Inorganica Chimica Acta, 51 (1981) 155–162
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Studies on the Metal–Amide Bond. VII*. Metal Complexes of the Flexible N_4 Ligand N,N′-Bis(2′-pyridinecarboxamide)1,2-ethane

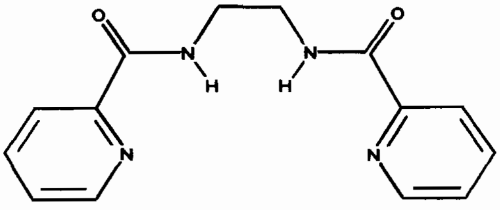
DAVID J. BARNES, ROSS L. CHAPMAN, FREDERICK S. STEPHENS and ROBERT S. VAGG
School of Chemistry, Macquarie University, North Ryde, N.S.W., 2113, Australia

Received March 4, 1981

The isolation and characterization of a series of transition metal complexes is described with the ligand bpenH$_2$ in both neutral and deprotonated forms. The ligand acts as a planar N_4 tetradentate in the monomeric deprotonated complexes of general form M(bpen)nH$_2$O (M = Cu^{II}, Ni^{II}, Pd^{II} or Pt^{II}). Metal chloride and perchlorate salts of the neutral ligand, of general formulae M(bpenH$_2$)Cl$_2$nH$_2$O and M$_2$(bpenH$_2$)$_3$(ClO$_4$)$_4$nH$_2$O, are reported (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} or Zn^{II}) with the ligand bonding through pyridine-N and amide-O atoms in a bridging bis-bidentate function. In the chloride complexes high-spin six-coordinate geometries are indicated for the polymeric solid products. The perchlorate complexes are dimeric and high-spin, with each metal atom exhibiting N_3O_3 six-coordination. Proton NMR studies on the ligand show coupling of the amide protons with those of the central ethylene group. Deprotonation is confirmed by loss of this coupling for the Ni^{II}, Pd^{II} and Pt^{II} chelates, $^1H-^{195}Pt$ coupling being observed in the latter compound. The neutral and deprotonated chelate forms also are readily differentiated by their IR absorption. Deuterium isotopic substitution of amide protons has been used to assist IR assignments.

Introduction

The ligand N,N′-bis(2′-pyridinecarboxamide)-1,2-benzene, bpbH$_2$, has been shown to coordinate to transition metal ions in several modes largely determined by the rigid nature of the central aromatic link [1, 2]. The more flexible ligand N,N′-bis(2′-pyridinecarboxamide)-1,2-ethane, bpenH$_2$, (I), should allow a lesser degree of electronic delocalization in its complexes than would its benzene homologue. Hence some marked differences in coordination behaviour between the two ligands might be expected.



(I)

The flexibility of bpenH$_2$ would allow a greater variation in possible geometries and metal/ligand ratios, especially for the non-deprotonated complexes where amide–oxygen coordination would be more favoured. A structural comparison between the bivalent copper complexes of the two deprotonated ligands [2, 3] demonstrates the effect on metal ion stereochemistry of the different central links. We report here details of the synthesis and characterization of a variety of metal complexes of bpenH$_2$.

Experimental

Synthesis of Compounds

The ligand was prepared by a previously described method [4]. A deuterated form, bpenD$_2$, was prepared by refluxing a solution of bpenH$_2$ in D$_2$O and allowing the product to crystallize slowly in a sealed flask. A hydroperchlorate salt of bpenH$_2$ was prepared by recrystallization of the ligand from a solution of 1 *M* perchloric acid. The solution slowly yielded a fine white microcrystalline product, [bpenH$_4$](ClO$_4$)$_2$ (*Anal.* Found: C, 35.7; H, 3.6 N, 11.7%. $C_{14}H_{16}N_4O_{10}Cl_2$ requires: C, 35.7; H, 3.4; N, 11.9%.)

Complexes of general formula M(bpenH$_2$)Cl$_2$·nH$_2$O were prepared by adding a hot solution of the ligand in aqueous ethanol to a warm ethanolic solution of the required metal chloride in slight excess. The zinc complex was prepared by adding a water/ethanol (5:1) solution of the ligand to a slightly acid aqueous solution of zinc chloride. Solid

---

*Part VI is reference [21].

TABLE I. Analyses of $bpenH_2$ Complexes (A check on metal analyses is provided in Table III).

