = alkyl, aryl; X = Cl, Br, –NCS; M = Sn, Pb; L = *N*-oxide) are trigonal bipyramidal with planar R_3M moieties[201,266,357]. $(C_6H_5)_3SnCl$ complexes with pyridine and quinoline *N*-oxides have fungicidal, bactericidal and molluskicidal properties and low phytotoxicity[358,359]. $R_2SnX_2 \cdot 2L$ complexes[131,201,212,266,273,357] involve two *N*-oxide ligands *trans* to one another[131,273,357] (see also Sects. C(*iii*), (*vi*) and structure XI), and are hexacoordinated; in the case of 2,4,6-CNO a pentacoordinated adduct of the type $(CH_3)_2SnCl_2 \cdot L$ is stabilized; formation of the 1:2 adduct in this case is sterically hindered[201]. A series of 4-substituted pyridine *N*-oxides with R_3M substituents (R = CH_3 or C_2H_5; M = C, Si, Ge, Sn) was recently prepared[360,361]. $Pb(PNO)_3(ClO_4)_2$ was also reported[111]. QNO and its derivatives react with $Pb(CH_3COO)_4$, forming *N*-acetoxycarbostyril, which is subsequently converted to *N*-hydroxycarbostyril, either on standing or by hydrolysis[362,363].

TABLE 13

Tin and lead complexes with aromatic amine *N*-oxides[a]

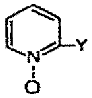
Complex	Ref.
$Sn(PNO)Cl_2$	182, 183
$Sn(PNO)_2Cl_2$	183
$Sn(PNO)(NCS)_2$	272
$Sn(PNO)_2F_4$	204
$Sn(PNO)_2Cl_4$	176
$Sn(PNO)_2Br_4$	176
$Sn(PNO)_2I_4$	176
$[Pb(PNO)_3](ClO_4)_2$	111
$(CH_3)SnBr_3 \cdot 2PNO$	176
$(CH_3)_2SnCl_2 \cdot 2PNO$	176
	201, 212
$(CH_3)_2SnCl_2 \cdot (2,4,6\text{-CNO})$	201
$(CH_3)_3SnCl \cdot PNO$	176
$(CH_3)_3PbCl \cdot PNO$	201

[a] Representative examples

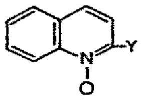
$SbCl_5$ forms a 1 1 adduct[364] with PNO, while $PCl_3 \cdot PNO$ (ref. 84) and $PCl_5 \cdot PNO$ (ref 92) adducts were proposed as intermediates of reactions between PCl_3 or PCl_5 and PNO (vide supra, Sect. C(*i*)) Adducts of the types $SO_3 \cdot L$ (ref 6), $TeCl_4 \cdot L$ (ref 174) and $TeCl_4 \cdot 2L$ with aromatic *N*-oxides have been reported. Phenol, alcohol and halogen adducts of *N*-oxides were discussed in Sect B(*iii*) Inorganic and organic acids form 1 1 and 1 2 adducts with *N*-oxides, for which structures IV and V respectively were proposed[56–58] (Sect B(*iii*)) Examples of *N*-oxide (L) adducts of these types are $[HL]X$ (X = Cl, Br, $SbCl_6$) (refs 5, 56, 365, 366), $[HL_2]X$ (X = Cl, Br, I (refs 56, 57), $SbCl_6$, SbF_6, PF_6, AsF_6 (refs 57, 58), BF_4 (ref 57), ClO_4 (refs 57, 367), $p\text{-}CH_3C_6H_4SO_3$ (ref 57), $AuCl_4$, $AuBr_4$ (refs. 368, 369)), $[LH]_2[Mo_2O_{11}]$ H_2O (ref 370) and $CCl_nH_{3-n}COOH$ L (n = 1–3)[371,372]. The crystal structure determination of $CCl_3COOH \cdot PNO$ revealed a rather short distance (2.41 Å) between the N–O oxygen atom and one of the carboxy oxygens[286]. Finally, kaolinite ($Al_4(Si_4O_{10})(OH)_8$) forms a PNO adduct, involving H-bonding from the hydroxyl hydrogens to the N–O oxygen[373]

D METAL COMPLEXES OF AROMATIC AMINE *N*-OXIDE AND DIAMINE *N,N*-DIOXIDE CHELATING AGENTS

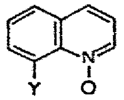
2-Substituted pyridine *N*-oxides and 2- or 8-substituted quinoline *N*-oxides (XII, XIII, XIV, respectively), involving substituents that can serve as donor sites, may act either as monodentate neutral ligands (e.g Y = NH_2, CN), coordinating through the N–O oxygen, or as neutral (e g Y = CN) or anionic (Y = O^-, S^-, COO^-, NH^-, etc) bidentate chelating agents Other *N*-oxide and *N,N*-dioxide chelating agents, reportedly forming metal complexes (vide infra) are 1,10-phenanthroline *N*-oxide, XV, 2,2'-bipyridine *N,N*-dioxide, XVI, 1,10-phenanthroline *N,N*-dioxide, XVII, and 2,3-di(2-pyridine *N*-oxide) quinoxa-



XII



XIII



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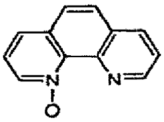

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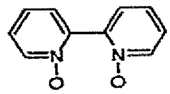

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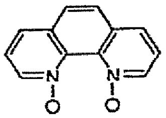
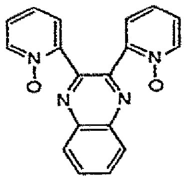


