Inorganica Chimica Acta, 117 (1986) 27–37

The Coordination Chemistry of *N*-(2-aminophenyl)- and *N*-(3-aminophenyl)-quinoline-2′-carboxamide; two Potentially Tridentate Ligands Containing Secondary Amide and *N*-donor Groups

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(Received November 8, 1985)

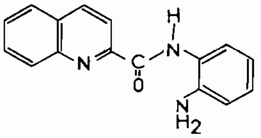
Abstract

New complexes of the general formulae Co(*o*-LH)$_2$X$_2$ (X = Cl, NCS), Co(*o*-LH)$_2$Br$_2$·EtOH (EtOH = ethanol), M(*o*-LH)(NO$_3$)$_2$ (M = Co, Ni), Ni(*o*-LH)$_2$X$_2$ (X = Cl, Br, NCS), Cu(*o*-L)X (X = Cl, Br), Zn(*o*-LH)X$_2$ (X = Cl, Br), Pd(*o*-L)Cl, Pt(*o*-LH)$_2$Cl$_2$·H$_2$O, M(*m*-LH)Cl$_2$·*n*H$_2$O (M = Co, Ni, Pd; *n* = 0, 0.5, 1), Cu(*m*-LH)Cl$_2$·EtOH, M(*m*-LH)$_2$Cl$_2$·*n*H$_2$O (M = Co, Zn, Pt; *n* = 0, 1), M(*m*-LH)Br$_2$ (M = Cu, Zn), M(*m*-LH)$_2$Br$_2$ (M = Co, Ni), Co(*m*-LH)(NCS)$_2$ and Co(*m*-LH)$_2$(NCS)$_2$, where *o*-LH = *N*-(2-aminophenyl)quinoline-2′-carboxamide and *m*-LH = *N*-(3-aminophenyl)quinoline-2′-carboxamide, have been prepared. The complexes were characterised by elemental analyses, conductivity measurements, X-ray powder patterns, thermogravimetric analyses, magnetic moments and spectral (^{1}H NMR, IR, and electronic) studies. Copper(II) and palladium(II) promote amide deprotonation at nearly acidic pH on coordination with *o*-LH. A variety of stereochemistries is assigned for the complexes prepared. The deprotonated copper(II) and the nickel(II) and palladium(II) complexes of *m*-LH appear to be polymeric. The neutral amide group of the ligands is coordinated to the metal ions through oxygen, while N(amide)-coordination is observed for the deprotonated complexes. Coordination of the secondary amide group is not observed for Zn(*m*-LH)$_2$Cl$_2$, Pd(*m*-LH)Cl$_2$·0.5H$_2$O and platinum(II) complexes. The neutral ligand *o*-LH shows bidentate N(ring), O-behaviour, while the anion *o*-L$^-$ exhibits tridentate N,N,N-coordination. *m*-LH acts as a monodentate, bidentate and tridentate ligand depending on the metal ion, the anion and the preparative conditions.

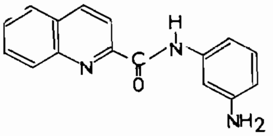
Introduction

The inorganic chemistry of organic amides is an important part of a number of current chemical problems [1–3]. The main results on the coordinating properties of the amide bond were reviewed by Sigel and Martin [1]. Their survey clearly shows that research interest is centred on the stability and structure 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 investigation of the metal–amide interactions [4–12], we report here the preparation and study of cobalt(II), nickel(II), copper(II), zinc(II), palladium(II) and platinum(II) complexes with *N*-(2-aminophenyl)quinoline-2′-carboxamide (**I**, *o*-LH) and *N*-(3-aminophenyl)-quinoline-2′-carboxamide (**II**, *m*-LH). These ligands exhibit interesting ligating possibilities because they have three donor groups; in *o*-LH two of these donor groups (the aromatic amino group and the quinoline N-atom) may serve as anchoring groups [1] to the secondary amide bond favouring deprotonated products.



(**I**, *o*-LH)



(**II**, *m*-LH)

The substituted picolinamide ligands *N*-(2-aminophenyl)- and *N*-(3-aminophenyl)pyridine-2′-carboxamide have been shown to coordinate to the bivalent metal ions in several modes [9–12], largely determined by the nature of the metal ion, the *o*- or *m*-position of the –NH$_2$ group and the pH of the reaction system. Particular attention was devoted to the cobalt ions' systems, because it was found that in the presence of oxygen *N*-(2-aminophenyl)pyridine-2′-carboxamide undergoes a cobalt(III) ion promoted amide hydrogen ionization, *i.e.*, lowering of reduction potential of metal couples and stabilization of high oxidation states. The less flexible ligands **I** and **II** of the present study should present a differ-

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0020-1693/86/$3.50

ent degree of electronic delocalization and a larger steric hindrance in their complexes than would their pyridine homologues. Hence some marked differences in coordination behaviour between **I**, **II** and the ligands of our previous work [9–12] might be expected.

Experimental

Analyses and physicochemical techniques were carried out by published methods [9].

Ligand Syntheses

The ligands *o*-LH and *m*-LH were prepared by hydrogenation of the nitro derivatives.

N-(2-nitrophenyl)quinoline-2'-carboxamide

To a solution of quinaldinic acid (10.0 g, 0.058 mol) in pyridine (35 ml) was added a solution of *o*-nitroaniline (8.0 g, 0.058 mol) in pyridine (15 ml). After warming the solution obtained to 70 °C, triphenylphosphite (15.2 ml, 0.058 mol) was added dropwise with vigorous stirring. After heating on a steam-bath with continuous stirring for 4 h, the reaction solution was allowed to stand overnight. After volume reduction and cooling, absolute ethanol was added under stirring until a permanent precipitate formed. The solid product was filtered off and recrystallised three times from absolute ethanol to yield 2.89 g (17%) of fine yellow needles (melting point (m.p.) 180–181 °C). *Anal.* Calc. for $C_{16}H_{11}N_3O_3$: C, 65.52; H, 3.79; N, 14.33. Found: C, 65.10; H, 3.71; N, 14.11%. The purity of the compound was also checked by TLC in a 4:1 chloroforme–hexane system giving one spot ($R_f = 0.90$). Mass spectrum: *m/e* (parent) 293 (calc. formula weight 293.30).

