Inorganica Chimica Acta, 52 (1981) 161–168

Studies on the Metal–Amide Bond.
IX*. Metal Complexes of Some Sterically Hindered Bis-Picolinamide Tetradentate Ligands

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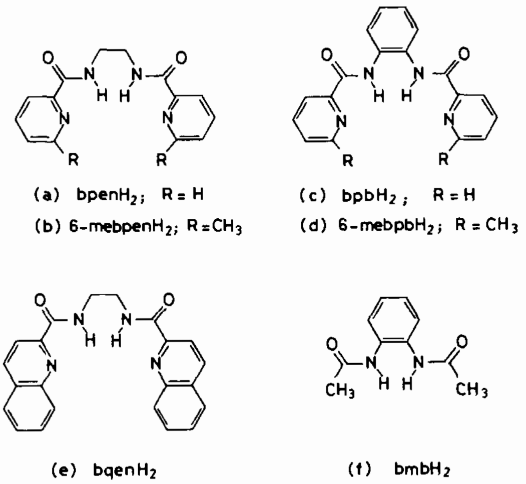
Received April 14, 1981

The synthesis is described of some bis-picolinamide ligands in which N_4 tetradentate function on coordination would enforce severe intramolecular steric interactions. These ligands are N,N'-bis-(6'-methylpyridine-2'-carboxamide)-1,2-ethane (6-mebpenH$_2$), N,N'-bis(6'-methylpyridine-2'-carboxamide)-1,2-benzene (6-mebpbH$_2$) and N,N'-bis(2'-quinolylcarboxamide)-1,2-ethane (bqenH$_2$). Their complexing abilities with bivalent Cu, Ni and Pd have been studied, and comparisons are made with analogous unhindered ligands reported previously. The complexes isolated each have been characterized by microanalysis, magnetic susceptibility, thermogravimetric analysis, and by visible, i.r. and n.m.r. spectral data. In the compound Pd(6-mebpenH$_2$)Cl$_2$ the ligand displays an apparent unique trans*-bidentate function. The deprotonated complexes isolated with the three ligands have N_4 tetradentate coordination, with resultant steric strain. Deuterium isotopic substitution has been used to assist with i.r. assignments.*

Introduction

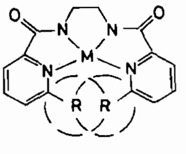
Evidence for steric hindrance between 6'-pyridyl hydrogen atoms obtained from the crystal structure of [Cu(bpb)H$_2$O] and [Cu(bpen)H$_2$O]H$_2$O [1, 2] prompted the synthesis of analogous ligands in which such steric interaction would be enhanced. These ligands, shown in *I* (b), (d) and (e) below, might be expected either to enforce alternative coordination modes or to undergo severe distortion in order to accommodate the tetradentate form of coordination, *II*, which is favoured in the absence of these steric interactions.



(a) bpenH$_2$; R = H
(b) 6-mebpenH$_2$; R = CH$_3$
(c) bpbH$_2$; R = H
(d) 6-mebpbH$_2$; R = CH$_3$
(e) bqenH$_2$
(f) bmbH$_2$

(I)

For deprotonated complexes of these ligands it was believed that coordination through the amide-oxygen atom, as found for the palladium complex of N-(2'-pyridyl)acetamide [3], may be enforced. Metal complexes of analogous sterically hindered imine compounds [4] show an enhanced tendency towards hydrolysis of C=N bonds to relieve steric strain.



(II)

The ligand 6-mebpbH$_2$, *I*(d), is considered to be especially interesting as this compound would retain both the strong tendency for deprotonation and lack of flexibility observed by bpbH$_2$ [1, 5], and thus variations in the mode of coordination are limited. An even more severe steric effect would be present in the complexes of bqenH$_2$, *I*(e), and planar N_4 function would appear to be impossible. Coordination studies on these ligands were limited to the copper(II), nickel(II) and palladium(II) systems, as these metal ions previously had shown the greatest

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*Part VIII is reference [14].

potential to promote amide deprotonation, in which form the desired effects would be most pronounced. We report here details of the coordination chemistry of these ligands.

Experimental

Physical measurements and analysis procedures were identical to those outlined earlier [6].

Ligand Syntheses

The ligands were prepared by a method similar to that previously described [7].

