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Mono-Ligand Complexes of 2,3,5,6-Tetrakis(6-methyl-2-pyridyl)pyrazine

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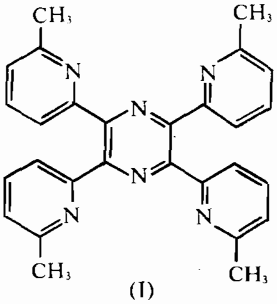
Mono-ligand metal complexes of the tridentate chelating agent 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)pyrazine (L) and of general formula [MLX_2] where M = Mn, Fe, Co, Ni, Cu and where X may be Cl, Br, I, NCS, NCSe or NO_3, have been prepared. Infrared, visible and near-ultraviolet spectral, conductance and magnetic data have been obtained for the complexes, and based on these data an attempt has been made to assign coordination numbers to the metal atoms. The evidence obtained indicates the presence of both five- and six-coordination in the compounds.

Introduction

The heterocyclic base 2,3,5,6-tetrakis(6-methyl-2-pyridyl)pyrazine (I) (L) has been shown to form complexes of the type [$MLCl_2$] where M = Fe, Co, Ni, Cu. A molecular model of the base (I) indicates that coordination as a double tridentate to two metal atoms is prevented because of steric interaction between the hydrogen atoms in the 3-positions of the pyridine rings. Because of this interaction the pyridine rings attached to the pyrazine ring in the 2 and 6 positions alone or those attached in the 3 and 5 positions alone may be coplanar with the pyrazine ring. No more than two pyridine rings may be simultaneously coplanar with the pyrazine ring. Thus the molecule is capable only of simple, planar tridentate behaviour. In an earlier work[1] it was reported that *bis*-ligand complexes of (I) could not be isolated and this was attributed to the steric hindrance offered to coordination of the ligand by the methyl groups in the 6-positions of the pyridine rings.



(I)

The ease with which (I) yields *mono* complexes and its observed failure to give rise to any isolable *bis* chelated species indicated that (I) would provide a useful system for investigation of complexes of the type [M(tridentate)X_2]. Such complexes have been the subject of much recent study, particularly from the viewpoint of the stereochemistry of the metal atom.[2-11] In these complexes a number of stereochemical possibilities can arise. Six-coordination of the metal atom can be achieved by the formation of ionic compounds of the type [(M(tridentate)$_2$]-[MX_4] or by the formation of a polymeric structure involving [M(tridentate)X_2] units with bridging coordinated anions. In addition, six-coordination can be achieved without bridging when the coordinated anion is capable of bidentate behaviour, as is possible with the nitrate ion; in such an instance both uni- and bidentate coordination of the anion would be involved. The metal atom can be four-coordinate if only one of the anions is coordinated and in complexes of the form [M(tridentate)X]X the metal atom may possess tetrahedral or square-planar stereochemistry depending upon the spatial demands of the metal atom and the chelate group. A complex of this type could, additionally, be five-coordinate if X is bridging or bidentate. Finally, the possibility arises where compounds of the form [M(tridentate)X_2] are monomeric and uncharged and where the metal atom is five-coordinate.

Molecular models of (I) demonstrate that the methyl groups present steric hindrance not only to the formation of *bis*-ligand complexes but also to the coordination of a fourth donor atom in the same plane, or very nearly so, as the three donor nitrogen atoms. Thus in a six-coordinate complex containing a molecule of (I) the arrangement of the donor atoms about the metal atom would be expected to be distorted from octahedral symmetry. Similarly a four-

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Table I. Complexes of 2,3,5,6-Tetrakis(6-methyl-2-pyridyl)pyrazine