N-(2-aminophenyl)quinoline-2'-carboxamide (I, o-LH)

To a suspension of *N*-(2-nitrophenyl)quinoline-2'-carboxamide (5.0 g, 0.017 mol) and 0.75 g of hydrogenation catalyst (10% Pd on activated carbon) in absolute ethanol (400 ml), pure hydrogen was admitted for 3 h under vigorous constant stirring. The reaction product was separated from the catalyst by filtration and the resulting solution after volume reduction (reduced pressure) yielded a dirty yellow solid. The solid product was filtered off and recrystallised from absolute ethanol to yield after drying *in vacuo* 4.26 g (95%) of golden yellow crystals (m.p. 149–150 °C). *Anal.* Calc. for $C_{16}H_{13}N_3O$: C, 72.98; H, 4.99; N, 15.96. Found: C, 72.49; H, 5.00; N, 16.20%. R_f (chloroforme–hexane 4:1) = 0.13. Mass spectrum: *m/e* (parent) 263 (calc. formula weight 263.32).

N-(3-nitrophenyl)quinoline-2'-carboxamide

Using *m*-nitroaniline as a starting material a quite similar isolation procedure, as outlined above for the 2-nitro compound, gave creamy-white needles (m.p. 187–188 °C). Yield 68%. *Anal.* Calc. for $C_{16}H_{11}N_3O_3$: C, 65.52; H, 3.79; N, 14.33. Found: C, 65.11; H, 3.71; N, 14.21%. R_f (chloroforme–hexane 4:1) = 0.79. Mass spectrum: *m/e* (parent) 293 (calc. formula weight 293.30).

N-(3-aminophenyl)quinoline-2'-carboxamide (II, m-LH)

To a suspension of *N*-(3-nitrophenyl)quinoline-2'-carboxamide (10.0 g, 0.034 mol) and 1.90 g of hydrogenation catalyst (10% Pd on activated carbon) in absolute ethanol (1000 ml), pure hydrogen was admitted for 4 h with continuous stirring. The reaction product was separated from the catalyst by filtration. Ethanol was then distilled off *in vacuo* leaving a thick brown oil. *n*-hexane (300 ml) was added and the oil scratched to give a light brown non-crystalline solid. The mixture was filtered off and the solid was recrystallised twice from absolute ethanol to yield after drying *in vacuo* 7.25 g (81% based on the corresponding nitro compound) of pale yellow crystals (m.p. 153–154 °C). *Anal.* Calc. for $C_{16}H_{13}N_3O$: C, 72.98; H, 4.99; N, 15.96. Found: C, 72,87; H, 5.24; N, 16.00%. R_f(chloroforme–hexane 4:1) = 0.14. Mass spectrum: *m/e* (parent) 263 (calc. formula weight 263.32).

Deuterium-substituted forms [13]

Due to their low solubilities in water the deuterated forms of *o*-LH and *m*-LH cannot be prepared by recrystallising these ligands from D_2O. They were prepared by dissolving the appropriate ligand in a small amount of hot ethanol, adding an equal volume of D_2O, then boiling off the more volatile ethanol. The deuterated samples crystallised out as the solutions cooled. An additional recrystallisation was found necessary for *m*-LH to give complete conversion.

Preparation of the complexes

The metal salts CoX_2 (X = Cl, Br, NCS), $M(NO_3)_2 \cdot 6H_2O$ (M = Co, Ni), $NiCl_2 \cdot 6H_2O$, $NiBr_2 \cdot 3H_2O$, $Ni(SCN)_2$, CuX_2 (X = Cl, Br), ZnX_2 (X = Cl, Br) and K_2MX_4 (M = Pd, Pt) were used as starting materials. Two general methods of preparation of complexes of *o*-LH and *m*-LH were used. The cobalt(II), nickel(II), copper(II) and zinc(II) complexes were prepared by the direct reaction of an ethanolic (refluxing methanolic in the case of nickel(II) thiocyanate) solution of the metal salt (10 mmol) with a warm ethanolic solution of *o*-LH or *m*-LH (10 or 20 mmol, see Table I). When hydrated metal salts were used as starting materials, 10–15 ml of triethyl orthoformate were added to the reaction mixture for

