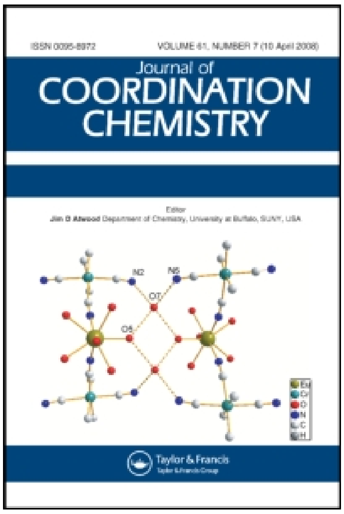

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DEPROTONATED AND NON-DEPROTONATED COMPLEXES OF *N*-(2-AMINOPHENYL) PYRIDINE-2-CARBOXAMIDE AND *N*-(3-AMINOPHENYL) PYRIDINE-2-CARBOXAMIDE WITH Co(II), Ni(II), Cu(II) AND Pd(II)

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DEPROTONATED AND NON-DEPROTONATED COMPLEXES OF *N*-(2-AMINOPHENYL) PYRIDINE-2-CARBOXAMIDE AND *N*-(3-AMINOPHENYL) PYRIDINE-2-CARBOXAMIDE WITH Co(II), Ni(II), Cu(II) AND Pd(II)

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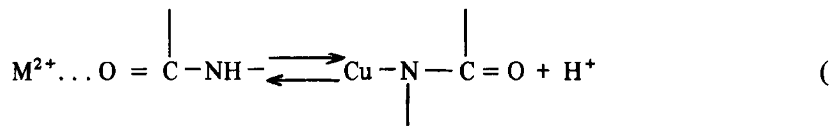
New deprotonated and non-deprotonated chelates of *N*-(2-aminophenyl)pyridine-2-carboxamide and *N*-(3-amino phenyl)pyridine-2-carboxamide with Co(II), Ni(II), Cu(II) and Pd(II) have been prepared. Properties, molar conductance measurement, magnetic moment and spectral (IR and visible) data are discussed in terms of possible structural types and the nature of the bonding. The metal ions used promote amide deprotonation on coordination with *N*-(2-aminophenyl)pyridine-2-carboxamide; only Pd(II) causes the same effect with *N*-(3-aminophenyl)pyridine-2-carboxamide. The neutral amide group is coordinated to the metal ions through oxygen, while an *N*(amide)-coordination is assigned for the deprotonated complexes.

INTRODUCTION

The binding of metal ions to amide groups has been a subject of increasing interest over the past two decades, largely because many of these reactions provide simple models for much more complex metal-peptide systems and enzymes.

It is now generally accepted[1] that for neutral amide groups both protonation and metal ion coordination occur at the amide oxygen. Metal ion coordination takes place at the amide nitrogen only upon substitution for an amide hydrogen. Since the discovery of metal ion induced amide (peptide) linkage deprotonation reactions[2] (Eqn. *1*), several studies have led to the conclusion that only Co(II), Ni(II), Cu(II) and Pd(II) are capable of inducing amide deprotonation reactions. The promotion of amide hydrogen ionization increases in the series Co(II) < Ni(II) < Cu(II) < Pd(II). The last three ions usually promote the deprotonation at $\mathrm{pH} \leqslant 7$. These ionizations are often accompanied by concomitant stereochemical changes about the metal ion; *e.g.*, the Ni(II) complex of triglycine undergoes a change from octahedral to square planar geometry upon amide proton ionization.[3]



$$M^{2+}\ldots O = C{-}NH{-} \rightleftarrows Cu{-}N{-}C = O + H^{+} \qquad (1)$$

The very recent discovery of the first case of amide deprotonation induced by Zn(II)[4] is important in that previous arguments that amide and presumably other deprotonation reactions are a result of large increases in ligand field stabilization energies due to increased σ-donor strengths of the ionized groups are apparently spurious; the d^{10} system

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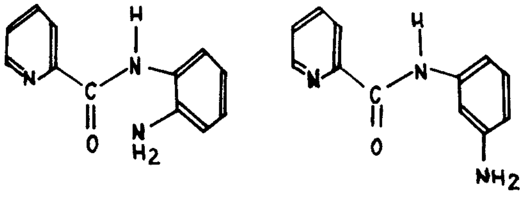
of Zn(II) can not attain increased ligand field stabilization. Such a stabilization, however, does provide an extra driving force which allows Cu(II), Ni(II) and Pd(II) to deprotonate amide groups below pH 7, in contrast to Co(II) and Zn(II) which promote the same reactions only at high pH.

Many studies have been made on cationic and non-ionic complexes of bivalent metal ions with *N*-substituted picolinamides containing one[5-8] or two[8-16] amide groups per ligand. In our continuing studies of metal-amide interactions[9,11,17-19] we now report the most important features of the coordination chemistry of *N*-(2-aminophenyl)pyridine-2-carboxamide and *N*-(3-aminophenyl)pyridine-2-carboxamide (Fig. 1), abbreviated as NopyH and NmpyH respectively. Analogous compounds with biological activity were previously reported.[20] The ligand NopyH was prepared for the first time, whereas the synthesis of NmpyH has been acheived earlier by an alternative method[21] to that described in this work. The two ligands have interesting ligating properties because they have three donor groups and the protons on the amide *N*-atoms can be removed and deprotonated chelates prepared. We were also interested in studying the possibility of amide hydrogen ionization promoted by Co(II), Ni(II), Cu(II) and Pd(II).

