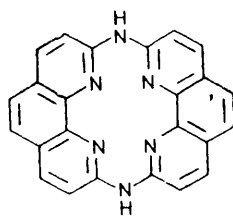


Chemistry of Polydentate Ligands. Part 5.† Complexes of 2,9-Dihydrazino-derivatives of 1,10-Phenanthroline. Dependence of Co-ordination Number of a Ligand on the Anion present

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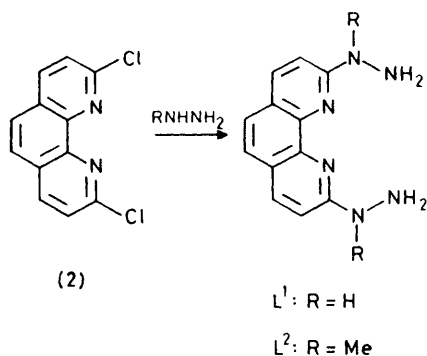
Two quadridentate ligands have been prepared by reaction of 2,9-dichloro-1,10-phenanthroline with hydrazine hydrate and methylhydrazine. The formation of complexes of Ag^{I} , Fe^{II} , Mn^{II} , Zn^{II} , Cd^{II} , Hg^{II} , and Ni^{II} with these ligands is described. Electrical conductivity, i.r., and ^1H n.m.r. spectral data of diamagnetic complexes are reported. The compound 2,9-dihydrazino-1,10-phenanthroline can also act as a tridentate ligand, as in the complex with nickel perchlorate, where the metal to ligand ratio is 1 : 2. Electronic spectral data of the nickel(II) complexes are presented. The preparation of a tridentate ligand, 2-(1-methylhydrazino)-1,10-phenanthroline, and of nickel(II) and iron(II) complexes of this ligand is also reported.

WHILE great interest in complexes of the ligands 2,2'-bipyridyl and 1,10-phenanthroline has been maintained for many years,¹ little effort has been directed towards substituting these ring systems so as to increase the co-



(1)

ordination number of the ligands. The few examples include studies by Goodwin² on some tridentate derivatives of phenanthroline, while Ogawa and Gotoh^{3,4} have prepared complexes of the quadridentate compound (1). Earlier papers in this series contain details



SCHEME

of work on quadridentate ligands incorporating 2,2'-bipyridyl,⁵⁻⁷ the parent ligands being prepared by condensation of hydrazines with 6,6'-dibromo-2,2'-bipyridyl. A similar route has been followed to the compounds L^1 and L^2 (Scheme). The preparation and chemistry of these ligands and some of their complexes are the subjects of this paper.

† Part 4, J. Lewis and K. P. Wainwright, *Inorg. Chim. Acta*, 1979, **34**, 57.

RESULTS AND DISCUSSION

The reactions of hydrazine hydrate and methylhydrazine with 2,9-dichloro-1,10-phenanthroline (2) under inert atmospheres yield yellow solids, L^1 and L^2 respectively (Scheme). Both compounds are unstable in alkaline solutions and solid L^1 decomposes over a period of days. Compound L^2 , which is isolated as the monohydrochloride salt, is stable when pure and dry. A satisfactory elemental analysis of L^1 was not obtained but a molecular ion at m/e 240 in the mass spectrum, elemental analyses of metal complexes of this ligand (Table 1), and the ^1H n.m.r. spectrum (Table 2) confirm the preparation of L^1 . A single methyl resonance in the n.m.r. of $\text{L}^2 \cdot \text{HCl}$ indicates that only one of the three possible isomers has been formed.⁷ The methyl-substituted nitrogen is a better nucleophile than the unsubstituted atom, and subsequent reactions of L^2 with carbonyl groups to produce hydrazone linkages confirm the product to be as drawn in the Scheme.⁷⁻⁹

Analytical data for L^2 and for complexes of L^1 and L^2 are contained in Table 1. The choice of metal ions was governed by possible template action of the cations in the formation of macrocycles and forms the subject of later papers.¹⁰ This Table also includes conductivity values, and the frequencies of any $\nu(\text{C}\equiv\text{N})$ signals for those complexes containing NCS^- groups. All the complexes appear to be indefinitely stable with the exception of the silver(I) and iron(II) compounds. The former are light sensitive and also give metallic silver when dissolved in dimethyl sulphoxide (dmsO). Decomposition of the iron(II) complexes, which is accompanied by a colour change from red to dark brown, is noticeable after a few months. Solutions of the iron(II) compounds are air sensitive.