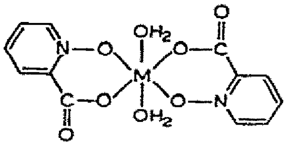
XVII



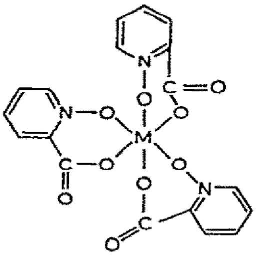
XVIII

line, XVIII. In contrast to the metal complexes of monodentate *N*-oxides, many of the metal chelates of these ligands can be isolated from aqueous solution

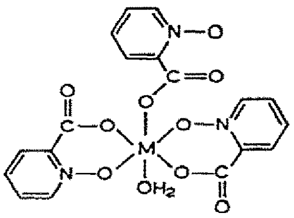
Picolinic acid *N*-oxide (PicANO-H, Y = COOH in XII) forms complexes with a variety of metal ions[213, 215, 374–379] (Table 14, see also Table 6 and Sect. C(*iv*)) Complexes[215] of the type $M(PicANO)_2 \cdot 2H_2O$ (M = Mg, Mn, Fe, Co, Ni, Cu) are bis-chelates, XIX; $M(PicANO)_3$ (M = Mn, Fe) are either monomeric tris-chelates, XX, or polymers based upon the anhydrous form of structure XXI, which was proposed[215] for $M(PicANO)_3 \cdot H_2O$ (M = Cr, Co).



XIX



XX



XXI

Other complexes reported by Lever et al. are. $Cu(PicANO)_2$ (monomeric, square planar chelate), $Zn(PicANO)_2 \cdot \frac{1}{2} H_2O$ (tetrahedral or pentacoordinated), $Ca(PicANO)_2$(probably polynuclear), $Fe(PicANO)_3(PicANO\text{-}H)$ (μ_{eff} = 5 98 B.M), $Fe(PicANO)_2OMe$ (μ_{eff} = 5 09 B M.), $HFe(PicANO)_4$, during oxidation of Fe^{II}, Co^{II} and Ni^{II}–PicANO complexes by chlorine or bromine, compounds of the types $FeCl_2(PicANO)$, $CoCl(PicANO)$, $Co(OOCCH_3)(PicANO)Br$ (μ_{eff} = 4.99 B M.), and $Ni(OOCCH_3)(PicANO)Br$ (μ_{eff} = 3 90 B.M) were isolated[215] Recently, the magnetic properties of $Fe(PicANO)_2 \cdot 2H_2O$ in the 80–300°K region were reported[378]. The patterns of the variation in stability constants with increasing atomic number led to the conclusion that PicANO acts as a bidentate ligand in its Ln^{III} (La to Lu) complexes[375]. However, the ratios of stepwise stability constants for the same complexes were suggestive of coordination of PicANO as a monodentate ligand[376]. A series of X_2BL (X = C_6H_5 or F, L = PicANO, 2-carboxyquinoline *N*-oxide, 2-OMePNO, 8-OQNO) complexes involve chelation of the ligand; 8-ethoxy-carbonylaminoquinoline *N*-oxide (LH) forms the $(C_6H_5)_2BL$ chelate, but its interaction with BF_3 leads to the formation of the adduct $BF_3 \cdot LH$, in which the ligand is neutral, coordinating

TABLE 14

Some metal chelates of aromatic amine *N*-oxides and *N*, *N* dioxides

Compound	μ_{eff} (B.M.)	ν_{N-O} (cm^{-1})	Other IR bands of interest (cm^{-1})	Ref.
PicANOH		1290, 1259	1626, 1393 (ν_{COO})	215
Ca(PicANO)$_2$		1280, 1238	1634, 1376 (ν_{COO})	215
Mg(PicANO)$_2$ · 2H$_2$O		1277, 1232	1634, 1387 (ν_{COO})	215
Mn(PicANO)$_2$ · 2H$_2$O	5.98	1282	1626, 1383 (ν_{COO})	215
Fe(PicANO)$_2$ · 2H$_2$O	5.36	1276, 1229	1615, 1379 (ν_{COO})	215
Co(PicANO)$_2$ · 2H$_2$O	4.90	1277, 1230	1623, 1385 (ν_{COO})	215
Ni(PicANO)$_2$ · 2H$_2$O	3.23	1272, 1232	1616, 1389 (ν_{COO})	215
Cu(PicANO)$_2$ · 2H$_2$O	1.88	1282, 1238	1634, 1380 (ν_{COO})	215
Zn(PicANO)$_2$ · 1½H$_2$O		1276	1618, 1381 (ν_{COO})	215
Cu(PicANO)$_2$	1.87	1259, 1230	1650, 1344 (ν_{COO})	215
Be(PicANO)$_2$		1261, 1247	1658, 1335 (ν_{COO})	215
Cr(PicANO)$_3$ · H$_2$O	3.77	1279^a, 1267, 1241, 1232	1647, 1336 (ν_{COO})	215
Mn(PicANO)$_3$	5.00	1276sh, 1266, 1241	1639, 1330 (ν_{COO})	215
Co(PicANO)$_3$ · H$_2$O	0	1277sh^a, 1267, 1245	1639, 1357, 1340 (ν_{COO})	215
Fe(PicANO)$_3$	5.88	1271, 1261, 1238	1634, 1333 (ν_{COO})	215
PTHNO		1115, 1090 or ~ 1248^b	1142 ($\nu_{C=S}$)	274, 386
Cr(PTNO)$_3$ · 1½H$_2$O	3.72	1080	1155, 1130 ($\nu_{C=S}$)	386
Mn(PTNO)$_2$ · H$_2$O	5.72	1080	1150 ($\nu_{C=S}$)	386
Fe(PTNO)$_3$	5.88–6.18	1075	1160, 1135 ($\nu_{C=S}$)	386
Co(PTNO)$_3$ · 2H$_2$O	0.40	1080	1150, 1120 ($\nu_{C=S}$)	386
Ni(PTNO)$_2$	0.34	1080	1150, 1135 ($\nu_{C=S}$)	386
Cu(PTNO)$_2$	1.68	1080	1155, 1140 ($\nu_{C=S}$)	386
Zn(PTNO)$_2$		1080	1140 ($\nu_{C=S}$)	386
Cd(PTNO)$_2$		1085	1150 ($\nu_{C=S}$)	386
Hg(PTNO)$_2$		1080	1140 ($\nu_{C=S}$)	386
Zr(PTNO)$_4$ · H$_2$O		1085	1150, 1125 ($\nu_{C=S}$)	386
Sn(PTNO)$_4$		1200	355 (ν_{Sn-O})	274
(C$_4$H$_9$)$_2$Sn(PTNO)$_2$		1205, 1195	340 (ν_{Sn-O})	274
(C$_6$H$_5$)$_2$Sn(PTNO)$_2$		1195	356 (ν_{Sn-O})	274

