

COMPLEXES OF IRON(II), COBALT(II), AND NICKEL(II) WITH α -DIIMINES AND RELATED BIDENTATE LIGANDS

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(Received April 18th, 1967)

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A. INTRODUCTION

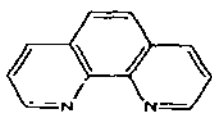
Metal chelates of numerous ligands containing the grouping $\text{—N}=\overset{|}{\underset{|}{\text{C}}}\text{—}\overset{|}{\underset{|}{\text{C}}}=\text{N—}$ have been investigated. A review by Brandt, Dwyer, and Gyarfas dealing with the metal complexes of 1,10-phenanthroline and related ligands appeared in 1954³⁶. Subsequently a considerable amount of research on the coordination chemistry of these ligands has been reported and some of this work has been discussed in recent reviews^{24,114}. In this review the iron(II), cobalt(II), and nickel(II) chelates of the various classes of bidentate ligands containing the grouping $\text{—N}=\overset{|}{\underset{|}{\text{C}}}\text{—}\overset{|}{\underset{|}{\text{C}}}=\text{N—}$ are discussed with particular reference to their magnetic susceptibilities. The restriction to iron, cobalt, and nickel has been deliberately made because these three metals in their bivalent oxidation state commonly display both "high-spin" and "low-spin" behaviour. The spin state of the central

metal ion often depends on minor structural variations in the chelating agent or on the nature of any other ligands present in the complex.

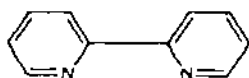
The metal chelates are classified according to the general type of ligand.

B. AROMATIC HETEROCYCLIC DIIMINES

(i) *Heterocyclic diimines containing six-membered aromatic rings.*—The aromatic heterocyclic diimines, 1,10-phenanthroline (I; phen) and 2,2'-bipyridyl (II; bipy) are among the most extensively investigated ligands.



(I)



(II)

The strong chelating ability of bidentate ligands containing the grouping $\text{—N}=\text{C}=\text{C}=\text{N—}$ is considered to result, in part, from $d_{\pi}\text{--}p_{\pi}$ bonding from the metal to the ligand^{49,152}. This π -bonding imparts some aromatic character to the chelate ring. The bonding of 2,2'-bipyridyl with certain transition metal ions has been discussed in terms of the valence bond⁴⁶ and molecular orbital^{11,244} theories. The thermodynamics of chelation of this ligand has been studied by calorimetry, potentiometry, and electron spin resonance^{2,5,36,144,167}. The thermal decomposition of bipyridyl complexes has been investigated^{65,155,182} and the electronic^{64,70,83,138,141,155,187,247}, infrared^{49,70,124,143,166,212}, and Mössbauer^{63,70,75,102,143} spectra of many complexes of each of these ligands have been discussed. A nuclear magnetic resonance study of electron transfer between the tris-1,10-phenanthroline iron(II) and iron(III) ions has been carried out⁶⁷ and several workers^{240,241,171,172,175} have studied the reduction of cobalt complexes of both these ligands by polarography. The resolution of the tris-iron(II) and -nickel(II) complexes has been effected³⁶ and the rate of racemization of the optical isomers has been studied^{21,214,216,246}.

In Table 1 are listed some representative metal complexes of these two ligands with iron(II), cobalt(II), and nickel(II). With iron(II), apart from the very stable spin-paired tris-complexes, mono- and bis-ligand chelates are also known. The effect of the other ligands in determining the spin state of iron(II) complexes of the type $\text{Fe}(\text{phen})_2\text{X}_2$ is well illustrated in Table 1. When $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{or } \text{N}_3$, the compounds are high-spin and the moment is essentially independent of temperature. When $\text{X} = \text{NCS}$ or NCSe the room-temperature moment is $\sim 5.0 \text{ BM}$; however, at a critical temperature (174°K for NCS and 232°K for NCSe) the moment drops sharply and at 77°K it is $< 1 \text{ BM}$ ¹⁴³. Baker and Bobonich¹² postulated dimeric structures involving bridging NCS or NCSe groups for these

TABLE I

MAGNETIC MOMENTS OF IRON(II), COBALT(II), AND NICKEL(II) COMPLEXES OF 1,10-PHENANTHROLINE AND 2,2'-BIPYRIDYL

Compound	Magnetic moment μ (BM)	Suggested structure	References
[Fe(phen) ₃] ²⁺	~1	6 coord.	51, 126, 212, 231
Fe(phen) ₃ X ₂ (X = Cl, Br, I, N ₃ , OCN, HCO ₂ , NCS, NCS ₂)	5.0-5.3	6 coord.	11, 12, 20, 28, 143, 169, 170
Fe(phen) ₃ X ₂ (X = CN, NCO, NO ₂)	~0	6 coord.	143, 168, 169, 206, 208
Fe(phen)Cl ₂	5.8	tetrahedral	39, 91
Fe(phen)F ₂	4.4	polymeric	170
[Fe(bipy) ₃] ²⁺	~1	6 coord.	46, 212, 231
Fe(bipy) ₃ X ₂ (X = Cl, NCS)	5.1, 5.15	6 coord.	12, 20, 83
Fe(bipy)Cl ₂	5.7	tetrahedral	20, 39, 91
Fe(bipy) ₂ (CN) ₂ · 3H ₂ O	0.6	6 coord.	206, 208
K ₂ [Fe(bipy)(CN) ₄] · 3H ₂ O	0.4	6 coord.	206
[Co(phen) ₃] ²⁺	~4.7	6 coord.	51, 89, 186, 196
Co(phen) ₃ Cl ₂ · 3.5 H ₂ O		4 or 6 coord.	36, 196
Co(phen) ₃ (CN) ₂ · 2H ₂ O	1.8	6 coord.	55, 56
Co(phen) ₂ X ₂ (X = Cl, Br)	5.0, 4.95	4 or 6 coord.	36, 55, 196
Co(phen)(NO ₂) ₂	1.7	square-planar	47, 55
[Co(bipy) ₃] ²⁺	~4.8	6 coord.	3, 46, 133
Co(bipy) ₃ Cl ₂	4.9	6 coord.	155
Co(bipy) ₃ (CN) ₂	3.65	6 coord.	47, 56
Co(bipy) ₂ X ₂ (X = Cl ^a , Br)	4.9-5.1	4 or 6 coord.	132, 155, 182, 250
Co(bipy) ₂ (CN) ₂	1.8	square-planar	47, 56
[Ni(phen) ₃] ²⁺	~3.1	6 coord.	50, 51, 53, 85, 116
Ni(phen) ₃ X ₂ (X = Cl, Br, NCS, ClO ₄)	3.2	6 coord.	116, 193, 210
Ni(phen) ₂ X ₂ (X = Cl, Br)	3.3	4 or 6 coord.	39
Ni(phen)(CN) ₂	1.7	polymeric	205
[Ni(bipy) ₃] ²⁺	~3.1	6 coord.	3, 46, 51, 116, 131
Ni(bipy) ₃ X ₂ (X = Cl, Br, I, NCS)	3.1-3.2	6 coord.	116, 155, 195
Ni(bipy) ₂ X ₂ (X = Cl, Br)	3.3, 3.5	6 coord.	39, 155