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

Compound number	Complex	Ligand: metal salt[a]	Yield (%)	Colour	Elemental analyses[b] (%)					Λ_M[c] (ohm^{-1} mol^{-1} cm^2)
					M	X	C	H	N	
1	Co(*o*-LH)$_2$Cl$_2$	1:1, 2:1	73	pink-yellow	8.5(9.0)	10.5(10.8)	58.7(58.5)	3.95(4.00)	12.5(12.8)	46[e]
2	Co(*o*-LH)$_2$Br$_2$·EtOH	1:1, 2:1	76	yellow	7.6(7.5)	20.4(20.2)	51.3(51.6)	3.78(4.08)	10.3(10.6)	67[e]
3	Co(*o*-LH)$_2$(NCS)$_2$	1:1, 2:1	64	pink	8.2(8.4)	16.4(16.5)	57.5(58.2)	3.91(3.74)	16.1(16.0)	14
4	Co(*o*-LH)(NO$_3$)$_2$	1:1	80	deep red	13.1(13.2)		43.6(43.1)	2.99(2.94)	15.2(15.7)	9
5	Ni(*o*-LH)$_2$Cl$_2$	1:1, 2:1	74	pale green	9.4(9.0)	10.6(10.8)	58.8(58.6)	4.15(4.00)	12.4(12.8)	57[e]
6	Ni(*o*-LH)$_2$Br$_2$	1:1, 2:1	63	lemon yellow	8.3(7.9)	20.6(21.4)	51.8(51.6)	3.53(3.52)	11.0(11.3)	62[e]
7	Ni(*o*-LH)$_2$(NCS)$_2$	1:1, 2:1	87	yellow–green	8.8(8.4)	16.4(16.6)	58.0(58.2)	3.91(3.74)	16.4(16.0)	7
8	Ni(*o*-LH)(NO$_3$)$_2$	1:1	69	pale green	13.5(13.2)		43.0(43.1)	2.81(2.94)	16.0(15.7)	3
9	Cu(*o*-L)Cl	1:1, 2:1	47	dark green	16.6(17.6)	9.8(9.8)	53.9(53.2)	3.39(3.35)	11.7(11.6)	9
10	Cu(*o*-L)Br	2:1	43	brown	15.4(15.7)	18.9(19.7)	49.2(47.4)	3.10(2.99)	10.1(10.4)	15
11	Zn(*o*-LH)Cl$_2$	1:1, 2:1	85	pale orange	17.0(16.4)	17.4(17.5)	48.8(48.1)	3.16(3.29)	11.0(10.5)	5
12	Zn(*o*-LH)Br$_2$	1:1, 2:1	90	pale yellow	13.3(13.4)	32.4(32.7)	39.0(39.3)	2.74(2.69)	8.8(8.6)	3
13	Pd(*o*-L)Cl	1:1	71	pale yellow	25.8(26.3)		47.6(47.5)	2.99(3.00)	10.6(10.4)	i
14	Pt(*o*-LH)$_2$Cl$_2$·H$_2$O	2:1	67	pale brown	23.9(24.1)		46.9(47.4)	3.33(3.49)	9.9(10.4)	i
15	Co(*m*-LH)Cl$_2$	1:1	78	blue–green	15.1(15.0)	17.8(18.0)	48.6(48.9)	3.55(3.34)	10.2(10.7)	20[e]
16	Co(*m*-LH)$_2$Cl$_2$	2:1	64	brown	9.1(9.0)	10.4(10.8)	57.6(58.5)	3.97(4.00)	12.9(12.8)	50[e]
17	Co(*m*-LH)$_2$Br$_2$	2:1	69	pink	7.7(7.9)	21.6(21.4)	51.8(51.6)	3.40(3.52)	11.0(11.3)	7
18	Co(*m*-LH)(NCS)$_2$	1:1	80	blue	13.2(13.4)	26.8(26.5)	49.6(49.3)	3.08(2.99)	16.2(16.0)	7
19	Co(*m*-LH)$_2$(NCS)$_2$	2:1	71	pink–brown	8.1(8.4)	16.8(16.6)	59.2(58.2)	3.76(3.74)	15.7(16.0)	9
20	Ni(*m*-LH)Cl$_2$·H$_2$O	1:1	97	yellow–green	14.1(14.3)	17.4(17.3)	47.5(46.8)	3.67(3.69)	10.5(10.2)	i
21	Ni(*m*-LH)$_2$Br$_2$	1:1, 2:1	98	green	8.3(7.9)	21.6(21.5)	51.7(51.6)	3.40(3.52)	11.4(11.3)	i
22	Cu(*m*-LH)Cl$_2$·EtOH	1:1, 2:1	91	brownish green	13.9(14.3)	16.0(16.0)	47.9(48.7)	4.34(4.32)	9.6(9.5)	19
23	Cu(*m*-LH)Br$_2$	1:1, 2:1	64	brown	12.9(13.1)	33.1(32.8)	38.9(39.5)	2.81(2.70)	8.8(8.6)	d
24	Zn(*m*-LH)$_2$Cl$_2$	1:1	71	white	9.8(9.9)	10.0(10.7)	58.0(58.0)	3.88(3.96)	12.3(12.7)	8
25	Zn(*m*-LH)Br$_2$	1:1, 2:1	84	white–yellow	13.6(13.4)	33.0(32.7)	39.2(39.3)	2.71(2.69)	8.8(8.6)	6
26	Pd(*m*-LH)Cl$_2$·0.5H$_2$O	1:1, 2:1	96	pale brown	23.6(23.7)		42.6(42.7)	2.99(3.14)	9.1(9.3)	i
27	Pt(*m*-LH)$_2$Cl$_2$·H$_2$O	1:1, 2:1	63	pale brown	24.1(24.1)		47.9(47.4)	3.37(3.49)	10.8(10.4)	3

[a] *Molar ratio.* [b] *Theoretical values in parentheses.* [c] *Values of molar conductivity for* ca. 10^{-3} *M solutions in DMSO at 25 °C.* [d] *This complex decomposes in solution.* [e] *The conductivities of the solutions increase with time.* M = metal; X = Cl, Br, NCS; i = insoluble.

dehydration purposes. The palladium(II) and platinum(II) complexes were prepared on adding an aqueous solution (20 ml) of K_2MCl_4 to a solution of ligand in ethanol at 35–40 °C.

Solid product formation was usually slow (1–3 h), although the precipitation of the nickel(II) and palladium(II) complexes of *m*-LH occurred immediately. All precipitates were collected by filtration after several hours stirring at 40 °C and washed with ethanol (aqueous ethanol in the case of palladium(II) and platinum(II) compounds). They were stirred again in warm ethanol or aqueous ethanol to remove unreacted starting materials, then filtered off and washed with ethanol and ether. They were dried *in vacuo* over P_4O_{10}. In the case of CoX_2, (X = Cl, NCS) and *m*-LH two series of complexes were obtained. Using 10 mmol of ligand and 10 mmol of anhydrous metal salts the compounds $Co(m\text{-}LH)X_2$ were prepared, while using a 2:1 ligand:metal ion molar ratio the complexes $Co(m\text{-}LH)_2X_2$ were isolated.

Efforts to prepare complexes with other stoichiometries, using various ligand:metal salt molar ratios, met with failure. In most cases the same complexes (those described in Table I), with lower yields, were again isolated. Several attempts were made to prepare cobalt(II) nitrate and nickel(II) nitrate or thiocyanate complexes with *m*-LH. However, varying metal ion-to-ligand ratios gave microanalyses for the products indicative of non-stoichiometric polymeric forms. No complexes of the ligands with manganese(II) salts could be prepared. Numerous attempts to isolate other deprotonated complexes from ethanolic, methanolic or ethanol–water solutions were unsuccessful. When an aqueous standard 1 N NaOH solution was added to the reaction mixtures till the pH was exactly 7, solids with poor analytical results were precipitated; when pH was adjusted in the 7.5–9.5 region hydroxo-derivatives of uncertain nature were obtained.

No evidence was obtained with any of the ligands for hydrolysis reactions occurring at the secondary amide group.

Results and Discussion

Preparative and analytical data, colours and molar conductivity values are given in Table I. The complexes are microcrystalline or powder-like, quite stable in atmospheric conditions, insoluble in non-polar solvents and soluble only in DMF and DMSO. The compounds **13**, **14**, **20**, **21** and **26** are, however, insoluble in DMF and DMSO. The molar conductivities of most of the complexes in DMSO are in accord with them being formulated as non-electrolytes [14]. The fact that the conductivities of the solutions of **1**, **2**, **5**, **6**, **15** and **16** increase with time can be attributed to the strong donor capacity of the solvent used, which leads to displacement of anionic ligands and change of electrolyte type [14]; thus the data for these complexes are somewhat difficult to interpret. X-ray powder diffraction patterns indicate that each compound represents a definite complex and not merely mixtures of simpler stoichiometric types or starting materials. The data also indicate the formation of four pairs of isomorphous compounds; the first pair includes the complexes **5** and **6**, the second the complexes **9** and **10**, the third the zinc(II) complexes **11** and **12** and the fourth includes the compounds **16** and **17**. The small number of diffraction lines observed for **9**, **10**, **20**, **21** and **26** complexes of *m*-LH suggests polynuclear arrangements. Thermogravimetric (TG) and differential thermogravimetric (DTG) studies in the 30–700 °C region show that ethanol present in **2** and **22** and water present in **14**, **26** and **27** are lattice held. The hydrated complexes begin their decomposition at 70–75 °C; they lose all water between 70 and 135 °C. Ethanol is completely removed between 55 and 85 °C. The high temperature (130–170 °C) loss of water in $Ni(m\text{-}LH)Cl_2 \cdot H_2O$, in connection with the relatively low decomposition temperature, shows that the water present is coordinated to the metal ion. Repeated thermograms for the chloride non-deprotonated complexes of *o*-LH and *m*-LH showed very low and varied residue weights and varying final decomposition patterns, indicating partial sublimation; similar sublimation processes have been observed previously with complexes of other secondary amide ligands [15–17]. No separate weight loss attributable to hydrogen chloride was demonstrated in the thermograms of any of the chloride non-deprotonated complexes of *o*-LH, in contrast with those of the nickel(II) and copper(II) complexes of *N*,*N*′-bis(2′-pyridinecarboxamide)-1,2-benzene [18] and with the complex of zinc(II) with *N*-(2-aminophenyl)pyridine-2′-carboxamide [11].