Compound	Colour	Conductivity [a]	μ (B.M.) at T°K
$[MnLCl_2]$	orange	0.1	5.9(299°)
$[MnLBr_2]$	orange	0.4	6.0(290°)
$[MnLI_2]$	yellow-orange	1.6	6.0(290°)
$[MnL(NCS)_2]$	orange	1.0	5.9(299°)
$[MnL(NCSe)_2]$	orange	2.1	5.9(298°)
$[MnL(NO_3)_2] . H_2O$	yellow	i [b]	6.0(292°)
$[FeLCl_2]$	deep green	0.2	5.4(293°)
$[FeLBr_2]$	deep green	0.2	5.4(293°)
$[FeLI_2]$	deep green	7.1	5.5(293°)
$[FeL(NCS)_2]$	green-brown	0.4	5.4(293°)
$[FeL(NCSe)_2]$	green-brown	1.0	5.1(293°)
$[FeL(NO_3)_2]$	deep green	0.6	5.1(293°)
$[CoLCl_2]$	green-brown	0.1	4.7(293°)
$[CoLBr_2]$	green-brown	0.2	4.9(293°)
$[CoLI_2]$	green-brown	2.4	4.9(293°)
$[CoL(NCS)_2]$	brown	0.7	4.5(293°)
$[CoL(NO_3)_2]$	orange-brown	i	4.6(293°)
$[NiLCl_2]$	yellow	0.1	3.3(299°)
$[NiLBr_2]$	yellow-orange	0.2	3.3(299°)
$[NiLI_2]$	brown	0.9	3.2(289°)
α–$NiL(NCS)_2]$	green	0.4	3.3(290°)
$[NiL(NO_3)_2] . O . 5H_2O$	green	i	3.3(292°)
$[CuL(NCS)_2]$	yellow-green	0.5	1.9(292°)
$[CuL(NO_3)_2] . H_2O$	green-brown	i	1.9(296°)

[a] Measured (in ohms^{-1} cm^2) in nitrobenzene at 25°. [b] Insoluble in nitrobenzene

coordinate complex would be expected to have a distorted square-planar configuration (a regular tetrahedral structure is not possible since coordination of (I) would require that the three donor nitrogen atoms and the metal atom be in the one plane). Again, a regular square-pyramidal structure in five-coordinate complexes of (I) would not be favoured but there would seem to be little steric resistance to the adoption of a trigonal-bipyramidal structure.

Results and Discussion

The addition of a lithium salt of a readily coordinating anion to an ethanolic solution containing equivalent amounts of (I) and a metal perchlorate resulted in the separation of the *mono*-ligand complex of the metal and that coordinating anion. The complexes could in many instances be prepared directly from the ligand and the appropriate transition metal salt of the coordinating anion. The compunds prepared are listed in Table I.

The interaction of (I) with nickel(II) thiocyanate was found to yield three different products. In ethanolic solution a bright green compound of composition $[NiL(NCS)_2]$ was produced, whereas it was found that if the ligand and nickel(II) thiocyanate were allowed to react in hot ethanol-ether mixture and the resulting solution left to stand undisturbed for three days a mixture of three compounds was produced. Only in some instances was the mixture obtained such that separation of the three products by hand-picking was possible. The three products proved to be (a) the bright green compound referred to above (hereafter designated α–$[NiL(NCS)_2]$); (b) an olive-green form of $[NiL(NCS)_2]$ (designated as the β-isomer); (c) bright green $[NiL(NCS)_2] . H_2O$. The quantities of β–$[NiL(NCS)_2]$ and the hydrated compound that could be obtained were insufficient to allow an adequate investigation of their properties.

Interestingly, both α– and β–$[NiL(NCS)_2]$ were found to react instantaneously with acetone at room temperature to produce a brown solid of composition $[NiL(NCS)_2] . 2[(CH_3)_2CO]$. The solvent molecules are lost when the solvated complex is washed with ethanol or ether, when it is heated for several minutes at 100°, or by allowing it to stand in air for several days.