^a Exists in at least two modifications.

compounds and suggested that the anomalous magnetic behaviour is due to metal-metal interaction. More recently, König and Madeja¹⁴³ have investigated these compounds and have interpreted the magnetic behaviour in terms of spin state equilibria between almost equi-energetic ⁵T₂ and ¹A₁ states. When X = CN, NCO or NO₂ the stronger field of these ligands, leads to compounds which are spin paired at room temperature.

The bis-ligand bipyridyl compounds are analogous to those of the phenanthroline series. The compound Fe(bipy)₂(NCS)₂ has been shown to exhibit similar anomalous magnetic behaviour to that of the corresponding phenanthroline compound¹².

Steric interaction between the hydrogen atoms of two phenanthroline or bipyridyl molecules in planar coordination leads to increased stability of the *cis*-

over the *trans*-isomer in an octahedral metal complex¹⁶³. It has been suggested that the splitting of an intense band at $\sim 770\text{ cm}^{-1}$, assigned as the in-phase, out of plane C-H bending mode, occurring in the spectra of some rhodium bis(bipyridyl) complexes, may be due to a *cis*-configuration¹⁷³. A similar splitting has been observed for $\text{Fe}(\text{bipy})_2(\text{NCO})_2$ ²⁵. The Mössbauer spectra of $\text{Fe}(\text{phen})_2\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}, \text{NCO}, \text{HCO}_2$) indicate a *cis*-structure for these iron(II) bis-(phenanthroline) complexes⁷⁰. The observed splitting of the C-N stretching mode in $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ and $[\text{Fe}(\text{phen})_2(\text{NCS}_2)_2]$ into two bands separated by $\sim 10\text{ cm}^{-1}$ has been considered to indicate the *cis*-configuration¹⁴³. The complexes $[\text{Fe}(\text{phen})_2(\text{CN})_2]$ and $[\text{Fe}(\text{bipy})_2(\text{CN})_2]$ exhibit appreciable dibasic character and react with acids to yield compounds in which the coordinated cyano group has been protonated^{109, 206, 207}. A similar reaction with dimethyl sulphate yields the complex $[\text{Fe}(\text{phen})_2(\text{CNMe})_2]^{2+}$; its infrared spectrum suggests a *cis*-configuration¹⁰⁹. Reaction of the thiocyanato complex $\text{Fe}(\text{phen})_2(\text{NCS})_2$ with dry hydrogen chloride yields adducts containing approximately four molar equivalents of hydrogen chloride; the evidence suggests that protonation of the thiocyanato groups has not occurred²¹⁰. Boron trifluoride forms bis-adducts with $\text{Fe}(\text{phen})_2(\text{CN})_2$ ²²⁰.

It is usual that there is a stepwise decrease in the affinity of a metal ion for the progressive addition of ligands; however, in the iron(II) phenanthroline and bipyridyl systems, $K_1 \gg K_2$ or $K_2^{23, 156}$. This orbital stabilization, which has been discussed by Irving and Williams¹²⁹, is accompanied by a strong band in the visible absorption spectra, giving rise to the intense red colour of these complexes^{134, 139, 225}.

The behaviour of $[\text{Fe}(\text{phen})_3]^{2+}$ as a reducing agent has been studied^{36, 69, 79, 97, 98, 105}.

With cobalt(II) and nickel(II), both ligands yield tris-complexes which are high spin. Palmer and Piper^{187a} have investigated the polarized crystal spectra of the tris(bipyridyl) complexes of these metals, together with those of iron(II), ruthenium(II), and copper(II). For the nickel(II) and cobalt(II) complexes Dq was found to be 1280 and 1270 cm^{-1} , respectively, whilst for the iron(II) complex, the estimated value of between 1650 and 1900 cm^{-1} indicates a substantial increase in Dq upon spin-pairing. Orgel¹⁸⁵ and Jørgensen¹³⁷ have pointed out that the decrease in the metal-ligand distance which accompanies the transfer of electron density from the e_g to the t_{2g} orbitals should result in an appreciable increase in Dq per electron transferred.

Mono- and bis-chelates of both cobalt(II) and nickel(II) are also known and, in general, these are high spin. However, the complex $\text{Co}(\text{phen})_2(\text{CN})_2 \cdot 2\text{H}_2\text{O}$, like its iron analogue, is spin-paired^{55, 56}. The moment of $\text{Co}(\text{bipy})_2(\text{CN})_2$ has been reported as 3.65 BM⁵⁶.

Several substituted derivatives of 1,10-phenanthroline and 2,2'-bipyridyl have been prepared and their analytical applications and chelating abilities with

* This paper lists many other references to the spectra of these compounds.