Compound	% Found				% Required			
	C	H	N	Other	C	H	N	Other
$[Cu(bpen)H_2O]H_2O$	45.7	4.5	15.3	Cu: 17.5	45.7	4.4	15.2	Cu: 17.3
$Ni(bpen)\cdot H_2O$	48.4	4.1	16.2	Ni: 17.1	48.7	4.1	16.2	Ni: 17.0
$Pd(bpen)\cdot 2H_2O$	41.0	3.6	13.8	Pd: 26.1	40.9	3.9	13.6	Pd: 25.9
$Pt(bpen)\cdot 4H_2O$	31.5	2.9	10.7	Pt: 36.2	31.4	3.7	10.5	Pt: 36.4
$Mn(bpenH_2)Cl_2\cdot 0.5H_2O$	41.4	3.7	13.7	Mn: 13.8	41.5	3.7	13.8	Mn: 13.6
$Fe(bpenH_2)Cl_2\cdot 0.5H_2O$	41.4	3.6	12.4	Cl: 17.5	41.4	3.7	13.8	Cl: 17.5
$Co(bpenH_2)Cl_2\cdot 2.5H_2O$	37.8	3.7	12.7	Cl: 15.8	37.8	4.3	12.6	Cl: 16.0
$Ni(bpenH_2)Cl_2\cdot 2.5H_2O$	37.0	4.2	12.4	Cl: 15.8	37.8	4.3	12.6	Cl: 16.0
$Cu(bpenH_2)Cl_2\cdot H_2O$	39.6	3.3	13.5	Cu: 15.0	39.8	3.8	13.3	Cu: 15.0
$Zn(bpenH_2)Cl_2\cdot 0.5H_2O$	40.1	3.5	13.4	Cl: 17.5	40.5	3.6	13.5	Cl: 17.1
$Co(bpenH_2)(NCS)_2$	42.9	3.3	18.9	S: 13.7	43.2	3.2	18.9	S: 14.4
$Cu(bpenH_2)(NO_3)_2$	36.5	3.0	17.9	Cu: 13.5	36.7	3.1	18.4	Cu: 13.9
$Ag(bpenH_2)NO_3\cdot 2H_2O$	35.5	3.4	14.7	Ag: 22.3	35.3	3.8	14.7	Ag: 22.7
$Mn_2(bpenH_2)_3(ClO_4)_4\cdot 2H_2O$	37.4	3.6	13.7	Mn: 7.9	37.2	3.6	12.4	Mn: 8.1
$Fe_2(bpenH_2)_3(ClO_4)_4\cdot 6H_2O$	35.2	3.3	11.4	Cl: 9.2	35.3	3.8	11.8	Cl: 9.9
$Co_2(bpenH_2)_3(ClO_4)_4\cdot 5H_2O$	36.0	3.3	12.7	Co: 8.3	35.6	3.7	11.9	Co: 8.3
$Ni_2(bpenH_2)_3(ClO_4)_4\cdot 6H_2O$	34.8	3.1	11.8	Ni: 8.1	35.2	3.8	11.7	Ni: 8.3
$Zn_2(bpenH_2)_3(ClO_4)_4\cdot 5H_2O$	35.1	3.3	11.7	Zn: 9.0	35.3	3.6	11.8	Zn: 9.2

product formation was often instantaneous although precipitation of the Fe(II), Zn(II) and Mn(II) compounds occurred slowly over 1–2 days. All complexes were collected by filtration after several days standing, were washed with a minimum of cold water and ethanol and dried at the pump. A deuterated analogue of the copper complex, $Cu(bpenD_2)Cl_2\cdot H_2O$, was prepared by refluxing a suspension of the non-deuterated complex in acidified (DCl) D_2O for 2 hrs.

Compounds of general formula $M_2(bpenH_2)_3(ClO_4)_4\cdot nH_2O$ were prepared by addition of a hot aqueous solution of the appropriate metal nitrate (in slight excess) to the ligand dissolved/suspended in hot water. The mixture was then stirred until all the ligand had dissolved. If necessary, a few drops of perchloric acid were added at this stage to prevent hydroxide formation. After filtration, followed by dropwise addition of a warm saturated solution of sodium perchlorate to the filtrate, fine precipitates formed slowly from the reaction solution. Several attempts were made to prepare a copper(II) perchlorate complex. However, varying metal-to-ligand ratios gave microanalyses for the products indicative of non-stoichiometric polymeric forms. $Cu(bpenH_2)(NO_3)_2$ and $Ag(bpenH_2)NO_3$ were prepared by addition of a warm ethanolic solution of the ligand to a warm aqueous solution of the corresponding nitrate salt. $Co(bpenH_2)(NCS)_2$ was prepared by addition of a warm saturated solution of potassium thiocyanate to a cobalt nitrate/$bpenH_2$ aqueous solution. The complexes were filtered off, washed well with water and/or ethanol and dried at the pump.