Infrared Spectra

The principal IR bands of interest are listed in Tables II and III. The presence of lattice ethanol in **2** and **22** is manifested by a broad band covering the 3600–3250 cm^{-1} region [19]. In the ν(O–H) region the spectrum of $Ni(m\text{-}LH)Cl_2 \cdot H_2O$ exhibits a medium, single and sharp band at 3410 cm^{-1} attributed to the presence of coordinated water [20]. In the spectra of the other hydrated compounds a very broad and weak continuous absorption (3550–3150 cm^{-1}), on top of the strong $\nu(NH_2)$ and $\nu(N\text{–}H)_{amide}$ bands, indicates that lattice water is present [20]; on dehydration of these compounds the broad band is not observed, with the main features of the spectra remaining unchanged from those of the hydrated forms.

TABLE II. Diagnostic Infrared Ligand Bands (cm^{-1}) of *o*-LH, *m*-LH and their Complexes and far-IR Bands

Compound	$\nu_{as}(NH_2)$[a]	$\nu_s(NH_2)$[b]	$\delta(NH_2)$[c]	Characteristic Amide Bands				$\nu(MX)$
				$\nu(N-H)$	amide I[d]	amide II[e]	amide III[e]	
o-LH	3425s	3345s	1655wm	3255mbr	1693vs	1528vs	1214m	
1	3430s	3335s	1660m	3200mbr	1614vs	1578s	1259wm, 1230m	240m
2	[f]	[f]	1655m	[f]	1626vs	1561m	1257wm, 1232m	[h]
3	3405sbr	3315sbr	1647m	3215mbr	1622vs	1564s	1259wm, 1232m	252s
4	3410s	3310s	1649sh	3225mbr	1620vs	1562s	1261wm, 1233m	301s, 289vs
5	3430sbr	3335s	1645sh	3195mbr	1625vs	1578m	1259wm, 1229m	271m
6	3410mbr	3322m	1645sh	3215mbr	1630vs	1564vs	1274m, 1232m	224s
7	3405s	3310m	1647m	3230mbr	1628vs	1562s	1276wm, 1234m	239s
8	3410s	3305s	1650m	3225mbr	1635sb	1560vs	1278wm, 1231m	309vs, 259s
9	3210s	3145s	1617m		1603vs	1401vs		349vs, 334s, 285m[i]
10	3265s	3185m	1623s		1601vs	1400vs		310m
11	3405s	3300s	1650w	3225mbr	1614m	1574m	1266w, 1235w	328vs, 283vs
12	3410s	3310m	1647w	3215mbr	1621vs	1569m	1263w, 1233m	257s, 216m
13	3255s	3190m	1619m		1603vs	1399vs		342vs
14	3295m	3210m	1611m	3235m	1675vs	1527s	1211m	340vs
m-LH	3430s	3335vs	1649sh	3280mbr	1678vs	1532vs	1212m	
15	3440mbr	3340mbr	1651sh	3260mbr	1625vs	1556vs	1269wm, 1224m	321vs, 285m
16	3420mbr	3335m	1655m	3240mbr	1621vs	1560vs	1267m, 1232m	232m
17	3415mbr	3320m	[g]	3265mbr	1623vs	1566vs	1270m, 1235m	[h]
18	3420m	3315sbr	1649w	3275mbr	1627vs	1560vs	1270wm, 1230m	307vs, 293vs
19	3415s	3320s	1652w	3270mbr	1621vs	1564vs	1269m, 1231m	233s
20	3320s	3195s	1612m	3280mbr	1629vs	1562m	1267m, 1230m	241vs
21	3305s	3200s	1609m	3250mbr	1625vs	1564m	1268m, 1235m	
22	[f]	[f]	1604sh	[f]	1633vs	1559s	1261m, 1228m	311s, 246m[i]
23	3425mbr	3310s	1650w	3270mbr	1635vs	1555vs	1261m, 1229m	244sh, 227vs
24	3335s	3220s	1610m	3260m	1679vs	1529vs	1209m	318s, 305s
25	3415sbr	3320vs	1647m	3255mbr	1624vs	1562vs	1270wm, 1230m	253s, 210s
26	3240m	3130s	1612m	3250mbr	1675vs	1535s	1214m	346vs
27	3315m	3255wbr	1608m	3210s	1675vs	1531vs	1209m	334vs

[a] Antisymmetric stretching. [b] Symmetric stretching. [c] Scissoring. [d] $\nu(C=O)$. [e] These bands in secondary amides arise from $\nu(C-N)$ and $\delta(NH)$ modes. [f] Obscured by the broad $\nu(O-H)$ band of ethanol. [g] Not observed. [h] Not observed above 215 cm^{-1}. [i] $\nu(CuCl)_b$. Where b = bridging; s = strong; m = medium; w = weak; v = very; br = broad; sh = shoulder; M = metal; X = Cl, Br, NCS, ONO_2.

TABLE III. Characteristic IR Thiocyanate and Nitrate Bands (cm^{-1}) of the Prepared Complexes

Complex	Thiocyanate bands[a]		Nitrate bands[b]				
	$\nu(CN)$	$\nu(CS)$	$\nu_1(A_1)$	$\nu_4(B_2)$	$\nu_2(A_1)$	$\nu_6(B_1)$	$\nu_3(A_1)$
3	2071vs	808vs					
4			1477s	1287vs	1018s	819m	739m
7	2076vs	811vs					
8			1473s	1283vs	1032s	824m	743m
18	2062vs	820vs					
19	2075vs	809s					

[a] The $\delta(NCS)$ band is obscured by the ligand bands. [b] The $\nu_5(B_2)$ mode of the C_{2v} nitrato groups was not assigned because the 680–725 cm^{-1} region is obscured by strong bands of the coordinated *o*-LH.

