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Studies on the Metal–Amide Bond. XIV*. The Coordination Chemistry of N-Methyl-N,N′-bis(2′-pyridinecarboxamide)-1,2-ethane; a Potentially Tetradentate Ligand Containing Both Secondary and Tertiary Amide Groups

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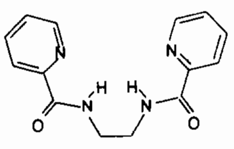
The isolation and characterization of a number of transition metal complexes of the ligand N-methyl-N,N′-bis(2′-pyridinecarboxamide)-1,2-ethane, bpenMeH, is described. Representative non-deprotonated 1:1 complexes of bivalent cobalt, nickel copper and zinc show the ligand to act as a bis-bidentate, forming five- or six-coordinate polymeric complexes involving coordination through pyridyl nitrogen and amide oxygen atoms. The complexes $Cu_2(bpenMeH)Cl_4$ *and* $Ni_2(bpenMeH)_3(ClO_4)_4 \cdot 7.5H_2O$ *also demonstrate this mode of bonding by the ligand. One complex alone, of bivalent palladium, was obtained in which coordination of the deprotonated secondary-amide nitrogen atom occurs. Coordination of the tertiary-amide nitrogen atom is not observed for any of the complexes.*

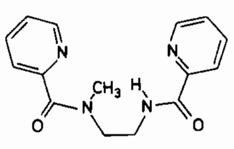
Introduction

Our previous studies [1, 2] on the coordination chemistry of the potentially tetradentate ligand N,N′-bis(2′-pyridinecarboxamide)-1,2-ethane, bpenH_2, (I), have shown that ligand to act either as a planar N_4-tetradentate when deprotonated or as a bis-bidentate in bridging metal ions through two pyridyl nitrogen and two amide oxygen atoms when in the neutral form. The mono-methylated analogue of bpenH_2, N-methyl-N,N′-bis(2′-pyridinecarboxamide)-1,2-ethane, bpenMeH, (II), now has been synthesised. In both ligands free rotation about the central ethylene linkage should minimize any steric interactions between the two picolinamide groups.



bpenH_2

(I)



bpenMeH

(II)

The non-deprotonated metal complexes of the two homologues should have similar structures, but for bpenMeH to act, like bpenH_2, as an N_4-tetradentate on deprotonation the methyl-substituted amide nitrogen atom would necessarily have a tetrahedral (sp^3) configuration. Such a geometry has not been observed previously, although considerable pyramidal distortions in deprotonated amide nitrogen atoms have been reported in similar chelates [3–5]. A loss of delocalization energy of 75–88 kJ/mol [6] would result from such a mode of coordination.

This investigation has been undertaken to study the effect of such substitution on the coordinating ability of the amide group, and in particular to determine whether coordination of a tertiary amide nitrogen atom may be enforced through a multidentate effect.

Experimental

Physical measurements and analysis procedures were identical to those outlined previously [2].

Ligand Synthesis

To a warm solution of 2-pyridinecarboxylic acid (49.2 g, 0.4 mol) in pyridine (160 ml) was added triphenylphosphite (124 g, 0.4 mol) and the mixture was heated for 10 minutes. N-Methyl-1,2-diaminoethane (14.8 g, 0.2 mol) in pyridine (40 ml) was then added dropwise with continuous stirring. The mixture was heated on a steam-bath for 5 hr. After volume reduction and cooling the resultant yellow oil was taken up in chloroform (30 ml) and washed several times with water (30 ml aliquots), then with a saturated solution of sodium bicarbonate

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*Part XIII, F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 57,* 43 (1982).

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TABLE I. Analyses of bpenMeH Complexes.

