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# Synthesis and Crystal Structure Determination of Some Asymmetrical and Symmetrical CR-Type Macrocyclic Schiff Base Complexes, with a Single Pendant Coordinating 2-Aminoethyl Arm

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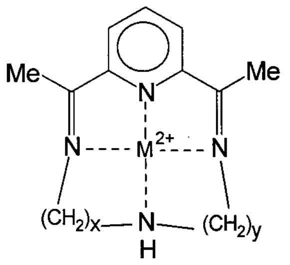
A novel, totally asymmetrical tripodal 2,3′,4″-tetraamine ligand, $N\{(CH_2)_2NH_2\}\{(CH_2)_3NH_2\}\{(CH_2)_4NH_2\}$, epb, has been synthesized. In the presence of copper(II) and nickel(II) ions it condenses with 2,6-diacetylpyridine in 1:1 ethanol−water solution, producing some new CR-type complexes with a pendant primary amino group. The X-ray crystal structure of the resulting copper(II) complex, $[Cu(3,4(2)\text{-}CR)](PF_6)_2$ (**1**), and two other related complexes, $[Cu(2,4(2)\text{-}CR)](ClO_4)_2$ (**2**) and $[Cu(3,3(2)\text{-}CR)](ClO_4)_2$ (**3**), are reported. Crystal data: complex **1**, monoclinic, $P2_1/n$, $a = 8.366(3)$ Å, $b = 15.549(3)$ Å, $c = 20.283(2)$ Å, $\beta = 98.73(2)°$, $V = 2607.8(11)$ Å$^3$, $Z = 4$, R1 = 0.0621, wR2 = 0.1615; complex **2**, monoclinic, $P2_1/c$, $a = 7.981(10)$ Å, $b = 18.882(3)$ Å, $c = 15.185(3)$ Å, $\beta = 96.40(2)°$, $V = 2275.7(6)$ Å$^3$, $Z = 4$, R1 = 0.0773, wR2 = 0.1635; complex **3**, monoclinic, $P2_1/n$, $a = 7.8764(10)$ Å, $b = 15.361(2)$ Å, $c = 19.370(2)$ Å, $\beta = 100.330(10)°$, $V = 2305.7(5)$ Å$^3$, $Z = 4$, R1 = 0.0537, wR2 = 0.1397. In all of these, copper atoms are bonded to four nitrogens of a macrocyclic ring and a nitrogen of the pendant arm. The arrangements are slightly distorted square-pyramidal in which the primary amino groups occupy apical positions and have the longest Cu−N distances. For all isomers, copper(II) ions are somewhat above the plane of the imino−pyridine system of the macrocyclic ring in the direction of the pendant coordinated primary amino group.

## Introduction

Study on macrocyclic complexes with pendant arms is growing because of their importance in biological systems and their utility as bioinorganic models for cobalamine.[1−4] A common method for preparation of these complexes is template condensation of 2,6-diacetylpyridine with an appropriate tripodal tetraamine in the presence of the required metal ion. The prototype is the CR system derived from $HN(CH_2CH_2CH_2NH_2)_2$[5] (Figure 1c), and we have reported[6−8] similar systems in which the size of the macrocycle has been modified and/or a pendant arm has been added. We have also devised improved synthesis of symmetrical and asymmetrical tripodal tetraamines and related ligands[7−9] which are necessary precursors. We now report the use of these techniques to prepare a novel totally asymmetrical 2,3′,4″-tetraamine in which all three chains are different (Figure 2). This ligand was synthesized because, from its condensation with diacetylpyridine in the presence of copper(II) and nickel(II) ions, some CR-type Schiff-base complexes with a pendant arm are produced (Figure 3a). In contrast to previous works,[6−8] there are always two possibilities of ring closure: 3,4(2)-CR and 2,4(3)-CR. Which occurs depends mainly upon the nature of the metal ions and the structure of the ternary complex involved.[10] We also report the crystal structure of $[Cu(3,4(2)\text{-}CR)](PF_6)_2$ **(1)** together with crystal structures of two other related copper(II) complexes,[8] $[Cu(2,4(2)\text{-}CR)](ClO_4)_2$ **(2)** and $[Cu(3,3(2)\text{-}CR)](ClO_4)_2$ **(3)**, for comparison.



