

The Coordination Chemistry of *N*-(2-Pyridyl)pyridine-2'-carboxamide; a Potentially Tridentate Ligand Containing one Secondary Amide and two 2-Pyridyl Donor Groups

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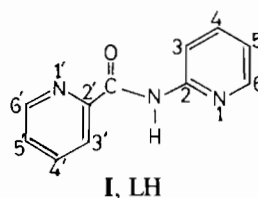
Abstract

New complexes of the general compositions $M(LH)X_2$ ($M = Co, Zn; X = Cl, Br, I$), $Zn(LH)(NCS)_2$, $Zn(LH)(NO_3)_2 \cdot H_2O$, $Cu(LH)X_2$ ($X = Cl, Br, ONO_2$), $Ni(LH)Cl_2 \cdot H_2O$, $Co(LH)_2X_2$ ($X = NCS, ONO_2$), $Ni(LH)_2X_2$ ($X = Cl, Br, NCS, ONO_2$), $Pt(LH)_2Cl_2$ and $MLCl \cdot nH_2O$ ($M = Ni, Cu, Pd; n = 2, 3$), where $LH = N$ -(2-pyridyl)pyridine-2'-carboxamide, have been isolated. The complexes were characterized by elemental analyses, conductivity measurements, X-ray powder patterns, thermal methods, magnetic susceptibilities and spectroscopic (IR, ligand field, 1H NMR) studies. Pseudotetrahedral, square planar, square pyramidal and distorted octahedral stereochemistries are tentatively assigned in the solid state. Most complexes appear to be monomeric, while polymeric structural types are attributed for $Ni(LH)Cl_2 \cdot H_2O$ and $CuLCl \cdot 2H_2O$. The neutral amide group of LH is coordinated to $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ through oxygen, while N-coordination is observed for $PdLCl \cdot 2H_2O$. The amide group of L^- is bound to different $Cu(II)$ atoms in $CuLCl \cdot 2H_2O$ through both its nitrogen and oxygen. The rare O-coordination of the deprotonated amide bond is proposed for $NiLCl \cdot 3H_2O$. The $N(1)$ atom is not involved in coordination except in the complexes $Ni(LH)Cl_2 \cdot H_2O$, $NiLCl \cdot 3H_2O$ and $CuLCl \cdot 2H_2O$, where both pyridine residues are coordinated. The variation in structural types observed is believed to be a consequence of the stereochemical adaptability of the ligand to the electronic demands of the metal ions.

Introduction

The coordination chemistry of amidic ligands plays an important role in a number of current research problems [1–6].

As part of our wide studies on the metal–amide interactions [7–14], we report here the preparation and study of $Co(II)$, $Ni(II)$, $Cu(II)$, $Zn(II)$, $Pd(II)$ and $Pt(II)$ complexes of the new ligand *N*-(2-pyridyl)pyridine-2'-carboxamide (**I**, LH),



which can be viewed either as a substituted picolinamide or as a substituted 2-aminopyridine. This ligand exhibits interesting ligating possibilities in three ways. Firstly, it has three donor groups and is capable, in principle, of several modes of coordination, secondly the amidic hydrogen may be removed and deprotonated L^- complexes prepared, and thirdly since the present ligand contains the $N(1')$, $N(\text{amide})$ donor set within a stable five-membered chelate ring it is possible, in principle, that the $N(1')$ atom may serve as an anchoring group to the secondary amide bond favouring deprotonation [1]. However, in contrast to the previous ligands *N*-(2-aminophenyl)pyridine-2'-carboxamide [9–11], *N*-(2-aminophenyl)quinoline-2'-carboxamide [12] and *N*-(2-carboxylphenyl)quinoline-2'-carboxamide [13], where two chelate rings with a common metal ion–deprotonated amide nitrogen bond could be formed per ligand, we selected LH in order to see the effect of the number of chelate rings per ligand on the deprotonation of the amide bond. Also the ligand of the present study should present a different degree of electronic delocalization and a smaller steric hindrance in its complexes than would the above mentioned ligands. Hence some marked differences in coordinating behaviour between **I** and the ligands of our previous work [9–14] might be expected.

Another reason for the selection of LH is the fact that there has been extensive interest [15–20] in the

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coordination chemistry of ligands formed by the linkage of two pyridine residues, in the *ortho* position, by various monatomic and diatomic groups. In most cases the bridging group is not involved in coordination to the metal. When coordination by the bridging group does occur, as it is possible with the amide group of LH, complexes of interesting structural features and important pharmacological applications are obtained.

Experimental

Elemental analyses, physicochemical measurements and spectroscopic techniques were carried out by published methods [9, 14, 21].

N-(2-Pyridyl)pyridine-2'-carboxamide (I, LH)

To a solution of picolinic acid (2.6 g, 21 mmol) in pyridine (8 ml) was added a solution of 2-aminopyridine (2.0 g, 21 mmol) in pyridine (3.5 ml). After warming the solution obtained to 40 °C, triphenylphosphite (3.3 g, 10 mmol) was added dropwise. After heating at 45 °C with continuous stirring for 24 h, the reaction solution was allowed to stand at -15 °C for 48 h. A solid product was precipitated, which was filtered off and washed with *n*-hexane. An analytical sample of the ligand was recrystallized three times from absolute ethanol to give white needles after drying *in vacuo* over P₄O₁₀. Yield: 70%. Melting point: 118 °C. *Anal.* Calc. for C₁₁H₉N₃O: C, 66.31; H, 4.56; N, 21.10. Found: C, 66.57; H, 4.32; N, 20.82%. The purity of the compound was also checked by TLC in a 4:1 chloroform: *n*-hexane system giving one spot (*R*_f = 0.88). Mass spectrum: *m/e* of the molecular ion was 199 (42%) (calc. formula weight 199.23); the intensity is expressed as a percentage of the intensity of the most abundant ion (base peak) which was found at *m/e* 121 (C₅H₄NCONH⁺ or C₅H₄NNHCO⁺).