The deprotonated 1:1 complexes of general formula $M(bpen)\cdot nH_2O$ were prepared by the dropwise addition of sodium hydroxide to a hot aqueous solution containing the ligand and appropriate metal salt. After filtering each solid product was washed with cold water and ethanol and air-dried. No hydroxide was used in the preparation of the platinum compound, which took several months to crystallize. The Cu(II) and Ni(II) chelates had been reported earlier [5] as part of a spectral investigation on deprotonated amide coordination.

Physical Measurements and Analyses

Infra-red spectra were recorded in KBr discs on a Perkin-Elmer 580 spectrometer. Diffuse visible reflectance spectra were recorded on a Carl-Zeiss PMQII spectrophotometer with RA3 attachment and calibrated against MgO. Magnetic moments were determined at room temperature using a Model SM-12 Newport Single Temperature Gouy Balance. Thermogravimetric studies were carried out on a

TABLE II. Spectral and Magnetic Properties of $bpenH_2$ Complexes.

Complex	Appearance	λ_{max} (nm)	Magnetic Moment (B.M.)
$Ni(bpen) \cdot H_2O$	yellow needles	~400	diam.
$[Cu(bpen)H_2O]H_2O$	dk. blue–violet rhomboids	570	1.83
$Pd(bpen) \cdot 2H_2O$	pale yellow needles	–	diam.
$Pt(bpen) \cdot 4H_2O$	yellow plates	–	diam.
$Mn(bpenH_2)Cl_2 \cdot 0.5H_2O$	pale yellow microcrystals		5.98
$Fe(bpenH_2)Cl_2 \cdot 0.5H_2O$	deep red powder	480, >1000	5.25
$Co(bpenH_2)Cl_2 \cdot 2.5H_2O$	beige powder	440, >1000	4.70
$Ni(bpenH_2)Cl_2 \cdot 2.5H_2O$	blue–grey powder	585(sh), 620, 910	3.15
$Cu(bpenH_2)Cl_2 \cdot H_2O$	blue powder	720	1.99
$Zn(bpenH_2)Cl_2 \cdot 0.5H_2O$	white microcrystals	–	diam.
$Co(bpenH_2)(NCS)_2$	pale brown powder	440(sh), >1000	4.72
$Cu(bpenH_2)(NO_3)_2$	blue powder	660	1.91
$Ag(bpenH_2)NO_3 \cdot 2H_2O$	grey–white powder	–	diam.
$Mn_2(bpenH_2)_3(ClO_4)_4 \cdot 2H_2O$	pale yellow powder		5.86
$Fe_2(bpenH_2)_3(ClO_4)_4 \cdot 6H_2O$	deep red crystals	470, 850	5.25
$Co_2(bpenH_2)_3(ClO_4)_4 \cdot 5H_2O$	pink powder	495, 1060	4.78
$Ni_2(bpenH_2)_3(ClO_4)_4 \cdot 6H_2O$	blue powder	600, 975	3.17
$Zn_2(bpenH_2)_3(ClO_4)_4 \cdot 5H_2O$	white powder	–	diam.

Stanton-Redcroft Model TG-750 Thermobalance in conjunction with a direct read-out recorder. Proton NMR spectra were recorded on a Varian XL-200 spectrometer and are reported in parts per million downfield from tetramethylsilane internal standard. C, H, N, S and Cl (perchlorate) were determined in the C.S.I.R.O. Microanalytical Laboratory, Melbourne. After acid digestion Ni, Cu and Zn were determined by titration with EDTA [6], Co was determined electrogravimetrically by deposition on platinum mesh electrodes [6] and Mn was determined by the bismuthate method [6]. Pd, Pt and Ag were determined using the thermobalance. Chloride was determined potentiometrically by silver ion titration [6].

Results

Table I shows the results of elemental analyses on the complexes. Table II gives the magnetic moment, physical appearance and spectral properties of the complexes. These data are consistent with high-spin octahedral environments for each of the paramagnetic non-deprotonated complexes. The yellow deprotonated nickel(II) complex is low-spin, indicating a square-planar environment, and the geometries of the bivalent palladium and platinum analogues would be identical. The coordination geometry of $[Cu(bpen)H_2O]H_2O$ is known to be a square-based pyramid [3].

Table III shows the results of thermogravimetric studies performed on the complexes. Repeated thermograms for the Cu(II) and Zn(II) chloride complexes showed very low and varied residue weights, and varying final decomposition patterns, indicating partial sublimation. No separate weight loss attributable to hydrogen chloride was demonstrated in the thermograms of any of the chloride complexes, in contrast with those of the Ni(II) and Cu(II) complexes of $bpbH_2$ [1].

