Studies on the Metal–Amide Bond.
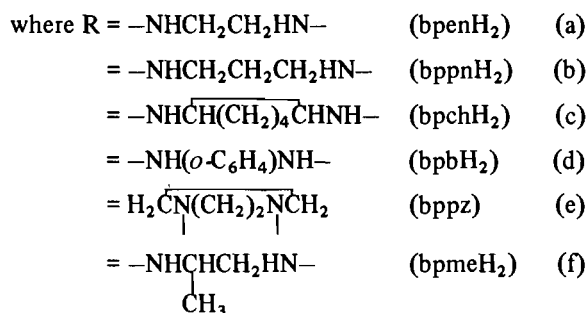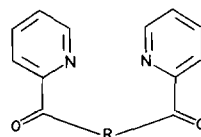# I. Metal Complexes of the Bis-amide Tetradentate Ligand N,N'-Bis(2'-pyridinecarboxamide)-1,2-benzene

ROSS L. CHAPMAN and ROBERT S. VAGG

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113, Australia

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Complexes of general formula $M(bpbH_2)Cl_2 \cdot nH_2O$, where $bpbH_2$ = N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene and M = Mn (n = 0), Co (n = 1), Co and Ni (n = 2) and Cu (n = 1.5) have been prepared. As well, the complexes $Ag(bpbH_2)(NO_3)$ and $Co(bpbH_2)(NCS)_2 \cdot 2.5H_2O$ were isolated. The copper and nickel complexes exhibit clear evidence of neutral amide-N coordination. Several of the metal ions used promote amide deprotonation on coordination, and a series of complexes of formula $M(bpb) \cdot H_2O$ (M = Co, Ni, Cu, Zn and Pd) are reported. A planar $M^{II}N_4$ system is proposed for these complexes. Stereochemistries for the complexes have been proposed utilising microanalyses, magnetic susceptibilities, thermogravimetric analyses and infrared and visible spectral data.

| where R = –NHCH₂CH₂HN– | (bpenH₂) | (a) |

where R = $-NHCH_2CH_2HN-$ (bpenH₂)   (a)

= $-NHCH_2CH_2CH_2HN-$ (bppnH₂)   (b)

= $-NHCH(CH_2)_4CHNH-$ (bpchH₂)   (c)

= $-NH(o\text{-}C_6H_4)NH-$ (bpbH₂)   (d)

= $H_2CN(CH_2)_2NCH_2$ (bppz)   (e)

= $-NHCHCH_2HN-$ (bpmeH₂)   (f)
        |
       CH₃

Introduction

It has been shown that deprotonated amide groups coordinate readily to metal ions through the amide-N atom, thus forming a stable delocalized electronic system [1–7]. Recently there has been some debate also over the coordination site of protonated amides [8]. Some authors have concluded that coordination of a protonated amide group occurs almost universally through the amide-O atom [8]. N-Substituted picolinamides have been found to coordinate to transition metal ions both as bidentate ligands (through ring-N and amide-O) for 1:2 complexes and as terdentate ligands in 1:1 complexes with coordination through the deprotonated amide-N.

Recently [9], we reported the synthesis of several potentially tetradentate ligands with the picolinamide unit as the basic component (Ia–e). These ligands would be expected to enforce amide-N coordination.

Most work on metal amide complexes, other than those of ligands derived from amino acids, has been limited to those containing one amide function per molecule or some which have only mono-bidentate potential. An exception is the work reported on *o*-phenylenebis(biuretate) [10], and that on some

potentially quinquedentate acid amides by Nonoyama [2]. In addition Ojima [3] has studied the spectroscopic properties of deprotonated copper(II) and nickel(II) complexes of three bisamides (Ia, b and f).

In the present work, the coordination chemistry of one of this series of compounds, namely N,N-bis-(2'-pyridinecarboxamide)-1,2-benzene (Id), has been studied.

Experimental

Synthesis of Compounds

N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene was prepared as described previously [9].

The 1:1 complexes of general formula $M(bpbH_2)Cl_2 \cdot nH_2O$ were prepared by mixing hot solutions of the metal chloride and the ligand in 95% ethanol. In most cases the complex formed immediately, was filtered off, was then washed with ethanol and dried at the pump. The manganese reaction solution slowly yielded large yellow crystals. However, on isolation, this compound rapidly lost its crystalline

TABLE I. Analyses of the Complexes (a check on metal analyses is provided in Table III).

