

Metal Complexes of 1-Methyl-3,4-diphenylpyrazole, a Ligand Formed by the Reaction between Benzil and N,N-dimethylhydrazine

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Received October 19, 1984

Abstract

New complexes of the general formulae MnX_2L_2 ($X = Cl, Br$), $MnBr_2L_3$, CoX_2L_2 ($X = Cl, Br, I, NCS, NO_3$), NiX_2L_2 ($X = Cl, NO_3$), $NiBr_2L_3 \cdot H_2O$, $NiI_2L_4 \cdot H_2O$, $CuCl_2L$, $CuBr_2L_2 \cdot H_2O$, $Cu(NO_3)_2L_2$, ZnX_2L_2 ($X = Cl, Br, NO_3$), $Zn(NCS)_2L_2 \cdot H_2O$, CdX_2L_2 ($X = I, NO_3$) and $HgCl_2L$, where L is 1-methyl-3,4-diphenylpyrazole, have been prepared and characterised by elemental analysis, conductivity measurements, magnetic moments and spectral (¹H-NMR, IR and electronic) studies. The ligand is formed by the reaction between benzil and N,N-dimethylhydrazine. The nitrogen of the $>C=N-$ bond is the donor atom to the metal ions. The bis-ligand halide complexes are pseudotetrahedral, while the nitrate complexes contain octahedrally coordinated metal ions. The IR spectra of MCl_2L ($M = Cu, Hg$) are indicative of the presence of both terminal and bridging metal-halogen bonds supporting polymeric structures. The stereochemistry and the nature of the nickel(II) complexes are markedly dependent upon the anions; the chloride complex is pseudotetrahedral, the iodide square planar, the nitrate polymeric octahedral, while the proposed structural formula for $NiBr_2L_3 \cdot H_2O$ comprises nickel(II) atoms present in both square planar and octahedral coordination environments.

Introduction

The interest in the study of hydrazones has been growing due to their use in biological systems [1] and analytical chemistry [2]. Ligands containing the $-N=C-C=N-$ grouping are amongst the best known chelating agents e.g. dimethylglyoxime, 2,2'-bipyridine and 1,10 phenanthroline. Other ligands containing this grouping can be synthesised by condensation reactions between 1,2-diketones

and hydrazines. Some iron(II), cobalt(II) and nickel(II) complexes of these ligands display both high-spin and low-spin behaviour [3–5]. 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.

As part of our systematic investigation of the coordination chemistry of α -dihydrazone ligands [6–9] we attempted to prepare benzilbis(N,N-dimethylhydrazine), but we unexpectedly obtained 1-methyl-3,4-diphenylpyrazole (I, L). In this paper, we report complexes of this heavily substituted pyrazole with manganese, cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II) salts. Complexes of other substituted pyrazoles have been prepared and studied previously [10–14].

Experimental

Experimental techniques were as described previously [6].

1-Methyl-3,4-Diphenylpyrazole (L)

A solution of benzil (150 g, 0.71 mol) in absolute ethanol (500 ml) was treated with N,N-dimethylhydrazine (60 ml, 0.79 mol). The mixture was heated under reflux for 10 h with vigorous stirring. The resulting solution was dark brown in colour. The ethanol was then distilled off in vacuo leaving a thick dark brown oil. Diethyl ether (550 ml) was added and the oil scratched to yield a light brown non-crystalline solid. The mixture was filtered and the insoluble product was washed with ether and dried in air. The solid was recrystallised twice from aqueous ethanol (ethanol: water = 2:1) to yield 67.5 g (41%) of creamy-white crystals (m.p. 154–5 °C). *Anal.* Found: C, 81.53; H, 6.07; N, 11.84%; $C_{16}H_{14}N_2$ requires C, 82.01; H, 6.03; N, 11.96%.