N,N'-bis[6'-methylpyridine-2'-carboxamide]-1,2-ethane, 6-mebpenH_2, I*(b)*

To a solution of 6-methylpyridine-2-carboxylic acid (13.72 g, 0.10 mol) in pyridine (120 ml), triphenylphosphite (26.1 ml, 0.10 mol) was added with stirring. After warming the solution to 80 ℃, 1,2-diaminoethane (3.33 ml, 0.05 mol) was added dropwise with continual stirring. After heating for 5 hrs on a steam-bath the reaction solution was allowed to stand overnight. Pyridine was removed under reduced pressure and the resulting brown oil was dissolved in chloroform, washed well with water and sodium bicarbonate solution, then dried over magnesium sulphate. The chloroform solution was reduced to 35 ml and added dropwise to ice-cold sodium-dried diethyl ether. A white solid resulted, 10.5 g (70%). An analytical sample was recrystallised from diethyl ether/chloroform to yield fine white plates (m.pt. 156–157 ℃).

N,N'-bis[6'-methylpyridine-2'-carboxamide]-1,2-benzene, 6-mebpbH_2, I*(d)*

Triphenylphosphite (26.1 ml, 0.10 mol) was added slowly to a warm solution of 6-methylpyridine-2-carboxylic acid (13.72 g, 0.10 mol) in pyridine (130 ml). 1,2-diamino-benzene (5.41 g, 0.05 mol) in pyridine (40 ml) was added slowly with stirring. The solution was heated on a steam-bath for 5 hrs then allowed to stand overnight. A similar isolation procedure as outlined for 6-mebpenH_2 above yielded 10.5 g (61%) of grey-white product. An analytical sample was twice recrystallised from chloroform to give fine white needles (m.pt. 134 ℃).

N,N'-bis(2'-quinolylcarboxamide)-1,2-ethane, bqenH_2, I*(e)*

Quinaldinic acid (20.0 g, 0.116 mol) was dissolved/suspended in hot pyridine (170 ml) and triphenylphosphite (30.1 ml, 0.116 mol) added slowly with stirring. After slow addition of 1,2-diaminoethane (3.91 ml, 0.058 mol) with stirring, the solution was heated on a steam-bath for 5 hr. After standing overnight a heavy white precipitate formed. This was filtered off and washed well with diethyl ether to yield 17.82 g (83%) of crude product. An analytical sample was recrystallised from ethanol/chloroform giving white needle clusters (m.pt. 215 ℃).

N,N'-bis(methylcarboxamide)-1,2-benzene, bmbH_2, I*(f)*

To a solution of acetic acid (6.0 g, 0.1 mol) in warm pyridine (80 ml) was added 1,2-diaminobenzene (5.41 g, 0.05 mol) in pyridine (40 ml). After addition of triphenylphosphite (26.1 ml, 0.10 mol) with stirring, the solution was heated on a steam-bath for 6 hr. On standing a white precipitate formed which was filtered off and washed well with diethyl ether. The yield was 8.44 g (88%). An analytical sample was recrystallised from water to give chunky white crystals (m.pt. 188–190 ℃).

Deuterium-Substituted Forms

A deuterated form of 6-mebpenH_2 was prepared by recrystallising this ligand from D_2O. Due to their low solubilities in water, deuterated forms of 6-mebpbH_2 and bqenH_2 necessarily were prepared by dissolving the appropriate ligand in a small amount of hot ethanol, adding an equal or greater volume of D_2O, then boiling off the more volatile ethanol. The deuterated compounds crystallized out as the solutions cooled. An additional recrystallization was sometimes found necessary for the latter compounds to give complete conversion.

Complexes of 6-MebpbH_2

The deprotonated copper(II) and nickel(II) complexes were prepared by addition of a hot solution of 6-mebpbH_2 in 50% aqueous ethanol to a hot solution of the metal acetate. The copper complex precipitated as a dark green microcrystalline solid soon after mixing. The reaction solution for the nickel complex was adjusted to pH 9.5 by dropwise addition of sodium hydroxide. This solution slowly yielded red-brown plates of the monohydrate. An anhydrous form of like appearance was produced using absolute ethanol alone. Upon recrystallization from chloroform the monohydrate returned as a mixture of two crystalline forms, both plates and fine needles. The palladium analogue precipitated immediately on adding an aqueous solution of K_2PdCl_4 to an equimolar solution of the ligand in aqueous ethanol. This fine yellow precipitate was washed with water and ethanol and dried at the pump. Numerous attempts to prepare non-deprotonated chloride complexes of each metal over a variety of pH conditions failed to yield solid products.