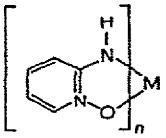
TABLE 14 (continued)

Compound	μ_{eff} (B M)	ν_{N-O} (cm^{-1})	Other IR bands of interest (cm^{-1})	Ref
$SnF_2(PTNO)_2$		1190	410, 387 (ν_{Sn-O})	274
$SnCl_2(PTNO)_2$		1186	402, 382 (ν_{Sn-O})	274
$SnBr_2(PTNO)_2$		1186	397, 373 (ν_{Sn-O})	274
$SnI_2(PTNO)_2$		1186	387, 371 (ν_{Sn-O})	274
$(C_6H_5)_2Sn(NCS)(PTNO)$		1205	390 (ν_{Sn-O})	274
$BiPO_2$		1262, 1255		407
$Sc(BiPO_2)_3(ClO_4)_3$		1225, 1210		120
$VO(BiPO_2)_2(ClO_4)_2$	1 64	1264, 1246	430 (ν_{M-O})	409
$Cr(BiPO_2)_3(ClO_4)_3 \cdot 2H_2O$	*c*	1215, 1210, 1199	434, 420 (ν_{M-O})	407
$Cr(BiPO_2)_3(NO_3)_3$	3.70	*c*		406, 407
$Mn(BiPO_2)_3(ClO_4)_3 \cdot 2H_2O$	4 97	*c*		405
$Mn(BiPO_2)_3(PtCl_4)$	6 34	1235, 1225, 1210	357 (ν_{M-O})	407
$Fe(BiPO_2)_3(ClO_4)_3 \cdot 3H_2O$	6 13	1225, 1213, 1200	408, 377 (ν_{M-O})	406, 407
$Co(BiPO_2)_3(ClO_4)_2 \cdot 2H_2O$	4 72	1220, 1202	362 (ν_{M-O})	406, 407
$Ni(BiPO_2)_3(ClO_4)_2 \cdot 2H_2O$	3 24	1220, 1209	370, 351 (ν_{M-O})	406, 407
$Cu(BiPO_2)_3(ClO_4)_2 \cdot 2H_2O$	2.10	1250, 1235, 1210	392 (ν_{M-O})	406, 407
$Zn(BiPO_2)_3(ClO_4)_2 \cdot 2H_2O$		1230, 1211	355, 340 (ν_{M-O})	406, 407
$Cd(BiPO_2)_3(ClO_4)_2 \cdot H_2O$		1230, 1211	348, 332 (ν_{M-O})	406, 407
$Y(BiPO_2)_4(ClO_4)_3$		1252, 1232, 1209	338 (ν_{M-O})	410
$Ln(BiPO_2)_4(ClO_4)_3$ (Ln = La–Yb)	*c*	1264–1249, 1238–1228, 1215–1204	345–332 (ν_{M-O})	410
$Ce(BiPO_2)_3(NO_3)_2(ClO_4)_2$		1260, 1239, 1210	355 (ν_{M-O})	411
$Th(BiPO_2)_4(ClO_4)_4$		1267, 1232	355 (ν_{M-O})	409
$UO_2(BiPO_2)_2(ClO_4)_2$		1260, 1218	361 (ν_{M-O})	409
$ZrO(BiPO_2)_3(ClO_4)_2 \cdot 2H_2O$		1261, 1225	388 (ν_{M-O})	409
$Mo_2O_4(BiPO_2)_2Cl_2 \cdot 2H_2O$	1 23	1264, 1256	394 (ν_{M-O})	409
$Mo_2O_3(BiPO_2)_4Cl_2 \cdot 2H_2O$	1 48	1261, 1230	404 (ν_{M-O})	409
$Mo(NO)_2(BiPO_2)Cl_2$	*c*	1215, 1199		323
$Re(CO)_3(BiPO_2)X$ (X = Cl, Br, I)	*c*	1206–1203, 1200–1196		96

