

Co(II) and Ni(II) Complexes of Linear Tridentate Nitrogenous Ligands

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The mono-ligand complexes of some linear tridentate nitrogenous ligands with nickel(II) and cobalt(II) salts are described. The compounds of formula $[\text{Ni}(\text{ligand})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ or NCS) appear to be bridged octahedral compounds on the basis of electronic and infrared spectral measurements. On the other hand, spectral results indicate that the similar compounds of cobalt(II), are monomeric five-coordinate species.

Magnetic data is reported for the compounds described, and details are given of infrared spectra for the pyridine ring vibration region, which indicate that in all cases the ligands act in a tridentate capacity.

Introduction

Extensive reviews of five-coordinate complexes of transition metals have been published [1, 2]. Detailed studies of five-coordinate complexes of cobalt(II) and nickel(II) have been made, and spectral characteristics of such complexes have been correlated with X-ray structure determinations. In this paper we report (i) the preparation of a series of cobalt(II) and nickel(II) complexes with linear tridentate nitrogenous ligands (NNN) of stoichiometry $[\text{M}(\text{NNN})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ or NCS), and (ii) the physical studies that have been carried out to assign the stereochemistry of these complexes.

This work has been undertaken to produce compounds of known stereochemistry, which can be compared with compounds of the type $[\text{Mn}(\text{NNN})\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ or NCS) in an attempt to extend the range of known five-coordinate manganese(II) compounds. The chemistry of five-coordinate manganese(II) complexes is not well documented; the electronic spectra being of little use in determining the stereochemistry. While some crystal structure determinations have been performed on five-coordinate manganese(II) complexes, most structural assignments have been based on either a comparison of X-ray powder photographs [4–9], or X-ray single crystal photographs [4, 10, 11], with those of other transition metal complexes of the

TABLE I. Tridentate Ligands^a.

Ligand No.	Formula	Substituents			Reference
		R ₁	R ₂	R ₃	
1a	I	CH ₃	H	H	22
1b	I	H	CH ₃	H	22
1c	I	H	H	CH ₃	22
IIa	II	H	H	–	30
IIb	II	CH ₃	H	–	–
IIc	II	H	CH ₃	–	–
IIIa	III	H	H	–	–
IIIb	III	H	CH ₃	–	–
IIIc	III	CH ₃	H	–	–
IVa	IV	H	H	–	31
IVb	IV	H	CH ₃	–	32

^aLigands VII, VIII and X shown in formulae. Ligands V, VI and IX, from which Mn(II) compounds were prepared [14], were not used in this study. However, the ligand numbering system has been kept common to both papers.

same ligand, or by infra-red studies of selected compounds containing thiocyanato groups [4, 12, 13].

The $[\text{Mn}(\text{NNN})\text{X}_2]$ compounds studied are reported in a following publication [14].

The ligands used in the preparation of cobalt(II) and nickel(II) complexes are shown in Table I. These ligands were prepared by the condensation of the appropriate aldehyde or ketone with the required hydrazine or amine.

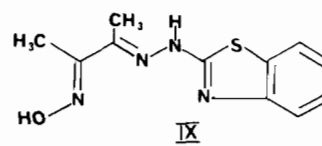
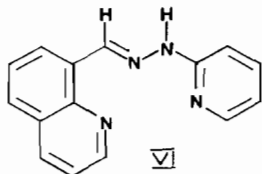
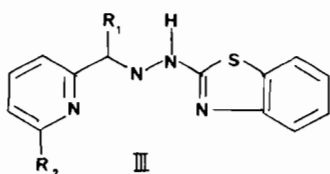
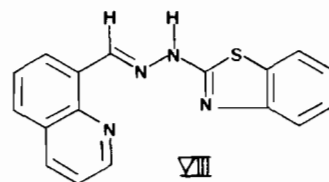
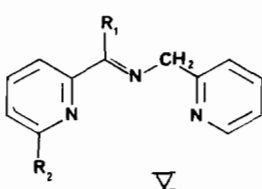
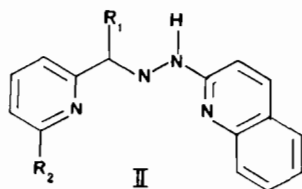
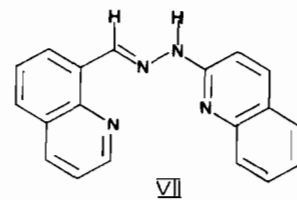
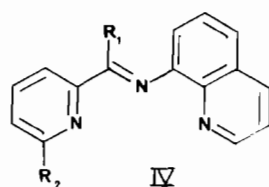
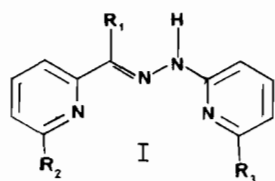
Nickel(II) Complexes

