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The coordination chemistry of isoxazoles

Mark S. Munsey and N.R. Natale*

Department of Chemistry, Renfrew Hall, University of Idaho, Moscow, ID 83843 (U.S.A.)

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CONTENTS

A. INTRODUCTION

Since the first preparation of isoxazole by Claisen in 1888, this heterocycle has found widespread use, and is the subject of several general reviews [1].

Isoxazole–metal complexes are often postulated as intermediates in reactions of considerable synthetic utility, for example the reductive ring opening of isoxazoles. Yet, comparatively little systematic information is available to the research investigator who wishes to make rational use of the complexation properties of the isoxazole ring.

Several isoxazole–metal complexes have been reported and well characterized. The most recent literature review available is that of Wakefield and Wright and covers the literature betwen 1974 and mid-1977 [1(a)]. However, an updated review of this chemistry is needed. Because the behaviour of isoxazoles as their metal complexes is of interest to the long-term goals of several of our own projects, it seemed expedient to conduct and report such a review at this time.

B. GENERAL DISCUSSION

As noted above, the review of isoxazole chemistry published in 1979 by Wakefield and Wright included a table which listed the metal complexes of isoxazoles reported between 1974 and mid-1977 [1a]. Their table is presented in Table 1 with the exception that the non-isoxazole ligands, such as isoxazolones, have not been included. The present literature survey updates this prior work through 1988, and the

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* To whom correspondence should be addressed.

TABLE 1

Metal complexes of isoxazoles, 1974 through mid-1977[a]

Ligand	Metal[b]	Ref.
Isoxazole, Isox, **1**	Cu, Ag(I), Zn, Cd, Hg Cr(III), Mn, Fe, Co, Ni, Pd, Pt	3, 4. 6, 8, 10, 14
5-Methylisoxazole, **2**	Cu, Ag(I), Zn, Co, Ni	2, 3
3,5-Dimethyl-isoxazole, DMI, **3**	Cu, Cu(I), Zn, Cd, Hg, Cr(0), Cr, Cr(III), Co, Ni, Pd, Pt	5. 7, 8, 10, 15, 21
3-Methyl-5-phenyl-isoxazole, **4**	Cu, Cu(I), Zn, Cd, Hg, Cr, Cr(III), Co, Ni, Pd, Pt	6, 9, 10, 12, 15, 21
3,5-Diphenyl-isoxazole, **5**	Cu, Zn, Cd, Hg, Cr(III), Co, Ni, Pd, Pt	9, 10, 12, 15, 17
3-Amino-5-methyl-isoxazole, **6**	Cu, Zn, Cd, Hg, Co, Ni, Pd, Pt	11, 13, 18, 20
4-Amino-3,5-dimethyl-isoxazole, **7**	Zn, Cd, Hg, Pd, Pt	12, 16
5-Amino-3,4-dimethyl-isoxazole, **8**	Cu, Zn, Cd, Hg, Co, Pd, Pt	11, 18, 19

[a] Ref. 1.

[b] M(II) unless otherwise noted.

results are given in Table 2. The same format is used in both tables to ease comparison of the data.

The previous authors felt that a rigorous discussion of the behavior of isoxazole–metal complexes was beyond the scope of their review [1a]. Just such a study is the purpose of the present work. So the detailed analysis of the isoxazole–metal complexes which follows will include those reports cited by the previous authors.

Tables 3–5 present these data [2–50] in the following general format. Each table lists the isoxazole ligands according to degree of substitution in the order of alkyl-, aryl-, alkyl/amino-, and alkyl/halo-substitution. The complexes of each ligand are listed approxiately in order of soft to hard metals. The coordination geometry of each complex is given when known followed by the molecular formula in parentheses where L refers to the isoxazole ligand and X and Y refer to the co-ligands. In some cases, a different co-ligand results in a change in the molecular formula of complexes of a given metal and isoxazole, and where this behavior is observed the complexes are listed with hard co-ligands first and proceeding to soft ones. Finally, the atom at which binding occurs on the ambidentate thiocyanate co-ligand is written first (i.e. NCS- indicates binding through N).

The structures of those isoxazoles for which metal complexes have been reported are shown in Chart 1. Table 3 presents those complexes in which isoxazoles were

TABLE 2

Metal complexes of isoxazoles, mid-1977 through 1988

Ligand	Metal[a]	Ref.
Isoxazole, **1**	Fe, Cr(0), Co(III), Ag(I), Pd, Pt, Pr(III), Eu(III), Yb(III), Gd(III), Pt(IV), Mn	24, 25, 29, 31, 36, 37–39, 44, 47
3-Phenylisoxazole, **9**	Mo(0), Fe(0)	43, 50
3,5-Dimethylisoxazole, **3**	Cu, Mn, Pt, Pd, Mo(0), Fe(0), Pt(IV)	25, 27–29, 31, 38, 43, 47
3-Methyl-5-phenylisoxazole, **4**	Cu, Pd, Pt, Mo(0), Fe(0), Mn	27–29, 31, 43, 48
3,5-Diphenylisoxazole, **5**	Mn, Pd, Pt, Mo(0), Fe(0), Fe(III)	30, 31, 35, 43
4,5-Naphthisoxazole, **10**	Ru	49
3-Phenyl-4,5-cycloalkylisoxazole, **11**	Mn(0), Fe(0)	43
3-Amino-5-methylisoxazole, **6**	Cr(III), Ni, Cu, Ca, Ba, Fe(III), Pd, Pt, Co, Mn	22, 26, 28, 32–35, 38, 40, 42, 45, 48
4-Amino-3,5-dimethylisoxazole, **7**	Co, Pd, Pt, Ni, Cu	23, 31
5-Amino-3,4-dimethylisoxazole, **8**	Cr(III), Ca, Ba, Pt, Pd	22, 34, 38, 48
4-Chloro-3,5-dimethylisoxazole, **12**	Pt	48
4-Chloro-3-methyl-5-phenylisoxazole, **13**	Cu	41
Hexakis (3,5-dimethylisoxazole-4-propane) phosphazene, **14**	Co, Cr(III), Mn	54

[a] Other than M(II) will be noted.

reported to act as monodentate ligands. In Table 4, the complexes in which isoxazoles exhibit bridging bidentate behavior are given. Many isoxazoles have been observed to exhibit both modes of binding; thus, for those ligands where this behavior is observed, information from Tables 3 and 4 has been contrasted and is presented in Table 5 so as to facilitate easier comparison.

The following complexes in Chart 1 will not be included in the detailed discussion which follows. 5-Methylisoxazole [2,3] and the zero-valent metal complexes [24,43] will not be discussed because sufficient information about their coordination geometries was not given.

TABLE 3

Comparison of coordination geometries and co-ligands in monodentate isoxazole–metal complexes

Ligand	Metal[a]	Coordination geometry[b]	Co-ligand[c]	Ref.
Isoxazole (Isox), **1**	Cr(0)	oct. (LX_5)	CO_t	24
	Pd, Pt	*tr*-sq. plnr. (L_2X_2)	$NO_3^-{}_t$, $Cl^-{}_t$, $Br^-{}_t$	7,31
	Pt(IV)	oct. (L_2X_4)	$Cl^-{}_t$	47
	Ag(I)	–(L_2X)	NO_3^-	3
	Ag(C=N)	lin. (LX)	tfa_t	44
	Cd	oct. ($L_6 + 2\ BF_4^-$)	–	14
	Cd	tet. (LX_2)	Cl^-, $NCS^-{}_{bbd}$, $I^-{}_t$	4
	Cd	tet. ($LX_2 \cdot 2H_2O$)	$Br^-{}_{t,bbd}$	4
	Hg(O_{ring})	tet. (LX_2)	$Cl^-{}_{t,bbd}$, $Br^-{}_{t,bbd}$	8
	Hg(O_{ring})	tet. ($LX_2 \cdot 2H_2O$)	$SCN^-{}_{t,bbd}$	8
	Fe	oct. ($L_6 + 2\ BF_4^-$ or ClO_4^-)	–	14,39
	Fe	oct. (LX_4Y)	N_{porph}; $NO^+{}_t$	37
	Co	oct. ($L_6 + 2\ BF_4^-$)	–	14
	Co	oct. (–)	NO_3^-	3
	Co	tet. (LX_2)	Br^-	4
	Co	oct. ($L_2X_2 \cdot 0.5H_2O$)	NCS^-	4
	Ni	oct. ($L_6 + 2\ BF_4^-$)	–	14
	Ni	oct. (–)	NO_3^-	3
3,5-Dimethyl-isoxazole (DMI), **3**	Fe(0), Mo(0)	–	CO	43
	Pd	*tr*-sq. plnr. (L_2X_2)	$NO_3^-{}_t$, $Cl^-{}_t$, $Br^-{}_t$, $I^-{}_t$	7,31
	Pt	*tr*-sq. plnr. (L_2X_2)	$Cl^-{}_t$, $Br^-{}_t$	7,31
	Pt(IV)	oct. (L_2X_4)	$Cl^-{}_t$	47
	Cu(I)	(M_2LX_2)	$Cl^-{}_{bbd}$	15
	Cd	tet. (LX_2)	$Cl^-{}_{bbd}$, $Br^-{}_{t,bbd}$, $I^-{}_{t,bbd}$	8
	Hg	tet. (LX_2)	$Cl^-{}_{bbd}$, $Br^-{}_{t,bbd}$	8
	Co	oct. ($L_4X_2 + 2\ ClO_4^-$)	H_2O	5
	Co	tet. (L_2X_2)	$Cl^-{}_t$, $Br^-{}_t$, $I^-{}_t$	5
	Co	tet. ($L_2X_2 \cdot 3H_2O$)	$NCS^-{}_t$	5

