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Nickel(II), Cobalt(II), Cobalt(III) and Copper(II) Complexes of N-(2-picolyl)- and N-2-(2'-pyridyl)ethyl-picolinamides

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Received July 8, 1970

N-(2-picolyl)picolinamide(pmpH) and N-2-(2′-pyridyl) ethylpicolinamide(pepH) were synthesized and their complexes with nickel(II), cobalt(II), and copper(II) studied. The amide-hydrogen of pmpH disosciates readily in the presence of transition metal ions, and deprotonated pmp coordinates through the amide-nitrogen atom to metals. The dissociation of the amide-hydrogen of pepH is more difficult than that of pmpH and only in alkaline medium are complexes like Cu(pep)Cl and $Co(pep)_2ClO_4 2/3H_2O$ *formed. The ligand pepH in the complexes* $M(pep)_2X_2$ *coordinates through the amide-ozygen atom. Copper perchlorate forms complexes in which both deprotonated pep (or pmp), and protonated pepH (or pmpH) are present as ligands.*

Introduction

Metal complexes with several heterocyclic terdentate Schiff bases and hydrazones recently have been reported.[1-4] The present authors who previously studied the metal complexes of picolinamide,[5,6] N-methyl- and N,N-dimethyl-picolinamides,[7] attempted in the present investigation to study the effects of substituents on the amide nitrogen atom and also the difference of coordinating power between acid amides and Schiff bases or hydrazones. The ligands studied in the present investigation are N-(2-picolyl)-picolinamide (abbreviated as pmpH) and N-2-(2′-pyridyl)ethylpicolinamide (abbreviated as pepH) which have the following structures similar to the Schiff bases and hydrazones (Figure 1). The abbreviations pmpH and pepH are used throughout the present paper.

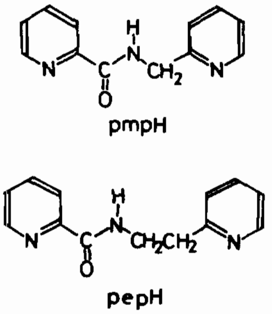

Figure 1. The Ligands.

The ligand pmpH coordinates to a metal mainly by deprotonation of the amide-hydrogen, forming two five-membered chelate rings, whereas pepH behaves either as a neutral or as a deprotonated anionic ligand. The deprotonated pep acts as a terdentate ligand and forms five- and sixmembered chelate rings. Two possible types of chelate formation of these ligands, N,N,N-, and N,O- coordination, are shown in Figure 2.

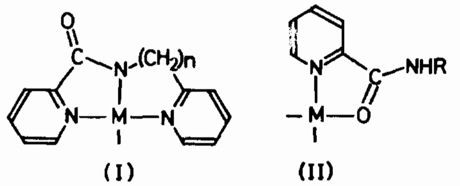

Figure 2. Coordination modes of the ligands.

Experimental Section

1. *Syntheses of the ligands.* (a) N–(2–picolyl)picolinamide. A mixture of methyl picolinate (12.6 g) and 2–picolylamine (10.0 g) was refluxed for four hours and then distilled under reduced pressure. The yield was 15.5 g. The amide is a yellow liquid which boils at 206-208 °C/8.5 mmHg and solidifies on standing. The pictrate melts at 192-193 °C. Calcd. for the picrate, $C_{18}N_6H_{14}O_8$: C, 48.88; H, 3.19; N, 19.00%. Found: C, 48.08, H, 3.14; N, 18.80%.

(b) N–2–(2′–pyridyl)ethylpicolinamide. A mixture of methyl picolinate (10.0 g) and 2–(2′–pyridyl)ethylamine (9.0 g) was refluxed for five hours and then distilled under reduced pressure. The amide is a slightly yellow liquid and boils at 223-226 °C/11.5 mmHg. The yield was 13.0 g. The picrate melts at 186.5-187.5 °C. Calcd. for the picrate, $C_{19}N_6H_{16}O_8$: C, 50.01; H, 3.53; N, 18.41%. Found: C, 49.17; H, 3.70; N, 18.30%.