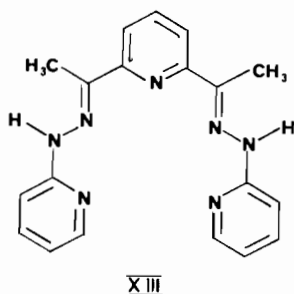
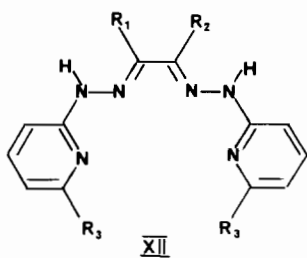
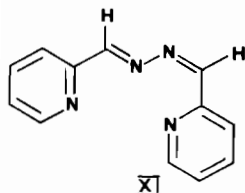
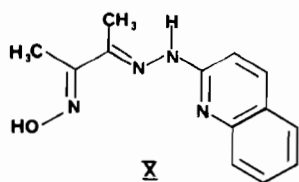
Complexes of nickel(II) are of the type $\text{Ni}(\text{NNN})\text{X}_2$ where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$ (Table II). These complexes are generally pale green or brown in colour. They are soluble, with difficulty, in polar organic solvents such as nitrobenzene without undergoing substantial decomposition. Magnetic moments indicate that the complexes are high spin.

Molar conductivities indicate that the complexes are non-electrolytes in nitrobenzene. Conductivities which appear to be high (up to 5 r.o.) are probably

TABLE II. Nickel(II) Complexes of NNN Ligands.

Complex		Analysis (%)				Prepn. (Method)	μ_{eff} (B.M.)
		C	H	N	Ni		
Ni(lig Ia)Cl ₂	Found	42.2	3.6	16.4	17.1	A	3.23
	Calc.	42.1	3.5	16.4	17.2		
Ni(lig Ib)Cl ₂	Found	42.3	3.6		17.2	C	3.32
	Calc.	42.1	3.5		17.2		
Ni(lig Ib)Br ₂	Found	33.0	2.9	12.5	13.8	D	3.25
	Calc.	33.4	2.8	13.0	13.7		
Ni(lig Ib)I ₂ ·H ₂ O	Found	26.7	2.7	10.0	10.8	D	3.18
	Calc.	26.5	2.6	10.3	10.9		
Ni(lig Ic)Cl ₂	Found	41.9	3.7	16.2	17.0	A	3.12
	Calc.	42.1	3.5	16.4	17.2		
Ni(lig IIa)Cl ₂	Found	47.3	3.5	14.2	15.5	A	3.07
	Calc.	47.7	3.2	14.8	15.5		
Ni(lig IIb)Cl ₂	Found	48.3	3.8	13.6	14.7	B	—
	Calc.	49.0	3.6	14.3	15.0		
Ni(lig IIc)Br ₂	Found	39.9	3.0	11.4	12.1	D	3.18
	Calc.	39.9	2.9	11.7	12.2		
Ni(lig IIc)(NCS) ₂	Found	50.6	3.4	18.5	13.2	D	3.43
	Calc.	49.5	3.2	19.2	13.4		
Ni(lig IIIb)(NCS) ₂	Found	43.3	2.9	18.2	13.1	D	3.22
	Calc.	43.4	2.7	19.0	13.3		
Ni(lig IIIc)Cl ₂	Found	42.2	3.2	14.1	14.5	B	3.21
	Calc.	42.2	3.0	14.1	14.8		
Ni(lig IVa)Cl ₂	Found	49.3	3.3	11.3	15.8	B	3.22
	Calc.	49.6	3.0	11.6	16.2		
Ni(lig IVb)Cl ₂ ·H ₂ O	Found	48.5	3.8	10.7	14.5	B	3.27
	Calc.	48.6	3.8	10.6	14.9		
Ni(lig VII)Cl ₂ ·H ₂ O	Found	50.9	3.4		13.2	C	3.22
	Calc.	51.1	3.6		13.2		





associated with slight decomposition of the complexes in solution. This decomposition may be attributed to the prolonged heating near the boiling point of nitrobenzene which is required to dissolve the complex.