The Deuterium Substituted Form LH + LD

A deuterated form of LH was prepared by recrystallizing this ligand from a 1:2 absolute ethanol-D₂O mixture. For a more efficient deuteration, the solid obtained was treated by dissolving it in a small amount of hot acetone, adding a double volume of D₂O and then boiling off the more volatile acetone. The deuterated solid was crystallized out as the solution cooled. The mixture was filtered off and the sample was dried *in vacuo* over P₄O₁₀ for several weeks. Spectroscopic (IR, ¹H NMR) results showed that the complete conversion of LH to LD was impossible, so the product isolated is better formulated as LD + LH.

Preparation of the Metal Complexes

The metal salts MX₂ (M = Co, Zn; X = Cl, Br, I), CuX₂ (X = Cl, Br), M(SCN)₂ (M = Co, Ni, Zn), NiCl₂·

6H₂O, NiBr₂·3H₂O, M(NO₃)₂·6H₂O (M = Co, Ni, Zn), Cu(NO₃)₂·3H₂O and K₂MCl₄ (M = Pd, Pt) were used as starting materials. Three general methods (see Table I) of preparation of complexes of LH and L⁻ were used.

The first method (method A) involved the direct reaction of an ethanolic (refluxing methanolic in the case of Ni(NCS)₂) solution of the appropriate metal salt with a solution of the required amount of LH in a small volume of warm absolute ethanol (for molar ratios see Table I). For the complex Ni(LH)₂Cl₂, the ligand was kept in slight excess of the stoichiometric requirement, whereas for Ni(LH)Cl₂·H₂O the nickel(II) salt was in small excess. The zinc(II) iodide, palladium(II) and platinum(II) complexes were prepared by adding an aqueous solution of the metal salt to a solution of ligand in ethanol at 40 °C in the required proportions (method B). In the third method (method C), to a solution of LH in warm ethanol, an equimolar amount of an ethanolic solution of the required metal chloride was added dropwise with stirring. The same precipitates as in method A were obtained. Over a period of 30 min, an equimolar amount of an aqueous standard 0.1 N NaOH solution was added to the above reaction mixtures under vigorous constant stirring (the final molar ratio was metal chloride:LH:NaOH = 1:1:1). The addition of the base caused slight colour changes and an immediate rise in pH (measured with an Orion 801 A pH-meter with glass and calomel electrodes) at first (9.5–10.0), followed by a slow fall. The new solid products were collected by filtration after 2 h stirring at 35 °C.

Working with methods A and B, solid product formation was usually rapid (5–10 min) although the precipitation of PdLCl₂·2H₂O and Pt(LH)₂Cl₂ occurred slowly over 7–8 h. The compound Co(LH)₂(NO₃)₂ did not crystallize from ethanol but it was precipitated, after volume reduction, by the addition of small quantities of ether. All precipitates were collected by filtration, washed with absolute ethanol (method A) or water and ethanol (methods B and C) and ether. They were dried *in vacuo* over silica gel (method A) or P₄O₁₀ (methods B and C).

Complexes of the type ML₂ (M = Ni, Cu) could not be formed. Attempts to prepare Co(II), Zn(II) and Pt(II) complexes working with method C were unsuccessful. Hydroxo-derivatives of uncertain nature, with poor analytical results, were precipitated in the case of Co(II) and Pt(II); with Zn(II) no solid product could be isolated from the alkaline solution.

Results and Discussion

Preparative data, colours and molar conductivity values are given in Table I. The complexes are microcrystalline or powder like, stable in atmospheric

TABLE I. Preparative Data, Colours and Molar Conductivity Values for the Complexes Prepared

Complex number	Complex	Method of preparation	Ligand:metal salt ^d	Yield (%)	Colour	$\Lambda_M^{g, h}$ (S cm ² mol ⁻¹)
1	Co(LH)Cl ₂	A	1:1, 2:1	85	blue	26
2	Co(LH)Br ₂	A	1:1, 2:1	90	blue	109
3	Co(LH)I ₂	A	1:1, 2:1	77	bluish-green	20
4	Co(LH) ₂ (NCS) ₂	A	1:1, 2:1	60	pink	62
5	Co(LH) ₂ (NO ₃) ₂	A	1:1, 2:1	30	pink	152
6	Ni(LH)Cl ₂ ·H ₂ O	A	1:1	45	light green	62
7	Ni(LH) ₂ Cl ₂	A	2:1	40	green	63
8	Ni(LH) ₂ Br ₂	A	1:1, 2:1	45	pale green	120
9	Ni(LH) ₂ (NCS) ₂	A	1:1, 2:1	65	pale violet	69
10	Ni(LH) ₂ (NO ₃) ₂	A	^e 2:1	72	green	12
11	Cu(LH)Cl ₂	A	1:1, 2:1	87	green	13
12	Cu(LH)Br ₂	A	1:1, 2:1	92	brick red	43
13	Cu(LH)(NO ₃) ₂	A	1:1 ^f	90	blue-green	112
14	Zn(LH)Cl ₂	A	1:1, 2:1	86	white	5
15	Zn(LH)Br ₂	A	1:1, 2:1	85	white	8
16	Zn(LH)I ₂	B	1:1, 2:1	75	white	89
17	Zn(LH)(NCS) ₂	A	1:1, 2:1	83	white	4
18	Zn(LH)(NO ₃) ₂ ·H ₂ O	A	1:1 ^f	70	white	133
19	Pt(LH) ₂ Cl ₂	B	1:1, 2:1	70	yellow	1
20	NiLCl·3H ₂ O	C ^a	1:1	90	green	4
21	CuLCl·2H ₂ O	C ^b	1:1	75	dark green	i
22	PdLCl·2H ₂ O	B ^c	1:1	88	dark yellow	i

