# Structure Variation Due to Ligand Flexibility: Syntheses and Structures of the Copper(II) Complexes [Cu(APPy)] and [$Cu_2$(AEPy)$_2$] Where $APPyH_2$ = Bis[3-(2-pyridinecarboxamido)propyl]-methylamine and $AEPyH_2$ = Bis[3-(2-pyridine-carboxamido)ethyl]methylamine

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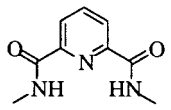
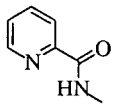
## Introduction

In recent years, we[1−16] and others[17−40] have been interested in the development of ligand systems that contain the pyridine-2-carboxamide functionality within larger ligand frames. Such ligands have been instrumental in developing an understanding of their influence on novel geometric and electronic properties imparted onto various metal centers. One such example is the recently reported pentadentate ligand $Py_3PH_2$ (Hs are the dissociable amide protons hereafter).[2] This ligand is based on the pyridine-2,6-dicarboxamide moiety and contains two additional pyridine donors connected by ethylene linkages. Once



Pyridine-2,6-dicarboxamide unit



Pyridine-2-carboxamide unit

deprotonated, the pyridine-2,6-dicarboxamido unit is strictly planar and maintains planarity in various metal complexes.[3] For example, in [Cu($Py_3P$)], the copper(II) complex of $Py_3PH_2$, the basal plane is defined by the $N_{amido}-N_{py}-N_{amido}$ coordination by the planar pyridine-2,6-dicarboxamido portion of the ligand.[2] In addition, there have been many reports on metal complexes of ligands that contain the planar pyridine-2,6-dicarboxamido moiety by itself[25,26] or included in larger organic frames.[3,7,9,11,13,27−29] It is now quite evident that planarity of the pyridine-2,6-dicarboxamido moiety is a stringent geometric requirement in metal complexes.

Complexes with a somewhat similar ligand $bpbH_2$ with two pyridine-2-carboxamide groups have been extensively studied in recent years.[30−39] In metal complexes of $bpbH_2$ and its derivatives,[37,38,40] the deprotonated $bpb^{2-}$ ligand is also planar due to resonance stabilization throughout the entire ligand framework. The situation is very similar with ligands such as $PypepOH_2$[1] and $PypepSH_2$[14] where the deprotonated tridentate ligands with one pyridine-2-carboxamido unit are strictly planar. In pursuit of ligands that will enhance our understanding of the structural requirements and electronic effects of pyridine-2-carboxamide group, we have synthesized two pentacoordinate ligands bis[3-(2-pyridinecarboxamido)propyl]methylamine (**1**)[41] and bis[3-(2-pyridinecarboxamido)eth-yl]methylamine (**2**), abbreviated as $APPyH_2$ and $AEPyH_2$, respectively. These two

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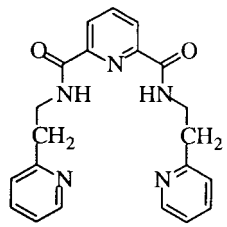
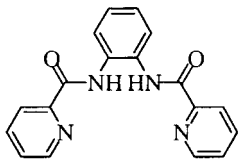
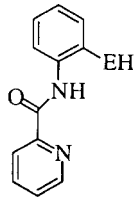


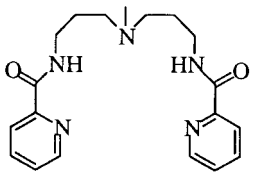

$Py_3PH_2$



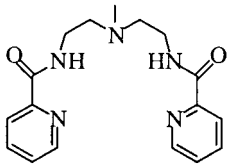

$bpbH_2$




E = S, $PypepSH_2$
E = O, $PypepOH_2$




$APPyH_2$ (**1**)




$AEPyH_2$(**2**)

designed pentadentate ligands differ from $Py_3PH_2$ in that the resonance stabilization of pyridine-2,6-dicarboxamide unit has been deliberately separated into two distinct pyridine-2-carboxamide moieties while retaining a similar nitrogen donor atom in the chain in between. We expected that such a change would result in a structurally less demanding coordination sphere for $M^{n+}$ centers since free rotation along the $-(CH_2)_n-$ links is readily allowed.

