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Bivalent Metal Complexes of Phototropic N-(2-pyridylmethyleneamino)-2-pyridinecarboxamide

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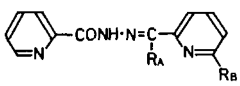
White N-(2-pyridylmethyleneamino)-2-pyridine-carboxamide (papH) turns yellowish green on exposure to sunlight, and the original white papH was recovered when the yellowish green sample was recrystallized or heated above 140° C. Its complexes, however, are no longer phototropic probably because of the fixed configuration of the coordinated ligand. The zinc(II) complexes are tetrahedral, and all the nickel(II) and cobalt(II) complexes are octahedral and show normal magnetic moments. The magnetic moments of the copper(II) complexes are all subnormal, and copper–copper interaction seems to be operative through delocalized orbitals over amide and azomethine groups.

Introduction

In previous papers[1–4] complexes of several potentially terdentate, N-substituted 2-pyridinecarboxamides have been studied to see how the mode of coordination of an acid amide group, O- or N-coordination, is varied with a substituent on the amide-N atom. In order to obtain further information, cobalt(II), nickel(II), copper(II), and zinc(II) complexes of N-(2-pyridylmethyleneamino)-2-pyridinecarboxamide (abbreviated as papH, formula I) were investigated.



$R_A=R_B=H$	papH
$R_A=CH_3$ $R_B=H$	β-Me-papH
$R_A=H$ $R_B=CH_3$	6′-Me-papH

I

The novel ligand papH has atoms of rigid sp^2 hybridization within the skeletons of its chelate rings, and is different from the terdentate ligands reported previously in that the latters have flexible methylene groups in their chelate rings. The effect of chelate ring flexibility on the properties of complexes is expected to be found out.

The ligand papH is unexpectedly phototropic and its white colour turns yellowish green on exposure to sunlight. The phototropic property of papH has been also studied briefly as well as its coordination chemistry. The only known phototropic compound containing the same methyleneamino-amide group (–CH=N-NHCO–) is yellow N-(2-nitrobenzylideneamino)-4-pyridinecarboxamide which turns red under light.[5]

Experimental

Syntheses of the Ligands

The mixture of 10.7 g of 2-pyridinecarboxaldehyde and 13.7 g of 2-pyridinecarbohydrazide was heated at 130° C until water had ceased to evolve. To the mixture cooled at *ca.* 80° C was added 30 ml of ethanol with stirring and this solution was allowed to stand in dark. White crystals separated were recrystallized from ethanol. The yield was 16.5 g. It melts at 161–162° C. The yellowish green form of papH was obtained when finely powdered papH was exposed to sunlight for several days. The yellowish green colour fades at *ca.* 140° C and it melts at the same temperature as white papH does.

The 6′-methyl derivative and the β-methyl derivative were prepared in the same way from 6-methyl-2-pyridinecarboxaldehyde and 2-acetylpyridine with 2-pyridinecarbohydrazide, respectively. The former melts at 100–101° C and the latter at 189.5–190.5° C. Analytical data for the three ligands are given in Table I.

Syntheses of the Complexes

$Cu_2(OH)(pap)SO_4 \cdot 4H_2O$

To a hot aqueous solution of 1.1 g of copper sulfate was added 0.5 g of papH in ethanol (15 ml) and then 0.1 g of sodium hydroxide in water (5 ml). The mixture was filtered and the filtrate was allowed to stand overnight at room temperature. Dark green crystals precipitated were washed with water and then dried in air. The yield was 0.7 g. The three complexes, $Cu_3(pap)_2(NO_3)_4 \cdot 2H_2O$, $Ni_3(pap)_2(SO_4)_2 \cdot 14H_2O$, and

TABLE I. Analytical Data and Colours of the Ligands and Complexes.