EXPERIMENTAL

All the chemicals used were of high purity. The solvents were purchased from Fluka and Ferak and were dried and purified using standard methods. Microanalyses were carried out by the microanalytical laboratory of the National Hellenic Research Foundation in Athens, and by the Organic Chemistry Department of the University of Thessaloniki. Melting points and decomposition temperatures were determined on a Buchi 510 apparatus and are uncorrected. The percentage of the water was determined thermogravimetrically. Conductance measurements were carried out at 25° using a Metrohm Herisau E-527, conductance bridge. Magnetic susceptibilities in the solid state were measured at room temperature by the Faraday method using a Cahn-Ventron RM-2 balance; mercuric tetrathiocyanatocobaltate(II) was used as the susceptibility standard. The magnetic susceptibilities were corrected for diamagnetic ligand contributions. IR spectra, in the 4000–250 cm^{-1} region, were recorded on a Perkin Elmer 577 spectrophotometer, calibrated with polystyrene. The samples were used in the form of KBr pellets or hexachlorobutadiene mulls between CsI plates. Diffuse reflectance spectra were obtained with a Varian 634 spectrophotometer at room temperature; spectroscopic grade MgO was used in the reference beam. ^{1}H NMR spectra of the organic liqands were recorded on a Varian A-60A 60 MHz spectrophotometer in $CDCl_3$ with tetramethylsilane as internal standard. Mass spectra were obtained with a Hitachi-Perkin Elmer RMU 6L spectrophotometer. An Orion Research model 801A pH-meter was used to measure pH during the preparation of the complexes.



NopyH NmpyH

FIGURE 1 The ligands.

Ligand Syntheses

N-(2-nitrophenyl)pyridine-2-carboxamide(NonpyH) To a solution containing picolinic acid (1.33 g, 0.0108 mol) and triethylamine (1.09 g, 0.0108 mol) in anhydrous THF (8 cm^3) cooled at − 15°, ethyl chloroformate (1.17 g, 0.0108 mol) was added with stirring. A cold solution of *o*-nitroaniline (1.38 g, 0.01 mol) in THF (2 cm^3) was added after 4 min. After stirring at − 15° for 30 min and at room temperature for 3h, the reaction mixture was evaporated to dryness under reduced pressure. The residue was taken up in dichloromethane (30 cm^3) and the mixture obtained was dried over sodium sulphate and filtered. The dry clear solution was reduced to a small volume and upon addition of absolute ethanol a yellow solid was obtained. An analytical sample was recrystallized three times from absolute ethanol to give yellow needles after drying *in vacuo* over P_4O_{10}. [*Anal.*; Calcd. for $C_{12}H_9N_3O_3$: C, 59.25; H, 3.72; N, 17.27%. Found: C, 58.95; H, 3.60; N, 17.20%].

N-(2-aminophenyl)pyridine-2-carboxamide(NopyH) To a suspension of NonpyH (1.0 g, 0.041 mol) and 0.2 g of hydrogenation catalyst (10% Pd on activated carbon) in absolute ethanol (100 cm^3), pure hydrogen was admitted for 3h with vigorous constant stirring. The reaction product was separated from the catalyst by filtration and the resulting solution after volume reduction yielded a yellow-brown oil. This crystallized from an 1:5 dichloromethane-hexane mixture. An analytical sample was recrystallized from absolute ethanol and dried *in vacuo* over P_4O_{10} to yield bright yellow crystals. [*Anal.*, Calcd. for $C_{12}H_{11}N_3O$: C, 67.69; H, 5.20; N, 19.71%. Found: C, 67.50; H, 5.10; N, 19.50%].

N-(3-nitrophenyl)pyridine-2-carboxamide(NmnpyH) and [N-(3-aminophenyl)pyridine-2-carboxamide(NmpyH) Using *m*-nitroaniline as a starting material quite similar isolation procedures, as outlined above for NonpyH and NopyH, gave white-yellow and yellow crystals of NmnpyH and NmpyH respectively. [*Anal.*, Calcd. for $C_{12}H_9N_3O_3$: C, 59.25; H, 3.72; N, 17.27%. Found: C, 59.32; H, 3.70; N, 17.21%; Calcd. for $C_{12}H_{11}N_3O$: C, 67.59; H, 5.20; N, 19.71%. Found: C, 67.70; H, 5.15; N, 19.80%].

Preparation of the Complexes

For the preparation of the complexes two general procedures were used, either mixing ethanolic solutions (90% ethanol) of ligands with ethanolic solutions of metal halides (method A), or mixing ethanolic solutions of ligands with aqueous solutions of metal halides (method B). The reaction solution for $Ni(Nopy)_2 \cdot 3H_2O$ was adjusted to pH 6.5 by dropwise addition of an equimolecular amount of ethanolic sodium hydroxide. For all other systems the pH reported in Table II was obtained by mixing the appropriate solutions without the addition of sodium hydroxide. Further increase of pH caused the precipitation of either hydroxides or solids of uncertain composition. Solid product formation at room temperature was usually instantaneous, although precipitation of Ni(Nopy)Br and $Ni(NopyH)_2Br_2 \cdot 5H_2O$ occurred slowly over 12-24h. All precipitates were collected by filtration after several hours stirring and standing. The complexes of Co(II), Ni(II) and Cu(II) were washed with aceton and ether and dried over $CaCl_2$; the Pd(II) compounds were washed with a minimum of warm water and ethanol and dried in the same way.

In the case of Cu(II) and Pd(II) with both ligands, attempts to prepare the 2:1 complexes using a molar ratio ligand: MX_2 = 2:1 met with failure; the 1:1 complexes were again isolated. It is worth noting that efforts to isolate a Co(II)-NopyH complex by following the preceding methods, were also made. Evidence was obtained for a Co(NopyH)(Nopy)Br•$3H_2O$ species, but because this compound was of uncertain nature it is not reported here; work on this system is under further investigation.

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

RESULTS AND DISCUSSION

General

Physical and spectroscopic data for the prepared organic compounds are given in Table I. Preparative, analytical and some physicochemical data of the new complexes are presented in Table II.