	Ni	oct. ($L_4X_2 + 2\ ClO_4^-$)	H_2O	5
	Ni	oct. (L_4X_2)	NCS^-_t	5
	Cu	sq. plnr. ($L_4 + 2\ ClO_4^-$)	–	5,28
	Cu	– (LX_2)	Br^-	27
	Zn (O_{ring})	tet. (L_2X_2)	Br^-_t	8
	Cr(III)	oct. ($L_3X_3 \cdot 6H_2O$)	Cl^-_t, Br^-_t, I^-_t	10
	Mn	oct. (L_4X_2)	SCN^-_t	29
3-Methyl-5-phenyl-isoxazole (MPI), **4**	Fe(0), Mo(0)	–	CO	43
	Pd, Pt	*tr*-sq. plnr. (L_2X_2)	$NO_3^-{}_t$, Cl^-_t, Br^-_t, SCN^-_t, I^-_t	12,31,48
	Pt(IV)	oct. (L_2X_4)	Cl^-_t	47
	Co	oct. ($L_4X_2 + 2\ ClO_4^-$)	H_2O	6
	Co	tet. (L_2X_2)	Cl^-_t, Br^-_t, I^-_t	6
	Co	tet. ($L_2X_2 \cdot 2H_2O$)	NCS^-_t	6
	Co	oct. (L_4X_2)	NCS^-_t	6
	Ni	oct. ($L_4X_2 \cdot H_2O$)	NCS^-_t	6
	Cu	sq. plnr. ($L_4 + 2\ ClO_4^-$)	–	6,28
	Cu	– (LX_2)	Br^-	27
	Zn (O_{ring})	tet. (L_2X_2)	Cl^-_t, Br^-_t	9
	Zn (O_{ring})	tet. ($L_2X_2 \cdot 2H_2O$)	I^-_t	9
	Cr(III)	oct. ($L_3X_3 \cdot 6H_2O$)	Cl^-_t	10
3,5-Diphenyl-isoxazole (DPI), **5**	Fe(0)	–	CO	43
	Mo(0)	–	CO, CH_3CN	43
	Pd	*tr*-sq. plnr. ($L_2X_2 \cdot 2H_2O$)	$NO_3^-{}_t$	12
	Pd, Pt	*tr*-sq. plnr. (L_2X_2)	Cl^-_t, Br^-_t, I^-_t	12,31
	Cd	tet. (L_2X_2)	Cl^-_t, Br^-_t	9
	Cd	tet. ($L_2X_2 \cdot 4H_2O$)	I^-_t	9
	Hg	tet. ($L_2X_2 \cdot nH_2O$)	Cl^-_t ($n = 0$), Br^-_t ($n = 1$)	9
	Co	oct. ($L_4X_2 \cdot 2X + 2\ ClO_4^-$)	H_2O	17
	Co	tet. ($L_2X_2 \cdot nH_2O$)	Cl^-_t ($n = 1$), NCS^-_t ($n = 2$)	17
	Co	tet. (L_2X_2)	Br^-_t, I^-_t	17
	Ni	oct. ($L_4X_2 \cdot 2X + 2\ ClO_4^-$)	H_2O	17
	Ni	oct. (L_4X_2)	NCS^-_t	17

TABLE 3 (continued)

Ligand	Metal[a]	Coordination geometry[b]	Co-ligand[c]	Ref.
	Cu	sq. plnr. ($L_4 \cdot 4H_2O + 2\ ClO_4^-$)	–	17
	Zn	tet. (LX_2)	Cl_{bbd}	9
	Zn	tet. ($L_2X_2 \cdot 4H_2O$)	Br_t	9
	Zn	tet. ($LX_2 \cdot 4H_2O$)	$I_{t,bbd}$	9
	Cr(III)	oct. ($L_3X_3 \cdot 6H_2O$)	Cl_t, Br^-_t	10
	Fe(III)	oct. ($L_4X_2 \cdot H_2O + X$)	$ClO_4{}^-_t$	35
	Fe(III)	oct. (L_3X_3)	Cl^-_t, Br^-_t	35
	Fe(III)	oct. ($L_6 + 3\ Cl^-$ or Br^-)	–	35
	Mn	oct. ($L_2X_2 \cdot 2H_2O$)	Cl_{bbd}	30
	Mn	oct. ($L_3X_2Y \cdot 2H_2O$)	Br^-_t; H_2O	30
4,5-Naphth-isoxazole, **10**	Ru	oct. ($L_2X_2Y_2$)	Cl^-; $CO_{t,cis}$	49
3-Phenyl-4,5-cyclo-alkylisoxazole, **11**	Fe(0), Mo(0)	-	CO	43
3-Amino-5-methyl-isoxazole (3-AMI), **6**	Pd (O_{ring})	*cis*-sq. plnr. (L_2X)	$C_2O_4^{2-}{}_{bbd}$	38
	Pd (O_{ring})	sq. plnr. ($L_3X + X$)	NO_3^-	11
	Pd(O_{ring})	sq. plnr. ($L_2X_2 \cdot H_2O$)	SCN^-_t	11
	Pd, Pt (O_{ring})	sq. plnr. (L_2X_2)	Cl^-, Br^-, I^-_t	11,48
	Cd (O_{ring})	tet. (LX_2)	Br^-_{bbd}	18
	Cd (O_{ring})	tet. (L_2X_2)	NCS^-_t, I^-_t	18
	Co	oct. ($L_4X_2 \cdot 6$)	$NO_3{}^-_t$	20
	Co	oct. ($L_4X_2 \cdot 3H_2O$)	$NO_3{}^-_t$	20
	Co	oct. ($L_6 + 2\ ClO_4^-$)	–	20
	Co	oct. ($L_4X_2 + 2\ ClO_4^-$)	H_2O	20
	Co	tet. (L_2X_2)	Cl^-_t, Br^-_t	20,40,46
	Co	oct. ($L_4X_2 \cdot 2H_2O$)	NCS_t	20
	Ni	oct. ($L_6 + 2\ ClO_4^-$)	–	13

	Ni	oct. ($L_4X_2 \cdot 0.5H_2O$)	Cl^-	13
	Ni	oct. (L_4X_2)	$NO_3{}^-_t$, Br^-_t, NCS^-_t	13,26
	Ni	oct. ($L_4X_2 \cdot 1H_2O$)	NCS^-_t	13
	Ni(N_{amino})	tet. ($L_2X_2 \cdot 2H_2O$)	Cl^-	13,40
	Cu	sq. pyrm. ($L_4X + X$)	$NO_3{}^-_t$, $ClO_4{}^-_t$, Br^-_t	20,26,32,33,43
	Cu	oct. (L_4X_2)	Cl^-_t	33,40
	Cu	– (L_2X_2)	Br^-	46
	Zn (O_{ring})	tet. (L_2X_2)	Cl^-_t, Br^-_t, NCS^-_t, I^-_t	18
	Cr(III)	oct. ($L_3X_3 \cdot 2H_2O$)	$NO_3{}^-_t$	22
	Cr(III)	oct. ($L_3X_3 \cdot 1H_2O$)	Cl^-_t	22
	Cr(III)	oct. ($L_2X_3Y \cdot 21Y$)	Br^-_t; H_2O	22
	Cr(III)	tet. (LX_3)	I^-_t	22
	Fe(III)	oct. ($L_6 \cdot H_2O + 3\ ClO_4{}^-$)		35
	Fe(III)	oct. ($L_4X_2 + X$)	Cl^-_t	35
	Fe(III)	oct. ($L_3X_3 \cdot H_2O$)	Cl^-_t	35
	Fe(III)	oct. ($L_6 + 3\ Br^-$)	–	35
	Ba	tet. (L_2X_2)	Cl^-_t	34
	Ca	tet. ($L_2X_2 \cdot H_2O$)	Cl^-_t	34
	Ca	oct. ($L_4X_2 \cdot 3H_2O$)	Br^-_t	34
4-Amino-3,5-dimethylisoxazole (4-ADI; N_{amino})a, **7**	Pd	*tr*-sq. plnr. ($L_2X_2 \cdot H_2O$)	$NO_3{}^-_t$	12
	Pd	*tr*-sq. plnr. ($L_2X_2 \cdot 2H_2O$)	Cl^-_t, Br^-_t	12,31
	Pd, Pt	*tr*-sq. plnr. (L_2X_2)	Cl^-_t, Br^-_t, NCS^-_t, I^-_t	12,31
	Co	tet. (L_2X_2)	Cl^-_t, Br^-_t, I^-_t	51
	Zn (O_{ring})	tet. (L_2X_2)	I^-_t	44
5-Amino-3,4-dimethylisoxazole (5-ADI), **8**	Pd (O_{ring})	*cis*-sq. plnr. (L_2X)	$C_2O_4{}^{2-}{}_{tbd}$	38
	Pd (N_{amino})	*tr*-sq. plnr. (L_2X_2)	Cl^-_t, Br^-_t	11
	Pd (N_{amino})	*tr*-sq. plnr. ($L_2X_2 \cdot 2H_2O$)	SCN^-_t	11
	Pd (N_{amino})	*tr*-sq. plnr. ($L_2X_2 \cdot H_2O$)	I^-_t	11
	Pt (N_{amino})	*tr*-sq. plnr. ($L_2X_2 \cdot 2H_2O$)	Cl^-_t	11
	Pt (N_{ring})	sq. plnr. (L_2X_2)	Br^-	48
	Pt (O_{ring})	*tr*-sq. plnr. (L_2X_2)	Br^-_t	11

TABLE 3 (continued)

Ligand	Metal[a]	Coordination geometry[b]	Co-ligand[c]	Ref.
	Pt (N_{amino})	*tr*-sq. plnr. (L_2X_2)	$SCN^-{}_t$	11
	Cd	tet. (L_2X_2)	$Br^-{}_{t,bbd}$	18
	Cd	sq. pyrm. (L_4X+X)	$NCS^-{}_t$	18
	Co	oct. ($L_4X_2+2\ ClO_4{}^-$)	H_2O	19
	Co (N_{amino})	tet. (L_2X_2)	$Cl^-{}_t$, $Br^-{}_t$	19
	Ni	oct. ($L_3X_2Y\cdot H_2O$)	$Cl^-{}_t$, $Br^-{}_t$; H_2O	13
	Ni	oct. ($L_4X_2\cdot H_2O$)	$I^-{}_t$	13
	Zn (N_{amino})	tet. (L_2X_2)	$Cl^-{}_t$, $Br^-{}_t$, $SCN^-{}_t$, $I^-{}_t$	18
	Cr(III)	oct. ($L_3X_3\cdot 2H_2O$)	$NO_3{}^-{}_t$	22
	Cr(III)	oct. ($L_3XY_2\cdot 1.4Y+2X$)	$Br^-{}_t$; H_2O	22
	Cr(III)	oct. ($L_2X_3Y\cdot 5Y$)	$Br^-{}_t$; H_2O	22
	Ba	tet. ($L_2X_2\cdot$**8**)	$Cl^-{}_t$	34
	Ba	oct. ($L_6+2\ SCN^-$)	–	34
	Ba	tet. ($L_2X_2\cdot 1.2H_2O$)	$I-{}_t$	34
	Ca	tet. ($L_2X_2\cdot 4H_2O$)	$Cl^-{}_t$	34
	Ca	tet. ($L_3X\cdot 2H_2O+X$)	$Br^-{}_t$	34
	Ca	tet. ($L_4\cdot 3H_2O+2\ I^-$)		34
4-Chloro-3-methyl-5R-isoxazole (R = methyl or phenyl), **12** and **13**, respectively	Pt	sq. plnr. (L_2X_2)	$Cl^-{}_t$	48
	Cu	sq. plnr. (L_2X_2)	$ClO_4{}^-{}_t$	41
	Cu	tet. (L_2X_2)	$Cl^-{}_t$	41
	Cu	tet. (LX_2)	$Br^-{}_{t,bbd}$	41

[a] Other than M(II) will be noted; deviations from N_{ring}-coordination will be shown.

[b] Abbreviated empirical formula in parentheses, where X and Y are the respective co-ligands.

