Synthesis and Electron Spin Resonance Studies of Copper(II) Complexes with Acid Amide Derivatives of 2-Amino and 2,6-Diaminopyridine**

M. F. EL-SHAZLY*

Department of Chemistry, Northeastern University, Boston, Mass. 02115, U.S.A.

A. EL-DISSOWKY, T. SALEM and M. OSMAN

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

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The reaction of copper(II) chloride, bromide, nitrate and perchlorate with acid amide ligands derived from 2-amino and 2,6-diamino pyridine was investigated. Electron spin resonance, magnetic and spectral data were used to determine the structure of the complexes. Acid amide derivatives of 2-amino pyridine formed distorted octahedral complexes while the acid amide ligands derived from 2,6-diamino pyridine formed a five coordinate square-based pyramidal compound. These five coordinated complexes react further with pyridine forming six coordinate base adducts.

Introduction

The coordination chemistry of acid amides is of considerable interest due to its biological importance. Recently there has been increasing interest in the metal complexes of the acid amide derivatives of 2-aminopyridine with transition metals as well as lanthanide salts [1–7]. Contiguous with our interest in the coordination behavior of heterocyclic ligands which have biological activity [8, 9], we synthesized new types of acid amide ligands derived from 2,6-diaminopyridine. We prepared these ligands to study their bulkiness effect on imposing a particular configuration around the metal ion, *e.g.*, a five-coordinate configuration. It has been shown [10, 11] that ligands which are suitable for imposing a five-coordinate arrangement around the central metal ion must fulfill the following conditions:
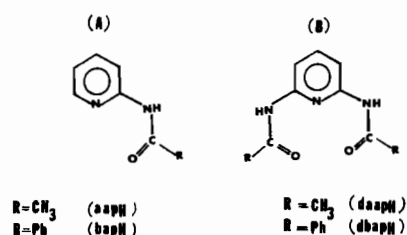

Fig. 1. The ligands.

the donor atoms must have strong coordinating ability and less tendency to form π-bonds with the metal ion; secondly, the ligand must be bulky and polydentate in order that crowding should prevent a six-coordinate complex from being attained. Ligand B, Fig. 1, fulfills these requirements and makes possible formation of bi- or polynuclear metal complexes due to its steric effect.

We report here a detailed preparation and characterization of 2,6-[(N,N′-diacetyl) diamino pyridine and 2,6-[(N,N′-dibenzoyl) diamino pyridine and their metal complexes with copper(II). We also further investigated the copper(II) complexes with 2-(N-acetyl) and 2-(N-benzoyl) amino pyridine, with special emphasis on their ESR spectra.

Experimental

Preparation of the Ligands

2-[(N-benzoyl)amino pyridine] (bapH)

2-Amino pyridine (0.5 mol) was dissolved in pyridine and cooled to −10 °C, then benzoyl chloride (0.5 mol) was added dropwise. The reaction mixture was then warmed to 10 °C with stirring for about ½ hr. The solution was poured into a water–ice mixture; the solid product was then recrystallized from ether to give white crystals, m.p. 86 °C. The yield was 90%.

TABLE I. Analytical Data.

Compound	Color	% Cu (Found)	% N (Found)	% Halogen (Found)
Cu(daapH)Cl$_2$	yellowish green	19.39 (19.38)	12.82 (13.0)	21.67 (21.58)
Cu(daapH)Br$_2$	Green	15.26 (15.28)	10.08 (10.21)	38.41 (38.52)
Cu(daapH)(NO$_3$)$_2$	Green	11.08 (11.03)	19.52 (19.50)	
Cu(dbapH)Cl$_2$	Pale green	14.06 (14.00)	9.30 (9.36)	15.72 (15.82)
Cu(dbapH)Br$_2$	Green	11.75 (11.80)	7.77 (7.63)	29.60 (29.80)
Cu(dbapH)(NO$_3$)$_2$	Pale green	12.58 (12.60)	13.87 (13.93)	
Cu(aapH)$_2$(ClO$_4$)$_2$[a]	Blue	11.80 (11.73)	10.47 (10.61)	
Cu(bapH)$_2$Cl$_2$	Green	11.97 (11.86)	10.55 (10.60)	13.38 (13.30)
Cu(bapH)$_2$Br$_2$	Green	10.25 (10.20)	9.03 (9.00)	25.92 (25.80)
Cu(bapH)$_2$(NO$_3$)$_2$	yellowish green	11.03 (11.10)	14.59 (14.70)	
Cu(bapH)(ClO$_4$)$_2$	yellowish green	9.64 (9.66)	8.50 (8.45)	

[a]Chloro, bromo and nitrate complexes with aapH, see ref. 2.