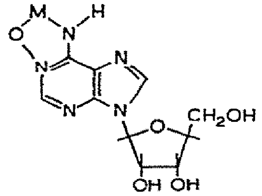
[a] Non-bonded N–O group [b] The ν_{N-O} of 1-hydroxypyridine-2-thione occurs at 1115, 1090 cm^{-1} (ref 383). Robinson has based his ν_{N-O} assignments on the shifts of these bands[386] The ν_{N-O} of the 2-pyridinethiol *N*-oxide tautomer has not been reported, Petridis et al , made ν_{N-O} assignments, by assuming that the ν_{N-O} of the thiol tautomer is close to that of 2-benzylthiopyridine *N*-oxide[274] which occurs at 1248 cm^{-1} (A.R. Katritzky and A.R. Hands, *J. Chem. Soc. London* (1958) 2105) [c] Not reported.

through the N–O oxygen[379a]. Other PicANO complexes reported are[374]. Be(PicANO)$_2$, MO$_2$(PicANO)$_2$·2H$_2$O (M = U, Pu), Zr(PicANO)(OH)$_3$ The 1 2 metal-to-ligand ratio in the UO$_2^{2+}$ complex was also determined by physicochemical studies[377].

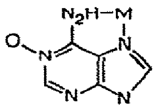
2-Aminopyridine *N*-oxide (LH) metal complexes of the type [M(LH)$_6$](ClO$_4$)$_2$ (M = Mn, Fe, Co, Ni, Zn, Mg) and [M(LH)$_4$](ClO$_4$)$_2$ (M = Cu, Ba), involving monodentate neutral ligands, coordinated through the N–O oxygen, were isolated during interaction of ligand and salt in methanol[380]. In highly alkaline aqueous media, the same ligand loses one proton, forming an anion, which can coordinate as a bidentate ligand to Cu^{II} and Fe^{III} (XXII), with other 3*d* metal ions hydrolysis occurs more easily than formation of metal chelates of the type shown in XXII[380].



XXII



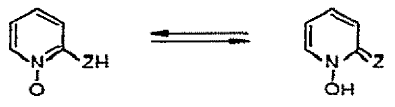
XXIII



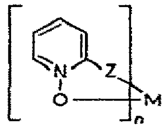
XXIV

Adenosine *N*-oxide behaves in a similar manner, forming 1.1 chelates, XXIII, with divalent 3*d* metal ions (M = Mn to Zn) in alkaline media[381a] However, adenine *N*-oxide forms chelates with the same metal ions, involving coordination of the nitrogen of the amino group and one nitrogen of the imidazole ring (in position 7) (XXIV), the N–O oxygen is not coordinated in the latter complexes[381] Adenosine-5′-monophosphate-*N*(1)-oxide forms Cu^{II} complexes involving coordination of the N–O oxygen, with other M^{II} ions (Mg, Ca, Ba, Mn, Co, Ni, Zn), coordination through this oxygen occurs, in solution, at high pH, while at neutral or weakly acid pH this ligand coordinates exclusively through the phosphate group to the above metal ions[382a]. Similar studies with inosine-*N*(1)-oxide and its 5′-monophosphate derivative established that the latter ligand coordinates mainly through the N–O oxygen to divalent 3*d* metal ions, whereas in the case of alkaline earth metal ions, an equilibrium between NO- and phosphato-bonded species exists in solution[382b]

2-Hydroxypyridine *N*-oxide (2-HOPNO) and 2-pyridinethiol *N*-oxide (PTNO-H) (XXV, Z = O, S) exist predominantly in their tautomeric forms of 1-hydroxypyrid-2-one and 1-hydroxypyridine-2-thione (XXVI, Z = O, S), respectively[383] (the 2-aminopyridine *N*-oxide exists predominantly in the *N*-oxide rather than the 1-hydroxypyridone-2-imine form[383])



XXV XXVI

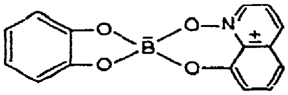


XXVII

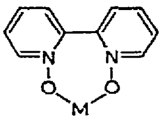
Both 2-HOPNO and PTNO-H (omadine) reportedly form metal chelates of type XXVII[271, 274, 275, 384–391](Table 14) Chelates of this type exhibit negative ν_{N-O} shifts[274, 386],

