

Metal Complexes Containing the Monoanion, Dianion and the Neutral Form of the Ligand *N*-(2-Carboxylphenyl)pyridine-2'-carboxamide

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Abstract

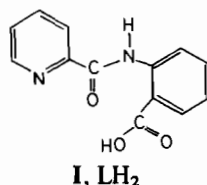
New complexes of the formulae $M(LH)_2 \cdot nH_2O$ ($M = Co, Ni, Cu, Zn; n = 2, 2.5, 3$), $Cu_2(LH)_2L \cdot 3H_2O$, $PdL \cdot H_2O$, $Pt_3(LH)_4L \cdot 7H_2O$, $M_2(LH)_2(OH)_2 \cdot nH_2O$ ($M = Co, Ni, Zn; n = 2, 4$), CuL , $M(LH_2)_2Cl_2 \cdot EtOH$ ($M = Co, Cu; EtOH = ethanol$), $Ni(LH_2)_2Cl_2 \cdot EtOH \cdot H_2O$, $M(LH_2)_2X_2$ ($M = Co, Ni; X = NCS, ONO_2$), $Zn(LH_2)_2(NO_3)_2$, $Zn(LH_2)(LH)Cl$, $Cu(LH_2)(LH)NO_3$ and $Cu_3(LH)_3L(NO_3)$, where $LH_2 = N$ -(2-carboxylphenyl)pyridine-2'-carboxamide, have been isolated. The complexes were characterised by elemental analyses, conductivity measurements, magnetic moments and spectral (IR, 1H NMR and electronic) studies. Varying stereochemistry is assigned for the complexes prepared in the solid state. The complexes $M(LH)_2 \cdot nH_2O$ ($M = Co, Ni, Cu, Zn$), $Cu_2(LH)_2L \cdot 3H_2O$ and $Cu_3(LH)_3L(NO_3)$ appear to be polymeric, while dimeric structural types are assigned for $M_2(LH)_2(OH)_2 \cdot nH_2O$ ($M = Co, Ni, Zn$) and CuL . Only palladium(II) at acidic pH and copper(II) at basic pH promote amide deprotonation on coordination and yield doubly deprotonated complexes. Coordination of the neutral carboxylic group is not observed for the complexes of LH_2 ; the carboxylate ion exhibits monodentate coordination in the compounds of LH^- and L^{2-} . The neutral amide group of the ligands LH_2 and LH^- is coordinated to the metal ions through oxygen, while N(amide)-coordination is observed for the L^{2-} complexes. The secondary amide bond shows the rare iminol type of coordination in $Cu(LH)_2 \cdot 2H_2O$.

Introduction

The coordination chemistry of amidic ligands is an important part of a number of current chemical problems. The review of Sigel and Martin [1] clearly shows that research interest is centred on the structure and stability of metal ion complexes of amides,

oligopeptides and related ligands; of special interest are the deprotonation processes and the species thereby formed.

As part of our systematic studies on the metal–amide bonds [2–6], we report here the preparation and study of cobalt(II), nickel(II), copper(II), zinc(II), palladium(II) and platinum(II) complexes of the new ligand *N*-(2-carboxylphenyl)pyridine-2'-carboxamide (**I**, LH_2). This ligand exhibits interesting ligating possibilities in three ways. Firstly, it has three donor groups and may coordinate to metal ions in several modes, secondly the hydrogen atom on the carboxylic group and perhaps on the amide-N atom can be removed and deprotonated LH^- and/or L^{2-} complexes prepared, and thirdly since the present ligand contains both N,N and N,O donor sets within stable five- and six-membered chelate rings, respectively, it is possible, in principle, that the other two donors may serve as anchoring groups [1] to the secondary amide bond, favouring deprotonation of this bond. However, in contrast to the previous ligands *N*-(2-aminophenyl)pyridine-2'-carboxamide [2–5] and *N*-(2-aminophenyl)quinoline-2'-carboxamide [6], where both anchoring groups were neutral, we selected a carboxylic group (which can be easily deprotonated) as one of the potential anchoring groups in order to see the effect of the charge on the deprotonation of the amide bond.



The ligand type can be viewed either as a substituted picolinamide or as a *N*-substituted 2-aminobenzoic acid. Complexes of picolinamide and its substituted derivatives have been extensively studied. The coordination chemistry of 2-aminobenzoic acid and its *N*-substituted derivatives has attracted some interest [7–11]. Ruthenium(II) [12], palladium(II) [13] and copper(II) [14] complexes with ligands con-

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taining the *ortho* $-\text{CONHC}_6\text{H}_4\text{COO}^-$ moiety have also been prepared and studied; these complexes show interesting chemical and structural features.

Experimental

Analyses and physicochemical techniques were carried out by published methods [2, 15].