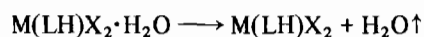
^aThe final pH before the filtration was 8.2. ^bThe final pH before the filtration was 7.5. ^cpH of precipitation = 3.7. ^dMolar ratio. ^eNo definite complex in the case of 1:1 molar ratio. ^fNo definite complex in the case of 2:1 molar ratio. ^gValues of molar conductivity for ca. 10⁻³ M solutions in DMF. ^hThe conductivities of most solutions increase with time. i = insoluble.

conditions and soluble only in DMF and DMSO, frequently with colour changes. The Λ_M values of some complexes in DMF are in accord with them being formulated as non-electrolytes [22]. Comparison of their solution and solid state (diffuse reflectance) electronic spectra reveals that they dissolve essentially unchanged, no solvolysis occurring. The Λ_M values of the other complexes indicate ionization [22]. However, the facts that the conductivities of the solutions increase with time and their solution and solid state d-d spectra differ can be attributed to the strong donor capacity of DMF, which frequently leads to displacement of anionic ligands and change of electrolyte type [22]. X-ray powder diffraction patterns indicate the formation of some pairs of isomorphous compounds; these are 1 and 14, 2 and 15, 3 and 16, 4 and 9, 5 and 10 and 7 and 8. The small number of diffraction lines observed for 21 may suggest a polynuclear arrangement [12]. Because of the insolubility of the prepared complexes in suitable solvents and inability to obtain samples for single-crystal X-ray diffraction, physical and spectroscopic studies in the solid state are the only practical means available for studying stereochemistry and probing which mode of coordination of the organic and inorganic ligands is adopted in the various cases.

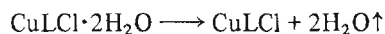
Thermal Studies

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of 6, 18 and 21 show a first mass loss between 60–110, 65–95 and 65–115 °C, respectively, which corresponds very well to the release of all the water content. The relatively low temperature of water loss shows that this is lattice held. The thermal behaviour of 20 and 22 is interesting. The TG-DTG curves show a first mass loss between 50–110 (20) and 65–125 °C (22). A plateau is reached at about 120 °C for 20 and 130 °C for 22. There is a second very distinct inflection in the regions 170–195 °C for 20 and 155–175 °C for 22; a clear plateau is not reached above these temperatures, because the decomposition of the complexes starts without formation of stable intermediates. The above experimental observations show clearly the simultaneous presence of crystal and coordinated water; this is also confirmed by IR spectroscopy (see later). Mass loss calculations prove that two water molecules per Ni(II) are coordinated in 20, while one water molecule per Pd(II) is coordinated in 22.

The activation energy values E_a of the reactions



(M = Ni, X = Cl; M = Zn, X = NO₃)



(M = Ni, $n = 3$; M = Pd, $n = 2$)

were determined by the variable heating rate method proposed by Flynn and Wall [23]; full experimental details of this method were also given in ref. 21. The average E_a values are 74.4 (6), 68.2 (18), 91.0 (20), 86.3 (21) and 104.1 (22) kJ mol^{-1} . These values are characteristic for the removal of crystal water [24]. Activation energies for solid state reactions are scarce but our values are in line with those reported [25].

By differential scanning calorimetry (DSC) at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ we have measured the enthalpy of dehydration of 6, 18 and 21. The ΔH values were found to be 39.8 (6), 24.5 (18) and 31.7 (21) kJ mol^{-1} ; these values are in the region expected for the removal of crystal water [25].

The thermal decomposition of the prepared complexes above $200\text{ }^\circ\text{C}$ is characterized by rather complex degradation mechanisms. Repeated thermograms for the non-deprotonated chloride complexes showed very low and varied residue weights, and varying final decomposition patterns, indicating partial sublimation; similar sublimation processes have been observed with complexes of other secondary amide ligands [12, 26]. No separate weight loss attributable to hydrogen chloride was demonstrated in the thermograms of the complexes $\text{M}(\text{LH})\text{Cl}_2$ (M = Co, Cu, Zn), $\text{Ni}(\text{LH})\text{Cl}_2\cdot\text{H}_2\text{O}$ and $\text{M}(\text{LH})_2\text{Cl}_2$ (M = Ni, Pt); so, compounds of the types MLCl (M = Co, Ni, Zn) and ML_2 (M = Ni, Pt) cannot be prepared from the non-deprotonated complexes by thermal decomposition. Also the complexes $\text{Co}(\text{LH})_2\text{X}_2$ (X = NCS, NO_3) and $\text{Ni}(\text{LH})_2\text{X}_2$ (X = Cl, Br, NCS, NO_3) decompose without the formation of stable intermediates, as no stoichiometric compounds can be assigned to the curves' inflections. So, the complexes $\text{Co}(\text{LH})\text{X}_2$ and $\text{Ni}(\text{LH})\text{X}_2$ cannot be prepared from the 1:2 complexes by thermal decomposition, in contrast with the cobalt(II) complexes of *N*-(3-carboxylphenyl)pyridine-2'-carboxamide [14].

Infrared Spectra

Table II gives some diagnostic IR bands; in this Table only selected representative complexes are listed. In the $\nu(\text{O}-\text{H})_{\text{water}}$ region, the spectra of 20 and 22 show one and two, respectively, strong and sharp bands attributed to the presence of coordinated water [27]. In the spectra of 6, 18 and 21, a weak to medium and broad continuous absorption (*ca.* $3550\text{--}3150\text{ cm}^{-1}$) indicates that lattice water is present [27]; on dehydration the broad band is not observed. The spectra of 20 and 22 exhibit, in addition to the strong and sharp bands of coordinated water, a weaker broad absorption; this is apparently due to

the simultaneous presence of coordinated and crystal water in these compounds.