Complexes of 6-MebpenH_2

The deprotonated palladium(II) complex was prepared following a similar method to that described above for the 6-mebpbH_2 compound, although addition of a small amount of sodium hydroxide solution was necessary. Formation of the deprotonated copper complex in aqueous solution was indicated by a dark green colour at high pH. However, numerous attempts to obtain a solid product from the solution were unsuccessful. Attempts to prepare a deprotonated nickel complex resulted only in the formation of nickel hydroxide. Non-deprotonated complexes of nickel(II), copper(II) and palladium(II) were prepared by mixing hot aqueous solutions of the ligand and the appropriate metal chloride in the presence of excess chloride ion at low pH. Fine microcrystalline products formed slowly in all cases. These were washed well with water and air dried at the pump.

Complexes of BqenH_2

The deprotonated palladium(II) complex was obtained by adding a hot acetone solution of the ligand to an aqueous solution of K_2PdCl_4 followed by dropwise addition of sodium hydroxide. The fine yellow product formed slowly from solution in low yield. The same compound was obtained in higher yields by using dimethylsulphoxide as solvent and adding a small amount of solid potassium hydroxide. This latter method when used with nickel nitrate plus bqenH_2 (or 6-mebpenH_2) yielded the deep red colour of the deprotonated nickel complex but no solid product was obtained. The non-deprotonated copper complex was formed by addition of an aqueous copper(II) chloride solution to an acidified aqueous solution of bqenH_2. A light green precipitate formed slowly. (Further addition of 1 *M* hydrochloric acid at this stage resulted in the solid redissolving, which could be reversed by addition of 1 *M* sodium hydroxide). Similar conditions failed to yield a Ni(II) complex.

The compound bmbH_2, *I*(f), did not yield a metal complex product under any of the various synthetic procedures employed, nor did it give any indication of metal coordination in reaction solutions.

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

Results

Table I gives the results of elemental analyses for the ligands and their associated metal complexes. Table II gives the appearance, magnetic moment and spectral properties of the complexes. The visible absorption and magnetic properties of the non-deprotonated copper(II) and nickel(II) complexes are consistent with six-coordinate geometries. The visible reflectance spectra for the complexes between 400 and 1100 nm are shown in Fig. 1. The deprotonated nickel complex gives identical spectra for both the anhydrous and monohydrate forms, indicating non-coordination of the water molecule. The spectra of the deprotonated copper(II) and nickel(II) complexes are consistent with a tetragonally distorted octahedral geometry for the copper complex and a square planar coordination geometry for the nickel complex.

Table III gives the results for the thermogravimetric analyses performed on the complexes. For the non-deprotonated chloride complexes no separate weight loss corresponding to hydrogen chloride was observed, as was the case for the bpbH_2 analogues [5]. Table IV gives the characteristic infra-red bands for the complexes. Assignment of amide bands for the ligands is assisted by deuterium isotopic substitution which highlights by difference any absorption associated with the N–H bond. Coordination of these

TABLE I. Analyses of Ligands and Complexes (A check on metal analyses is provided in Table III).

Compound	% Found				% Required			
	C	H	N	Metal	C	H	N	Metal
6-mebpenH_2	63.9	6.1	18.6		64.4	6.1	18.6	
6-mebpbH_2	69.3	5.1	16.4		69.4	5.2	16.2	
bqenH_2	71.3	4.9	14.9		71.3	4.9	15.1	
bmbH_2	62.4	6.2	14.7		62.5	6.3	14.6	
Ni(6-mebpb)	59.8	3.9	14.0		59.6	4.0	13.9	
Ni(6-mebpb)·H_2O	56.5	4.3	13.4	14.0	57.0	4.3	13.3	13.9
Cu(6-mebpb)	59.2	4.2	13.9	15.6	59.0	4.0	13.7	15.5
Pd(6-mebpb)·H_2O	51.4	4.0	12.4	23.2	51.2	3.9	12.0	22.7
Pd(6-mebpen)·2H_2O	43.6	4.7	12.6	24.2	43.8	4.6	12.8	24.2
Pd(bqen)·0.5H_2O	54.8	3.6	11.7	21.9	54.6	3.5	11.6	22.0
Ni(6-mebpenH_2)Cl_2·4H_2O	39.1	4.9	11.2	11.6	38.4	5.2	11.2	11.8
Cu(6-mebpenH_2)Cl_2·H_2O	42.8	4.5	13.1	14.3	42.6	4.5	12.4	14.1
Pd(6-mebpenH_2)Cl_2	39.9	3.9	11.7	21.8	40.4	3.8	11.8	22.4
Cu(bqenH_2)Cl_2·H_2O	50.3	4.1	10.7	11.9	50.5	3.5	10.7	12.1

TABLE II. Spectral and Magnetic Properties of the Complexes.