Preparation of the Complexes

The complexes were prepared by adding a warm solution of the required metal salt (4 mmol) in

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absolute ethanol to a, vigorously stirred, hot solution of the ligand (16.5 mmol) in 25–30 ml of absolute ethanol. When $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$, $\text{NiI}_2 \cdot x\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were used as starting materials, 3–5 ml of triethyl orthoformate were added to the reaction mixture for dehydration purposes because without this reagent the products were often contaminated with metal hydroxides. All cobalt(II) complexes were prepared under an atmosphere of nitrogen. Solid product formation was usually instantaneous, although the precipitation of CoI_2L_2 and $\text{Cd}(\text{NO}_3)_2\text{L}_2$ occurred slowly over 1–2 h. The compounds NiCl_2L_2 and $\text{Zn}(\text{NO}_3)_2\text{L}_2$ did not crystallise from ethanol but were precipitated by the addition of small quantities of 1:2 heptane–ether mixture and ether respectively, to the cooled solutions. The precipitates were collected by filtration and washed with ethanol and ether. All complexes except NiCl_2L_2 which was soluble, were refluxed in absolute ethanol to remove unreacted starting materials, then filtered off and washed as above. They were dried in vacuo over silica gel.

Efforts to prepare complexes with other stoichiometries, using various metal salt: ligand molar ratios, met with failure. In the case of manganese(II) bromide two different complexes were obtained.

Using 17 mmol of ligand and 4 mmol of anhydrous manganese(II) bromide the complex MnBr_2L_3 was prepared, while using a 2:1 ligand:metal ion molar ratio MnBr_2L_2 was isolated. The analogous chloride complex MnCl_2L_3 could not be isolated although a vast excess (*ca.* 6:1) of ligand was used. It is worth noting that attempts to prepare iron(II) complexes under an atmosphere of nitrogen were also made, but solid products with poor analytical results and of uncertain nature were obtained.

Results and Discussion

The product we expected from the reaction of *N,N*-dimethylhydrazine and benzil was benzilbis-(dimethylhydrazone); we expected the reaction to resemble that between diacetyl and *N,N*-dimethylhydrazine [7]. This however, was not the case, the product being instead 1-methyl-3,4-diphenylpyrazole. This type of ring formation is common with β -diketones [15] but as far as we are aware it is unknown amongst α -diketones.

Colours, analytical results and molar conductivity values for the prepared compounds are given in Table I. The complexes were readily prepared by direct reaction between the metal salt and an excess of ligand in hot ethanol. The complexes are micro-

TABLE I. Colours, Analytical and Conductivity Data for Complexes of 1-Methyl-3,4-diphenylpyrazole.

Complex	Colour	Elemental analyses ^a (%)			$\Lambda_{\text{M}}^{\text{b}}$ ($\text{ohm}^{-1} \text{mol}^{-1} \text{cm}^2$)
		C	H	N	
MnCl_2L_2	cream	64.7(64.6)	4.91(4.76)	9.3(9.4)	22
MnBr_2L_2	pale pink	56.3(56.2)	4.26(4.14)	8.1(8.2)	21
MnBr_2L_3	pale pink	62.5(62.8)	4.57(4.62)	8.7(9.2)	24
CoCl_2L_2	blue	64.0(64.2)	4.76(4.72)	9.4(9.4)	2
CoBr_2L_2	blue	55.4(55.9)	4.21(4.11)	8.3(8.2)	5
CoI_2L_2	bluish-green	50.3(49.2)	3.72(3.62)	7.3(7.2)	33
$\text{Co}(\text{NCS})_2\text{L}_2$	blue	62.1(63.4)	4.32(4.38)	12.9(13.1)	5
$\text{Co}(\text{NO}_3)_2\text{L}_2$	deep red	59.2(59.0)	4.36(4.34)	13.0(12.9)	23
NiCl_2L_2	bluc	64.1(64.2)	4.61(4.73)	9.2(9.4)	17
$\text{NiBr}_2\text{L}_2 \cdot \text{H}_2\text{O}$	yellow	62.0(61.4)	4.94(4.73)	9.0(9.0)	42
$\text{NiI}_2\text{L}_4 \cdot \text{H}_2\text{O}$	yellow-orange	60.6(60.6)	4.72(4.62)	8.6(8.8)	152
$\text{Ni}(\text{NO}_3)_2\text{L}_2$	pale-green	59.6(59.0)	4.56(4.34)	12.8(12.9)	80 ^c
CuCl_2L	green	51.5(52.1)	3.51(3.79)	7.5(7.6)	^d
$\text{CuBr}_2\text{L}_2 \cdot \text{H}_2\text{O}$	brown	53.7(54.0)	4.03(4.26)	7.5(7.9)	^d
$\text{Cu}(\text{NO}_3)_2\text{L}_2$	dull green	57.9(58.6)	4.36(4.31)	12.6(12.8)	83 ^c
ZnCl_2L_2	white	64.3(63.5)	4.60(4.67)	9.3(9.3)	3
ZnBr_2L_2	white	55.4(55.4)	4.09(4.08)	8.2(8.1)	5
$\text{Zn}(\text{CNS})_2\text{L}_2 \cdot \text{H}_2\text{O}$	white	61.3(61.1)	4.27(4.50)	12.4(12.6)	7
$\text{Zn}(\text{NO}_3)_2\text{L}_2$	white	58.3(58.4)	4.32(4.30)	12.6(12.8)	22
CdI_2L_2	white	46.0(46.0)	3.32(3.35)	6.8(6.7)	7
$\text{Cd}(\text{NO}_3)_2\text{L}_2$	white	54.7(54.5)	4.04(4.01)	11.8(11.9)	14
HgCl_2L	white	38.0(38.0)	2.86(2.79)	5.4(5.5)	18