N-(2-Carboxylphenyl)pyridine-2'-carboxamide (I, LH₂)

Ethyl chloroformate (0.88 g, 8.13 mmol) was added with stirring to a solution containing picolinic acid (1.0 g, 8.13 mmol) and anhydrous triethylamine (0.82 g, 8.13 mmol) in a mixture of absolute THF (2.5 ml) and DMSO (0.5 ml) cooled at -15°C . A cold (0°C) solution of 2-aminobenzoic acid (1.11 g, 8.13 mmol) and anhydrous triethylamine (0.82 g, 8.13 mmol) in a mixture of absolute THF (1 ml) and DMSO (1 ml) was added to the previous solution after 4 min. After stirring at -15°C for 15 min and at room temperature for 3 h, the reaction mixture was concentrated at 55°C under reduced pressure. The residue was cooled to 0°C and 0.5 N HNO_3 or H_2SO_4 was added under vigorous stirring until the pH was 4; a solid product was obtained, which was filtered off. An analytical sample of the ligand was recrystallised three times from absolute ethanol to give fine white needles after drying *in vacuo* over P_4O_{10} . Melting point: $173.5\text{--}174.0^\circ\text{C}$. Yield: 38%. *Anal.* Calc. for $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.64; H, 3.87; N, 11.00%. The purity of the compound was also checked by TLC in a 9:1 ethyl acetate–methanol system giving one spot ($R_f = 0.36$). Mass spectrum: *m/e* of the molecular ion was 242 (27%) (calc. formula weight 242.24). Some other fragment ions were found at *m/e* values 225 ($\text{C}_5\text{H}_4\text{NCONHC}_6\text{H}_4\text{CO}^+$, 2%), 197 ($\text{C}_5\text{H}_4\text{NCONHC}_6\text{H}_4^+$, base peak), 106 ($\text{C}_5\text{H}_4\text{NCO}^+$, 11%), 90 ($\text{C}_5\text{H}_4\text{NC}^+$, 17%), 78 ($\text{C}_5\text{H}_4\text{N}^+$, 88%) and 45 (COOH^+ , 8%). The intensities are expressed as a percentage of the intensity of the most abundant ion (base peak).

N-(2-Carboxylatephenyl)pyridine-2'-carboxamide Sodium Salt Hydrate, $\text{LH}^-\text{Na}^+\cdot\text{H}_2\text{O}$

To a solution of *N*-(2-carboxylphenyl)pyridine-2'-carboxamide (1.0 g, 4.13 mmol) in 15 ml of absolute ethanol, an ethanolic solution (20 ml) of sodium hydroxide (0.165 g, 4.13 mmol) was added dropwise under vigorous stirring. A white precipitate was immediately obtained. The solid was collected by filtration and washed with absolute ethanol (3×5 ml). The product was refluxed in acetone, filtered, washed with absolute ethanol and acetone and dried *in vacuo* over calcium chloride. Yield: 95%. *Anal.* Calc. for $\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_4\text{Na}$: C, 55.32; H, 3.93; N, 9.92. Found: C, 58.40; H, 3.23; N, 10.04%.

The Deuterium Substituted Form LHD + LD₂

A deuterated form of LH₂ was prepared by recrystallising this ligand from a 1:1 ethanol– D_2O mixture. For a more efficient deuteration, the solid obtained was treated by dissolving it in a small amount of hot acetone, adding an equal or greater volume of D_2O , then boiling off the more volatile acetone. The deuterated form was slowly crystallised out as the solution cooled. The mixture was filtered off and the sample was dried *in vacuo* over P_4O_{10} . Spectroscopic (IR, ^1H NMR) results showed that the complete conversion of LH₂ to LD₂ was impossible, so the product obtained is better formulated as LD₂ + LHD, where H is the non-deuterated percentage of the amidic hydrogen. The deuteration of the carboxylic group was complete and easy.

Preparation of the Complexes

The metal salts MCl_2 (M = Co, Cu, Zn), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{M}(\text{NCS})_2$ (M = Co, Ni), $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (M = Co, Ni, Zn), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and K_2MCl_4 (M = Pd, Pt) were used as starting materials. Three general methods (see Table I) of preparation of the complexes were used.

In the first method (method A), to a suspension of LH₂ in water, an equimolar amount of an aqueous standard 1 N NaOH solution was added dropwise with stirring. An aqueous solution of the required metal chloride was added to the clear solution obtained (pH = 6.0–6.5). A precipitate was immediately obtained. All precipitates were collected by filtration after 2–3 h stirring and washed with water and ethanol. The solid products were refluxed in ethanol for 1 h (aqueous ethanol in the case of palladium(II) and platinum(II) compounds), then filtered off, washed with water and ethanol and dried *in vacuo* over $\text{CaCl}_2\text{--P}_4\text{O}_{10}$. In the case of CuCl_2 two complexes were obtained. Using 9 mmol of ligand and 8.9 mmol of metal salt the complex $\text{Cu}_2(\text{LH})_2\text{L} \cdot 3\text{H}_2\text{O}$, with a 99% yield based on the ligand, was prepared, while using a 2:1 ligand:metal ion molar ratio the compound $\text{Cu}(\text{LH})_2 \cdot 2\text{H}_2\text{O}$ was isolated.

In the second method (method B), an equimolar amount of an aqueous standard 1 N NaOH solution was added dropwise with stirring to a suspension of LH₂ in water. To the clear solution obtained, an aqueous solution of the required metal salt was added in a 1:1 molar ratio. The same precipitates as in method A were immediately obtained. Over a period of 1 h, another equimolar amount of the aqueous standard 1 N NaOH solution was added to the above reaction mixtures under vigorous constant stirring (the final molar ratio was metal chloride:LH₂:NaOH = 1:1:2). The addition of the base caused colour changes and an immediate rise in pH at first (10.0–10.5), followed by a slow fall. All new solid products were collected by filtration after 2–3 h stirring. They were purified and dried as described in

method A. Attempts to isolate a platinum complex by method B was unsuccessful; solids with very poor analytical results were obtained.