TABLE 2

STABILITY CONSTANTS OF IRON(II), COBALT(II), AND NICKEL(II) COMPLEXES OF 2,2'-BIPYRIDYL AND 1,10-PHENANTHROLINE AND ITS DERIVATIVES

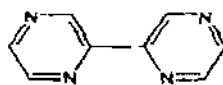
Unless otherwise stated the measurements were made in aqueous solution at 20 or 25°.

Ligand	Iron(II)	Cobalt(II)	Nickel(II)
2,2'-Bipyridyl	K_1 4.43 β_3 17.58 ¹³⁰	K_1 6.06, K_2 5.36, K_3 4.60 ³	K_1 6.80, K_2 6.46, K_3 5.20 ⁶
1,10-Phenanthroline	K_1 5, K_2 9.85 β_3 21.3 ¹¹¹	K_1 7.25, K_2 6.70, K_3 5.95 ²	K_1 8.8, K_2 8.3, K_3 7.7 ³
5-Methyl-1,10-phenanthroline	K_1 6.05 β_3 22.3 ¹⁸	"	"
5-Phenyl-1,10-phenanthroline	" β_3 21.1 ²⁷	"	"
5-Chloro-1,10-phenanthroline	" β_3 19.7 ¹²	"	"
5-Bromo-1,10-phenanthroline	K_1 5.45 β_3 19.7 ¹⁸	"	"
2-Methyl-1,10-phenanthroline	K_1 4.2, K_2 3.7, K_3 2.9 ¹²³	"	"
4,7-Diphenyl-1,10-phenanthroline	" β_3 21.8 ¹⁷⁸	"	"
2,9-Dimethyl-1,10-phenanthroline	"	"	K_1 2.6–2.8 ²²⁸

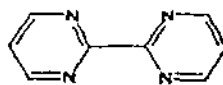
" not measured; ^b in 50% dioxane; ^c in 10% alcohol.

iron(II), cobalt(II), and nickel(II) have been studied^{36, 99, 114, 117, 164, 233, 244}. The presence of substituents in the aromatic rings gives rise to electronic effects with concomitant alteration of the pK values of the ligands. Those complexes in which steric interference also occurs are discussed in the next section. The stability constants of the complexes of iron(II), cobalt(II), and nickel(II), with 2,2'-bipyridyl and 1,10-phenanthroline and its derivatives are listed in Table 2.

Some metal complexes of bipyrazinyl (III; bpz) have been reported and their electronic absorption spectra have been obtained. The complexes [Fe(bpz)₃]-



(III)



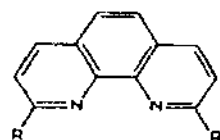
(IV)

(ClO₄)₂ (μ , 0 BM), [Co(bpz)₃](ClO₄)₂ (μ , 4.75 BM), Co(bpz)₂Br₂ (μ , 4.9 BM), [Ni(bpz)₃](ClO₄)₂ (μ , 3.3 BM) are similar to their 2,2'-bipyridyl analogues; the tris-chelated iron complex is dark red. Addition compounds of uncertain structure containing two and three metal atoms per ligand—*e.g.*, Ni₂bpzCl₄—were also obtained^{1, 30}. Spectral data show that 2,2'-bipyrimidinyl (IV) also forms a red tris-chelated complex with iron(II) but its stability (β_3 , 7.5) is much less than that of the 2,2'-bipyridyl complex³¹.

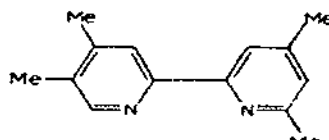
(ii) *Sterically hindered heterocyclic diimines*.—Although substitution of methyl groups in the 2,9-positions of 1,10-phenanthroline or the 6,6'-positions of 2,2'-bipyridyl is expected to raise the base strength of the donor nitrogens, it has been well established that in many cases, these ligands coordinate less strongly

than the parent ligands^{45,125,127}. An increase in basicity of the donor atoms will normally give rise to more stable metal chelates²⁷; however, lower stability of the metal chelates of these substituted ligands is due to steric interference^{91,125,127} which occurs in certain configurations⁹¹.

The analytical applications of these two ligands have been investigated^{36,107,118,127,128,224} and their failure to produce intense red colorations with ferrous salts is due to steric hindrance which inhibits the formation of tris-chelated complexes^{57,121,125,162,165}. Nevertheless, 2,9-dimethyl-1,10-phenanthroline (V; $R = R' = \text{Me}$) forms both mono- and bis-chelated complexes with iron(II)^{91,104} and mono-complexes with cobalt(II) and nickel(II) are known¹⁰⁶. Stable mono-complexes with iron(II) and stable mono- and bis-complexes with cobalt(II) and nickel(II) are known with 4,5,4',6'-tetramethyl-2,2'-bipyridyl (VI)¹⁰⁸. All these complexes are spin-free.



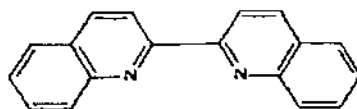
(V)



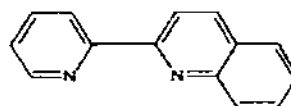
(VI)

2-Methyl-1,10-phenanthroline (V; $R = \text{Me}$; $R' = \text{H}$) is a stronger base ($\text{p}K_a = 5.42$) than 1,10-phenanthroline ($\text{p}K_a = 4.92$) and forms tris-complexes with iron(II) and nickel(II)¹⁹². The orange tris-chelated iron compound is much less stable than the corresponding red phenanthroline complex (see Table 2). In contrast to the behaviour with phenanthroline, the reaction of ferrous ion with the 2-methyl derivative follows the normal stability pattern with the successive stability constants decreasing in the order $K_1 > K_2 > K_3$ ^{125,127}. It is significant that the tris-complex is spin-free at room temperature¹²⁷; however, Goodwin and Sylva¹⁰⁴ have recently found that at lower temperatures a colour change from orange through red to deep purple occurs and the compound approaches the spin-paired state.