The IR spectrum of LH shows the characteristic bands of a *trans* secondary hydrogen-bonded amide with two chemically non-equivalent 2-pyridyl residues [9–19, 26]. Assignments of the amide bands of LH were assisted by deuterium isotopic substitution [13, 14, 26]. The absence of large systematic shifts of the $\nu(\text{N}-\text{H})$ and amide V bands in the spectra of the non-deprotonated complexes, in comparison with these bands in LH, confirms the inability of the amide nitrogen to participate in coordination, if undeprotonated. In the spectra of 1–18 the amide I band shifts to a lower frequency, while the amide II and III bands shift to higher frequencies compared with these modes in LH; these shifts indicate amide–O coordination [26, 28]. For 19 there are no shifts in the characteristic amide bands, which suggests that the neutral amide group is not coordinated to Pt(II). As would be expected from the stoichiometries the $\nu(\text{N}-\text{H})$ and amide V bands are absent in the spectra of 20, 21 and 22. Also the amide II and III bands are replaced by a very strong absorption in the $1400\text{--}1350\text{ cm}^{-1}$ region, which is characteristic for deprotonated secondary amide complexes [26, 28]; this replacement might be expected, since on removal of the amide proton the band becomes a pure C–N stretch. However, some IR features of 20 are different from those of 21 and 22. For 20 the amide I band is observed at a very low frequency, while the $\nu(\text{C}-\text{N})_{\text{amide}}$ band is situated $30\text{--}40\text{ cm}^{-1}$ higher compared with the frequency of this vibration in 21 and 22. These shifts can be explained by the larger decrease of the double bond character of C=O and the subsequent increase of the amide C–N double bond character, due to more considerable degree of charge delocalization of the deprotonated amide group in 20. The above spectroscopic evidence suggests that the rare O-coordination of the deprotonated amide bond may be assigned in 20 [29, 30] (for further comments of this structural type see 'Conclusions').

It is well known that the IR spectra of complexes containing ligands with two pyridine residues may be reliably used as a guide to pyridine coordination and the criteria employed have been adequately discussed [15–19, 31, 32]. The careful study of the multiplicity and shifts of mid- and far-IR bands associated with internal modes of vibration of the pyridine rings, can lead to fairly clear structural conclusions. The bands of interest, mostly affected by coordination, are the four $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ bands observed between 1608 and 1413 cm^{-1} , the ring breathing mode near 1000 cm^{-1} , an out-of-plane CH deformation near 770 cm^{-1} and the two in-plane and out-of-plane ring deformation bands at *ca.* 600 and 400 cm^{-1} , respectively [15–18, 31, 32]. These characteristic bands of the pyridine ring are doubled in the

TABLE II. Diagnostic Infrared Bands (cm^{-1}) of LH and some Selected Representative Complexes

Assignment	LH	1	6	7	13	19	20	21	22
$\nu(\text{O}-\text{H})_{\text{cryst. water}}$			3600–3100mb				3600–3100mb	3550–3200wb	3600–3100wb
$\nu(\text{O}-\text{H})_{\text{coord. water}}$							3485s, 3403ss		3535ss
$\nu(\text{N}-\text{H})$	3321mb 1676vs	3265wb 1623vs	3290sb 1626vs	3225mb 1659vs, 1652sh, 1634m	3250mb 1621s	3240sh 1681vs		1628vs	1637sb
Amide I ^a							1528vs		
Amide I ^a [+ Ring stretching vibration]									
Amide II ^b	1511s	1518s	1519m	1519vsb	1520sh	1512s			
Ring's stretching vibrations, <i>i.e.</i>	1589m, 1580m, 1561s, 1552m, 1482m, 1466m, 1433s, 1414s	1596sh, 1578s, 1569s, 1557m, 1504m, 1464m, 1451s, 1426m	1604s, 1584m, 1568s, 1558m, 1499m, 1476s, 1450sh, 1432vs	1608vs, 1592m, 1580m, 1572m, 1557sh, 1505s, 1475s, 1434m, 1418m	1601m, 1580sh, 1572s, 1556sh, 1504m, 1476m ^d , 1445m, 1435m, 1433s, 1423s	1600s, 1580sh, 1564vs, 1551m, 1487vs, 1456m, 1433s, 1423s	1594m, 1573vs, 1563s, 1518vs, 1500w, 1461vs, 1426vs 1392vs	1594s, 1587s, 1565m, 1556m, 1470vsb, 1440m, 1422vs 1352vs	1602sh, 1581vs, 1570m, 1555m, 1499m, 1468vs, 1431s, 1417sh 1364vs
$\nu(\text{C}-\text{N})_{\text{amide}}$	1214m	1231m	1235m	n.a.	1224m	1216w			
Amide III ^b	995s, 986m	1027m, 1001s	1020s, 1011m	1026m, 1018m, 997s	1030m, 1002s	1030m, 995s	1050s, 1022s, 1017s	1042s, 1027s, 1021s	1050s, 992m
Ring breathing mode							782s, 752m	810m, 774vs, 753s	777vs, 767vs
Out-of-plane CH deformation	775s, 758m	781vs, 763s	743m, 713m	812m, 779vs, 761m	780vs, 751s	779vs, 749m			
Amide V ^c	684sb	694s	688mb	692s, 681sh	690sb	687sb			
$\delta(\text{Py})$ in-plane	620s, 596s	651m, 590w	644s, 637m	648m, 611s	655s, 631m, 590w	620m, 606s	645m, 622w	650s, 621m	661m, 620m, 605w
$\delta(\text{Py})$ out-of-plane	407m, 400m	413m, 399m	442m, 427m	430m, 410m, 403sh	411m, 401m	418w, 400m	454w, 435m	453m, 431m	442m, 414w, 398w

^a $\nu(\text{C}=\text{O})$.^bIn secondary amides these bands arise from $\nu(\text{C}-\text{N})$ and $\delta(\text{NH})$ modes.^c $\pi(\text{NH})$.^dOverlapping with the $\nu_1(\text{A}_1)$ band of the bidentate C_{2v} nitrate groups. Py = pyridine ring; s = strong; ss = strong and sharp; m = medium; w = weak; b = broad; v = very sh = shoulder; n.a. = not assigned.

spectrum of LH, due to the presence of two non-equivalent pyridine residues, *i.e.* C₅H₄NCO⁻ and C₅H₄NNH⁻. The complexes can be divided into two series, A and B, on the basis of their IR spectra. The series A complexes (**6**, **20**, **21**) have spectra in which many of the key ring bands indicative of metal coordination are doubled. Since these bands are significantly shifted from their positions in the free ligand spectrum (the shift is to higher frequencies for the $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ vibrations, the ring breathing mode and the $\delta(\text{Py})$ modes), the implication is that both pyridine-N atoms are coordinated [15–18, 31, 32]. Ring bands of the coordinated ligand in the spectra of series B complexes (**1–5**, **7–19**, **22**) are again generally doubled, one band being nearly coincident with the corresponding one of the free ligand and the other occurring at a higher frequency; these results have been interpreted in terms of presence of both coordinated and uncoordinated pyridine residues on the same ligand molecule [15, 18, 19, 31, 32].