An Orion Research model 801A pH-meter with glass and Calomel electrodes was employed to measure pH during the preparations of the complexes with methods A and B.

The third method (method C) involved the direct reaction of an ethanolic solution (refluxing methanolic solution in the case of nickel(II) thiocyanate) of the appropriate metal salt with a solution of the required amount of LH_2 in a small volume of absolute ethanol (for molar ratios, see Table I). When hydrated metal salts were used as starting materials, a few ml of triethyl orthoformate were added to the reaction mixtures for dehydration purposes. Solid product formation was rapid. All precipitates were collected by filtration, washed with absolute ethanol and dried *in vacuo* over silica gel.

Results and Discussion

Preparative and analytical data, colours and molar conductivity values are given in Table I. The complexes are soluble only in DMSO and DMF, frequently with colour changes; however, the compounds prepared by method C, except 22, have low to moderate solubility in nitromethane. The Λ_M values of the complexes prepared by methods A and B in DMSO are in accord with them being formulated as non-electrolytes [16]. The complex 17 appears to be a 1:2 electrolyte in DMSO [16]. The Λ_M values of the other complexes, except 20, indicate ionisation. However, the fact that the conductivities of the solutions of 12–22 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 [16].

Infrared Spectra

Tables II and III give the principal IR bands of interest. In Table II only selected representative complexes are listed. The presence of crystal water in 1–5, 7–9 and 13 and lattice ethanol in 12–14 are both manifested by a broad weak band in the high frequency region [17, 18] (for 9 the crystal water band is not included in Table II). In the $\nu(\text{O}-\text{H})_{\text{water}}$ region, the spectra of 6, 7, 9 and 10 show one or two sharp bands attributed to the presence of coordinated water [18]. The spectra of 8–10, formulated as containing bridging OH^- , exhibit two fairly sharp absorptions at 3600 and 3530 cm^{-1} [19].

The wavenumber of the $\nu(\text{N}-\text{H})$ band in the complexes of LH_2 and LH^- is almost unchanged from that in the corresponding free neutral ligand and its sodium salt, which confirms the inability of the amide nitrogen to participate in coordination, if un-deprotonated.

In the spectra of the non-amide deprotonated complexes, except 7, the amide I, II and III band shifts indicate amide-O coordination [20–22]. The $\nu(\text{N}-\text{H})$ band is absent in the spectra of 6 and 11. Also the amide II and III bands are replaced by a strong band at 1400 cm^{-1} , which is characteristic for deprotonated secondary amide complexes [20–22]. The spectra of 5 and 22 are very similar. They show amide bands indicative of both O-coordinated neutral amide groups of the LH^- ligands and N-coordinated deprotonated amide group of the L^{2-} ligand, thus confirming their formulation as mixed LH^- , L^{2-} complexes. Some spectral features of $\text{Cu}(\text{LH})_2 \cdot 2\text{H}_2\text{O}$ (4) are different from those of all the prepared complexes. The appearance of the $\nu(\text{OH})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})_{\text{amide}}$ modes is strong evidence that an iminol structure is present [23–25]. The spectrum of 4 does, however, exhibit the amide I, II and III bands in the regions expected for amide-O coordination. Thus one of the amide O-atoms is proposed to be protonated (iminol structural type), while the other is normally coordinated to copper(II).

In the spectra of all the complexes studied, the in-plane and out-of-plane deformation bands of the pyridine ring shift to higher frequencies to indicate coordination of the ring N-atom [26].

The absence of large systematic shifts of the $\nu(\text{C}=\text{O})_{\text{acid}}$, $\delta(\text{OH})_{\text{acid}}$ and $\tau(\text{OH})_{\text{acid}}$ bands in the spectra of 12–19, in comparison with the same bands in the spectrum of LH_2 , implies that there is no interaction between the neutral carboxylic group and the metal ions.

In the spectra of 1–6, 8–11 and 20–22, $\Delta_{\text{complex}} > \Delta_{\text{LH}^- \text{Na}^+ \cdot \text{H}_2\text{O}}$, where Δ is the separation between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$. This indicates that the carboxylate group of LH^- or L^{2-} is coordinated to the metal ions as a monodentate ligand [27, 28]. The spectra of 20 and 21, which contain both LH_2 and LH^- groups, are similar. The unusual high frequency of the carboxylic absorption, assigned as $\nu_{\text{as}}(\text{COO}^-)$ in Table II, and the resulting large Δ value are analogous with those observed for $[\text{H}(\text{O}_2\text{CMe})_2]^- \text{Na}^+$, where the hydrogen as a pseudo-metal bridges strongly to acetate ions giving two 'unidentate' acetate groups [27]; we conclude that there is a similar structural type in these complexes (see Conclusion).