On complexing with Pd(II), Cu(II) and Ni(II), the amide proton of NopyH becomes extremely labile, all deprotonated complexes forming at pH values below 7. The results obtained indicate that Pd(II) is the most effective metal ion for inducing amide hydrogen ionization. We found that the ionization of the amide hydrogen atom and precipitation of the complexes occurs at pH 3.5–4.0 with Pd(II) complexation, whereas the corresponding reactions with Cu(II) occur at pH 4.5-5.0 and with Ni(II) at pH 6. This observation is in agreement with previous work[22,23] describing the relatively high thermodynamic stability of the Pd–N(amide) bond and the promotion of amide deprotonation by Pd(II). Generally the pK_a value for Pd(II)-induced deprotonation of the amide hydrogen atom in peptides is about 3.5; this value is approximately 2, 5 and 7 pK_a units less than for the respective Cu(II)-, Ni(II)- and Co(II)- promoted peptide hydrogen ionizations.[24] Except for compound **16**, all complexes of NmpyH are not deprotonated.

The prepared complexes are crystalline and stable under normal laboratory conditions over a long period. They are insoluble in nonpolar solvents, alcohols, acetone and CH_3NO_2, soluble in DMF and DMSO (except **16**) and decomposed by dilute mineral acids. The high temperature loss of H_2O in **7**, **9** and **10** in connection with the relatively low decomposition temperature may indicate that some of the water molecules are coordinated. However, a report by Nuttall and Stalker[25] concluded that the temperature of water elimination does not reliably differentiate between the types of water present in metal complexes; thus water elimination above 200° is not *a priori* indicative of coordinated water.[25] From the conductance measurements it is concluded that **1**, **4**, **5** and **13** are non-electrolytes in DMF or DMSO.[26] The other complexes were found to have appreciable conductivities. It must be pointed that for the calculation of the Λ_M values in Table II the compounds were assumed to be monomeric and DMF and DMSO have strong donor capacities, which frequently lead to displacement of anionic ligands and change of the electrolyte type. Thus the molar conductance data are somewhat difficult to interpret.

IR Spectral Studies

Table III gives some characteristic IR bands of the compounds prepared. In general, the spectra are very complex, but a careful study can lead to fairly important structural conclusions.

In the ν(O – H) region the spectra of **4**, **6**, **11-16** exhibit a medium, very broad, continuous absorption covering the whole 3600-3100 cm^{-1} region and this is attributable to the presence of exclusively lattice water.[27] **7**, **9** and **10** also exhibit a strong maximum at 3440-3395 cm^{-1} on top of the weaker extremely broad absorption mentioned above.

TABLE I
Preparative, physical and spectroscopic data for the prepared amides

Compound	Yield(%)	R_f^a	MP(°)	IR^b (cm^{-1})	NMR (ppm)	Mass spectrum^c (m/e, parent)
NonpyH	40	0.66	167	3290m, 2920w, 2850w, 1695s, 1610s, 1584s 1500s, 1450m, 1425s, 1342s, 1310w, 1295w 1272m, 1240w, 742s, 682m, 620w, 595w 530w, 400w, 340w	2.3 mt 1.2 mt	243 (243.22)
NopyH	90	0.17	94	3410m, 3340m, 3310m, 3270w, 3240w, 1680vs 1650m, 1600s, 1575w, 1535s, 1500w, 1465s 1440m, 1290m, 1238w, 745s, 720w, 700w 688w, 650m, 620m, 600w, 545w, 475w, 450w 430w, 405m, 330w	5.9 ss 2.9 mt 1.8 mt	213 (213.24)
NmnpyH	70	0.43	170	3320m, 3130w, 1691s, 1622m, 1593m, 1535s 1440w, 1429m, 1359s, 1290m, 1271w, 1121w 997m, 877m, 818m, 808m, 791m, 741m, 730s 672s, 617m, 581w, 467w, 438w	2.5 mt 1.8 mt	243 (243.22)
NmpyH	80	0.15	135	3425s, 3345s, 3320s, 3240m, 1689vs, 1640s 1600s, 1549s, 1465s, 1440m, 1332m, 1310w 1294m, 1241m, 1170m, 875s, 810s, 775s, 745w 730m, 685s, 620w, 600m, 590m, 530w, 455w 402m, 330w	6.6 ss 3.1 mt 1.9 mt	213 (213.24)

[a] The purity of the compounds was checked by TLC in a 4:1 chloroforme-hexane system giving one spot.

[b] The most characteristic features.

[c] Calculated formula weights in parentheses.

Abbreviations: s=strong, m=medium, w=weak, ss=singlet and sharp, mt=multiplet, v=very.

TABLE II
Preparative data, analytical results and some physicochemical features of the new complexes