The spectra of *o*-LH and *m*-LH show the characteristic bands of secondary hydrogen-bonded amides with quinoline and aromatic $-NH_2$ moieties. Assignments of $-NH_2$ and amide bands for the ligands were assisted by deuterium isotopic substitution. In the spectra of **9**, **10**, **13**, **14**, **20**–**22**, **24**, **26** and **27** large frequency decreases (90–215 cm^{-1}) for the $\nu(NH_2)$ bands and $\delta(NH_2)$ band (*ca.* 40 cm^{-1}) indicate $-NH_2$ coordination [21]. The absence of large systematic shifts of these bands in the spectra of the other complexes implies that there is no interaction between the amino group and the metal ions. The relatively small shift of the $\nu(\mathrm{NH_2})$ modes to lower frequencies and the rather broad character of these bands is expected to arise from hydrogen bonding to the $\mathrm{NH_2}$ protons with the bonded anions, but any reductions in $\nu(\mathrm{NH_2})$ are not as large as expected if coordination had occurred.

As would be expected from the stoichiometries the $\nu(\mathrm{N{-}H})_{\mathrm{amide}}$ band is absent in the spectra of the deprotonated complexes. Other differences in the spectra of these complexes and those of the non-deprotonated ones are readily noticeable. The amide II and III bands are replaced by a strong absorption band at about 1400 $\mathrm{cm^{-1}}$, which is assigned to a pure C–N stretch; this frequency value is typical for deprotonated secondary amide complexes [13, 15, 16]. In the spectra of the most non-deprotonated complexes the amide I band shifts to a lower frequency, while the amide II and III bands shift to higher frequencies; these shifts indicate amide-0 coordination [13, 15, 16, 18]. The observeration of only one sharp absorption band for each amide I and II mode in the spectra of the 1:2 complexes indicates that both amide groups are coordinated to the metal ions [15]. For **14**, **24**, **26** and **27** there are no shifts in the characteristic amide bands, which suggests that the amide groups remain uncoordinated in these complexes.

The spectra of all complexes prepared, except **14**, **24** and **27**, show medium to strong bands at *ca.* 495, 530, 640, 780, 1310, 1380, 1435, 1450 and 1595 $\mathrm{cm^{-1}}$, which are due to vibrational modes of the coordinated quinoline moiety [22–24]. The effect of coordination is mainly on the heterocyclic ring causing noticeable changes in the position and intensity of the bands. This effect is probably not transmitted to the benzene ring and consequently there is a very small change in the position of the bands arising out of the benzene ring.

The IR spectra of the thiocyanate complexes exhibit $\nu(\mathrm{CN})$ and $\nu(\mathrm{CS})$ modes all in the regions characteristic of terminal N-bonded isothiocyanate groups [25]. Further the spectrum of **18** shows the two strong $\nu(\mathrm{Co{-}NCS})_t$ bands expected for pseudotetrahedral symmetry [26], while the spectra of **3**, **7** and **19** exhibit one strong band in the 233–242 $\mathrm{cm^{-1}}$ region which probably arises from the $\nu(\mathrm{M{-}NCS})_t$ vibration in a *trans* octahedral structure [27]. The values of the frequencies assigned as vibrational modes of the nitrate group (Table III) are strongly indicative of the presence of coordinated bidentate nitrates [28, 29], because the separation of the two highest frequency bands is *ca.* 200 $\mathrm{cm^{-1}}$. The 1700–1800 $\mathrm{cm^{-1}}$ region is viewed as the key to differentiate between bidentate and unidentate coordination of nitrato groups [28, 30]. The separation of the combination bands $\nu_2 + \nu_3$ and $\nu_2 + \nu_5$, appearing around 1765 and 1720 $\mathrm{cm^{-1}}$, is about 45 $\mathrm{cm^{-1}}$ and this fact indicates bidentate nitrato groups [28]. Lever *et al.* have reported [30] that the spectra of the complexes containing bridging nitrate groups almost invariably exhibit a combination band at a higher frequency (near 1800 $\mathrm{cm^{-1}}$) than those observed in non-bridging systems; the absence of such a band in the spectra of the nitrate complexes prepared confirms that bridging nitrates are absent. In addition the spectra of **4** and **8** exhibit strong $\nu(\mathrm{M{-}O})$ bands in the far-IR region [26].

The region of the free ligands' spectra between 450 and 215 $\mathrm{cm^{-1}}$ contains only four weak bands. This would indicate that some of the other bands observed in this region would be assignable to $\nu(\mathrm{M{-}N_{ring}})$, $\nu(\mathrm{M{-}NH_2})$, $\nu(\mathrm{M{-}O_{amide}})$ and $\nu(\mathrm{MX})$, where X = Cl, Br, NCS, $\mathrm{ONO_2}$. The $\nu(\mathrm{MX})$ bands of the prepared complexes give an insight into the structure and bonding in the solid state. Assignments of these bands in Table II have been made by noting: (a) the frequencies of internal modes of the organic ligands, (b) bands principally dependent on X, (c) the variation in band position with changing metal ion, and (d) the reports of the literature [26, 27, 29, 31]. The far-IR spectra of the complexes **11**, **12**, **15**, **18**, **23**, **24** and **25** show the terminal M–X frequencies in the region expected for pseudotetrahedral monomeric stereochemistry. The spectra of Cu(*o*-L)Cl and Cu(*m*-LH)$\mathrm{Cl_2}$·EtOH are indicative of the presence of both terminal and bridging Cu–Cl bonds. The far-IR spectra of the palladium(II) and platinum(II) complexes prepared exhibit strong singlet absorption bands associated with terminal Pd–Cl and Pt–Cl stretches; the presence of one $\nu(\mathrm{M{-}Cl})_t$ vibration in each spectrum confirms their *trans* structures. A strong band at frequencies lower than 280 $\mathrm{cm^{-1}}$ in the spectra of **1**, **3**, **5**, **6**, **7**, **16**, **19** and **20** probably arises from the $\nu(\mathrm{M{-}X})_t$ vibration in a *trans* octahedral structure.