In this account, we report the syntheses, structures, and properties of [Cu(APPy)] (**3**) and $[Cu_2(AEPy)_2]$ (**4**), the copper(II) complexes of **1** and **2**, respectively. As discussed below, ligand **1** in deprotonated form binds copper(II) ion to form the pentadentate mononuclear copper(II) complex **3**. This complex adds to the list of mononuclear copper(II) complexes that contain dicarboxamido ligation in [N5] chromophores.[2,4] It is also shown that the shorter ethylene chains in **2** only allows formation of the dimeric complex **4**. No synthetic procedure affords a monomeric copper(II) complex with this ligand.

## Experimental Section

**Preparation of Compounds.** 3,3′-Diamino-*N*-methyldipropylamine, 2-picolinic acid, and ACS reagent grade copper(II) chloride dihydrate were procured from Aldrich Chemical Co. and were used without further purification. *N*′-Methyl-2,2′-diaminodiethylamine was obtained from TCI America. Triethylamine ($Et_3N$) was distilled from NaOH. All solvents were purified by standard techniques and distilled prior to use. The acid chloride of 2-picolinic acid was synthesized by heating 2-picolinic acid in excess thionyl chloride followed by removal of unreacted thionyl chloride under vacuum.

**$APPyH_2$ (1).** A batch of 4.798 g (33.9 mmol) of 2-picolinic acid chloride was placed in a mixture of 40 mL of tetrahydrofuran (THF) and 8.5 g (84.0 mmol) of $Et_3N$. To this mixture was then added dropwise a solution of 2.462 g (16.9 mmol) of 3,3′-diamino-*N*-methyldipropylamine in 15 mL of THF at 0 °C. The resulting solution was allowed to stir at 0 °C for 20 min and then warmed at 50 °C for another 20 min. The light brown solution was cooled to 0 °C and filtered to remove $Et_3N$.HCl (s). Crude **5** was obtained as a viscous oil upon removal of THF. The resulting oil was dissolved in $CH_2Cl_2$, and the solution was washed with aqueous NaOH (3 × 30 mL). The $CH_2Cl_2$ layer was collected and dried with $CaSO_4$. It was then filtered and the solvent was removed in vacuo to obtain pure **1** as a light yellow oil (yield 70%). $^1$H NMR (303K, $CDCl_3$, 250 MHz): $\delta$ (ppm from TMS) 8.50 (s, 2H), 8.44 (d, 2H), 8.07 (d, 2H), 7.73 (t, 2H), 7.30 (m, 1H), 3.49 (q, 4H), 2.5 (t, 4H), 2.24 (s, 3H), 1.82 (t, 4H). Selected IR frequency (NaCl plates): $\nu_{co} = 1666$ cm$^{-1}$.

**$AEPyH_2$ (2).** This ligand was synthesized by following the procedure for the synthesis of **1** with the exception that *N*′-methyl-2,2′-diaminodiethylamine was used in place of 3,3′-diamino-*N*-methyldipropylamine. From 3.499 g (24.7. mmol) of 2-picolinic acid chloride and 1.448 g (12.3 mmol) of 3,3′-diamino-*N*-methyldipropylamine, a batch of pure **2** was obtained as a light yellow oil in 75% yield. $^1$H NMR (303 K, $CDCl_3$, 250 MHz): $\delta$ (ppm from TMS) 8.93 (s, 2H), 8.32 (d, 2H), 8.08 (d, 2H), 7.74 (t, 2H), 7.29 (t, 3H), 3.54 (q, 4H), 2.68 (t, 4H), 2.36 (s, 3H). Selected IR frequency (NaCl plates): $\nu_{co} = 1670$ cm$^{-1}$.