	Complex	Method of preparation	pH of precipitation	Yield^a (%)	Ligand: salt	Analyses^b (%)					Colour	Λ_M^c(S cm^2 mol^{-1})	Effect of heat(°)	
						C	H	N	M	X			Loss of water^g	Decomp. temp.
1	Cu(Nopy)Cl	A	4.5–5.0	72	1:1, 2:1	46.34 (46.31)	2.99 (3.21)	13.49 (13.50)	20.57 (20.42)	11.30 (11.39)	dark green	6^d 4^f		210
2	Cu(Nopy)Br	B	4.5–5.0	71	1:1, 2:1	40.50 (40.52)	2.67 (2.83)	11.62 (11.81)	17.90 (17.87)	22.42 (22.47)	light green	20^f		240
3	Ni(Nopy)Br	B	5.5–6.0	35	1:1	40.88 (41.08)	2.90 (2.87)	11.69 (11.98)	16.70 (16.73)	23.00 (22.78)	red-brown	74^d		160
4	Ni(Nopy)$_2$·3H$_2$O	B	6.5	40	2:1	53.50 (53.66)	4.42 (4.88)	15.60 (15.64)	11.30 (10.93)		yellow-green	5^f	80–160	220
5	Pd(Nopy)Cl	B	3.5–4.0	53	1:1, 2:1	40.37 (40.71)	2.83 (2.85)	11.50 (11.87)	30.11 (30.05)	10.01 (10.00)	yellow-green	3^d		260
6	Ni(NopyH)$_2$Br$_2$·5H$_2$O	B	5.0	44	2:1	39.30 (39.22)	4.64 (4.39)	11.63 (11.43)	7.96 (7.99)	21.64 (21.74)	yellow-green	142^d	60–160	160
7	Cu(NmpyH)Cl$_2$·2H$_2$O	A	6.0–6.5	80	1:1, 2:1	38.01 (37.56)	3.47 (3.94)	10.95 (11.00)	16.60 (16.56)	18.46 (18.48)	khaki	245^e	60–200	80
8	Cu(NmpyH)Br$_2$·H$_2$O	A	6.0–6.5	78	1:1, 2:1	31.52 (31.70)	2.82 (2.88)	9.01 (9.24)	14.00 (13.98)	35.00 (35.15)	khaki	48^d	100–200	240
9	Ni(NmpyH)Cl$_2$·5H$_2$O	A	6.0–6.5	95	1:1	35.30 (35.29)	4.49 (4.89)	9.80 (9.71)	13.60 (13.56)	16.95 (16.38)	light green	131^d	60–310	100
10	Ni(NmpyH)Br$_2$·5H$_2$O	B	6.0–6.5	81	1:1	27.50 (27.62)	3.61 (4.06)	8.25 (8.05)	11.28 (11.25)	30.50 (30.62)	light green	131^d	60–250	200
11	Ni(NmpyH)$_2$Cl$_2$·H$_2$O	A	6.0–6.5	71	2:1	49.88 (50.21)	4.12 (4.21)	14.24 (14.64)	10.24 (10.23)	12.28 (12.35)	green	58^f	80–120	200
12	Ni(NmpyH)$_2$Br$_2$·4H$_2$O	B	6.0–6.5	62	2:1	40.19 (40.20)	3.99 (4.22)	11.95 (11.72)	8.20 (8.19)	22.20 (22.20)	green	66^f	60–180	250
13	Co(NmpyH)Cl$_2$·2H$_2$O	A	6.0–6.5	80	1:1	38.11 (38.02)	3.99 (3.99)	11.05 (11.08)	15.43 (15.55)	18.62 (18.70)	emerald	33^d	60–150	160
14	Co(NmpyH)$_2$Br$_2$·3H$_2$O	B	6.0–6.5	61	2:1	40.70 (41.22)	4.37 (4.04)	12.00 (12.02)	8.50 (8.43)	22.80 (22.87)	pale green	121^d	50–130	210
15	Co$_2$(NmpyH)$_3$Cl$_4$·3H$_2$O	A	6.0–6.5	68	2:1	45.01 (45.35)	3.99 (4.12)	13.66 (13.22)	12.50 (12.36)	14.48 (14.87)	emerald	57^d	40–140	190
16	Pd(Nmpy)Cl·3.5H$_2$O	B	3.5–4.0	66	1:1, 2:1	34.60 (34.55)	4.02 (4.11)	9.98 (10.07)	25.93 (25.51)	8.46 (8.50)	light yellow	insoluble	80–150	310

[a] Based on the metal.

[b] Calculated values in parentheses.

[c] Values of molar conductance for *ca* 10^{-3} M solutions at 25°.

[d] In DMF.

[e] In water.

[f] In DMSO.

[g] Found thermogravimetrically.

This is due to the simultaneous presence of water molecules as ligands.[27] The complex 8 seems to contain only coordinated water. The rocking, wagging and metal-oxygen stretching modes of coordinated water are seen in the 900-350 cm^{-1} region, together with other absorptions. On dehydration of the complexes containing lattice water the very broad band is not observed, with the other main features of the spectra remaining unchanged from those of the hydrated forms.

Assignment of $-NH_2$ and amide bands for the ligands was assisted by deuterium isotopic substitution, which highlights any absorption associated with the N – H bonds. As would be expected the N(amide) – H stretching band is absent in the deprotonated complexes. The small shift of this band in the spectra of the non-deprotonated chelates indicates that the amide – N atom is not involved in coordination; the *ca* 60 cm^{-1} shift of $\nu(N-H)_{amide}$ to lower frequencies in **7**, **9**, **10** and **14** could be due to stronger hydrogen bonding to the halide ions or oxygen atoms by the amidic hydrogen compared to hydrogen bonding in pure NmpyH. The 3600-3000 cm^{-1} region of the spectrum is somewhat difficult to interpret for the hydrated compounds due to the broad bands associated with the O – H stretch. The $\nu_{as}(N-H)$ and $\nu_s(N-H)$ modes of the aromatic $-NH_2$ group in the spectra of NopyH and NmpyH are assigned to the strong and sharp absorptions at 3410, 3340 and 3420, 3345 cm^{-1}, respectively. In the deuterated ligands they are shown at *ca* 2550 and 2460 cm^{-1} ($\nu(N-H)/\nu(N-D) = 1.34$-1.36). The relatively low frequencies of these motions may indicate the existence of intramolecular hydrogen bonding. In the spectra of **1-10**, **13** and **15** these bands shift to lower frequencies by more than 100 cm^{-1}; this large shift is explained by the weakening of the N – H bonds, resulting from the electron drainage from the nitrogen atom on account of its coordination to metal ions.[28] The spectra of **11**, **12** and **14** are indicative of both coordinated and uncoordinated $-NH_2$ groups, while for **16** a weak Pd – N(amine) bond is suggested.

The amide I band consists mainly of $\nu(C=O)$[29] and the amide II and III bands in secondary amides arise from $\nu(C-N)$ as well as from $\delta(N-H)$ modes, although the latter two modes are coupled to one another.[29] For a neutral secondary amide group coordinated through the oxygen atom, the amide I band will shift to a lower frequency and the amide II and III bands to higher frequencies; these facts may be explained by the decrease of the double bond character of C = O and the subsequent increase of the C – N double bond character.[5,16] On the other hand, if the non-deprotonated amide – N atom coordinates, the amide I, II and III bands should shift in the opposite directions. On coordination *via* the deprotonated amide – N atom the amide I band shifts to lower frequencies, while the amide II band undergoes a sizable shift to lower frequencies.[14] This might be expected since on removal of the amide proton the band reflects a pure C – N stretch. Differences in the spectra of our deprotonated and non-deprotonated complexes are readily noticeable. The data for the non-deprotonated complexes reveal that the amide I, II and III bands shift towards the region expected for amide oxygen coordination, while the spectra of **1-5** and **16** are indicative of coordination *via* the deprotonated N-atom. As has been shown previously for chelates of secondary amides[10,12] the presence of both coordinated and uncoordinated amide groups in a complex is easily detected by the considerably more complicated IR spectrum obtained. The observation of only one sharp absorption for each amide I and II band in the spectra of 2:1 and 3:2 complexes indicates that all amide groups are coordinated.