The characteristic infra-red bands of the free ligand and its metal complexes are given in Table IV. On deuteration, absorption associated with the N–H bond in the ligand is displaced markedly to lower frequencies. The amide I band, which is composed almost exclusively of $\nu_{C=O}$ [7], shows very little shift on deuteration. The relatively large difference in the ν_{N-H} (or ν_{N-D}) and amide I absorptions between the solid state and dichloromethane solution suggest that hydrogen bonding is an important factor in the solid form. The perchlorate salt of the ligand shows additional peaks in the 3200–3500 cm^{-1} region associated with N^+–H stretching, small shifts in the frequencies of the amide bands, and strong absorption around 1100 cm^{-1} due to the perchlorate ion.

Differences in the spectra of the deprotonated and non-deprotonated complexes are readily noticeable.

TABLE III. Results of Thermogravimetric Studies.

Complex	Temp. Range (°C)	Volatile Products	Wt. Loss (%)		Metal (%)	
			Calc.	Found[a]	Calc.	Found[b]
$Ni(bpen)\cdot H_2O$	95–150	H_2O	5.2	5.3		
	300–550	bpen	77.8	77.4		
		Total loss	83.0	82.7	17.0	17.3
$[Cu(bpen)H_2O]H_2O$	80–130	$2H_2O$	9.8	10.0		
	310–600	bpen	73.0	72.4		
		Total loss	82.8	82.7	17.2	17.3
$Pd(bpen)\cdot 2H_2O$	40–90	H_2O	4.4	4.5		
	105–130	H_2O	4.4	4.4		
	350–370	bpen	65.3	65.0		
		Total loss	74.1	73.9	25.9	26.1
$Pt(bpen)\cdot 4H_2O$	30–133	$4H_2O$	13.5	12.6		
		bpen	50.1	50.9		
		Total loss	63.6	63.5	36.4	36.6
$Mn(bpenH_2)Cl_2\cdot 0.5H_2O$	110–170	$0.5H_2$	2.2	1.4		
	370–800	$bpenH_2 + Cl_2$	84.2	84.4		
		Total loss	86.4	85.8	13.6	14.2
$Fe(bpenH_2)Cl_2\cdot 0.5H_2O$	50–120	$0.5H_2O$	2.2	1.5		
	290–760	$bpenH_2 + Cl_2$	84.0	83.9		
		Total loss	86.2	85.4	13.8	14.7
$Co(bpenH_2)Cl_2\cdot 2.5H_2O$	30–190	$2.5H_2O$	10.1	10.0		
	350–760	$bpenH_2 + Cl_2$	76.6	76.6		
		Total loss	86.7	86.6	13.3	13.4
$Ni(bpenH_2)Cl_2\cdot 2.5H_2O$	50–170	$2.5H_2O$	10.1	10.3		
	330–650	$bpenH_2 + Cl_2$	76.7	76.5		
		Total loss	86.8	86.8	13.2	13.2
$Cu(bpenH_2)Cl_2\cdot H_2O$[c]	85–170	H_2O	4.3	3.7	–	–
$Zn(bpenH_2)Cl_2\cdot 0.5H_2O$	70–180	$0.5H_2O$	2.2	1.9	–	–
$Mn_2(bpenH_2)_3(ClO_4)\cdot 2H_2O$	$\leqslant 200$[d]	$2H_2O$	2.7	4.1	–	–
$Fe_2(bpenH_2)_3(ClO_4)_4\cdot 6H_2O$	$\leqslant 200$[d]	$6H_2O$	7.5	7.2	–	–
$Co_2(bpenH_2)_3(ClO_4)_4\cdot 5H_2O$	$\leqslant 200$[d]	$5H_2O$	6.4	6.4	–	–
$Ni_2(bpenH_2)_3(ClO_4)_4\cdot 6H_2O$	$\leqslant 200$[d]	$6H_2O$	7.5	7.3	–	–
$Zn_2(bpenH_2)_3(ClO_4)_4\cdot 5H_2O$	$\leqslant 200$[d]	$5H_2O$	6.3	6.1	–	–
$Co(bpenH_2)(NCS)_2$	340–430	$bpenH_2$	60.7	59.1		
		HCN, H_2S	26.1	26.7		
		Total loss	86.8	85.8	13.3	14.2
$Cu(bpenH_2)(NO_3)_2$	300	decomp.	–	–	–	–
$Ag(bpenH_2)NO_3\cdot 2H_2O$	40–95	$2H_2O$	7.6	7.5	–	–
	185–550	$bpenH_2 + NO_2$	69.7	70.2		
		Total loss	77.3	77.3	22.7	22.3

[a] Final weight loss corrected for uptake of oxygen. [b] Assuming the following to be the remaining solids for the respective metals: Mn_3O_4, Co_3O_4, NiO, CuO, ZnO, Pd, AgO and Pt. [c] Above 400 °C decomposition patterns and residue weights for these compounds were not found to be reproducible, possibly due to partial sublimation. [d] All perchlorate complexes were removed from thermobalance at 200 °C to prevent possible explosion.