2. *Preparation of the complexes.* Complexes were prepared by the reaction of stoicheiometric amounts of the ligand and an appropriate metal salt. The com-

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plexes were precipitated immediately after mixing or crystallized upon evaporation on a water bath. The preparative methods are divided into A, B, and C according to the solvent used. In method A, an ethanol solution of the ligand mixed with an aqueous solution of the metal salt, and in method B, ethanol solutions of both the ligand and the metal salt, were mixed. In method C, the same procedure as method A was used

Table I. Analytical data of the complexes.

Complex	Color	Prep. method	Analytical results (Calculated values in parentheses) Metal %	C %	H %	N %	Others %
$Co^{III}(pmp)_2ClO_4$	dark red	C	10.01(10.11)	49.12(49.46)	3.60(3.46)	14.62(14.42)	
$Co^{III}(pep)_2ClO_4 2/3H_2O$	dark red	C	9.42(9.46)	49.72(50.13)	4.22(4.10)	13.41(13.49)	H_2O: 1.91(1.93)
$Co(pepH)Cl_2\tfrac{1}{2}HCl$	blue	B	15.71(15.70)	41.54(41.60)	3.86(3.63)	11.18(11.20)	Cl: 23.34(23.61)
$Co(pepH)_2Cl_2$	red	B	10.15(10.09)	53.18(53.44)	4.47(4.49)	14.15(14.38)	
$Co(pepH)_2(NCS)_2$	red	B	9.25(9.36)	53.34(53.41)	4.54(4.16)	17.30(17.80)	
$Co(pepH)_2(ClO_4)_2 2H_2O$	orange	A	7.89(7.88)	41.14(41.73)	4.30(4.04)	11.19(11.23)	H_2O: 4.91(4.81)
$Ni(pmp)(NCO)H_2O$	orange	A	17.51(17.74)	47.43(47.18)	3.71(3.65)	16.71(16.93)	H_2O: 5.00(5.44)
$Ni(pmp)(NCS)1\tfrac{1}{2}H_2O$	orange	A	16.59(16.49)	43.93(43.86)	3.91(3.68)	15.96(15.74)	H_2O: 7.08(7.59)
$Ni(pmp)Cl$	yellowish brown	B	19.20(19.16)	46.88(47.04)	3.51(3.29)	13.58(13.71)	
$Ni(pmp)Br\tfrac{1}{2}HBr$	green	B	15.05(15.00)	36.75(36.83)	3.04(2.71)	10.61(10.74)	Br: 30.52(30.63)
$Ni(pmp)_2 6H_2O$	gray	C	9.84(9.93)	49.24(48.75)	5.63(5.46)	14.43(14.21)	H_2O: 18.45(18.28)
$Ni(pmpH)_2(NO_3)_2 2H_2O$	blue	B	8.08(7.99)	38.97(39.21)	3.47(3.29)	18.74(19.05)	
$Ni(pepH)_2Br_2 3H_2O$	blue	B	8.11(8.08)	42.96(42.95)	4.58(4.44)	11.33(11.56)	H_2O: 7.55(7.43)
$Ni(pepH)_2(NCS)_2$	blue	B	9.12(9.33)	53.45(53.43)	4.32(4.16)	17.04(17.80)	
$Cu(pmp)Cl$	blue	A	20.38(20.42)	46.14(46.31)	3.59(3.24)	13.38(13.50)	
$Cu(pmpH)_2(ClO_4)_2$	blue	A	9.19(9.22)	41.83(41.84)	3.60(3.22)	11.56(12.20)	
$Cu(pep)Cl$	blue	A	19.53(19.54)	48.08(48.01)	3.83(3.72)	12.43(12.92)	
$Cu(pep)_2HClO_4 2H_2O$	blue	C	9.73(9.74)	47.90(48.01)	4.52(4.48)	12.54(12.88)	H_2O: 5.89(5.52)
$Cu(pepH)_2(ClO_4)_2 2HClO_4$	blue	A	6.96(6.92)	34.27(34.07)	3.27(3.07)	9.71(9.15)	

Table II. Characteristic amide bands of the ligands and the complexes(in cm^{-1})