Found: C, 72.75; H, 5.048; N, 14.23%. Calcd. for C$_{12}$H$_{10}$ON$_2$: C, 72.72; H, 5.05; N, 14.14.

2-[N-acetyl amino pyridine] (aapH)

It was prepared from 2-amino pyridine and acetic anhydride according to the reported method [2] to give 80% yield of white crystals, m.p. 68–70 °C.

2,6[(N,N'-diacetyl) diamino pyridine] (daapH)

2,6-Diaminopyridine (0.04 mol) was refluxed with acetic anhydride (0.1 mol) for one hr. Then 100 ml water was added and the mixture was refluxed for another 20 minutes. The resultant solution was poured into an ice–water mixture. The crude pale brownish product was washed with a sodium carbonate solution and then recrystallized from water to give pale brown needle crystals, m.p. 203 °C. The yield was 70%. Found: C, 76.0; H, 4.10; N, 11.35%. Calcd for C$_9$H$_{11}$N$_3$O$_2$: C, 76.01; H, 4.04; N, 11.32.

2,6[(N,N'-dibenzoyl) diamino pyridine] (dbapH)

This was prepared from 2,6-diamino pyridine (0.04 mol) and benzoyl chloride (0.08 mol) in pyridine at 10 °C as previously described for the preparation of bapH. The crude product was washed several times with sodium carbonate solution and then crystallized from a benzene–ethanol mixture to give very pale brown crystals, m.p. 176 °C. Found: C, 56.0;

H, 5.72; N, 21.52; Calcd for C$_{19}$H$_{15}$N$_3$O$_2$: C, 55.96; H, 5.69; N, 21.76.

Preparation of the Complexes

All the copper complexes were prepared according to the following general method. An ethanolic solution of 0.01 mol of the copper salts was mixed with 0.02 mol of the ligands in ethanol. The mixture was stirred, the crystalline product formed was filtered off, washed several times with ethanol, and dried under vacuum over P$_2$O$_5$. Elemental analyses are given in Table I.

Physical Measurements

Electronic spectra were recorded with Unicam Sp 600 and Cary 14 spectrophotometers. IR spectra were measured using KBr discs with a Perkin Elmer 21 spectrophotometer. ESR data were obtained with an x-band, 1000 HZ field modulation as previously described [9]. Magnetic measurements were carried out at room temperature using the Faraday method and the diamagnetic corrections were calculated by the use of Pascal's constants [12].

Results and Discussion

IR spectra of the free acid amides A and B, Fig. 1, were measured using KBr discs and the characteristic

TABLE II. Characteristic Amide Bands of the Ligands and the Complexes (in cm^{-1}).[a]

Compound	N–H	Amide			Pyridine	NO_3 or ClO_4
		I	II	III		
(daapH)	3300	1665	1515	1280	1580	
Cu(daapH)Cl$_2$	3282	1625	1500	1280	1555	
Cu(daapH)Br$_2$	3290	1630	1490	1280	1553	
Cu(daapH)(NO$_3$)$_2$	3230	1600	1500	1275	1580	1375(s), 1310(s), 780(m)
(dbapH)	3210(br)	1640	1520	1280	1580	
Cu(dbapH)Cl$_2$	3195	1525(br)	1470	1275	(1550)[b]	
Cu(dbapH)Br$_2$	3100	1600	1480	1280	1555	
Cu(dbapH)(NO$_3$)$_2$	3200	1605	1510	1260	1560	1380(s), 1320(s), 825(m)
(bapH)	3200	1675	1580(s)	1245	1600	
Cu(bapH)$_2$Cl$_2$	3240(b)	1620	1580(m)	1338	1620	
Cu(bapH)$_2$Br$_2$	3240(b)	1635(m)	1580(m)	1334	1620	
Cu(bapH)$_2$(NO$_3$)$_2$	3230	1660(sh)	1570	1331	1610	1280(s), 1020(s)
Cu(bapH)$_2$(ClO$_4$)$_2$	3320(b)	1635	1585	1331	1615	
Cu(aapH)$_2$(ClO$_4$)$_2$	3320(b)	1640	1535(m)	1338	1615	1140(s), 1080, 935(w)

[a]b = broad, s = strong, m = medium and w = weak.   [b]Obscured by the amide-I band at 1520 cm^{-1}.