Electronic spectra have been measured in the solid state in the range 11.8–23.3 kK. Intense bands in the region 21–23 kK are presumably due to charge transfer bands. In this region d–d bands may appear as shoulders.

Infra-red spectra have been measured in the range 4000–250 cm^{-1} . Absorption peaks in both the spectra of ligands and metal complexes are numerous and meaningful interpretation is difficult. However, the spectra have been used (a) to detect the presence of solvent coordination; (b) to distinguish between monomeric and bridging thiocyanato complexes; (c) to consider the consequence of coordination of ligands on pyridine ring frequencies (see Table IV);

(d) to make tentative assignments on the metal–ligand stretching frequencies [14].

X-ray diffraction powder photographs have been taken of selected nickel(II) complexes and the d-spacings calculated. These photographs have been used in conjunction with X-ray powder diffraction photographs of cobalt(II) and manganese(II) complexes to deduce the structures of the manganese(II) complexes. d-Spacings of significant lines are shown in a following paper [14].

Halogeno-Complexes of Nickel(II)

The complexes $\text{Ni}(\text{lig I a})\text{Cl}_2$, $\text{Ni}(\text{lig I b})\text{Cl}_2$, $\text{Ni}(\text{lig I c})\text{Cl}_2$, $\text{Ni}(\text{lig II a})\text{Cl}_2$, $\text{Ni}(\text{lig II b})\text{Cl}_2$, $\text{Ni}(\text{lig III c})\text{Cl}_2$, $\text{Ni}(\text{lig IV a})\text{Cl}_2$, $\text{Ni}(\text{lig IV b})\text{Cl}_2 \cdot \text{H}_2\text{O}$ are proposed as having a six coordinate, octahedral halogen-bridged structure. Magnetic properties, which indicate all the nickel(II) complexes are high spin with two unpaired electrons, discount the possibility of the structure $[\text{Ni}(\text{NNN})\text{X}] \text{X}$. Conductivity measurements, which indicate the complexes to be non-electrolytes in nitrobenzene do not favour the structure $[\text{Ni}(\text{NNN})_2] [\text{NiX}_4]$ being assigned to the complexes.

Examination of the electronic spectra of five-coordinate nickel(II) complexes indicate a significant band in the 10–15 kK region. The spectra of the complexes listed above show no band in this region to be present. Furthermore, the spectra of these complexes closely resemble that of the complexes $\text{Ni}(\text{PAPHY})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$ or I ; $\text{PAPHY} = \text{lig I}, \text{R}_1 = \text{R}_2 = \text{R}_3 = \text{H}$) which have been proposed as being six coordinate halogen bridged by Lions, Dance and Lewis [4]; These authors base their proposed structure on a comparison of spectra both in the solid state and in water or $\text{Ni}(\text{PAPHY})\text{X}_2$ and $\text{Ni}(\text{terpy})\text{X}_2$, ($\text{terpy} = 2,2',2''\text{-terpyridine}$), the latter being known to be five-coordinate. The reflectance spectrum of $\text{Ni}(\text{PAPHY})\text{Cl}_2$ resembles the solution spectra of $[\text{Ni}(\text{PAPHY})_2]^{2+}$ and $\text{Ni}(\text{terpy})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ both of which are octahedral complexes. Furthermore, the $\text{Ni}(\text{PAPHY})\text{Cl}_2$ spectrum shows no band in the 5 kK region, whereas the complex $\text{Ni}(\text{terpy})\text{Cl}_2$ absorbs at *ca.* 5 kK.

It is possible, therefore, that a more conclusive argument could be made if reflectance spectra in the region 5–12 kK were available. In the absence of this data, the comparison of spectra with the nickel(II) complexes of the similar ligand PAPHY are used to assign the six-coordinate halogen bridged structure.

The compound $\text{Ni}(\text{lig I b})\text{I}_2 \cdot \text{H}_2\text{O}$ is assigned a monomeric octahedral structure. The spectrum of this compound is similar to those octahedral halogen bridged structures already mentioned. The infra-red spectrum (Table IV), however, shows bands at 3530 cm^{-1} , 3360 cm^{-1} and 885 cm^{-1} . The bands at 3530 cm^{-1} and 3360 cm^{-1} may be assigned as antisymmetric and symmetric O–H stretching modes [14],

and that at 885 cm^{-1} as a wagging or rocking mode of coordinated water (δ_{MOH}) [15]. The structure of $\text{Ni}(\text{lig Ib})\text{I}_2 \cdot \text{H}_2\text{O}$ is therefore proposed as monomeric octahedral with the sixth coordination position being occupied by a water molecule.