Typical conductivity measurements for 1 : 1 electrolytes in dmsO¹¹ fall in the range 20–40 $\text{S cm}^2 \text{mol}^{-1}$, while 2 : 1 electrolytes give values between 50 and 80 $\text{S cm}^2 \text{mol}^{-1}$. The majority of the complexes in Table 1 are 2 : 1 electrolytes. However with $\text{Hg}(\text{L}^1)\text{Cl}_2$ the chloride ions are co-ordinated in solution, and the complexes $\text{Zn}(\text{L}^2)\text{Cl}_2$ and $\text{Cd}(\text{L}^2)\text{Cl}_2$ are partially dissociated since they act as 1 : 1 electrolytes. The cor-

TABLE 1
Analytical, electrical-conductance, and selected i.r. data for L² and complexes of L¹ and L²

Compound	Analysis (%) ^a			Λ ^b S cm ² mol ⁻¹	$\nu(\text{C}\equiv\text{N})$ cm ⁻¹
	C	H	N		
L ² ·HCl·0.5H ₂ O	53.6 (53.7)	5.8 (5.7)	26.8 (26.5)		
L ² ·HClO ₄	45.4 (45.6)	4.7 (4.7)	22.9 (22.8)	99 ^c	
L ² ·H ₂ PF ₆	40.4 (40.6)	4.2 (4.2)	20.2 (20.3)		
Mn(L ¹)Cl ₂	39.6 (39.4)	3.4 (3.3)	23.1 (23.0)	50	
Zn(L ¹)(SO ₄)	35.7 (35.9)	3.0 (3.0)	21.0 (20.9)	<i>d</i>	
Cd(L ¹)(NCS) ₂	36.2 (35.9)	2.7 (2.6)	24.4 (23.9)	64	2 078, 2 090
Ag(L ¹)(ClO ₄)	32.4 (32.2)	2.7 (2.7)	19.5 (18.8)	<i>e</i>	
Hg(L ¹)Cl ₂	28.1 (28.2)	2.7 (2.4)	16.7 (16.4)	6	
Mn(L ²)Cl ₂	42.6 (42.7)	4.1 (4.1)	21.7 (21.3)	59	
Mn(L ²)(NCS) ₂	43.4 (43.7)	3.8 (3.7)	25.6 (25.5)	67	2 080
Zn(L ²)Cl ₂	41.4 (41.5)	4.1 (4.0)	20.9 (20.8)	20	
Zn(L ²)Cl(O ₂ CMe)	45.3 (45.1)	4.5 (4.5)	19.8 (19.7)	<i>d</i>	
Cd(L ²)I ₂	26.8 (26.5)	3.0 (2.6)	13.3 (13.3)		
Cd(L ²)Cl ₂	37.2 (37.2)	3.7 (3.6)	18.7 (18.6)	21	
Cd(L ²)(NCS) ₂	38.7 (38.7)	3.3 (3.3)	22.4 (22.5)		2 065, 2 085, 2 096
Ag(L ²)(ClO ₄)	34.1 (34.1)	3.4 (3.7)	16.9 (17.0)	<i>e</i>	
Fe(L ²)Cl ₂ ·H ₂ O	40.8 (40.7)	3.9 (4.4)	20.1 (20.4)		
Fe(L ²)(NCS) ₂ ·2H ₂ O	40.3 (40.3)	3.9 (4.2)	24.1 (23.5)		2 080
[(Fe(L ²)Cl ₂) ₂ O]·2H ₂ O	39.8 (39.9)	4.5 (4.2)	19.4 (19.5)		

^a Calculated values are given in parentheses. ^b 10⁻³ mol dm⁻³ solutions in dmso at 22 °C. ^c 10⁻³ mol dm⁻³ solution in methanol at 22 °C. ^d Insoluble in dmso. ^e Decomposes in dmso.

TABLE 2
Hydrogen-1 n.m.r.^a data for L¹, L², and their zinc(II) and cadmium(II) complexes