Complex	Found (%)					Required (%)				
	C	H	N	Metal	H_2O^a	C	H	N	Metal	H_2O
$Cu(bpenMeH)Br_2 \cdot 0.5H_2O$	34.4	3.2	10.9	12.1	1.5	34.8	3.3	10.8	12.3	1.7
$Cu(bpenMeH)(NO_3)_2$	38.1	3.6	17.9	13.3	–	38.2	3.4	17.8	13.5	–
$Cu(bpenMeH)(ClO_4)_2$	33.2	3.1	10.3	11.3	13.3[b]	32.9	2.9	10.3	11.6	13.0[b]
$Cu_2(bpenMeH)Cl_4$	33.3	3.3	10.2	23.3	–	32.6	2.9	10.1	23.0	–
$Ni(bpenMeH)Cl_2 \cdot 3H_2O$	38.5	4.8	11.4	12.8	11.5	38.5	4.7	11.9	12.6	11.5
$Ni(bpenMeH)Br_2 \cdot 4H_2O$	31.2	3.8	9.8	10.6	12.0	31.3	4.1	9.7	10.2	12.6
$Ni(bpenMeH)(NO_3)_2 \cdot 2H_2O$	36.0	4.2	16.5	11.6	7.0	35.8	4.0	16.7	11.7	7.2
$Ni_2(bpenMeH)_3(ClO_4)_4 \cdot 7.5H_2O$	35.5	3.8	11.6	8.1	8.1	35.9	4.2	11.2	7.8	9.0
$Co(bpenMeH)Br_2 \cdot 4H_2O$	30.9	3.6	9.6	10.4	11.8	31.3	4.2	9.7	10.2	12.5
$Co(bpenMeH)(NO_3)_2 \cdot 1.5H_2O$	36.3	3.8	16.6	11.7	6.5	36.4	3.8	17.0	11.9	5.5
$Zn(bpenMeH)Br_2 \cdot 3H_2O$	32.0	3.3	9.6	12.0	3.0	31.9	3.9	9.9	11.6	3.2[c]
$Zn(bpenMeH)I_2 \cdot 2H_2O$	28.0	2.9	8.2	10.1	5.0	28.1	3.1	8.7	10.2	5.6
$Zn(bpenMeH)(NO_3)_2 \cdot 1.5H_2O$	35.9	3.6	16.9	13.0	4.8	36.0	3.8	16.8	13.1	5.4
$Zn(bpenMeH)(ClO_4)_2$	32.5	3.3	10.5	11.5	12.5[b]	32.8	2.9	10.2	11.9	12.9[b]
Pd(bpenMe)Cl	42.4	3.5	13.1	25.2	–	42.2	3.7	13.1	25.0	–

[a] Determined by the thermogravimetric analysis on a Stanton-Redcroft TG-750 instrument. [b] Elemental Cl analysis values. [c] After initial loss of 1 mol of water of hydration decomposition patterns suggest sublimation of the dihydrate residue.

(20 ml aliquots), and finally again with water (30 ml aliquots). After volume reduction and cooling absolute ethanol (5–10 ml) was added followed by dropwise addition of dry diethyl-ether to yield an off-white solid (28.4 g, 50%). This was recrystallized from ethanol to give white needles [m.p. 115–117 °C. *Anal.* Found: C, 63.3; H, 5.7; N, 20.1%. Calcd. for $C_{15}H_{16}N_4O_2$: C, 63.4; H, 5.6; N, 19.7%. Mass spectrum: m/e (parent) 284].

Preparation of Complexes

Complexes of general formula $Cu(bpenMeH)X_2 \cdot nH_2O$ (where X = Br, n = 0.5, and X = NO_3, ClO_4, n = 0) were prepared by mixing a hot solution of the ligand in n-butanol with a hot equimolar ethanolic solution of the appropriate hydrated copper(II) salt. A chloride 2:1-complex, $Cu_2(bpenMeH)Cl_4$, formed also from an equimolar reaction mixture.