Complex	% Found					% Required				
	C	H	N	Other		C	H	N	Other	
Co(bpb)·H$_2$O	54.3	3.7	14.2	Co:	15.3	55.0	3.6	14.3	Co:	15.0
Ni(bpb)	57.4	3.3	15.0	Ni:	15.7	57.6	3.2	14.9	Ni:	15.7
Cu(bpb)	56.8	3.3	14.8	Cu:	16.4	56.9	3.2	14.8	Cu:	16.7
Zn(bpb)·H$_2$O	54.0	3.8	14.3	Zn:	15.9	54.1	3.5	14.0	Zn:	16.4
Pd(bpb)·H$_2$O	49.1	3.6	12.8	Pd:	24.0	49.1	3.2	12.7	Pd:	24.2
Mn(bpbH$_2$)Cl$_2$	48.9	3.7	13.0	Cl:	15.8	48.7	3.2	12.6	Cl:	16.0
Co(bpbH$_2$)Cl$_2$·H$_2$O	46.8	3.6	11.8			46.4	3.5	12.0		
Co(bpbH$_2$)Cl$_2$·2H$_2$O	44.7	3.5	11.5	Cl:	14.5	44.7	3.8	11.6	Cl:	14.6
Ni(bpbH$_2$)Cl$_2$·2H$_2$O	45.0	3.5	11.7	Cl:	15.0	44.7	3.7	11.6	Cl:	14.7
Cu(bpbH$_2$)Cl$_2$·1.5H$_2$O	44.8	3.4	11.3	Cu: Cl:	13.5 15.1	45.0	3.5	11.7	Cu: Cl:	13.3 14.8
Ag(bpbH$_2$)·NO$_3$	43.1	3.2	13.7			42.7	3.2	13.8		
Co(bpbH$_2$)(NCS)$_2$·2.5H$_2$O	44.5	3.3	15.3	S:	11.6	44.6	3.6	15.6	S:	11.9
Zn(bpbH)$_2$	61.6	4.0	16.5	Zn:	9.3	61.8	3.7	16.0	Zn:	9.4
bpbH$_2$	67.8	4.5	17.7			67.9	4.4	17.6		

TABLE II. Spectral and Magnetic Properties of Complexes.

Complex	Appearance	λ_{max} (nm)	Magnetic Moment (B.M.)
Co(bpb)·H$_2$O	fine dk. brown needles	505(sh), 735	2.26
Ni(bpb)	deep-orange needles	440, 600(sh)	diam.
Cu(bpb)·H$_2$O	fine brown prisms	510(sh)	2.06
Zn(bpb)·H$_2$O	yellow plates		diam.
Pd(bpb)·H$_2$O	deep-yellow powder		diam.
Mn(bpbH$_2$)Cl$_2$	cream-white powder		5.65
Co(bpbH$_2$)Cl$_2$·2H$_2$O	pink powder	515, 680(sh)	4.67
Ni(bpbH$_2$)Cl$_2$·2H$_2$O	pale blue powder	620, ~1000	3.18
Cu(bpbH$_2$)Cl$_2$·1.5H$_2$O	green powder	790	1.92
Ag(bpbH$_2$)NO$_3$	fine white needles		diam.
Co(bpbH$_2$)(NCS)$_2$·2.5H$_2$O	flesh-red powder	480(sh), 525, 630(sh)	4.74
Zn(bpbH)$_2$	bright yellow powder		diam.

properties to become an amorphous off-white powder. The nickel complex appeared to absorb moisture on standing — it was therefore left open to the atmosphere for two weeks before analysis. The cobalt compound formed initially as a monohydrate; however, on standing for several weeks thermogravi-metric and chloride analyses results indicated the formation of a stable dihydrate form. This was verified by a second microanalysis. The preparation of a satisfactory complex of Fe(II) was found to be very difficult. A brown complex of apparent formula Fe(bpbH$_2$)Cl$_2$ was isolated which afforded reasonable microanalyses for C,H,N and Cl. However a large value of 6.0 B.M. was found for its magnetic moment,

suggesting the presence of paramagnetic impurities. Recrystallisation of the complex proved impossible. The complexes Ag(bpbH$_2$)NO$_3$ and Co(bpbH$_2$)(NCS)$_2$·2.5H$_2$O were prepared from an aqueous ethanol system using silver nitrate and cobalt thio-cyanate respectively.