Compound	Solvent	H ³	H ⁴	H ⁵	H ⁹	H ¹⁰	H ¹¹	<i>J</i> (H ³ H ⁴) ^b
L ¹	[² H ₆]dmso	6.92	7.93	7.36				9
L ² ·HCl	CD ₃ OD ^c	7.5	8.0	7.4		3.5		9
1,10-Phenanthroline	[² H ₆]dmso	7.63	8.29	7.60		3.50		9.1
	[² H ₆]dmso ^d	7.88	8.61	8.12				8.4
	tfa ^e	8.54	9.45	8.59				8.5
Zn(L ¹)(SO ₄)	[² H ₆]dmso	7.11	8.11	7.54				8.1
Zn(L ²)Cl(O ₂ CMe)	[² H ₆]dmso	7.29	8.23	7.54		3.40		9.0
Cd(L ¹)(NCS) ₂	[² H ₆]dmso	7.01 ^f	8.14	7.53	9.14		5.13	9.0
		6.89 ^g	8.03	7.51	8.79		4.54	8.8
		7.41 ^f	8.36	7.65		3.51	5.52	9.2
Cd(L ²)(NCS) ₂	[² H ₆]dmso	7.33 ^g	8.31	7.64		3.51	4.89	9.1
		7.33	8.30	7.61		3.43	5.23	9.1
		7.32	8.33	7.63		3.49	4.89	9.1

^a Chemical shifts in p.p.m. relative to SiMe₄ as the zero. ^b Coupling constants in Hz. ^c Run at 60 MHz. ^d Ref. 15. ^e Ref. 16, tfa is trifluoroacetic acid; the phenanthroline ion is present. ^f More abundant species. ^g Less abundant species. The ratio of the more abundant to the less abundant species is 3 : 1. ^h Separation between aromatic region signals from the species present is small and they are unresolved. The H¹¹ signals are resolved, and the less abundant resonances are found at δ 4.84 for Cd(L²)Cl₂ and 5.40 for Cd(L²)I₂.

responding manganese(II) complex is fully dissociated in this solvent.

The i.r. spectra of the various complexes and the free ligands are similar when allowance is made for signals from the axial ligands and/or counter ions. General features include two bands in the N-H stretching region, between 3 100 and 3 300 cm^{-1} ,¹² an N-H bending mode at *ca.* 1 650, and a strong band at *ca.* 850 cm^{-1} , the C-H deformation of the phenanthroline hydrogens.¹³ The $\nu(\text{N-H})$ signals normally occur at 3 300 and 3 210 cm^{-1} for the complexes, and *ca.* 30 cm^{-1} higher in the spectra of the free ligands. The spectra of the cadmium(II) complexes contain at least one additional signal in this region. With $\text{Cd}(\text{L}^2)\text{X}_2$ this band occurs at 3 255 cm^{-1} , while $\text{Cd}(\text{L}^1)(\text{NCS})_2$ gives five N-H signals: two in the usual positions and three at higher frequencies, the highest appearing at 3 390 cm^{-1} . The compounds $\text{Cd}(\text{L})(\text{NCS})_2$ ($\text{L} = \text{L}^1$ or L^2) also give extra $\nu(\text{C}\equiv\text{N})$ bands (Table 1). A sole resonance at 2 080 cm^{-1} , indicative of N-bonded isothiocyanato-ligands,¹⁴ is recorded for $\text{Mn}(\text{L}^2)(\text{NCS})_2$ whereas two bands of equal intensity are observed for $\text{Cd}(\text{L}^1)(\text{NCS})_2$, while $\text{Cd}(\text{L}^2)(\text{NCS})_2$ provides three signals, the band at 2 065 cm^{-1} being slightly weaker than the other two. The i.r. spectra indicate that the co-ordination of L^1 and L^2 to cadmium(II) differs from the simple *trans* equatorial binding expected for the other complexes in Table 1.

The ^1H n.m.r. spectral data for the ligands and the diamagnetic zinc(II) and cadmium(II) complexes are contained in Table 2. A broad region around 5 p.p.m. in each spectrum is assigned to the terminal NH_2 hydrogens while hydrogen atoms attached to secondary nitrogens present in L^1 and its complexes give resonances at *ca.* δ 9. The high-field signal for any methyl groups present occurs at *ca.* δ 3.5, close to the value expected for a methyl bound to a substituted nitrogen when the other substituent is an aromatic ring.¹² The relative ordering of the aromatic signals from H^3 and H^4 was assigned by comparison with the positions of these atoms in the spectrum of 1,10-phenanthroline.¹⁵ Complex formation produces only slight alterations in the chemical shifts of the aromatic hydrogens in L^1 and L^2 , with H^3 , the hydrogen *ortho* to the position of substitution, being the most susceptible to change. The disparity in chemical shifts between $\text{L}^2\cdot\text{HCl}$ and the phenanthroline ion¹⁶ indicates that, as expected, the site of protonation in $\text{L}^2\cdot\text{HCl}$ is a hydrazine nitrogen. Spectra of the cadmium(II) complexes are again atypical as they demonstrate the existence, in solutions, of two forms of the ligands. The relative abundance of the two species present in the NCS^- salts, measured from the integration of the signals, is roughly 3 : 1, with signals from the more abundant types occurring at lower fields.