**[Cu(APPy)] (3).** A batch of 0.172 g (0.50 mmol) of $APPyH_2$ was dissolved in 15 mL of N,N′-dimethylformamide (DMF) and the ligand was deprotonated by adding dropwise a slurry of 0.025 g (1.10 mmol) of NaH in 5 mL of DMF with constant stirring. To this solution of deprotonated ligand was then added a solution of 0.085 g (0.50 mmol) of $CuCl_2 \cdot 2H_2O$ in 5 mL of DMF. The resulting blue solution was allowed to stir overnight. It was then filtered, and the DMF was removed in vacuo. The resulting blue oil solidified after successive THF washes (3 × 10 mL). The blue solid was dissolved in 10 mL of $CH_3CN$, and the solution was filtered to remove NaCl(s). Crystalline **3** was obtained upon cooling solution of the complex in $CH_3CN$/diethyl ether mixture (1:1 v/v) containing a trace of water. Yield: 30%. Anal. Calcd for $C_{19}H_{29}N_5O_5Cu$ (**3**·$3H_2O$): C, 48.45; H, 6.21; N, 14.87. Found: C, 48.91; H, 6.29; N, 14.76. Selected IR frequencies (KBr disk, cm$^{-1}$): 3384 (vs), 2938 (m), 2837 (m), 1615 (s), 1585 (s), 1561 (s), 1395 (s), 1262 (m), 1093 (m), 1046 (m), 1013 (m), 763 (m), 695 (m). Absorption spectrum in $CH_3OH$, $\lambda_{max}$ nm ($\epsilon$, M$^{-1}$ cm$^{-1}$): 260 (13 800), 285 sh, 590 (200), 770 sh. Value of $\mu_{eff}$ (298 K, polycryst): 1.83 $\mu_B$.

**[$Cu_2$(AEPy)$_2$] (4).** A solution of 0.034 g (1.42 mmol) of NaH in 5 mL of DMF was slowly added to a solution of 0.183 g (0.56 mmol) of $AEPyH_2$ in 20 mL of DMF. To this solution of the deprotonated ligand was then added with stirring a solution of 0.095 g (0.56 mmol) of $CuCl_2 \cdot 2H_2O$ in 5 mL of DMF. The resulting deep blue solution was allowed to stir for 1 h, and the DMF was removed in vacuo. The dark blue oil thus obtained solidified after successive THF washes (3 × 10 mL). The blue solid was dissolved in hot $CH_3CN$ and the solution was filtered to remove NaCl(s). Crystaline **4**·$H_2O$ was obtained from the $CH_3CN$ solution upon standing at room temperature (Yield 50%). Anal. Calcd for $C_{34}H_{40}N_{10}O_5Cu_2$:C, 51.31; H, 5.06; N, 17.60. Found: C, 51.2; H, 4.98; N, 17.70. Selected IR frequencies (KBr disk, cm$^{-1}$): 3397 (br, s), 2852 (m), 1630 (s), 1613 (s), 1589 (s), 1567 (s), 1471 (m), 1404 (m), 1288 (m), 1089 (w), 1046 (m), 880 (w), 755 (m), 701 (m). Absorption spectrum in $CH_3OH$, $\lambda_{max}$ nm ($\epsilon$, M$^{-1}$ cm$^{-1}$): 260 (12 200), 580 (200), 750 sh.

**Physical Measurements.** Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. A Perkin-Elmer 1600 FTIR spectrophotometer was employed to monitor the infrared spectra. EPR spectra at X-band frequencies were obtained with a Bruker ESP-300 spectrometer. $^1$H NMR spectra were recorded at 25 °C on a Bruker 250 MHz spectrometer.

**X-ray Data Collection and Structure Solution and Refinement.** Blue blocks of **3**·$3H_2O$ suitable for X-ray analysis were obtained from a solution of the complex in $CH_3CN$/diethyl ether/water mixture stored at −28 °C. Deep blue plates of **4**·$H_2O$ were obtained from slow cooling of aqueous $CH_3CN$ solutions of **4**. Diffraction data for **3** were collected at 90 K on a Bruker SMART 1000 system while data for **4** were collected at 130 K on a Siemens P4 machine. Mo K$\alpha$ (0.71073 Å) radiation was used and the data were corrected for absorption. Intensities of two standard reflections showed only random fluctuations of less

(41) A brief report on the copper(II) and nickel(II) complexes of this ligand has been published by Nonoyama (Nonoyama, M.; Yamasaki, K. *Inorg. Chim. Acta* **1974**, *10*, 59). However, no structural data are available for these complexes.