The deprotonated 1:1 complexes of general formula M(bpb)·nH$_2$O were prepared by addition of a warm aqueous solution of metal acetate to a warm ethanolic solution of the ligand. K$_2$PdCl$_4$ in a sodium acetate solution was used for the Pd complex. With Cu, Ni and Pd a precipitate formed immediately on addition; for the Zn complex the initial reaction solu-tuion was filtered and fine yellow crystals formed
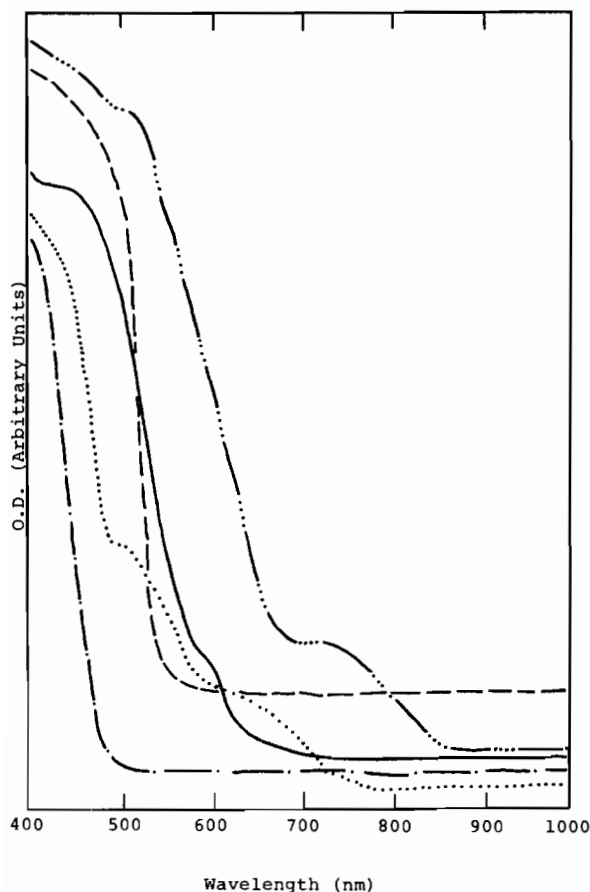
Figure 1. Diffuse reflectance spectra of deprotonated complexes. $-\cdots-\cdots$ Co(bpb)·H_2O; $————$ Ni(bpb); $\cdots\cdots\cdots$ Cu(bpb); $-\cdot-\cdot-$ Zn(bpb)·H_2O; $————$ Pd(bpb)·H_2O.

recorded in the range 400–1000 nm on a Carl-Zeiss PMQII spectrophotometer with RA3 reflectance attachment and calibrated against MgO.

Infrared spectra were recorded in the range 4000–600 cm^{-1} on a Perkin-Elmer 621 spectrometer using KBr discs.

Thermogravimetric studies were carried out on a Stanton-Redcroft Thermobalance (Model TG-750) in conjunction with a direct readout recorder.

Analyses

Ni, Cu and Zn were determined by titration with EDTA [11]. Co was determined electrogravimetrically by deposition on platinum mesh electrodes [11]. Pd was determined as the metal using the thermobalance; the molecular weight of the Pd complex was confirmed by mass spectrometry (m/e parent $422 = M_r - H_2O$) using an AEI MS12 electron impact source mass spectrometer. Chloride was determined potentiometrically using silver and calomel reference electrodes [11]. C, H, N and S were determined in the C.S.I.R.O. Microanalytical Laboratory, Melbourne, Australia.

Results

Table I shows the results of elemental analyses on the ligand and metal complexes. The copper and nickel deprotonated complexes, Ni(bpb) and Cu(bpb), were dried before analysis; it was found later that each forms a stable monohydrate species, however they were studied in the anhydrous forms. Table II gives the magnetic moment, appearance and spectral properties of each of the complexes prepared. The data are consistent with high-spin octahedral environments for all of the complexes containing the neutral amide group. The nickel and cobalt deprotonated complexes are low-spin indicating a probable square planar environment in each case. The low value of λ_{max} for the brown copper deprotonated complex (as compared to the non-deprotonated form) indicates a high degree of tetragonal distortion [12] and this complex may be thought of as being essentially square planar. Figures 1 and 2 show the visible reflectance spectra for the complexes between 400 and 1000 nm. The results obtained correlate well with those expected for the geometries indicated by magnetic data.