$\nu_{C=S}$ in M(PTNO)$_n$ complexes did not diminish in intensity or approximate position, as would be expected, although, in certain cases, the absorption was split into two bands[386]. 2-OPNO (L) chelates of the types $[SiL_3]X$ (X = Cl, $FeCl_4$), $[SiL_3]_2[SnCl_6]$, $[AlL_3]$, $[FeL_3]$ and $[SnL_3]_2[SnCl_6]$ have been reported[384,391] The Si^{IV} complexes involve an octahedral complex cation[384], which was partially resolved into its optical enantiomers by treatment with disodium (–)-dibenzoyl-L-tartrate[391]. Zn^{II} complexes of this ligand may be used as antifungal agents[392]. An early paper[389] reported the preparation of various 2-pyridine-thiolate *N*-oxide M(PTNO)$_n$ complexes (M = Na^{I}, Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Ag^{I}, Au^{III}, Zn^{II}, Cd^{II}, Hg^{I}, Hg^{II}, Pb^{II}, Sb^{III}, As^{III}, Bi^{III}) Polarographic studies of some of these complexes[388] and determination of formation constants of divalent 3*d* metal ion chelates with 2-OPNO and PTNO[385] were later reported The following PTNO(L) metal chelates have been isolated and characterized $CrL_3 \cdot 1.5H_2O$, NaL, KL, $MnL_2 \cdot H_2O$, FeL_3, $CoL_3 \cdot 2H_2O$, NiL_2, CuL_2, ZnL_2, CdL_2, $ZrL_4 \cdot H_2O$, HgL_2 (ref. 386), R_2SnL (R = *n*-C_4H_9, C_6H_5), SnX_2L (X = F, Cl, Br, I), SnL_4, $(C_6H_5)_2Sn(NCS)L$ (ref 274). $RSnClL_2$ (R = *n*-C_4H_9, C_6H_5) (ref 275) Mossbauer studies of FeL_3 (ref 271) and the Sn^{IV} complexes[274, 275] have already been mentioned (Sect. C(*vi*)). NiL_2 (μ_{eff} = 0 34 B M.) and CuL_2 are square planar, $MnL_2 \cdot H_2O$ is tetrahedral (μ_{eff} = 5.72 B M , yellow-green color) and the Cr^{III}, Fe^{III} and Co^{III} chelates are octahedral, a *Dq* value of 1884 cm^{-1} was derived from the electronic spectrum of $CoL_3 \cdot 2H_2O$(μ_{eff} = 0.40 B M.)[386]. PTNHO[387] and 4-methylpyridine-2-thiol *N*-oxide[390] have been used for the analytical determination of Fe^{III} The Fe^{III} chelates with both these ligands can be used for the selective differential absorptiometric determination[390] of Hg^{II}. M(PTNO)$_n$ complexes have found application as components of fungicides and bactericides and as repellents, reducing deer-browsing[393] The Na^{I} and Zn^{II} complexes of 2-quinolinethiol *N*-oxide are used in anti-dandruff shampoos[394]. Co^{II}, Ni^{II}, Cu^{II} and Cd^{II} chelates of 1-hydroxypyrazole-2-oxide[395a] and Cu^{II} complexes o[illegible]oxazoline oxide derivatives[395b] have also been reported

8-Quinolinol *N*-oxide (oxine *N*-oxide) and substituted derivatives have been extensively used for the extraction and analytical determination of various metal ions (e g Mn^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Ln^{3+}, Ru^{3+}, Ir^{4+}, Ce^{4+}, U^{6+})[396–400] The stability constants of 8-quinolinol *N*-oxide complexes are generally smaller than those of the corresponding 8-quinolinol complexes[400] Spectrophotometric, stability constant and other investigations of metal complexes of 8-quinolinol *N*-oxide (LH) and substituted derivatives (e g 5,7-dichloro-8-quinolinol *N*-oxide (L'H)) of various types (i.e NiL'_2, CuL_2, PdL_2 $[MLCl_4]^{(5-n)-}$ (M = Ru^{III}, Rh^{III}, Os^{IV}, Ir^{IV}, Pt^{IV}, *n* = 3 or 4), etc.), led to the assignment of structures invariably involving chelating L or L' ligands to these compounds[396, 399, 400–402]. Although many metal ions can be precipitated with 8-quinolinol *N*-oxide (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ce^{4+}, UO_2^{2+}, Tl^{+}, etc)[398], the only 3*d* metal complex obtained in crystalline form and characterized is $VO(8\text{-}OQNO)_2$ (μ_{eff} = 1 77 B.M)[403]. Reaction of 8-quinolinol *N*-oxide and 2-*n*-butoxy-1,3,2-dioxaborole in CH_2Cl_2 results in the precipitation of the tetraoxa-azaspiroborate, XXVIII[404].



XXVIII



XXIX

1-Hydroxyphenazine-*N*,*N*-dioxide reportedly behaves in a similar manner to 8-quinolinol *N*-oxide, forming Cu^{II} chelates by coordination of one of the NO oxygens and the oxygen of the hydroxyl group[401b].