[c] t = terminal; tbd = terminal bidentate; bbd = bridging bidentate.

TABLE 4

Comparison of coordination geometries and co-ligands for bridging bidentate isoxazole–metal complexes

Ligand	Mode[a]	Metal[b]	Coordination geometry[c]	Co-ligand[d]	Ref.
Isoxazole (Isox), **1**	A	Pd	*cis*-sq. plnr. (LX)	$C_2O_4{}^{2-}{}_{tbd}$	38
	A	Pd, Pt	*cis*-sq. plnr. (LX_2)	$SCN^-{}_t$, $I^-{}_t$	7
	A	Co	oct. (LX_2)	$Cl^-{}_{bbd}$	4
	A	Ni	oct. ($LX_2 \cdot 0.5H_2O$)	$Cl^-{}_{bbd}$	4
	A	Cu	oct. (LX_2)	$Cl^-{}_{bbd}$	4,25
	A	Zn	oct. ($LX_2 \cdot 0.5\ H_2O$)	$Cl^-{}_{bbd}$	8
	A	Zn	oct. (L_2X_2)	$Br^-{}_t$, $I^-{}_t$	8
	A	Zn	(LX_2)	$NCS^-{}_t$	8
	A	Mn	oct. (L_2X_2)	$Cl^-{}_t$, $Br^-{}_t$, $NCS^-{}_t$	29
	A	Mn	oct. ($L_2X_2 \cdot H_2O$)	$I^-{}_t$	29
3,5-Dimethylisoxazole (DMI), **3**	A	Pd	*cis*-sq. plnr. (LX)	$C_2O_4{}^{2-}{}_{tbd}$	38
	A	Pt	*cis*-sq. plnr. (LX_2)	$I^-{}_t$	7
	A	Cu(I)	(M_2LX_2)	$Br^-{}_{bbd}$	5
3-Methyl-5-phenylisoxazole (MPI), **4**	A	Cu	oct. (LX_2)	Cl^-	6
	A	Cr(III)	oct. ($M_2L_3X_6 \cdot 6H_2O$)	$Br^-{}_t$	10
	A	Mn	oct. (L_2X_2)	$Br^-{}_t$	29
	A	Mn	oct. ($L_2X_2 \cdot 1.5H_2O$)	$NCS^-{}_t$	29
	A	Mn	oct. ($L_2X_2 \cdot H_2O$)	$I^-{}_t$	29
3,5-Diphenylisoxazole (DPI), **5**	A	Ni	oct. ($L_2X_2 \cdot H_2O$)	Cl^-	17
	A	Ni	oct. ($L_2X_2 \cdot 2H_2O$)	Br^-	17
	A	Ni	oct. (L_2X_2)	$NCS^-{}_t$, $I^-{}_t$	17

TABLE 4 (continued)

Ligand	Mode[a]	Metal[b]	Coordination geometry[c]	Co-ligand[d]	Ref.
	A	Cu	oct. ($LX_2 \cdot H_2O$)	Cl^-_{bbd}	17
	A	Cu	oct. (L_2X_2)	Br^-_t	17
3-Amino-5-methylisoxazole (3-AMI), **6**	A	Pd	*cis*-sq. plnr. (L_2X_2)	I^-	11
	A	Cd	oct. (LX_2)	Cl^-_{bbd}	18
	A	Hg	tet. (LX_2)	Cl^-_t, Br^-_t	18
	A	Cu	sq. pyrm. (L_2X_2)	NO_3^-, Cl^-_t, Br^-_t	20,32,33
	A	Cr(III)	oct. (L_2X_3)	Cl^-_t	22
	A	Cr(III)	oct. ($L_2X_3 \cdot 5H_2O$)	Br^-_t	22
	A	Mn	oct. (L_2X_2)	Cl^-_t, Br^-_t, I^-_t	30
	A	Mn	oct. ($L_2X_2 \cdot H_2O$)	NCS^-_t	30
4-Amino-3,5-dimethylisoxazole (4-ADI), **7**	B	Cd	tet. ($LX_2 \cdot H_2O$)	Cl^-_t	16
	B	Cd	oct. ($LX_2 \cdot H_2O$)	Br^-_{bbd}	16
	A	Cd	oct. (LX_2)	NCS^-_{bbd}	16
	A	Cd	oct. ($L_2X_2 \cdot 2H_2O$)	I^-_t	16
	A	Hg	tet. (LX_2)	Cl^-_t, $Br^-_{t,bbd}$	16
	B	Hg	tet. (LX_2)	SCN^-_t	16
	B	Co	oct. (L_2X_2)	NCS^-_t	23
	B	Ni	oct. ($L_2X_2 \cdot 2H_2O$)	Cl^-_t	23
	B and -NH_2 mono-	Ni	oct. ($L_3X_2 \cdot 4H_2O$)	Cl^-_t	23
	B	Ni	oct. ($L_2X_2 \cdot 0.4H_2O$)	Br^-_t	23
	B	Cu	oct. ($L_3 + 2\ ClO_4^-$)	..	23
	B	Cu	oct. ($LX_2 \cdot 2H_2O$)	Cl^-_{bbd}	23
	B	Cu	oct. ($L_2X_2 \cdot H_2O$)	Cl^-_t	23
	B	Cu	oct. ($L_2X_2 \cdot 2H_2O$)	Br^-_t	23
	B	Zn	tet. ($LX_2 \cdot H_2O$)	Cl^-_t	16

	B	Zn	oct. (LX_2)	Br^-_{bbd}	16
	B	Zn	oct. ($LX_2 \cdot H_2O$)	NCS^-_{bbd}	16
5-Amino-3,4-dimethyl-isoxazole (5-ADI), **8**	C	Pd	*cis*-sq. plnr. ($M_2L_3X_4$)	$NO_3{}^-_t$	11
	A	Cd	oct. (L_2X_2)	Cl^-_{bbd}	18
	C	Cd	oct. (L_2X_2)	I^-_t	18
	C	Hg	tet. (LX_2)	Cl^-_t	18
	A	Hg	tet. (LX_2)	Br^-_t	18
	A	Co	oct. (L_2X_2)	$NO3^-_t$	19
	B	Co	tet. ($M_2L_7X_4$)	I^-	19
	B	Co	tet. and oct. ($M_4L_{11}X_8$)	I^-	19
	A	Ni	oct. ($L_2X_2 \cdot 2H_2O$)	$NO3^-_t$	13
	A	Ni	oct. ($L_3 \cdot 4H_2O + 2\ ClO_4{}^-$)	–	13
	A	Ni	oct. ($L_3X_2 \cdot H_2O$)	NCS^-_t	13
	A	Cu	oct. ($M_2L_5X_4$)	$NO3^-_t$	19
	A	Cu	sq. plnr. ($L_2 \cdot 4H_2O + 2\ ClO_4{}^-$)	–	19
	A	Cu	oct. ($M_2L_3X_4$)	$Br^-_{t,bbd}$	19
	A	Cu	oct. ($M_4L_3X_8$)	$I^-_{t,bbd}$	19
	A	Cr(III)	oct. ($LX_3 \cdot 4H_2O$)	$Cl^-_{t,bbd}$	22
	A	Cr(III)	oct. ($L_2X_3 \cdot H_2O$)	$Cl^-_{t,bbd}$	22
	A	Mn	oct. ($L_2X_2 \cdot H_2O$)	Cl^-_t	30
	A	Mn	oct. (L_2X_2)	Br^-_t	30
	A	Mn	oct. ($L_2X_2 \cdot 3H_2O$)	SCN^-_t	30
	A	Mn	oct. ($L_2X_2 \cdot H_2O$)	I^-_t	30
4-Chloro-3-methyl-5-phenylisoxazole, **13**	A	Cu	*cis*-sq. plnr. ($LX_2 \cdot H_2O$)	$NO_3{}^-_t$	41

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[a] See Fig. 2.

[b] Other than M(II) will be noted.

[c] Abbreviated empirical formula in parentheses where X and Y are the respective co-ligands.

[d] t = terminal; tbd = terminal bidentate; bbd = bridging bidentate.

TABLE 5

Comparison of coordination geometries and co-ligands for monodentate and bridging bidentate isoxazole–metal complexes

Ligand	Mode[a]	Metal[b]	Coordination geometry[c]	Co-ligand[d]	Ref.
Isoxazole (Isox), **1**	M	Cr(0)	oct. (LX_5)	CO_t	24
	A	Pd	*cis*-sq. plnr. (LX)	$C_2O_4{}^{2-}{}_{tbd}$	38
	M	Pd, Pt	*tr*-sq. plnr. (L_2X_2)	$NO_3{}^-{}_t$, $Cl^-{}_t$, $Br^-{}_t$	7,31
	A	Pd, Pt	*cis*-sq. plnr. (LX_2)	$SCN^-{}_t$, $I^-{}_t$	7
	M	Pt(IV)	oct. (L_2X_4)	$Cl^-{}_t$	47
	M	Ag(I)	–(L_2X)	$NO_3{}^-$	3
	C=N	Ag(I)	lin. (LX)	tfa_t	44
	M	Cd	oct. ($L_6 + 2\ BF_4{}^-$)	–	14
	M	Cd	tet. (LX_2)	Cl^-, $NCS^-{}_{bbd}$, $I^-{}_t$	4
	M	Cd	tet. ($LX_2 \cdot 2H_2O$)	$Br^-{}_{t,bbd}$	4
	M (O_{ring})	Hg	tet. (LX_2)	$Cl^-{}_{t,bbd}$, $Br^-{}_{t,bbd}$	8
	M (O_{ring})	Hg	tet. ($LX_2 \cdot 2H_2O$)	$SCN^-{}_{t,bbd}$	8
	M	Fe	oct. ($L_6 + 2\ BF_4{}^-$ or $ClO_4{}^-$)	–	14,39
	M	Fe	oct. (LX_4Y)	N_{porph}; $NO^-{}_t$	37
	M	Co	oct. ($L_6 + 2\ BF_4{}^-$)	–	14
	M	Co	oct. (–)	$NO_3{}^-$	3
	A	Co	oct. (LX_2)	$Cl^-{}_{bbd}$	4
	M	Co	tet. (LX_2)	Br^-	4
3,5-Dimethyl-isoxazole (DMI), **3**	M	Fe(0), Mo(0)–		CO	43
	A	Pd	*cis*-sq. plnr. (LX)	$C_2O_4{}^{2-}{}_{tbd}$	38
	M	Pd	*tr*-sq. plnr. (L_2X_2)	$NO_3{}^-{}_t$, $Cl^-{}_t$, $Br^-{}_t$, $I^-{}_t$	7,31
	M	Pt	*tr*-sq. plnr. (L_2X_2)	$Cl^-{}_t$, $Br^-{}_t$	7,31
	A	Pt	*cis*-sq. plnr. (LX_2)	$I^-{}_t$	7
	M	Pt(IV)	oct. (L_2X_4)	$Cl^-{}_t$	47
	M	Cu(I)	– (M_2LX_2)	$Cl^-{}_{bbd}$	15
	A	Cu(I)	– (M_2LX_2)	$Br^-{}_{bbd}$	5