Table III gives the results for the thermogravimetric studies performed on the complexes. The cobalt, copper and nickel non-deprotonated complexes show pronounced colour changes on dehydration. Spectral examination of the dehydration products (Figures 2 (a) and (b)) indicates that the colour changes are caused by a red shift with an accompanying intensity increase in the charge transfer bands of those com-

after 1 day. For the preparation of Co(bpb)·H_2O the above method continually gave a mixture of products, fine brown needles and larger green crystals. Physical separation proved impossible. The brown needle form was isolated alone by using a Soxhlet apparatus, with the ligand in the Soxhlet thimble and an aqueous solution of cobalt acetate as the refluxing medium.

The sole 1:2 complex was prepared by recrystallizing the deprotonated 1:1 Zn complex from pyridine. This yielded an unstable yellow complex, of apparent formula Zn(bpbH)$_2$(py)$_2$, which slowly lost pyridine. Thermogravimetric analysis showed that rapid loss of the base occurred at 165 °C. Thus the compound was heated at 170 °C for 10 hours, yielding a bright yellow solid of formula Zn(bpbH)$_2$.

Physical Measurements

Magnetic moments were determined at room temperature using a Newport Single Temperature Gouy Balance (Model SM-12). Visible spectra were

Figure 2a. Diffuse reflectance spectra of non-deprotonated complexes. $- - - -$ Co(bpbH$_2$)(NCS)$_2 \cdot$2.5H$_2$O; $\underline{\quad\quad}$ Co(bpbH$_2$)Cl$_2 \cdot$2H$_2$O; $\cdots\cdots\cdots$ Co(bpbH$_2$)Cl$_2$.
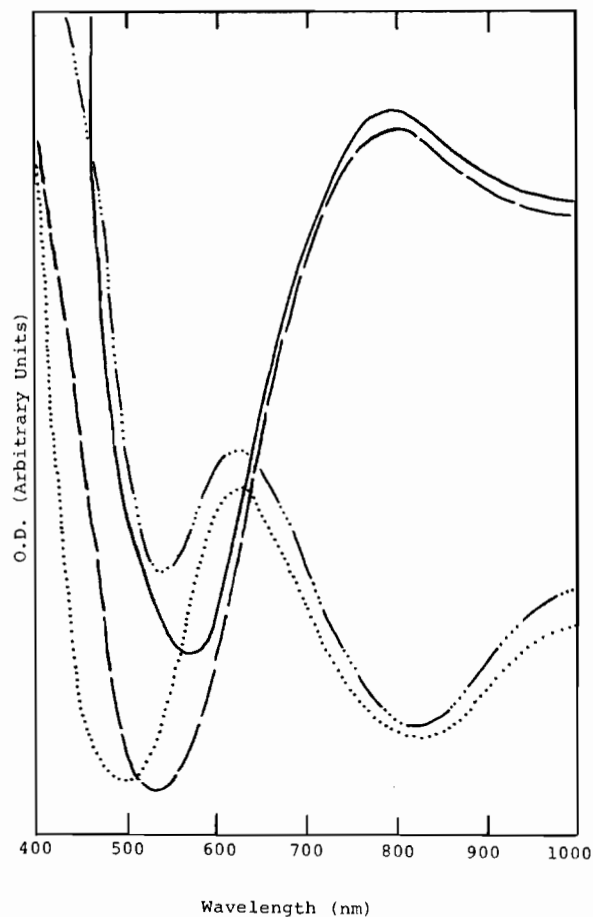
Figure 2b. Diffuse reflectance spectra of non-deprotonated complexes. $\cdots\cdots\cdots$ Ni(bpbH$_2$)Cl$_2 \cdot$2H$_2$O; $- \cdots - \cdots$ Ni-(bpbH$_2$)Cl$_2$; $- - - -$ Cu(bpbH$_2$)Cl$_2 \cdot$1.5H$_2$O; $\underline{\quad\quad}$ Cu-(bpbH$_2$)Cl$_2$.