The behaviour with iron(II) and other transition metals of a number of sterically hindered bidentates related to bipyridyl has been investigated^{36,38,45,121,122,142,223}. Except in the case of 2,2'-biquinolyl (VII) and 2,2'(pyridyl)-quinoline (VIII) no systematic study of their coordination chemistry has been made⁶¹. Although high-spin complexes of iron(II), cobalt(II), and nickel(II) with 2,2'-biquinolyl have been prepared⁶¹ no tris-chelated complexes are known.

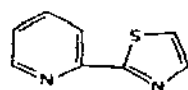


(VII)

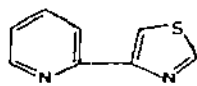


(VIII)

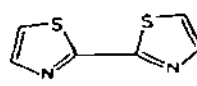
(iii) *Heterocyclic diimines containing five-membered aromatic rings.*—It has been pointed out that heterocyclic nitrogen atoms in five-membered rings are less favourably positioned for coordination to a metal ion than are the donor nitrogens in, *e.g.*, 2,2'-bipyridyl^{62, 78, 103}. In agreement with this, 2-(2-pyridyl)thiazole (IX) and 4-(2-pyridyl)thiazole (X) form less intensely coloured solutions with iron(II) than does 1,10-phenanthroline or 2,2'-bipyridyl¹⁴². Although 2,2'-bithiazolyl (XI), 4,4'-bithiazolyl (XII) and pyrido-(2,3)-benzothiazole (XIII) are reported to coordinate poorly to iron(II), it is possible to isolate complexes of the type $\text{Fe}(\text{thiaz})_2\text{Br}_2 \cdot 2\text{H}_2\text{O}$ ^{76, 78} (thiaz = XI, XII, or XIII); however, no tris-chelated complex has been isolated. Complexes of these ligands with nickel(II) and other bivalent metals have also been prepared⁷⁷.



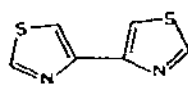
(IX)



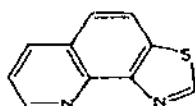
(X)



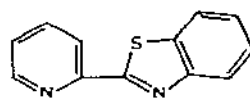
(XI)



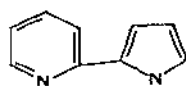
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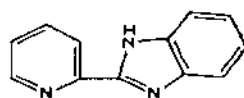
(XIII)



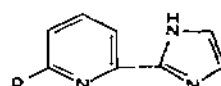
(XIV)



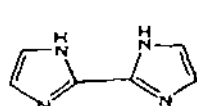
(XV)



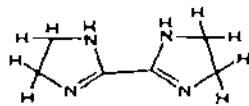
(XVI)



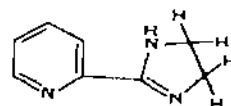
(XVII)



(XVIII)



(XIX)



(XX)

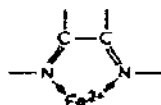
2-(2-Pyridyl)benzothiazole (XIV, pbth) which is closely related to (IX), yields a bright red solution with iron(II); however, several attempts at isolation of the complex as its perchlorate salt were unsuccessful. This ligand forms complexes with several bivalent ions¹⁵⁹. The magnetic moment ($\mu = 3.36 \text{ BM}$) of $\text{Ni}(\text{pbth})(\text{CH}_3\text{CO}_2)_2(\text{H}_2\text{O})_2$ ¹⁵⁹ is above the upper limit of the range (2.9–3.3 BM) generally found for octahedral nickel(II) and is within the range (3.3–3.5 BM) of many tetragonal nickel(II) complexes¹⁵⁷.

By loss of a proton from the pyrrole nitrogen, 2-(2-pyridyl)pyrrole (XV) forms a red neutral bisligand complex with iron(II) which is unstable in air and

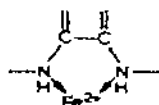
is rapidly oxidized to an iron(III) complex⁷²; a bis-ligand neutral nickel(II) complex is also known⁷⁴

Freiser *et al.*^{113,242} have studied the infrared spectra of some metal chelates of 2-(2-pyridyl)benzimidazole (XVI, pbim) which forms the metal chelates $[M(pbim)_3]X_2$ ($M = Ni, Co$; $X = Br, I, ClO_4$). Coordination with a metal ion increases the acidity of the imino hydrogen of the imidazole group in (XVI) and this increase bears some relationship to the particular metal used¹¹². Lions *et al.*⁶² prepared the complexes $M(pbim)_2Cl_2$ ($M = Co, Ni$) and $M(pbim)_3Cl_2$ ($M = Fe, Ni$). Although no moment was given for the red iron complex, it is most likely spin-free as is the analogous red complex with 2-(2'-pyridyl)imidazole (XVII; $R = H$) which has a moment of 5.42 BM. Bis- and tris-ligand cationic complexes of (XVII; $R = H$) with cobalt(II) and nickel(II) have also been reported^{62,120}. In general, these are spin-free; however, it is surprising that the pale orange complex $[Co(chelH)_2](ClO_4)_2 \cdot 2H_2O$ ($chelH = 2-(2'-pyridyl)imidazole$) is spin-paired with a moment of 2.11 BM. Substitution of a methyl group in the 6-position of (XVI) completely inhibits the isolation of complexes with group VIII metals, yet complexes were obtained with copper(II), silver(I), and cadmium(II)⁶². The cations of some of the iron(II), cobalt(II), and nickel(II) complexes of (XVII; $R = H$) can be deprotonated^{62,120} to yield the neutral 2-(2'-pyridyl)-imidazolato complexes, *viz.*, $Fe(chel)_2 \cdot 2H_2O$ ($\mu = 5.26$ BM), $Co(chel)_2 \cdot 2H_2O$ ($\mu = 2.06$ BM), and $Ni(chel)_2 \cdot H_2O$ ($\mu = 3.15$ BM)⁶². The greenish-yellow bis[2-(2'-pyridyl)benzimidazolato]nickel complex has also been obtained by a similar procedure⁶².