Proton Magnetic Resonance Spectra

The ^{1}H NMR assignments of *o*-LH, *m*-LH and their diamagnetic complexes in $\mathrm{D_6}$-DMSO are based on comparisons with the corresponding nitro organic compounds and a number of other amide complexes [3, 10–13, 32]. The complexes **13**, **14** and **26** are insoluble in DMSO, so that NMR spectral studies have been precluded. The spectrum of *o*-LH shows a complex of peaks between δ 8.73 and 6.71 ppm downfield from TMS assigned to the quinoline and benzene protons, a broad singlet at 5.00 ppm assigned to the $-\mathrm{NH_2}$ protons and another broad singlet at δ 10.84 ppm assigned to the –CO–NH– hydrogen; in $\mathrm{D_2O}$ the amide proton signal disappears indicating a rapid exchange. The corresponding signals of *m*-LH appear at δ 8.73 and 6.36, 5.13 and 10.69 ppm. The integrations of the signals were in the ratio 10:2:1. In the spectra of the diamagnetic complexes the signals of the aromatic hydrogen atoms shift slightly (*ca.* 0.1–0.3 ppm) downfield compared with those of free ligands, suggesting that the donor-atoms are far removed from the regions of these hydrogens. Also, the amide proton undergoes only a marginal shift (*ca.* 0.05 ppm) indicating non-involvment of the amide-N atom in coordination. The shift observed for $-NH_2$ protons in the spectra of **11**, **12** and **25** is insignificant (*ca.* 0.05–0.1 ppm), indicating that the aromatic amino group remains uncoordinated in these complexes. The spectrum of $Pt(m\text{-}LH)_2Cl_2 \cdot H_2O$ shows a characteristic downfield shift (0.7 ppm) of the $-NH_2$ resonance relative to the free ligand, clearly suggesting the coordination of the anilinic nitrogen to Pt(II) [3]. For $Zn(m\text{-}LH)_2Cl_2$, if the spectrum is run immediately after dissolution the $-NH_2$ signal appears at 5.90 ppm indicating binding through this group; if the spectrum is run again after 1–2 h this signal remains, but another signal appears at 5.15 ppm indicative of the simultaneous presence of uncomplexed $-NH_2$. NMR evidences for iminol structures [33] were not found.

Magnetic 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 [34] and electronic spectral data of $Co(m\text{-}LH)X_2$ (X = Cl, NCS) indicate pseudotetrahedral stereochemistry around Co(II) with the band assigned to the $^4A_2 \rightarrow {}^4T_1(F)$ transition being split (by virtue of reduction of symmetry from T_d to C_{2v} or lower) into bands representing the transitions to the $^4B_1$, $^4A_2$ and $^4B_2$ states [35]. The μ_{eff} values of the cobalt(II) complexes **1**, **2**, **3**, **16**, **17** and **19** lie in the 4.75–5.13 BM range, characteristic of octahedral stereochemistry. Their electronic spectra exhibit bands typical of octahedral structure; the 10 *Dq* values for the isothiocyanate complexes are higher than those found in the other complexes, as expected from the relatively high position of this group in the spectrochemical series. While the magnetic moment of $Co(o\text{-}LH)(NO_3)_2$ is in the region expected for tetrahedral complexes, the electronic spectrum of this compound in the solid state (Table IV) and in DMSO (not included in Table IV) differs from spectra of typical tetrahedral cobalt(II) complexes. The absorption maximum at *ca.* 18 500 cm^{-1}, although similar in general contour to the visible bands of other tetrahedral complexes, is at a higher energy than would have been expected. Moreover, the molar extinction coefficient of the visible band in DMSO (180 l cm^{-1} mol^{-1}) is appreciably lower than those found for other tetrahedral cobalt(II) complexes [35]. Also the near-IR spectrum consists of two bands. This magnetic and spectral behaviour, which has been found for some other *cis*-$CoL_2(NO_3)_2$ compounds where L is a phosphine or arsine oxide [36] or a hindered monodentate amine [37] or 1-methyl-3,4-diphenylpyrazole [38], has been explained [36] by postulating that the six-coordinated complex can be regarded as having a rather quasi-tetrahedral structure with bonds directed toward the centres of the bidentate nitrate groups instead of toward the oxygen atoms. However, Lever [37] suggested that the assumption of a quasi-tetrahedral coordination is perhaps unnecessary. These molecules have a distorted six-coordinated structure of C_2 symmetry (in the case of **4** the symmetry is lower because of the N,O-bidentate behaviour of *o*-LH); the degeneracy of the ground state of the cobalt ion is lifted ($^4T_{1g}(O_h) \rightarrow {}^4A$, 2^4B 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 for a normal octahedral stereochemistry; this was observed in **4**. The absence of a centre of symmetry could produce a fairly high intensity d–d spectrum, since both p and d orbitals span common representations in C_2; this was also observed.

The μ_{eff} values of the nickel(II) complexes show only small orbital contribution, in accord with octahedral stereochemistry [34]. Their electronic spectra exhibit the well-defined transitions between the triplet states in this geometry [35]. The doublet structure of $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ in **5** and **6** has been ascribed to a gaining of intensity of the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition through configurational interaction with the $^3T_{1g}(F)$ level and also to spin–orbit coupling. The doublet structure of $^3A_{2g} \rightarrow {}^3T_{2g}$ in the spectra of $Ni(o\text{-}LH)_2X_2$ (X = Cl, Br, NCS) is indicative of a *trans* tetragonally distorted octahedral structure [35].

The μ_{eff} values, measured at room temperature, indicate that the copper(II) complexes are magnetically dilute. The diffuse reflectance maxima in the 22 900–26 100 cm^{-1} region are assignable to halogen-to-copper(II) charge-transfer bands [39] and together with the far-IR spectra help to confirm their coordination to the metal center. It is expected that chloro- and bromo-ligand to metal charge-transfer bands will be found at lower energies than those involving oxygen or nitrogen donor atoms from the organic ligands, with the band of the bromo ligand being found at the lowest energy [39]. The electronic spectra of **9**, **10** and **22** are fairly typical of a tetragonally distorted octahedral stereochemistry, exhibiting one absorption band in the visible region [35, 39]. The d–d bands of $Cu(m\text{-}LH)Br_2$ are indicative of tetrahedral stereochemistry [35, 40, 41]. For truly tetrahedral copper(II) complexes, crystal field theory predicts only one transition due to $^2T_2 \rightarrow {}^2E$. However, Furlani and Morpurgo [42] have shown that the flattening of the tetrahedron results in the splitting of both the ground and excited levels so that four transitions are to be expected.