The exact causes of the unusual n.m.r. and i.r. spectra of the cadmium(II) complexes are debatable. The rigidity of the quadridentate ligands L^1 and L^2 ensure

* Linear quadridentate ligands can co-ordinate in any of three stereochemistries; *trans*, *cis- α* , and *cis- β* . See ref. 6 and E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.

that these compounds adopt *trans* conformations in complexes, and rules out an explanation for the $\nu(\text{C}\equiv\text{N})$ signals, involving *cis* stereochemistries, that is valid for related ligands based on 2,2'-bipyridyl.* The information from $\text{Cd}(\text{L}^1)(\text{NCS})_2$ is compatible with L^1 being a tridentate ligand. A rotation about one phenanthroline-hydrazine bond (Figure) would remove one NH_2

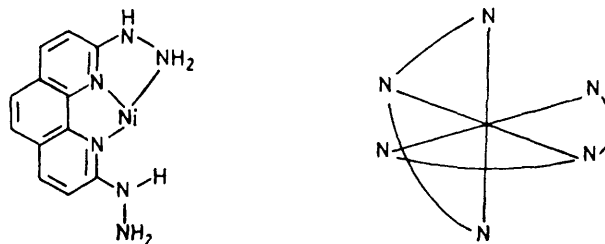


FIGURE Co-ordination mode of L^1 in $\text{Ni}(\text{L}^1)_2(\text{ClO}_4)_2$

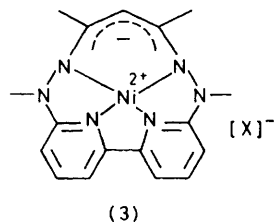
group from the co-ordination sphere of the metal ion. This mode of binding is proposed below for a nickel(II) complex but is considered unlikely here. The n.m.r. evidence indicates that both L^1 and L^2 adopt similar co-ordination geometries in solution, but L^2 cannot act as a tridentate ligand. An equivalent rotation to the above would produce a large non-bonded interaction between the methyl group and the metal ion. A possible explanation of the spectra involves the co-ordination number of the cadmium(II) ions varying. Equilibria between cadmium halide complexes, $[\text{CdX}_n]^{(n-2)-}$ ($n = 0-4$), are well known,¹⁷ and similar equilibria could be present here. Differentiation between the species in solution will occur in the axial co-ordination of anions. Support for this interpretation is provided by the n.m.r. spectra of $\text{Cd}(\text{L}^2)\text{Cl}_2$ and $\text{Cd}(\text{L}^2)\text{I}_2$. The expected anion dependence of the equilibrium constants should result in different ratios of the species present for different anions. This is found to be the case since the ratio is 2 : 1 for chloride ions in solution and 1 : 5 for $\text{Cd}(\text{L}^2)\text{I}_2$, the figures being determined from the H^{11} resonances in the n.m.r. spectra.

The Mössbauer spectrum of $\text{Fe}(\text{L}^2)(\text{NCS})_2\cdot 2\text{H}_2\text{O}$ was recorded at room temperature. The isomer shift of 1.0 mm s^{-1} and quadrupole splitting of 3.06 mm s^{-1} are characteristic of high-spin octahedral iron(II).¹⁸ Reaction of $\text{L}^2\cdot\text{HCl}$ with $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ gave an immediate precipitate of a dark brown solid which analyses as the oxygen-bridged dimer $[\{\text{Fe}(\text{L}^2)\text{Cl}_2\text{O}\}]_2\cdot 2\text{H}_2\text{O}$, a common reaction when iron(III) and 1,10-phenanthroline derivatives are allowed to interact in the presence of water.^{19,20}

Nickel(II) Complexes. The nickel(II) complex of L^2 was regarded as a possible intermediate in macrocycle formation in view of previous work in this laboratory.⁷ Compound (3) is formed by condensation of pentane-

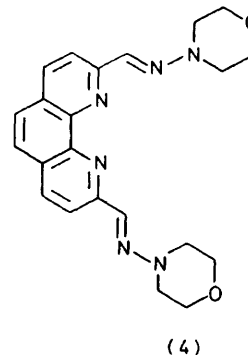
† Ratios are given as lower-field resonances: higher-field resonances. Chemical-shift separations between equivalent aromatic hydrogens in equilibrated complexes are much smaller with halides as counter ions than with NCS^- groups, and signals in the aromatic region for complexes containing halide ions are poorly resolved.