^aTheoretical values in parentheses. ^bValues of molar conductivity for *ca.* 10^{-3} solutions in nitromethane at 25 °C. ^cIn DMSO. ^dThese complexes decompose in solution.

crystalline or powder-like, stable in atmospheric conditions, insoluble in benzene, moderately soluble in chloroform, soluble in nitromethane, DMF and DMSO; they are decomposed by dilute mineral acids. The molar conductivities of most of the complexes in nitromethane are in accord with them being formulated as non-electrolytes. The molar conductivities of some complexes indicate very little ionisation (1:1 electrolytes have Λ_M values $\sim 80 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$ on average [16]), while $\text{Ni}_2\text{L}_4 \cdot \text{H}_2\text{O}$ behaves as an 1:2 electrolyte [16]. The insolubility of the complexes $\text{M}(\text{NO}_3)_2\text{L}_2$ ($\text{M} = \text{Ni}, \text{Cu}$) in nitromethane hindered conductivity measurements. They appear to be 1:2 electrolytes in DMSO [16]. However, the fact that the conductivities of these solutions increase with time can be attributed to the strong donor capacity of DMSO which frequently leads to displacement of anionic ligands and change of electrolyte type; thus the data in DMSO are somewhat difficult to interpret.

Infrared Spectra

The principal IR bands of interest are listed in Table II. In the $\nu(\text{O-H})$ region the spectra of the hydrated complexes exhibit a broad continuous absorption, covering the region $3550\text{--}3200 \text{ cm}^{-1}$, attributed to the presence of lattice water [17].

The significant changes in the ligand bands upon complexing are the increases in $\nu(\text{C=N})$ and $\nu(\text{N-N})$. The band due to $\nu(\text{C=C})$ does not shift in the spectra of most complexes. The assignment of the 1592 cm^{-1} band in L to $\nu(\text{C=N})$ is in agreement with other pyrazoles [18] and the movement of this band to higher wavenumber is as has been observed in alkyl cyanide complexes [19] and in complexes of ligands containing the $>\text{C=N-N}<$ grouping [6-9]. Similarly the band at 1118 cm^{-1} in the spectrum of L we assign to $\nu(\text{N-N})$ in accord with the assignments of this band in N-N bonded compounds [6-9, 20, 21]. Shift of $\nu(\text{N-N})$ to higher frequencies has been observed in hydrazine [21] and α -dihydrazone [6-9] complexes. These shifts in the case of L, however, are smaller than those observed for complexes of α -dihydrazones. Both of the above shifts are compatible with the nitrogen of the $>\text{C=N-}$ bond being the donor atom to the metal ions.

The IR spectra of the thiocyanate complexes exhibit $\nu(\text{CN})$, $\nu(\text{CS})$ and $\nu(\text{NCS})$ modes all in the regions characteristic of terminal N-bonded isothiocyanate groups [22]. Further they show the two strong $\nu(\text{M-NCS})$ bands expected for tetrahedral complexes of C_{2v} symmetry [23]. In compounds containing ionic nitrate, the $\nu_3(\text{E}')$ mode of the ion occurs as a single strong band at *ca.* $1350\text{--}1400 \text{ cm}^{-1}$ [24]; the absence of such a band in the spectra of the nitrate complexes