TABLE IV. Solid State Magnetic Moments and Ligand Field Electronic Spectral Data of Complexes of *N*-(2-aminophenyl)- and *N*-(3-aminophenyl)quinoline-2′-carboxamide

Complex	μ_{eff}[a,b] (BM)	Solid state[b] electronic (diffuse reflectance) spectra (10^3 cm^{-1})					10 *Dq* (cm^{-1})	*B* (cm^{-1})	β
Tetrahedral Co(II) complexes		$^4A_2 \rightarrow {}^4T_1(P)$		$^4A_2 \rightarrow {}^4T_1(F)$					
Co(*m*-LH)Cl_2	4.59	15.27		7.62, 6.40, 5.81			3280	694	0.71
Co(*m*-LH)$(NCS)_2$	4.67	15.81		8.45, 7.12, 5.88			4160	700	0.72
Octahedral Co(II) complexes		$^4T_{1g} \rightarrow {}^4T_{1g}(P), {}^4A_{2g}$		$^4T_{1g} \rightarrow {}^4T_{2g}$					
Co(*o*-LH)$_2Cl_2$	4.77	20.41, 15.87		7.96			9060	755	0.78
Co(*o*-LH)$_2Br_2$•EtOH	4.85	19.61, 16.95		7.93			9000	762	0.78
Co(*o*-LH)$_2(NCS)_2$	5.03	20.88, 19.37, 18.43		9.18			10360	813	0.84
Co(*o*-LH)$(NO_3)_2$	4.59	19.08sh, 18.38		8.80, 7.39			9155	763	0.79
Co(*m*-LH)$_2Cl_2$	4.75	19.83, 15.62		7.83			8880	734	0.76
Co(*m*-LH)$_2Br_2$	4.84	19.30, 15.92		7.80			8845	731	0.75
Co(*m*-LH)$_2(NCS)_2$	5.13	20.50, 19.84sh, 19.01, 18.25		9.02			10160	770	0.79
Octahedral Ni(II) complexes		$^3A_{2g} \rightarrow {}^3T_{1g}(P)$	$^3A_{2g} \rightarrow {}^1T_{1g}$[c]	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^1E_g$[c]	$^3A_{2g} \rightarrow {}^3T_{2g}$			
Ni(*o*-LH)$_2Cl_2$	3.15	22.73		15.43, 13.42	12.40sh	9.49, 8.10	8795	698	0.66
Ni(*o*-LH)$_2Br_2$	3.04	22.57	20.01sh	15.38, 13.33		9.19, 8.23	8710	702	0.67
Ni(*o*-LH)$_2(NCS)_2$	3.02	25.25		15.70		10.15, 8.75	9450	815	0.77
Ni(*o*-LH)$(NO_3)_2$	3.17	22.95	20.22sh	14.55		8.85	8850	708	0.67
Ni(*m*-LH)Cl_2•H_2O	3.18	23.25		14.14	11.07sh	8.60	8600	768	0.73
Ni(*m*-LH)$_2Br_2$	2.99	24.80	20.23sh	15.27	13.01sh	9.25	9250	804	0.76
Cu(II) complexes		CT	d–d						
Cu(*o*-L)Cl	1.85	25.97	16.13						
Cu(*o*-L)Br	1.79	23.81	15.62						
Cu(*m*-LH)Cl_2•EtOH	1.89	26.10	14.33						
Cu(*m*-LH)Br_2	2.14	22.91	16.13, 13.89, 6.71						
Square planar Pd(II) and Pt(II) complexes		$^1A_{1g} \rightarrow {}^1E_g$	$^1A_{1g} \rightarrow {}^1B_{1g}$	$^1A_{1g} \rightarrow {}^1A_{2g}$	Other bands				
Pd(*o*-L)Cl	dia	27.78sh	24.10	15.46	22.22, 20.70sh				
Pt(*o*-LH)$_2Cl_2$•H_2O	dia	d	24.81	15.43	18.69				
Pd(*m*-LH)Cl_2•0.5H_2O	dia	27.78sh	23.53	16.95					
Pt(*m*-LH)$_2Cl_2$•H_2O	dia	28.17	22.73	15.50					

[a] Per metal ion. [b] Measured at room temperature. [c] Spin-forbidden bands frequently observed in octahedral nickel(II) complexes. [d] Not observed. CT = charge-transfer; dia = diamagnetic.

TABLE V. Observed Coordinating Behaviours of the Ligands and Stereochemistries of their Complexes

Coordinating behaviour of the organic ligands	Stereochemistry	Complex
Non-deprotonated complexes		
N_{ring}, O_{amide}, $-NH_2$ tridentate bridging	polymeric octahedral	**20, 21, 22**[a]
N_{ring}, O_{amide} bidentate chelated	monomeric tetrahedral[b] (**III**, **IV**)	**11, 12, 15, 18, 23, 25**
N_{ring}, O_{amide} bidentate chelated	monomeric *trans* octahedral[c] (V)	**1, 2, 3, 5, 6, 7, 16, 17, 19**
N_{ring}, O_{amide} bidentate chelated	monomeric *cis* octahedral[d]	**4, 8**
N_{ring}, $-NH_2$ bidentate bridging	polymeric *trans* square planar[b] (VI)	**26**
$-NH_2$ monodentate	monomeric *trans* square planar[b]	**14, 27**
$-NH_2$ monodentate	monomeric tetrahedral[b]	**24**
Deprotonated complexes		
N_{ring}, N_{amide}, $-NH_2$ tridentate chelated	monomeric square planar[e] (VII)	**13**
N_{ring}, N_{amide}, $-NH_2$ tridentate bridging	polymeric octahedral[f]	**9, 10**

[a] Probably dimeric. [b] The coordination is completed by two X groups (X = Cl, Br, NCS). [c] The chromophore appears to be $[M^{II}O_2N_2X_2]$ in these 1:2 complexes (M = Co, Ni; X = Cl, Br, NCS). [d] $[M^{II}O_5N]$ chromophore with bidentate chelate nitrato groups. [e] The coordination around Pd(II) is completed by the chloride ion. [f] Not assigned with certainty.

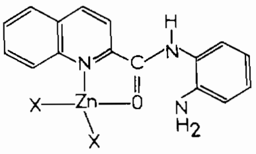
The combination bands of the various ν(N–H) and ν(C–H) IR modes of *m*-LH was the major difficulty in assignment; we have excluded all the narrow bands in the near-IR region. Hence the three bands presented for **23** in Table IV can be assigned with certainty to ligand field transitions; the fourth band expected may be located below 5900 cm^{-1} or may be hidden by the intense charge-transfer band [40].

Square planar structures are assigned for the palladium(II) and platinum(II) complexes prepared on the basis of their electronic spectra [35]. The highest energy $^1A_{1g} \rightarrow {}^1E_g$ transition is normally a shoulder associated with the intense charge-transfer maximum in the 31 000–34 000 cm^{-1} region.