Conductivities. The conductivities in nitrobenzene solution at 25° were measured for those compounds soluble in that solvent and are listed in Table I. All the values obtained indicate that the complexes are essentially non-electrolytes in nitrobenzene and that, at least in solution, the complexes do not exist as ionic species.

Magnetic Properties. The room-temperature magnetic moments of the complexes (Table I) are not at all diagnostic of the stereochemistry of the metal atom in any of the compounds. Those of the manganese complexes are very close to the spin-free, spin-only value as expected for high-spin Mn^{II} complexes of any stereochemistry.[12] The values obtained for the nickel and copper complexes are slightly above the spin-only values.

The magnetism of the iron and cobalt complexes was measured over the temperature range 80-293°K. The data are given in Table II. The magnetic moments of the Fe^{II} compounds at room temperature are above the spin-free, spin-only value and these vary to only a small extent with change in temperature: a Curie-Weiss law ($\chi'_M = C/(T-\theta)$) is obeyed in all instances with small θ values (these are included in Table II), indicating that the complexes are magnetically dilute. The cobalt complexes were also

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Table II. Magnetic data for Iron and Cobalt Complexes

Compound	Magnetic moments at T°K 293°	263°	233°	203°	173°	143°	113°	80°	Curie Weiss θ value
[$FeLCl_2$]	5.39	5.36	5.37	5.37	5.32	5.29	5.27	5.19	—10°
[$FeLBr_2$]	5.36	5.36	5.36	5.37	5.38	5.35	5.32	5.27	—2°
[$FeLI_2$]	5.52	5.50	5.48	5.47	5.45	5.43	5.36	5.26	—10°
[$FeL(NCS)_2$]	5.38	5.36	5.34	5.33	5.30	5.25	5.19	5.07	—14°
[$FeL(NCSe)_2$]	5.14	5.12	5.11	5.13	5.10	5.07	5.02	4.94	—12°
[$FeL(NO_3)_2$]	5.13	5.10	5.09	5.08	5.05	5.02	4.98	4.89	—12°
[$CoLCl_2$]	4.74	4.71	4.69	4.69	4.65	4.60	4.56	4.44	—16°
[$CoLBr_2$]	4.87	4.84	4.81	4.78	4.73	4.69	4.61	4.50	—22°
[$CoLI_2$]	4.92	4.90	4.88	4.85	4.84	4.78	4.69	4.56	—17°
[$CoL(NCS)_2$]	4.47	4.46	4.44	4.41	4.34	4.29	4.19	4.08	—25°
[$CoL(NO_3)_2$]	4.58	4.57	4.57	4.50	4.46	4.41	4.33	4.23	—22°

Table III. Infrared Data for Thiocyanato and Selenocyanato Complexes

Compound	C—N Stretching Frequency (cm^{-1})
[$MnL(NCS)_2$]	2075, 2060
[$MnL(NCSe)_2$]	2070, 2065
[$FeL(NCS)_2$]	2080, 2055
[$FeL(NCSe)_2$]	2075, 2070
[$CoL(NCS)_2$]	2090, 2065
α—[$NiL(NCS)_2$] [a]	2060
α—[$NiL(NCS)_2$] [b]	2060
β—[$NiL(NCS)_2$]	2120, 2085
[$NiL(NCS)_2$] . 2[$(CH_3)_2CO$]	2075, 2060, 1712 (carbonyl band)
[$NiL(NCS)_2$] . H_2O	2100
[$CuL(NCS)_2$]	2095, 2070

[a] Prepared from ethanol. [b] Prepared from ethanol-ether

found to possess room-temperature moments above the spin-free, spin-only value and which also varied little with change in temperature. That the magnetism of cobalt(II) complexes does not necessarily provide a means of distinguishing between five-and six-coordinate Co^{II} is illustrated by the two isomers of [Co-(paphy)Cl_2] (paphy = pyridine-2-aldehyde-2′-pyridylhydrazone), one of which is five- and the other six-coordinate and both of which have essentially the same magnetic properties.[10]

Infrared Spectra. The C—N stretching vibration frequencies exhibited by the thiocyanato and selenocyanato complexes are given in Table III. Because of ligand absorptions it was not found to be possible to attribute bands to C—S and C—Se stretching frequencies or to NCS and NCSe bending modes.