2,2'-Biimidazolyl (XVIII) forms tris-chelated complexes with iron(II), cobalt(II), and nickel(II). The yellow colour of the iron complex is unusual and the authors suggest that this ligand may not chelate strongly to $Fe(II)$ ¹²⁰. However, the yellow colour may arise from the ligand's being coordinated through the two $-NH$ groups, as the chromophore(XXI) is absent in the structure (XXII). In its deprotonated form, (XVII) forms a neutral, bis-ligand complex with nickel(II),



(XXI)



(XXII)

which is brown, and an impure, purple, bis-ligand cobalt(II) complex. Iron, cobalt, and nickel complexes of the related ligand, 2,2'-bi-2-imidazoline (XIX) have also been reported and there is evidence to suggest that coordination may occur through the secondary nitrogens of the imidazoline rings²⁴³. Metal complexes of another ligand containing an imidazoline ring, namely 2-(2-pyridyl)imidazoline (XX), have also been investigated^{111,112,113,242}. However, again there is evidence

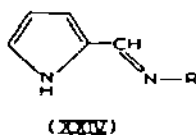
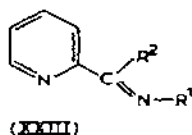
that the α -diimine structure in this ligand is not involved in chelation¹⁵⁴. It should be pointed out that (XIX) and (XX) do not contain aromatic five-membered rings.

C. LIGANDS CONTAINING A HETEROCYCLIC NITROGEN AND AN ALIPHATIC IMINE AS DONORS

Ligands containing functional groups of both the cyclic aromatic amine type and the imine type are known. This class of ligand is illustrated by 2-pyridinal-methylimine (XXIII; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$) and provides a structural link between the aromatic diimines such as 2,2'-bipyridyl and the aliphatic α -diimines which are discussed in the following section.

The very stable tris-ligand complexes of (XXIII; $\text{R}^1 = \text{Me}$; $\text{R}^2 = \text{H}$) with iron(II)^{8,49,86} and nickel(II)^{86,198} exhibit similar magnetic behaviour to that of the analogous compounds of bipyridyl and phenanthroline; however, the room-temperature moment of the tris-cobalt(II) complex⁸⁶ is slightly below the range normally accepted for high-spin octahedral cobalt(II)¹⁸¹. Stoufer *et al.*²²⁹ have shown that this compound becomes spin-paired on cooling and this behaviour has been explained in terms of the existence of a Boltzmann distribution between high- and low-spin states. The infrared spectra of the tris-ligand iron(II), cobalt(II), and nickel(II) complexes²³⁰ and the electron paramagnetic resonance spectrum of the cobalt complex²¹³ have been reported.

Some metal complexes of (XXIII) in which $\text{R}^2 = \text{H}$; $\text{R}^1 =$ various straight chain alkyl groups⁸, Ph ¹⁰, $i\text{-Pr}$ ¹⁹⁸, CH_2Ph ¹⁹⁸, $\text{C}_6\text{H}_4 \cdot \text{CH}_3$ ^{10,227}, are also known. The latter ligand, 2-pyridinal-*p*-tolylimine (pti) forms the complexes $\text{M}(\text{pti})_2\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Fe}$, Co , Ni ; $\text{X} = \text{Cl}$, I or ClO_4) and $\text{M}(\text{pti})_3\text{I}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Fe}$, Ni) which, except for the tris-ligand iron(II) complex, are all high-spin. The low moment (0.8 BM) of the iron complex is typical of the values found for many



similar low-spin iron complexes^{88,160}. The other ligands also form similar tris-chelated iron complexes.

Krumholz¹⁵¹ has shown that the 2-pyridyl ketoimines (XXIII; $\text{R}^1 = \text{H}$, aliphatic or aromatic groups; $\text{R}^2 = \text{Me}$, Ph) also form tris-ligand iron(II) complexes.

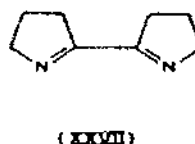
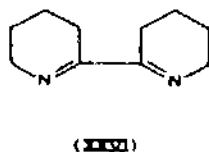
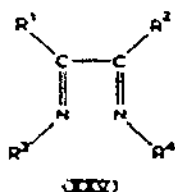
By loss of a proton from the pyrrole nitrogen the pyrrolidine imines (XXIV; $\text{R} = \text{H}$ ¹⁹⁴ or alkyl group^{59,74,119,234}) form a series of neutral complexes with bivalent and trivalent metals. Holm *et al.*¹¹⁹ have studied the solution equilibria of some of the bis(pyrrole-2-aldimino)metal(II) complexes. The bis-ligand cobalt(II) complex of (XXIV; $\text{R} = t\text{-Bu}$) has a moment in the solid state of 4.67 BM and

in toluene solution of 4.74 BM and this, together with X-ray evidence, indicates a tetrahedral stereochemistry. The nickel(II) complex (μ , 3.30 BM) is pseudo-tetrahedral. In chloroform solution the complexes with sec-alkyl groups, such as *i*-Pr, are involved in a configurational equilibrium between planar and pseudo-tetrahedral forms. In the planar form of such complexes it is apparent that a sufficiently bulky alkyl group will suffer substantial steric interaction with the hydrogen attached to the 5-position of the pyrrole ring. This has been postulated to destabilize the planar form such that the free energy difference between the two configurations is reduced sufficiently to allow population of both configurations at room temperature. When R is a small alkyl group such as *n*-Pr the diamagnetism of the nickel(II) compounds in the solid state and in solution demonstrates the essential planarity of these complexes.

D. NON-AROMATIC α -DIIMINES

It has been well established^{49, 152, 153} that the octahedral iron(II) complexes of bidentate α -diimine ligands such as glyoxal-bis(methylimine) (gmi; XXV; R¹, R² = H; R³, R⁴ = Me), together with aromatic diimines such as 2,2'-bipyridyl and those ligands containing an aromatic imine and a single imine nitrogen such as 2-pyridinalmethylimine (XXIII; R¹ = Me, R² = H), constitute a single class of compound with similar spectral and magnetic properties. The infrared spectra of all these compounds show displacements of the $>C=N-$ band towards longer wavelengths corresponding to linkages intermediate between single and double bonds^{24, 49}.