2,4-dione with 6,6'-di(1-methylhydrazino)-2,2'-bipyridyl in the presence of a nickel(II) template. Molecular models show that the macrocyclic ring in (3) is highly strained; indeed the strain present is invoked to explain



why copper(II) does not act as a template for this reaction, while it does so for a similar preparation of another macrocyclic ring containing 13 atoms.²¹ The inability to prepare the phenanthroline analogue of (3) adds some support to the strain hypothesis as the 1,10-phenanthroline residue is less flexible than 2,2'-bipyridyl. During the course of this investigation an unusual reaction was encountered where the product is dependent on the anion present. Addition of Ni[ClO₄]₂·6H₂O to a hot solution of L²·HCl in aqueous ethanol produced a transient green colour before giving a yellow solution. The yellow solid isolated on cooling is the monohydrop perchlorate salt of L². A similar reaction with NiCl₂·6H₂O yielded a green paramagnetic solid Ni(L²)Cl₂ (Table 3). The i.r. spectrum of Ni(L²)(NCS)₂ contains just one ν(C≡N) signal, at 2 090 cm⁻¹, which implies axial co-ordination of the NCS⁻ groups. Introduction of [NH₄]-

2 : 1. There are two possible arrangements of the pairs of planar L¹ molecules such that they provide the required octahedral co-ordination geometry about the metal ion: (i) each molecule acts as a tridentate ligand, and (ii) one ligand molecule is quadridentate and the other bidentate. Both (i) and (ii) could give rise to the three ν(N-H) bands in the i.r. spectrum. However, the latter arrangement is unlikely. Only *trans* equatorial binding of the linear quadridentate group is feasible so the bidentate ligand would have to co-ordinate in both



axial sites, and the bite of L¹ is insufficient to span these positions. Each molecule is therefore believed to be acting as a tridentate ligand as shown in the Figure, and the i.r. signal at 3 375 cm⁻¹ is assigned to the unco-ordinated NH₂ group. Indirect support for this interpretation is provided by the crystal structure of bis-

TABLE 3

Analytical, electrical-conductance, magnetic moment, and spectral data for nickel(II) complexes of L¹ and L²

Complex	Analysis (%) ^a			Λ ^b S cm ² mol ⁻¹	μ _{eff.} B.M.	ν ₁ ^c cm ⁻¹
	C	H	N			
Ni(L ¹) ₂ (ClO ₄) ₂	39.0 (39.0)	3.3 (3.3)	22.8 (22.8)	184	3.12	10 900
Ni(L ¹)Cl ₂ ·0.75EtOH	39.8 (40.1)	4.5 (4.1)	20.8 (20.8)	185	3.16	10 000
Ni(L ²)Cl ₂	41.9 (42.2)	4.2 (4.1)	21.3 (21.1)	202	3.06	10 360
Ni(L ²)(NCS) ₂ ^d	43.2 (43.4)	3.8 (3.6)	24.8 (25.3)			^e

^a Calculated values are given in parentheses. ^b 10⁻³ mol dm⁻³ solutions in methanol at 22 °C. ^c Spectra run in methanol or water. ^d ν(C≡N) at 2 090 cm⁻¹ in the i.r. spectrum. ^e Insoluble in these solvents.

[PF₆]⁻ to a solution containing Ni(L²)Cl₂, prepared *in situ*, gives the yellow solid L²·HPF₆. Metathesis is the preferred reaction to complex formation when the anion is weakly co-ordinating.

The reaction of nickel(II) with L¹ is also anion dependent. The octahedral complex Ni(L¹)Cl₂ is formed when NiCl₂·6H₂O is added to a solution of L¹, but the product from mixing equimolar quantities of L¹ and Ni[ClO₄]₂·6H₂O in solution is now a green paramagnetic complex. A broad resonance at 1 085 cm⁻¹ in the i.r. spectrum of this compound demonstrates that ionic perchlorate is present,²² while the ν(N-H) region contains three bands, the additional signal being found at 3 375 cm⁻¹. Analytical data are consistent with the formula Ni(L¹)₂(ClO₄)₂; that is a ligand to cation mole ratio of

[2,9-di(morpholinoiminomethyl)-1,10-phenanthroline]-nickel(II) tetrafluoroborate, a complex with compound (4).²³ The two molecules of the potentially quadridentate ligand are, by means of a rotation about one phenanthroline-carbon bond on each, both acting as tridentate species. Compound L² cannot be transformed into a tridentate ligand (see above) and so does not undergo a similar reaction to L¹. Quite why nickel(II) is reluctant to form square-planar complexes with L¹ and L² is uncertain.