In the deprotonated complex absorption bands associated with the N–H bond are necessarily absent. The amide II and amide III bands, combinations of ν_{C-N} and δ_{N-H} modes [7], are replaced by a strong absorption at about 1415 cm^{-1} which may be assigned to a C–N stretching mode. This value is typical

TABLE IV. Characteristic Infra-red Bands of $bpenH_2$ and its Complexes (cm^{-1}).[a]

Compound	ν_{N-H}	Amide I[b]	Amide II[b]	Amide III[b]	Other Bands
$bpenH_2$	3300(ss)	1660(s)	1535(s)	1330(m)	π_{N-H} (Amide V)[b] 680(s,br)
$bpenD_2$	2480(mss)[c]	1655(ss)	1425(mss)	942(m)	π_{N-D} 520(m,br)
$bpenH_2$ (in CH_2Cl_2)	3400(ms)	1680(s)	1530(s)	[d]	
$bpenD_2$ (in CH_2Cl_2)	2520(ms)[c]	1675(s)	1422(ms)	[d]	
$[bpenH_4](ClO_4)_2$	3330(m), 3220(m)	1680(s)	1565(s), 1530(s)	1340(m) 1350(sh)	3500 (ν_{N^+-H}), 1150–1030[f]
$Ni(bpen)\cdot H_2O$		1640(sh), 1630(s)		1420(ms)	
$[Cu(bpen)H_2O]H_2O$		1635(s) 1620(s)		1410(s)	
$Pd(bpen)\cdot 2H_2O$		1635(sh) 1620(s)		1410(ss)	
$Pt(bpen)\cdot 4H_2O$		1645(sh), 1630(s)		1415(ms)	
$Mn(bpenH_2)Cl_2\cdot 0.5H_2O$	[e]	1645(s) 1630(ms)	1550(ms)	1340(ms)	
$Fe(bpenH_2)Cl_2\cdot 0.5H_2O$	[e]	1645(s), 1630(s)	1560(ms)	1350(ms)	
$Co(bpenH_2)Cl_2\cdot 2.5H_2O$	[e]	1630(s)	1560(ms)	1345(ms)	
$Ni(bpenH_2)Cl_2\cdot 2.5H_2O$	[e]	1630(s)	1560(ms)	1350(ms)	
$Cu(bpenH_2)Cl_2\cdot H_2O$	[e]	1620(s)	1550(ms)	1355(ms)	π_{N-H} 675(sh)
$Cu(bpenD_2)Cl_2\cdot D_2O$	2495(s,br)[c]	1620(s)	1500(s)	1115(mw)	π_{N-D}555(m,br)
$Zn(bpenH_2)Cl_2\cdot 0.5H_2O$	[e]	1655(s), 1640(s)	1545(s)	1340(ms)	
$Mn_2(bpenH_2)_3(ClO_4)_4\cdot 2H_2O$	[e]	1655(ms), 1645(sh) 1625(s)	1555(m), 1530(m)	1360(s)	1140–1060(s)[f]
$Fe_2(bpenH_2)_3(ClO_4)_4\cdot 6H_2O$	[e]	1625(s)	1560(ms)	1360(m)	1140–1080(s)[f]
$Co_2(bpenH_2)_3(ClO_4)_4\cdot 5H_2O$	[e]	1625(s)	1560(ms)	1385(m), 1360(m)	1140–1060(s)[f]
$Ni_2(bpenH_2)_3(ClO_4)_4\cdot 6H_2O$	[e]	1635(s)	1570(s)	1370(sh), 1345(ms)	1150–1080(s)[f]
$Zn_2(bpenH_2)_3(ClO_4)_4\cdot 5H_2O$	[e]	1655(sh), 1630(s)	1570(ms)	1360(m)	1140–1060(s)[f]
$Co(bpenH_2)(NCS)_2$	3240(ms)	1630(s)	1555(ms)	1340(m)	2090(s) ($\nu_{C\equiv N}$)
$Cu(bpenH_2)(NO_3)_2$	3240(m)	1630(s)	1565(ms)	obsc.	π_{N-H} 685(ms,br), 1380–1330(s) (ν_{N-O})
$Ag(bpenH_2)NO_3\cdot 2H_2O$	3340(m)	1660(s)	1535(s)	1290(ms)	π_{N-H} 680(s,br), 1390(s) (ν_{N-O})