Condensation of methylamine with glyoxal in the presence of iron(II) leads to the isolation of the dark reddish-purple spin-paired complex $Fe(gmi)_3I_2 \cdot 3H_2O$ which is remarkably stable to acid^{49, 152}. The stability of the α -diimineiron(II) chelate ring is demonstrated by the fact that, in the absence of iron(II), it is not possible to isolate the free Schiff's base, only polymeric condensation products being obtained^{86, 87}. The infrared spectra of the tris-chelated iron(II) and nickel(II) complexes of glyoxal-bismethylimine have been obtained and Nakamoto has carried out a normal coordinate analysis for the iron complex^{177, 178}. Substitution of biacetyl, methylglyoxal, phenylglyoxal, or 1,2-cyclohexanedione for glyoxal also gives similar ferrous complexes. However, replacement of *N*-methyl by *N*-phenyl or *N*-ethyl leads to steric interference and no tris-ligand complexes are obtained¹⁵².



The alicyclic Schiff bases 2,2'-bipiperidine (XXVI) and 2,2'-bipyrroleine (XXVII) also have been reported to form red tris-ligand iron(II) complexes^{24,152}.

Nickel(II) and cobalt(II) complexes of (XXV; $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4$ = various alkyl or aryl groups) have also been investigated^{79,198}. Spectral studies on the high-spin, tris[biacetylbis(methylimine)]-nickel(II) complex show that the ligand-field strength of this α -diimine is comparable to those of 2,2'-bipyridyl and 1,10-phenanthroline¹⁹⁸. In contrast to the analogous complexes of these last two ligands, the tris-ligand cobalt(II) complex of biacetylbis(methylimine) has a room temperature moment (μ , 2.91 BM) which is intermediate between the high- and low-spin values. This value decreases to 1.91 BM at 100 °K and then falls within the range expected for low-spin octahedral cobalt(II) complexes. This behaviour has been explained in terms of an equilibrium between the high- and low-spin states²²⁹.

E. HYDRAZONES CONTAINING THE GROUP $\text{—N}=\overset{\text{I}}{\text{C}}\text{—}\overset{\text{I}}{\text{C}}=\text{N—}$

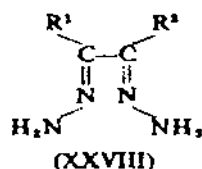
2-Pyridinalhydrazone (pah; XXIII; $\text{R}^2 = \text{H}$, $\text{R}^1 = \text{NH}_2$) and biacetylhydrazone (bdh; XXV; $\text{R}^1, \text{R}^2 = \text{Me}$, $\text{R}^3, \text{R}^4 = \text{NH}_2$) form tris-complexes with bivalent iron, cobalt, and nickel similar to the analogous complexes of bipyridyl^{49,227}. The tris-complex $[\text{Co}(\text{pah})_3]\text{I}_2$ has a moment of 4.71 BM at 300 °K and 4.06 BM at 100 °K ($\theta = 19^\circ$). The moment of the analogous complex $[\text{Co}(\text{bdh})_3]\text{I}_2$ decreases from 4.20 BM at 300 °K to 3.35 BM at 100 °K ($\theta = 142^\circ$)²²⁹.

The complexing ability of several *N*-substituted derivatives of 2-pyridinalhydrazones has been studied and in some cases the results obtained were somewhat different to those obtained with the unsubstituted ligand¹⁹⁷. The ligands (XXIII; $\text{R}^2 = \text{H}$, $\text{R}^1 = \text{NHMe}$, NMe_2) form stable tris-complexes with cobalt(II) and nickel(II) and also less stable bis-complexes which readily disproportionate in water to the tris-complexes. All these complexes have magnetic moments which indicate spin-free octahedral structures. The greater stability of the tris-complex of iron(II) is further demonstrated by the fact that these two ligands yield only tris-complexes with iron, regardless of the metal-to-ligand ratio used in their preparation. The moment of the octahedral iron(II) 2-pyridinalmethylhydrazone complex follows the usual pattern of such complexes in that it is spin-paired. In contrast, the tris-ligand iron(II) complex of 2-pyridinaldimethylhydrazone is spin-free with a moment of 5.45 BM. This is the first reported example of a tris-complex from the pyridinalimine or pyridinalhydrazone class in which the ferrous ion is not spin-paired. With this ligand the presence of *N*-methyl groups, together with the very definite steric requirements of the hydrazone grouping when coordinated, leads to a diminution in donor capacity which has been ascribed to inter-ligand repulsion. If such is the case, the metal-nitrogen bond distance would be lengthened in comparison to that in the 2-pyridinalhydrazone complex and such a forced

extension of the bond distance will result in a decreased ligand-field strength¹⁹⁸.

It is significant that the *N*-phenyl substituted ligands (XXIII; $R^1 = H$; $R^2 = NHPH, NPh_2$) form only bis-chelated complexes with iron(II), cobalt(II), and nickel(II) and the failure to isolate tris-complexes has also been ascribed to inter-ligand crowding in the octahedral configuration¹⁹⁸.

The iron(II), cobalt(II), and nickel(II) complexes of a number of related α -dihydrazones, namely, biacetyldihydrazone (XXVIII; $R^1, R^2 = Me$), benzildihydrazone (XXVIII; $R^1, R^2 = Ph$), pyruvaldihydrazone (XXVIII; $R^1 = H$; $R^2 = Me$), glyoxaldihydrazone (XXVIII; $R^1, R^2 = H$), have been investigated^{90, 227}.



Tris-ligand ferrous complexes are formed with the biacetyl-, benzil-, and glyoxal-dihydrazones and are low-spin with moments of 0.62, 1.29 and 1.11 BM, respectively. The dichlorobis-ligand complexes of pyruval- and glyoxal-dihydrazone have moments of 2.90 BM ($\theta = 4^\circ$) and 3.32 BM ($\theta = 8^\circ$), respectively. It has been suggested that the magnetic properties of these two complexes are consistent with the coordination of two bidentate ligands in a plane about the metal ion with the chloride ions lying above and below this plane in such a manner that a significant tetragonal distortion results. The configurational limit of such a distortion is a square-plane and the moments of these two compounds correspond rather closely to the spin-only value of two unpaired electrons (2.83 BM) expected for a low-spin planar iron(II) complex.