All complexes exhibit a sharp maximum in the 1610-1590 cm^{-1} region attributable to the coupled stretching modes of the pyridyl C – C and C – N bonds, which have been shown[30] to give rise to small frequency shifts and a marked intensity increase on coordination of the pyridyl – N atom. The in-plane and out-of-plane deformation bands of the pyridine ring occur at *ca* 620 and 405 cm^{-1}, respectively, for the free ligands. For **1-15** the δ(Py) modes shift to higher frequencies to indicate coordination of the pyridyl

TABLE III

IR spectral assignments[a] of diagnostic bands in the 4000–250 cm^{-1} region

Compound	$\nu(O-H)$	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(N-H)_{amide}$	Amide absorptions			$\delta(Py)^c$	$\delta(Py)^d$
					I	II	III		
NopyH		3410s	3340s	3310m	1680vs	1535s	1290m, 1238w	620m	405w
1		3285m	3220m	n.o.	1639s	1400vs	1295w, 1251w	648m	415sh
2		3280m	3223m	n.o.	1638s	1396vs	1294w, 1250w	649m	415sh
3[e]		3180mb	3120w	n.o.	1632m	1403s	1270w	653w	420w
4	3620-3150 mvb	3250s	3208m		1620sh	1386vs	1291m, 1270w	639m	420w
5[f]		3225s	3180m	n.o.	1649s	1381vs	1271w	641m	420sh
6	3500-3150 mvb	3210s	n.a.	3320m	1632s	1548m	1309m, 1270m	640m	438m
NmpyH		3420s	3345s	3320s	1689vs	1549s	1294m, 1241m	620m	402m
7	3550-3050 mvb	3220m	3143m	3260m	1632s	1578m	1312w, 1269m	647m	439w
	3440s								
8	3465m	3220s	3130s	3282m	1641m	1572m	1322w, 1267m	646m	450mb
9	3600-3000 mvb	3250[b]vsb	3160s	3250[b]vsb	1644s	1572vs	1311m, 1270s	642m	441w
	3405s								
10	3600-3000 mvb	3250[b]vsb	3155s	3250[b]vsb	1645s	1572vs	1310w, 1269m	641m	440w
	3395s								
11	3550-3050 mvb	3415s	3345sh	n.a.	1635vs	1574s	1311w, 1270m	642m	441w
		3228s	3115s						
12	3550-3050 mvb	3405s	3340m	n.a.	1638vs	1576vs	1312w, 1270m	646m	443m
		3238s	3125s						
13[g]	3600-3100 mvb	3280[b]sb	3155m	3280[b]sb	1635s	1565s	1311w, 1271m	641m	440m
14	3500-3050 mvb	3420m	3340m	3260sh	1630vs	1570s	1313w, 1269m	640m	439m
		3220s	3105s						
15	3550-3050 mvb	3230s	3110s	3340m	1638vs	1572vs	1315w, 1270m	640m	440w
16	3550-3150wvb	3320m	3270m		1623s	1382s	1293w, 1269w	620w	n.a.

[a] From refs. 5, 8, 10–14, 16, 27–29 and 31. The assignments for the amide ligands were assisted by deuterium substitutions.

[b] Overlapping.

[c] In-plane pyridine ring deformation.

[d] Out-of-plane ring deformation.

[e] $\nu(Ni-Br)_t$ at 315 cm^{-1} (m).

[f] $\nu(Pd-Cl)_t$ at 348 cm^{-1} (s).

[g] $\nu(Co-Cl)_t$ at 277 cm^{-1} (s). Abbreviations: n.a.=not assigned, n.o.=not observed, ν_{as}=antisymmetric stretching, ν_s=symmetric stretching, t=terminal, s=strong, m=medium, w=weak, sh=shoulder, b=broad, v=very.

– N atom.[31] In the spectrum of **16** the characteristic bands of coordinated pyridine ring are absent.

The region of the free ligands' spectra between 550 and 250 cm^{-1} has several weak absorption bands. This would indicate that other bands observed in this region in the spectra of the complexes could be assignable to metal-ligand stretching frequencies. However, a comparison of the far-IR spectra of NopyH, NmpyH and their metal complexes fails to give clear cut assignments since other ligand vibrations, activated by complex formation, may appear in the same spectral region. Of the several bands observed in the far-IR spectra, some may be assinged to M – O(water), M – N(amide), M – N(amine), M – N(ring) and terminal M – X stretching vibrations. A strong and sharp peak at 348 cm^{-1} in **5**, which does not appear in the spectrum of NopyH, is assigned to a Pd – Cl stretching mode.[13]

Magnetic Moments and Electronic Spectra

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

The relative energies of the 4d orbitals in tetragonal Pd(II) are difficult to determine because they are closely spaced and because electron-transfer transitions interfere at short wavelengths. A likely order of inreasing energies for the 4d orbitals of Pd(II) in our systems is $z^2 < xz \sim yz < xy < x^2\text{-}y^2$.[24] In the D_{4h} group the above ordering is described by the representations $a_{1g} < e_g < b_{2g} < b_{1g}$. In d^8 Pd(II) the three spin-allowed one-electron d-d transitions in order of increasing energies are $b_{2g} \longrightarrow b_{1g}$, $e_g \longrightarrow b_{1g}$ and $a_{1g} \longrightarrow b_{1g}$; of these three transitions only the highest energy one is magnetic dipole forbidden to the extent that D_{4h} microsymmetry is maintained.[24] Application of the above ordering in our spectra does not lead to clear assignments.