[a] ss = strong and sharp; s = strong; mss = medium-strong and sharp; ms = medium strong; m = medium; mw = medium–weak; br = broad; sh = shoulder. [b] From reference [7]. [c] ν_{N-D}. [d] Obscured by solvent absorption. [e] Broad ν_{O-H} bands dominate this region. [f] Perchlorate ion absorption.

of deprotonated amide complexes [8]. The spectra of the non-deprotonated complexes, particularly those containing water molecules, are somewhat more complicated. The amide I absorption is again shifted to a lower frequency but the frequencies of the amide II and amide III bands increase. Identifica-

TABLE V. Results of NMR Studies on $bpenH_2$ Compounds.

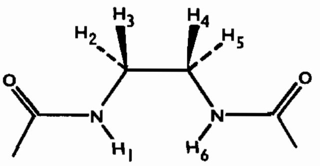
Compound	Solvent	Chemical Shifts^a					
		(amide) N–H	pyridyl protons				–CH_2–
			H_3	H_4	H_5	H_6	
$bpenH_2$	$CDCl_3$	8.46(br,s)	8.24(d)	7.87(t)	7.42–7.50(t)	8.60(d)	3.80(ct)
	DMSO	8.85(br,s)	8.04(d)	7.96(t)	7.57(t)	8.62(d)	3.55(ct)
$bpenD_2$	$CDCl_3$	–	8.30(d)	7.90(t)	7.40–7.55(t)	8.63(d)	3.80(s)
$[bpenH_4](ClO_4)_2$^{c}	DMSO	9.17(br,s)	8.1–8.4(m)		7.7–8.0(m)	8.6–8.9 (br. unres.)	3.65(ct)
$Ni(bpen)\cdot H_2O$^{e}	DMSO	–	7.67–7.60(m) (with H_5)	8.16(t)	7.67–7.60(m) (with H_3)	8.52(d)	3.22(s)
$Pd(bpen)\cdot 2H_2O$^{e}	DMSO	–	7.84(d)	8.24(t)	7.74(t)	8.72(d)	3.58(s)
$Pt(bpen)\cdot 4H_2O$^{e}	DMSO	–	7.78–7.70(m) (with H_5)	8.23(t)	7.78–7.70(m) (with H_3)	8.96(d)^d	3.60(s)^d
$Zn(bpenH_2)Cl_2\cdot 0.5H_2O$^{e}	DMSO	8.95(br.s)	8.01(m)	7.97(m)^b	7.58(m)	8.63(d)	3.52(ct)
$Zn_2(bpenH_2)_3(ClO_4)_4\cdot 5H_2O$^{e}	DMSO	9.06(br,s)	8.04(m)	7.99(m)^b	7.61(m)	8.63(d)	3.54(ct)

[a] m = multiplet; t = triplet; d = doublet; s = singlet; br = broad; ct = compound triplet (see text). All peaks due to pyridyl protons showed considerable fine splitting due to long range coupling. [b] These peaks partially overlapped in spectrum, relative positions in multiplet determined from decoupling studies. [c] An additional strong peak occurred at 10.71 ppm, assigned to (py) N^+–H. [d] These signals show additional structure due to ^{195}Pt–^1H coupling: J_{Pt-H} = 26 Hz. [e] Signal due to H_2O at 3.21 ppm.

tion of the latter two bands was facilitated by a comparison of the spectrum for the copper chloride complex with that of its deuterated analogue.

All complexes exhibit a sharp maximum in the 1590–1600 cm^{-1} region attributable to the coupled stretching modes of the pyridyl C–C and C–N bonds, which have been shown [9] to exhibit small frequency shifts and a marked intensity increase on coordination of the pyridyl-nitrogen atom. The perchlorate complexes show strong absorption around 1100 cm^{-1}, of very similar nature and frequency to that shown by the perchlorate salt of the ligand. $Co(bpenH_2)(NCS)_2$ shows a strong band at 2090 cm^{-1} attributable to the C≡N stretching mode for the N-bonded thiocyanate ion [10]. Both nitrato complexes show broad absorption around 1380 cm^{-1} due to the N–O stretching mode. The spectrum of the silver complex is almost identical to that of the ligand, with small frequency shifts and increased intensities for the bands associated with the pyridyl ring being the sole differences. Coordination through the pyridyl nitrogen atoms only is suggested, as was found for the analogous complex of $bpbH_2$ [1].