All four dihydrazones form tris-complexes with cobalt(II). The moment of the benzildihydrazone complex ($\mu = 4.93$ BM) is within the range expected for high-spin octahedral cobalt(II), whereas the low moments of the other three complexes ($\mu = 3.1$ – 4.26 BM), together with the fact that they exhibit anomalous Curie-Weiss behaviour, is suggested to arise from the presence of equilibrium mixtures of high- and low-spin species. Biacetyldihydrazone forms a dichloro-bis-ligand complex with cobalt(II) ($\mu = 4.91$ BM).

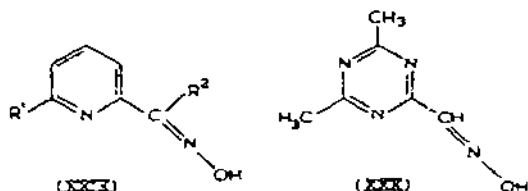
Biacetyl-, pyruval-, and glyoxal-dihydrazones form high-spin ($\mu = 3.0$ – 3.1 BM) bis- and tris-complexes with nickel, whereas benzildihydrazone gives only a bis-ligand complex.

From a study of the complexes formed and their electronic and infrared spectra, it has been deduced that intra-ligand repulsions occur between R^1 and R^2 when these ligands are coordinated. The data are consistent with a decreasing intra-ligand repulsion in the order: biacetyldihydrazone > benzildihydrazone > pyruvaldihydrazone > glyoxaldihydrazone⁹⁰. The infrared spectra of the complexes

of biacetyldihydrazone indicate strong multiple bonding in the diamagnetic iron tris-complex, whereas the bonding is weaker in the paramagnetic cobalt and nickel complexes²²⁸.

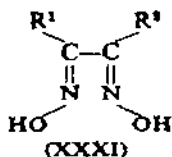
F. OXIMES CONTAINING THE GROUP $-\text{N}=\overset{\text{I}}{\underset{\text{I}}{\text{C}}}-\text{C}=\text{N}-$

2-Pyridinaldoxime (paoH; XXIX; $\text{R}^1, \text{R}^2 = \text{H}$), like the related ligands (XXIII) discussed above, forms high-spin nickel(II) chelates of the type $\text{Ni}(\text{paoH})_2\text{Cl}_2$ and $\text{Ni}(\text{paoH})_2\text{I}_2$ ^{145,146,148}. The high-spin complexes $\text{Ni}(\text{pao})-(\text{paoH})\text{I}$ and $\text{Ni}(\text{pao})_2$ have also been prepared^{145,146} and the stabilities of some iron(II), cobalt(II), and nickel(II) complexes of this ligand have been studied^{33,40,110,130}. The infrared spectra of complexes of this oxime have been determined^{147,208} and the behaviour of some complexes with organic reagents, such as acetyl chloride, has been investigated^{99,149}. The reactions of methyl- α -pyridyl ketoxime (XXIX; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Me}$) with nickel(II)⁷³ and phenyl- α -pyridyl ketoxime (XXIX; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}$) with iron(II) and cobalt(II)²¹⁷ have also been studied.



6-Methyl-2-pyridinaldoxime (XXIX; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{H}$) and 4,6-dimethyl-2-pyridinaldoxime (XXX) readily yield high-spin dihalogeno bis-ligand complexes with nickel. Apparently the steric effect of the methyl groups inhibits the formation of stable tris-ligand complexes¹⁴⁸.

Various aspects of the coordination chemistry of *vic*-dioximes have been reviewed^{14,66,71,115}. The best-known *vic*-dioxime is dimethylglyoxime (dmgH; XXXI; $\text{R}^1, \text{R}^2 = \text{Me}$).



The insoluble red complex $\text{Ni}(\text{dmg})_2$ is formed under alkaline conditions. The crystal structure of this compound has been determined and the square-planar molecules are stacked one above the other such that the nickel atoms lie in chains which extend throughout the crystal^{101,248}. The analogous palla-

dium^{188,248} and platinum⁹³ compounds have been shown to be isomorphous with the nickel compound. The close intermetallic distances in these compounds have been rationalized in terms of metal-metal bonds and several workers have attempted to investigate the nature of these bonds^{15,16,17,201,202,249}. However, other investigators have suggested that metal-metal bonds, as originally proposed, may not be present in these compounds and the unusual structure of these complexes may in fact be mainly due to favourable crystal packing^{22,123,174,251}.

Binary metal dimethylglyoximates containing nickel, palladium, or platinum have been prepared^{22,161} and their unit-cell dimensions have been obtained by X-ray diffraction¹⁶¹. These binary complexes are isomorphous with the simple dimethylglyoximates of nickel, palladium, and platinum and have short metal-metal distances. The X-ray and spectral data show that the binary metal complexes are not mixed crystals consisting of domains of the individual metal glyoximates but are homogeneous in that both metal dimethylglyoximate molecules are stacked in a statistically ordered manner¹⁶¹.

The behaviour of $\text{Ni}(\text{dmg})_2$ towards oxidizing agents has been studied^{6,13,34,80,81,176,180,183,221}. The complexes of iron(II)^{41,42,43,52,136,237} and cobalt(II)^{41,42,43,44,54,140} have been investigated. Both the iron and cobalt complexes are low-spin and the Mössbauer spectrum of the iron complex indicates the presence of metal \rightarrow ligand π -bonding⁴¹. The infrared spectra of these and other dimethylglyoxime complexes have been obtained^{29,30,43,96,100,203}. The data for the complexes $\text{M}(\text{dmg})_2$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}, \text{Cu}, \text{Co}$) are consistent with the presence of hydrogen bridges between the ligands.