Electronic spectra of the nickel(II) complexes were recorded in aqueous or methanolic solutions, the choice being governed by solubility of the compounds. Intense π→π* bands obscure all but the lowest energy d-d signal, ν₁. The frequency of this band, which corres-

ponds to the transition ${}^3A_{2g} \rightarrow {}^3T_{2g}$, provides a rough measure of the ligand-field splitting, Δ , in the pseudo-octahedral complexes.²⁴ The results, recorded in Table 3, show L^2 to have slightly greater ligand field (ν_1 at $10\,360\text{ cm}^{-1}$) than L^1 (ν_1 at $10\,000\text{ cm}^{-1}$). Both values are *ca.* $1\,000\text{ cm}^{-1}$ lower than the figures measured for the analogous substituted bipyridyl complexes.²⁵ It is interesting to note the proximity of these results to the

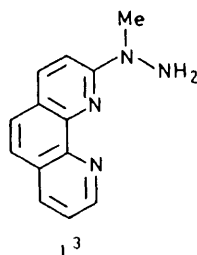


figure of $9\,900\text{ cm}^{-1}$ estimated to be the minimum value of Δ required for the formation of diamagnetic, as opposed to paramagnetic, square-planar nickel(II) complexes.²⁶ To the best of our knowledge no paramagnetic square-planar nickel(II) complexes have been isolated to date.²⁷

Complexes of L^3 . An intermediate in the preparative route to (2) is 2-chloro-1,10-phenanthroline. Condensation of this compound with methylhydrazine gives L^3 as the hydrochloride salt. Analytical data for $L^3 \cdot HCl$ and some complexes of this ligand are contained in Table 4: the iron(II) complexes are stable in air for about 1

TABLE 4
Analytical data (%) for L^3 and some complexes of this ligand

Compound	Analysis (%) ^a		
	C	H	N
$L^3 \cdot HCl$	59.7 (59.9)	5.1 (5.0)	21.4 (21.5)
$Ni(L^3)_2(ClO_4)_2$ ^b	44.4 (44.2)	3.6 (3.4)	15.6 (15.9)
$Fe(L^3)_2Cl_2$ ^c	54.1 (54.3)	4.4 (4.2)	19.3 (19.5)
$Fe(L^3)_2(BF_4)_2 \cdot 1.5H_2O$	44.3 (44.4)	3.6 (3.6)	15.9 (15.9)

^a Calculated values are given in parentheses. ^b The electronic spectrum taken on a methanolic solution of this compound contains one *d-d* transition (ν_1) at $11\,500\text{ cm}^{-1}$ with an absorption coefficient of $71\text{ m}^2\text{ mol}^{-1}$. The room-temperature magnetic moment μ_{eff} is 3.35 B.M. ^c $\mu_{\text{eff}} = 5.08\text{ B.M.}$ at 20°C .

month. Again the only *d-d* band visible in the electronic spectrum of the nickel(II) complex is ν_1 . This value is 600 cm^{-1} higher than that measured for L^1 when acting as a tridentate ligand, a difference that is possibly due to slight steric interactions present in the complex. The room-temperature magnetic moment of $Fe(L^3)_2Cl_2$, $\mu_{\text{eff}} = 5.08\text{ B.M.}$, is noticeably lower than the expected value of 5.3 B.M. for a quintet ground state.*

EXPERIMENTAL

Infrared spectra of Nujol mulls supported between sodium chloride discs were recorded using Perkin-Elmer 257 and

457 spectrometers, over the range $625\text{--}4\,000\text{ cm}^{-1}$. Conductance measurements were made with a Wayne-Kerr Universal bridge. Hydrogen-1 n.m.r. spectra were recorded at 80 MHz on a Varian CFT-20, apart from one example when a 60-MHz Perkin-Elmer R24 was used. Magnetic moments were obtained on a Newport Gouy balance; the readings were corrected for ligand and inner-core diamagnetism using Pascal's constants.²⁸ A Cary model 14M-50 recording spectrophotometer was used to measure the electronic spectra. The mass spectrum was obtained with an A.E.I. MS12 spectrometer. The Mössbauer spectrum was recorded on equipment previously described.²⁹ Microanalyses were performed by the University Chemical Laboratory Microanalytical Department.

Dimethyl sulphate was fractionally distilled before use while phosphorus oxychloride was purified by a published method.³⁰ All other reagents were used without further purification.