bands are given in Table II. The free ligand A has been reported [2] to have the following resonance structures
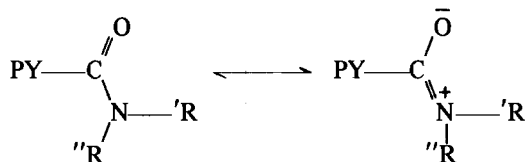
If the coordination takes place with the metal ion through the oxygen atom the amide I band, which consists mainly of $\nu(C=O)$, will shift to a lower frequency while the amides (II) and (III) which arise from $\nu(C-N)$ and $\delta(N-H)$ will shift to higher frequencies [2, 5]. On the other hand, if the amide-nitrogen atom coordinates to the metal ions, amide I, II and III bands should shift in the opposite directions. The ir spectra of the complexes with ligands A and B (Table II) are in accordance with the oxygen atom being bonded without deprotonation of the amide nitrogen in all the cases. The ir spectra showed that the pyridine band for the free ligands at 1580 cm^{-1} shifted to lower frequency while the $\delta(py)$ at 630 cm^{-1} shifted to higher frequency with splitting, indicating coordination of the pyridine-nitrogen atom.

Copper(II) Complexes of N-(2-pyridyl) acetamide and N-(2-pyridyl) benzamide

The reaction of aapH and bapH with CuX$_2$ where x = Cl, Br, NO$_3$ and ClO$_4$ gave 1:2 complexes, Fig. 2. The ir spectra of the complexes showed that the
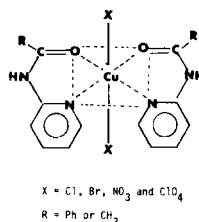

Fig. 2. The 1:2 complexes.
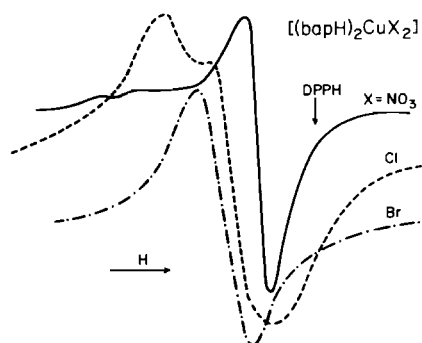

Fig. 3. The X-band ESR spectra of the polycrystalline solids of (bapH)$_2$ CuX$_2$ complexes at 25 °C.

coordination took place through the amide-oxygen atom and the pyridine-N atom. The most characteristic bands for the copper complexes are given in Table II. The magnetic moments measured at 25 °C, Table III, lie within the range 1.85–1.88 B.M. The normal magnetic moments of these chelates indicate

TABLE III. Esr and Electronic Spectra of Copper(II) Complexes of Acid Amide Derivatives of 2-Aminopyridine.

Compound	Meff[a] (BM)	Esr data				Electronic Spectra[b] ν_{max} 10^3 cm^{-1}
		$g_\parallel$	$g_\perp$	$\langle g \rangle$	G	
Cu(aapH)$_2$Cl$_2$	1.85	2.282	2.068	2.14	4.15	16.4; 13.9(sh)
Cu(aapH)$_2$Br$_2$	1.86	2.234	2.074	2.13	3.16	14.9; 12.5(sh)
Cu(aapH)$_2$(NO$_3$)$_2$	1.88	2.223	2.064	2.12	3.48	17.2(sh); 15.4; 13.9(sh)
Cu(aapH)$_2$(ClO$_4$)$_2$	1.86	2.231	2.061	2.12	3.79	16.1; 13.9
Cu(bapH)$_2$Cl$_2$	1.88	2.354	2.076	2.17	4.66	14.0; 12.5(sh)
Cu(bapH)$_2$Br$_2$	1.85	2.135				14.30
Cu(bapH)$_2$(NO$_3$)$_2$	1.88	2.241	2.065	2.12	3.71	15.2; 13.0(sh)
Cu(bapH)$_2$(ClO$_4$)$_2$	1.85	2.231	2.062	2.12	3.73	14.70

[a]Room temperature; $\langle g \rangle = 1/3 g_\parallel + 2/3 g_\perp$; [b], diffuse reflectance spectra; G = $(g_\parallel - 2)/(g_\perp - 2)$.

TABLE IV. Esr and Electronic Spectral Data of Copper(II) Complexes of the Acid Amide Derivatives of 2,6-Diaminopyridine.