a) x = 3, y = 4 $[M(3,4\text{-}CR)]^{2+}$ [ M = Ni, Cu, Zn ]
b) x = 2, y = 4 $[M(2,4\text{-}CR)]^{2+}$ [ M = Cu ]
c) x = y = 3 $[M(CR)]^{2+}$ [ M = Fe, Co, Cu, Ni, Zn ]

**Figure 1.** The proposed chemical structures of the $[M(x,y\text{-}CR)]^{2+}$ cations.

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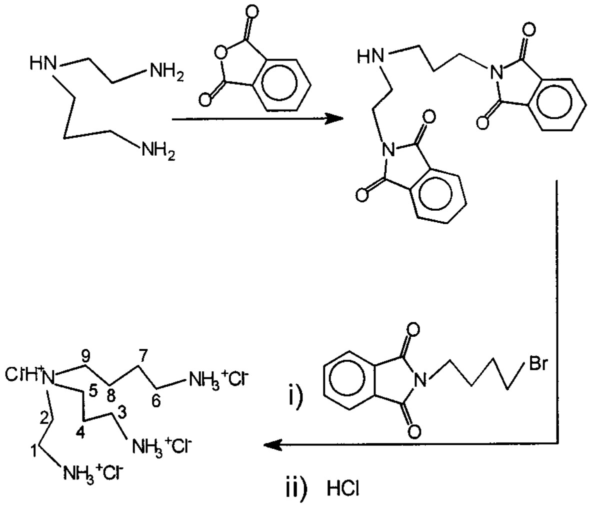
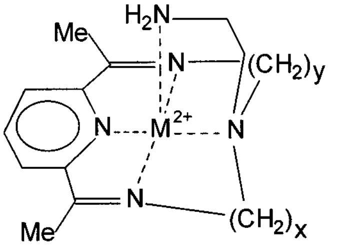


**Figure 2.** The procedure of ligand synthesis.



a) x = 3, y = 4  [ M(3,4(2)-CR)]$^{2+}$  [ M = Cu, Ni ]
b) x = 2, y = 4  [ M(2,4(2)-CR)]$^{2+}$  [ M = Cu, Ni ]
c) x = y = 3  [ M(3,3(2)-CR)]$^{2+}$  [ M = Cu ]

**Figure 3.** The proposed chemical structures of the [M(*x*,*y*(2)-CR)]$^{2+}$ cations.

## Experimental Section

**General Information.** 2,6-Diacetylpyridine was obtained from Aldrich and used without further purification. The tripodal tetraamine ligands N{CH$_2$)$_4$NH$_2$}{(CH$_2$)$_2$NH$_2$}$_2$ bee and N{(CH$_2$)$_3$NH$_2$}$_2${(CH$_2$)$_2$-NH$_2$} ppe, and their resulting macrocyclic complexes, [Cu2,4(2)-CR]-(ClO$_4$)$_2$ (**2**) and [Cu3,3(2)-CR](ClO$_4$)$_2$ (**3**), were synthesized according to methods that we have earlier reported.[8] 2,3′-Diphthalimidoethylpropylamine and *N*-(4-bromobutyl)phthalimide were prepared according to the literature methods.[8,11] IR, UV−vis, and NMR spectra were measured on Shimadzu IR-435, UV-265 FW, and Bruker DPX 300 NMR spectrometers, respectively.