prepared confirms that ionic nitrates are absent. The values of the frequencies assigned as vibrational modes of the nitrate group (Table II) are strongly indicative of the presence of coordinated bidentate nitrates [24, 25], because the separation of the two highest frequency bands is *ca.* $170\text{--}200 \text{ cm}^{-1}$. The $\nu_2(\text{A}_1)$ and $\nu_3(\text{A}_1)$ and $\nu_5(\text{B}_2)$ modes of the C_{2v} nitrate groups [24] were not assigned because the $990\text{--}1050$ and $700\text{--}800 \text{ cm}^{-1}$ regions are obscured by strong bands of the coordinated ligand. The IR spectrum is very complex in the nickel(II) and copper(II) complexes, and supports a complex structure with possible bidentate and bridging nitrates being simultaneously involved [26, 27]. The $1700\text{--}1800 \text{ cm}^{-1}$ region is viewed as the key to differentiate between bidentate and unidentate coordination of nitrate groups [24, 25, 28]. The separation of the combination bands $\nu_2 + \nu_3$ and $\nu_2 + \nu_5$, appearing around 1760 and 1720 cm^{-1} , is about 40 cm^{-1} and this fact indicates bidentate nitrate groups [24]. Lever *et al.* have reported [28] that the spectra of the complexes containing bridging nitrate groups almost invariably exhibit a combination band at a higher frequency (near 1800 cm^{-1}) than those observed in non-bridging systems. In the spectra of $\text{M}(\text{NO}_3)_2\text{L}_2$ ($\text{M} = \text{Ni}, \text{Cu}$) the band at *ca.* 1800 cm^{-1} is consistent with the presence of a bridging nitrate group, whilst the bands at *ca.* 1760 and 1720 cm^{-1} represent the pair of bands arising from a bidentate nitrate group [28]. In addition all spectra exhibit strong $\nu(\text{M-O})$ bands in the far-IR region [23].

The far-IR spectra of the complexes MnX_2L_2 ($\text{X} = \text{Cl}, \text{Br}$), CoX_2L_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), NiCl_2L_2 , $\text{Cu-Br}_2\text{L}_2 \cdot \text{H}_2\text{O}$ and ZnX_2L_2 ($\text{X} = \text{Cl}, \text{Br}$) show the terminal metal-halogen frequencies in the region expected for tetrahedral monomeric complexes [23]. The spectra of MCl_2L ($\text{M} = \text{Cu}, \text{Hg}$) are indicative of the presence of both terminal and bridging metal-halogen bonds [23]. The spectra of MnBr_2L_2 and MnBr_2L_3 are similar in the far-IR region, differing slightly only in the mid-IR region.

Proton Magnetic Resonance Spectra

The ^1H NMR spectrum of the ligand in CDCl_3 shows a complex of peaks at δ 7.75, 7.63, 7.59, 7.51, 7.35, 7.27 and 7.22 ppm downfield from TMS assigned to the C_6H_5 and $=\text{CH-}$ protons and a sharp singlet at δ 3.51 ppm assigned to the CH_3 group protons; the integrations of the signals were in the ratio 11:3. In the ^1H NMR spectra of the diamagnetic zinc(II) (CDCl_3), cadmium(II) (CDCl_3), mercury(II) ($\text{D}_6\text{-DMSO}$) and $\text{Ni}_2\text{L}_4 \cdot \text{H}_2\text{O}$ ($\text{D}_6\text{-DMSO}$) and $\text{Ni}_2\text{L}_4 \cdot \text{H}_2\text{O}$ ($\text{D}_6\text{-DMSO}$) complexes the signals of the C_6H_5 , $=\text{CH}$ and CH_3 hydrogen atoms shift slightly (*ca.* 0.3 and 0.1 ppm respectively) downfield compared with those of free ligand,

TABLE II. Diagnostic Infrared Bands (cm^{-1}) of 1-Methyl-3,4-diphenylpyrazole and its Complexes.