For full assignments of all characteristic IR thiocyanate and nitrate bands as well as of the diagnostic far-IR stretching vibrations for all the prepared complexes see 'Supplementary Material'. The spectra of **4**, **9** and **17** exhibit $\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ modes all in the regions characteristic of terminal N-bonded isothiocyanato groups [33]. In the spectra of **5**, **10** and **18** the vibrational fundamentals of the nitrate groups are strongly indicative of the presence of monodentate nitrates [13, 33, 34], because the separation of the two highest frequency bands is *ca.* 120 cm⁻¹. The complex **13** seems to contain two chelated bidentate nitrate groups, as the above separation is *ca.* 200 cm⁻¹ [12, 33, 34]. The possibility of bridging nitrate groups is ruled out, because the highest frequency nitrate mode appears below 1550 cm⁻¹ [35]. The number and the frequencies of the $\nu(\text{MX})$ far-IR bands (X = Cl, Br, I, NCS, ONO₂) fully support [33, 34] the proposed structures of the

complexes (see 'Conclusions'). The far-IR spectra of **1–3**, **11**, **12** and **14–18** show the two $\nu(\text{M-X})_t$ bands in the regions expected for pseudotetrahedral monomeric stereochemistry. A strong metal- and X-sensitive band at a frequency lower than 270 cm⁻¹ in the spectra of **4**, **5** and **7–10** arises from the $\nu(\text{M-X})_t$ vibration in a monomeric *trans* octahedral structure. The spectrum of **6** is indicative of the presence of both terminal and bridging Ni–Cl bonds, while the spectra of **20–22** exhibit a terminal M–X stretching frequency. The presence of one $\nu(\text{M-X})_t$ band at 334 cm⁻¹ in the spectrum of **19** confirms its *trans* planar structure.

¹H NMR Spectra

Table III gives the ¹H NMR chemical shifts for LH and its diamagnetic complexes in d₆-DMSO (downfield from TMS). The study was based on comparisons with a number of related ligands and complexes [10–14, 26, 28–30, 36, 37], on deuterium exchange and on resonance decoupling experiments.

The data for H₃, H₄, H₅, H₆ and –CONH– in the free ligand are in excellent agreement with the corresponding data for *N*-(2-pyridyl)acetamide, which have been interpreted [29, 30, 36, 37] in terms of a planar structure with a *trans* secondary amide group and the aromatic ring *trans* to the methyl group. So, in the case of the present ligand the structure shown in **I** with a *trans* amide group and *trans* pyridine rings, is the most possible. The appearance of the H₃ signal at a considerably low field may be rationalized as the result of long range deshielding by the amide carbonyl group which is *cis* to, and approximately coplanar with, the 2-aminopyridine ring [36, 37]; in **I** the carbonyl group exerts its maximum deshielding effect. The observed conformational preference can be explained by the strong dipole–dipole interactions between the aminopyridine ring and the amide bond [36, 37]; this stabilization also hinders rotation about the N(amide)–C(ring) bond. In agreement with this,

TABLE III. Results of ¹H NMR (δ , ppm)^a Studies on LH and its Diamagnetic Complexes in d₆-DMSO

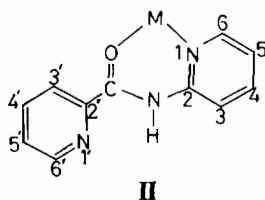
Assignment ^b	LH	14	15	16	17	18	19
–CONH–	10.40sb	10.43sb	10.46sb	10.36sb	10.47sb	10.45sb	10.55sb
Water						3.65sb	
H ₃	8.22d	8.32d	8.25d	8.33d	8.21d	8.24d	8.30d
H ₄	7.83t	7.90t	7.85t	7.93t	7.87t	7.85t	7.92t
H ₅	7.25t	7.36t	7.30t	7.36t	7.27t	7.26t	7.35t
H ₆	8.42d	8.48d	8.44d	8.51d	8.40d	8.41d	8.45d
H ₃ '	8.09d	8.18d	8.13d	8.21d	8.07d	8.10d	8.19d
H ₄ '	7.93t	8.03t	7.97t	8.07t	7.98t	7.96t	8.05t
H ₅ '	7.74t	7.79t	7.75t	7.72t	7.77t	7.76t	7.83t
H ₆ '	8.72d	8.92d	8.96d	9.05d	8.94d	8.93d	8.93d ^c

^aThe spectrum of **22** could not be recorded because of its low solubility.

^bAssignments for individual ring protons assisted by resonance decoupling studies. ^cThis signal shows additional structure due to ¹⁹⁵Pt–H coupling; $J(\text{Pt-H}) = 25$ Hz. s = singlet; d = doublet; t = triplet; b = broad.

variations in temperature gave no new features in the spectrum of LH. That the ^1H NMR spectrum is not affected by varying the temperature indicates that there is a large energy barrier to rotation around the amide C–N bond in this *trans* amide group of the free ligand [37, 38].