The electronic spectra of complexes $\text{Ni}(\text{lig Ib})\text{Br}_2$, $\text{Ni}(\text{lig IIc})\text{Br}_2$, and $\text{Ni}(\text{lig VII})\text{Cl}_2 \cdot \text{H}_2\text{O}$ show absorption bands at 14.6 kK, 15.5 kK and 14.3 kK respectively. However, it is not possible to assign five-coordinate structures to these complexes with any confidence since the structure of $\text{Ni}(\text{lig IIIb})(\text{NCS})_2$ which has a similar absorption band at 16.2 kK is proposed as octahedral thiocyanato bridged on the basis of its infra-red spectrum. In these cases, the presence of absorption bands in the 5 kK region would be required to establish beyond doubt the five-coordination of the complexes. In this context it should be noted that a band in the region of 10–15 kK exists for $\text{Ni}(\text{PAPHY})\text{I}_2$ [4] and that considerable variety is apparent in the reflectance spectra of high spin nickel(II) compounds with approximately square-pyramidal stereochemistry. It is likely, therefore, that these compounds may well be of six-coordinate bridged structure although no definite assignment may be made. The possible exception is the compound $\text{Ni}(\text{lig VII})\text{Cl}_2 \cdot \text{H}_2\text{O}$ which has an identical X-ray powder diffraction pattern to the analogous cobalt(II) complex and may therefore be five-coordinate. In order to confirm this structure, electronic spectra in the region 5–10 kK would be required.

Thiocyanato Complexes of Nickel(II)

The complexes $\text{Ni}(\text{lig IIc})(\text{NCS})_2$ and $\text{Ni}(\text{lig IIIb})(\text{NCS})_2$ are assigned octahedral six-coordinate bridged structures on the basis of their infra-red spectra (Table IV). Infra-red spectra exhibit two bands at 2110 and 2150 cm^{-1} for $\text{Ni}(\text{lig IIIb})(\text{NCS})_2$ and 2115 and 2098 cm^{-1} for $\text{Ni}(\text{lig IIc})(\text{NCS})_2$. These bands appear indicative of bridging thiocyanato groups. If a thiocyanato group is terminally N-bonded to a metal atom the $\text{C}\equiv\text{N}$ stretching frequency usually occurs in the region 2050 – 2100 cm^{-1} . For a terminally S-bonded thiocyanato group the $\text{C}\equiv\text{N}$ stretching frequency occurs in the region 2110 – 2140 cm^{-1} . Bridging thiocyanato groups may possess $\text{C}\equiv\text{N}$ stretching vibrations which span both regions. However, these vibrations have usually been observed at frequencies greater than 2090 cm^{-1} . It is also found that although a number of absorptions due to $\text{C}\equiv\text{N}$ stretching occur, the position of the bands rather than the number of absorptions is the best indication of the nature of the bonding of the thiocyanato group to the metal atom [16]. This method of assignment has been used to detect thiocyanato bridging in a number of metal complexes. Some caution may be needed in using the above criteria as Harris and McKenzie [17] mention a thiocyanato bridged silver complex with a band at 2090 cm^{-1}

and Chatt and Duncanson [18] use higher frequency ranges (2182 – 2150 cm^{-1} ; 2120 – 2100 cm^{-1}) to distinguish bridging and terminal NCS groups in platinum complexes.

Electronic spectra of the two complexes in the solid state are dissimilar. However, in the absence of spectral data in the near infra-red region, it is not possible to assign structures with any degree of certainty on the basis of electronic spectra.

Cobalt(II) Complexes

The complexes of cobalt(II) with tridentate NNN ligands are of the type $\text{Co}(\text{NNN})\text{X}_2$ where $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$ (Table III). The colour of these complexes varies from green to red or brown and they are soluble, with some difficulty, in polar organic solvents such as nitrobenzene. Conductivity measurements on these solutions indicate that decomposition in solution occurs in some complexes. *e.g.*, $\text{Co}(\text{lig Ia})\text{Cl}_2$; $\text{Co}(\text{lig IIb})\text{Cl}_2$; $\text{Co}(\text{lig IIIb})(\text{NCS})_2$; $\text{Co}(\text{lig IIIc})\text{Cl}_2$. The degree of decomposition appears to be greater than is the case in the corresponding nickel(II) compounds.