Compound	Colour	M% (Calcd.)	N% (Calcd.)	Other % (Calcd.)					
papH	White		24.42 (24.79)	C	63.51 (63.75)	H	4.46 (4.46)		
6′-Me-papH	White		23.18 (23.32)	C	65.27 (64.99)	H	4.89 (5.03)		
β-Me-papH	White		23.25 (23.32)	C	65.39 (64.99)	H	5.03 (5.03)		
yg-$Cu_2Cl_3(pap)$	Yellowish green	27.55 (27.71)	12.12 (12.21)	Cl	22.90 (23.19)				
dg-$Cu_2Cl_3(pap)$	Dark green	27.74 (27.71)	12.13 (12.21)	Cl	23.10 (23.19)				
$Cu_2(OH)(pap)SO_4 \cdot 4H_2O$	Dark green	23.54 (23.65)	10.30 (10.42)	C	26.31 (26.82)	H	3.34 (3.17)	H_2O	13.32 (13.41)
$Cu_3(NO_3)_4(pap)_2 \cdot 2H_2O$	Dark green	21.00 (20.79)	18.28 (18.33)	H_2O	3.88 (3.93)				
$Ni_2Cl_3(pap) \cdot 3H_2O$	Yellow	23.53 (23.34)	11.09 (11.14)	C	29.05 (28.65)	H	3.08 (3.08)	Cl	20.94 (21.14)
$Ni_3(pap)_2(SO_4)_2 \cdot 14H_2O$	Brown	16.52 (16.42)	10.29 (10.45)	C	26.59 (26.45)	H	3.99 (4.32)	S	5.41 (5.98)
$Co_3(pap)_2(SO_4)_2 \cdot 12H_2O$	Orange	17.34 (17.07)	10.66 (10.82)	H_2O	20.25 (20.88)				
$ZnCl_2(papH)$	Yellow	18.25 (18.03)	15.23 (15.46)	Cl	19.55 (19.56)				
$ZnBr_2(papH)$	Yellow	14.36 (14.48)	12.37 (12.41)	Br	35.31 (35.40)				

$Co_3(pap)_2(SO_4)_2 \cdot 12H_2O$ were prepared in a similar way.

yg-$Cu_2Cl_3(pap)$ (yellowish green isomer)

A hot ethanolic solution(20 ml) of 1.5 g of papH was added to a hot ethanolic solution(30 ml) of 1.0 g of copper chloride. The mixture was heated on a hot plate for two hours. The product was washed with ethanol and dried in air. The yield was 0.6 g. The three complexes, $Ni_2Cl_3(pap) \cdot 3H_2O$, and ZnX_2 (papH)(X = Cl, Br) were prepared in a similar way.

dg-$Cu_2Cl_3(pap)$ (dark green isomer)

To a hot aqueous solution(25 ml) of 1.0 g of copper chloride was added a solution of 1.5 g of papH in ethanol(15 ml). The mixture was heated on a hot plate with stirring until all the precipitates had turned dark green. The product was washed with water and dried in air. The yield was 0.7 g.

Measurements

Measurements were carried out in the same method as reported previously.[1,2]

Results and Discussion

Properties of papH

The ligand papH remains white indefinitely when kept in dark, but the crystal surface turns yellowish green in sunlight after several minutes, and the colour change is complete on prolonged exposure to sunlight. The original white colour is not restored in dark, but the yellowish green colour fades completely when heated above 140° C or recrystallized, and white papH is recovered.

The properties of the white and yellowish green forms are identical in solution and the solution shows no colour change in light. In solid state, however, some differences are observed between the white and yellowish green forms. In the visible region the mull spectrum of the yellowish green papH have two peaks at 20.7 and 22.3 $\times 10^3$ cm^{-1}, whereas the white papH shows no peak in this region (Fig. 1). The difference of the infrared spectra between the two forms is remarkable in the amide bands (Table II), and the amide group seems to be related partially with the colour change. The mechanism of colour change reported for N-(2-nitrobenzylideneamino)-4-pyridinecarboxamide[5] can not be suitably applied to this case, since papH has no nitro group*. Both the white and yellowish green forms are diamagnetic, so that a radical-formation mechanism is excluded.