2,2′-Bipyridine *N*,*N*-dioxide (XVI, $BiPO_2$) acts as a neutral bidentate ligand, forming metal complexes involving seven-membered chelate rings XXIX[96,120,222,320,323,405–413] (Table 14). Metal complexes of the general types $[M(BiPO_2)_3]X_n$ ($M = Al^{3+}, Sc^{3+}, Cr^{3+}, Mn^{2+}, Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}$, X = Br, I, ClO_4, NO_3, S_2O_8, $PtCl_4$, $n = 0.5$–3)[120,405–408], $[M(BiPO_2)_2]X_n$ ($M = Co^{2+}$, X = Cl, Cu^{2+}, X = $PtCl_4$, Ag^+, Pb^{2+}, X = ClO_4)[406–408] are generally characterized by bidentate $BiPO_2$ ligands. ν_{M-O} values are in agreement with the Irving–Williams series, i.e. they vary in the following order[407] for 3*d* metal ions $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. Stereochemical considerations and infrared studies suggest that the seven-membered chelate rings involve a staggered (*gauche*) configuration of the pyridine rings[406,407]. NMR data for $[M(BiPO_2)_3][PF_6]_2$ (M = Co, Ni) complexes (contact and dipolar shifts and the corresponding geometrical factors) were best interpreted[413] by assuming a 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 $BiPO_2$ ligand, involving an angle of 67° between the planes of the two aromatic rings and a M–O–N angle of 115°. Two out of eight possible optical isomers appear to be present in appreciable amounts in the $[M(BiPO_2)_3]^{2+}$ (M = Co, Ni) cationic complexes, these are the Δ*ddd* (≡Λ*lll*) and the Δ*lll* (≡Λ*ddd*) isomers[413]. Other $BiPO_2$ chelates with transition metal ions reported are $VCl_4 \cdot L$ (L = $BiPO_2$, 1,10-phenanthroline *N*,*N*-dioxide, XVII, $\mu_{eff} = 1.50$ and 1.60 B.M., respectively)[222], $[VO(BiPO_2)_2](ClO_4)_2$ ($\mu_{eff} = 1.63$ B.M.), $[ZrO(BiPO_2)_3](ClO_4)_2$ (ref. 409), $[(Nb_6Cl_{12})Cl_2(BiPO_2)_2]$ (ref. 320), $[Mo_2O_4Cl_2(BiPO_2)_2] \cdot 2H_2O$, $[Mo_2O_3Cl(BiPO_2)_2] \cdot 2H_2O$ ($\mu_{eff} =$ 1.23 and 1.48 B.M., respectively)[409], $Mo(NO)_2(BiPO_2)Cl_2$ (ref. 323) and $Re(CO)_3(BiPO_2)X$ (X = Cl, Br, I)[96]. Y^{III} and Ln^{III} form chelates of the type $[M(BiPO_2)_4](ClO_4)_3$ (M = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) (refs. 410, 411). The Eu^{III} and Tb^{III} complexes of this type are fluorescent, and their fluorescence spectra in solution were reported[411]. IR and conductance data[410] indicate that the metal–ligand bond is weaker in the lanthanide than in the corresponding transition metal chelates with $BiPO_2$. A Ce^{IV} complex of the type $[Ce(BiPO_2)_3(NO_3)_2](ClO_4)_2$ was recently prepared[411]. Chelates of the actinide ions with $BiPO_2$ have also been reported, viz. $[Th(BiPO_2)_4](ClO_4)_4$, $[UO_2(BiPO_2)_2](ClO_4)_2$ (ref. 409), $UO_2(NO_3)_2(BiPO_2)$, and $PuO_2Cl_2(BiPO_2 \cdot HCl)_2$ (ref. 412). Finally, $BiPO_2$ forms 1:1 adducts with the following inorganic acids: $HClO_4$, $DClO_4$, HCl, HBr, $HSbCl_6$ (ref. 414). Other *N*,*N*-dioxides, reportedly forming metal complexes, are 4,4′-dinitro (or dihydroxy)-glycosine-3,3′-dioxide and indigo-3,3′-dioxide (2,2′-dibenzdimidazyl-3,3′-dioxide)[415]. 2,2′-Bipyridine-*N*-oxide complexes have not been reported, but a series of $ML_2Cl_2 \cdot nH_2O$ (M = Co, Ni, Cu, n = 0, 0.5 and 2, respectively) with 1,10-phenanthroline *N*-oxide, XV, were prepared[416]. These complexes are dissociated in water to regenerate the *N*-oxide and the hydrated metal ion[416], no characterization studies were reported for these compounds.

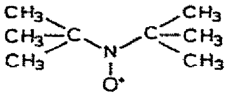
Quite recently, a number of Co^{II}, Ni^{II} and Cu^{II} halide complexes with the ligand 2,3-di(2-pyridine *N*-oxide) quinoxaline (XVIII, DPNOQ) were synthesized[417] (Table 14). DPNOQ can act as a monodentate, mono-bidentate or bis-bidentate (bridging) ligand. In the latter two cases, six-membered chelate rings are formed by coordination of one N–O oxygen and one nitrogen of the quinoxaline ring to the metal ion. Monomeric tetrahedral structures, involving mono-bidentate DPNOQ were assigned to $CoX_2(DPQNO)\cdot nH_2O$ ($X = Cl, Br, I, n = 1-1.5$), complexes of the type $NiX_2(DPNOQ)_2\cdot H_2O$ ($X = Br, I$) are monomeric, octahedral, and also contain mono-bidentate ligands[417]. Oligomeric $NiCl_2$ complexes of the types $Ni_3Cl_6(DPNOQ)_4\cdot 4H_2O$ and $Ni_5Cl_{10}(DPNOQ)_4\cdot 4H_2O$ contain bridging bis-bidentate DPNOQ ligand molecules, coordination of terminal mono-bidentate DPNOQ groups was proposed for the former complex, while the formulation of the latter complex involves only bridging DPNOQ ligands and terminal aquo and chloro groups. $CuX_2(DPNOQ)$ complexes are probably hexacoordinated, polynuclear, DPNOQ-bridged. A complex in which this ligand is monodentate[417] is the adduct $ICl\cdot DPNOQ$. Finally, 2-CNPNO acts as a monodentate ligand in $[M(2\text{-}CNPNO)_6](ClO_4)_2$ (M = Co, Ni), while for $Ag(2\text{-}CNPNO)_2(ClO_4)$ the possibility of chelation of the ligand was discussed[148] (vide supra, Sect. C(*viii*)(*b*)).