A thiocyanato group which is terminally N-bonded to a metal atom usually possesses C—N stretching frequency bands in the 2050-2100 cm^{-1} region, whereas in a terminally S-bonded group this frequency occurs in the 2110-2140 cm^{-1} region. Bridging thiocyanate groups can possess C—N stretching frequencies which span both regions but which usually occur at frequencies greater than 2090 cm^{-1}.[10,13-18] Parallel correlations occur for selenocyanate complexes, though this is not so extensively documented.[15,19-22] Complexes which contain bridging thiocyanate and selenocyanate groups usually exhibit several C—N stretching frequencies but the presence of more than one such frequency is not necessarily indicative of the bifunctional behaviour of the group. It would seem to be the position rather than the number of the absorptions due to the C—N stretching which is diagnostic of the nature of the bonding of the group to the metal atom.[10,16,22,23]

The C—N stretching frequencies of the thiocyanato and selenocyanato complexes of (I) with the single exception of β—[$NiL(NCS)_2$] are consistent with terminal N-bonding of the groups and thus five-coordination of the metal atom. In β—[$NiL(NCS)_2$] the frequencies are consistent with bridging thiocyanate and thus six-coordination of the metal atom.

The spectrum of the acetone adduct of α—[NiL-$(NCS)_2$] possesses a carbonyl band at 1712 cm^{-1}, indicating that the acetone is simply incorporated into the lattice without being coordinated to the metal. The carbonyl band shown by pure acetone is shifted only slightly in lattice acetone,[23,24] but occurs at much lower frequencies in compounds containing coordinated acetone.[25]

The infrared spectra of the nitrato complexes show several bands attributable to various vibrations of the coordinated anion[26,27] and the frequencies of these are listed in Table IV. Because of the complexity of the spectra of the complexes only bands in the regions 1273-1305 cm^{-1} and 1460-1475 cm^{-1} could be readily identified. It should be noted that while the bands in the lower frequency region are quite distinct those in the higher region are superimposed on heterocyclic ligand bands and only one band in this region could be reliably attributed to the presence of the coordinated anion.

The single, intense band shown by ionic nitrate at approximately 1400 cm^{-1} [28] is split into two components on coordination of the anion, irrespective

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(16) I. Bertini and A. Sabatini, *Inorg. Chem.*, *5*, 1025 (1966).
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(21) S. M. Nelson and T. M. Shepherd, *Inorg. Chem.*, *4*, 813 (1965).
(22) J. L. Burmeister and L. E. Williams, *Inorg. Chem.*, *5*, 1113 (1966).
(23)C. M. Harris and E. D. McKenzie, *J. Inorg. Nucl. Chem.*, *29*, 1047 (1967).
(24) L. F. Lindoy, S. E. Livingstone, and N. C. Stephenson, *Austral. J. Chem.*, *19*, 1165 (1966).
(25) D. Cassimatic and B. P. Suez, *Helv. Chim. Acta*, *43*, 852 (1960).

of whether the ion is uni- or bidentate. However, the degree of splitting is less for unidentate than for bidentate nitrate, this behaviour paralleling that of the carbonate ion.[27] A compound containing both uni- and bidentate nitrate ion ought, then, to exhibit four bands, two at about 1300 cm^{-1} and two at about 1450 cm^{-1}, as had been observed for dinitrato-diethylenetriamine-nickel(II).[27]