Of the Cu(II) compounds only **7** has a normal magnetic moment; the subnormal moments of **1**, **2** and **8** indicate dimeric or polymeric structures.[32] The electronic spectra of **1** and **2** are fairly typical of octahedral complexes with a medium to small tetragonal distortion.[33] The khaki colours of **7** and **8** were rather surprising. The shift of the d-d manifold to longer wavelengths allows the charge-transfer bands to dominate the colour. The relatively low energies of the d-d electronic absorptions of these complexes would indicate a distorted tetrahedral or five-coordinate trigonal bipyramidal structure as the most likely configuration.[33,34]

The magnetic moments of **6**, **9**, **11** and **12** are consistent with an octahedral arrangement of ligands around Ni(II),[35] while those of **4** and **10** are slightly higher than usual for this metal ion; several low symmetry six-coordinated Ni(II) complexes exhibit μ_{eff} values exceeding 3.30 B.M.[36] The diffuse reflectance spectra are indicative of octahedral[37] (**6**, **9**, **11**, **12**) or tetragonally distorted octahedral[38] (**4**, **10**) structures. Ni(Nopy)Br has unusual magnetic and spectral properties. The magnetic moment found (1.07 B.M.) corresponds very well to the average of μ_{eff} for two low-spin and one high-spin Ni(II) atoms per molecular unit. It seems likely that the diamagnetic subunits are of square planar stereochemistry and that the paramagnetic one is octahedral. This is further supported by the electronic spectrum in the solid state. The maximum at 12.66 kK is assigned to the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition in O_h symmetry. The shoulder at 18.52 kK suggests square-planar coordinated Ni(II).[39] Planar complexes of Ni(II) are invariably diamagnetic. They are frequently red, yellow or brown owing to the presence of an absorption band of medium intensity in the range 16.60-22.20 kK.[39] It is proposed that such a value for the moment and the spectral data arise from the coexistence[35] of both paramagnetic octahedral and diamagnetic square planar nickel atoms in the solid; a trimeric structure with one octahedrally and two planar coordinated Ni(II) atoms is very probable.

TABLE IV
Magnetic moments[a] and diffuse reflectance[a] (11.50–31.00 kK) spectral data

Complex	μ_{eff}(B.M.)	Band positions[b] and assignments[c]	Comments[e]
5	dia	13.33 ? 15.27sh d–d 26.31sh d–d/charge transfer	square planar Pd(II)
16	dia	12.05 ? 15.62sh d–d 26.74sh d–d/charge transfer	square planar Pd(II)
1	1.36	15.87 $^2B_{1g} \longrightarrow {}^2E_g$ 26.74sh charge transfer	octahedral structure with medium tetragonal distortion (D_{4h} symmetry)
2	1.60	15.38 $^2E_g \longrightarrow {}^2T_{2g}$ 22.22sh charge transfer [Br(π) $\longrightarrow$ Cu(d)] 26.73sh charge transfer	octahedral structure with small tetragonal distortion
7	1.88	12.34 d–d 13.33sh d–d 24.39sh charge transfer	distorted tetrahedral or five-coordinate configuration
8	1.66	12.34 d–d 26.31 charge transfer	distorted tetrahedral or five-coordinate configuration
3	1.07	12.66 $^3A_{2g} \longrightarrow {}^3T_{2g}[O_h]$ 18.52 $^3A_{2g} \longrightarrow {}^3T_{1g}(F)[O_h]/{}^1A_{1g}(b_{1g}+b_{2g}) \longrightarrow {}^1A_{2g}$[square planar structure]	mixed structure containing low-spin square-coordinated and high-spin octahedrally coordinated nickel atoms
4	3.50	12.05 $^3B_{1g} \longrightarrow {}^3B_{2g}$ 23.04sh $^3B_{1g} \longrightarrow {}^3A_{2g}(F), {}^3E_g(F)$ 26.31sh $^3B_{1g} \longrightarrow {}^3A_{2g}(P)$/charge transfer	tetragonally distorted octahedral structure with a NiN_6 chromophore; the site symmetry was assumed to be D_{4h}; $D_q^{xy} = 1205$ cm^{-1}
6	2.93	11.90 $^3A_{2g} \longrightarrow {}^3T_{2g}[\nu_1]$ 17.24 $^3A_{2g} \longrightarrow {}^3T_{1g}(F)[\nu_2]$ 27.03sh $^3A_{2g} \longrightarrow {}^3T_{1g}(P)[\nu_3]$/charge transfer	octahedral configuration with $NiN_2O_2N_2$ chromophore; $D_q = 1120$ cm^{-1}, B = 711 cm^{-1}, $\beta = 0.67$
9	2.86	12.82 $^3A_{2g} \longrightarrow {}^3T_{2g}[\nu_1]$? 15.62sh $^3A_{2g} \longrightarrow {}^3T_{1g}(F)[\nu_2]$ 27.78sh $^3A_{2g} \longrightarrow {}^3T_{1g}(P)[\nu_3]$/charge transfer	octahedral coordination; $D_q = 940$ cm^{-1}, B = 1013 cm^{-1}, $\beta = 0.96$
10	3.55	12.75 $^3B_{1g} \longrightarrow {}^3B_{2g}$ 13.81 $^3B_{1g} \longrightarrow {}^3B_{2g}$ 15.38sh $^3B_{1g} \longrightarrow {}^3E_g(F), {}^3A_{2g}(F)$ 28.25sh $^3B_{1g} \longrightarrow {}^3A_{2g}(P), {}^3E_g(P)$/charge transfer	tetragonally distorted octahedral structure (D_{4h} site symmetry); $D_q^{xy} = 1328$ cm^{-1}