Complex	Appearance	λ_{max} (nm)	Magnetic Moment (B.M.)
Ni(6-mebpb)	fine dk. brown plates	410, 575 (sh)	diam.
Ni(6-mebpb)$\cdot H_2O$	dk. brown plates *or* fine needles	410, 575 (sh)	diam.
Cu(6-mebpb)	dk. green prisms	410, 605	2.03
Pd(6-mebpb)$\cdot H_2O$	deep yellow powder	–	diam.
Pd(6-mebpen)$\cdot 2H_2O$	yellow powder	–	diam.
Pd(bqen)$\cdot 0.5H_2O$	yellow-cream powder	–	diam.
Ni(6-mebpenH_2)$Cl_2\cdot 4H_2O$	lt. blue powder	~600 (sh), 680, 1040	3.34
Cu(6-mebpenH_2)$Cl_2\cdot H_2O$	lt. blue-green powder	1030 (v. br.)	1.89
Pd(6-mebpenH_2)Cl_2	fine, lt. yellow crystals	–	diam.
Cu(bqenH_2)$Cl_2\cdot H_2O$	lime-green powder	935 (br.)	2.00

TABLE III. Results of Thermogravimetric Studies.

Complex	Temp. Range (°C)	Volatile Products	Wt. Loss (%)		Metal (%)	
			Calc.	Found[a]	Calc.	Found
Ni(6-mebpb)$\cdot H_2O$	50–130	H_2O	4.3	4.5		
	300–650	6-mebpb	81.8	81.0		
		Total loss	86.1	85.5	13.9	14.5
Cu(6-mebpb)	440–505	6-mebpb	84.5	84.4	15.5	15.6
Pd(6-mebpb)$\cdot H_2O$	55–140	H_2O	3.8	3.6		
	335–460	6-mebpb	73.5	73.2		
		Total loss	77.3	76.8	22.7	23.2
Pd(6-mebpen)$\cdot 2H_2O$	25–80	$2H_2O$	8.2	8.3		
	295–430	6-mebpen	67.6	67.5		
		Total loss	75.8	75.8	24.2	24.2
Pd(bqen)$\cdot 0.5H_2O$	30–95	$0.5H_2O$	1.9	1.1		
	260–475	bqen	76.1	77.0		
		Total loss	78.0	78.1	22.0	21.9
Ni(6-mebpenH_2)$Cl_2\cdot 4H_2O$	40–160	$4H_2O$	14.4	13.8		
	340–600	6-mebpenH_2 + Cl_2	73.8	74.2		
		Total loss	88.2	88.0	11.8	12.0
Cu(6-mebpenH_2)$Cl_2\cdot H_2O$	40–170[b]	H_2O	3.9	2.8		
Cu(bqenH_2)$Cl_2\cdot H_2O$	50–170[c]	H_2O	3.4	3.4		
Pd(6-mebpenH_2)Cl_2	270–650	6-mebpenH_2 + Cl_2	77.6	78.2	22.4	21.8

[a] Final weight loss corrected for uptake of oxygen. The following oxides are assumed to be the remaining solids for the respective metals: NiO, CuO and PdO. [b] Compound appears to sublime above ~450 °C. [c] Compound appears to sublime above ~600 °C.

ligands to metal ions produces effects similar to those noted for the ligands bpbH_2 [5], bpenH_2 [6] and bpchH_2 [8]. Bands associated with the N–H bond disappear on formation of the deprotonated complexes, and the amide II and amide III bands are replaced by a new band at ~1410 cm^{-1}. The amide I band again undergoes a shift to lower frequency for both deprotonated and non-deprotonated complexes. The one exception to this trend is the non-deprotonated palladium complex of 6-mebpenH_2. The amide I band shifts to slightly higher frequencies for this complex, while the other amide bands show a

TABLE IV. Characteristic Infra-red Bands of the Ligands and Related Metal Complexes.