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{N}-\text{N})$	$\nu(\text{CN})$	$\nu(\text{CS})$	$\nu(\text{NCS})$	$\nu_1(\text{A}_1)$	$\nu_4(\text{B}_2)$	$\nu_6(\text{B}_1)$	1820–1700 cm^{-1} region	$\nu(\text{MX})^a$
L	1592	1574	118								
MnCl ₂ L ₂	1600	1571	1123								310, 283
MnBr ₂ L ₂	1599	1573	1122								241, 227
MnBr ₂ L ₃	1601	1573	1124								240, 229
CoCl ₂ L ₂	1602	1577	1129								322, 308
CoBr ₂ L ₂	1602	1578	1127								251 sh, 244, 238
CoI ₂ L ₂	1599	1573	1122								216
Co(NCS) ₂ L ₂	1600	1583	1126	2058	816	481	1490 sh, 1477	1298, 1275	808	1761, 1722	305, 295
Co(NO ₃) ₂ L ₂	1600	1574	1127								303, 285
NiCl ₂ L ₂	1601	1577	1125								311, 303 sh, 293
NiBr ₂ L ₃ ·H ₂ O	1600	1579	1133								b
Ni ₂ L ₄ ·H ₂ O	1599	1575	1132								
Ni(NO ₃) ₂ L ₂	1600	1570	1128				1522, 1498 sh, 1476	1288 sh, 1279, 801,	1804, 1761, 1718		311, 263
CuCl ₂ L	1602	1574	1131								309, 277, 248 ^e
CuBr ₂ L ₂ ·H ₂ O	1601	1574	1133								247 sh, 232
Cu(NO ₃) ₂ L ₂	1600	1571	1132				1529, 1490 sh, 1478	1276, 1262 sh	803	1805, 1758, 1722	322, 271
ZnCl ₂ L ₂	1602	1576	1126								310, 298
ZnBr ₂ L ₂	1599	1573	1123								248 sh, 230, 215
Zn(NCS) ₂ L ₂ ·H ₂ O	1600	1575	1129	2065	819	485	1491 sh, 1474	1307, 1285	811	1760, 1718	304, 280
Zn(NO ₃) ₂ L ₂	1599	1576	1129								279
CdI ₂ L ₂	1599	1575	1121								b
Cd(NO ₃) ₂ L ₂	1599	1577	1127				1503 sh, 1475	1290, 1267	810	1760, 1703	b
HgCl ₂ L	1599	1578	1129								308, 231 ^d

^aX = Cl, Br, I, NC, ONO₂.^bNot observed above 215 cm^{-1} .^c $\nu(\text{CuCl})_p$; sh = shoulder.^d $\nu(\text{HgCl})_p$.

suggesting that the donor-atom is far removed from the region of these hydrogens. The integration of these two groups of peaks is again 11:3 in the zinc(II), cadmium(II) and mercury(II) compounds. The spectrum of $\text{Ni}_2\text{L}_4 \cdot \text{H}_2\text{O}$ exhibits the water hydrogens signal at δ 3.01 ppm; the overall integration is 11:3:2. We believe therefore that in our complexes the pyrazole is bonded to the metal via the pyridine-type i.e. unsubstituted nitrogen atom. This is the atom known from crystal structure studies to co-ordinate to nickel(II) in $\text{Ni}(\text{pyrazole})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$) [40, 41].

Magnetic and Ligand Field Spectral Studies

Table III gives the room temperature magnetic moments and details of the electronic spectra of the prepared complexes.

The magnetic moments and electronic spectral data of CoX_2L ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$) in the solid state indicate pseudotetrahedral stereochemistry around cobalt(II), the band at *ca.* 16 000 cm^{-1} being assigned to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ transition with the band assigned to the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$ transition being split (by virtue of reduction of symmetry from T_d to C_{2v}) into bands representing the transitions to the ${}^4\text{B}_1$, ${}^4\text{A}_2$ and ${}^4\text{B}_2$ states [29]. These assignments give rise to 10 Dq values, which lie between those found for $[\text{CoX}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) ions and cobalt(II) tetrahedrally surrounded by four nitrogen atoms [29]. In nitromethane solution the complexes remain tetrahedral as is evidenced by the positions of the absorption maxima and magnitudes of the molar absorption coefficients for the ligand field bands.