Compound	μ_{eff} (BM)	ESR data					Electronic Spectra[b] ν_{max} 10^3 cm^{-1}
		g_1	g_2	g_3	$\langle g \rangle$[a]	R[c]	
Five Coordinate Complexes							
Cu(daapH)Cl$_2$	1.89	2.043	2.149	2.238	2.140	1.08	13.16; 11.90(sh)
Cu(daapH)Br$_2$	1.87	2.134					13.16; 11.63(sh)
Cu(daapH)(NO$_3$)$_2$	1.89	2.041	2.099	2.140	2.09	0.53	13.33; 11.74(sh)
Cu(dbapH)Cl$_2$	1.88	2.058	2.150	2.240	2.15	1.02	12.99; 11.76(sh)
Cu(dpapH)Br$_2$	1.87		2.140				13.2; 11.11(sh)
Cu(dbapH)(NO$_3$)$_2$	1.88	2.052	2.093	2.177	2.11	0.49	12.9; 11.76(sh)
Six Coordinate Complexes		$g_\parallel$	$g_\perp$		$\langle g \rangle$[a]	G	
[Cu(daapH)Cl$_2$·Py]	1.80	2.215	2.069		2.12	3.12	14.49
[Cu(daapH)Br$_2$·Py]	1.83	2.211	2.055		2.07	3.84	15.38
[Cu(daapH)(NO$_3$)$_2$·Py]	1.84	2.188	2.037		2.09	5.08	16.13
[Cu(dbapH)Cl$_2$·Py]	1.87	2.215	2.067		2.12	3.21	15.30
[Cu(dbapH)Br$_2$·Py]	1.86	2.064					14.38
[Cu(dbapH)(NO$_3$)$_2$·Py]	1.88	2.185	2.038		2.09	4.87	17.40

[a]$\langle g \rangle = 1/3 g_\parallel + 2/3 g_\perp$; or $\langle g \rangle = 1/3(g_1 + g_2 + g_3)$.   [b]Diffuse reflectance spectra.   [c]R = $(g_2 - g_1)/(g_3 - g_2)$; G = $(g_\parallel - 2)/(g_\perp - 2)$.

their monomeric nature. The nujol mull electronic spectra showed absorption maxima at (14.0–17.0) $\times 10^3$ cm^{-1}, which are in accordance with expectations for tetragonal copper(II) complexes [13, 14]. These results are in agreement with previous results reported by Nonoyama *et al.* [2].

The x-band esr spectra of the polycrystalline complexes at 25 °C are typical of those reported for axial type copper(II) complexes [14, 15] with two g-values, $g_\parallel$ and $g_\perp$. Typical spectra are shown in Fig. 3, and the results are given in Table III. In an axial symmetry the g-values are related by the expression,

G = $(g_\parallel - 2)/(g_\perp - 2)$, which measures the exchange interaction between copper centers in the polycrystalline solid [16]. According to Hathaway [14–18] if the value of G is larger than four, exchange interaction is negligible while G less than four indicates considerable exchange interaction in the solid complexes. The calculated G-values are given in Table III. The average g-values were calculated according to the relation $\langle g \rangle = 1/3\ g_\parallel + 2/3\ g_\perp$ and gave values in the range of 2.12–2.17, which are in agreement with an orbitally non-degenerate ground state.
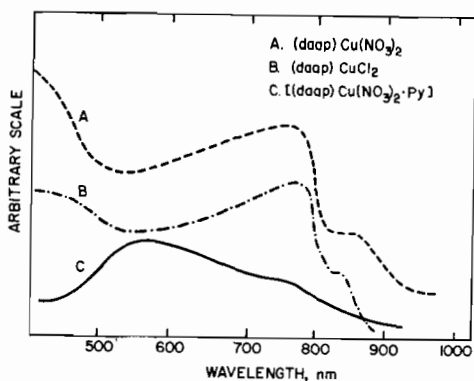
Fig. 4. The nujol mull electronic absorption spectra of some representative five coordinate copper(II) complexes and their pyridine adduct.
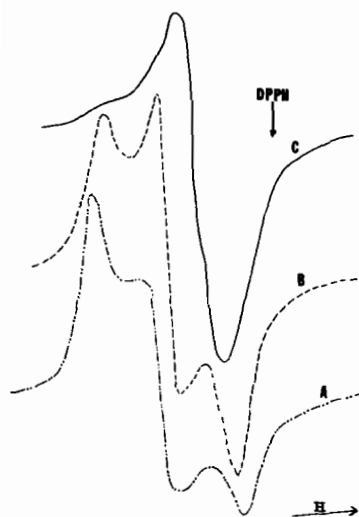

Fig. 5. The X-band ESR spectra of (A) Cu(daapH)Cl$_2$, (B) Cu(daapH)(NO$_3$)$_2$ and (C) [Cu(daapH)(NO$_3$)$_2$·py] at 25 °C.