The two methyl derivatives (Formula I) prepared are insensitive to light both in the solid state and in solution, and no additional information is available.

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* The nitro group of the 4-pyridinecarboxamide derivative was reported to be concerned with its colour change (ref. 5).

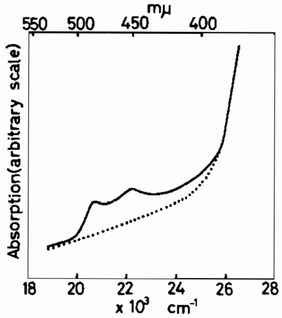


Figure 1. Mull spectra of white papH(· · ·) and yellowish green papH(——).

Some complexes of papH are also examined, but they are not phototropic because of the fixed configuration of papH by chelation. In view of the mechanisms of phototropy of compounds containing ethylene, azomethine, or azo groups,[6,7] a possible mechanism for the phototropy of papH seems to be the *cis–trans* isomerization of either the amide or azomethine, or both groups.

Properties of the Complexes

The complexes listed in Table I except those of zinc are not monomeric, but di- or tri-meric on the basis of analytical results. The complexes cannot be recrystallized, owing to their low solubility in common solvents. In the case of copper chloride, two isomers are isolated and they are differenciated by infrared and electronic spectra.

Electronic spectra

The diffuse reflectance spectra of the nickel complexes are those of octahedral ones and this is consistent with the normal magnetic moments observed (Table III). The cobalt complex seems to be octahedral, since the ligand field bands are weak. If the structure is other than octahedral, intense bands would be observable as for tetrahedral or five-coordinate complexes. The resemblance of the infrared spectra of $Ni_3(pap)_2(SO_4)_2 \cdot 14H_2O$ and $Co_3(pap)_2(SO_4)_2 \cdot 12H_2O$ confirms this assumption.

The spectra of the copper complexes are more intense and the bands below 17 × 10^3 cm^{-1} may be due to ligand field transitions. The bands shift to higher

TABLE II. Infrared Spectra of the Ligands and Zinc Complexes (cm^{-1}).

Compound	Amide bands						
	νN–H	I	II	III	δC=O	πN–H	νN–N
papH (white)	3298	1694	1513	1236	703	615	1138
papH (chloroform solution)	3295	1691	1515 1490	1236	[a]	[a]	1105
papH (yellowish green)	3302	1699	1517	1234	693	600	1145
papD (white)[b]	2452	1693	1408	951	685	451	1093
$ZnCl_2(papH)$	3188	1664	1496	1234	675	643	1109
$ZnBr_2(papH)$	3180	1661	1494	1236	674	640	1108

[a] Obscured by chloroform absorption. [b] The amide group is deuterated and νN–H and πN–H should be replaced with νN–D and πN–D, respectively.

TABLE III. Electronic Spectra and Magnetic Moments of the Complexes.

Complex	μ_{eff}[a] B.M.	Absorption Maximum in 10^3 cm^{-1}			
yg-$Cu_2Cl_3(pap)$	1.59	10.7sh[b]	13.8	22.5sh	25.5
dg-$Cu_2Cl_3(pap)$	1.58	13.4	15.2sh	21.0sh	26.5
$Cu_2(OH)(pap)SO_4 \cdot 4H_2O$	0.63	13.5sh	16.3	21.5sh	23.5sh
$Cu_3(NO_3)_4(pap)_2 \cdot 2H_2O$	1.67	15.4	23.4sh	26.2	
$Ni_2Cl_3(pap) \cdot 3H_2O$	3.03	9.9	12.5sh	15.0sh	23.0sh
$Ni_3(pap)_2(SO_4)_2 \cdot 14H_2O$	3.09	11.8	17.5sh	23.5	
$Co_3(pap)_2(SO_4)_2 \cdot 12H_2O$	4.66	9.0sh	15.5sh	20.5sh	24.5
$ZnCl_2(papH)$	Dia.[c]	27.5sh			
$ZnBr_2(papH)$	Dia.	25.8sh			

[a] At room temperature. [b] sh = Shoulder. [c] Dia = Diamagnetic.

frequencies in the order of anions: Cl < NO_3 < SO_4, implying coordination of the anion. The marked shoulders near 21 × 10^3 cm^{-1} are considered to be due to the same origin as that for nearultraviolet bands of copper complexes with subnormal magnetic moments,[8,9] since the copper complexes of pap are all magnetically subnormal (Table III).