Table IV. Infrared Data for Nitrato Complexes

Compound	Frequencies (cm^{-1})
$[MnL(NO_3)_2] . H_2O$	1277, 1302, 1475
$[FeL(NO_3)_2]$	1305, 1475
$[CoL(NO_3)_2]$	1278, 1303, 1470
$[NiL(NO_3)_2] . O . 5H_2O$	1273, 1298, 1460
$[CuL(NO_3)_2] . H_2O$	1280, 1303, 1460

With the exception of $[FeL(NO_3)_2]$ the spectra of the nitrato complexes all show two distinct and intense bands in the 1273-1303 cm^{-1} region. Since neither unidentate nor bidentate nitrate *alone* would be expected to show two bands in this region, these data suggest the existence of two modes of bonding of the nitrate ion. The two bands in this region cannot be attributed to weak splitting as a result of exclusively unidentate behaviour, because there is at least one band definitely present in the 1460-1475 cm^{-1} region which is absent in the other metal complexes of (I) and must therefore be the result of the presence of the nitrate ion. It would appear from this that in the nitrato complexes of Mn^{II}, Co^{II}, Ni^{II} and Cu^{II} the metal atoms achieve six-coordination by virtue of the presence of both uni- and bidentate coordination of the nitrato groups. The spectrum of $[FeL(NO_3)_2]$ differs in that only a single absorption is observed in the 1300 cm^{-1} region and this might indicate only one mode of bonding of the anion and hence five-coordination of the metal atom.

Electronic Spectra. Electronic spectra of the Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} compounds were determined both in the solid state and in chloroform solution in the range 400-2000 mμ. The solution spectra do not appear to be significantly different from the corresponding diffuse reflectance spectra. The differences which were observed could be attributed to interference caused by the extensive charge-transfer bands present in all the spectra. In table V the results of the diffuse reflectance spectral measurements only are given.

The spectra of the iron compounds appear to exhibit charge-transfer bands alone. These occur in the range 570-675 mμ and the extinction coefficients of the bands depend on the coordinated anion, increasing in the order $NO_3^- < NCSe^- \sim NCS^- < Cl^- < Br^- < I^-$. This sequence indicates that the bands result from metal-anion rather than metal-heterocyclic ligand electronic transitions.

Table V. Diffuse Reflectance Spectral Data

Compound	Bands: mμ
$[FeLCl_2]$	675
$[FeLBr_2]$	660
$[FeLI_2]$	630
$[FeL(NCS)_2]$	570(sh)
$[FeL(NCSe)_2]$	615(sh)
$[FeL(NO_3)_2]$	570, 590(sh)
$[CoLCl_2]$	590(sh), 900(sh), 1080, $\geqslant$2000
$[CoLBr_2]$	440, 570(sh), 900(sh), 1120, $\geqslant$2000
$[CoLI_2]$	460, 590, 750, 870, 1180, $\geqslant$2000
$[CoL(NCS)_2]$	570(sh), 850, 1900(sh)
$[CoL(NO_3)_2]$	580(sh), 730, 900, 1700
$[NiLCl_2]$	725, 1130(sh), 1250
$[NiLBr_2]$	750, 1210(sh), 1290
$[NiLI_2]$	460, 580(sh), 970, 1160, 1725
α–$[NiL(NCS)_2]$	650, 850, 1125, $\geqslant$2000
β–$[NiL(NCS)_2]$	680, 900
$[NiL(NCS)_2] . H_2O$	640, 1050, 1150(sh)
$[NiL(NO_3)_2] . O . 5H_2O$	640, 1000, 1680
$[CuL(NCS)_2]$	800
$[CuL(NO_3)_2]$	420, 850

The spectra of $[CoLX_2]$, where X = Cl, Br, I, NCS, do not differ significantly from one another. The essential difference between these spectra and the spectrum of the nitrato complex is the absence in the latter of absorption in the vicinity of 2000 mμ. The appearance of a band in this region has been observed in the spectra of numerous Co^{II} compounds for which five-coordination has been either postulated or established.[8,10,11] This evidence suggests, then, that all the cobalt complexes are five coordinate except the nitrato complex which may have a distorted octahedral structure, and this is consistent with the interpretation of the infrared spectral data obtained for the thiocyanato and nitrato complexes.