While the magnetic moment of $\text{Co}(\text{NO}_3)_2\text{L}_2$ is in the region expected for tetrahedral complexes, the electronic spectrum of this compound in the solid state and in solution differs from spectra of typical tetrahedral cobalt(II) complexes. The absorption band at *ca.* 18 500 cm^{-1} , although similar in general contour to the visible bands of other tetrahedral complexes, is at rather higher energy than would have been expected. Moreover, the molar extinction coefficient of the visible band in nitromethane is appreciably lower than those found for other tetrahedral cobalt(II) complexes [29]. Also the near-IR spectrum consists of two bands. This magnetic and spectral behaviour, which has been found for some other $\text{Co}(\text{NO}_3)_2\text{L}_2$ complexes where L is a hindered amine or a phosphine or arsine oxide, has been explained by postulating that the six-coordinated complex can be regarded as having a rather distorted quasi-tetrahedral structure with bonds directed toward the centres of the bidentate nitrate groups instead of toward the oxygen atoms [30]. The trimethylphosphine oxide complex is known [31] to have a distorted *cis* octahedral structure. Lever [32] suggested that the assumption of a quasi-tetrahedral

coordination is perhaps unnecessary. These molecules have a distorted six-coordinated structure of C_2 symmetry; the degeneracy of the ground state of the cobalt ion will be lifted (${}^4\text{T}_{1g}(\text{O}_h) \rightarrow {}^4\text{A}, {}^2\text{B}$ in C_2). The new ground state being an orbital singlet gives rise to a magnetic moment much closer to the spin-only value than that observed in an octahedral complex. This was observed in our complex. The absence of a centre of symmetry could produce a fairly high intensity electronic spectrum (since both p and d orbitals span common representations in C_2); this was also observed.

The magnetic and spectral data on NiCl_2L_2 indicate tetrahedral stereochemistry [29] with the ${}^3\text{T}_1 \rightarrow {}^3\text{A}_2$ transition being split markedly. The band on the higher side of the ${}^3\text{T}_1 \rightarrow {}^3\text{T}_1(\text{P})$ transition is assigned as a spin-forbidden transition to a component of the ${}^1\text{G}$ level; the intensity of this band in nitromethane is abnormally large for a spin forbidden transition. The magnetic moment and diffuse reflectance spectrum of $\text{Ni}(\text{NO}_3)_2\text{L}_2$ are easy to assign on the basis of octahedral symmetry [29]. The doublet structure of ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ has been ascribed to a gaining of intensity of the spin-forbidden ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$ transition through configurational interaction with the ${}^3\text{T}_{1g}(\text{F})$ level and also to spin-orbit coupling. The compound is not soluble in nitromethane but in DMSO solution, its electronic spectrum is the same as the spectrum of the $[\text{Ni}(\text{DMSO})_6]^{2+}$ cation [29]. The ligand field spectrum of $\text{Ni}_2\text{L}_4 \cdot \text{H}_2\text{O}$ shows no electronic transitions below 20 000 cm^{-1} . This suggests that the ground state of nickel(II) ion in this complex is ${}^1\text{A}_{1g}$, in accordance with its diamagnetism. The above data indicate a square planar stereochemistry. The frequency of the lowest energy transition (21 300 cm^{-1}) [29] and the fact that $\text{Ni}_2\text{L}_4 \cdot \text{H}_2\text{O}$ behaves as an 1:2 electrolyte in nitromethane (see Table I) are indicative of the existence of the $[\text{NiL}_4]^{2+}$ complex cation. The complex $\text{NiBr}_2\text{L}_3 \cdot \text{H}_2\text{O}$ has unusual magnetic and spectral properties. The effective magnetic moment found (1.85 BM) corresponds very well to the average value for one low-spin and one high-spin nickel(II) atom per molecular unit. It seems likely that the diamagnetic subunit is of square planar stereochemistry and that the paramagnetic one is distorted octahedral; this is further supported by the solid state electronic spectra. If the compound contained a square planar unit of formula NiBr_2L_2 we would expect a band between 15 000 and 18 000 cm^{-1} as is observed when L is a substituted pyridine [29, 33]. The band at 14 400 cm^{-1} could derive from a similar unit, but this is unlikely because of the absence of $\nu(\text{Ni}-\text{Br})_t$ above 260 cm^{-1} in the far-IR spectrum [33]. The presence of a $[\text{NiL}_4]^{2+}$ unit is most likely, because these types of complex cations (where L is a nitrogen donor) have been shown to

TABLE III. Magnetic Moments and Ligand Field Spectral Data of Complexes of 1-Methyl-3,4-diphenylpyrazole.