Infrared spectra

The infrared spectra of the complexes except the two zinc ones are, generally, similar to one another down to 400 cm^{-1}. In the spectra, νN–H of papH disappears and instead of the amide I, II, and III bands, two strong bands, one at 1530–1560 and the other at 1350–1390 cm^{-1}, are observed. This indicates amide-N coordination.[1] Further the band due to νC = N,[10] which is at 1620 cm^{-1} for free papH, appears between 1610–1630 cm^{-1} in the complexes.

The amide bands of the zinc complexes (Table II) are very different from those of the other complexes and suggest amide-O coordination. The scarce shifts of the amide II and III bands, however, disagree with those expected from previous works.[1,2,4] This fact may arise from the coupling of the amide bands with those of the azomethine group, the N-atom of which seems to be coordinated.

$Ni_3(pap)_2(SO_4)_2\cdot 14H_2O$ and $Co_3(pap)_2(SO_4)_2\cdot 12H_2O$ show a broad, strong band at *ca.* 1100 and a medium one at *ca.* 610 cm^{-1}, so that the sulfate groups are not coordinated. On the other hand, strong bands at 1169, 1135, 1028, and 601, and a medium one at 948 cm^{-1} are observed for $Cu_2(OH)(pap)SO_4\cdot 4H_2O$. This indicates clearly the coordination of the sulfate group.[11] In $Cu_3(NO_3)_4(pap)_2\cdot 2H_2O$ the coordination of the nitrate ions is implied by the presence of bands at 1467, 1313, 1024, and 825 cm^{-1}.

Far infrared spectra

The deformation mode of the pyridine rings of free papH at 620 cm^{-1} shows no shift in the zinc complexes indicating non-coordination of the rings.[12] The band, however, shifts to 641–654 cm^{-1} in the other complexes suggesting the coordination of the rings.

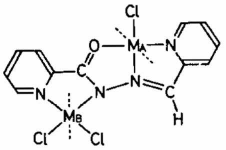
The two strong bands observed for $ZnCl_2(papH)$ at 329 and 298 cm^{-1}, which shift to 250 and 227 cm^{-1} in the bromo analogue, are assigned to νZn–X. The mean ratio 0.76 for νZn–Br/νZn–Cl and the band positions agree well with those reported for tetrahedral zinc complexes.[13] The two zinc complexes, therefore, are determined to be tetrahedral.

$Ni_2Cl_3(pap)\cdot 3H_2O$ shows νNi–Cl at 257 and 201 cm^{-1} and these values are close to those of six-coordinate nickel(II) complexes.[14] $Ni_3(pap)_2(SO_4)_2\cdot 14H_2O$ and $Co_3(pap)_2(SO_4)_2\cdot 12H_2O$ show no band assignable to νM–OSO_3, while $Cu_2(OH)(pap)SO_4\cdot 4H_2O$ shows an additional band at 350 cm^{-1}, which is tentatively assigned to νCu–OSO_3. The band observed at 334 cm^{-1} for $Cu_3(NO_3)_4(pap)_2\cdot 2H_2O$ is assigned to νCu–ONO_2 and the value is compatible with the reported one.[15] The coordination of SO_4 and NO_3 ions is also indicated by the splitting of their internal modes.[11]

Two strong bands at 307 and 282 cm^{-1} are observed for yg-$Cu_2Cl_3(pap)$ and at 319 and 285 for the dg-isomer, and these bands are assigned to νCu–Cl. In the strictly square-planar copper complex,[16] $CuCl_2$(4-methylpyridine-N-oxide)$_2$, νCu–Cl has been found at 339 cm^{-1}, so that in both isomers the chlorine atoms may be bridged between copper ions.