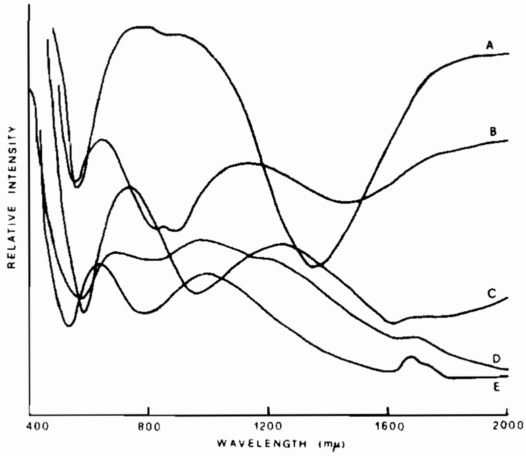

Figure 1. Diffuse reflectance spectra of A. $[Ni(terpy)Cl_2]$; B. α–$[NiL(NCS)_2]$; C. $[NiLCl_2]$; D. $[Ni(paphy)Cl_2]$; E. $[NiL(NO_3)_2] . O . 5H_2O$.

In the Figure are shown the spectra of α–$[NiL(NCS)_2]$, $[NiLCl_2]$ and $[NiL(NO_3)_2]O . 5H_2O$ together with, for comparative purposes, those of $[Ni(terpy)Cl_2]$ (terpy = 2,2′,2″-terpyridine) and $[Ni(paphy)Cl_2]$. The latter two complexes are included since, on the one hand $[Ni(terpy)Cl_2]$ is known to be

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(26) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957), *J. Inorg. Nucl. Chem.*, *8*, 75 (1958).

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five-coordinate while on the other [Ni(paphy)Cl_2] is believed to be six-coordinate with chlorine bridges.[10] It will be seen from the Figure that the greatest differences in the spectra are in the vicinity of 2000 $m\mu$. The presence of bands in this near-infrared region for a number of Ni^{II} compounds has been taken to be indicative of five-coordination while their absence has been considered to indicate six-coordination.[10] Prominent absorption in the spectrum of α–[NiL$(NCS)_2$] in this region, comparable to that of [Ni(terpy)Cl_2] would suggest that the former complex also is five-coordinate. This conclusion is certainly consistent with the interpretation given for the infrared data obtained for this compound. The spectra of [NiL$(NO_3)_2$]O . $5H_2O$ and [Ni(paphy)Cl_2] exhibit close similarity and indicate that the nitrato complex is six-coordinate, again as suggested by the infrared data. The similarity of the spectrum of [NiLI_2] to that of [NiL$(NO_3)_2$]O . $5H_2O$ would seem to be sufficiently close to suggest that the former compound is also six-coordinate. The spectrum of [NiLCl_2] and also that of [NiLBr_2] are such that no clear assignment of the coordination numbers of the metal atoms in these compounds can be made.

Because only small quantities of β–[NiL$(NCS)_2$] could be obtained its spectrum could not be determined beyond 1400 $m\mu$. Within the range common to the spectra obtained for the α– and β–isomers differences in band positions were observed (Table V), but these differences, unlike the infrared spectral data, do not provide evidence for the structure of the β–isomer.

The spectra of the copper compounds show an extremely unsymmetrical band at about 800 $m\mu$, this tailing off to beyond 1400 $m\mu$. This absorption obviously consists of an envelope of bands and is not indicative of the stereochemistry of the copper atoms in the complexes.