The spectra of 15 and 16 exhibit $\nu(\text{CN})$ and $\delta(\text{NCS})$ modes both in the regions characteristic of terminal N-bonded isothiocyanate groups [29]. Further, the spectra show one far-IR band, which arises from the $\nu(\text{M}-\text{NCS})_t$ vibration in a *trans*-octahedral structure [30]. The appearance of a strong band at 1379 cm^{-1} in 22 confirms that an ionic D_{3h} nitrate group is present [31]. In the spectra of 17–19 the vibrational fundamentals of the nitrate groups are strongly indicative of the presence of

TABLE I. Preparative Data, Colours, Analytical Results and Conductivity Measurements for the Complexes Prepared

Compound number	Complex	Method of preparation	Ligand: metal salt ^a	Yield (%)	Colour	Elemental analyses ^b (%)				Λ_M^c (S cm ² mol ⁻¹)
						M	C	H	N	
1	Co(LH) ₂ ·3H ₂ O	A	1:1, 2:1	73	beige-pink	9.8(9.9)	52.3(52.4)	3.68(4.06)		5
2	Ni(LH) ₂ ·3H ₂ O	A	1:1, 2:1	70	pale green	10.0(9.9)	52.1(52.5)	4.10(4.06)		d
3	Zn(LH) ₂ ·2.5H ₂ O	A	1:1, 2:1	80	white	11.3(11.0)	52.3(52.7)	3.66(3.91)		d
4	Cu(LH) ₂ ·2H ₂ O	A	2:1	77	pale green	11.1(10.9)	55.0(53.7)	3.30(3.81)		d
5	Cu ₂ (LH) ₂ L·3H ₂ O	A	1:1	99	deep green	14.1(14.1)	52.1(51.8)	3.03(3.57)		d
6	PdL·H ₂ O	A	1:1	82	yellow	29.5(29.2)	44.2(42.8)	2.22(2.76)		d
7	Pt ₃ (LH) ₄ L·7H ₂ O	A	1:1	61	pale brown	30.5(30.6)	41.6(40.8)	2.47(2.90)		d
8	Co ₂ (LH) ₂ (OH) ₂ ·4H ₂ O	B	1:1	55	pale green	17.7(16.9)	44.0(44.2)	4.07(4.00)		d
9	Ni ₂ (LH) ₂ (OH) ₂ ·4H ₂ O	B	1:1	72	pale green	17.3(16.6)	43.3(44.2)	3.96(4.00)		d
10	Zn ₂ (LH) ₂ (OH) ₂ ·2H ₂ O	B	1:1	74	white	20.1(19.1)	44.7(45.7)	3.56(3.54)		d
11	CuL	B	1:1	84	green	20.8(20.9)	51.3(51.4)	2.43(2.65)		d
12	Co(LH) ₂ Cl ₂ ·EtOH	C	1:1, 2:1	86	beige	9.5(8.9)	49.1(50.9)	3.52(3.97)		31
13	Ni(LH) ₂ Cl ₂ ·EtOH·H ₂ O	C	2:1	91	pale green	8.6(8.7)	50.2(49.6)	4.19(4.16)		35
14	Cu(LH) ₂ Cl ₂ ·EtOH	C	1:1, 2:1	83	green	9.2(9.6)	49.4(50.6)	3.99(3.94)		17
15	Co(LH) ₂ (NCS) ₂	C	2:1	56	beige	9.0(8.9)	51.1(51.0)	2.96(3.06)		52
16	Ni(LH) ₂ (NCS) ₂	C	2:1	77	pale green	8.4(8.9)	50.6(51.0)	3.22(3.06)		34
17	Co(LH) ₂ (NO ₃) ₂	C	2:1	56	pink	8.8(8.8)	47.0(46.8)	3.28(3.02)		70
18	Ni(LH) ₂ (NO ₃) ₂	C	2:1	91	pale green	8.9(8.8)	46.8(46.8)	3.22(3.02)		52
19	Zn(LH) ₂ (NO ₃) ₂	C	2:1	83	white	10.5(9.7)	45.5(46.3)	2.94(2.99)		51
20	Zn(LH) ₂ (LH)Cl	C	2:1	70	pale yellow	11.0(11.2)	55.4(53.5)	3.56(3.28)		d
21	Cu(LH) ₂ (LH)NO ₃	C	2:1	97	pale green	10.4(10.4)	51.7(51.3)	3.19(3.14)		43
22	Cu ₃ (LH) ₃ L(NO ₃)	C	1:1	99	deep green	15.5(15.7)	50.3(51.3)	2.98(2.90)		57

^aMolar ratio. ^bTheoretical values in parentheses. ^cValues of molar conductivity for ca. 10⁻³ M solutions in DMSO at 25 °C. ^d $\Lambda_M < 1$ S cm² mol⁻¹. M = metal; X = Cl, Br, NCS. EtOH = ethanol.