E. METAL COMPLEXES OF ALIPHATIC AMINE *N*-OXIDES AND SECONDARY AMINE NITROXIDE FREE RADICALS

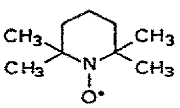
The present section gives a brief account of the metal complexes reported for aliphatic amine *N*-oxides and secondary amine nitroxide free radicals. Trimethylamine *N*-oxide (TMNO) forms complexes with a variety of transition metal salts[18, 100, 110, 293, 418–425], coordination occurring through the N–O oxygen. Complexes of the following types were reported: $[M(TMNO)_4](ClO_4)_2$ (M = Mn, Co, Ni, Cu, Zn)[18, 100, 418–422], $[M(TMNO)_6](ClO_4)_3$ (M = Sc, Cr)[100, 293], $[M(TMNO)_2X_2]$ (M = Mn, Co, Zn, Cd; X = Cl, Br, I, NCS, NO_3)[18, 110, 419, 420, 422, 423], $[Co(TMNO)_3I]I$ (ref. 18), $[Co(TMNO)_4]X_2$ ($X = NO_3$ (ref. 110), BF_4, ClO_4, Br, I, $CH_3C_6H_4SO_3$ (tosylate))[421], $[M(TMNO)X_2]$ (M = Cd, Hg, X = Cl, Br, I)[423] and $M(TMNO)_2Cl_4$ (M = Ti, Zr)[422, 424]. TMNO behaves in a manner similar to sterically hindered aromatic amine *N*-oxides (e.g. 2,6-LNO[145], ANO)[149], in that it forms $[ML_4]^{2+}$ and $[ML_6]^{3+}$ cationic complexes. However, the $[M(TMNO)_4]^{2+}$ complexes are tetrahedral, with the exception of the Cu^{II} complex, which is probably distorted square-planar (D_{2d} symmetry)[100], whereas the $[M(2,6\text{-}LNO)_4]^{2+}$ complexes are square-planar[145]. Thus, TMNO resembles the corresponding phosphine and arsine oxides[101, 102, 135–139] in that it favors the stabilization of tetrahedral cationic complexes. Square pyramidal $[ML_5]^{2+}$ and $[ML_4(OClO_3)]^+$ cationic $3d$ metal complexes with trialkyl- and tri-arylphosphine oxides have been reported[136, 140, 426]. Nevertheless, attempts at the isolation of $[M(TMNO)_5](ClO_4)_2$ were unsuccessful, although solutions of $[M(TMNO)_4](ClO_4)_2$ (M = Co, Ni) containing excess ligand exhibit electronic spectra indicating the attainment of a coordination higher than four[140]. Conclusions regarding the stereochemistry of $[M(TMNO)_5]^{2+}$ would be of considerable interest, since $[ML_5]^{2+}$ cations are square pyramidal for L = phosphine or arsine oxide[136, 140, 426] and trigonal bipyramidal for L = aromatic amine *N*-oxide (2-PicNO)[123, 133]. $[Co(TMNO)_2X_2]$ (X = Cl, Br, I, NCS) complexes are pseudo-tetrahedral in solution, but pentacoordinated (most probably TMNO-bridged and dimeric) in the solid state[419, 420]. The paramagnetic metal ion TMNO complexes mentioned above are generally of the high-spin type. Other metal complexes of TMNO reported are $BX_3\cdot TMNO$ (X = F, Cl, Br)[11, 15, 424, 427], $AlX_3\cdot TMNO$

(X = Cl, Br), $GaCl_3 \cdot TMNO$, $InCl_3 \cdot 2TMNO$ (ref 424), $(CH_3)_3M \cdot TMNO$ (M = Al, Ga, In)[428], $SiF_4 \cdot 2TMNO$, $SiX_4 \cdot 4TMNO$ (X = Cl, Br)[11,354], $GeCl_4 \cdot 2TMNO$, $GeCl_4 \cdot 4TMNO$ (ref. 424), $SnX_4 \cdot 2TMNO$ (X = F, Cl, Br)[422,424], $PCl_3 \cdot n$TMNO (ref. 11), $SO_2 \cdot TMNO$ (refs 10, 13), $SO_3 \cdot TMNO$ (refs. 13, 15). TMNO·HCl and $TMNO \cdot 2H_2O$ have also been studied[429,430]: Triethyl- and tripropylamine *N*-oxides (TENO, TPNO, respectively) form $[CoL_2X_2]$ (X = Cl, Br, I, NCS) and $[CoL_4](ClO_4)_2$ complexes[422,425]. TENO complexes of these types form the pentacoordinated complex $[Co(TENO)_5]^{2+}$ in solution and in the presence of excess ligand, treatment of TPNO complexes with excess ligand does not lead to the formation of species with a coordination number higher than four. ($[Co(TPNO)X_2]$ forms the $[Co(TPNO)_4]^{2+}$ cation, under these conditions[425]. Rare earth complexes of the type $[M(TENO)_6][Cr(NCS)_6] \cdot 2H_2O$ (M = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er) have also been reported[431] *N,N*-Dimethylethylenediamine *N*-oxide ($(CH_3)_2N(O)$-$CH_2CH_2NH_2$) acts as a bidentate chelating agent, coordinating through one oxygen and one nitrogen atom, $[ML_3](ClO_4)_{2 \text{ or } 3}$ (M = Fe^{3+}, Co^{3+}, Ni^{2+}), $[ML_2](ClO_4)_2$ (M = Cu, Zn), MLX_2 (M = Mn, Co, Cu, Zn; X = Cl, I), $NiLCl_2 \cdot 2H_2O$, $MLCl_2 \cdot 2HCl$ (M = Mn, Pd, Cd) and L·2HCl complexes of this ligand have been prepared[432]. Complexes with other R_3NO ligands reported are $C_6H_5MgBr \cdot C_6H_5(CH_3)_2$ (ref 12), $ZnBr_2 \cdot 2C_6H_5(C_6H_5CH{=}CHCH{=})NO$ (ref. 14), and a series of F_3NO adducts with BF_3, AsF_5 and SbF_5 (ref 433).