Complexes of general form $Ni(bpenMeH)X_2 \cdot nH_2O$ (where X = Cl, n = 3; X = Br, n = 4; and X = NO_3, n = 2) were prepared in a similar manner to the Cu(II) complexes using the appropriate hydrated nickel(II) salts. The use of nickel perchlorate hexahydrate under like conditions yielded the compound $Ni_2(bpenMeH)_2(ClO_4)_4 \cdot 7.5H_2O$.

The compounds $Co(bpenMeH)Br_2 \cdot 4H_2O$ and $Co(bpenMeH)(NO_3)_2 \cdot 1.5H_2O$ were prepared by adding a hot ethanolic solution of the hydrated salts of cobalt(II) bromide or nitrate to a hot equimolar solution of the ligand in n-butanol. Complexes of the form $Zn(bpenMeH)X_2 \cdot nH_2O$ (where X = Br, n = 3; X = I, n = 2, X = NO_3, n = 1.5 and X = ClO_4, n = 0) were prepared by a method similar to the Cu(II) and Ni(II) analogues described above using the appropriate bivalent zinc salt.

The solid products, which generally formed immediately, were filtered off and washed with a minimum of absolute ethanol and dried under vacuum.

The deprotonated palladium complex, [Pd(bpenMe)Cl], was prepared by mixing a hot solution of the ligand in chloroform with a warm aqueous solution of K_2PdCl_4 in slight excess. The warm mixture was stirred continuously for several hours with chloroform being added from time to time to compensate for evaporation. The chloroform layer was then separated and the volume reduced on a steam-bath. After cooling diethyl ether was added dropwise with stirring until a yellow precipitate formed. This was filtered off and re-crystallized from a chloroform/ethanol (2:1) mixture to yield yellow-orange crystals.

Several attempts to isolate other deprotonated complexes of this ligand from aqueous solutions were unsuccessful.

Results

The analytical data for the complexes prepared are given in Table I. Table II gives the magnetic moments, appearance, and spectral properties of the

TABLE II. Spectral and Magnetic Properties of bpenMeH Complexes.

Complex	Appearance	Magnetic Moment (B.M.)	λ_{max} (nm)
Cu(bpenMeH)$Br_2 \cdot 0.5H_2O$	pale green	2.00	700
Cu(bpenMeH)$(NO_3)_2$	blue	2.05	660
Cu(bpenMeH)$(ClO_4)_2$	pale blue	1.98	640
Cu_2(bpenMeH)Cl_4	green	1.81	800
Ni(bpenMeH)$Cl_2 \cdot 3H_2O$	pale blue	3.42	925, 640, 570(sh)[a]
Ni(bpenMeH)$Br_2 \cdot 4H_2O$	pale blue	3.38	900, 640, 570(sh)
Ni(bpenMeH)$(NO_3)_2 \cdot 2H_2O$	pale blue	3.23	900, 640, 570(sh)
Ni_2(bpenMeH)$_3(ClO_4)_4 \cdot 7.5H_2O$	pale blue	3.16	995, 620
Co(bpenMeH)$Br_2 \cdot 4H_2O$	pink	4.82	700, 480(sh), <400
Co(bpenMeH)$(NO_3)_2 \cdot 1.5H_2O$	pink	4.69	
Zn(bpenMeH)$Br_2 \cdot 3H_2O$	white	diam.	
Zn(bpenMeH)$I_2 \cdot 2H_2O$	yellow	diam.	
Zn(bpenMeH)$(NO_3)_2 \cdot 1.5H_2O$	white	diam.	
Zn(bpenMeH)$(ClO_4)_2$	white	diam.	
[Pd(bpenMe)Cl]	yellow-orange	diam.	

[a] sh = shoulder.