**Table 1.** Summary of Crystal Data and Intensity Collection and Structural Refi,nement Parameters for [Cu(APPy)]·3$H_2O$ (**3**·3$H_2O$) and [$Cu_2$(AEPy)$_2$]·$H_2O$ (**4**·$H_2O$)

| | **3** | **4** |
|---|---|---|
| formula (mol wt) | $C_{19}H_{29}CuN_5O_5$ | $C_{34}H_{40}Cu_2N_{10}O_5$ |
| (mol wt) | (471.01) | (795.84) |
| cryst color, habit | blue plate | blue plate |
| *T*, K | 89(2) | 133(2) |
| cryst system | monoclinic | monoclinic |
| space group | *C*2/*c* | P$2_1$/n |
| *a*, Å | 15.2171(10) | 10.501(2) |
| *b*, Å | 13.7051(9) | 25.305(5) |
| *c*, Å | 20.1824(14) | 13.022(3) |
| α, deg | 90° | 90° |
| *β*, deg | 91.3050(10)° | 93.18(3)° |
| *γ*, deg | 90° | 90° |
| *V*, Å$^3$ | 4208.0(5) | 3455.0(12) |
| *Z* | 8 | 4 |
| $d_{calced}$, g cm$^{-3}$ | 1.487 | 1.530 |
| abs coeff, $\mu$, mm$^{-1}$ | 1.079 | 2.000 |
| GOF[a] on $F^2$ | 1.064 | 1.062 |
| $R_1$,[b] % | 4.87 | 6.54 |
| $R_{w2}$,[c] % | 10.68 | 16.74 |

[a] GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$ ($M$ = number of reflections, $N$ = number of parameters refined). [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_{w2} = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

than 1% during the course of data collection. The structures were solved using the standard SHELXS-97 package.

Machine parameters, crystal data, and data collection parameters for **3**·3$H_2O$ and **4**·$H_2O$ are summarized in Table 1 while selected bond distances and angles are listed in Table 2. Complete crystallographic data for [Cu(APPy)]·3$H_2O$ and [$Cu_2$(AEPy)$_2$]·$H_2O$ have been submitted as Supporting Information.

## Results and Discussion

We have previously demonstrated that ligands with carboxamide group(s) are easily converted to their deprotonated forms (sodium salts) by the addition of NaH in DMF solution.[1] In the present work, the same synthetic procedure has been utilized to deprotonate both the ligands. The deprotonated form of **1**, $APPy^{2-}$, is a strong ligand and readily forms the deep blue copper(II) complex **3** upon addition of copper(II) salts such as $CuCl_2$·2$H_2O$ or Cu($ClO_4$)$_2$·6$H_2O$ (Caution: perchlorate salts should be handled with care since they could lead to explosions upon heating). When $CuCl_2$·2$H_2O$ is used, the reaction generates 2 equiv of NaCl which can be easily removed by filtration. The dimeric copper(II) complex **4** is obtained by following the same general procedure. Multiple attempts to obtain any monomeric species by changing the reaction conditions such as changes in the starting materials or solvents were all unsuccessful.

**Structure of [Cu(APPy)]·3$H_2O$ (3·3$H_2O$)**. Crystallographic study reveals that the crystals are composed of monomeric units of [Cu(APPy)]. An ORTEP drawing of **3** is shown in Figure 1 while the metric parameters are listed in Table 2. The $APPy^{2-}$ ligand employs five nitrogen donors (two pyridine nitrogens, two carboxamido nitrogens, and one tertiary amine nitrogen) to bind the copper(II) center and the geometry around copper is distorted square-pyramidal. The base of the square pyramid is comprised of one pyridine-2-carboxamido moiety, the tertiary amine nitrogen and the carboxamido nitrogen of the second pyridine-2-carboxamide group which lies perpendicular to the basal plane (Figure 1). The pyridine ring nitrogen of this second pyridine-2-carboxamide group occupies the apical position to complete the square pyramid geometry. In this configuration, the two carboxamido nitrogens are trans to each other and are nearly collinear ($N_{amido}$−Cu−$N_{amido}$ angle is ∼173°). Due to the close bite of the pyridine-2-carboxamido units, both five membered rings force the $N_{amido}$−Cu−$N_{py}$ angles very close to 80°(Table 2). Similar small $N_{amido}$−Cu−$N_{py}$ angles have been noted in copper(II) complexes of ligands with pyridine-2-carboxamide group(s).[2,18,19,29]