Complex	μ_{eff} (BM) ^a	Electronic spectra (10^3 cm^{-1})		Solution (CH_3NO_2) spectra ^b ϵ ($1 \text{ cm}^{-1} \text{ mol}^{-1}$) in parentheses	$10 Dq^d$ B (cm^{-1})	β^d
		Solid state (diffuse reflectance)				
Tetrahedral Co(II) complexes						
CoCl_2L_2	4.62	$4A_2 \rightarrow 4T_1(P)$	$4A_2 \rightarrow 4T_1(F)$	15.8(985)	4245	0.72
CoBr_2L_2	4.53	15.8	8.6, 7.2, 6.1	15.7(490)	4205	0.70
CoI_2L_2	4.60	16.3, 15.4, 14.7	7.6, 7.2	16.4, 15.4(621), 14.6	4010	0.71
$\text{Co(NCS)}_2\text{L}_2$	4.72	16.0	8.5, 7.1, 5.9	16.0(1180)	4570	0.69
Octahedral Co(II) complexes						
$\text{Co(NO}_3)_2\text{L}_2$	4.54	$4T_{1g} \rightarrow 4T_{1g}(P)$	$4T_{1g} \rightarrow 4T_{2g}$	18.1(282)	9400	0.77
Tetrahedral Ni(II) complexes						
NiCl_2L_2	3.63	$3T_1 \rightarrow 1T_2$	$3T_1 \rightarrow 3T_1(P)$	17.7(167), 16.0sh(138)	4610	0.78
Octahedral Ni(II) complexes						
$\text{Ni(NO}_3)_2\text{L}_2$	2.96	$3A_{2g} \rightarrow 3T_{1g}(P)$	$3A_{2g} \rightarrow 3T_{1g}(F)$	24.1(111), 14.3sh(3), 13.0(4)	8850	0.66
Square planar Ni(II) complexes						
$\text{NiL}_2\text{L}_4 \cdot \text{H}_2\text{O}$	dia	$1A_{1g} \rightarrow 1B_{1g}$	$1A_{1g} \rightarrow 1A_{2g}$	21.2(233)		
$\text{NiBr}_2\text{L}_3 \cdot \text{H}_2\text{O}$	1.85	21.5 ($1A_{1g} \rightarrow 1A_{2g}$), 14.4 ($3A_{2g} \rightarrow 3T_{1g}(F)$), 13.2 ($3A_{2g} \rightarrow 1E_g$), 8.8 ($3B_{1g} \rightarrow 3B_{2g}$), 7.5 ($3B_{1g} \rightarrow 3E_g$)		17.4(114), 14.5sh(86)	9.8(35), 8.9sh(20)	
Cu(II) complexes						
CuCl_2L	1.94	26.9, 19.8, 12.7, 6.7		c		
$\text{CuBr}_2\text{L}_2 \cdot \text{H}_2\text{O}$	2.10	22.8, 16.0, 13.8, 6.6		c		
$\text{Cu(NO}_3)_2\text{L}_2$	1.47	24.3, 17.5, 14.0		12.1(39)		
Mn(II) complexes						
MnCl_2L_2	6.01	28.2, 23.3, 22.5, 20.8sh		21.7sh(24), 21.4(25), 20.8(21)		
MnBr_2L_2	5.85	27.8, 23.0sh, 22.2, 20.8sh		21.5(29)	20.8(25), 19.8(19)	
MnBr_2L_3	6.34	27.8, 23.0sh, 22.2, 21.0sh		21.3(27)	20.8(23)	

^aMeasured at room temperature. ^bThe spectra of $\text{M(NO}_3)_2\text{L}_2$ (M = Ni, Cu) were obtained in DMSO. ^cThese complexes decompose in solution. ^dThe ligand field parameters were calculated from solid state spectra.