TABLE II. Diagnostic Infrared Bands (cm^{-1}) for Ligands of LH_2 , $\text{LH}^-\text{Na}^+\cdot\text{H}_2\text{O}$ and some Selected Representative Complexes

Assignment	LH_2	$\text{LHD} + \text{LD}_2$	$\text{LH}^-\text{Na}^+\cdot\text{H}_2\text{O}$	1	4	5	6	9	12	20
$\nu(\text{O}-\text{H})_{\text{hydroxyl}}$								3620m, 3530m		
$\nu(\text{O}-\text{H})_{\text{ethanol}}$									3600-3350wb	
$\nu(\text{O}-\text{H})_{\text{water}}$								3440ss		
$\nu(\text{N}-\text{H})$	3235m	3235vw	3500wb	3500-3100wb	3500-3300wb	3600-3300wb	3590, 3520mss	3215mb	3220mb	3245wb
$\nu(\text{N}-\text{D})$		2335m		3175m, 3140m	3200mb	3200wb				
$\nu(\text{OH})_{\text{iminoal}}$					3635w, 2880wb, 2600wb					
$\nu(\text{OH})_{\text{acid}}$	2885wb, 2640wb, 2545wb								2890wb, 2740mb, 2565wb	2770mb
$\nu(\text{O}-\text{D})$										
$\nu(\text{C}=\text{O})_{\text{acid}} [+ \nu_{\text{as}}(\text{C}=\text{O})]^{\text{a}}$		2055s								
$\nu(\text{C}=\text{O})_{\text{acid}}$	1670-1660vsb	1686vsb								
Amide I ^a		1655vs	1678s	1620s	1624m	1623s, 1612m	1630vs	1623vs	1676s	1625vs
$\nu(\text{C}=\text{N})_{\text{iminoal}}$					1642m					
Ring-stretching vibrations	1598m, 1572s, 1500sh, 1444m, 1425m	1593m, 1572m, 1562s, 1481s, 1441m, 1415m	1602m, 1579s, 1491s, 1441s, 1420m	1581s, 1562m, 1499s, 1473m, 1442s, 1432s	1600sh, 1585vs, 1562m, 1468m, 1440s	1595sh, 1573s, 1562s, 1469m, 1448s, 1439s	1600m, 1586s, 1562vs, 1487s, 1432m	1585vs, 1562m, 1499vs, 1472m, 1445s, 1436s	1604m, 1582s, 1513m, 1473m, 1459sh, 1446s	1580s, 1562m, 1540m, 1469m, 1444vs, 1430m
Amide II ^b		1415m								
Amide II ^b [+ Ring vibrations]	1514vsb	1514m			1527m	1530m			1532sb	1531m
Amide II ^b [+ $\nu_{\text{as}}(\text{COO}^-)^{\text{c}}$]										
$\nu_{\text{as}}(\text{COO}^-)^{\text{c}}$			1500vsb	1510vsb	1505m	1502s	1520s	1510sb		1735sb
$\nu(\text{C}-\text{N})$						1394s	1402s			
$\nu(\text{C}-\text{O})_{\text{iminoal}}$					1390m					
$\nu(\text{COO}^-)^{\text{d}}$			1382vs	1388s	1338sb	1339vsb	1325vs	1360vs		1348sb
$\delta(\text{OH})_{\text{acid}} [+ \nu(\text{C}-\text{O})_{\text{acid}}]$	1403vs, 1260vs	1400mb, 1255mb							1370s, 1201vs	
$\delta(\text{OD})$		960m								
Amide III ^b	1291m	890m		1301m	1307w	n.o.		1300m	1332s, 1300m	1295m
$\tau(\text{OH})_{\text{acid}}$	900sb								912s	
$\tau(\text{OD})$		741s								
Pyridine ring (in-plane)	585m	579m	585m	593m	591m	593m	591m	596m	593m	590w
Vibrations (out-of-plane)	403m, 397m	396m	409m	437m	444m	447m	463m	440w	442w	441w

^a $\nu(\text{C}=\text{O})_{\text{amide}}$. ^bThese bands in secondary amides arise from $\nu(\text{C}-\text{N})$ and $\delta(\text{NH})$ modes. ^cAntisymmetric stretching. ^dSymmetric stretching. ^eThese modes couple strongly in organic acids. s = strong; ss = strong and sharp; m = medium; w = weak; b = broad; sh = shoulder; n.o. = not observed.

TABLE III. Characteristic Infrared and Far-Infrared Bands (cm^{-1}) for Inorganic Anions of the Prepared Complexes

Complex	Isothiocyanate bands ^a		Nitrate bands				$\nu(\text{M}-\text{X})_t$
	$\nu(\text{CN})$	$\delta(\text{NCS})$	$\nu_4(\text{B}_2)$	$\nu_1(\text{A}_1)$	$\nu_6(\text{B}_1)$	$\nu_3(\text{A}_1)$ or $\nu_5(\text{B}_2)$	
12							232s
13							229s
14							367s
15	2079vs	471wm					243m
16	2085vs	469m					252s
17 ^b			1417m	1316m	817m	728w	310m
18 ^b			1420m	1318m	814m	729w	279m
19 ^{b, c}			^d	1322m	819m	723w	277m
20							298ms
21 ^e			1310m	1545m ^f	823m	^d	340m, 301m
22							1379s

^aThe $\nu(\text{CS})$ band is obscured by the ligand bands. ^bThe $\nu_2(\text{A}_1)$ and one of the $\nu_3(\text{A}_1)$ or $\nu_5(\text{B}_2)$ modes of the monodentate C_{2v} nitrate groups were not assigned because the regions at *ca.* 1000 and 770–670 cm^{-1} are obscured by bands of coordinated LH_2 . ^cThe IR spectra of 19 in Nujol or hexachlorobutadiene and of its powdered KBr pellet differ; the obtained spectrum in KBr is indicative of the simultaneous presence of ionic and bidentate nitrates. ^dObscured. ^eThe $\nu_2(\text{A}_1)$, $\nu_3(\text{A}_1)$ and $\nu_5(\text{B}_2)$ bands of the bidentate C_{2v} nitrate group were not assigned because the regions at *ca.* 1000 and 800–700 cm^{-1} are obscured by strong bands of the organic ligand. ^fOverlapping with ring vibrations. M = metal; X = Cl, NCS, ONO_2 ; $\nu(\text{M}-\text{X})_t$ is the stretching vibration of the terminal M–X bond.