plexes. These observations suggest [13] that, on dehydration, chloride ions replace the water molecules in the coordination sphere. This low temperature initial loss of coordinated water in many of the complexes is at first surprising. However, a recent report by Nuttall and Stalker [14] concluded that the temperature of water elimination does not reliably differentiate between the types of water present in metal complexes. For the non-deprotonated nickel and copper complexes a weight loss at 160 °C has been assigned to loss of HCl. This was verified by examination of the product directly after the weight loss. In both cases the compounds gave visible reflectance spectra and magnetic moments corresponding to those obtained for the respective deprotonated complexes. This ease of halide elimination suggests a structure for these complexes in which a minimum of molecular rearrangement is required in the solid state to give the deprotonated square planar forms.

Table IV gives details of the infra-red spectra of the complexes together with tentative assignments for most bands. The amide I band (consisting primarily of νC=O) [15] shifts to lower frequencies on coordination for both the neutral and deprotonated amide complexes. As would be expected the N–H stretching bands [15] are absent in the deprotonated amide forms. This region of the spectrum is somewhat difficult to interpret for the hydrated complexes due to the broad bands associated with O–H stretch [15]. The amide II band, generally considered to be a combination of C–N stretch and N–H band in secondary amides [15], undergoes a sizable shift to higher frequencies in the deprotonated complexes. This might be expected since on removal of the amide proton this band becomes a pure C–N stretch. The Zn 1:2 complex shows absorption indicative of both coordinated and uncoordinated amide groups. This suggest a bis-bidentate structure for

TABLE III. Results of Thermogravimetric Studies.

Complex	Temp. Range (°C)	Vol. Products[a]	Wt. Loss (%)		Metal (%)	
			Calc.	Found[b]	Calc.	Found[c]
Co(bpb)·H$_2$O	160–200	H$_2$O	4.6	4.1		
	340–600	bpb	80.4	80.8		
		Total Loss	85.0	84.9	15.0	15.0
Ni(bpb)	410–610	bpb	84.3	84.1	15.7	15.6
Cu(bpb)	410–640	bpb	83.1	83.0	16.7	16.7
Zn(bpb)·H$_2$O	140–213	H$_2$O	4.5	4.6		
	415–545	bpb	79.1	78.8		
		Total Loss	83.6	83.4	16.4	16.3
Pd(bpb)·H$_2$O	60–110	H$_2$O	4.1	4.0		
	400–575	bpb	71.9	71.8		
		Total Loss	76.0	75.8	24.2	24.0
Mn(bpbH$_2$)Cl$_2$	350–790	bpbH$_2$ + Cl$_2$	87.6	88.1	12.4	11.8
Co(bpbH$_2$)Cl$_2$·2H$_2$O	20–165	2H$_2$O	7.5	8.0		
	180–740	bpbH$_2$ + Cl$_2$	80.4	80.3		
		Total Loss	87.9	88.3	12.1	11.7
Ni(bpbH$_2$)Cl$_2$·2H$_2$O	40–130	H$_2$O	4.0	3.7		
	160–270	H$_2$O + 2HCl	18.0	18.8		
	350–600	bpb	65.8	65.3		
		Total Loss	87.8	87.8	12.2	12.1
Cu(bpbH$_2$)Cl$_2$·1.5H$_2$O	50–100	H$_2$O	3.8	3.8		
	160–270	0.5 H$_2$O + 2HCl	17.1	16.7		
	330–580	bpb	65.9	66.1		
		Total Loss	86.7	86.6	13.3	13.6
Ag(bpbH$_2$)NO$_3$	80–770	bpbH$_2$ + NO$_2$	77.9	77.9	22.1	22.1
Co(bpbH$_2$(NCS)$_2$·2.5H$_2$O	35–100	2.5H$_2$O	8.4	9.1		
	190–670	2SO$_2$ + bpbH$_2$	71.0	71.4		
	760–820	2HCN	9.6	8.1		
		Total Loss	89.0	88.6	11.0	11.5
Zn(bpbH)$_2$	270–420	bpbH$_2$	45.4	45.2		
	500–590	bpb	45.2	45.0		
		Total Loss	90.6	90.2	9.4	9.8

[a]bpbH$_2$ = N,N'-bis(2'-pyridinecarboxamide)-1,2-benzene. [b]Final weight loss corrected for uptake of oxygen. [c]Assuming the following oxides to be the remaining solids for the respective metals: Mn$_3$O$_4$, Co$_3$O$_4$, NiO, CuO, ZnO and AgO. For Pd remaining solid is metallic palladium.

the complex. The silver complex shows very little variation from the free ligand. This is best explained by weak coordination through the two pyridyl nitrogens only, a coordination number that is often found for this metal [16].