Concluding Remarks. The ligand (I) obviously provides an ideal tridentate for preparation of potentially five-coordinate complexes with bivalent metal atoms. An extensive series of well-defined, highly crystalline complexes was readily obtained. Determination of molecular weights of the compounds was not possible because of low solubility in suitable solvents. In the absence of X-ray crystallographic data it is of course not possible to assign unequivocally coordination numbers to the metal atoms in the complexes obtained in this investigation, but where other evidence could be expected to be diagnostic of the stereochemistry of the metal atom the evidence certainly has indicated the presence of both five- and six-coordination in the series of compounds.

The adoption of a particular coordination number by a metal atom obviously must depend upon the interrelationships of a number of factors such as the preferred stereochemistry of the metal, the nature of the coordinated anions, the stereochemical rquirements of the chelating agent and the macroscopic forces involved in the formation of a crystal lattice.

Experimental Section

Preparation of Complexes. Unless otherwise indicated the metal complexes were prepared by the following general method. To a hot solution of 2,3,5,6-tetrakis-(6-methyl-2-pyridyl)pyrazine (0.44 g, 1.0 mmole) in ethanol (20 ml) was added a hot solution of the metal perchlorate hexahydrate (1.0 mmole) in ethanol (10 ml). To this mixture was then added an excess of the appropriate lithium salt (*ca.* 0.5 g) dissolved in hot ethanol (10 ml). The selenocyanato complexes were prepared using the correct stoichiometric amount of lithium selenocyanate.

The complexes crystallized when the solutions were allowed to cool to room temperature. They were collected, washed with ethanol and ether, and dried over calcium chloride. Analytical data for the complexes are given in Table VI.

Table VI. Analytical Data

Compound	Found (%)			Calculated (%)		
	C	H	M	C	H	M
[MnLCl_2]	58.7	4.4	9.6	59.0	4.2	9.6
[MnLBr_2]	50.6	3.7	8.5	51.0	3.7	8.3
[MnLI_2]	44.7	3.3	7.0	44.6	3.2	7.3
[MnL$(NCS)_2$]	58.5	4.0	8.8	58.5	3.9	8.9
[MnL$(NCSe)_2$]	50.4	3.6	7.8	50.8	3.4	7.7
[MnL$(NO_3)_2$] . H_2O	52.6	3.9	8.7	52.4	4.1	8.6
[FeLCl_2]	58.5	4.5	10.0	58.9	4.2	9.8
[FeLBr_2]	51.3	3.6	8.3	50.9	3.7	8.5
[FeLI_2]	44.5	3.1	7.3	44.6	3.2	7.4
[FeL$(NCS)_2$]	58.5	4.0	8.9	58.4	3.9	9.1
[FeL$(NCSe)_2$]	50.7	3.6	7.6	50.7	3.4	7.6
[FeL$(NO_3)_2$]	53.6	4.1	8.6	53.9	3.9	8.9
[CoLCl_2]	58.5	4.3	10.3	58.6	4.2	10.3
[CoLBr_2]	50.2	3.7	8.5	50.7	3.6	8.9
[CoLI_2]	44.3	3.2	7.6	44.4	3.2	7.8
[CoL$(NCS)_2$]	58.0	4.0	9.2	58.2	3.9	9.5
[CoL$(NO_3)_2$]	53.3	3.9	9.0	53.6	3.9	9.4
[NiLCl_2]	58.6	4.3	10.1	58.6	4.2	10.2
[NiLBr_2]	50.4	3.8	8.8	50.7	3.6	8.8
[NiLI_2]	44.1	3.6	7.6	44.4	3.2	7.8
α–[NiL$(NCS)_2$]	57.8	4.0	9.6	58.2	3.9	9.5
[NiL$(NO_3)_2$] . O . $5H_2O$	52.8	4.2	9.0	52.9	4.0	9.2
[CuL$(NCS)_2$]	57.4	3.8	10.3	57.7	3.9	10.2
[CuL$(NO_3)_2$] . H_2O	51.3	4.0	9.4	51.7	4.0	9.8

Dinitrato[2,3,5,6-tetrakis(6-methyl-2-pyridyl)pyrazine]-manganese(II) Monohydrate. To a hot solution of (I) (0.44 g, 1.0 mmole) in ethanol (20 ml) was added a solution of manganese(II) nitrate hexahydrate (0.29 g, 1.0 mmole) in ethanol (10 ml). The mixture was concentrated to about 20 ml and then cooled to room temperature whereupon the complex crystallized. It was recrystallized from ethanol, washed with ethanol and ether, and air-dried. Analytical data are given in Table VI.