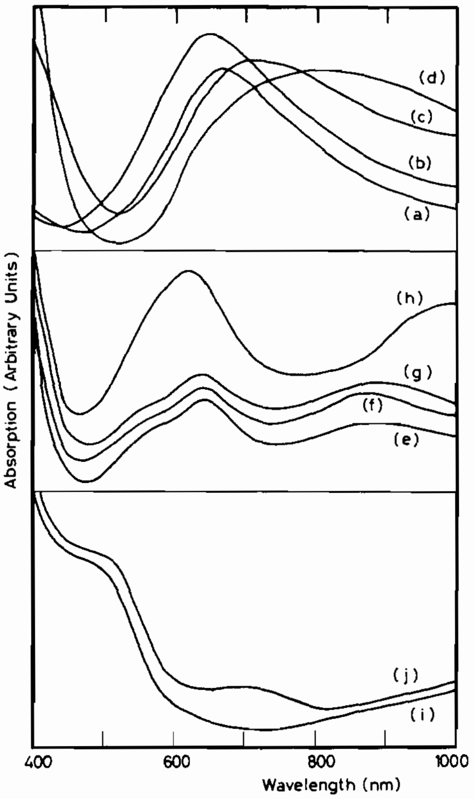


Fig. 1. Diffuse reflectance spectra of bpenMeH complexes. (a) Cu(bpenMeH)$(NO_3)_2$; (b) Cu(bpenMeH)$(ClO_4)_2$; (c) Cu(bpenMeH)$Br_2 \cdot 0.5H_2O$; (d) Cu_2(bpenMeH)Cl_4; (e) Ni(bpenMeH)$Cl_2 \cdot 3H_2O$; (f) Ni(bpenMeH)$(NO_3)_2 \cdot 2H_2O$; (g) Ni(bpenMeH)$Br_2 \cdot 4H_2O$; (h) Ni_2(bpenMeH)$_3(ClO_4)_4 \cdot 7.5H_2O$; (i) Co(bpenMeH)$(NO_3)_2 \cdot 1.5H_2O$; (j) Co(bpenMeH)$Br_2 \cdot 4.5H_2O$.

complexes. The reflectance spectra of the paramagnetic complexes in the range 400–1000 nm are shown in Fig. 1.

The complexes of copper, nickel and cobalt each have magnetic moments and spectral features typical of the spin-free forms. The reflectance spectra of the copper complexes are characteristic of distorted octahedral copper(II) and the band positions are observed to be anion dependent. The spectra of the nickel complexes show two bands around 900 and 640 nm which are typical of octahedral Ni(II) complexes. The two cobalt complexes show differing spectra. The bromide complex has maxima at 480 and 700 nm, whilst in the spectrum of the nitrate complex the latter band is not observed, inferring coordination of the bromide ion in the solid state. The solution spectra of these complexes were not obtained due to their lack of solubility in suitable solvents.

Thermogravimetric studies show the halide complexes of copper and zinc to undergo sublimation after loss of water of hydration. The thermograph of Zn(bpenMeH)$Br_2 \cdot 2H_2O$ shows an initial loss of one water molecule but the pattern of subsequent weight loss was not reproducible. Sublimation of these halides complexes was confirmed by the observation of a condensed sublimate at the outlet of the furnace after each run. Like sublimation processes have been observed previously with complexes of similar ligands [2, 7].

The characteristic infrared bands of the ligand and its complexes are given in Table III together with tentative assignments. The spectrum of the free