give one band between 21 500 and 23 400 cm^{-1} [29]. We, therefore, assign the band at 21 500 cm^{-1} to an allowed transition in the square planar $[\text{NiL}_4]^{2+}$ unit. The four lower energy bands are assigned to a six-coordinated tetragonal nickel(II) centre. The ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ transition cannot be observed as it is obscured by the high energy charge-transfer bands. The presence of two absorption maxima at 8800 and 7500 cm^{-1} is quite typical for tetragonally distorted octahedral structures; these bands are assigned, in D_{4h} symmetry, as transitions to the ${}^3\text{B}_{2g}$ and ${}^3\text{E}_g$ (components of ${}^3\text{T}_{2g}$ in O_h) levels. For all the data obtained on the compound in its solid state, we can conclude that the structure comprises planar $[\text{NiL}_4]^{2+}$ and distorted octahedral $[\text{NiL}_2\text{Br}_4]^{2-}$ subunits. Complexes in which nickel(II) ions are present in both square planar and octahedral environments have been reported previously e.g. [34]. Nitromethane solutions of $\text{NiBr}_2\text{L}_3 \cdot \text{H}_2\text{O}$ are blue and exhibit spectra characteristic of tetrahedral species.

The μ_{eff} values, measured at room temperature, indicate that the copper(II) halide complexes are magnetically dilute. The diffuse reflectance maxima at ca. 27 000 and 23 000 cm^{-1} in the chloro and bromo derivatives, respectively, are due to charge-transfer bands [35]. The d-d bands are indicative of tetrahedral stereochemistry [29, 36]. For truly tetrahedral copper(II) complexes, Crystal Field Theory predicts only one transition due to ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ transition [37]. Nevertheless Furlani and Morpurgo [38] have shown that the flattening of the coordination tetrahedron results in the splitting of both the ground and the excited levels so that four transitions are to be expected. Hence the three bands observed for both complexes can be assigned to ligand field transitions of the copper(II) ion. The other band expected may be located below 6000 cm^{-1} or may be hidden by the more intense charge-transfer bands [36]. The low magnetic moment of the nitrate complex supports a dimeric or polymeric structure. The reflectance spectrum is fairly typical of a tetragonally distorted octahedral stereochemistry exhibiting one absorption band in the visible region which is resolved into two components [29].

The μ_{eff} values for the manganese(II) compounds are as expected for high-spin $3d^5$ systems. The electronic spectra of the prepared complexes, however, provide evidence to their tetrahedral structures in two ways. Firstly, the fact that the reflectance triplet in the 25 000–20 000 cm^{-1} region is clearly observed indicates tetrahedrally coordinated manganese(II) [39], and secondly tetrahedral complexes where the Laporte restriction is not so rigid exhibit spectra with molar extinction coefficients in the range 1–10 $1 \text{ cm}^{-1} \text{ mol}^{-1}$ are commonly observed [29]. In our solution spectra

high values are observed in agreement with tetrahedral structures; the much more intense spectra obtained probably arise from intensity stealing from charge-transfer states.

Conclusion

Whilst pyrazole forms six co-ordinate complexes with metal ions e.g. $\text{Ni}(\text{pyrazole})_6(\text{NO}_3)_2$ [40], the heavily substituted ligand 1-methyl-3,4-diphenylpyrazole forms tetrahedral bis-ligand complexes with manganese(II), cobalt(II), and zinc(II) halides and thiocyanates; the copper(II) bromide complex is also tetrahedral. In the copper(II) mono-ligand chloride complex tetrahedral coordination is attained by chloride bridging. The nitrate complexes $\text{M}(\text{NO}_3)_2\text{L}_2$ contain octahedrally coordinated metal ions with bidentate chelate ($\text{M} = \text{Co}, \text{Zn}, \text{Cd}$) or bidentate bridging ($\text{M} = \text{Ni}, \text{Cu}$) nitrate groups. This behaviour is similar to that for metal nitrate complexes with other bulky monodentate ligands [30–32]. The reason for this octahedral preference of the metal nitrates has been discussed [32]. The data available on MnBr_2L_3 , CdI_2L_2 and HgCl_2L complexes cannot be assigned with certainty to any stereochemistry. The stereochemistry and the nature of the nickel(II) halide complexes are independent on the preparative conditions (metal salt:ligand molar ratio) but are markedly dependent upon the anions. This is not surprising, since it is known that the structures of nickel(II) complexes are influenced to a large extent by the steric and electronic requirements of the ligands. The poorer donor strength of the iodide ions has a great influence on the structure, as shown by the square planar $[\text{NiL}_4]_2 \cdot \text{H}_2\text{O}$ complex.

Acknowledgements

S.P.P. wishes to thank the Chemistry Department of the University of Ioannina for leave of absence and Prof. J. M. Tsangaris for encouragement.

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