	M	Cd	tet. (LX_2)	Cl^-_{bbd}, $Br^-_{t,bbd}$, $I^-_{t,bbd}$	8
	M	Hg	tet. (LX_2)	Cl^-_{bbd}, $Br^-_{t,bbd}$	8
	M	Co	oct. ($L_4X_2 + 2\ ClO_4^-$)	H_2O	5
	M	Co	tet. (L_2X_2)	Cl^-, Br^-, I^-_t	5
	M	Co	tet. ($L_2X_2 \cdot 3H_2O$)	NCS^-_t	5
	M	Ni	oct. ($L_4X_2 + 2\ ClO_4^-$)	H_2O	8
	A	Ni	oct. ($L_2X_2 \cdot H_2O$)	Cl^-	5
	A	Ni	oct. (LX_2)	Br^-_{bbd}	5
	A	Ni	oct. (L_2X_2)	NCS^-_t	5
	M	Ni	oct. (L_4X_2)	NCS^-_t	5
	M	Cu	sq. plnr. ($L_4 + 2\ ClO_4^-$)	–	5,28
	M	Cu	– (LX_2)	Br^-	27
	A	Cu	oct. (LX_2)	Cl^-_{bbd}, Br^-_{bbd}	5,25
	A	Zn	tet. (LX_2)	$Cl^-_{t,bbd}$, I^-_t	8
	M (O_{ring})	Zn	tet. (L_2X_2)	Br^-_t	8
	M	Cr(III)	oct. ($L_3X_3 \cdot 6H_2O$)	Cl^-_t, Br^-_t, I^-_t	10
	A	Mn	oct. ($LX_2 \cdot 0.5H_2O$)	Cl^-_{bbd}	29
	A	Mn	oct. (LX_2)	Br^-_{bbd}	29
	M	Mn	oct. (L_4X_2)	SCN^-_t	29
	A	Mn	oct. ($L_2X_2 \cdot 4H_2O$)	I^-_t	29
3-Methyl-5-phenylisoxazole (MPI), **4**					
	M	Fe(0), Mo(0)	–	CO	43
	A	Pd	*cis*-sq. plnr. (LX_2)	Br^-_t	12
	A	Pd	*cis*-sq. plnr. ($LX_2 \cdot H_2O$)	I^-_t	12
	M	Pd, Pt	*tr*-sq. plnr. (L_2X_2)	$NO_3^-{}_t$, Cl^-_t, Br^-_t, SCN^-_t, I^-_t	12,31,48
	M	Pt(IV)	oct. (L_2X_4)	Cl^-_t	47
	A	Cu(I)	– (M_2LX_2)	Br^-_{bbd}	6
	A	Cu(I)	– (L_3X)	Br^-_{bbd}	6
	A	Cd	oct. ($L_2X_2 \cdot 2H_2O$)	Cl^-_t, Br^-_t	9
	A	Cd	oct. ($LX_2 \cdot 2H_2O$)	$I^-_{t,bbd}$	9
	A	Hg	tet. (L_2X_2)	Cl^-_t	9

TABLE 5 (continued)

Ligand	Mode[a]	Metal[b]	Coordination geometry[c]	Co-ligand[d]	Ref.
	A	Hg	tet. ($L_2X_2 \cdot 2H_2O$)	Br^-_t	9
	M	Co	oct. ($L_4X_2 + 2\ ClO_4^-$)	H_2O	6
	M	Co	tet. (L_2X_2)	Cl^-_t, Br^-_t, I^-_t	6
	M	Co	tet. ($L_2X_2 \cdot 2H_2O$)	NCS^-_t	6
	M	Co	oct. (L_4X_2)	NCS^-_t	6
	A	Ni	oct. (L_2X_2)	$ClO_4^-{}_t$	6
	A	Ni	oct. ($M_2LX_4 \cdot 3H_2O$)	Br^-	6
	M	Ni	oct. ($L_4X_2 \cdot H_2O$)	NCS^-_t	6
	A	Ni	oct. (L_3X_2)	NCS^-_t	6
	M	Cu	sq. plnr. ($L_4 + 2\ ClO_4^-$)	–	6,28
	A	Cu	oct. (LX_2)	Cl^-	6
	M	Cu	– (LX_2)	Br^-	27
	M (O_{ring})	Zn	tet. (L_2X_2)	Cl^-_t, Br^-_t	9
	M (O_{ring})	Zn	tet. ($L_2X_2 \cdot 2H_2O$)	I^-_t	9
	M	Cr(III)	oct. ($L_3X_3 \cdot 6H_2O$)	Cl^-_t	10
	A	Cr(III)	oct. ($M_2L_3X_6 \cdot 6H_2O$)	Br^-_t	6
	A	Mn	oct. (L_2X_2)	Br^-_t	29
	A	Mn	oct. ($L_2X_2 \cdot 1.5H_2O$)	SCN^-_t	29
	A	Mn	oct. ($L_2X_2 \cdot H_2O$)	I^-_t	29
3,5-Diphenyl-isoxazole (DPI), 5	M	Fe(0)	–	CO	43
	M	Mo(0)	–	CO,CH_3CN	43
	M	Pd	*tr*-sq. plnr. ($L_2X_2 \cdot 2H_2O$)	$NO_3^-{}_t$	12
	M	Pd, Pt	*tr*-sq. plnr. (L_2X_2)	Cl^-_t, Br^-_t, I^-_t	12,31
	M	Cd	tet. (L_2X_2)	Cl^-_t, Br^-_t	9
	M	Cd	tet. ($L_2X_2 \cdot 4H_2O$)	I^-_t	9
	M	Hg	tet. (L_2X_2)	Cl^-_t	9
	M	Hg	tet. ($L_2X_2 \cdot H_2O$)	Br^-_t	9

	M	Co	oct. ($L_4X_2 \cdot 2X + 2\ ClO_4^-$)	H_2O	17
	M	Co	tet. ($L_2X_2 \cdot H_2O$)	Cl^-_t	17
	M	Co	tet. ($L_2X_2 \cdot 2H_2O$)	NCS^-_t	17
	M	Co	tet. (L_2X_2)	Br^-_t, I^-_t	17
	M	Ni	oct. ($L_4X_2 \cdot 2X + 2\ ClO_4^-$)	H_2O	17
	A	Ni	oct. ($L_2X_2 \cdot H_2O$)	Cl^-	17
	A	Ni	oct. ($L_2X_2 \cdot 2H_2O$)	Br^-	17
	M	Ni	oct. (L_4X_2)	NCS^-_t	17
	A	Ni	oct. (L_2X_2)	NCS^-_t, I^-_t	17
	M	Cu	sq. plnr. ($L_4 \cdot 4H_2O + 2\ ClO_4^-$)	–	17
	A	Cu	oct. (LX_2)	Cl^-_{bbd}	17
	A	Cu	oct. (L_2X_2)	Br^-_t	17
	M	Zn	tet. (LX_2)	Cl^-_{bbd}	9
	M	Zn	tet. ($L_2X_2 \cdot 4H_2O$)	Br^-_t	9
	M	Zn	tet. ($LX_2 \cdot 4H_2O$)	$I^-_{t,bbd}$	9
	M	Cr(III)	oct. ($L_3X_3 \cdot 6H_2O$)	Cl^-_t, Br^-_t	10
	M	Fe(III)	oct. ($L_4X_2 \cdot H_2O + X$)	ClO_4^-	35
	M	Fe(III)	oct. (L_3X_3)	Cl^-_t, Br^-_t	35
	M	Fe(III)	oct. ($L_6 + 3\ Cl^-$ or Br^-)	–	35
	A	Mn	oct. ($L_2X_2 \cdot 2H_2O$)	Cl^-_{bbd}	30
	A	Mn	oct. ($L_3X_2Y \cdot 2H_2O$)	Br^-_t; H_2O	30
3-Amino-5-methyl-isoxazole (3-AMI), **6**	M (O_{ring})	Pd	*cis*-sq. plnr. (L_2X)	$C_2O_4^{2-}{}_{tbd}$	38
	M (O_{ring})	Pd	sq. plnr. ($L_3X + X$)	NO_3^-	11
	M (O_{ring})	Pd	sq. plnr. (L_2X_2)	Cl^-, Br^-	11
	M (O_{ring})	Pd	sq. plnr. ($L_2X_2 \cdot H_2O$)	SCN^-_t	11
	A	Pd	*cis*-sq. plnr. (L_2X_2)	I^-	11
	M (O_{ring})	Pt	sq. plnr. (L_2X_2)	Cl^-, Br^-, I^-	11,48
	A	Cd	oct. (LX_2)	Cl^-_{bbd}	18
	M (O_{ring})	Cd	tet. (LX_2)	Br^-_{bbd}	18
	M (O_{ring})	Cd	tet. (L_2X_2)	NCS^-_t,I^-_t	18
	A	Hg	tet. (LX_2)	Cl^-_t, Br^-_t	18

TABLE 5 (continued)

Ligand	Mode[a]	Metal[b]	Coordination geometry[c]	Co-ligand[d]	Ref.
	M	Co	oct. ($L_4X_2\cdot\mathbf{6}$)	$NO_3^-{}_t$	20
	M	Co	oct. ($L_4X_2\cdot 3H_2O$)	$NO_3^-{}_t$	20
	M	Co	oct. ($L_6+2\ ClO_4^-$)	–	20
	M	Co	oct. ($L_4X_2+2\ ClO_4^-$)	H_2O	20
	M	Co	tet. (L_2X_2)	Cl^-, Br^-	20,40,46
	M	Co	oct. ($L_4X_2\cdot 2H_2O$)	$NCS^-{}_t$	20
	M	Ni	oct. ($L_6+2\ ClO_4^-$)	–	13
	M	Ni	oct. ($L_4X_2\cdot 0.5H_2O$)	$Cl^-{}_t$	13
	M	Ni	oct. (L_4X_2)	$NO_3^-{}_t$, $Br^-{}_t$, $NCS^-{}_t$	13,26
	M	Ni	oct. ($L_4X_2\cdot\mathbf{6}\cdot H_2O$)	$NCS^-{}_t$	13
	M (N_{amino})	Ni	tet. ($L_2X_2\cdot 2H_2O$)	Cl^-	13,40
	M	Cu	sq. pyrm. (L_4X+X)	$NO_3^-{}_t$, $ClO_4^-{}_t$, $Br^-{}_t$	20,26,32,33,42
	M	Cu	oct. (L_4X_2)	$Cl^-{}_t$	33,40
	A	Cu	sq. pyrm. (L_2X_2)	NO_3^-, $Cl^-{}_t$, $Br^-{}_t$	20,32,33
	M	Cu	– (L_2X_2)	Br^-	46
	M (O_{ring})	Zn	tet. (L_2X_2)	$Cl^-{}_t$, $Br^-{}_t$, $NCS^-{}_t$, $I^-{}_t$	18
	M	Cr(III)	oct. ($L_3X_3\cdot 2H_2O$)	$NO_3^-{}_t$	22
	M	Cr(III)	oct. ($L_3X_3\cdot\mathbf{6}\cdot H_2O$)	$Cl^-{}_t$	22
	A	Cr(III)	oct. (L_2X_3)	$Cl^-{}_t$	22
	A	Cr(III)	oct. ($L_2X_3\cdot 5H_2O$)	$Br^-{}_t$	22
	M	Cr(III)	oct. ($L_3X_3Y\cdot 2\ \mathbf{6}\cdot Y$)	$Br^-{}_t$; H_2O	22
	M	Cr(III)	tet. (LX_3)	$I^-{}_t$	22
	M	Fe(III)	oct. ($L_6\cdot H_2O+3\ ClO_4^-$)	–	35
	M	Fe(III)	oct. (L_4X_2+X)	$Cl^-{}_t$	35
	M	Fe(III)	oct. ($L_3X_3\cdot H_2O$)	$Cl^-{}_t$	35
	M	Fe(III)	oct. ($L_6+3\ Br^-$)	–	35
	M	Ba	tet. (L_2X_2)	$Cl^-{}_t$	34
	A	Mn	oct. (L_2X_2)	$Cl^-{}_t$, $Br^-{}_t$, $I^-{}_t$	30
	A	Mn	oct. ($L_2X_2\cdot H_2O$)	$NCS^-{}_t$	30