**Ligand Synthesis. 2,3′,4″-Triaminoethylpropylbutylamine Tetrahydrochloride (epb·4HCl).** 2,3′-Diphthalimidoethylpropylamine (15 g, 40 mmol) and *N*-(4-bromobutyl)phthalimide (11.28 g, 40 mmol) were fused together at 160 °C with constant stirring for 1 h. The resulting solid was pulverized and stirred in boiling 2:1 methanol−chloroform for about 30 min. The insoluble materials were filtered off, the filtrate was evaporated to dryness, and the residue was heated under reflux with HCl (300 cm$^3$, 25%w/w) for 12 h. The phthalic acid which formed on cooling was removed by filtration, and the filtrate was evaporated to small bulk and poured into absolute EtOH. The viscous residue was recrystallized from EtOH−H$_2$O, washed several times with small amounts of cooled absolute EtOH and Et$_2$O, and dried in vacuo; yield 5.2 g (40%). Analysis suggests the presence of some ethanol and water: $C_9H_{24}N_4$·4HCl·2.5H$_2$O·0.2C$_2$H$_5$OH. Anal. Calcd for $C_{9.4}H_{34.2}N_4Cl_4O_{2.7}$: C, 29.0; H, 8.8; N, 14.4. Found: C, 28.7; H, 9.0; N, 14.4. FAB MS (positive FAB in nitrobenzyl alcohol): *m*/*z* 189 (epbH$^+$, 100%). $^1$H NMR ($\delta$ (ppm), D$_2$O): 1.1 (C*H*$_3$−CH$_2$OH, t), 1.77 (4 H, m, 7-H and 8-H), 2.1 (2 H, m, 4-H), 2.9 (4 H, m, 3-H and 6-H), 3.4 (8 H, m, 1-H, 2-H, 5-H, and 9-H), 3.56 (CH$_3$−C*H*$_2$OH, q). $^{13}$C NMR ($\delta$ (ppm), D$_2$O): 20.88 (C-8), 21.99 (C-4), 24.16 (C-7), 34.08 (C-2), 36.83 (C-5), 39.21 (C-9), 49.57 (C-1), 50.79 (C-3), 53.30 (C-6).

**Complex Synthesis.** Both complexes were readily prepared by template condensation. 2,6-Diacetylpyridine and epb·4HCl were refluxed for 24 h in 1:1 EtOH−H$_2$O with the metal salt (usually the perchlorate) in equimolar ratio. The initial pH was adjusted to ca. 8−9, and typical concentrations were 0.002 M. The solvent was evaporated to small bulk, and, after cooling and addition of NaClO$_4$, crystalline products were obtained as needles. The nickel(II) complex was found to be hydrated.

**[Ni(3,4(2)-CR)](ClO$_4$)$_2$·H$_2$O.** Yield: 0.1 g (30%). Anal. Calcd for $C_{18}H_{31}N_5Cl_2O_9Ni$: C, 36.5; H, 5.2; N, 11.8. Found: C, 37.1; H, 5.0; N, 11.3. FAB MS (positive FAB in nitrobenzyl alcohol): *m*/*z* 472 (M − ClO$_4^+$, 100%).

**[Cu(3,4(2)-CR)](ClO$_4$)$_2$.** Yield: 0.2 g (60%). Anal. Calcd for $C_{18}H_{29}N_5Cl_2O_8Cu$: C, 37.4; H, 5.0; N, 12.1. Found: C, 37.2; H, 5.9; N, 12.0. FAB MS (positive FAB in nitrobenzyl alcohol): *m*/*z* 477 (M − ClO$_4^+$, 78%).

Recrystallization of 1 g of the above compound in methanol in the presence of an excess of NaPF$_6$ gave green needle crystals of [Cu(3,4-(2)-CR)](PF$_6$)$_2$ (**1**), yield 0.9 g (80%). Anal. Calcd for $C_{18}H_{29}N_5F_{12}P_2Cu$: C, 32.3; H, 4.3; N, 10.5. Found: C, 32.2; H, 4.3; N, 10.3.

**X-ray Crystal Structure Analysis.** Crystal data and the major experimental parameters for the three crystal structures ([Cu(3,4(2)-CR)](PF$_6$)$_2$ (**1**), [Cu(2,4(2)-CR)](ClO$_4$)$_2$ (**2**), and [Cu(3,3(2)-CR)](ClO$_4$)$_2$ (**3**)) are reported in Table 2. Single crystals of **2** and **3** were obtained by recrystallization from water, and **1** by slow diffusion of diethyl ether vapor into a methanol solution. Three-dimensional X-ray data were collected on a Rigaku AFC65 diffractometer by the $\omega-2\theta$ method, using Mo K$\alpha$ radiation for **2** and Cu K$\alpha$ radiation for **1** and **3**. The structures was solved by Patterson and Fourier techniques and refined by full-matrix least-squares regression (SHELX-97).[12] Complex scattering factors were taken from ref 13 and from SHELX-97.