monodentate nitrates [32, 33], because the separation of the two highest frequency bands is *ca.* 100 cm^{-1} . The complex 21 most probably contains a chelated bidentate nitrate group, as the above separation is *ca.* 230 cm^{-1} . The possibility of a bridging nitrate group in the complexes can be ruled out, because the highest frequency IR mode appears below 1570 cm^{-1} [31]. A strong far-IR band in the spectra of 12–14 arises from the $\nu(\text{M}-\text{Cl})_t$ vibration in a *trans*-octahedral structure [32, 33].

The solution IR spectra of LH_2 , $\text{LH}^-\text{Na}^+\cdot\text{H}_2\text{O}$ and the complexes in DMSO were also studied in the 3350–3000, 2800–1440, 1380–1310 and 1280–1090 cm^{-1} regions. Distinctive differences between the two phases were observed in the spectra of 1–3, 8–10 and 20. The appearance of the characteristic $\nu(\text{OH})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ modes at *ca.* 2800–2500, 1660 and 1370 cm^{-1} , respectively, is consistent with protonation of the amide-O atom to form the iminol tautomers [23–25].

Magnetic and Ligand Field Spectral Studies

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

The μ_{eff} values and the d–d spectra of the cobalt(II) complexes 1, 12, 15, 17 and nickel(II) complexes are characteristic of octahedral high-spin stereochemistry [34, 35]. The doublet structure of ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ in the spectra of the nickel(II) complexes is indicative of *trans*-tetragonally distorted octahedral structures [35]. The pale green high-spin complex $\text{Co}_2(\text{LH})_2(\text{OH})_2\cdot 4\text{H}_2\text{O}$ has an electronic spectrum

which agrees quite well with the energy level diagram for a d^7 ion in square pyramidal fields [36].

The μ_{eff} values, measured at room temperature, indicate that the copper(II) complexes are magnetically dilute. The electronic spectra of 4, 14 and 21 are fairly typical of a tetragonally distorted octahedral stereochemistry [35]. The chromophores appear to be CuN_2O_4 in 4 and 21 [37] and $\text{CuN}_2\text{O}_2\text{Cl}_2$ in 14 [37]. The ligand field spectrum of 5 provides strong evidence of its 5-coordinate square pyramidal structure [38]; however, a symmetry lower than C_{4v} with a splitting of the tetragonal ${}^2\text{E}$ state, leading to a partial overlap of two of the four possible electronic transitions, cannot be ruled out. The number and the frequencies of the d–d bands observed in the spectra of 11 and 22 are consistent with essentially planar structures, probably with *trans*- CuN_2O_2 chromophores [35].

Square planar structures are assigned for 6 and 7 on the basis of their solid-state electronic spectra (not included in Table IV) [35].

${}^1\text{H}$ NMR Spectra

The ${}^1\text{H}$ NMR study of the diamagnetic complexes in d_6 -DMSO (downfield from TMS) was based on comparisons with a number of other amide complexes and on deuterium assisted experiments. The spectrum of LH_2 shows four groups of peaks between δ 8.92 and 7.21 ppm (rings' protons) and a broad singlet at 13.10 ppm (hydrogen-bonded $-\text{CO}-\text{NH}-$ proton); the integrations were exactly in the ratio 8:1. The spectrum also shows two very broad singlet peaks at 13.63 and 3.36 ppm, which are due to the