Table V summarises the results of proton magnetic resonance studies. The unusual splitting pattern observed for the methylene protons of the ligand (approximating a 2:1:2 triplet) is sensitive to loss of the amide proton; decoupling of the N–H resonance causes collapse to a singlet. The deuterated ligand, $bpenD_2$, also exhibits a singlet for the methylene protons. Computer simulation of the spectrum indicates that the pattern may best be produced assuming both free rotation about the H_2C–CH_2 and N–CH_2 bonds and the coupling constants shown in (II) below.



(II)

$J_{12} = J_{13} = J_{46} = J_{56} = 5.5$ Hz

$J_{23} = J_{45} = 13.0$ Hz

$J_{24} = J_{35} = 9.5$ Hz

The deprotonated complexes exhibit a singlet for the methylene protons, verifying removal of the protons from the amide nitrogen atoms. The spectrum of $Pt(bpen)\cdot 4H_2O$ shows ^{195}Pt–^1H coupling in the signals of both the methylene and the 6′-pyridyl hydrogen atoms, confirming a planar tetradentate coordination. For the two Zn(II) non-deprotonated

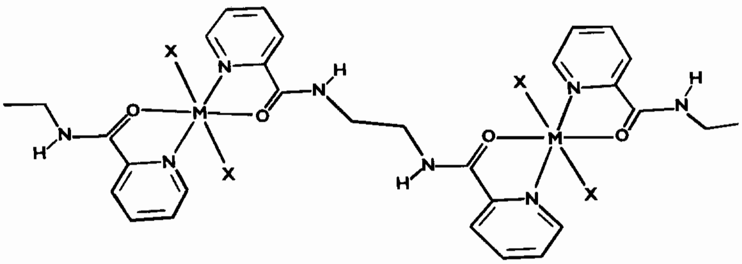


Fig. 1. Proposed *trans*-bis-bidentate bridging arrangement for 1:1 non-deprotonated complexes (X = Cl or H_2O).

complexes the appearance of a splitting pattern for the methylene protons similar to that recorded for the ligand suggests amide-O coordination with free rotation about that central ethylene link.

Discussion

The infra-red spectra of the non-deprotonated 1:1 complexes exhibit a pattern of frequency shifts previously associated with amide-O coordination of neutral amides [1, 8, 9, 11]. Thus coordination of pyridyl-N and amide-O atoms is generally concluded for the non-deprotonated chelates. This form of coordination would produce polymeric compounds allowing a considerable amount of hydrogen bonding, accounting for the low solubility of these complexes. The NMR results for the zinc chloride complex supports this hypothesis of bonding although a polymeric nature in solution is unlikely. The lower energy *anti* conformation about the ethylene link might be expected as this would also relieve steric hindrance between pyridyl groups. Although *cis* conformations about the metal ions can not be discounted, a *trans* arrangement involving bis-bidentate bridging behaviour (Fig. 1) would seem to be the more likely. The different metal-to-ligand ratios for the chloride and perchlorate complexes suggest coordination of the chloride ions in the former, as was concluded for like complexes of $bpbH_2$ [1].

The non-deprotonated 2:3 complexes formed only as the perchlorate salts. These compounds most probably exist in dimeric form with each metal atom exhibiting N_3O_3 coordination (Fig. 2). A complex hydrogen bonding scheme involving water molecules, amide protons and perchlorate anions could bind these dimeric units strongly in the crystal lattice. Similar compounds were obtained with the analogous ligand derived from 1,2-diaminocyclohexane [12].

As has been shown previously for complexes of secondary amides [1, 8, 13] the presence of both coordinated and uncoordinated amide groups in a complex is easily detected by the considerably more complicated infra-red spectrum obtained. The observation of only one sharp absorption for each amide band in the infra-red spectra of these 2:3 complexes indicates that all amide groups are coordinated, almost certainly through the oxygen atoms, with the pyridyl-N atoms completing the chelate rings. This is consistent with the proposed dimeric structure, as is the coupling of the amide and methylene protons observed in the NMR spectrum of the $[Zn_2(6bpenH_2)_3]^{4+}$ cation. This bridging arrangement is similar to that proposed by Stratton and Busch [14] for 2:3 complexes of pyridinaldazine and bis-acetylhydrazoneazine.