Burger *et al.*^{42,43} have discussed the importance of the hydrogen bridges and also of the effect of metal-to-ligand π -bonds in the stabilization of dioxime complexes of several transition metals. As an extension of this study^{199,200}, these workers prepared cobalt(II), nickel(II), and copper(II) complexes of acetylacetonedioxime and found that these complexes are less stable than the corresponding compounds of dimethylglyoxime. The stability decrease is attributed to firstly, the changed "chelate effect" and secondly, the lack of a conjugated system in the acetylacetonedioxime complexes. However, it is pointed out that the stability decrease is compensated in part by the formation of stronger H-bridges. Metal chelates of this ligand have also been investigated by other workers^{26,232}. Charles and Freiser⁶⁰ have prepared metal complexes of dimethylglyoxime monomethyl ether in order to investigate the changes that occur in these complexes when no hydrogen bonding can occur. However, the situation in this case is somewhat complicated by the presence of the methyl groups which may cause changes in the donor capacity of the nitrogens due to electronic effects or may even cause steric hindrance.

Acylation of the coordinated oxime group in $\text{Ni}(\text{dmg})_2$ has been reported²¹⁹, but this reaction was later disputed¹⁴⁹. The interaction of this complex with organic reactants has been investigated^{19,48,84,235}. The reaction with the boron

halides is particularly interesting and results in each of the oxime protons being replaced by $-(BX_2)-$ bridges to yield macrocyclic compounds. The stable complex with $-(BF_2)-$ bridges forms adducts with nitrogen bases in which the nickel ion is spin-paired and has a coordination number of six²¹⁵.

The diamagnetism of Ni(dmg)₂ indicates that the ligand, in its deprotonated form, exerts a strong field which is undoubtedly related to the presence of H-bridges and also to the higher polarizabilities of the nitrogen atoms in the charged ligand. If Ni(dmg)₂ is treated with hydrochloric acid, the high-spin bluish-grey complex Ni(dmgH)₂Cl₂ is formed^{189,219,236}; the visible spectrum of this complex indicates that it is octahedral³⁵ and thus similar to the nickel complexes of the other ligands discussed in previous sections of this review. The mono-ligand complex Ni(dmgH)Cl₂ ($\mu = 3.2$ BM) has been assigned a polymeric structure consisting of octahedra joined by chloro-bridges^{68,149,189}.

Treatment of Ni(dmg)₂, suspended in methanol, with hydrochloric or hydrobromic acid yields solutions of the corresponding high-spin complexes of protonated dimethylglyoxime; the addition of copper or cobalt salts results in ligand-exchange and solid complexes of the latter metals can be isolated¹⁵⁹.

Complexes of iron(II), cobalt(II), and nickel(II) with other *vic*-dioximes (XXXI; R¹, R² = alkyl, aryl) have been investigated^{15,17,26,42,52,58,82,92,94,135,190,204,218,238,239}. The stability constants of the complexes of some of these ligands are listed in Table 3.

TABLE 3

STABILITY CONSTANTS OF IRON(II), COBALT(II), AND NICKEL(II) COMPLEXES OF α -DIOXIMES

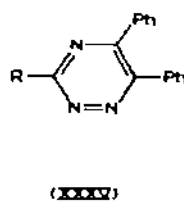
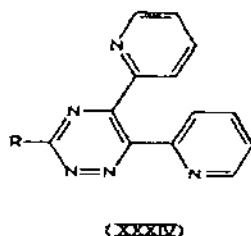
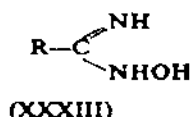
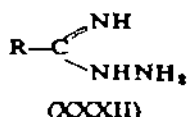
Ligand	Iron(II)	Cobalt(II)	Nickel(II)
Diaminoglyoxime	b	b	^a K ₁ 2.69 ^a , K ₂ 4.70 ^b , K ₃ 7.33 ^{92,135}
Methylglyoxime	b	K ₁ 9.5, K ₂ 9.1 ³²	K ₁ 9.6, K ₂ 9.2 ³²
Dimethylglyoxime	β_2 7.25 ²³³	K ₁ 9.80, K ₂ 9.14 ⁹⁵	K ₁ 11.16, K ₂ 10.54 ⁶⁰
Dimethylglyoxime <i>O</i> -methyl ether	b	K ₁ 10.00, K ₂ 7.1 ⁹⁵	K ₁ 6.38, K ₂ 5.69 ⁶⁰
Ethylmethylglyoxime	b	K ₁ 12.86 ³²	K ₁ 11.5, K ₂ 11.0 ³²
Cyclohexanedione-1,2-dioxime (nioxime)	b	K ₁ 13.0, K ₂ 12.5 ¹⁹¹	b
Phenylglyoxime	b	K ₁ 10.3, K ₂ 9.0 ¹⁹¹	K ₁ 9.9, K ₂ 9.4 ¹⁹¹
<i>p</i> -Methoxyphenylglyoxime	b	K ₁ 9.3, K ₂ 8.6 ¹⁹¹	K ₁ 9.1, K ₂ 8.6 ¹⁹¹
Benzil- α -dioxime	b	K ₁ 11.2, K ₂ 8.3 ¹⁹¹	b
α -Furyl dioxime	b	K ₁ 9.7, K ₂ 8.5 ¹⁹¹	K ₁ 8.4, K ₂ 6.3 ¹⁹¹

^a in aqueous solution; all other measurements were made in 50% dioxane at 25°; ^b not measured.

G. OTHER LIGANDS

Schilt²⁰⁹ has investigated the analytical applications of the iron(II) and cobalt(II) complexes of hydrazidines (XXXII), amidoximes (XXXIII), and 3-substituted-5,6-bis(2-pyridyl)-1,2,4-triazines (XXXIV), and 3-substituted-5,6-diphe-

nyl-1,2,4-triazines (XXXV) (R = 2-pyridyl, 4-methyl-2-pyridyl, 4-ethyl-2-pyridyl, 4-phenyl-2-pyridyl, 2-quinolyl, 2-pyrimidyl, or 2-thiazolyl).



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