Fig. 6. The X-band ESR spectrum of the powder solid of (daapH)CuBr$_2$ at 77 K.
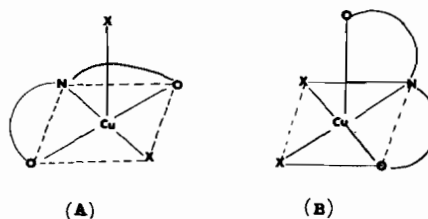
Fig. 7. The possible configurations of the five coordinate copper(II) complexes.

Copper(II) Complexes with 2,6-[N,N'-diacetyl)diami-no pyridine] and 2,6-[(N,N'-dibenzoyl)diamino Pyri-dine]

The reactions of daapH and dbapH with CuX$_2$ where x = Cl, Br and NO$_3$ gave 1:1 complexes LCuX$_2$. The infrared spectra of all the complexes showed that the ligands coordinate with the metal ion through the two amide-oxygen atoms and the pyridine-N atom, Table II. The Nujol mull electronic spectra for all the complexes are very similar in the d–d region and consist of a band around 13.000 cm^{-1} with a shoulder around 11.600 cm^{-1}, Fig. 4. These data are compatible with a square-based pyramidal structure [15, 16]. The magnetic susceptibilities were measured at 25 °C. All the compounds showed normal magnetic moments (Table IV).
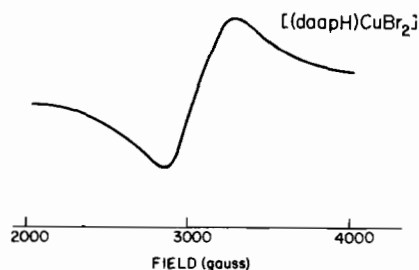
The polycrystalline ESR spectra of the Cu(II) complexes were measured at room temperature, as well as at 77 K. The spectra were analyzed by Kneubuhl's method [19] and the g-factor values obtained are presented in Table IV. All the complexes under investigation gave anisotropic ESR spectra. The calculated average ⟨g⟩ factor lie in the range 2.11 ± 0.03, which would be in agreement with an orbitally non-degenerate ground state [20].

The copper complexes with the anions X = Cl$^-$ and NO$_3^-$ exhibit essentially orthorhombic ESR spectra, Fig. 5, and the corresponding g-values are rather consistent. For the rhombic system with g$_3$ > g$_2$ > g$_1$ it is found that if the value of the parameter R defined by the ratio (g$_2$ − g$_1$)/(g$_3$ − g$_2$) is greater than one, then a predominantly d$_{z^2}$ ground state is present, while for a d$_{x^2-y^2}$ ground state R is expected to be less than one. The calculated values of R, Table IV, indicate a d$_{x^2-y^2}$ ground state which is consistent with a distorted square-based pyramidal structure which is in agreement with the electronic absorption spectra. However, since the crystal structures of these complexes are not known, we cannot conclude to what extent the g-values reflect the actual molecular structure. The ESR spectra of the bromo complexes are characterized by one broad signal and Δ$_{(peak to peak)}$ = 600 gauss, Fig. 6. This kind of behaviour is very common in many copper-(II) bromo complexes [21]. These isotropic ESR spectra are most commonly due to dipolar broadening and enhanced spin–lattice relaxation of the bromide ion [22]. Therefore, there are two possible configurations A and B for these five coordinate complexes (Fig. 7).

We have not been successful in growing single crystals for X-ray analysis to determine the exact structure due to the partial solubilities of the complexes in most of the non-coordinating organic solvents. Therefore, configuration A may be assigned to these complexes because of the steric arrangement of the ligands and also the strain in their sidechains.

Five coordinate copper(II) complexes are known to form six-coordinate tetragonally distorted complexes by reaction with amine bases such as pyridine. All the compounds dissolved readily in pyridine forming solutions from which blue solids precipitated. The pyridine adducts exhibit a broad band around $(15–17) \times 10^3$ cm^{-1}. The results are given in Table IV and Fig. 5. The polycrystalline ESR spectra of the copper pyridinate adduct are typical of axially-elongated complexes [14, 15]. They are characterized by two g-values, $g_\parallel > g_\perp$. The ESR data are given in Table IV and Fig. 5. The exchange interaction, G, was calculated and the results are shown in Table IV. The calculated values for the chloro and bromo compounds are less than 4.0, which may indicate strong spin interaction between the copper centers in the solid complexes. Much reliance, however, cannot always be placed on this criterion, since many planar copper(II) complexes are known to have $G < 4.0$ even in the magnetically diluted state [22–26].

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