Magnetic moments for these complexes lie in the range 4.37–5.03 B.M. indicating the complexes are high spin. Electronic spectra of the complexes in the solid state are similar to the spectra of known five-coordinate cobalt(II) complexes.

Halogeno Complexes of Cobalt(II)

The complexes of the type $\text{Co}(\text{NNN})\text{X}_2$, $\text{X} = \text{Cl}, \text{Br}$ are proposed to be five-coordinate in the solid state. Conductivity measurements indicate that the complexes are non-electrolytes. This eliminates the possibility of the complexes existing in the form $[\text{Co}(\text{NNN})_2]^{2+}[\text{CoX}_4]^{2-}$. The presence of strong bands in the electronic spectra of the complexes at 14–16 kK (which might indicate the presence of the species $[\text{CoX}_4]^{2-}$) is not at variance with this conclusion as such bands also occur in the electronic spectra of five-coordinate cobalt(II) complexes.

The magnetic moments, with the exception of $\text{Co}(\text{lig VII})\text{Cl}_2$ lie in the range 4.50–5.03 B.M. Magnetic moments of tetrahedral complexes of the type $\text{Co}(\text{NN})\text{X}_2$ where NN is a bidentate ligand have been calculated as being not greater than 4.49 B.M. [4]. It is reasonable to assume, therefore, that the complexes are either five-coordinate monomeric or six-coordinate dimeric (or polymeric) with halogen bridging.

Comparison of the electronic spectra of the complexes with the spectra of known five-coordinate complexes of cobalt(II) indicate that the spectra are similar. This similarity with that of known five-coordinate compounds is consistent with the existence of structural similarity, hence the compounds are probably monomeric five-coordinate.

TABLE III. Cobalt(II) Complexes of NNN Ligands.

Complex		Analysis (%)				Prepn. (Method)	μ_{eff} (B.M.)
		C	H	N	Co		
Co(lig Ia)Cl ₂	Found	41.8	3.7	15.9	17.0	B	4.51
	Calc.	42.1	3.5	16.4	17.3		
Co(lig Ib)Cl ₂	Found	41.8	3.6	16.7	17.2	D	5.06
	Calc.	42.1	3.5	16.4	17.2		
Co(lig Ib)Br ₂	Found	33.7	3.0	12.6	13.6	D	4.86
	Calc.	33.4	2.8	13.0	13.7		
Co(lig Ib)(NCS) ₂	Found	43.1	3.2	21.5	15.4	D	4.54
	Calc.	43.4	3.1	21.7	15.3		
Co(lig Ic)Cl ₂	Found	41.7	3.5	16.2	17.3	A	4.45
	Calc.	42.1	3.5	16.4	17.3		
Co(lig IIa)Cl ₂	Found	47.2	3.2	14.4	15.4	A	4.71
	Calc.	47.6	3.2	14.8	15.6		
Co(lig IIb)Cl ₂	Found	48.6	3.8	13.9	14.9	B	4.64
	Calc.	49.0	3.6	14.3	15.1		
Co(lig IIc)Cl ₂ ·H ₂ O	Found	47.2	4.1	13.3	14.3	A	4.58
	Calc.	46.8	3.9	13.7	14.4		
Co(lig IIc)Br ₂ ·H ₂ O	Found	38.5	3.3	11.2	12.0	A	4.57
	Calc.	38.5	3.2	11.2	11.8		
Co(lig IIc)(NCS) ₂	Found	49.3	3.3	18.2	13.3	D	4.40
	Calc.	49.4	3.2	19.2	13.4		
Co(lig IIIa)Cl ₂	Found	40.6	2.7	15.0	15.2	A	4.66
	Calc.	40.6	2.6	14.6	15.4		
Co(lig IIIc)Cl ₂	Found	42.2	3.3	14.0	14.8	B	4.82
	Calc.	42.2	3.0	14.1	14.8		
Co(lig IIIb)Cl ₂	Found	42.2	3.1	14.1	14.6	C	4.53
	Calc.	42.2	3.0	14.1	14.8		
Co(lig IIIb)Br ₂	Found	34.3	2.6	11.6	11.8	C	4.67
	Calc.	34.5	2.5	11.5	12.1		
Co(lig IIIb)(NCS) ₂	Found	42.9	2.8	18.2	13.1	D	4.44
	Calc.	43.3	2.7	19.0	13.3		
Co(lig X)Cl ₂	Found	41.8	3.8	14.5	15.9	C	4.64
	Calc.	41.9	3.8	15.1	15.9		
Co(lig VII)Cl ₂	Found	52.8	3.4	13.4	13.8	C	4.37
	Calc.	53.3	3.3	13.1	13.8		
Co(lig VIII)Cl ₂	Found	46.8	3.0	13.1	13.5	C	4.79
	Calc.	47.0	2.8	12.9	13.6		
Co(lig IVb)Cl ₂	Found	51.0	3.6	11.5	15.6	B	4.50
	Calc.	50.9	3.5	11.1	15.6		