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

Complex	$\mu_{eff}^{a, b}$ (BM)	Solid state ^b electronic (diffuse reflectance) spectra (10^3 cm^{-1})				$10Dq$ (cm^{-1})	B (cm^{-1})	β
Octahedral Co(II) complexes		${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$	${}^4T_{1g} \rightarrow {}^4T_{2g}$	Calc. ${}^4T_{1g} \rightarrow {}^4A_{2g}$	Other bands			
Co(LH) ₂ ·3H ₂ O	4.78	20.12, 19.34	8.89	18.86		9980	805	0.83
Co(LH) ₂ Cl ₂ ·EtOH	5.01	19.23, 18.18	8.26	17.53		9390	776	0.80
Co(LH) ₂ (NCS) ₂	4.92	20.83, 19.51	9.80	20.77	17.39, 16.67	10970	773	0.80
Co(LH) ₂ (NO ₃) ₂	4.90	20.30	8.93	18.99		10100	842	0.87
5-Coordinate Co(II) complexes ^c		${}^4A_2(F) \rightarrow {}^4A_2(P)$	${}^4A_2(F) \rightarrow {}^4E(P)$	${}^4A_2(F) \rightarrow {}^4B_1(F)$	${}^4A_2(F) \rightarrow {}^4E(F)$	${}^4A_2(F) \rightarrow {}^4B_2(F)$		
Co ₂ (LH) ₂ (OH) ₂ ·4H ₂ O	4.82	19.42	16.26	15.04	8.00	ca. 6.67		
Octahedral Ni(II) complexes		${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$	${}^3A_{2g} \rightarrow {}^4E_g$ ^d	${}^3A_{2g} \rightarrow {}^3T_{2g}$			
Ni(LH) ₂ ·3H ₂ O	3.11	27.03	16.26	13.79sh	10.99, 8.93	9960	889	0.85
Ni ₂ (LH) ₂ (OH) ₂ ·4H ₂ O	3.31	26.67	15.21	13.51sh	10.53, 8.85	9690	713	0.68
Ni(LH) ₂ Cl ₂ ·EtOH·H ₂ O	3.26	27.40	16.53, 15.27	12.82sh	9.66, 8.85	9250	944	0.91
Ni(LH) ₂ (NCS) ₂	3.28	27.40	18.43, 15.15	13.24sh	11.24, 9.26	10250	884	0.85
Ni(LH) ₂ (NO ₃) ₂	3.20	27.59	16.00	13.51sh	10.75, 8.97	9860	880	0.84
Octahedral Cu(II) complexes		CT	d-d	Other bands				
Cu(LH) ₂ ·2H ₂ O	2.18		14.93	21.50sh				
Cu(LH) ₂ Cl ₂ ·EtOH	2.12	26.88	15.38sh, 13.51					
Cu(LH) ₂ (LH)NO ₃	1.91	26.32	14.29					
5-Coordinate Cu(II) complexes ^e			$B_1 \rightarrow E$	$B_1 \rightarrow B_2$	$B_1 \rightarrow A_1$			
Cu ₂ (LH) ₂ L·3H ₂ O	2.02	27.02	18.18	14.54	8.59			
Square planar Cu(II) complexes ^f			${}^2B_{1g} \rightarrow {}^2E_g$	${}^2B_{1g} \rightarrow {}^2B_{2g}$	${}^2B_{1g} \rightarrow {}^2A_{1g}$			
CuL	1.81	25.16	21.28sh	18.87sh	15.15			
Cu ₃ (LH) ₃ LNO ₃	1.89	26.32	21.74sh	18.96	14.98			

^aPer metal ion. ^bMeasured at room temperature. ^cAssignments have been given assuming C_{4v} symmetry (square pyramidal structure). ^dA spin-forbidden band frequently observed in octahedral nickel(II) complexes. ^eAssignments have been given assuming a ligand field of C_{4v} (square pyramidal) symmetry; the spectrum fits this model well.

^fAssignments in D_{4h} symmetry resulting from an elongated octahedron. CT = charge transfer; sh = shoulder.

intermediate rate intermolecular exchange of protons between the carboxylic group and water contained in the solvent [39,40]. In the spectrum of 19, the amide proton undergoes only a marginal shift (0.07 ppm) to indicate the non-involvement of the amide-N atom in coordination.

The spectrum of $\text{LH}^-\text{Na}^+\cdot\text{H}_2\text{O}$ exhibits a complex of peaks between δ 8.78 and 6.91 ppm (rings' protons) and a relatively broad singlet at 14.85 ppm assigned to the amide proton; the integrations were in the ratio 8:1. A large deshielding effect is exerted on the amide proton, via a strong intramolecular hydrogen bond to one of the O-atoms of the ionised carboxylate group, giving a stable 6-membered ring, with the resonance occurring at very low fields [39, 40]. The signal due to the amide proton is absent in 6, providing conclusive evidence that this proton is lost during complexation. The spectra of 3 and 10 are indicative of the iminol type of coordination [23] in solution.

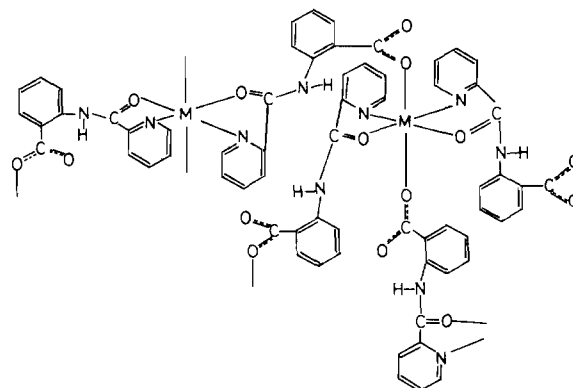
In the spectra of the diamagnetic complexes, the signals of the 6'-pyridyl hydrogen atom shift 0.25–0.40 ppm downfield compared with those of LH_2 and its sodium salt, suggesting that the pyridine-N atom of the picolinamide unit is coordinated to the metal ions [41].