TABLE III. Characteristic Infrared Bands with Tentative Assignments.^{a}

Compound	ν(N–H)	Amide I^b	Amide II^b	δ(NCO)^c	Py Ring^d	Other Bands
bpenMeH	3320(ss)	1663(ss) 1620(ss)	1540(s)	740(s)	618(s)	
Cu(bpenMeH)Br$_2$·0.5H$_2$O	e	1632(s) 1604(s)	1585(s)	760(s)	660(s)	
Cu(bpenMeH)(NO$_3$)$_2$	f	1635(ss) 1608(ms)	1587(ms)	760(s)	660(ms)	1380(br) ν(N–O)
Cu(bpenMeH)(ClO$_4$)$_2$	3320(ms)	1630(s) 1600(ms)	1580(ms)	750(s)	655(s)	1100(br)^g
Cu$_2$(bpenMeH)Cl$_4$	f	1628(ss) 1600(s)	1585(ms)	760(ss)	650(s)	
Ni(bpenMeH)Cl$_2$·3H$_2$O	e	1632(s) 1600(ms)	1572(s)	765(s)	650(s)	
Ni(bpenMeH)Br$_2$·4H$_2$O	e	1630(s) 1600(ms)	1570(s)	765(s)	650(w)	
Ni(bpenMeH)(NO$_3$)$_2$·2H$_2$O	e	1632(s) 1600(ms)	1572(s)	765(s)	650(w)	1380(br) ν(N–O)
Ni$_2$(bpenMeH)$_3$(ClO$_4$)$_4$·7.5H$_2$O	e	1635(s) 1595(ms)	1570(ms)	758(s)	630(s)	1100(br)^g
Co(bpenMeH)Br$_2$·4H$_2$O	e	1630(s) 1600(s)	1570(s)	760(s)	648(w)	
Co(bpenMeH)(NO$_3$)$_2$·1.5H$_2$O	e	1632(s) 1600(s)	1572(s)	760(s)	645(w)	1380(br) ν(N–O)
Zn(bpenMeH)Br$_2$·3H$_2$O	e	1640(s) 1600(s)	1570(s)	755(ss)	650(s)	
Zn(bpenMeH)I$_2$·2H$_2$O	e	1640(s) 1600(s)	1570(ms)	755(s)	645(w)	
Zn(bpenMeH)(NO$_3$)$_2$·1.5H$_2$O	e	1640(s) 1600(s)	1572(ss)	752(s)	650(ms)	1380(br) ν(N–O)
Zn(bpenMeH)(ClO$_4$)$_2$	3325(ms)	1650(s) 1600(s)	1572(s)	760(s)	650(w) 625(ss)	1100(br)^g
[Pd(bpenMe)Cl]		1630(s) 1595(s)		760(s)	665(w)	1395(s) ν(C–N)

^{a}ss = strong and sharp; s = strong; ms = medium strong; br = broad; w = weak. ^{b}From refernece [8]. ^{c}From reference [9]. ^{d}Pyridine ring in-plane deformation [10, 11]. ^{e}Broad ν(O–H) bands dominate this region. ^{f}Broad band due to H-bonding. ^{g}Ionic perchlorate absorption.

ligand shows a strong band at 3200 cm^{-1} attributable to ν(N–H). The anhydrous copper nitrate and chloride complexes show this band to be broadened suggesting the presence of hydrogen-bonding involving the anion. In the palladium complex this band disappears with deprotonation, and in the non-deprotonated hydrated complexes it is obscured by broad ν(O–H) absorption in this region.

Since bpenMeH has both a secondary and a tertiary amide group it shows two separate strong absorption maxima at 1663 and 1620 cm^{-1} assignable as Amide I absorption [8]. In the metal complexes both of these bands shift to lower frequencies, whilst the Amide II absorption at 1540 cm^{-1} shifts to higher frequencies on coordination. The deprotonated Pd complex shows a strong band at 1395 cm^{-1} assignable to pure ν(C–N) [12]. The band at 618 cm^{-1} in the free ligand, attributable to the deformation of the pyridine ring, shifts to higher frequency in all complexes indicating coordination of each of the pyridine nitrogen atoms. The nitrate complexes exhibit broad absorption centred at 1380 cm^{-1} attributable to ν(N–O) [13]. All perchlorate complexes have strong absorption at 1100 cm^{-1} due to the presence of ionic perchlorate.