Compound	ν_{N-H}	Amide I[a]	Amide II[a]	Amide III[a]	Other bands
6-mebpenH_2	3310 (ms)	1660 (s)	1530 (s)	1320 (m)	π_{N-H} (amide V)[a] 685 (m, sh)
6-mebpenD_2	2460 (ms)[b]	1650 (s)	1475 (ms), 1450 (m)	950 (m)	π_{N-D} 510 (m, br)
Pd(6-mebpen)·$2H_2O$	–	1625 (sh), 1620 (s)	1420–1410 (m)		
Ni(6-mebpenH_2)Cl_2·$4H_2O$	c	1640 (s)	1560 (ms)	1350 (m), 1340 (m)	
Cu(6-mebpenH_2)Cl_2·H_2O	c	1630 (ms)	1555 (ms)	1360 (m)	
Pd(6-mebpenH_2)Cl_2	3350 (sh), 3340 (m)	1680–1670 (s)	1550 (sh), 1540 (s)	1355 (m), 1320 (ms)	π_{N-H} 570 (m, br) ν_{Pd-Cl} 350 (ms)
6-mebpbH_2	3325 (m)	1690 (s)	1500 (s)	1320 (mw)	π_{N-H} 635 (m, br)
6-mebpbD_2	2460 (mw)[b]	1690 (s)	1410 (mw)	945 (w)	π_{N-D} 510 (sh, br)
Ni(6-mebpb)·H_2O	–	1645 (s)	1410 (ms)		
Cu(6-mebpb)	–	1640 (ms)	1410 (ms)		
Pd(6-mebpb)·H_2O	–	1630 (s)	1405 (m)		
bqenH_2	3400 (mss)	1670 (s)	1525 (s)	1295 (m)	π_{N-H} 590 (ms, br)
bqenD_2	2525 (m)[b]	1665 (s)	1470 (ms), 1445 (m)	900 (sh)	π_{N-D} 435 (m, br)
Pd(bqen)·$0.5H_2O$	–	1635 (s)	1400 (m, br)		
Cu(bqenH_2)Cl_2·H_2O	3550 (m), 3430 (m)	1620 (s)	1570 (ms)	1350 (m)	
bmbH_2	3230 (m, br)	1670 (s)	1535 (s, br)	1315 (ms)	π_{N-H} 715 (ms, br)

[a] From reference [11]. [b] ν_{N-D}. [c] Obscured by broad ν_{O-H} bands. Band shapes are described as in reference [6].

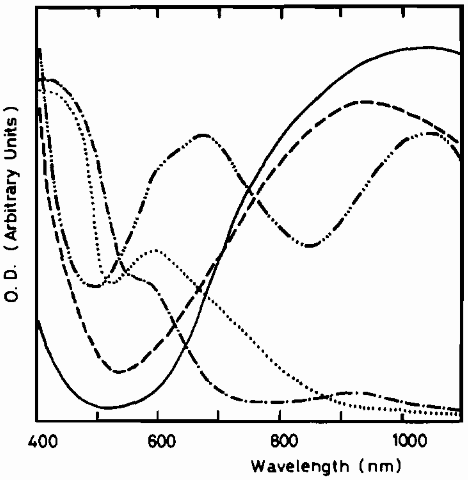


Fig. 1. Diffuse reflectance spectra of copper and nickel complexes. —·—·—·— $Ni(6\text{-}mebpb)\cdot H_2O$; ···—···—··· $Ni(6\text{-}mebpenH_2)Cl_2\cdot 4H_2O$; ········ $Cu(6\text{-}mebpb)$; ——— $Cu(6\text{-}mebpenH_2)Cl_2\cdot H_2O$; – – – – $Cu(bqenH_2)Cl_2\cdot H_2O$.

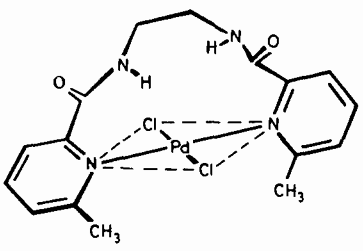
complicated pattern unlike that for any complex previously characterised. A sharp peak at 350 cm^{-1} which does not appear in the spectrum of the free ligand is assigned to a Pd–Cl stretching mode, consistent with a *trans*-arrangement [9, 10].