	M	Ca	tet. ($L_2X_2 \cdot H_2O$)	Cl^-_t	34
	M	Ca	oct. ($L_4X_2 \cdot 3\ H_2O$)	Br^-_t	34
4-Amino-3,5-dimethyl-isoxazole (4-ADI), **7**	M (N_{amino})	Pd	*tr*-sq. plnr. ($L_2X_2 \cdot H_2O$)	$NO_3{}^-_t$	12
	M (N_{amino})	Pd	*tr*-sq. plnr. ($L_2X_2 \cdot 2\ H_2O$)	Cl^-_t,Br^-_t	12,31
	M (N_{amino})	Pd, Pt	*tr*-sq. plnr. (L_2X_2)	Cl^-_t, Br^-_t, NCS^-_t, I^-_t	12,31
	B	Cd	tet. ($LX_2 \cdot H_2O$)	Cl^-_t	16
	B	Cd	oct. ($LX_2 \cdot H_2O$)	Br^-_{bbd}	16
	A	Cd	oct. (LX_2)	NCS^-_t	16
	A	Cd	oct. ($L_2X_2 \cdot 2H_2O$)	I^-_t	16
	A	Hg	tet. (LX_2)	Cl^-_t, $Br^-_{t,bbd}$	16
	B	Hg	tet. (LX_2)	SCN^-_t	16
	M	Co	tet. (L_2X_2)	Cl^-_t, Br^-_t, I^-_t	23
	B	Co	oct. (L_2X_2)	NCS^-_t	23
	B	Ni	oct. ($L_2X_2 \cdot 2H_2O$)	Cl^-_t	23
	B and N_{amino}	Ni	oct. ($L_3X_2 \cdot 4H_2O$)	Cl^-_t	23
	B	Ni	oct. ($L_2X_2 \cdot 4H_2O$)	Br^-_t	23
	B	Cu	oct. ($L_3 + 2\ ClO_4{}^-$)	–	23
	B	Cu	oct. ($LX_2 \cdot 2H_2O$)	Cl^-_{bbd}	23
	B	Cu	oct. ($L_2X_2 \cdot H_2O$)	Cl^-_t	23
	B	Cu	oct. ($L_2X_2 \cdot 2H_2O$)	Br^-_t	23
	B	Zn	tet. ($LX_2 \cdot H_2O$)	Cl^-_t	16
	B	Zn	oct. (LX_2)	Br^-_{bbd}	16
	B	Zn	oct. ($LX_2 \cdot H_2O$)	NCS^-_{bbd}	16
	M (O_{ring})	Zn	tet. (L_2X_2)	I^-_t	16
5-Amino-3,4-dimethyl-isoxazole (5-ADI), **8**	M (O_{ring})	Pd	*cis*-sq. plnr. (L_2X)	$C_2O_4{}^{2-}{}_{tbd}$	38
	C	Pd	*cis*-sq. plnr. ($M_2L_3X_4$)	$NO_3{}^-_t$	11
	M (N_{amino})	Pd	*tr*-sq. plnr. (L_2X_2)	Cl^-_t, Br^-_t	11
	M (N_{amino})	Pd	*tr*-sq. plnr. ($L_2X_2 \cdot 2H_2O$)	NCS^-_t	11
	M (N_{amino})	Pd	*tr*-sq. plnr. ($L_2X_2 \cdot H_2O$)	I^-_t	11

TABLE 5 (continued)

Ligand	Mode[a]	Metal[b]	Coordination geometry[c]	Co-ligand[d]	Ref.
	M (N_{amino})	Pt	*tr*-sq. plnr. ($L_2X_2\cdot2H_2O$)	Cl^-_t	11
	M (N_{ring})	Pt	sq. plnr. (L_2X_2)	Br^-	48
	M (O_{ring})	Pt	*tr*-sq. plnr. (L_2X_2)	Br^-_t	11
	M (N_{amino})	Pt	*tr*-sq. plnr. (L_2X_2)	SCN^-_t	11
	A	Cd	oct. (L_2X_2)	Cl^-_{bbd}	18
	M	Cd	tet. (L_2X_2)	$Br^-_{t,bbd}$	18
	M	Cd	sq. pyrm. (L_4X+X)	NCS^-_t	18
	C	Cd	oct. (L_2X_2)	I^-_t	18
	C	Hg	tet. (LX_2)	Cl^-_t	18
	A	Hg	tet. (LX_2)	Br^-_t	18
	M	Co	oct. ($L_4X_2+2\ ClO_4^-$)	H_2O	19
	A	Co	oct. (L_2X_2)	$NO_3^-{}_t$	19
	M (N_{amino})	Co	tet. (L_2X_2)	Cl^-_t, Br^-_t	19
	B	Co	tet. ($M_2L_7X_4$)	I^-	19
	B	Co	tet. and oct. ($M_4L_{11}X_8$)	I^-	19
	A	Ni	oct. ($L_2X_2\cdot2H_2O$)	$NO_3^-{}_t$	13
	A	Ni	oct. ($L_3\cdot4H_2O+2\ ClO_4^-$)	–	13
	M	Ni	oct. ($L_3X_3Y\cdot H_2O$)	Cl^-_t, Br^-_t; H_2O	13
	A	Ni	oct. ($L_3X_2\cdot H_2O$)	NCS^-_t	13
	M	Ni	oct. ($L_4X_2\cdot H_2O$)	I^-_t	13
	A	Cu	oct. ($M_4L_5X_4$)	$NO_3^-{}_t$	19
	A	Cu	sq. plnr. ($L_2\cdot4H_2O+2\ ClO_4^-$)	–	19
	A	Cu	oct. ($M_2L_3X_4$)	$Br^-_{t,bbd}$	19
	A	Cu	oct. ($M_4L_3X_8$)	$I^-_{t,bbd}$	19
	M (N_{amino})	Zn	tet. (L_2X_2)	Cl^-_t, Br^-_t, NCS^-_t, I^-_t	18
	M	Cr(III)	oct. ($L_3X_3\cdot2H_2O$)	$NO_3^-{}_t$	22
	A	Cr(III)	oct. ($LX_3\cdot H_2O$)	$Cl^-_{t,bbd}$	22
	A	Cr(III)	oct. ($LX_3\cdot4H_2O$)	$Cl^-_{t,bbd}$	22
	M	Cr(III)	oct. ($L_3XY_2\cdot8\cdot4H_2O+2\ X$)	Br^-_t; H_2O	22

	M	Cr(III)	oct. ($L_2X_3Y \cdot 5H_2O$)	Br^-_t; H_2O	22
	M	Ba	tet. ($L_2X_2 \cdot \mathbf{8}$)	Cl^-_t	34
	M	Ba	oct. ($L_6 + 2\ NCS^-$)	–	34
	M	Ba	tet. ($L_2X_2 \cdot \mathbf{8} \cdot 2H_2O$)	I^-_t	34
	M	Ca	tet. ($L_2X_2 \cdot 4H_2O$)	Cl^-_t	34
	M	Ca	tet. ($L_3X \cdot 2H_2O + X$)	Br^-_t	34
	M	Ca	tet. ($L_4 \cdot 3H_2O + 2\ I^-$)	–	34
	A	Mn	oct. ($L_2X_2 \cdot H_2O$)	Cl^-_t	30
	A	Mn	oct. (L_2X_2)	Br^-_t	30
	A	Mn	oct. ($L_2X_2 \cdot 4H_2O$)	NCS^-_t	30
	A	Mn	oct. ($L_2X_2 \cdot H_2O$)	I^-_t	30
4-Chloro-3-methyl-5R-isoxazole (R = methyl, phenyl), **12** and **13**, respectively	M	Pt	sq. plnr. (L_2X_2)	Cl^-_t	48
	A	Cu	*cis*-sq. plnr. ($LX_2 \cdot H_2O$)	$NO_3{}^-_t$	41
	M	Cu	sq. plnr. (L_2X_2)	$ClO_4{}^-_t$	41
	M	Cu	tet. (L_2X_2)	Cl^-_t	41
	M	Cu	tet. (LX_2)	$Br^-_{t,bbd}$	34