## Results and Discussion

Previously known tripodal ligands either are completely symmetrical (all three arms identical) or have two arms of one type and the third different. Using a method similar to those we have employed previously,[7−9] we have now prepared the first tripodal ligand containing three different arms: N{(CH$_2$)$_2$-NH$_2$}{(CH$_2$)$_3$NH$_2$}{(CH$_2$)$_4$NH$_2$} (epb). Both chloride and perchlorate salts of this amine were prepared, and both were hygroscopic. IR, $^{13}$C NMR, $^1$H NMR, and mass spectra of the hydrochloride salt of this amine were consistent with its asymmetrical structure.

**Complexes Derived from epb.** Macrocyclic Schiff base complexes [M(3,4(2)-CR)]$^{2+}$ with nickel(II) and copper(II) were obtained by template condensation of the tetraamine with diacetylpyridine in the presence of appropriate metal salts (usually perchlorate salts). The absence of (C═O) absorptions at ca. 1700 cm$^{-1}$ in the IR spectrum and the presence of $\nu$(C═N) bands [in addition to the pyridine $\nu$(C═N)] in the correct positions for Schiff base linkages indicate that cyclization has indeed occurred,[14] giving complexes of a new macrocylic ligand. The presence of a pair of sharp $\nu$(N−H) bands is as expected for a single primary amine group.[15] Broad intense bands at ca. 1100 cm$^{-1}$ due to ClO$_4^-$ show no splitting,

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**Table 1.** IR Data ($cm^{-1}$) and Electronic Spectroscopy Data ($cm^{-1}$) for the CR-Type Complexes

| compound[a,b] | $\nu$(C=N)[c] | $\nu$(N−H) | $\nu$(O−H) | $\lambda_{max}$ (soln, $H_2O$)[d] | ref |
|---|---|---|---|---|---|
| $[Cu(3,4(2)\text{-}CR)](PF_6)_2$ (**1**) | 1626 | 3387, 3337 | | | this work |
| $[Cu(3,4(2)\text{-}CR)](ClO_4)_2$ | 1623 | 3338, 3281 | | 15151 (138.4), 11111 (85.8) | this work |
| $[Cu(2,4(2)\text{-}CR)](ClO_4)_2{\cdot}0.5H_2O$[e] | 1650s, 1622 | 3340, 3290 | 3480m | 16583 (244), 12048 (121) | 8 |
| $[Cu(3,3(2)\text{-}CR)](ClO_4)_2$ (**3**) | 1625 | 3356, 3285 | | 16129 (134), 11764 (80) | 8 |
| $[Cu(3,4\text{-}CR)](ClO_4)_2{\cdot}H_2O$ | 1635 | | | 16393 (110) | 14 |
| $[Cu(2,4\text{-}CR)](ClO_4)_2$ | 1650, 1615 | 3240 | | 16920 (160) | 6 |
| $[Ni(2,4(2)\text{-}CR)](ClO_4)_2{\cdot}1.5H_2O$ | 1649s, 1611sh | 3330, 3282 | 3420s | 18050sh (46), 12853 (40) | 8 |
| $[Ni(3,4(2)\text{-}CR)](ClO_4)_2{\cdot}H_2O$ | 1623.8 | 3321, 3265 | 3430s | 19569 (42), 18018 (32), 11905 (27) | this work |
| $[Ni(3,4\text{-}CR)](ClO_4)_2{\cdot}2H_2O$ | 1628 | | | 27777 (2), 21053 (3), 12837 (14), 12077 (18) | 14 |

[a] ***CAUTION***: Perchlorate salts can be dangerously explosive. The compounds described here have never detonated in our hands, but they should be treated with care. [b] In all cases (except **1**) a single broad, intense $\nu$(Cl−O) band is found at ca. 1100 $cm^{-1}$ for the $ClO_4^-$ ion. [c] Schiff base. [d] Figures in parentheses are extinction coefficients ($dm^3\ mol^{-1}\ cm^{-1}$). [e] Suitable single crystals of compound **2** were obtained by recrystallization of this compound.