2,9-Dichloro-1,10-phenanthroline.—The preparation of this compound has been described previously,^{3,4,31} but as extensive alterations in work-up procedures were made details of the synthesis are reported here. The route is the same as in earlier papers and consists of six steps.

(i). 1,10-Phenanthroline hydrate (70 g) was dissolved in hot benzene (750 cm^3) and dimethyl sulphate (45 cm^3) added slowly over 2 h. **CAUTION:** This solution must not be allowed to come into contact with the skin. A white solid appears during the addition and the mixture was refluxed for another hour before allowing it to cool. The mother liquor was then decanted and the solid dried *in situ* by evacuating the flask. This took 3 d.

(ii). Potassium ferricyanide (275 g) was dissolved in water ($1\,250\text{ cm}^3$) and the solution thoroughly cooled in ice. Sodium hydroxide (300 g) was also dissolved in water ($1\,000\text{ cm}^3$) and cooled, as was the product from step (i) ($1\,250\text{ cm}^3$). These two solutions were added dropwise, over 3 h, to the aqueous $K_3[Fe(CN)_6]$ with rapid stirring. The temperature was kept below 5°C . The slurry was then stirred for another hour before filtering and the solid was washed several times with cold water. Several batches of hot $CHCl_3$ were then added to dissolve the solid, each aliquot being filtered under suction into a separating funnel. The aqueous layer was separated from the organic solvent, as were several washings with water. The chloroform layer was then dried with $Mg[SO_4]$ and boiled with charcoal before filtering. Reduction of the volume of solvent on a rotary evaporator, with a minimal amount of heating, gave a yellow solid, which was filtered off and allowed to dry in air.

(iii). This product was dissolved in phosphorus oxychloride (600 cm^3), and phosphorus pentachloride (85 g) added. The solution was refluxed, under nitrogen, for 8 h before the solvent was distilled off to leave a solid residue. Ice was carefully added to the solid until no further reaction occurred, followed by sufficient aqueous ammonia to make the solution basic. The white solid was filtered off, heated in an excess of $CHCl_3$, and filtered again while hot. Decolourising charcoal was added to the hot solution and, after filtering, the volume was reduced to yield a brown solid. This was recrystallised several times from CCl_4 to give 2-chloro-1,10-phenanthroline as white needles.

(iv). This solid (40 g) was dissolved in Me_2SO_4 (300 cm^3) and the solution kept at 100°C for 2 h. The liquid was

* Throughout this paper: $1\text{B.M.} = 9.27 \times 10^{-24}\text{ A m}^2$.

then poured into 3 000 cm³ of diethyl ether. The resulting white solid was filtered and dissolved in water (400 cm³) ready for the next step.

(v). The slow addition of this solution and of aqueous Na[OH] (85 g in 550 cm³) to the aqueous K₃[Fe(CN)₆] (130 g in 550 cm³) was again performed with the temperature < 5 °C. The same work-up procedure as in step (ii) was used here.

(vi). The dark brown solid was added to POCl₃ (600 cm³), followed by PCl₅ (30 g). The procedure was then the same as step (iii). The crude product is dark brown, the white solid only appearing after several recrystallisations from CHCl₃, using decolourising charcoal.

Yield for all six reactions was 32%.

2,9-Dihydrazino-1,10-phenanthroline, L¹.—2,9-Dichloro-1,10-phenanthroline (4 g) was added to refluxing degassed hydrazine hydrate (30 cm³), under a nitrogen atmosphere, and the solution refluxed for 1 h. Cooling gave yellow crystals which were filtered and washed with chloroform (5 cm³). The solid was recrystallised twice from methanol. Yield 70%.

2,9-Di(1-methylhydrazino)-1,10-phenanthroline Monohydrochloride, L²·HCl.—2,9-Dichloro-1,10-phenanthroline (4 g) was added to refluxing degassed methylhydrazine (30 cm³) under an inert atmosphere. An immediate exothermic reaction occurred. The solvent was rapidly distilled off to leave a yellow solid. This was filtered off, washed with CHCl₃ (5 cm³), and recrystallised from methanol. A second crop of crystals can be obtained by reducing the volume of the methanol and adding a little dilute HCl. Yield 60%.

2,9-Di(1-methylhydrazino)-1,10-phenanthroline Monohydroperchlorate.—The compound L²·HCl (0.15 g, 0.5 mmol) was dissolved in water (20 cm³) at 60 °C and a solution of Ni[ClO₄]₂·6H₂O (0.5 mmol) in ethanol (10 cm³) added dropwise over 20 min. The solution was then heated to 80 °C for 1 h before cooling to yield a yellow solid. This was filtered off, washed with ice-water, and recrystallised from a 90% water-ethanol mixture. The yield was almost quantitative.