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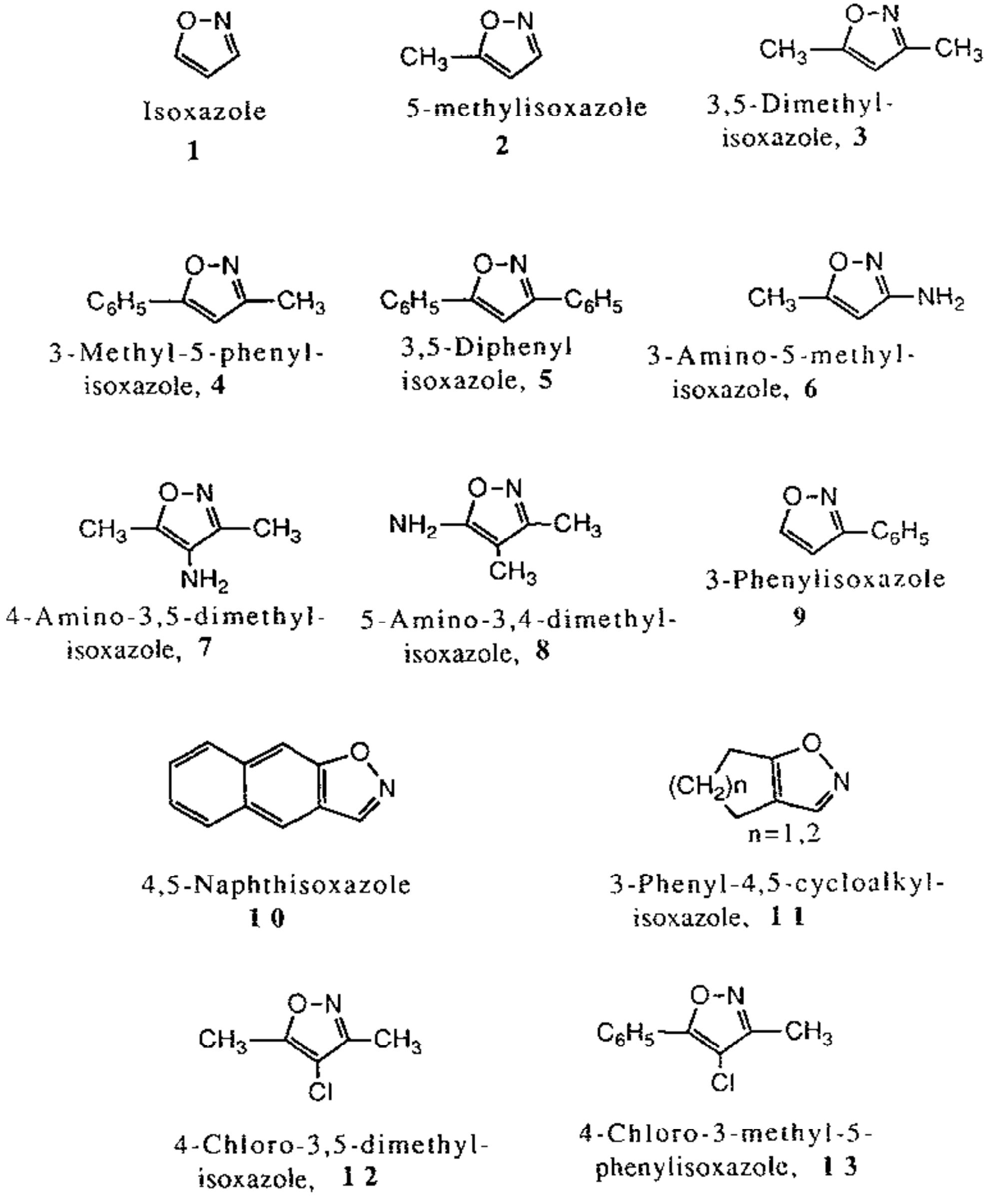
[a] A, B and C are bridging modes (see Fig. 2); M modes are monodentate (see Fig. 1).

[b] Other than M(II) will be noted.

[c] Abbreviated empirical formula in parentheses where X and Y are the respective co-ligands.

[d] t = terminal; tbd = terminal bidentate; bbd = bridging bidentate.



Isoxazole **1**

5-methylisoxazole **2**

3,5-Dimethylisoxazole, **3**

3-Methyl-5-phenylisoxazole, **4**

3,5-Diphenyl isoxazole, **5**

3-Amino-5-methylisoxazole, **6**

4-Amino-3,5-dimethylisoxazole, **7**

5-Amino-3,4-dimethylisoxazole, **8**

3-Phenylisoxazole **9**

4,5-Naphthisoxazole **10**

3-Phenyl-4,5-cycloalkylisoxazole, **11**

4-Chloro-3,5-dimethylisoxazole, **12**

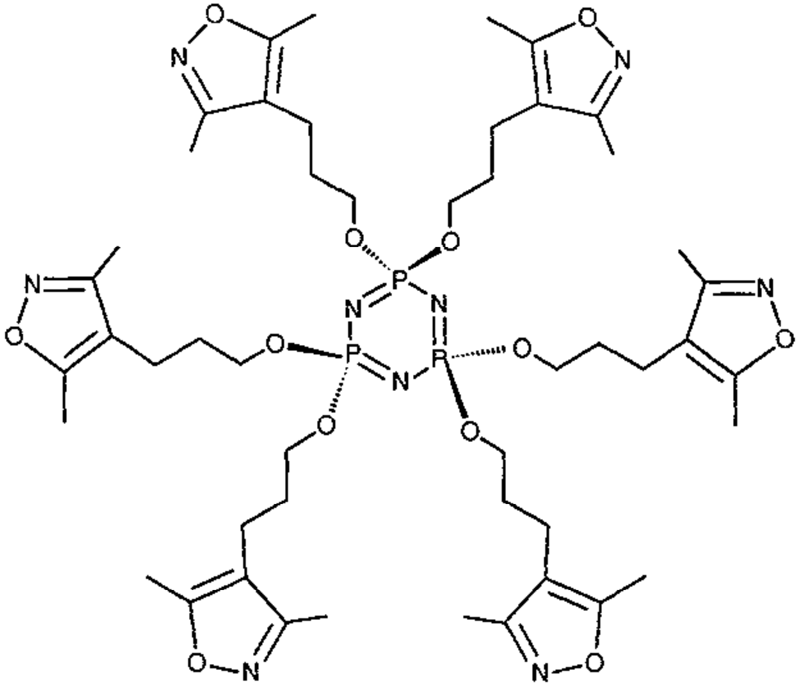
4-Chloro-3-methyl-5-phenylisoxazole, **13**

Chart 1. Structures of isoxazole ligands.

Garnovskii et al. claimed to have made chromium, molybdenum, and tungsten complexes of 3-methyl-5-phenyl- and 3,5-diphenylisoxazole in which the phenyl substituents were η^6 π-bound to the metal centers [21]. They reported only elemental analysis data for these purported complexes, however. They mentioned that IR data had been obtained and were consistent with the proposed structures, but these data were not reported. Thus, since no other investigators have reported this bonding behavior and our own studies have produced reductive ring opening of the isoxazole, their claims must await replication [43].

Dey et al. [50] reported a diiron complex which possessed two 3-phenylisoxazole substituents, each of which was bound to an iron atom via the carbon in the 5 position of the isoxazole ring. They report IR data which confirm only the presence of a bridging carbonyl, and their elemental analysis data do not agree with their proposed structure. They state that their conclusion must be considered tentative. So this compound will not be discussed any further for these reasons. Finally, the recent report of isoxazolyl-phosphazene, **14**, complexes [54] in which the isoxazole–metal bonding was evidenced by UV–VIS studies, only inferred the coordination geometry by comparison with earlier studies [5,10].

Generalizations in the discussion which follows should be regarded as narrow rather than broad, pK_a values of -2.97 and -1.61 have been reported for *N*-protonated isoxazole and 3,5-dimethylisoxazole, respectively [1]. (See Chart 1 for structures and compound numbers.) Stability constant measurements between 0.48



Isoxazolyl-Phosphazene, **14**

and 9.70 have been reported for Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Ag^{+} complexes of isoxazole and 5-methylisoxazole and also bear witness to the weak Lewis basic character of isoxazoles [2,3]. Thus, anomalous binding characteristics should be expected.

C. DETAILED DISCUSSION

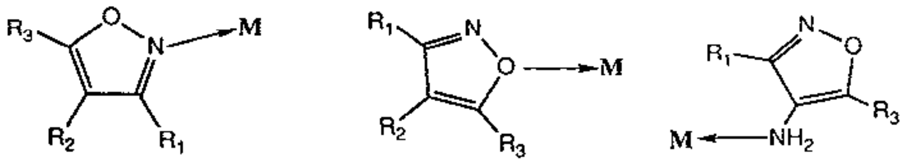
Excluding the reports as discussed in the preceding section still leaves nearly 300 complexes from which to attempt to glean an understanding of the behavior of isoxazoles as ligands. Some general information about the study of these complexes should be noted as follows.

First, the metals of the first row from manganese to zinc have been the most thoroughly studied. Iron is the only M(II) member of this row for which fewer than 20 examples (only three) have been reported. Several complexes of Cr(III), Fe(III), and Co(III) have also been reported. Second, two groups have been fairly well studied, those being the nickel–palladium–platinum and zinc–cadmium–mercury groups. Third, though it may appear that the effects of isoxazole substitution and of differing co-ligands have been thoroughly examined, it should become evident that a considerable need for a systematic study of this topic still exists. In some cases the synthesis of adducts which are lacking have been attempted but have met with failure, but attempts at making other needed complexes have not as yet been made. Finally, approximately equal numbers of alkyl/aryl- and amino-substituted adducts have been reported.

Characterization of the complexes has most often been made using UV–VIS, mid-IR and far-IR spectrophotometric techniques. Elemental analysis, magnetic properties, solution conductivity, and color data are also usually reported. NMR [24,39,40,44,45,47] and EPR [25,27,28,29,32,33,37,41,42] spectroscopic techniques have been used to further study several of the complexes. Most of the complexes are reported to be microcrystalline solids, thus only a few X-ray structural determinations have been reported [15,26].

Perhaps the first specific characteristic which should be noted is that almost equal numbers of monodentate and bridging bidentate isoxazole complexes have been reported. For most metals the predominant mode of monodentate binding is through the ring nitrogen when the isoxazole is alkyl- or aryl-substituted (Fig. 1, Mode A). The Hg complexes of isoxazole [9] (Isox, 1) are exceptions to this, as are the $ZnBr_2$ complex of 3,5-dimethylisoxazole [9] (DMI, 3) and all of the Zn(3-methyl-5-phenylisoxazole)$_2$ (MPI, 4) adducts [10] which are bound through the oxygen (Fig. 1, Mode B).

The Isox-Ag(I)trifluoroacetate complex represents the only complex in which π electrons are involved in bonding to the metal [44]. As shown in the tables, the electrons involved are those of the carbon–nitrogen double bond and not the entire π cloud.



A. N_{ring} B. O_{ring} C. N_{amino}

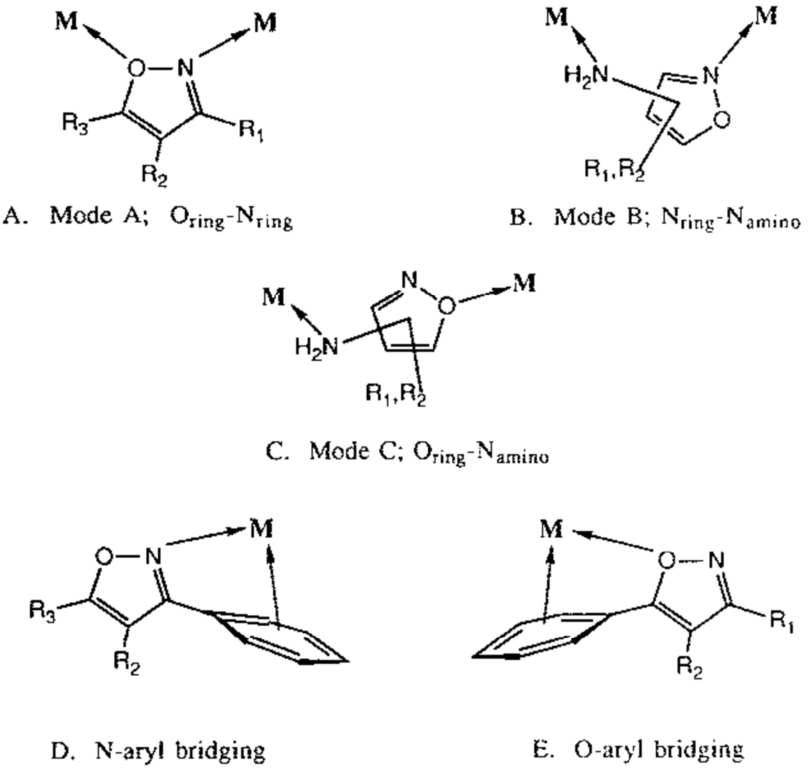
Fig. 1. Monodentate chelation modes of isoxazoles.