**Table 2.** Selected Bond Distances (Å) and Angles (Deg) for [Cu(APPy)]·3$H_2O$ (**3**·3$H_2O$) and [$Cu_2$(AEPy)$_2$]·$H_2O$ (**4**·$H_2O$)

| | | | |
|---|---|---|---|
| | Complex **3** | | |
| Cu−N1 | 2.0689(19) | N2−C6 | 1.332(3) |
| Cu−N2 | 1.9608(18) | N2−C7 | 1.467(3) |
| Cu−N3 | 2.1056(19) | N3−C9 | 1.499(3) |
| Cu−N4 | 1.9636(18) | N3−C10 | 1.498(3) |
| Cu−N5 | 2.2129(19) | N3−C19 | 1.486(3) |
| O1−C6 | 1.255(3) | N4−C12 | 1.463(3) |
| O2−C13 | 1.269(3) | N4−C13 | 1.320(3) |
| N1−C5 | 1.350(3) | N5−C14 | 1.352(3) |
| N1−Cu−N2 | 80.92(7) | Cu−N2−C6 | 117.50(15) |
| N1−Cu−N3 | 154.59(8) | Cu−N2−C7 | 127.94(14) |
| N1−Cu−N4 | 93.16(7) | Cu−N3−C9 | 112.18(13) |
| N1−Cu−N5 | 97.95(7) | Cu−N3−C10 | 108.39(13) |
| N2−Cu−N3 | 95.98(7) | Cu−N3−C19 | 111.14(14) |
| N2−Cu−N4 | 172.50(8) | Cu−N4−C12 | 118.18(14) |
| N2−Cu−N5 | 106.58(7) | Cu−N4−C13 | 120.02(15) |
| N3−Cu−N4 | 87.38(8) | Cu−N5−C14 | 109.62(14) |
| N3−Cu−N5 | 107.03(7) | N2−C6−O1 | 126.5(2) |
| N4−Cu−N5 | 78.69(7) | N4−C13−O2 | 126.8(2) |
| Cu−N1−C5 | 112.35(14) | N5−C14−C13 | 116.13(19) |
| | Complex **4** | | |
| Cu1−N1 | 2.091(4) | Cu1−Cu2 | |
| Cu1−N2 | 1.909(4) | O1−C6 | 1.245(6) |
| Cu1−N3 | 2.153(4) | N2−C6 | 1.317(7) |
| Cu1−N9 | 1.960(4) | O2−C12 | 1.234(7) |
| Cu1−N10 | 2.172(4) | N4−C12 | 1.347(7) |
| Cu2−N4 | 1.958(4) | O3−C23 | 1.239(7) |
| Cu2−N5 | 2.173(5) | N7−C23 | 1.318(7) |
| Cu2−N6 | 2.068(4) | O4−C29 | 1.240(6) |
| Cu2−N7 | 1.922(4) | N9−C29 | 1.342(7) |
| Cu2−N8 | 2.155(5) | C29−C30 | 1.512(7) |
| N1−Cu1−N2 | 79.98(17) | N4−Cu2−N5 | 80.16(18) |
| N1−Cu1−N3 | 152.97(16) | N4−Cu2−N6 | 97.65(18) |
| N1−Cu1−N9 | 96.22(17) | N4−Cu2−N7 | 178.08(19) |
| N1−Cu1−N10 | 99.36(17) | N4−Cu2−N8 | 100.01(17) |
| N2−Cu1−N3 | 82.37(17) | N5−Cu2−N6 | 100.53(18) |
| N2−Cu1−N9 | 176.12(17) | N5−Cu2−N7 | 99.17(18) |
| N2−Cu1−N10 | 100.97(18) | N5−Cu2−N8 | 104.75(17) |
| N3−Cu1−N9 | 100.91(16) | N6−Cu2−N7 | 80.50(19) |
| N3−Cu1−N10 | 103.99(16) | N6−Cu2−N8 | 151.12(18) |
| N9−Cu1−N10 | 80.33(17) | N7−Cu2−N8 | 81.89(17) |