The complexes exhibit strong bands in the region 14–16 kK and most exhibit weak bands in the 11–14 kK region. In some cases this latter band is somewhat obscured by the intense 14–16 kK band. Other bands appear as shoulders on a rising ligand adsorption (charge-transfer) band. In some cases the d–d transition bands in this region (16–23 kK) may be masked completely by these very intense ligand bands.

As the instrumental limitations prevented the observation of spectra in the region 5–12 kK, the assignment of structures based on electronic spectra in these limited regions (23–11.8 kK) must be viewed with caution. The presence of bands in the 5 kK region has been used as an indication of five-coordina-

tion by several workers [4, 19, 20]. A confirmation of the proposed structures, therefore, would require examination of the electronic spectra in the near infra-red region. Further evidence supporting the five-coordinate structure for cobalt(II) complexes is supplied by a consideration of the X-ray diffraction powder photographs of cobalt(II) and nickel(II) complexes. With the exception of Ni(lig VII)Cl₂·H₂O and Co(lig VII)Cl₂, a lack of similarity is observed in a comparison of the photographs of the cobalt(II) and nickel(II) complexes of the same ligand. As the structures of the nickel(II) complexes are considered to be six-coordinate halogen bridged, the structure of the cobalt(II) complexes is probably

TABLE IV. Infra-red Spectral Data of Cobalt(II) and Nickel(II) Complexes.

Ligand or Complex	$\nu_{\text{N-H}}$	$\nu_{\text{C}\equiv\text{N}}$	PyI	PyII	Other
Ligand Ib	3160w		1597m	1573s	
Ni(lig Ib)Cl ₂			1620s	1572m	
Ni(lig Ib)Br ₂			1622s	1570m	
Ni(lig Ib)I ₂ ·H ₂ O	3170m		1622s	1569m	3530m($\nu_{\text{O-H}}$), 3360m($\nu_{\text{O-H}}$), 885m($\delta_{\text{M-O-H}}$)
Co(lig Ib)Cl ₂	3190m		1620s	1572m	
Co(lig Ib)Br ₂	3190m		1620s	1570m	
Co(lig Ib)(NCS) ₂	3190w	2100 } 2075 }s	1615s	1570m	
Ligand Ic	3180w		1602s	1572s	
Ni(lig Ic)Cl ₂	3165w		1615s	1580m	
Co(lig Ic)Cl ₂	3180s		1612s	1581m	
Ligand IIa	3180w		1602sh	1572s	
Ni(lig IIa)Cl ₂	3160w		1612s	1568m	
Co(lig IIa)Cl ₂	3160m		1612s	1568m	
Ni(lig IIc)(NCS) ₂	3160w	2115sh } 2098s }			
Co(lig IIc)(NCS) ₂	3190br	2085s			
Ni(lig IIb)(NCS) ₂		2150s } 2110s }			
Co(lig IIb)(NCS) ₂		2085s			
Ligand X					3340s($\nu_{\text{O-H}}$)
Co(lig X)Cl ₂	3160m				3290m($\nu_{\text{O-H}}$)

five-coordinate monomeric. Details of the powder photographs and their d spacings are shown in a following paper [14].

The structure of the cobalt(II) complexes is most likely to be distorted square pyramidal. Lions, Dance and Lewis [4] have indicated that the substitution of methyl groups at the 6-position in the pyridine rings of PAPHY (lig I; R₁ = R₂ = R₃ = H) causes "strong modification of the properties and structures of the cobalt(II) mono chelate complexes". No further details of the complexes prepared have been published. These authors also state that distortion of a square pyramidal structure by reducing the symmetry of the basal plane is accompanied by a decrease in the magnetic moment from a value of 5.0 B.M., the value of 5.0 B.M. indicating high symmetry; and also note that the expected pattern of electronic spectral bands in five-coordinate square pyramidal cobalt(II) complexes becomes irregular with increasing angular distortion. An examination of the magnetic moments of the cobalt(II) complexes indicates that the range of these moments (4.37–5.04 B.M.) is consistent with a distorted square pyramidal geometry similar to that of β -Co(PAPHY)Cl₂ [21]. The magnetic moments appear to be lower than those of the five-coordinate Co(PAPHY)X₂ complexes (X = Cl, Br). This may indicate distortions in the complexes caused by the presence of quinolyl, benzothiazyl and

methyl substituted pyridyl components of the Schiff's base ligand.