The substitution of an amino group on the ring markedly affects monodentate binding behavior, though in a much less predictable manner than might be thought. N_{ring} binding predominates among the 3-amino-5-methylisoxazole (3-AMI, **6**) complexes. But Pd [11,38], Pt [11,47], Cd [18], and Zn [18] favor the oxygen in adducts of this ligand. This behavior is consistent with the known oxaphilicity of Pd and Pt, but it is not observed among the alkyl/aryl-substituted isoxazole adducts. Only one example of N_{amino} complexation has been observed for 3-AMI, **6**, that being [Ni(3-AMI)Cl_2] [13,40] (Fig. 1, Mode C). Interestingly, this is also the only example of a tetrahedral Ni complex.

Of the 29 reported adducts of 4-amino-3,5-dimethylisoxazole (4-ADI, **7**), monodentate complexation occurs in 12 examples. Eight of these are N_{amino}. Binding of 4-ADI to Pd and Pt [12,31] takes place in this manner exclusively, and in one $NiCl_2$ complex the 4-ADI, **7**, is both monodentate N_{amino} and bridging bidentate Mode B bound [23]. Only the Co–halide complexes of 4-ADI, **7**, exhibit N_{ring} binding [23], and only in the $Zn(4\text{-ADI})_2I_2$ adduct is the ligand O_{ring}-bound [16].

The complexes of 5-amino-3,4-dimethylisoxazole (5-ADI, **8**) exhibit the broadest range of binding modes, with the greatest variation being seen among the Pd and Pt adducts [11,38,47]. In monodentate complexes of this ligand with these metals, examples of N_{ring}, O_{ring}, and N_{amino} binding occur (see Fig. 1, Structure C for the latter), though N_{amino} is the principal mode observed. With regard to the other metals, the complexes of 5-ADI, **8**, are nearly equally divided between monodentate N_{ring} and bridging bidentate binding, whereas the former predominates among 3-AMI complexes and the latter among 4-ADI complexes. CoX_2 ($X=Cl^-$, Br^-) and ZnX_2 ($X=Cl^-$, Br^-, NCS^-, and I^-) adducts of 5-ADI are also reported to be N_{amino}-bound [19,18].

The most commonly observed bridging binding modes of isoxazoles are illustrated in Fig. 2. As noted above, nearly equal numbers of alkyl/aryl- and amino-substituted examples have been reported. Isox and DMI can, of course, exhibit only Mode A binding (Fig. 2, Mode A). MPI and DPI are reported to form only Mode A complexes. The presence of the aromatic substituents adjacent to the oxygen and/or nitrogen could conceivably give rise to the modes illustrated in Fig. 2, Mode D and E, particularly since they are known to be non-coplanar with the isoxazole ring



A. Mode A; O_{ring}-N_{ring}

B. Mode B; N_{ring}-N_{amino}

C. Mode C; O_{ring}-N_{amino}

D. N-aryl bridging

E. O-aryl bridging

Fig. 2. Bridging bidentate chelation modes of isoxazoles.

[50–53]. These modes have not been observed as yet, though (except as noted above [21]). Isoxazoles are electron-poor aromatic systems and should, therefore, act as electron-withdrawing groups towards the phenyl rings. Thus, it is expected that substitution of electron-donating groups on the phenyl substituents could induce Mode D and Mode E behavior.

Among the amino-substituted ligands, all three bridging bidentate modes are reportedly observed. 3-AMI, **6**, exhibits only Mode A binding [11,18,20,22,30,32,33]. This behavior is reported in only 13 of its 57 complexes, the others being monodentate complexes. 4ADI, **7**, is observed to bind via Mode B [16,23] (Fig. 2, Mode B) in 14 of its 18 bridging bidentate adducts and Mode A in the other four [16]. 5-ADI is reported to exhibit bridging bidentate behavior in 21 of its 51 complexes. Sixteen of these are Mode A [13,18,19,22,30], two are Mode B [19], and three are Mode C [11,18] (Fig. 2, Mode C). 5-ADI is the only ligand of the three aminoisoxazoles to exhibit Mode C behavior.

It would appear that steric, co-ligand hard/soft factors, and isoxazole substitution symmetry can affect the monodentate vs. bridging bidentate behavior of the alkyl- and alkyl/aryl-substituted isxoxazoles. As noted previously, though, several anomalies can be found for whatever generalizations are made.

The influences of steric and co-ligand parameters are best illustrated by the complexes of Pd and Pt^{2+} ($4d^8$ and $5d^8$ metals, respectively) with the symmetrically substituted Isox, DMI, and DPI ligands [7,12,31,38]. First, the hard, bidentate chelating ligand $C_2O_4^-$ causes Isox and DMI to form bidentate bridges and thus dimeric *cis*-square planar complexes with Pd. In the Pd–Isox adducts with monodentate hard (NO_3^- and Cl^-) or intermediate (Br^-) co-ligands, Isox is monodentate nitrogen-bound, the complexes are monomeric, and they adopt *trans*-square planar geometries. The softer SCN^- co-ligand induces Isox to form bridges and, thus, a dimeric *cis*-square planar complex. However, in the DMI– and DPI–Pd complexes, the steric bulk of the isoxazole ligand seems to supercede hard/soft co-ligand characteristics. The isoxazoles in these complexes are reported to be monodentate and nitrogen-bound, and the complexes have *trans*-square planar geometries.

The isoxazoles in the PtX_2 complexes ($X = Cl^-$ or Br^-) of Isox and DPI behave the same as in their Pd adducts. The PtI_2 complex of Isox also compares well with the $Pd(SCN)_2$ analogue, Isox acting as a bidentate bridge in both cases. However, the Pt(II)–DMI complexes appear to exhibit a slight co-ligand-dependent binding variability. When $X = Cl^-$ or Br^-, DMI acts as a monodentate ligand, but it forms bidentate bridges with the soft I^- co-ligand.

The MPI ligand exhibits binding variability in its complexes with Pd and Pt(II) which may be the result of the unsymmetrical substitution of the isoxazole [7,12]. In its NO_3 adducts with Pd and its Cl complexes with both metals, MPI is monodentate with binding occurring through the nitrogen. Monodentate binding is also observed in MPI's $Pd(SCN)_2$ adduct, behavior which is in contrast to the bridging behavior of Isox in $Pd(Isox)(SCN)_2$. The PdX_2 ($X = Br^-$ or I^-) complexes of MPI have a bridging bidentate isoxazole, but this stands in contrast to the analogous complexes of the more symmetrical ligands Isox, DMI, and DPI, the last of which is even bulkier than MPI itself. However, in its complexes with PtX_2 salts, the binding behavior of MPI is the same as that of DPI, both ligands forming monodentate, *trans*-square planar complexes. Thus, it appears that the unsymmetrical substitution of MPI perturbs its binding behavior from the more systematic changes observed among the Isox, DMI, and DPI series.

Similarly anomalous behavior of MPI is also observed in complexes of Cd ($4d^{10}$). Isox–, DMI–, and DPI–CdX_2 compounds all have nitrogen-bound monodentate isoxazoles, are dimeric, and are of tetrahedral coordination geometry [4,8,9]. The MPI–CdX_2 complexes, though, are seen to be of octahedral stereochemistry, and the MPI is a bridging bidentate ligand. A small co-ligand dependence may also be expressing itself in the MPI complexes in that the Cl^- and Br^- are terminal co-ligands, and the complexes are of ML_2X_2 molecular formula. In the CdI_2 adduct, though, I^- is a bridging species, and the molecular formula is MLX_2.

No change in stereochemistry is observed in any of the Hg complexes (a $5d^{10}$

metal) [8,9]. Isox is O_{ring}-bound, but no co-ligand dependence is apparent. However, in the Isox, DMI, and DPI complexes the isoxazole is monodentate, whereas in the MPI complexes the isoxazole again forms bidentate bridges as it also does in the CdX_2 analogues. Thus, it is again seen that the binding is perturbed not with the increase in steric bulk of the isoxazole but with its symmetry. The irregular behavior (in comparison with Isox, DMI, and DPI) exhibited consistently by the MPI ligand as discussed in the last few paragraphs appears to demonstrate that isoxazole substitution symmetry can influence their binding behavior.

Ni and Zn represent the other metals in the d^8 and d^{10} groups, respectively ($3d$ orbitals). Steric effects are expressed somewhat differently in complexes of Ni [4–6,8,17] from those of Pd and Pt, but the Zn adducts [8,9,14] are similar to Cd and Hg.

All of the Ni adducts reported are octahedrally coordinated. The very hard BF_4^- induces ML_6 monodentate coordination of Isox, as it does for all metals except Cu [14]. The hard but bulkier ClO_4^- induces ML_4X_2 ($X=H_2O$) coordination of DMI and DPI, ClO_4^- being present as a counter ion. However, the $Ni(MPI)_2$ complex has coordinated ClO_4^- and bridging MPI. Br^- and NCS^- Ni–Isox adducts have monodentate Isox; but DMI, MPI, and DPI all act as bridging ligands, as does Isox, in its $NiCl_2$ complex. Furthermore, for each ligand except Isox, NCS^- is observed to form complexes in which the isoxazole ligand exhibits both binding behaviors. Thus, whereas sterically bulky ligands led to monodentate binding in Pd and Pt complexes, the opposite is true of the complexes of Ni.

In the Zn complexes, a change from octahedral to tetrahedral coordination geometry is observed. Isox acts as a bidentate bridge irrespective of co-ligand, and all of its complexes are octahedral. The complexes formed with DMI, MPI, and DPI are all of tetrahedral sterochemistry. DMI shows some co-ligand dependence in its binding behavior, though it is anomalous, forming bridges in the Cl^- and I^- adducts and being monodentate in the Br^- compound. The isoxazoles are monodentate in the MPI (O_{ring}-bound) and DPI complexes. Thus, the influence of steric and co-ligand parameters is again observed.