In the spectra of the diamagnetic complexes, the amide proton undergoes only a marginal shift to indicate the non-involvement of the amide-N atom in coordination. The signal of the 6'-pyridyl hydrogen shifts downfield compared with that of LH, suggesting that the N(1') atom of the picolinamide unit is coordinated to Zn(II) and Pt(II) [39]. The shift observed for H_6 is insignificant (0.01–0.09 ppm), indicating that the N(1) atom of the aminopyridine unit remains uncoordinated in **14**–**19**. If N(1) coordination had occurred (coordinating behaviour **II**), the H_3 signal would have shifted to a much higher field because on N(1), O(amide) chelation LH must have changed its configuration from **I** to **II** [37]; the H_3 in **II** is no longer deshielded by the carbonyl group. The δ value of H_3 is almost unchanged from that in LH, which rules out **II**.



Magnetochemical and Ligand Field Spectral Studies

Table IV gives the room temperature magnetic moments and details of the solid state electronic spectra of the prepared complexes.

The magnetic moments [40] and electronic spectral data [41] of $\text{Co}(\text{LH})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) indicate a pseudotetrahedral stereochemistry around $\text{Co}(\text{II})$ with the band assigned to the $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{F})$ transition in **1** and **3** being split (by virtue of reduction of symmetry from T_d to C_{2v} or lower) into bands representing the transitions to the $^4\text{B}_1$, $^4\text{A}_2$ and $^4\text{B}_2$ states, in order of increasing energy. The μ_{eff} values, d–d frequencies and the calculated ligand field parameters of the $\text{Co}(\text{II})$ complexes **4**, **5** and $\text{Ni}(\text{II})$ complexes are all characteristic of octahedral high-spin stereochemistry [40, 41]. The doublet structure of $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$ in the spectra of **7**, **8**, **9**, **10** and **20** is indicative of *trans* tetragonally distorted structures [41]; as the symmetry is lowered from O_h to D_{4h} , the $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}$ transition is split into $^3\text{B}_{1g} \rightarrow ^3\text{B}_{2g}$ and $^3\text{B}_{1g} \rightarrow ^3\text{E}_g$ transitions.

The room temperature μ_{eff} values for the $\text{Cu}(\text{II})$ complexes would appear to exclude very strong antiferromagnetic coupling, but it is difficult to rule out ferromagnetic interactions or relatively weak

antiferromagnetic interactions. In order to try to clarify the situation we have measured the susceptibilities of **11**, **12**, **13** and **21** over the temperature range 310–85 K (for the experimental data see 'Supplementary Material'). The compound **13** has a normal μ_{eff} value, which shows practically no variation with temperature. Its reciprocal corrected molar susceptibility χ'_M varies linearly with temperature, the curve intercepting the T axis very close to the origin ($\theta \approx 0$ K); thus **13** is a magnetically dilute compound obeying a simple Curie law [42]. For **11** and **12** the data strictly obey the Curie–Weiss law down to 90 K. The extrapolation from the 310–85 K region gave the Weiss constant θ for each complex. The very small θ values (+2.0 K for **11** and –8.5 K for **12**) indicate the absence of any significant magnetic interaction between $\text{Cu}(\text{II})$ ions in these complexes [42]; their μ_{eff} values are not therefore temperature dependent. Such a behaviour is consistent with the proposed mononuclear structures of **11**, **12** and **13** (see 'Conclusions'). The room temperature magnetic moment of **21** is normal but the sizeable negative Weiss constant ($\theta = -42.0$ K), which is obtained from the variable-temperature study, implies an appreciable antiferromagnetic interaction [42] between the $\text{Cu}(\text{II})$ atoms; this interaction is most probably operated via the deprotonated amidic group $-\text{CON}^-$ which is proposed to bridge two adjacent metal centres in a binuclear or polynuclear structure. The μ_{eff} values decrease as the temperature is lowered ($\mu_{\text{eff}} = 1.63$ BM at 89.1 K).

In the diffuse reflectance spectra of the $\text{Cu}(\text{II})$ complexes the maxima in the 31 010–20 000 cm^{-1} are assignable to ligands-to-copper(II) charge transfer bands [41]. The bromo complex **12** shows a more complex halogen-to-copper(II) charge transfer spectrum, compared with that of the chloro complex **11**, due to spin–orbit splitting of the orbital triplets [41]. The d–d spectra of **11** and **12** are indicative of pseudotetrahedral stereochemistry [12, 16, 41, 43]. In the absence of spin–orbit splitting, a regular tetrahedral (T_d) $\text{Cu}(\text{II})$ complex should yield a single transition ($^2\text{T}_2 \rightarrow ^2\text{E}$) at a relatively low energy. The appearance of three d–d bands in each spectrum can be explained by the fact that tetrahedral $\text{Cu}(\text{II})$ complexes are almost invariably distorted; the usual distortion is a flattening of the tetrahedron along a two-fold axis. This will result in a structure of D_{2d} symmetry (or in a further distortion to D_2 or C_s) which would retain the degeneracy of d_{yz} and d_{xz} and lead to three possible transitions from the ground state $^2\text{B}_2$ to ^2E , $^2\text{B}_1$ and $^2\text{A}_1$ [41]. Regular tetrahedral $\text{Cu}(\text{II})$ complexes, having an orbital triplet ground state, should theoretically have temperature-dependent magnetic moments, being of the order of 2.2 BM at room temperature and falling to 1.9 BM at *ca.* 100 K [40, 44]. However, the μ_{eff} values of **11** and **12** are lower than 2.00 BM at *ca.* 300 K and

TABLE IV. Solid State Magnetic Moments and Electronic Spectral Data for the Co(II), Ni(II) and Cu(II) Complexes of *N*-(2-Pyridyl)pyridine-2'-carboxamide