**Table 2.** Crystal Data and Structure Refinement for the Complexes **1**, **2**, and **3**

| | **1** | **2** | **3** |
|---|---|---|---|
| empirical formula | $C_{18}H_{29}CuF_{12}N_5P_2$ | $C_{17}H_{27}Cl_2CuN_5O_8$ | $C_{17}H_{27}Cl_2CuN_5O_8$ |
| fw | 668.94 | 563.88 | 563.88 |
| temp (K) | 295(2) | 203(2) | 295(2) |
| wavelength (Å) | 1.54178 | 0.71073 | 1.54178 |
| space group | monoclinic, $P2_1/n$ | monoclinic, $P2_1/c$ | monoclinic, $P2_1/n$ |
| $a$ (Å) | 8.366(3) | 7.9871(10) | 7.8764(10) |
| $b$ (Å) | 15.549(3) | 18.882(3) | 15.361(2) |
| $c$ (Å) | 20.283(2) | 15.185(3) | 19.370(2) |
| $\beta$ (deg) | 98.73(2) | 96.40(2) | 100.330(10) |
| $Z$ | 4 | 4 | 4 |
| $V$ (Å$^3$) | 2607.8(11) | 2275.7(6) | 2305.7(5) |
| $\rho_{calcd}$ (g $cm^{-3}$) | 1.704 | 1.646 | 1.624 |
| $\mu$ ($mm^{-1}$) | 3.330 | 1.249 | 3.954 |
| $F$(000) | 1356 | 1164 | 1164 |
| cryst size ($mm^3$) | 0.3 × 0.15 × 0.1 | 0.3 × 0.15 × 0.05 | 0.3 × 0.2 × 0.1 |
| $\theta$ range for data collection (deg) | 4.41−65.10 | 1.73−24.96 | 3.70−60.15 |
| index ranges | $-4 \le h \le 9$ | $0 \le h \le 9$ | $-8 \le h \le 8$ |
| | $-9 \le k \le 17$ | $0 \le k \le 22$ | $-8 \le k \le 17$ |
| | $-23 \le l \le 23$ | $-18 \le l \le 17$ | $-21 \le l \le 21$ |
| reflns collected | 4757 | 4219 | 3696 |
| GOF on $F^2$ | 1.025 | 0.998 | 0.996 |
| final $R(F_o^2)$[a] | 0.0621 | 0.0773 | 0.0537 |
| weighted $R(F_o^2)$[b] | 0.1615 | 0.1635 | 0.1397 |

[a] $R1 = \Sigma||F_o| - |F_c|/\Sigma|F_o||$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for the Complexes **1**, **2**, and **3**

| | **1** | **2** | **3** |
|---|---|---|---|
| Cu−N(1) | 1.936(5) | 1.901(5) | 1.908(5) |
| Cu−N(2) | 2.054(6) | 2.003(6) | 2.052(5) |
| Cu−N(3) | 2.121(6) | 1.959(6) | 2.041(5) |
| Cu−N(4) | 2.024(8) | 2.048(6) | 1.987(5) |
| Cu−N(5) | 2.155(9) | 2.152(9) | 2.182(8) |
| N(2)−C(6) | 1.261(9) | 1.239(10) | 1.279(9) |
| N(3)−C(7) | 1.249(11) | 1.262(9) | 1.277(9) |
| N(1)−Cu−N(2) | 78.5(2) | 80.2(3) | 78.8(2) |
| N(1)−Cu−N(3) | 76.8(3) | 78.9(2) | 79.3(2) |
| N(1)−Cu−N(4) | 175.0(3) | 160.1(3) | 175.1(3) |
| N(1)−Cu−N(5) | 101.2(3) | 110.4(3) | 100.4(3) |
| N(2)−Cu−N(3) | 150.0(3) | 152.4(3) | 152.6(2) |
| N(2)−Cu−N(4) | 98.3(3) | 112.4(3) | 99.9(2) |
| N(2)−Cu−N(5) | 105.6(3) | 98.3(3) | 100.4(3) |
| N(3)−Cu−N(4) | 104.9(3) | 83.8(2) | 100.4(2) |
| N(3)−Cu−N(5) | 95.7(3) | 105.8(3) | 99.6(3) |
| N(4)−Cu−N(5) | 83.3(4) | 83.7(3) | 84.6(3) |
| N(2)−C(6)−C(8) | 126.7(7) | 126.3(9) | 125.9(7) |
| N(3)−C(7)−C(9) | 127.8(9) | 125.2(7) | 125.4(7) |