The unusual behavior of the amino-substituted isoxazoles can be fairly well accounted for by considering the possible resonance structures for each (Fig. 3.). In Fig. 3, A and C illustrate that donation of a pair of electrons from the oxygen ultimately increases the electron density on the ring nitrogen of 3-AMI and 5-ADI (structures A*iii* and C*iii*). Interaction of the lone electron pair of the amino group with the π cloud of the ring should have the same effect (structures A*iv* and C*v*). Figure 3B, however, illustrates that similar electron donation by the oxygen of 4-ADI should increase the electron density on the amino group, if only indirectly (structure B*ii*). Though structure B*iii* is similar to A*iii* and C*iii*, and this resonance structure results directly in increased electron density on the ring nitrogen (it possesses a full formal negative charge), it is apparent from the observed behavior of the ligands that structure B*ii* plays a larger role in the monodentate binding of 4-ADI. Thus, that

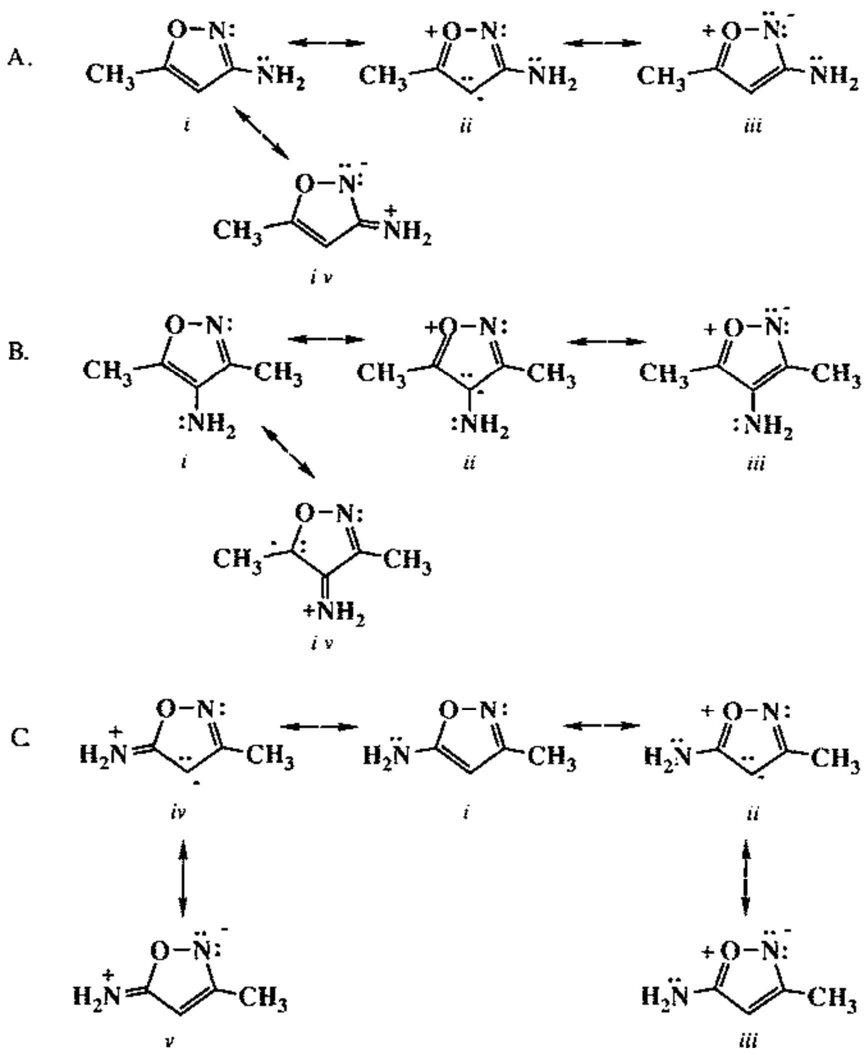


Fig. 3. Resonance structures of 3-AMI (A), 4-ADI (B) and 5-ADI (C).

N_{ring} binding should be the primary monodentate behavior exhibited by 3-AMI and 5-ADI, and N_{amino} the principal monodentate binding mode in 4-ADI complexes (among metals other than Pd and Pt), is not surprising.

Resonance arguments also account well for the observed bridging bidentate behaviors of these ligands. For, again, when electrons are donated by the amino functionalities of 3-AMI and 5-ADI, the electron density is increased on the ring nitrogen (Fig. 3, A*iv* and C*v*). Oxygen is more electronegative than nitrogen; and since its lone pair electrons are left free in these resonance structures, an increase in the electron density on nitrogen will also result in an increase in oxygen's electron density and thus increase its donor capability. Structures B*ii* (as discussed above) and B*iii* account for the N_{ring}–N_{amino} binding predominance among 4-ADI complexes. And though structure B*iv* must have some influence in the observation of Mode A bidentate binding in the Cd and Hg adducts of 4-ADI, it seems that co-ligand effects may also have a part in this apparently anomalous behavior. Finally, it must also be said that none of the arguments discussed above account for either the unusual behavior of 3-AMI and 5-ADI towards Pd and Pt, the preference in 4-ADI complexes of Pd and Pt for monodentate binding, or for the lack of a truly dominant bonding mode in complexes of 5-ADI.

Consideration of the complexes of the remaining metals represents approximately half of the reported data. This discussion will serve rather well to illustrate the difficulty in generalizing about isoxazole ligand behavior, for either too few examples are available or the isoxazoles appear to act capriciously in regards to the foregoing discussion.

Ba and Ca are the only alkali earth metals studied, and the only ligands considered were 3-AMI and 5-ADI [34]. Only the $Ca(3\text{-}AMI)Br_2$ adduct had octahedral geometry, all the other complexes being tetrahedral.

Cr(III) is the only d^3 metal for which isoxazole complexes were reported [6,10,22]. Monodentate N_{ring} behavior predominates among the alkyl/aryl isoxazoles, though the $Cr_2(MPI)_3Br_6 \cdot 6H_2O$ adduct has a bridging MPI. The exception to octahedral stereochemistry is found in the $Cr(3\text{-}AMI)I_3$ complex, which is tetrahedral. 3-AMI and 5-ADI are the only ligands for which bridging behavior is observed (the ML_2X_3 Cl^- and Br^- and the MLX_3 Cl^- derivatives, respectively).

In all but three of the 22 complexes of Mn(II) [14,29,30] the isoxazoles are observed to act as bidentate Mode A bridges. It should be noted, however, that no 4-ADI complexes have been reported. The only monodentate isoxazoles occur in $Mn(Isox)_6(BF_4)_2$ [14] and the $Mn(DPI)_4X_2$ adducts ($X=Cl^-$ or Br^-) [30]. All of the Mn complexes are octahedral and are predominantly of ML_2X_2 empirical formula. Complexes of the other d^5 metal [Fe(III)] are also reported to be octahedrally coordinated, though only monodentate N_{ring}-bound isoxazoles have been reported [35]. Very unusual isoxazole behavior is observed in some of these complexes. In the $Fe(DPI)_4(ClO_4)_3$ adduct, two of the ClO_4^- co-ligands remain coordinated to the metal center even though the isoxazole itself is very bulky. The Cl^- and Br^- DPI analogues are reported to be hexacoordinated by the isoxazole. The 3-AMI compounds, by comparison, are ML_6 (ClO_4^- counter ion), ML_4X_2 and ML_3X_3 ($X=Cl^-$), and ML_6 ($X=Br^-$ counter ion), respectively.

Too few Fe(II) and Co(III) examples have been reported to be able to generalize about isoxazole ligand behavior with d^6 metals except that hard BF_4^- and ClO_4^- induce hexacoordination by the isoxazole and the complexes reported are all of octahedral stereochemistry [14,36,37,39].

d^7 Co(II)[4–6,14,17,19,20,23,40,45] preferentially forms N_{ring}-bound complexes and slightly favors tetrahedral over octahedral sterochemistry. $Co(Isox)Cl_2$ is the only alkyl/aryl complex with a bridging isoxazole ligand. However, no clear trend can be discerned as to why Co changes its stereochemistry. 3-AMI is N_{ring}-bound in all of its complexes, and this is surprisingly true of all but the NCS^- adduct of 4-ADI. The ClO_4^- complex of 5-ADI is 5-ADI's only N_{ring} adduct, but the Cl^- and Br^- 5-ADI analogues are N_{amino}-bound. The isoxazole is bridging bidentate Mode A in the $Co(5\text{-ADI})_2(NO_3)_2$ complex, and Mode B in its I^- adducts. Both of these latter species are polymeric, and the $Co_4(5\text{-ADI})_{11}I_8$ possesses both tetrahedral and octahedral metal centers.

The Cu(II)-isoxazole complexes exhibit the widest range of stereochemistries of all the metals studied. Octahedral complexes predominate with 15 examples [4–6,14,17,25]. One of these $[Cu(4\text{-ADI})_3(ClO_4)_2]$ is one of only two ML_3 complexes reported [the other being $Ni(5\text{-ADI})_3(ClO_4)_2$]. The isoxazole is bridging bidentate in both cases. And the octahedral $Cu(Isox)_4\ (BF_4)_2$ is the only complex in which BF_4^- is reported to remain coordinated [14]. Two examples of tetrahedral [34,41], six of square planar[5,6,17,19,28,41] and square pyramidal [20,26,32,33,42], and three of unknown stereochemistry [25,27] have also been reported. All of the square pyramidal adducts are complexes of 3-AMI. Three of the square planar complexes are adducts of alkyl/aryl isoxazoles in which the ClO_4^- is a free ion. This is also true in the $Cu(5\text{-ADI})_2\ 2ClO_4^-$ complex. However, the 5-ADI forms bridges, and thus the only ML_2 complex reported [19]. The remaining square planar Cu(II) complexes are adducts of 4-chloro-3-methyl-5-R-isoxazole (R = methyl, phenyl; **12** and **13**, respectively), as are the two tetrahedral complexes.

D. CONCLUSION

A thorough review of the literature of isoxazole–metal complexes reported between 1974 and 1988 has been conducted. The binding characteristics of the isoxazoles in these complexes have been examined, and some tentative conclusions regarding the regularity of isoxazole complexation behavior have been discussed.

It was shown that the behavior of alkyl/aryl-substituted isoxazoles can be influenced by steric, co-ligand, and symmetry effects. The regular variation in the binding behavior of isoxazoles arising from these influences was, however, seen to have only limited predictability value.

The difference in the behavior of the alkyl/arylisoxazole ligands from that of the aminoisoxazoles was discussed. The presence of the amino group was seen to effect the binding of the isoxazole somewhat differently than was at first expected. The behavior of the aminoisoxazoles was seen to be fairly well, but not entirely, explained by resonance arguments.

Finally, it was shown that anomalous isoxazole binding behavior is exhibited in nearly half of the complexes reported. This behavior is consistent with their known chemical characteristic of being weak Lewis bases, but it was also seen to make it difficult to generalize about the behavior of isoxazoles in metal complexes.

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