Complex	$\mu_{\text{eff}}^{\text{a, b}}$ (BM)	Solid state ^b electronic (diffuse reflectance) spectra (10^3 cm^{-1})	$10Dq$ (cm^{-1})	B (cm^{-1})	β
Tetrahedral Co(II) complexes					
1	4.62	$^4A_2 \rightarrow ^4T_1(\text{P})$ 18.52sh, 17.86, 15.81	$^4A_2 \rightarrow ^4T_1(\text{F})$ 8.02sh, 7.84, 7.66	4545	0.77
2	4.66	17.86sh, 17.24, 15.70	7.55vb	4390	0.75
3	4.70	17.39sh, 16.81, 15.50	7.94, 7.34, 6.56	4220	0.75
Octahedral Co(II) complexes					
4	5.01	$^4T_{1g} \rightarrow ^4T_{1g}(\text{P})$ 21.74sh, 20.72, 20.00, 19.29sh	$^4T_{1g} \rightarrow ^4T_{2g}$ 9.52vb	10705	0.83
5	4.92	21.72sh, 21.05, 20.12, 19.23	8.93vb	10150	0.86
Octahedral Ni(II) complexes					
6	3.18	$^3A_{2g} \rightarrow ^3T_{1g}(\text{P})$ $^3A_{2g} \rightarrow ^1T_{2g}^{\text{c}}$ 23.53	$^3A_{2g} \rightarrow ^3T_{1g}(\text{F})$ 13.89	8540	0.77
7	3.32	26.67	11.67sh	9170	0.91
8	3.29	25.71sh	12.87	8770	0.86
9	3.14	26.60	15.09, 14.44	10460	0.76
10	3.17	27.53	16.61	10100	0.87
20	3.07	26.67	13.12sh	9930	0.84
Tetrahedral Cu(II) complexes					
11	1.83 ^f	LMCT 28.17, 23.26sh	d-d 13.87, 10.53, 7.41sh		
12	1.93 ^f	29.63, 24.39, 20.47, 20.00	13.51, 9.80, 7.35sh		
Octahedral Cu(II) complexes					
13	1.88 ^f		d-d 12.51vb ^d		
Five-coordinate Cu(II) complexes ^e					
21	1.97 ^f	31.01, 30.07, 28.99, 27.40	$B_1 \rightarrow E$ 19.23sh	$B_1 \rightarrow A_1$ 11.11	

^aPer metal ion. ^bMeasured at room temperature. ^cSpin-forbidden bands frequently observed in octahedral Ni(II) complexes. ^dThis maximum is very asymmetric.

^eAssignments have been given assuming a ligand field of C_{4v} (square pyramidal symmetry); the spectrum fits this model well. ^fFor variable temperature data see text and supplementary material. LMCT = ligand-to-metal charge transfer; sh = shoulder; vb = very broad.

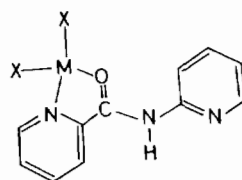
practically temperature-independent. This discrepancy is due to the distortion from tetrahedral symmetry, which removes the degeneracy of the ground state and leads to a decrease in the dependence of the moment with temperature and to a reduction of the room-temperature moment to the range normally observed for octahedral complexes [44].

The electronic spectrum of **13**, which exhibits a very broad and asymmetric band at *ca.* 12 500 cm^{-1} , is fairly typical of octahedral stereochemistry with small tetragonal distortion [16, 41]. The ligand field spectrum of **21** provides strong evidence of a five-coordinate square pyramidal structure [13, 45]. The spectrum exhibits three d-d maxima, which are assigned to the $B_1 \rightarrow A_1$, $B_1 \rightarrow B_2$ and $B_1 \rightarrow E$ transitions in the C_{4v} square pyramidal field; however, a lower symmetry with a splitting of the tetragonal 2E state, leading to a partial overlap of two of the four possible transitions, is the most probable [45].

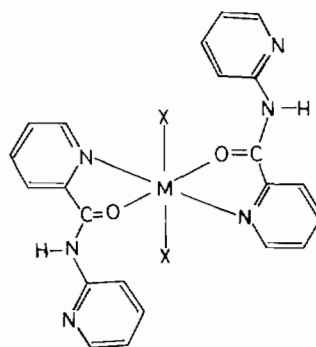
Square planar structures are assigned for **19** and **22** on the basis of their solid-state electronic spectra (not included in Table IV) [41].

Conclusions

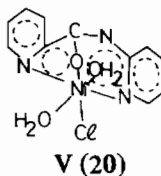
From the overall study presented a variety of stereochemistries is assigned in the solid state for the complexes prepared. Full details about the various coordinating behaviours of LH and L^- and the stereochemistries of their complexes are given in Table V. Some of the structural formulae proposed are **III**, **IV**, **V** and **VI**. A full discussion for the coordinating properties of the secondary amide bond has been



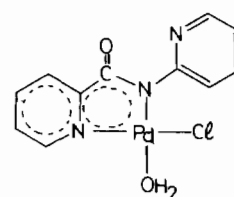
III ($M = \text{Co, Cu, Zn}$; $X = \text{Cl, Br, I, NCS, ONO}_2$)



IV ($M = \text{Co, Ni}$; $X = \text{Cl, Br, NCS, ONO}_2$)



V (**20**)



VI (**22**)

given in refs. 1, 10–13, 29, 30. Below only some important and unexpected features, observed in the present work, are outlined.

TABLE V. Proposed Coordinating Behaviours of the Organic Ligand and Stereochemistries of its Complexes

Coordinating behaviour of the organic ligand	Stereochemistry	Complex
Non-deprotonated complexes		
N(1'),O(amide) bidentate chelated	monomeric pseudotetrahedral ^a (III)	1, 2, 3, 11, 12, 14, 15, 16, 17, 18
N(1'),O(amide) bidentate chelated	monomeric <i>trans</i> octahedral ^b (IV)	4, 5, 7, 8, 9, 10
N(1'),O(amide) bidentate chelated	monomeric <i>cis</i> octahedral ^c	13
N(1'),O(amide),N(1) tridentate bridging	polymeric octahedral ^d	6
N(1') monodentate	monomeric <i>trans</i> square planar ^e	19
Deprotonated complexes		
N(1'),O(amide),N(1) tridentate chelated	monomeric <i>trans</i> octahedral (V) ^f	20
N(1'),O,N(amide),N(1) tetradentate bridging	polymeric or dimeric square pyramidal ^g	21
N(1'),N(amide) bidentate chelated	monomeric <i>cis</i> square planar (VI) ^h	22