Discussion

Because of its planar nature a coordination behaviour employing the two amide-oxygens necessarily would involve a decrease in the potential chelating ability of this ligand. Hence a tetradentate N$_4$ function would be expected. A very stable planar system involving maximum electronic delocalization thus would be achieved on deprotonation (II). This mode of coordination is similar to that found by X-ray analyses for disodium triglycylglycino copper-(II) [17], potassium bis-biuretato copper(II) tetra-

(II)
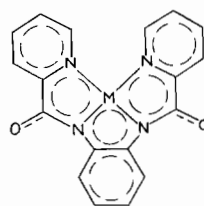
hydrate [18], and the closely related *o*-phenylene-bis(biuret) complex of copper(III) [10].

On complexing with Pd(II), Cu(II) or Ni(II), the amide protons of the ligand become extremely labile, all three deprotonated complexes forming at pH values close to 7. In particular the Pd(II) complex will form even under acidic conditions. This observation is in agreement with previous work [19] describing the relatively high thermodynamic stability of the Pd(N-amide) bond and the promotion of amide

TABLE IV. Infrared Absorption Analysis of the Complexes.

Tentative Band[a] Assignment	bpbH₂	Co(bpb)·H₂O	Ni(bpb)	Cu(bpb)	Zn(bpb)·H₂O	Pd(bpb)·H₂O	Mn(bpbH₂)Cl₂
νN–H	3320(mss)						3360(s)
	3260(sh)						3330(sh)
νO–H		3320(mbr)			3430(mbr)	3450(mbr)	
	3060(w)	b	3060(w)	3050(w)	3060(sh)	3060(w)	3080(w)
νC–H	2930(w)				2930(w)		
Amide I	1675(s)	1615(mss)	1640(ss)	1635(s)	1612(m)	1622(s)	1660(ss)
	1665(s)						
Aromatic Ring	1595(m)	1595(ss)	1605(mss)	1600(s)	1595(ms)	1598(ss)	1595(mss)
Skeletal Vibrations	1590(m)	1585(sh)	1570(m)	1590(ms)	1570(sh)		
	1570(w)						
Amide II	1525(sh)	1580(s)	1560(sh)	1585(sh)	1560(s)	1565(s)	1550(sh)
	1515(s)						1525(s)
Aromatic Ring	1485(m)		1485(ms)				1500(sh)
Skeletal Vibrations	1465(w)	1475(m)		1475(mss)	1470(m)	1475(ms)	1470(m)
and C–H	1450(w)	1455(m)	1450(m)	1450(w)	1455(sh)	1450(w)	1445(m)
Deformation	1430(w)						1430(sh)
	1310(sh)						
	1305(m)	1390(m)	1390(ms)	1385(ms)	1395(ms)	1380(ms)	1335(ms)
	1295(m)						1305(m)
Amide III	1280(w)	1290(w)	1280(w)	1290(w)	1290(w)	1290(w)	1280(w)
	1240(w)	1275(w)			1270(w)	1280(w)	1270(w)
	1145(w)	1160(w)	1160(sh)	1160(sh)			1240(w)
	1125(w)	1145(w)	1150(w)	1145(w)	1145(w)	1150(w)	1130(w)
	1040(w)	1090(w)	1090(w)	1090(w)	1085(w)	1090(w)	1050(w)
	1000(m)	1030(w)	1030(w)	1022(w)	1015(w)	1030(w)	1010(w)
C–H Deformation	920(w)	960(w)		950(w)	940(sh)	970(w)	920(w)
	900(w)	940(sh)		935(w)	925(w)		900(w)
	815(w)			805(w)	815(w)	805(w)	815(w)
C–H Deformation	760(ms)	778(ms)	762(sh)	763(m)	755(m)	760(w)	770(mss)
	750(ms)	742(m)	750(ms)	750(m)	745(sh)	745(mss)	750(m)
	690(m)	680(m)	680(m)	685(m)	695(m)	680(ms)	695(m)
Amide V	670(br, sh)						685(m)
				645(w)	640(w)		645(m)