α–Dithiocyanato[2,3,5,6-tetrakis(6-methyl-2-pyridyl)-pyrazine]nickel(II). To a hot solution of (I) (0.44 g, 1.0 mmole) in ethanol (20 ml) was added a hot solution of nickel(II) thiocyanate (0.18 g, 1.0 mmole) in ethanol (50 ml). The mixture was concentrated to about 20 ml and cooled to room temperature whereupon the green complex crystallized. It was recrystallized from ethanol, washed with ethanol and ether, and dried over calcium chloride. Analytical data are given in Table VI.

The acetone solvate was prepared by heating a sample of the unsolvated product with acetone for a few minutes. The brown product so formed was washed with acetone and dried at the pump. (Found: acetone, 15.7; Ni, 7.8; calculated for $[NiL(NCS)_2] \cdot 2[(CH_3)_2CO]$: acetone, 15.8; Ni, 8.0).

The Reaction Between (I) and Nickel(II) Thiocyanate in Ethanol-Ether. The ligand (I) (1.78 g, 4.0 mmole) and nickel(II) thiocyanate (0.72 g, 4.0 mmole) were heated together in ethanol (250 ml) until the process of solution was complete (about 30 minutes). The solution was diluted with ether (250 ml), and allowed to stand in a stoppered flask at room temperature for three days. After this time, small quantities of three different products had crystallized, these being distinguishable by their colours. The crystals were collected, washed with ether, and dried over calcium chloride. The reaction was repeated several times but only in some instances were sufficient quantities of the products obtained in large enough crystals to allow their separation by hand-picking. $[NiL(NCS)_2] \cdot H_2O$ formed large (up to 15 mm), light green, readily fractured needles. α–$[NiL(NCS)_2]$ was present as darker green, irregularly shaped crystals (up to 5 mm in length). β–$[NiL(NCS)_2]$ was produced as olive-green circular clusters of many small needles, the clusters being about 0.5 to 1.00 mm in diameter and of similar depth. A quantity of about 25 mg of each product was separated. *Anal.* (a) $[NiL(NCS)_2] \cdot H_2O$. Found: C, 56.3; H, 4.6; Ni, 8.6. Calcd. C, 56.5; H, 4.1; Ni, 9.2. (b) α–$[NiL(NCS)_2]$. Found: C, 58.0; H, 3.9; N, 18.1. (c) β–$[NiL(NCS)_2]$. Found: C, 58.2; H, 3.9; N, 17.8. Calcd. C, 58.2; H, 3.9; N, 18.1.

Physical Measurements. The room-temperature magnetic moments were determined by the Gouy method. The temperature dependence of the magnetism of the iron and cobalt complexes was measured using a Newport variable temperature Gouy balance. Diamagnetic corrections were calculated using Pascal's constants.[29]

The infrared spectra were obtained using a Perkin-Elmer 337 grating spectrophotometer. In the 4000-1300 cm^{-1} region halocarbon mulls of the compounds were used with sodium chloride optics; in the 1300-400 cm^{-1} region Nujol mulls were employed with potassium bromide optics.

The visible and near-infrared spectra were measured using a Zeiss PMQ II spectrophotometer. In the 400-1400 mμ region the diffuse reflectance spectra were measure using a small sample of the compound spread on filter paper. Measurements made in the 1400-2000 mμ region were obtained using either the pure solid compound or a mixture of the compound and magnesium oxide.

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