^aThe coordination is completed by two terminal X ($X = \text{Cl, Br, I}$) ligands (**1, 2, 3, 11, 12, 14, 15, 16**), two monodentate isothiocyanato (**17**) or two monodentate nitrate (**18**) ligands. ^bThe coordination is completed by two terminal X (**7, 8**), monodentate isothiocyanato (**4, 9**) or monodentate nitrate groups in apical positions. ^c $[\text{Cu}^{\text{II}}\text{O}_5\text{N}]$ chromophore with bidentate chelated nitrate groups. ^dA $[\text{Ni}^{\text{II}}\text{ON}_2\text{Cl}_3]$ chromophore is tentatively proposed with both terminal and chloro ligands. ^eThe coordination around Pt(II) is completed by two terminal chloro ligands. ^fTwo aqua ligands in apical positions. ^gA $[\text{Cu}^{\text{II}}\text{ON}_3\text{Cl}]$ chromophore is assigned. ^hThe coordination around Pd(II) is completed by one terminal chloro ligand and one aquo group.

In **20** the amide nitrogen is proposed to be deprotonated but not coordinated. This very unusual coordinating behaviour of the deprotonated amide bond has been structurally characterized [30] and studied by spectroscopic methods [29] only once in the past. A tridentate chelation of L^- including the deprotonated amide nitrogen is unlikely due to the requirement for a four-membered chelate ring. Thus, the deprotonated uncoordinated amide nitrogen in **20** is accountable by the enforced chelate stereochemistry and the relatively weak amide nitrogen basicity [30]. Molecular models reveal that such a complex could form with considerable angular strain of L^- . A five-coordinate square pyramidal dimeric or polymeric structure is assigned for **21**. In this complex the L^- ligand seems to exhibit the rare $N(1')$, O_{amide} (to one Cu(II)), N_{amide} (to another Cu(II)), $N(1)$ tetradentate bridging behaviour. Thus the deprotonated amide group of L^- is bound to different Cu(II) atoms through both its deprotonated nitrogen and oxygen; this unusual coordinating mode, which was also present in other deprotonated Cu(II) complexes [13, 14], has been structurally characterized in aquo- μ -bis(cyclo-(L-histidyl-L-histidyl)-dicopper(II) [46] and (L-methionylglycinate)-copper(II) [47]. The antiferromagnetic character of **21** is most probably due to the bridging deprotonated amide group which provides the dominant contribution to the exchange pathway between the Cu(II) $3d_{x^2-y^2}$ magnetic orbitals. The square pyramidal structure, proposed for **21**, can explain this character assuming that the oxygen and nitrogen atoms of the bridging $-CON^-$ group lie in the basal planes of two adjacent metal centres. The unpaired electron of Cu(II) (d^9 configuration) in a trigonal bipyramidal ligand field should exist in the $3d_{z^2}$ orbital directed toward apical positions, while it is in the $3d_{x^2-y^2}$ orbital in a square pyramidal structure (the xy plane is the equatorial plane). In a square pyramidal structure, where both donor atoms of the $-CON^-$ group occupy equatorial coordination sites, the bridging group mediates efficiently electron spins in $3d_{x^2-y^2}$ orbitals of copper(II) ions; in this case an appreciable interaction is expected [48]. The relatively small antiferromagnetic interaction observed (the room temperature μ_{eff} value of **21** is normal) may result from the fact that the central metal ion in this geometry usually moves from the basal plane to the apical donor site [48]. Square pyramidal structures, where both donor atoms of the bridging deprotonated amide group are coordinated at the apical positions or one is coordinated at the apical position and the other at an equatorial site, can be ruled out. In these structures magnetic interaction would be expected to be zero or very small, respectively, because the apical site has no spin density of $3d_{x^2-y^2}$ orbital.

On complexing with Ni(II) and Cu(II) in slightly alkaline medium and with Pd(II) at acidic pH, the

amide proton of LH becomes extremely labile; **20**, **21** and **22** are the only complexes which contain the deprotonated L^- ligand. It is worth noting that throughout most of the pH range, in the absence of metal ions, the amide group is neutral [1]. A comparison of the deprotonating ability of LH with that of analogous amide ligands [9–13] demonstrates the effect of the number of chelate rings per ligand. The $N(1)$ donor atom cannot serve as an anchoring group [1] to the amide bond; so, the presence of only one chelate ring per LH does not favour deprotonation of the secondary amide bond.

The ability of LH to form complexes in various different geometries is, for a complicated ligand such as this, moderately uncommon, and betokens unusual adaptability to different environments [16]. With ions such as Zn(II), Pd(II) and Pt(II) for which stereochemical requirements are quite severe, only tetrahedral (Zn(II)) or square planar (Pd(II), Pt(II)) complexes were prepared. With Co(II), an ion for which the energy barrier from tetrahedral to octahedral stereochemistry is small, both stereochemistries were observed. However, with Cu(II), an ion whose ability to form variable and distorted stereochemistries is quite remarkable, an even wider range (pseudotetrahedral, square pyramidal, octahedral) of structures were assigned. Thus the extraordinary adaptability of LH and L^- to the electronic demands of the metal ion has been demonstrated by the existence of metal complexes in a wide range of stereochemistries. The rationale for this behaviour originates from the flexibility of the ligand used. It can adopt conformations which allow a variety of possible angles to be subtended at the metal ion, and can therefore coordinate in various stereochemical modes. It is also likely that the high polarizability of the electron cloud on the pyridine residues allows the metal–nitrogen bond lengths to vary somewhat without a serious loss in bond energy.

Supplementary Material

Table I', analytical results for the complexes prepared; Table II', characteristic infrared isothiocyanate and nitrate bands (cm^{-1}) of the prepared complexes; Table III', diagnostic far-IR metal–ligand stretching frequencies (cm^{-1}); and Table IV', temperature dependence of the magnetochemical data for the Cu(II) complexes prepared are available on request from the authors in Ioannina.

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