Table V gives the result of proton magnetic resonance studies on $bpbH_2$, the substituted ligands and their diamagnetic metal complexes. On formation of the deprotonated nickel complex $Ni(6\text{-}mebpb)\cdot H_2O$, the benzene protons show similar frequency shifts to those found for analogous complexes of $bpbH_2$. Pyridyl protons also show similar changes in chemical shift. The methyl groups are found to be shielded to a greater extent on complex formation; this could well be due to mutual interaction of these groups brought about by the geometry of the complex. The two palladium complexes of $6\text{-}mebpenH_2$ show obvious differences highlighting the deprotonation of the ligand. The complex pattern of the methylene signal in $Pd(6\text{-}mebpenH_2)Cl_2$ changes to a singlet on decoupling the (amide) N–H resonance at 8.31 p.p.m., verifying that the amide-N atom is not coordinated [6]. The disappearance of this amide proton peak in the spectrum of $Pd(6\text{-}mebpen)\cdot 2H_2O$, and the collapse of the splitting pattern for the methylene protons, clearly demonstrate coordination of the deprotonated amide-N atom in this compound [6].

Discussion

The non-deprotonated nickel and copper complexes of $6\text{-}mebpenH_2$ almost certainly have a structure similar to the analogous complexes of $bpenH_2$ reported previously [6]. Thus each molecule would act as a bis-bidentate ligand coordinating through pyridyl-N and amide-O atoms and bridging two metal ions. Either *cis* or *trans* configurations are possible as both allow reasonable steric freedom for the methyl groups. The copper complex of $bqenH_2$ could have a similar structure; the slightly greater steric hindrance between the 8′-substituted hydrogen atoms of the quinoline ring may be alleviated by a greater distortion away from a regular octahedral arrangement. It is of interest that no non-deprotonated complexes were isolated with $6\text{-}mebpbH_2$. This may be due to the lack of flexibility in the central link of this sterically hindered ligand.

The non-deprotonated palladium chloride complex of $6\text{-}mebpenH_2$, apart from being the only palladium complex of this type isolated so far with any ligand, shows several significant differences from the other non-deprotonated complexes. It forms slowly from aqueous solution yielding small yellow crystals which are quite stable on storage. The infra-red spectrum of the compound is quite unusual, showing a slight frequency increase on coordination for the amide I absorption. The slow formation of crystals from aqueous solution suggests that the species is not polymeric. Nuclear magnetic resonance data indicate that both protons are located on the amide-nitrogen atoms. These observations, plus the identification of a ν_{Pd-Cl} band in the infra-red spectrum, suggest the structure shown in *III*, where each ligand bonds through the pyridine-N atoms alone in a *trans*-bidentate function. Molecular models show that such a species could form readily with no obvious steric strain, although rotation about the C(*pyridine*)-C(*amide*) bonds would be required. A large deshielding effect on the methyl groups is observed in the n.m.r. spectrum of this complex, which may be a consequence of their unusual positioning relative to the coordination plane. Loss of steric interaction between these methyl groups would result from such an arrangement. The increased frequency observed for the amide I i.r. band of this compound then may be explained by comparison with $[bpenH_4](ClO_4)_2$ [6], where an increased frequency was noticed for this pyridinium salt.



(III)

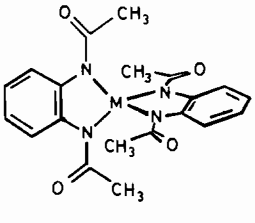
The lack of reactivity of the potential bidentate $bmbH_2$ demonstrates the importance of coordination

TABLE V. Results of N.m.r. Studies.