Thiocyanato Complexes of Cobalt(II)

The complexes of Co(lig Ib)(NCS)₂, Co(lig IIc)(NCS)₂ and Co(lig IIb)(NCS)₂ are proposed as being five-coordinate structures on the basis of their infra-red absorption in the 2050–2110 cm⁻¹ region. The absorption bands for the $\nu_{\text{C}\equiv\text{N}}$ vibration occur in the 2050–2110 cm⁻¹ region, and this is indicative of a terminal rather than a bridged NCS group. In each case, the complexes show no bands in the 2110–2150 cm⁻¹ region.

Examination of X-ray powder diffraction photographs of the nickel(II) and cobalt(II) thiocyanato complexes of ligands IIc and IIb indicate that the nickel(II) and cobalt(II) complexes are not isostructural [14]. This is consistent with the conclusions reached from infra-red spectral data. The electronic spectra of the cobalt(II) thiocyanato complexes are similar to those of other designated five-coordinate cobalt(II) complexes.

Infra-red Spectra of Cobalt(II) and Nickel(II) Complexes

Infra-red spectral studies of the complexes were concentrated in the following areas: $\nu_{\text{N-H}}$ vibrations,

pyridine ring vibrations, $\nu_{\text{M-Ligand}}$ and $\nu_{\text{M-X}}$ (X = Cl, Br, I) vibrations as well as the $\nu_{\text{C}\equiv\text{N}}$ vibrations already considered in the structure determination of thiocyanato complexes.

Studies in the $\nu_{\text{N-H}}$ vibrations (Table IV) yielded little structural information except to confirm that no deprotonation of the N-H group in the ligand had taken place on coordination to the metal atom. The absence of a $\nu_{\text{N-H}}$ band in the spectra of metal complexes has been used as an indication of deprotonation [22]. However, in a number of cases, the presence of substituents such as quinolyl or benzothiazyl group on the basic PAPHY structure appeared to weaken considerably the intensity of $\nu_{\text{N-H}}$ bands in this region and make spectral studies in this region of little consequence.

Pyridine ring vibrations (Table IV) were assigned to absorptions in the 1550–1650 cm^{-1} spectral range. The assignments were consistent with those shown by other workers who have used these assignments to deduce whether or not the pyridine rings are coordinated to the metal atom [23–26].

Two pyridine ring vibrations were observed in the ligand; one at approximately 1600 cm^{-1} (Pyl) and one at approximately 1570–1580 cm^{-1} (PylI). On coordination, the 1600 cm^{-1} band shifted to a higher frequency with an increase of 10–20 cm^{-1} whereas the 1570 cm^{-1} band remained virtually the same. The presence of a band in the spectrum of the metal complex at the original Pyl ligand vibration is taken as an indication that the pyridine ring has not coordinated. In the metal complexes of cobalt(II) and nickel(II) with PAPHY-type ligands no significant absorption was noted at the original Pyl frequency indicating the expected result that all pyridine rings were coordinated to the metal atom.

It is possible that the Pyl band mentioned might overlap with the band due to $\nu_{\text{C}=\text{N}}$. However, the values of $\nu_{\text{C}=\text{N}}$ in ligands of a similar type appear to be of a higher frequency and have not been reported to shift to a higher frequency on coordination of the ligand to a metal atom. This band may account for the shoulder present on the strong Pyl band in the spectra. It is also noted that the intensity of the PylI band decreases on coordination. This feature has been noted by Gibson and Mackenzie [27], in a study of complexes of cobalt(II), nickel(II) and palladium(II) with 1,6-bis(2'-pyridyl)-2,5-diazahexane and related compounds. The presence of quinolyl and benzothiazyl components in the PAPHY like ligands produced complicated spectra in the region making the assignment of pyridine ring vibrations impossible.

The discussion of the spectral bands in the far infra-red region of cobalt(II) and nickel(II) complexes is treated in conjunction with the manganese(II) complexes [14].