11	3.17	11.90	$^3A_{2g} \longrightarrow {}^3T_{2g}[\nu_1]$?	octahedral coordination; $D_q = 940\ cm^{-1}$, $B = 1013\ cm^{-1}$, $\beta = 0.96$
		15.62	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)[\nu_2]$	
		23.81sh	$^3A_{2g} \longrightarrow {}^3T_{2g}(D)$[spin-forbidden]	
		27.78sh	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)[\nu_3]$/charge transfer	
12	3.30	11.84	$^3A_{2g} \longrightarrow {}^3T_{2g}[\nu_1]$?	octahedral coordination; $D_q = 938\ cm^{-1}$, $B = 947\ cm^{-1}$, $\beta = 0.90$
		15.47	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)[\nu_2]$	
		23.25sh	$^3A_{2g} \longrightarrow {}^1T_{2g}(D)$[spin-forbidden]	
		26.88sh	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)[\nu_3]$/charge transfer	
13	1.87	11.76	?	low-spin octahedral; the true symmetry is lower than O_h because of the Jahn-Teller effect; for assignments it is assumed that the symmetry decreased to D_{4h}
		14.39	?	
		15.06	$^2A_{1g} \longrightarrow {}^2E_g$	
		15.87	$^2A_{1g} \longrightarrow {}^2B_{2g}$	
		16.23sh	$^2A_{1g} \longrightarrow {}^2A_{2g}$	
		27.78sh	charge transfer	
14	4.65	13.77	spin-forbidden	mixed structure containing high-spin tetrahedrally and octahedrally coordinated cobalt atoms
		14.28	$^4A_2 \longrightarrow {}^4T_1(P)[T_d]$	
		15.06	$^4A_2 \longrightarrow {}^4T_1(P)[T_d]$	
		15.62	$^4A_2 \longrightarrow {}^4T_1(P)[T_d]$	
		18.86	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)[O_h]$	
		26.59sh	charge transfer	
15	3.25[d]	14.37	d-d and spin-forbidden	octahedral environment (equilibrium between low-spin ^2E_g and high-spin $^4T_{1g}$ ground states) or mixed structure containing high-spin tetrahedral and low-spin octahedral units
		15.06	d-d and spin-forbidden	
		15.53sh	d-d and spin-forbidden	
		15.87	d-d and spin-forbidden	
		16.23sh	d-d and spin-forbidden	
		18.87sh	d-d and spin-forbidden	
		20.00sh	d-d and spin-forbidden	
		27.03sh	charge transfer	

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[a] At room temperature.

[b] All the spectra exhibit another maximum at *ca* 32 kK, which is attributed to the $n \rightarrow \pi^*$ electronic transition of the organic ligands.

[c] From refs. 24, 33, 34, 37–39, 42.

[d] Per Co(II) ion.

[e] The crystal field parameters for the octahedral Ni(II) complexes were calculated from the Underhill-Billing equations.[40] D_q^{xy} values for the tetragonally distorted octahedral complexes **4** and **10** were calculated from the equation cited in ref. 41. The parameters D_t and D_q^z were not calculated because the transition $^3B_{1g} \longrightarrow {}^3E_g^a$ (ref. 41) occurs below 11.50 kK (the low-frequency limit of the instrument used).

Both the magnetic and visible reflectance data indicate that **13** has a low-spin pseudo-octahedral configuration.[39,42] It follows from the Tanabe-Sugano diagram that strong ligand fields (10Dq > 15000 cm^{-1}) can cause a ^2E state, originating in the ^2G state of the free Co^{2+} ion, to become the ground state. The electronic configuration of the low-spin octahedral Co(II) complexes is $t_{2g}^6e_g^1$. In reality, the true symmetry of **13** would be lower than O_h because of the Jahn-Teller effect; if the symmetry decreases to D_{4h} there is additional removal of orbital degeneracy. The admixture of the $^2T_{2g}$ term with ^2E_g, owing to spin-orbit coupling, is responsible for the slight increase of the effective magnetic moment compared with the spin only value.[42] It should be noted that very few six-coordinate low-spin Co(II) complexes have been reported.[39] A square planar structure for **13** can be ruled out with certainty. Planar Co(II) chelates have magnetic moments in the region 2.2-2.7 B.M. at room temperature[39] and exhibit absorption maxima at different energies.[43] The μ_{eff} value of **14** is in the borderline between the tetrahedral and octahedral regions for Co(II),[35] while the electronic spectrum is typical for a coexistence of both pseudotetrahedral and high-spin octahedral units in the solid state. At room temperature compound **15** shows a magnetic moment (3.25 B.M.) between the two extreme values of $\mu_{eff} \simeq 5.0$ for a pure octahedral quartet ground state ($^4T_{1g}$) and $\mu_{eff} \simeq 2.0$ B.M. for a pure doublet ground state (^2E_g). Assuming a thermal equilibrium between the two spin states,[44,45] about 30% of the high-spin states should be occupied with electrons at room temperature. Various Co(II) complexes afford examples of the d^7 spin-crossover situation.[44-46] The possibility of spin equilibrium is under investigation at this laboratory, in parallel with the coordination chemistry of *o*-aminobenzylamine.[47] The value of μ_{eff} and the reflectance spectrum can also be interpreted on the basis of a mixed structure containing high-spin tetrahedral and low-spin octahedral units.[48] In fact, the magnetic