The Cu(II)−$N_{amido}$ bond distances of **3** (1.9608(18) and 1.9636(18) Å for Cu−N2 and Cu−N4, respectively) are well within the range of Cu−$N_{amido}$ distances noted in similar complexes.[2,18,19,29] There are two distinctly different Cu−$N_{py}$ bond distances (2.0689(19) and 2.2129(19) Å) in **3** that correspond to the basal and apical Cu(II)-pyridine bonds. The long apical bond (Cu−N5) reflects a weak axial interaction as expected for Jahn−Teller sensitive copper(II) complexes.

Although the N2−Cu−N4 angle is close to 180°, the N1−Cu−N3 angle is quite small (154.59 (8)°), and this results in significant distortion from ideal square pyramidal geometry. This distortion presumably arises from steric repulsion between the methyl group of the tertiary amine group and the pyridine ring occupying the axial position (Figure 1). This is supported by the greater-than-90° value of the N3−Cu−N5 angle (107.03-(7)°). Additional distortion may arise from steric requirements of the propyl linkage. Overall, the copper center is lifted 0.279 Å away from the average basal plane toward the apical pyridine nitrogen.[42]

(42) The calculation was performed by computing the least squares plane defined by N1, N2, N3, and N4 and noting the extent of displacement of the copper(II) center from that plane.

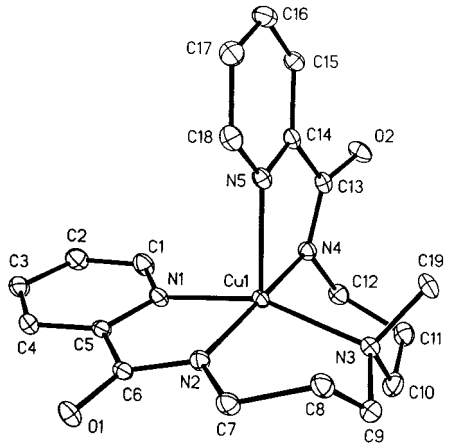



**Figure 1.** Thermal ellipsoid (probability level 50%) plot of [Cu(APPy)] (complex **3**) with the atom-labeling scheme. H atoms are omitted for the sake of clarity.

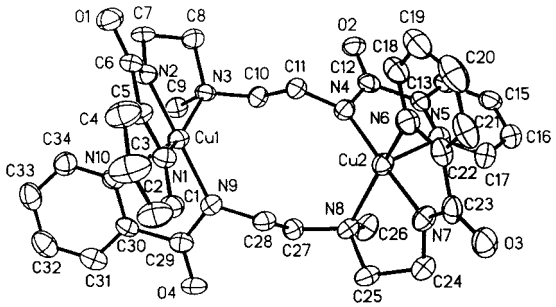



**Figure 2.** Thermal ellipsoid (probability level 50%) plot of $[Cu_2(AEPy)_2]$ (complex **4**) with the atom-labeling scheme. H atoms are omitted for the sake of clarity.

**Structure of $[Cu_2(AEPy)_2]\cdot H_2O$ ($4\cdot H_2O$).** An ORTEP diagram of the dimeric copper(II) complex **4** is shown in Figure 2. Each copper(II) center resides in a distorted square pyramidal geometry generated by the $N_{py}-N_{amido}-N_{amine}$ portion of one ligand and one pyridine-2-carboxamido end of the other. The base of the square pyramid around each copper is completed by the $N_{py}-N_{amido}-N_{amine}$ portion of one ligand and $N_{amido}$ donor center of the sharing ligand while the apical position is occupied by the second $N_{py}$ of the shared ligand (Figure 2). The carboxamido nitrogen donors occupy trans positions in the basal plane of each copper center. The two copper(II) centers, connected by the pendant ethylene linkages, are 5.3433(14) Å apart. The copper(II)$-N_{amido}$ bonds of **4** (1.909(4)−1.960(4) Å) are slightly shorter than those observed in **3**.