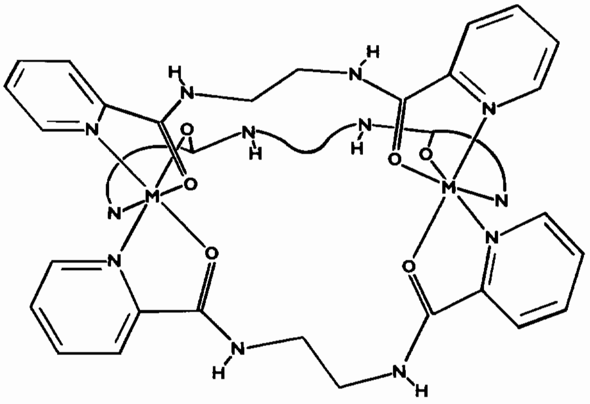


Fig. 2. Proposed dimeric arrangement for 2:3 non-deprotonated complexes. Details of third molecule have been omitted for clarity.

A strong signal at 10.71 ppm in the NMR spectrum of $[bpenH_4](ClO_4)_2$ has been assigned to a proton bonded to the pyridyl-nitrogen atom. Broadening and loss of resolution for the 6′-pyridyl hydrogen signal indicates that the adjacent pyridyl-nitrogen atom is the site of protonation rather than the amide-O or -N atoms. This effect has been found previously for pyridinium ion systems [15], and the conclusion relating to site of protonation agrees with that deduced from a potentiometric study on the ligand [16].

The deprotonated amide-nitrogen atom is a strong field ligand favouring planar coordination [17]. This is exemplified in the diamagnetic complex Ni(bpen)-H_2O, which is obviously square-planar. A similar planar N_4 arrangement is proposed for the palladium and platinum analogues; the observation of specific $^{195}Pt-^{1}H$ coupling in the NMR spectrum confirms this for the latter species. Significant differences are found for the chemical shift of the analogous protons in each complex. In particular the chemical shift of the 6′-pyridyl hydrogen atoms (H_6) occurs at higher frequencies in the order Ni < Pd < Pt, a trend observed also in the shielding of the methylene protons. These effects may be ascribed both to the different deshielding abilities of each metal and to differences in the ionic radii of the metal ions. For example, as the effective radius of the metal ion decreases, the 6′-pyridyl hydrogen atoms are brought closer to the adjacent aromatic ring and differing shielding effects may be observed [18, 19]. Close intramolecular contacts between 6′-pyridyl hydrogen atoms have been observed in the structures of the five-coordinate copper complexes previously reported [2, 3, 20, 21], and more pronounced interactions might be expected in the square-planar chelates of Ni(II), Pd(II) and Pt(II). This aspect of the structural chemistry of these chelates will receive some emphasis in future articles.

Acknowledgement

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

References

1 R. L. Chapman and R. S. Vagg, *Inorg. Chim. Acta, 33,* 227 (1979).

2 R. L. Chapman, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 43,* 29 (1980).

3 R. L. Chapman, F. S. Stephens and R. S. Vagg, *Acta Cryst., B37,* 75 (1981).

4 D. J. Barnes, R. L. Chapman, R. S. Vagg and E. C. Watton, *J. Chem. Eng. Data, 23,* 349 (1978).

5 H. Ojima, *Nippon Kagaku Zasshi, 88,* 333 (1967).

6 A. Vogel, 'Quantitative Inorganic Analysis', Longmans, 3rd Edition (1968).

7 L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules', Chapman and Hall, 3rd Edition, London (1975).

8 M. Nonoyama and K. Yamasaki, *Inorg. Chim. Acta, 5,* 124 (1971).

9 J. Bould and B. J. Brisdon, *Inorg. Chim. Acta, 19,* 159 (1976).

10 R. A. Bailey, S. L. Kozak, T. W. Michelson and W. N. Mills, *Coord. Chem. Rev., 6,* 407 (1971).

11 M. Nonoyama and K. Yamasaki, *Inorg. Chim. Acta, 3,* 585 (1969); *ibid, 7,* 373, 676 (1973).

12 M. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 53,* L91 (1981).

13 M. F. Iskander, L. El Sayad, A. F. M. Hefny and S. E. Zayan, *J. Inorg. Nucl. Chem., 38,* 2209 (1976).

14 W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc., 82,* 4834 (1960).

15 T. J. Batterham, 'NMR Spectra of Simple Heterocycles', Wiley–Interscience, New York (1973).

16 Pham D. Hung, M. Sc. (Hons.) Thesis, Macquarie University (1978).

17 H. C. Freeman, 'Inorganic Biochemistry', Vol. 1 (Ed. G. L. Eichorn), Elsevier Scientific Publishing Co., Amsterdam, p. 121 (1973).

18 R. S. Drago, 'Physical Methods in Inorganic Chemistry', Reinhold Publishing Corp., New York, p. 306 (1965).

19 R. D. Gillard and P. R. Mitchell, *J. Chem. Soc. Chem. Comm.,* 428 (1978).

20 M. Mulqi, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 51,* 9 (1981).

21 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 51,* 149 (1981).