Compound	Solvent	Chemical Shift (p.p.m.)[a]								
		H (*amide*)	Pyridyl protons				Central link			
			H_3	H_4	H_5	H_6	Hb_α	Hb_β	H_e	CH_3
$bpbH_2$	$CDCl_3$	10.26 (br, s)[b]	8.32 (d)	7.90 (t)	7.46 (m)	8.56 (d)	7.83 (m)	7.31 (m)	–	–
	DMSO	10.72 (s)	8.16 (d)	8.05 (t)	7.64 (t)	8.63 (d)	7.76 (m)	7.29 (m)	–	–
$Ni(bpb)\cdot H_2O$	DMSO	–	7.74 (d)	8.20 (t)	7.67 (t)	8.45 (d)	8.13 (m)	6.75 (m)	–	–
$Pd(bpb)\cdot H_2O$	DMSO	–	7.88 (d)	8.25 (t)	7.74 (t)	8.69 (d)	8.30 (m)	6.85 (m)	–	–
$Zn(bpb)\cdot H_2O$	DMSO	–	8.39 (d)	8.25 (t)	7.77 (t)	9.00 (d)	8.49 (m)	6.83 (m)	–	–
6-$mebpbH_2$	$CDCl_3$	10.35 (br, s)	8.11 (d)	7.76 (t)	7.29 (m)	–	7.92 (m)	7.27 (m)	–	2.46 (s)
Ni(6-mebpb)$\cdot H_2O$	$CDCl_3$	–	7.72 (d)	7.81 (t)	7.18 (d)	–	8.13 (m)	6.85 (m)	–	2.37 (s)
6-$mebpenH_2$	$CDCl_3$	8.50 (br, s)	8.05 (d)	7.71 (t)	7.30 (d)	–	–	–	3.75 (ct)	2.54 (s)
	DMSO	8.80 (br, s)	7.83 (d)	7.83 (t)	7.43 (d)	–	–	–	3.52 (ct)	2.53 (s)
Pd(6-mebpen)$\cdot 2H_2O$	$CDCl_3$	–	7.86 (m)	7.90 (t)	7.37 (d)	–	–	–	3.74 (s)	2.56 (s)
Pd(6-$mebpenH_2Cl_2$	DMSO	8.31 (br, s)	7.66 (d)	7.88 (t)	7.58 (d)	–	–	–	3.85 (ct)	3.58 (s)
	$CDCl_3$	8.67 (br, s)	7.66 (d)	7.79 (t)	7.38 (d)	–	–	–	4.08 (ct)	3.71 (s)

[a] Assignments for individual protons assisted by resonance decoupling studies. [b] m = multiplet; t = triplet; d = doublet; s = singlet; ct = compound triplet (see reference [6]). All signals due to pyridyl protons show fine splitting due to long range coupling effects.

of the pyridyl groups in the tetradentate ligands. The only possible metal geometry which coordination of deprotonated $bmbH_2$ would allow is tetrahedral; this limitation is due to the steric effects of the methyl groups as shown in *IV*. That such compounds do not form is in keeping with the general observation that the high ligand field deprotonated peptide or amide nitrogen atoms prefer to coordinate as part of a planar arrangement around a metal atom [12].


(IV)

The deprotonated complexes of these sterically hindered ligands exhibit an interesting trend for the three metal ions studied. Palladium(II) readily forms such complexes with all three ligands. Copper(II) appears to form complexes with each, but those of 6-mebpenH_2 and bqenH_2 could not be successfully isolated. Nickel(II) forms a complex with 6-mebpbH_2 alone. All data obtained for the deprotonated complexes suggest similar tetradentate N_4 coordination geometry as found in the structures of the nickel(II) and copper(II) complexes previously described [1, 2, 13, 14]. Palladium has been shown to maintain a planar MN_4 configuration even at the expense of considerable steric effects in the ligands used [15, 16]. For the nickel and copper complexes it would appear that the strong stabilising effect of extensive delocalization possible on deprotonation is sufficient to overcome the severe steric interaction of the methyl groups in this type of coordination. The crystal structure of Cu(6-mebpb) [17] shows that this steric hindrance is lessened by significant deformations within the ligand, in particular in the pyridine and amide groups. The square-pyramidal geometries observed for $[Cu(bpb)(H_2O)]$ [1] $[Cu(bpen)H_2O]H_2O$ [2] and $[Cu(bpch)H_2O]H_2O$ [13] would not be allowed in these sterically hindered copper chelates, hence the anhydrous nature of Cu(6-mebpb). The distortions present in Cu(6-mebpb) should be even more extreme in Ni(6-mebpb) due to the smaller effective radius of the latter metal ion. In fact, it is a little surprising that such a complex forms; the constraints on ligand geometry are considerably more rigid for low-spin d^8 metal ions than for d^9 ions [12].

The solubility of these complexes provide further interesting comparisons. While the deprotonated Cu(II), Ni(II) and Pd(II) complexes of $bpbH_2$ are almost insoluble in most solvents, Ni(6-Mebpb)H_2O is soluble in a wide range of solvents including chloroform and carbon tetrachloride. The copper complex also shows considerably higher solubility in water than does its $bpbH_2$ analogue. Such a solubility increase has been linked previously to steric strain in metal complexes [18].

Acknowledgement

One of us (R.L.C.) wishes to thank the Australian Government for the grant of a Commonwealth Postgraduate Research Award.

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