Structures

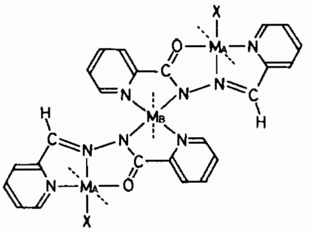
The subnormal magnetic moments of the copper complexes suggest the presence of copper–copper interaction.[8] In view of the above results, the mode of coordination of papH is presumed to be as shown in Formula II.



II

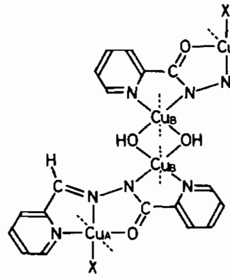
In this model a plausible pathway through which electron spins of the two copper atoms interact may be delocalized p-π orbitals over the amide and azomethine groups.[17] It seems to be a novel pathway.[8]

The two isomers of $Cu_2Cl_3(pap)$ may arise from joining apically together the dimer units (Formula II) in different manners. The apical positions are indicated by dotted lines in Formulae. The proposed structure for $Cu_3(NO_3)_4(pap)_2\cdot 2H_2O$ is shown in Formula III, where the positions X and apical sites are occupied by either H_2O or NO_3.



III

The supposed structure for $Cu_2(OH)(pap)SO_4\cdot 4H_2O$ with a much lower magnetic moment is shown in Formula IV. The empty positions of Formula IV are occupied by H_2O or SO_4. This proposal is supported by the fact that magnetically subnormal copper complexes of bipy and phen have a dimeric hydroxo-bridged structure $[LCu(OH)_2CuL]^{2+}$ (L = bipy,



IV

phen*).[18] Further a hydroxo-bridged complex with a subnormal magnetic moment,[4] $[(mepia)Cu(OH)_2Cu(mepia)] \cdot 4H_2O$, have been prepared.** In this complex mepia is coordinated with the pyridine-N and amide-N atoms and the mode of coordination corresponds to the central hydroxo-bridged part of Formula IV (around Cu_B).

From the similarity of infrared spectra, the mode of coordination of papH in other complexes except the two zinc ones appears to be identical (Formula II). $Ni_2Cl_3(pap) \cdot 3H_2O$ has, in principle, a structure similar to that of $Cu_2Cl_3(pap)$, apical positions of Formula II being occupied by H_2O. A structure similar to that of $Cu_3(NO_3)_4(pap)_2 \cdot 2H_2O$ is assigned to $Ni_3(pap)_2(SO_4)_2 \cdot 14H_2O$ and $Co_3(pap)_2(SO_4)_2 \cdot 12H_2O$, where instead of NO_3 groups H_2O molecules occupy the remaining sites of coordination (Formula III).

Conclusion

The phototropic ligand papH is quite different in coordinating behaviour from the potentially terdentate ligands reported previously, $R-(CH_2)_n-NHCO-C_5H_4N$ (LH) where R is a coordinating group and $n = 1$, 2, or 3. Therefore, the first purpose to obtain information about the influence of chelate ring rigidity on coordinating behaviour of an acid amide group has not been achieved. The terdentate ligands form either $MLX \cdot mH_2O$ or $M(LH)_2X_2 \cdot mH_2O$, where the ligand acts as a ter- or bi-dentate, respectively, while papH forms di-, tri- or tetra-meric complexes and acts as a quinquedentate ligand. The most important factor causing the difference may arise from the presence of an azomethine group of coordinating ability in papH. The presence of an azomethine group adjacent to an acid amide group appears to favour the deprotonation of the amide group. A methyleneamino-amide group (–CH=N–NHCO–) is coordinated through its azomethine-N, amide-N, and amide-O atoms under deprotonation and the group is found to be a novel pathway exchanging electron spins between copper ions.

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* phen = 1,10-phenanthroline and bipy = 2,2'-bipyridine.

** mepiaH = N-methyl-2-pyridinecarboxamide.

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