Compound	ν_{N-H}	Amide II	Amide I	$\nu_{C=O}$*	ν_{C-N}*
pmpH	3378	1666	1517		
pepH	3378	1664	1525		
$Co^{III}(pmp)_2ClO_4$				1641	1398
$Co^{III}(pep)_2ClO_4 2/3H_2O$				1635	1389
$Co(pepH)_2(NCS)_2$	3228	1632	1556		
$Co(pepH)Cl_2\tfrac{1}{2}HCl$	3160	1633	1554		
$Ni(pmp)(NCS)1\tfrac{1}{2}H_2O$				1630	1402
$Ni(pmp)(NCO)H_2O$				1637	1413
$Ni(pmpH)_2(NO_3)_2 2HNO_3$	3180	1635	1551		
$Cu(pmp)Cl$				1642	1400
$Cu(pep)Cl$				1618	1394 1382
$Cu(pmpH)_2(ClO_4)_2$**	3300	1647	1546	1626	1413
$Cu(pep)_2HClO_4 2H_2O$**	3276	1648	1564	1623	1399
$Cu(pepH)_2(ClO_4)_2 2HClO_4$	3280	1633	1560		
$Cu(pepD)_2(ClO_4)_2 2DClO_4$	2440	1632	1508		

* These bands are of a deprotonated amdie group. ** These complexes should be formulated as $Cu(pmp)(pmpH)ClO_4HClO_4$ and $Cu(pep)(pepH)ClO_4 2H_2O$, respectively.

Table III. Magnetic moments and electronic spectra of the cobalt(III), cobalt(II) and copper(II) complexes

Complex	μ_{eff} (20°C) B.M.	State*	Electronic spectrum Absorption max. in 10^3cm^{-1} (logε)**				
$Co^{III}(pmp)_2ClO_4$	diamag.	aq.	31.3(3.66)	25.5sh(2.4)	20.4(2.68)	13.2(0.51)	
$Co^{III}(pep)_2ClO_4 2/3H_2O$	diamag.	aq.	31.5sh(3.6)	24.9(2.26)	19.5(2.36)	12.3(0.26)	
$Co(pepH)_2(NCS)_2$	4 74	refl.	21sh	19.6	17sh	8.7	
		MeOH	20.7sh(1.4)	19.3(1.60)	16sh(0.7)	10sh(0.6)	8.8(0.84)
$Co(pepH)_2(ClO_4)_2 2H_2O$	4.59	refl.	22.0	18sh	9.2		
$Co(pepH)Cl_2\tfrac{1}{2}HCl$	4.64	refl.	20.5	19.2	16.6	15.4	8.2sh
		DMF	19sh(1.1)	16.5(2.39)	14.9(2.59)	7.4(1.20)	
$Cu(pmp)Cl$	1.88	refl.	15.6				
$Cu(pep)Cl$	1.86	refl.	15.7				
$Cu(pmpH)_2(ClO_4)_2$	1.82	refl.	17.4	14sh			
$Cu(pep)_2HClO_4 2H_2O$	1.85	refl.	16.9	13sh			
$Cu(pepH)_2(ClO_4)_2 2HClO_4$	1.87	refl.	15.9				

* aq = aqueous solution, MeOH = methanol solution, DMF = dimethylformamide solution, refl. = diffuse reflectance spectrum.
** ε = molar extinction coefficient.

with the addition of an equivalent amount of sodium hydroxide. The cobalt(III) complexes were prepared by the aerial oxidation of a mixed solution of the ligand and a cobalt(II) salt after the addition of sodium hyroxide. The analytical results of the complexes prepared are presented in Table I.

3. *Measurements.* Apparatus used for the measurement of infrared and electronic spectra, and magnetic moments, was the same as reported in the previous paper.[7]

Results and Discussion

1. *Cobalt(III) complexes.* The infrared spectra of $Co(pmp)_2ClO_4$ and $Co(pep)_2ClO_4 2/3H_2O$ lacked the N–H stretching vibrations, indicating loss of the hydrogen atoms on the amide group (Table II). In these complexes all the pyridine-nitrogen atoms are coordinated to the metal and their magnetic and absorption spectral data are listed in Table III. If only the coordinating nitrogen atoms are considered, the symmetry of the complex may be O_h, but this is not the cases, because the ligand forms two pucekred chelate rings. The symmetry of the complex may better be represented by D_{4h}, *i.e.* *trans* coordination of two amide-nitrogen atoms of the ligands, and the low-intensity band at *ca.* 13×10^3 cm^{-1} was assigned to the spin-forbidden transition and the next two bands at *ca.* 20 and 25×10^3 cm^{-1} to the transitions from $^1A_{1g}$ to $^1A_{1g}$, and to $^1E_{1g}$, respectively.[8] No band corresponding to the transitions from $^1A_{1g}$ to $^1B_{2g}$ and ^1E_g ($^1T_{2g}$) has been found, probably because they overlap an intense band at *ca.* 31×10^3 cm^{-1} which may possibly be a charge transfer absorption. A comparison of the electronic spectra of these two complexes reveals that the deprotonated ligand, pmp, has a stronger ligand field than pep, and that the five-membered chelate ring is more stable than the six-membered one (Figure 2-I).