[a]Ref. 15.   [b]Obscured by O–H stretch.   [c]Ionic nitrate, νN–O.   [d]Thiocyanate, νC–N.   [e]Broad, overlapped band.
s = strong; ss = strong and sharp; ms = medium-strong; mss = medium-strong and sharp; m = medium; w = weak; br = broad, sh = shoulder.

deprotonation by palladium. Also, Hung and Vagg [20], as part of an equilibrium study on metal complexes of the ligand Ia above, have obtained a measured pK_a value of 3.50 for the corresponding palladium complex. Square planar geometries are most likely for all the deprotonated complexes, although it is possible that the water molecule in the zinc complex may occupy a fifth coordination site.

Attempts to produce pyridine adducts of the nickel and copper deprotonated complexes, resulted only in the original complex being recrystallized. In both cases the original monohydrate was recovered from the pyridine solvent. This suggests that the water molecule is involved in strong hydrogen-bonding within the crystal lattice. The same method, when applied to the zinc complex yielded an unstable yellow powder of approximate composition Zn(bpbH)₂(py)₂. This product was quite unexpected as, to form this species, the original complex, Zn(bpb)·H₂O, must have undergone disproportionation as well as hydrolysis in order to protonate the amide groups. A possible explanation is the reaction of the displaced zinc with the water molecule to give Zn(OH)₂ and the partially deprotonated Zn(bpbH)₂-(py)₂ complex. As outlined in the experimental section this powder was heated to remove the base yielding the 1:2 complex. Infra-red data on this complex indicate the presence of both coordinated and uncoordinated amide groups. The most likely structure therefore is one with bidentate behaviour of the ligands with each molecule losing one amide proton and coordinating through one pyridyl nitrogen atom

| Co(bpbH$_2$)Cl$_2$·2H$_2$O	Ni(bpbH$_2$)Cl$_2$·H$_2$O	Cu(bpbH$_2$)Cl$_2$·1.5H$_2$O	Ag(bpbH$_2$)·NO$_3$	Zn(bpbH$_2$)$_2$	Co(bpbH$_2$)(NCS)$_2$·2.5H$_2$O
b	3320(ms)	3170(m)	3320(m)	3320(m)	3240(m)
	3220(ms)	3130(m)	3250(w)	3260(sh)	
3380(mbr)	3260(mbr)	3450(mbr)			3560(mbr)
3050(w)	3050(w)	3050(w)	3060(w)	3060(w)	3060(w)
					2090(ss)[d]
1637(s)	1638(s)	1633(s)	1675(ms)	1680(s), 1625(m)	1642(m)
			1665(s)	1670(s), 1610(m)	
1590(ss)	1590(ss)	1593(s)	1590(m)	1590(s)	1595(s)
1570(w)	1570(w)	1570(w)	1570(w)	1575(s)	1570(w)
1540(ms)	1545(ms)	1550(m)	1520(s)	1560(s), 1525(sh)	1535(ms)
				1520(s)	
	1495(w)	1495(w)	1482(w)	1485(m)	1495(w)
1465(w)	1470(m)	1475(m)	1465(w)	1470(ms)	1465(ms)
1450(w)	1450(w)	1455(m)	1450(w)	1450(w)	1460(sh)
			1430(w)	1430(w)	1440(w)
			1385(s)[c]		
1340(m)	1345(m)	1353(m)	1308(w)	1380(s), 1308(w)	1333(m)
1305(w)	1310(w)	1310(m)	1300(w)	1300(m)	1305(w)
1280(sh)	1280(sh)	1275(m)	1240(w)	1275(w)	1280(w)
1265(w)	1260(w)			1240(w)	1270(w)
1160(w)	1160(w)	1160(w)	1145(m)	1150(w)	1165(w)
	1100(w)	1100(w)		1100(w), 1087(w)	1100(w)
1050(w)	1055(w)	1060(w)	1040(w)	1050(w), 1020(w)	1050(w)
1020(w)	1025(w)	1030(m)	1000(w)	1000(w)	1020(w)
925(w)	925(w)	915(m)	920(w)	920(w), 940(w)	922(w)
910(w)	910(w)	910(w)	900(w)	900(w)	902(w)
815(w)	815(w)	815(w)	820(w)	820(w)	815(w)
755(ms)	755(ms)	755(mss)	760(ms)	760(ms)	753(m)
			750(ms)	750(ms)	
685(m)	685(m)	685(m)	690(m)	695(m)	690(m)
e	e	e	675(sh)	675(sh)	660(w)
640(w)	645(w)	645(w)		642(w)	640(w)