Close comparison of the structural parameters of **4** with those of **3** reveal similarities in the coordination structure of the copper(II) centers. For example, in **4**, the N1−Cu−N3 angle is 152.97(16)° and is very close to the corresponding angle found in **3** (154.59(8)°). Additionally, the apical pyridine ring is pushed away from the methyl group on the amine nitrogen and this steric interaction results in an increase in the corresponding $N_{py}-Cu-N_{amine}$ bond angle (Table 2). In both **3** and **4**, the carboxamido nitrogen donors lie in trans positions in the basal plane and are nearly linear. Finally, in both **3** and **4**, two different Cu(II)$-N_{py}$ bond lengths (shorter basal plane Cu$-N_{py}$ bond and a longer apical Cu$-N_{py}$ bond) are observed.

**Properties.** Coordination of $APPy^{2-}$ to copper(II) is indicated by the IR spectrum of this complex. Ligation of the carboxamido nitrogens results in a red shift in the carbonyl stretching frequency ($\nu_{co}$) from 1666 $cm^{-1}$ in **1** to 1604 $cm^{-1}$ in **3**.[1] A similar red shift of the $\nu_{co}$ is noted for **4** upon ligation of $AEPy^{2-}$ to copper(II) (1670 $cm^{-1}$ in the free ligand to 1612 $cm^{-1}$ in the complex). As mentioned earlier, the spectroscopic properties of [Cu(APPy)] (**3**) are very similar to those of $[Cu(Py_3P)]$. For example, **3** readily dissolves in solvents such as methanol and $CH_3CN$ to give deep blue solutions. In methanol, **3** exhibits a broad absorption band with $\lambda_{max}$ at 590 nm and a shoulder at 770 nm. The blue solution of $[Cu(Py_3P)]$ in methanol also displays a broad absorption band with $\lambda_{max}$ at 613 nm and a shoulder at 750 nm. The extinction coefficients of these bands are very similar (Figure S1, Supporting Information).

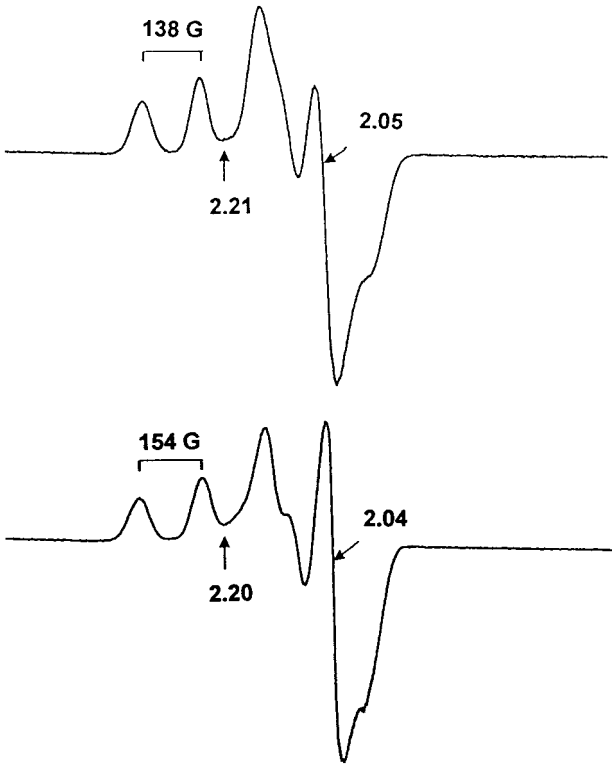



**Figure 3.** X-band EPR spectra of [Cu(APPy)] (top) and $[Cu(Py_3P)]$ (bottom) in methanol/toluene glass (80 K). Selected $g$ and $A$ values are indicated. Spectrometer settings: microwave frequency, 9.43 GHz; microwave power, 25 mW; modulation frequency, 100 kHz; modulation amplitude, 2G.