Comparison of the spectra of the ligand X with its cobalt(II) complex $\text{Co}(\text{lig X})\text{Cl}_2$ indicates that the

bonding to the metal atom occurs via the three nitrogen atoms and not via two nitrogens and the -OH of the oxime group. The ligand shows a sharp band attributed to ν_{OH} at 3340 cm^{-1} . This band is also present in the complex as a broader band at slightly lower frequency at 3290 cm^{-1} .

Experimental

Preparation of Ligands and their Metal Complexes

Starting Materials

(i) Pyridine-2-aldehyde, 6-methylpyridine-2-aldehyde, 2-acetylpyridine, 2,6-diacetylpyridine were obtained from commercial sources and purified as required.

(ii) Quinoline-8-aldehyde was prepared by selenium dioxide oxidation of 8-methylquinoline using the method of Seyham and Fernelius [28].

(iii) 6-methyl-2-hydrazinopyridine was prepared by the action of hydrazine hydrate on 2-bromo-6-methylpyridine according to the procedure described by Chiswell [29]. The hydrazine was not isolated but combined directly with the required aldehyde to form the desired ligand.

(iv) 2-hydrazinopyridine, 2-hydrazinoquinoline, 2-hydrazinobenzothiazole and 2-aminomethylpyridine were obtained commercially and purified if necessary.

(v) Diacetylmonoxime was obtained commercially as analytical reagent grade and used without further purification.

Preparation of Ligands

The ligands were prepared by refluxing an ethanolic solution of the appropriate aldehyde or ketone with an ethanolic solution of the hydrazine or amine in equimolar quantities. The ligands, if crystalline, at room temperature, were purified by recrystallization from ethanol or aqueous ethanol to constant melting point. No further characterization was made. Ligands which were oils at room temperature were prepared *in situ* by refluxing equimolar quantities of ketone or aldehyde with amine or hydrazine in ethanol solution. The ligand was then used in the preparation of metal complexes without isolation. References to the preparation and characterization of ligands are shown in Table I.

Preparation of Metal Complexes

The preparation of metal complexes may be classified into several standard types as follows:

Method A. A hot, filtered, ethanolic solution of the ligand was added slowly to a hot, filtered, ethanolic solution of the metal salt (the metal salt being in a slight excess of a 1:1 molar ratio of ligand: metal). The metal complex crystallized immediately or on slight evaporation of solvent.

Method B. This method is the same as method A except that the ligand is prepared *in situ* from the appropriate aldehyde or ketone and hydrazine or amine and used without isolation.

Method C. The ligand and metal salt were suspended in ethanol and refluxed together for at least one hour. The metal complex separated out, was allowed to digest for 30 minutes and filtered off after cooling.

Method D. The hot filtered ethanolic solution of the ligand prepared either as in method A or B was added to a hot filtered ethanolic solution of the metal salt (in slight excess) prepared *in situ*. The metal salt was prepared *in situ* by adding an appropriate lithium salt in ethanol to a solution of the metal perchlorate in ethanol. As above, the metal complex crystallized immediately or on slow evaporation. In some cases, acetone was preferred to ethanol as a solvent, the metal complex perchlorates being less likely to crystallize from this solvent than from ethanol.

Method E. A hot, filtered, ethanolic solution of the metal perchlorate was added to a hot, filtered, ethanolic solution of the ligand, the mole ratio of ligand:metal being in slight excess of 2:1. The bis-ligand complex perchlorates crystallized on cooling and was recrystallized from either ethanol or aqueous ethanol.

Spectra

Infrared spectra were obtained using a Perkin-Elmer model 457 spectrophotometer. Samples were examined in nujol mulls supported by (a) potassium bromide discs in the region 4000–400 cm^{-1} and by (b) caesium iodide discs in the region 400–250 cm^{-1} .

Electronic spectra were recorded using a Unicam SP800 spectrophotometer for solutions and a Unicam SP800 spectrophotometer with a SP890 diffuse reflectance attachment for spectra in the solid state.

Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were made using the Gouy method. The magnetic field was produced by a permanent magnet of field strength 6.58 kG and the force developed on the sample measured using a Mettler balance with digital readout to 0.01 mg. Measurements were made at room temperature. The apparatus was calibrated using mercury(II) tetrathiocyanatocobaltate(II), $\text{Hg}[\text{Co}(\text{NCS})_4]$.

Diamagnetic corrections for the ligands were calculated from Pascal constants. Molar susceptibilities are expressed in $\text{cm}^3 \text{mol}^{-1}$ using the unrationalized c.g.s. e.m.u. system.

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