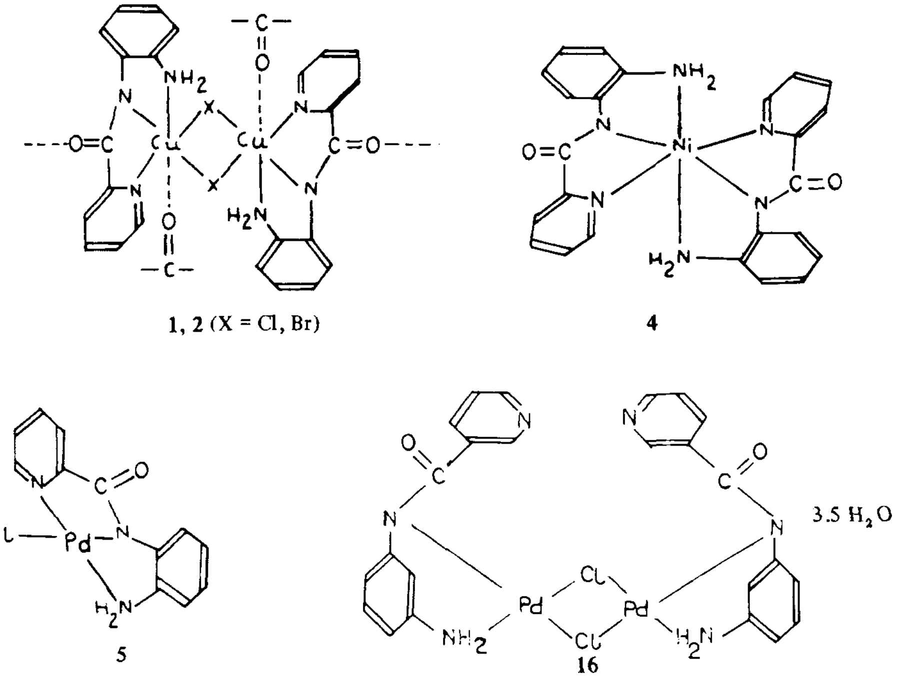
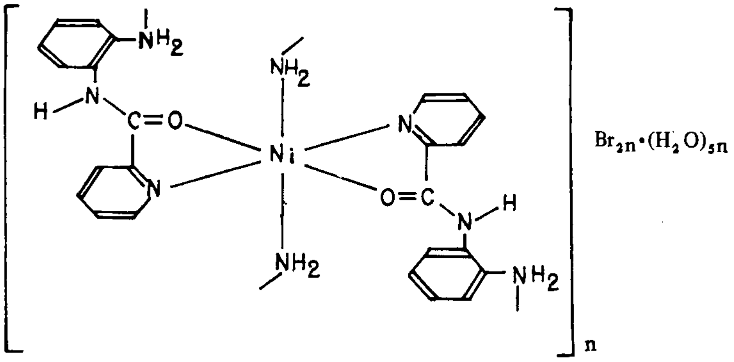


FIGURE 2 The most probable structural arrangements for complexes with deprotonated ligands (1-2, 4, 5, 16).



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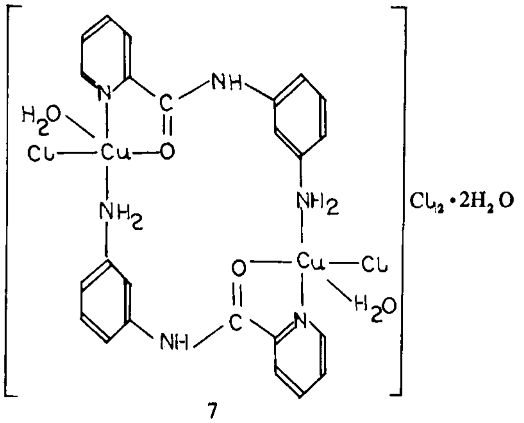

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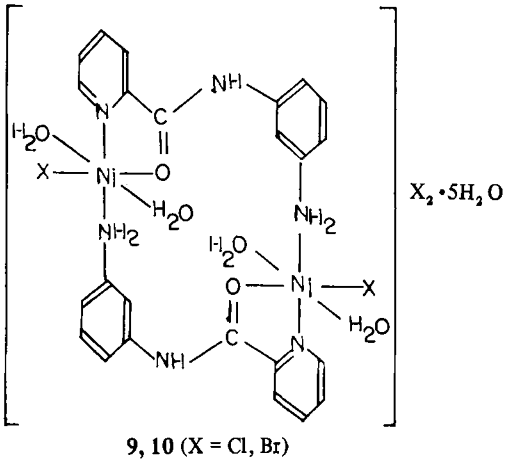

9, 10 (X = Cl, Br)

FIGURE 3 The most probable structural arrangements for complexes with non-deprotonated ligands (6, 7, 9–10).

moment corresponds well to the average of μ_{eff} for low-spin octahedrally (1.8-1.9 B.M.) and high-spin tetrahedrally (4.4-4.8 B.M.) coordinated Co(II) atoms, and the reflectance spectrum contains a large number of d-d bands.

CONCLUDING REMARKS

The most probable structural arrangements for some complexes of NopyH and NmpyH are given in Figures 2 and 3, respectively. For the other complexes several oligomeric or polymeric structural possibilities exist. In the absence of detailed structural studies the modes of coordination in **3**, **8**, **11**, **12**, **13**, **14** and **15** remain somewhat speculative; we are continually trying to obtain crystals suitable for X-ray analysis, but have not so far been successful. The *m*- position of the aromatic $-NH_2$ group in NmpyH was expected to produce dimeric or polymeric compounds allowing a considerable amount of hydrogen bonding. This would account for the lower solubility of these complexes.

The free acid amide groups have planar configurations with large resonance stabilization energy. Amide nitrogen coordination without deprotonation will change the sp^2 hybridization of the nitrogen atoms into an sp^3 hybridization with loss of the planar configuration and the stabilization energy, while amide oxygen coordination will require only the donation of the lone pair of the metal ion without change in hybridization and loss of the resonance energy.[49] Hence the latter is expected for the non-deprototonated complexes. An iminol type of coordination is ruled out in these complexes, because of the non-appearance of the $\nu(C = N)$ and $\nu(C - O)$ IR bands.[50] This type seems to be an intermediate for deprotonated nitrogen coordination.[51,52] On the other hand, the deprotonated amide nitrogen atom is a strong field ligand,[16] favoring planar coordination or tetrahedrally distorted octahedral structures. This is exemplified in the diamagnetic Pd(II) complexes, which are obviously square planar, and in **1**, **2**, **3** and **4**.

In conclusion, it should be pointed out that the systems studied in the present work are more complicated than the complexes of the *bis*-amide tetradentete ligand *N*, *N*'-(dipicolyl)-1,8-naphthylenediamine,[9-11] because this ligand lacks the flexibility of NopyH and NmpyH.

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