The X-band EPR spectrum of **3** in $CH_3OH$ glass (80 K) is displayed in Figure 3. The spectrum is typical for monomeric copper(II) complexes in tetragonal geometry ($g_\perp = 2.05$, $g_\parallel = 2.21$, $A_\parallel = 138$ G) with $d_{x2-y2}$ ground state. The $g$ values of **3** are also very close to those reported for $[Cu(Py_3P)]$ ($g_\perp = 2.04$, $g_\parallel = 2.20$, $A_\parallel = 154$ G; Figure 3) and are within the expected range of values noted for other distorted square-pyramidal copper(II) centers with [N5] ligation.[2,16,22−24,43] Miyoshi et al. have demonstrated that larger $A_\parallel$ values are consistent with stronger in-plane ligand strength in square pyramidal copper(II) complexes.[43] When the coordination structures of the two complexes **3** and $[Cu(Py_3P)]$ are compared, it becomes evident that the smaller $A_\parallel$ value of **3** (138 G)) arises from weaker in-plane crystal field associated with the tertiary amine nitrogen.

Overall, comparison of the structural and spectral parameters of complex **3** with those of $[Cu(Py_3P)]$ reveals that although the structure of the copper(II) complex changes upon replacement of the pyridine-2,6-dicarboxamide unit with two pyridine-2-carboxamide units tethered with flexible $-(CH_2)_3-N(Me)-(CH_2)_3-$ link, the less resonance-stabilized structure of **3** displays spectral properties very similar to those of $[Cu(Py_3P)]$.

(43) Miyoshi, K.; Tanaka, H.; Kimura, E.; Tsuboyama, S.; Murata, S.; Shimizu, H.; Ishizu, K. *Inorg. Chim. Acta* **1983**, *78*, 23.

Thus, the planarity of the pyridine-2,6-dicarboxamido moiety could be removed without disrupting the spectral properties of the pentacoordinate copper(II) center.

In $[Cu_2(AEPy)_2]$ (**4**), the two Cu(II) centers are too far apart to interact with each other. Susceptibility measurement at room temperature shows that polycrystalline **4** has a magnetic moment of 1.78 $\mu_B$ per copper. Also in solid state, **4** exhibits a broad EPR signal around $g = 2$ with no visible hyperfine interaction in the temperature range 80−300 K. Since the EPR spectrum of **4** in methanol or DMF glass at 80 K resembles monomeric Cu(II) EPR spectrum ($g_\perp = 2.06$, $g_\parallel = 2.20$, $A_\parallel = 135$ G), it appears that the dimer dissociates in solution. However, as pointed out earlier, attempts to crystallize the monomeric species always results in isolation of **4** in high yields.

## Conclusion

We have reported the syntheses and characterization of the copper(II) complexes of two ligands ($APPyH_2$ and $AEPyH_2$) that contain two pyridine-2-carboxamide units connected by $-(CH_2)_n-N(Me)-(CH_2)_n-$ links. In the deprotonated form, $APPy^{2-}$ binds copper(II) to afford the pentacoordinate complex [Cu(APPy)] (**3**) with distorted square pyramidal geometry. In contrast, $AEPy^{2-}$ only affords the dimeric copper(II) complex $[Cu_2(AEPy)_2]$ (**4**). Thus, our results demonstrate that the propylene linkages in $APPyH_2$ (**1**) are sufficient in length to allow complete coordination to a single copper(II) ion (to yield **3**) while the ethylene linkages in $AEPyH_2$ (**2**) are too short to bind a single copper(II) center and hence give rise to the ligand-shared dimer **4**. Research is currently underway to establish the coordination characteristics of the two reported ligand with various $M^{n+}$ ions.

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**Supporting Information Available:** Electronic absorption spectra of [Cu(APPy)] (**3**) and $[Cu(Py_3P)]$ in methanol (Figure S1) and the X-ray crystallographic files (in CIF format) for the structure determination of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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