The nitroxides of secondary amines are free radicals; properly substituted radicals of this type are stable substances[434–436] (e g. di-*tert*-butylnitroxide, XXX, DBNO and 2,2,6,6-tetramethylpiperidine nitroxide, XXXI, TMPNO·)



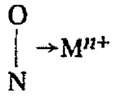
XXX



XXXI

These compounds have found wide application as spin labels for probing biomolecular structure[437], interest in their coordination compounds has started developing in recent years The donor properties of TMPNO· towards various phenols and alcohols were recently investigated[438]; protonation of TMPNO·, not involving destruction of the paramagnetic center, has been reported[439] The 1 1 complexes of non-transition metal ions with nitroxide free radicals (i e $AlCl_3$ with DBNO· and TMPNO· (ref. 105), and MX_3 (M = Al, Ga, X = Cl, Br, I) with 2,2,6,6-tetramethyl-4-pyridone nitroxide[103]) are paramagnetic[103,105]. Solution EPR spectra of the free radicals consist of three lines produced by interaction of the unpaired electron with a single ^{14}N nucleus The Al^{III} complexes exhibit 18-line EPR spectra in which each of the three ^{14}N lines is split into six by interaction with a single ^{27}Al nucleus[105] In the case of Ga^{III} complexes, 24 lines are observed in their EPR spectra, this is due to interactions between ^{14}N and ^{69}Ga or ^{71}Ga nuclei[103]. In complexes with paramagnetic metal ions, spin–spin interactions between the ligand and metal ions unpaired electrons occur, as indicated by magnetic susceptibility and EPR studies[104,105,440–444]. $[Co(DBNO\cdot)_2X_2]$ (X = Cl, Br, I) complexes were initially found[104] to exhibit μ_{eff} of ca 2.7 B M.; recently, μ_{eff} of the $CoBr_2$ complex was redetermined[440] and found to be 4.23 B.M. The complexes are tetrahedral and their electronic spectra establish that Co is in the

+2 oxidation state[440]. The interaction between ligand and metal ion unpaired electrons is obvious, since the theoretical μ_{eff} value[440] for a system containing three unpaired electrons on cobalt, which are not interacting with one unpaired electron on each ligand, is 4 8 B M. The solid-state EPR spectra of these complexes are unusual for tetrahedral Co^{II}. It resembles an $S = \frac{1}{2}$ system with g values[440] comparable to that expected for tetrahedral Co^{II}. Beck et al [104] assumed a total spin of $S = \frac{1}{2}$, but Brown et al.[440] concluded that $S \neq \frac{1}{2}$. Similar magnetic properties and EPR spectra were reported for a number of 3*d* metal perchlorate–TMPNO· complexes. $[Fe(TMPNO\cdot)_2(ClO_4)_2]_x$ (μ_{eff} = 3.47 B M.), $[Co(TMPNO\cdot)(ClO_4)_2]_x$ (μ_{eff} = 4 58 B M), $[Ni(TMPNO\cdot)(ClO_4)_2]_x$ (μ_{eff} = 3 63 B M.), $[Zn(TMPNO\cdot)_2(ClO_4)_2]_x$ (μ_{eff} = 2.06 B M)[106] These compounds are most probably binuclear, the presence of bridging perchlorato ligands was considered as more probable than that of bridging TMPNO ·, in view of the steric features of the later ligand [106] Bis-(β-ketoenolato)–Cu^{II} chelates form 1 1 adducts with DBNO · and TMPNO ·, exhibiting low magnetic moments (1 05 B M) [441,444]. The Cu^{II} salt of the 2,2,5,5-tetramethyl-3-carboxypyrroline nitroxide radical does not exhibit an EPR signal[442]. A labile $Cu(ClO_4)_2$ complex with TMPNO· was isolated but not characterized, the reaction was carried out in triethyl orthoformate, and this complex was attacked by the ethanol produced, forming 2,2,6,6-tetramethylpiperidinium perchlorate and a mixture of elemental copper and copper oxides[445] Addition of 3*d* metal acetylacetonates (VO^{2+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{2+}, Cu^{2+}) to solutions of DBNO· or TMPNO· results in a broadening of the lines of the EPR and NMR spectra of the free radical, the line widths depend on the number of spins on the metal and the geometry of the complexes[443]. A number of diamagnetic Pd^{I} complexes of the type $[Pd(DBNO\cdot)X]_2$ (X = Cl, Br) reported, are binuclear halogen-bridged [107] The complexes mentioned above involve, with the possible exception of CuL_2 (L = 2,2,5,5-tetramethyl-3-carboxypyrroline nitroxide)[442] coordination of the nitroxide group to the metal ion Coordination through the N–O oxygen is suggested by negative ν_{N-O} frequency shifts [104, 106, 445] and the fact that the nitrogen hyperfine splittings in the EPR spectra of diamagnetic metal ion-free radical complexes are increased relative to the splittings of the uncomplexed free radicals[441] The possibility of π-bonding of the type



$$\begin{array}{l} O \\ | \rightarrow M^{n+} \\ N \end{array}$$

was also advanced [103] Complexes of nitroxide free radicals, not involving coordination of the nitroxide group, are also known For example, during spin-labeling of vitamin B_{12} it was suggested that TMPNO· and its 4-hydroxy derivative coordinates to Co^{III} through the nitroxide group, while 4-bromoacetamido-2,2,6,6-tetramethylpiperidine nitroxide radical coordinates through the carbon of the $BrCH_2$ group[446], and in Pd(porphyrexide)$_2$-Cl_2 complexes, the bidentate ligands coordinate through two imino group nitrogens[447]

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