2. *Cobalt(II) complexes.* The complexes, $Co(pepH)_2(NCS)_2$ and $Co(pepH)_2(ClO_4)_2 2H_2O$ were prepared in ethanol, and in water respectively. $Co(pepH)_2Cl_2$ was also prepared in addition to these two complexes. The diffuse reflectance spectrum of $Co(pepH)_2(NCS)_2$ resembled those of $Co(piaH)_2(NCS)_2$ and $Co(mepiaH)_2(NCS)_2$, where piaH and mepiaH denote picolinamide and N-methylpicolinamide, respectively.[7] Therefore they presumably have structures similar to those of picolinamide complexes determined by X-ray.[9] Their presumed structures are consistent with the infrared spectral data of amide groups as well (Table II). The nitrogen coordination of NCS ion is indicated by the infrared bands, $\nu_{N\equiv C}=2075$, 2090sh, $\nu_{C-S}=807$ and $\delta_{NCS}=474$ cm^{-1}. The absorption spectrum of $Co(pepH)_2(NCS)_2$ in methanol resembled that of an octahedral cobalt(II) complex (Figure 3 and Table III), and the bands at 8.8×10^3 and $19.3\times{}^3$ cm^{-1} may be assigned to the transition, $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$, and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$, respectively, and the two shoulders at 10 and 16×10^3 cm^{-1} to the spin-forbidden, or two electron, transitions.[10] In $Co(pepH)_2(ClO_4)_2 2H_2O$, water molecules are presumed to be coordinated to cobalt, because the electronic spectrum is quite similar to that of $[Co(mepiaH)_2(H_2O)_2]^{2+}$,[7] in which two water molecules are in the trans positions, above and below the plane of two mepiaH ligands.

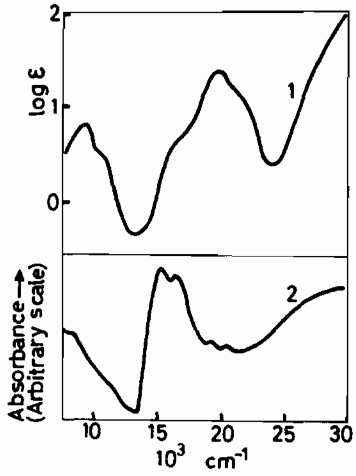

Figure 3. Electronic spectra of cobalt(II) complexes: (1) Absorpion spectrum of $Co(pepH)_2(NCS)_2$ in methanol; (2) Diffuse reflectance spectrum of $Co(pepH)Cl_2 \frac{1}{2}HCl$.

In the preparation of the chloride complex, if cobalt chloride was added in excess, a blue complex $Co(pepH)Cl_2 \frac{1}{2}HCl$ was precipitated. The diffuse reflectance spectrum in the solid state and the absorption spectrum in dimethylformamide of this blue 1:1 complex indicate a tetrahedral cobalt(II) complex,[10] furthermore, the infrared spectrum showed that the amide-oxygen is coordinated to the metal, because the amide I and amide II bands shifted as shown in Table II. Two Co–Cl stretching bands, at 301 and 281 cm^{-1}, appear in the far infrared region as expected for the C_{2v} configuration from group theory. Based on these data the structure of $Co(pepH)Cl_2 \frac{1}{2}HCl$ is assigned as tetrahedral. In all the cobalt(II) complexes the mode of cordination of pepH may be as in Figure 2-II.