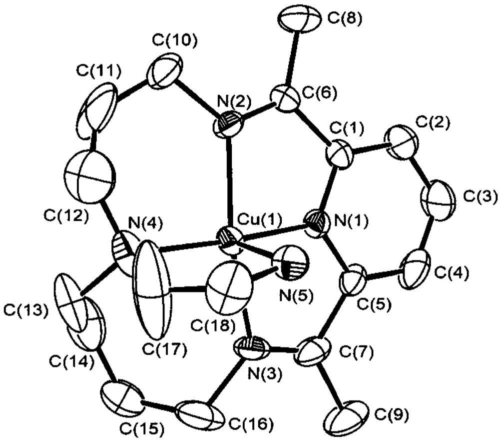

**Figure 4.** ORTEP plot of the complex $[Cu(3,4(2)\text{-}CR)](PF_6)_2$ (**1**). The atoms are drawn with 30% probability ellipsoids. $PF_6^-$ ions and hydrogen atoms are omitted for clarity.

indicating that the anion is uncoordinated in both complexes. For **1**, a single intense band due to $PF_6^-$ appears at 830 $cm^{-1}$, showing that this anion is also not coordinated. The spectra of both nickel(II) and copper(II) complexes in the region 1500−1700 $cm^{-1}$ are similar to those of 3,4-CR[14] rather than 2,4-CR[6] or 2,4(2)-CR.[8] Electronic absorption data for both complexes together with those of related complexes are shown in Table 1. It seems that their structures are probably square-pyramidal.[16]

Molecular models show not only that the 2,2(4)-CR, 2,3(3)-CR, and 2,3(4)-CR types (12- and 13-membered rings) would have a smaller aperture than 2,4(2)-CR, 3,3(2)-CR, and 3,4(2)-

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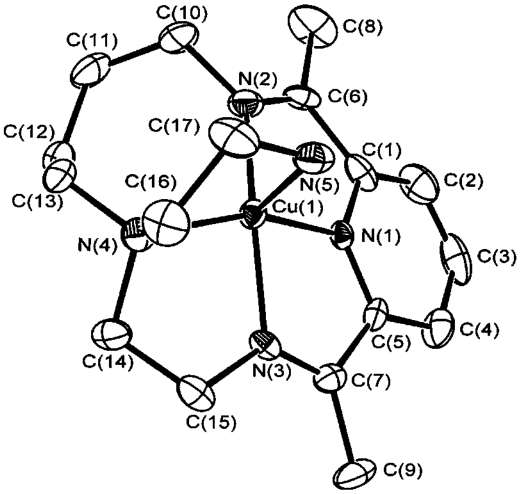

**Figure 5.** ORTEP plot of the complex [Cu(2,4(2)-CR)](ClO$_4$)$_2$ (**2**). The atoms are drawn with 30% probability ellipsoids. Perchlorate ions and hydrogen atoms are omitted for clarity.