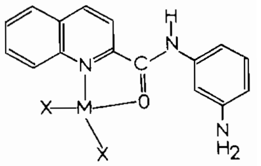
Conclusion

From the overall study presented a variety of stereochemistries is assigned for the complexes prepared. Full details about the various coordinating behaviours of *o*-LH, *o*-L$^-$ and *m*-LH and the stereochemistries of their complexes are given in Table V. Some of the proposed structural formulae are **III**, **IV**, **V**, **VI** and **VII**; for **V** only the structural type with *o*-LH is shown.

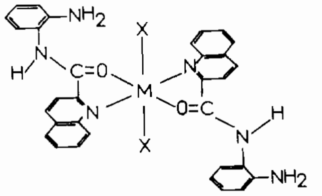
It has been shown [43] that free peptide or amide groups are invariably planar due to resonance stabilization. The coordination of a non-deprotonated amide nitrogen atom would cause loss of this stability with a change to tetrahedral geometry. Hence O-coordination is more favoured for the non-deprotonated complexes and, in fact, the neutral amide group of the ligands is coordinated to the metal ions through oxygen.



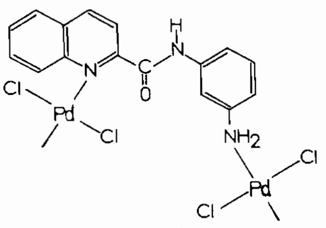
III (X = Cl, Br)



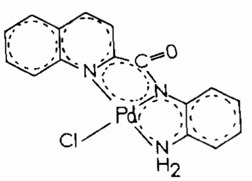
IV (M = Co, Cu, Zn; X = Cl, Br, NCS)



V (M = Co, Ni; X = Cl, Br, NCS)



VI (**26**)



VII (**13**)

Coordination of the neutral secondary amide group is not observed for Zn(*m*-LH)$_2$Cl$_2$, Pd(*m*-LH)Cl$_2$·0.5H$_2$O and both platinum(II) complexes.

This behaviour was expected for the platinum(II) complexes, but it was quite unexpected for $Zn(m\text{-}LH)_2Cl_2$. The palladium(II) chloride complex of *m*-LH, apart from being non-deprotonated while the analogous complex with *N*-(3-aminophenyl)pyridine-2′-carboxamide [9] is deprotonated, shows some significant differences from the other non-deprotonated complexes. It forms immediately from a water–ethanol solution yielding medium pale brown crystals which are stable on storage. It has a very poor X-ray pattern. The IR spectrum of the compound is quite unusual, showing an uncoordinated amide group and coordinated N_{ring} and $-NH_2$ atoms. The immediate formation of crystals and the poor X-ray spectrum suggest that the species is polymeric. These observations, plus the identification of one $\nu(Pd-Cl)_t$ band in the far-IR region, suggest the structure shown in **VI**, where *m*-LH bonds through the nitrogen atoms alone in a polymeric *trans* bidentate function. Molecular models show that such a complex could form readily with no large steric strain.

In general, *o*-LH shows bidentate chelated N_{ring}, O_{amide}-behaviour. *m*-LH acts as a $-NH_2$ monodentate, N_{ring}, O_{amide} bidentate chelated, N_{ring}, $-NH_2$ bidentate bridging and N_{ring}, O_{amide}, $-NH_2$ tridentate bridging ligand, depending on the metal ion, the anionic ligands and the preparative conditions. Thus *m*-LH appears to be a very versatile ligand. The *m*-position of the $-NH_2$ group favours the bridging coordination of this group. This form of coordination produces the oligomeric or polymeric compounds **20**, **21**, **22** and **26**, allowing a considerable amount of hydrogen bonding and accounting for the lower solubilities and poorer X-ray powder patterns observed for these complexes.

On complexing with Pd(II) and Cu(II), the amide proton of *o*-LH becomes extremely labile, all three deprotonated complexes precipitating at pH values, near to 7. In particular Pd(*o*-L)Cl forms even under acidic conditions. This observation is in agreement with previous works [9, 10, 13, 15, 16, 18, 32] describing the high thermodynamic stability of the $Pd(II)-N_{amide}$ bond and the promotion of amide deprotonation by this metal ion. The deprotonated amide-nitrogen is a strong field ligand favouring planar coordination [18]. This is exemplified in the diamagnetic square planar complex Pd(*o*-L)Cl (**VII**) and in the tetragonally distorted copper(II) complexes **9** and **10**; that planar copper(II) complexes do not form is due to the steric requirements of the ligand. Palladium(II) has been shown to maintain a planar configuration even at the expense of considerable steric effects in the ligands [13]. Deprotonation leads to systems having a considerable degree of delocalization. The iminol form of coordination [33, 44], which seems to be an intermediate for deprotonated N-coordination of the amide bond, was not observed in the complexes studied.

Since the discovery of metal ion induced amide-(peptide) deprotonation reactions [45], several studies have led to the conclusion that only Pd(II), Cu(II), Ni(II), Co(II) and Zn(II) are usually capable of promoting these reactions. The promotion of amide hydrogen ionization [1] increases in the series $Zn(II) \simeq Co(II) < Ni(II) < Cu(II) < Pd(II)$; only the last three ions promote the deprotonation at $pH \leqslant 7$. It is worth noting that throughout most of the pH range, in the absence of metal ions, the amide group is neutral [1]. The ligand *o*-LH was thought to present one of the most favourable cases for metal-ion promoted amide hydrogen deprotonation like *N*-(2-aminophenyl)pyridine-2′-carboxamide [9–12]. The presence of two strong anchoring [1] groups (quinoline *N*-atom and aromatic $-NH_2$ group), capable of forming two stable 5-membered chelate rings per $o\text{-}L^-$ with the amide nitrogen, would reduce the importance of metal ions' hydrolysis and bring out metal ions' full binding capabilities favouring deprotonation. In addition the planarity of the amide group is maintained in the deprotonated trigonal amide nitrogen. Unexpectedly only three deprotonated complexes were prepared. Ni(II) and Zn(II) do not promote amide deprotonation on coordination with *o*-LH; also *o*-LH does not undergo a cobalt(III) ion promoted amide hydrogen ionization in the pH region 4–6. Both of these phenomena were observed in the case of *N*-(2-aminophenyl)pyridine-2′-carboxamide [9–12]. A comparison of the coordinating ability of *o*-LH with its pyridine analogue demonstrates the effect of the presence of the quinoline ring. Because of steric requirements and electronic reasons (delocalization is not easy with the quinoline part of the ligand) the deprotonating ability of *o*-LH is poor.

Acknowledgements

Some of the spectroscopic material of this work was obtained by S.P.P. at Donnan Laboratories in the University of Liverpool, U.K.; we wish to thank Dr. David Nicholls for this convenience. One of us (V.L.) wishes to thank the Research Committee of the University of Ioannina for a postgraduate research award.

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