2,9-Di(1-methylhydrazino)-1,10-phenanthroline Monohydrofluorophosphate.—The compound L²·HCl (0.2 mmol) was suspended in water (20 cm³) and solid NiCl₂·6H₂O (0.2 mmol) added. The mixture was stirred until the solid dissolved and then [NH₄][PF₆] (0.4 mmol) introduced. A yellow solid came out of solution after 20 min, and was filtered off and washed with ethanol. Yield 90%.

2-(1-Methylhydrazino)-1,10-phenanthroline Monohydrochloride, L³·HCl.—2-Chloro-1,10-phenanthroline (2 g) was added to refluxing degassed methylhydrazine (20 cm³) under an inert atmosphere. A vigorous reaction took place and the excess of solvent was distilled off to give a yellow solid, which was filtered off and recrystallised from ethanol. Yield 70%.

Complexes of L¹ and L² with Mn^{II}, Zn^{II}, Cd^{II}, and Hg^{II}.—A general method involved dissolving the ligand in either hot water or methanol and adding a solution of a salt of the appropriate metal ion. Any addition of large anions to induce precipitation was performed after cooling the solution. The product was filtered off, washed, and vacuum dried. The salts used were MnCl₂·4H₂O, Zn[O₂CMe]₂·2H₂O, CdCl₂·2.5H₂O, Cd[O₂CMe]₂, and HgCl₂. Yields were almost quantitative.

Silver(I) Complexes of L¹ and L².—The ligand (0.5 mmol) was dissolved in methanol (25 cm³) at room temperature,

and Ag[ClO₄] (0.5 mmol) added. The mixture was shielded from light throughout the experiment. After stirring for 1 h, the solid was filtered off and washed with ethanol before being vacuum dried. The yield was quantitative.

Iron(II) Complexes of L². The example given is the chloride complex. The complex Fe(py)₄Cl₂ (py = pyridine) (0.7 mmol) was added to a refluxing degassed solution of L²·HCl (0.7 mmol) in acetonitrile (50 cm³). Heating was continued until all the solid had dissolved; ca. 2 h. A red solid appeared on cooling, and was filtered off under nitrogen and washed with diethyl ether. Yield 80%.

[{Fe(L²)Cl₂]₂O}·2H₂O.—The salt FeCl₃·6H₂O (1 mmol) was added to a degassed refluxing solution of L²·HCl (1 mmol) in methanol (30 cm³). A dark brown solid formed immediately. After cooling, this solid was filtered off and washed with water and ethanol. The yield was quantitative.

Ni(L²)Cl₂.—A solution of NiCl₂·6H₂O (0.3 mmol) in methanol (15 cm³) was added dropwise to L²·HCl (0.3 mmol) in hot ethanol (30 cm³), and the mixture refluxed for 15 min. On cooling, a green solid appeared which was filtered off and washed with ethanol and diethyl ether. Yield 80%.

Ni(L¹)Cl₂.—A solution of NiCl₂·6H₂O (0.6 mmol) in methanol (10 cm³) was slowly added to L¹ (0.6 mmol) in refluxing ethanol (25 cm³). Cooling, after 5 min reflux, and addition of diethyl ether gave a green solid which was filtered off and washed with diethyl ether. The yield was quantitative.

Ni(L¹)₂(ClO₄)₂.—Slow addition of Ni[ClO₄]₂·6H₂O (0.2 mmol) in methanol (10 cm³) to L¹ (0.2 mmol) in hot methanol (15 cm³) produced a green solution. Refluxing for 20 min, cooling, and addition of diethyl ether yielded a green solid. This was filtered off and air dried. The yield was quantitative.

Ni(L³)₂(ClO₄)₂.—The compound L³·HCl (0.4 mmol) was added to a refluxing solution of Ni[ClO₄]₂·6H₂O (0.2 mmol) in acetonitrile (20 cm³). The solution was refluxed for 1 h before the volume was reduced on a rotary evaporator to give a green solid. This was filtered off and washed with ethanol before recrystallising from ethanol-acetonitrile. Yield 80%.

Iron(II) Complexes of L³.—Method given is for the chloride. The complex Fe(py)₄Cl₂ (0.3 mmol) and L³·HCl (0.6 mmol) were added to refluxing degassed acetonitrile (40 cm³) and the mixture heated until the solids dissolved. A red product was precipitated on cooling. This solid was filtered off and vacuum dried. The yield was quantitative.

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