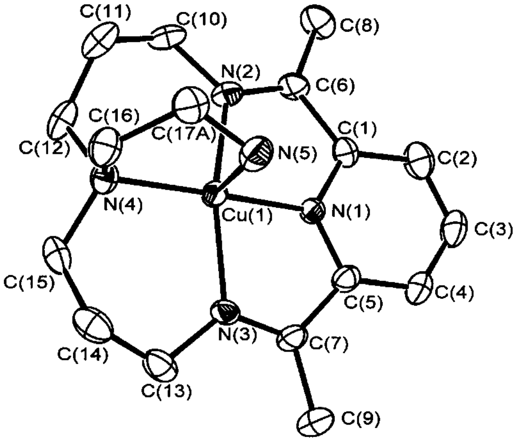

**Figure 6.** ORTEP plot of the complex [Cu(3,3(2)-CR)])](ClO$_4$)$_2$ (**3**). The atoms are drawn with 30% probability ellipsoids. Perchlorate ions and hydrogen atoms are omitted for clarity.

CR derivatives for coordination of metal ion but also that the former macrocycles would experience a much greater ring strain even without the metal being present.[5,6,8,14,17] This implies a minimum ring size (14) for the formation of this kind of macrocycle by tetraamine−diketone condensation.

**Description of the X-ray Structures.** Crystallographic data for the new complex [Cu(3,4(2)-CR)](PF$_6$)$_2$ (**1**) and the previously known[8] copper complexes [Cu(2,4(2)-CR)](ClO$_4$)$_2$ (**2**) and [Cu(3,3(2)-CR)](ClO$_4$)$_2$ (**3**) are given in Tables 2 and 3. These complexes are derived from the ligands epb, bee, and ppe, respectively. The data reveal that in each case the pendant arm is an ethylene unit: [Cu(3,3(2)-CR)]$^{2+}$, [Cu(2,4(2)-CR)]$^{2+}$, and [Cu(3,4(2)-CR)]$^{2+}$. As shown in Figures 4−6, the metal atoms have five-coordinate, square-pyramidal geometry. The nitrogen donor atoms of the macrocyclic ligands form an approximate plane, and the pyramid is completed by the amine nitrogen from the pendant arm. The imino−pyridine section of the ring is planar, and the copper atoms lie slightly above this plane [N(2)−Cu−N(3) ca. 151°], toward N(5), an effect which has been reported previously.[19] The bridgehead nitrogen atom, N(4), is effectively in the plane for **1** and **3** but rather below it for **2**, [N(1)−Cu−N(4) = 160°]; this may reflect the greater variation in sizes of the chelate rings. This distortion pulls the pendant arm, and N(5)−Cu−N(1) is greater for this complex. In all cases, the other N−Cu−N bond angles increase with the size of the chelate rings: five-membered, 76.8−84.6°; six-membered, 98.3−100.4°; seven-membered, 104.9−112.4°.

The Cu−N bond lengths in the macrocyclic rings are marginally longer for **1**, which has 15-membered rings, than for the 14-membered **2** and **3**. As would be expected, all Cu−N(macrocyclic) are shorter than the corresponding Ni−N bonds in [Ni(3,3(3)-CR)]$^{2+}$.[18] The Cu−N(5) bonds are similar in all complexes and are elongated by the Jahn−Teller effect.

## Conclusions

The present data confirm and extend our previous observations: when complexes of unsymmetrical tripodal ligands undergo cyclization with diacetylpyridine, ring closure involves preferentially the longer arms of the ligand, and the shorter arms becomes a pendant ligand. This preference follows the criterion of “best fit” between the size of the cation and the cavity offered by the ligand and also the structure of ternary complex precursors and partially condensed intermediate to macrocyclic complex.[20] The structures reported here are similar to those previously reported[7,18] for the related nickel(II) and copper(II) complexes [Ni(3,3(3)-CR)]$^{2+}$ and [Cu(3,3(3)-CR)]$^{2+}$. Rybak-Akimova et al. have also reported a second product obtained with the latter copper(II) complex in which one of the C=N double bonds has migrated into the initially saturated six-membered chelate ring.[18] In the present work our observations (IR, X-ray) do not show this type of isomerization in any of the products isolated.

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**Supporting Information Available:** Tables of crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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