3. *Nickel(II) complexes.* Diamagnetic complexes, $Ni(pmp)(NCS)1\frac{1}{2}H_2O$, $Ni(pmp)(NCO)H_2O$, and $Ni(pmp)Cl$ are readily soluble in chloroform and moderately soluble in other organic solvents. Infrared spectra of these complexes are similar to each other, showing no N–H stretching vibration, which indicates the presence of the deprotonated ligand, pmp (Table II). The maximum in the diffuse reflectance spectra at 12-15×10^3 cm^{-1} corresponds to the low intensity band at 13-15×10^3 cm^{-1} in chloroform solution with log $\varepsilon=0.3$-0.5 (Table IV), and this band may be assigned to a spin-forbidden transition, because spin-allowed transitions of a square planar complex may be more intense with log $\varepsilon=2$-3.[10] Consequently intense bands at 17.3-21.7×10^3 cm^{-1} were assigned to a spin-allowed transition. The low intensity band showed a red shift in the order of the spectro-chemical series, $NCS>NCO>Cl$. It is remarkable that a weak field li-

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[10] A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968, p. 317.

Table IV. Magnetic moments and electronic spectra of nickel complexes

Complex	μ_{eff} (20°C) B.M.	State*	Electronic spectrum Absorption max. in 10^3 cm^{1-} (logε)**				
$Ni(pmp)(NCO)H_2O$	diamag.	refl.	18sh	13.6	9.7sh		
		$CHCl_3$	25.2(3.25)	21.5sh(2.4)	18.7sh(2.0)	13.8(0.28)	
$Ni(pmp)(NCS)1\frac{1}{2}H_2O$	diamag.	refl.	18.5sh	14.7	8.4sh		
		$CHCl_3$	25.6(3.29)	24.8sh(3.3)	21.7sh(2.5)	18.7sh(2.1)	14.5sh(0.5)
$Ni(pmp)Cl$	diamag.	refl.	17.3sh	12.1			
		$CHCl_3$	26.2(3.05)	24.8(3.10)	20.3(2.20)	17.3sh(1.7)	13sh(0.3)
$Ni(pmp)Br\frac{1}{2}HBr$	3.28	refl.	22sh	14.4	11.5sh		
		DMF	25sh(2.3)	20.2(1.44)	16.4(1.06)	11.5(1.03)	8.3(0.84)
$Ni(pmp)_2 6H_2O$	3.12	refl.	18.1	11.6			
		EtOH	18.4(1.19)	11.5(1.69)			
$Ni(pepH)_2(NCS)_2$	3.18	refl.	16.5	13.2	9.9		
$Ni(pmpH)_2(NO_3)_2 2HNO_3$	3.25	refl.	18sh	15.7	11.1	9.8	
$Ni(pepH)_2Br_2 3H_2O$	3.19	refl.	16.9	13.5sh	11.1		
		aq.	17.1(0.86)	13.5(0.72)	12.2(0.80)	9.8(0.69)	

*, ** Symbols used are the same as in Table III.

gand, Cl ion formed a square planar complex. A possible reason for such a complex may be a strong ligand field of amide-nitrogen and large tendency of an amide group to have a planar configuration.

In contrast to nickel thiocyanate, cyanate and chloride, nickel bromide formed a green paramagnetic complex, $Ni(pmp)Br\frac{1}{2}HBr$, showing an unusual absorption spectrum (Figure 4). This spectrum agreed neither with that of an octahedral nor that of a tetrahedral complex. It is interesting to note that the chloride complex is diamagneic, while the bromide complex is paramagnetic in spite of a small difference of ligand field strength between chloride and bromide ions.

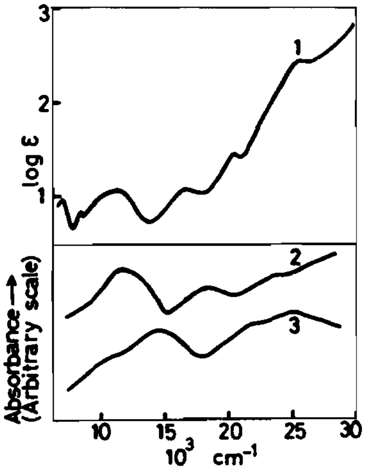

Figure 4. Electronic spectra of nickel(II) complexes: (1) Absorption spectrum of $Ni(pmp)Br\frac{1}{2}HBr$; (2) Diffuse reflectance spectrum of $Ni(pmp)_2 6H_2O$; (3) Diffuse reflectance spectrum of $Ni(pmp)Br\frac{1}{2}HBr$.