and an amide-oxygen atom. This structure would involve coordination of a deprotonated amide oxygen atom and as such, is somewhat unusual. However, it appears to be the most viable proposal considering the conformational requirements of the ligand and the data obtained for the complex. The zinc atom would most likely be in either a tetrahedral environment, or the carbonyl oxygens of neighbouring protonated amide groups could complete a five or six coordination.

For complexes of the neutral ligand, several structural possibilities exist. Some authors have stated that neutral amides coordinate almost universally through the amide-oxygen atom [2, 6, 7]. Examples of neutral amides coordinating through the nitrogen atom have appeared however [5, 19–22]. The direction and magnitude of the frequency shift associated with the amide I and II bands has often been used to

determine the mode of bonding in non-deprotonated amides. Farona *et al.* [21] have shown that this method is not always applicable to coordinated amides. Farona *et al.* [23] have shown that this may be drawn from the infra-red data with respect to the mode of bonding of the amide. This is due in the main to the complexity of the spectra, caused by the presence of two amide groups per molecule which do not necessarily have the same vibrational modes [24].

The thermogravimetric results for the chloride complexes suggest that there are two quite different structural groups. The most logical arrangement for the nickel and copper chloride salts is one in which the metal ion is coordinated to the four nitrogen atoms of the ligand with the water molecules (or, after dehydration, the chloride ions) coordinated in axial positions. Loss of HCl would occur relatively

easily in the solid state to give the stable deprotonated complex. Thus the bonding mode described in III is postulated for the copper and nickel protonated complexes. Infra-red spectra of the 'dehydrated' forms of these complexes did not improve the resolution of bands in the 4000–3000 region, thus, little may be said concerning the nature of the N–H or O–H bonds.
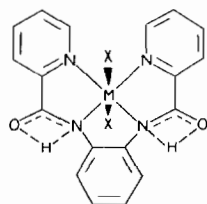
(III)

$X = H_2O, Cl$

For the cobalt and manganese non-deprotonated complexes the polymeric structure IV is a possibility. This is suggested by the insolubility of these complexes and the decomposition pattern in their thermogravimetric analyses. The thiocyanate ion in the cobalt complex exhibits C–N stretching absorption centred at 2090 cm^{-1}. This suggests a coordinated N-bonded ion [25] as might be expected in this type of complex.
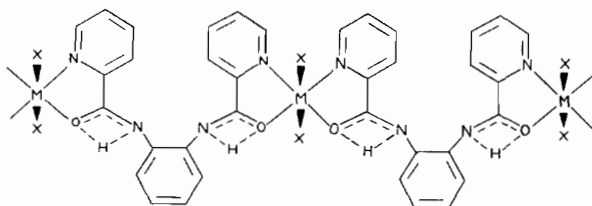
(IV)

$X = H_2O, Cl, NCS$

The silver complex, as outlined in the previous section, most probably involves coordination through the pyridyl nitrogen atoms only. Two coordination is quite common for the silver (I) ion [16].

The location of the amide-proton in complexes which involve neutral amide coordination is open to question. Several neutral N-coordinated amide complexes have been found previously [5, 19–22]; those workers have proposed an 'iminol' form, with the proton bonded to the oxygen atom. It is quite feasible that the proton is involved in hydrogen-bonding between both amide nitrogen and oxygen atoms, as exemplified by III and IV; water molecules or halide ions also may be involved. Both structures would allow a high degree of electronic delocalization and planarity with a resultant enhancement of stability.

Our continuing work [20, 26] on these and similar bis-amide complexes, including high resolution nmr spectroscopy, electrochemical techniques and X-ray structural analyses, should provide further information on the ambivalent nature the metal–amide bond.

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