Conclusion

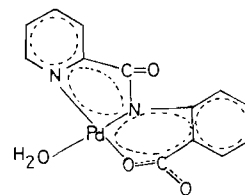
Some of the proposed structural formulae are shown in II–VII. The complexes 1, 2, 3 (II) appear to be polymeric with a N_{ring} , O_{amide} , monodentate COO^- tridentate bridging coordinating behaviour for LH^- . An analogous polymeric octahedral structure is also proposed for 4, but the secondary amide bond of one LH^- per Cu(II) exhibits the rare iminol type of coordination. In the 5-coordinate square pyramidal polymeric complex 5, the LH^- ligands behave as above, while the L^{2-} ligand seems to exhibit the rare N_{ring} , O_{amide} (to one Cu(II)), deprotonated N_{amide} (to another Cu(II)) and monodentate COO^- tetradentate bridging behaviour, producing an N_2O_3 environment around each Cu(II) . Thus the deprotonated amide group of L^{2-} is bound to different Cu(II) atoms through both its deprotonated nitrogen and oxygen; this unusual coordinating behaviour, which is also present in 11 (V), has been structurally characterised [42]. All data for 6 (III) suggest a square planar geometry. Dimeric structures are assigned for 8, 9 (IV), 10 (IV) and 11 (V). In the complexes 12–19 the ligand LH_2 shows bidentate chelated N_{ring} , O_{amide} behaviour; this form of coordination produces the monomeric *trans*-octahedral structural type VI. For 20 the structural type VII is proposed; the IR $\nu(\text{Zn-Cl})_t$ value at 298 cm^{-1} is strong evidence that the coordination number of Zn(II) is five [43]. There is similar coordinating

behaviour for the $\text{LH}_2\text{-LH}^-$ ligand system in 21; however, this complex is 6-coordinate with a chelated bidentate nitrate group.

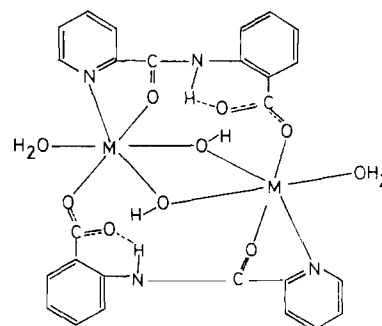
On complexing with Pd(II) , Pt(II) and Cu(II) , the amide proton of the present ligand becomes extremely labile, the only five complexes which



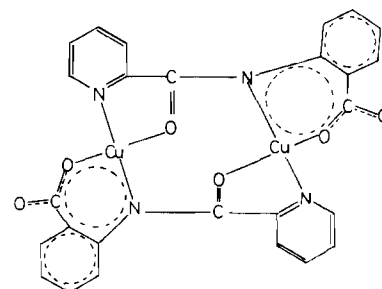
II (1, 2, 3; M = Co, Ni, Zn)



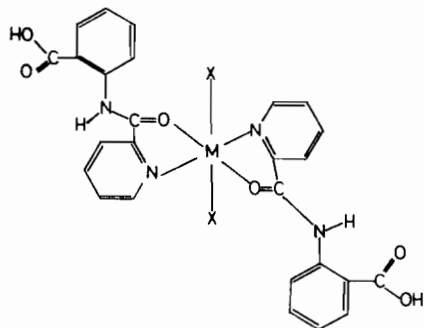
III (6)



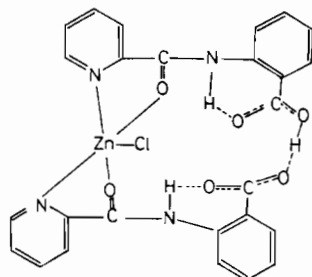
IV (9, 10; M = Ni, Zn)



V (11)



VI (12, 13, 14, 15, 16, 17, 18, 19; M = Co, Ni, Cu, Zn; X = Cl, NCS, ONO₂)

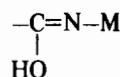


VII (20)

contain, exclusively or in part, the doubly deprotonated L^{2-} ligand precipitating at pH values 2 (5), 1.7 (6), 3.5 (7), 10 (11) and 1.5 (22). It is worth noting that throughout most of the pH range, in the absence of metal ions, the amide group is neutral [1]. Since the discovery of metal ion-induced amide (peptide) deprotonation reactions [44], several studies have led to the conclusion that only Pd(II), Cu(II), Ni(II), Co(II), Zn(II) and perhaps Pt(II) are capable of promoting these reactions. The promotion increases in the series Zn(II) \approx Co(II) < Ni(II) < Cu(II) < Pd(II). The anion LH^- was selected as ligand because it was thought to present one of the most favourable cases for metal-ion promoted amide deprotonation. The presence of two anchoring [1] groups (ring-N atom and aromatic $-COO^-$ group), capable of forming one 5- and one 6-membered stable chelate ring per L^{2-} with the amide nitrogen, would reduce the importance of hydrolysis and bring out the full binding capabilities of the metal ions favouring deprotonation. However, only five complexes containing L^{2-} could be prepared. A comparison of the coordinating ability of LH^- with that of our previous ligands [2–6] demonstrates the effect of the presence of a negative charge in one of the anchoring groups; the $-COO^-$ donor is inefficient in promoting amide deprotonation by Ni(II), Co(II) and Zn(II); at basic pH values the hydroxo complexes 8, 9 and 10 containing a neutral secondary amide group were isolated. Under the same conditions Cu(II) gives the fully deprotonated complex 11, while under

acidic conditions the mixed LH^- , L^{2-} species 5 and 22 were obtained; the situation is surprising for 22, because the starting material was LH_2 and not $LH^-Na^+ \cdot H_2O$. This fact indicates the high thermodynamic stability of the Cu(II)-deprotonated N_{amide} bond.

The iminol form of coordination



which is an intermediate [45] for deprotonated N-coordination of the amide bond, was assigned in 4 which was prepared in a $LH^-:Cu(II)$ molar ratio of 2:1. This structure seems to dominate in DMSO solutions of 1–3, 8–10 and 20, suggesting that the situation is different in solution.

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