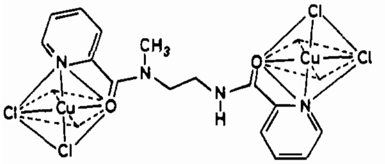
Discussion

It has been shown [6, 14] that free peptide or amide groups are invariably planar due to resonance stabilization. Hence coordination of an N,N-disubstituted (*i.e.* tertiary) amide nitrogen atom would cause loss of this stability with a change to tetrahedral geometry. In the non-deprotonated complexes both the secondary and the tertiary amide nitrogen atoms of bpenMeH obviously remain uncoordinated. Thus a bis-bidentate function of this ligand via the pyridine nitrogen and amide oxygen atoms would be favoured both on geometric and energetic grounds. Again this was concluded for the 1:1 non-deprotonated complexes of $bpchH_2$ [15], $bpbH_2$ [16] and the unsubstituted analogue $bpenH_2$ [2]. A *gauche* or *anti*-configuration of the two picolinamide units with respect to the ethane linkage is possible due to rotation about the central C–C bond, the latter arrangement being the more probable as it would minimize steric interactions both between the pyridine rings and between the amide-N substituents.

The characteristic shifts of the infrared amide bands for these complexes are similar to those reported for complexes of N-methyl derivatives of pyridine-2-carboxamide [10], N-substituted picolinamides [17], pyridine-2-acetamide [18], 2-[(N-acetyl)-amino]pyridine [19] and of pyrazine-2,3-dicarboxamide [20] for which amide oxygen coordination was proposed in each case.

It is interesting that although with this ligand the perchlorate complexes of copper and zinc are obtained as 1:1 forms, a 2:3 nickel complex was isolated. The structure of this latter complex is most likely dimeric and similar to like complexes of $bpenH_2$ [2] and $bpchH_2$ [15] in which octahedrally coordinated metal ions, each with N_3O_3 coordination, was proposed. The compound's visible and infrared spectral features closely parallel those of the unsubstituted-ligand complexes.

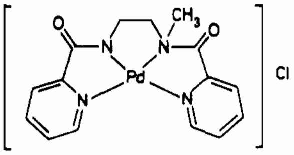
In the complex $Cu_2(bpenMeH)Cl_4$ the ligand is most probably acting as a bis-bidentate, as shown in (III), with five- or six-coordination being completed by bridging chloride ions or amide oxygen atoms. The infrared spectrum of this complex shows a broadening of the ν(N–H) absorption which could be due to intermolecular hydrogen bonding involving the chloride ions. An alternative formulation involving a chlorocuprate anionic species does not appear to be consistent with the visible spectrum of this complex.



(III)

Divalent palladium is most effective in inducing ionization of amide protons [21]. The palladium complex of bpenMeH was the only deprotonated complex isolated. From a potentiometric study on the unsubstituted ligand $bpenH_2$ and its metal complexes [22], a very high proton dissociation constant was observed for palladium compared with the copper and nickel chelates. Similar results have been obtained with peptide complexes of palladium(II) [23]. These low pK_a values were interpreted as being due to the relatively high stability of the square-planar deprotonated palladium complex and the high affinity of Pd(II) for nitrogen donor ligands.

This compound is of particular interest in that coordination of both pyridine nitrogen atoms and one deprotonated amide nitrogen, as indicated by its infrared spectrum, may result in the enforced coordination of the N-methylated amide nitrogen atom also, as shown in (IV) below. However, the appearance of a strong infrared absorption band at 370 cm^{-1} may be consistent with Pd–Cl bonding [8, 11]. The molecular structure of this complex has been investigated in detail by X-ray diffraction and high-resolution proton magnetic resonance methods. The results of that investigation are reported in the following article in this issue [24].



(IV)

A comparison of the chelating ability of bpenMeH with its unsubstituted analogue $bpenH_2$ [2] demonstrates the effect of methyl-substitution. In the non-deprotonated forms like complexes involving amide-oxygen coordination are obtained, and their thermal and magnetic properties and infrared and visible spectral features are closely comparable. Alkyl-substitution, however, obviously has a marked effect on the ability of these ligands to act as linear N_4-tetradentates, and complexes of bpenMeH involving this coordination mode were not obtained. The coordination chemistries of some bis-picolinamide ligands in which both amide nitrogen atoms are substituted have been investigated also. Details will be given in papers to follow.

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