When an aqueous solution containing a nickel salt and pmpH in the ratio 1:2 was made alkaline, gray paramagnetic $Ni(pmp)_2 6H_2O$ was obtained. The diffuse reflectance spectrum, shown in Figure 4, is similar to that of an octahedral complex, but higher absorption intensity may be due to a distorted structure(11) (Table IV). Only one complex with the protonated pmpH, $Ni(pmpH)_2(NO_3)_2 2HNO_3$, was obtained. Its structure may be six-coordinate with to nitrate ions as additional ligands because its electronic spectrum is similar to that of a distorted octahedral complex with two split bands at 9.8 and 11.1×10^3 cm^{-1} which may possibly be the transition, $^3A_{2g} \rightarrow {}^3T_{2g}(O_h)$ Table IV). The infrared bands of coordinated nitrate ion(12) are observed at 1431, 1398 and 1318 cm^{-1}. Further the amide bands of this complex revealed that pmpH is coordinated as in Figure 2-II (Table II).

With deprotonated pep no nickel complex was obtained, while with pepH, $Ni(pepH)_2(NCS)_2$, $Ni(pepH)_2Cl_2$, $Ni(pepH)_2Br_2 3H_2O$ and $Ni(pepH)_2(NO_3)_2 2HNO_3$ were obtained. The diffuse reflectance spectrum of the thiocyanate complex is quite similar to those of the corresponding complexes of picolinamide and its N-methyl derivatives.[7] The same spectrum of the bromide complex is also similar to that of $[Ni(piaH)_2(H_2O)_2]^{2+}$ whose structure has been determined by X-rays.[9] In this complex two water molecules are in the trans positions, above and below the plane of the ligand, piaH, while in the pepH complexes two ligand molecules occupy the trans positions and two other groups like NCS, NO_3, Cl, H_2O are situated above and below the nickel atom in an octahedron[9] (Figure 2-II). This conclusion is borne out by the infrared spectral data of the amide groups as well.

4. *Copper (II) complexes.* All the copper complexes of pmpH and pepH showed normal magnetic moments at room temperature and their electronic spectral data are shown in Table III. Infrared spectra of Cu(pmp)Cl and Cu(pep)Cl revealed that the amide-nitrogen atom coordinates to the metal on deprotonation, giving a structure similar to the diamagnetic nickel complexes, while in $Cu(pepH)_2(ClO_4)_2 2HClO_4$ the ligand pepH coordinates through the amide-oxygen atom. The assignment of the amide bands of the latter was further confirmed by deuteration of the amide-hydrogen atom (Table II). No evidence for strong interaction of perchlorate ion with copper has been found in the infrared spectrum. From these spectral data the structure of the perchlorate complex is presumed to be

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elongated tetragonal like $Cu(mepiaH)_2(ClO_4)_2$[7] which shows a maximum at $16.3\times10^{3-1}$ in the diffuse reflectance spectrum, the position being different from 14.8×10^3 cm^{-1} shown by six-coordinate $[Cu(mepiaH)_2(H_2O)_2]Cl_2 2H_2O$.[7]

Two complexes, $Cu(pmpH)_2(ClO_4)_2$ and $Cu(pep)_2$-$HClO_4 2H_4O$ showed complicated infrared spectra which indicated the presence of both protonated and deprotonated ligands as shown in Table II. Therefore, these two complexes should be formulated as five coordinate $Cu(pmp)(pmpH)ClO_4HClO_4$ and Cu(pep)-$(pepH)ClO_4 2H_2O$, respectively. In the electronic spectra of these complexes a shoulder is observed at *ca.* 13×10^3 cm^{-1} (Table III), which is also found in some other five coordinate copper complexes.[13] This fact supports the above mentioned structure of these two complexes, *i.e.* five coordinate with one protonated bidentate ligand and one deprotonated terdentate ligand. The main bands of the five coordinate complexes are found at 16.9 and 17.4×10^3 cm^{-1} in shorter wavelength region than that of tetragonal Cu(pmp)Cl and Cu(pep)Cl (Table III). The reason for this blue shift which is rather unusual is not clear yet. Perhaps the presence of coordinating atoms, 4N and O, in these five coordinate complexes instead of 3N and Cl in the four coordinate complexes may be responsible for it.

Acknowledgment. The present investigation has been supported by the Scientific Research Grant of the Ministry of Education.

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