

Steric influences in the formation of complexes of Schiff base derivatives of 2-acetylpyrrole with Cu(II)

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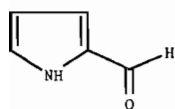
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Abstract

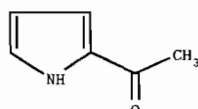
A series of Cu(II) complexes of Schiff base derivatives of 2-acetylpyrrole with ammonia, n-butylamine and benzylamine have been synthesized, as well as the bis chelate complex of 2-acetylpyrrole with Cu(II). The stoichiometry of each complex is shown to depend on the amine used. Small amines (NH_3 and CH_3NH_2) produce *trans* bis ketimine Cu(II) chelates, while ethylamine and the larger primary amines effect mixed ligand products containing one 2-acetylpyrrole chelate and one Schiff base chelate per metal center with pyrrole groups *cis* to one another. Cu(II) is shown to mediate Schiff base formation while also maintaining a square planar stereochemistry. Crystals of the *trans* bis Schiff base derivative of 2-acetylpyrrole with ammonia, $\text{Cu}(\text{C}_6\text{H}_7\text{N}_2)_2$ (**1a**), are monoclinic with space group $P2_1/n$ with $a = 11.698(2)$, $b = 5.406(1)$, $c = 10.687(3)$ Å, $\beta = 115.92(1)^\circ$, $V = 607.8$ Å³ and $Z = 2$. Crystals of the *trans* bis Schiff base adduct of 2-acetylpyrrole with benzylamine, $\text{Cu}(\text{C}_{13}\text{H}_{13}\text{N}_2)_2$ (**3b**), are monoclinic with space group $P2_1/c$ with $a = 10.647(3)$, $b = 12.737(4)$, $c = 16.371(3)$ Å, $\beta = 90.31(2)^\circ$, $V = 2220.1$ Å³ and $Z = 4$. $\text{Cu}(\text{C}_6\text{H}_6\text{NO})_2$ (**4a**), the bis Cu(II) chelate of 2-acetylpyrrole, is monoclinic with space group $P2_1/a$ with $a = 8.143(2)$, $b = 14.452(3)$, $c = 5.189(1)$ Å, $\beta = 106.82(2)^\circ$, $V = 584.5$ Å³ and $Z = 2$.

Introduction

A number of divalent metal ion complexes containing bis Schiff base derivatives of pyrrole-2-aldehyde have been structurally characterized [1–5].



pyrrole-2-aldehyde



2-acetylpyrrole

Those containing Cu(II) vary in stereochemistry according to the imino-nitrogen substituent; small groups such as H permit the molecule to assume a planar four-coordinated configuration, while bulky tert-butyl groups force a distorted tetrahedral structure [1, 3]. Solution studies also show that large imine bonded substituents cause distortions from planarity in bis pyrrole-2-aldehyde Cu(II) complexes [6]. In contrast, Zn(II) bis pyrrole-2-aldehyde compounds are tetrahedral, with little variation in stereochemistry due to the size of imino-nitrogen substituents [5].

Crystal structures of Schiff base derivatives of 2-acetylpyrrole with Cu(II) and Zn(II) have also been published, where ethyl substitution is present on the imine-nitrogen atom [7, 8]. The Zn(II) adduct assumes a distorted tetrahedral geometry, while two forms of distorted square planar Cu(II) complexes have been characterized, one a mixed-ligand product containing one Schiff base and one 2-acetylpyrrole chelate per metal center with pyrrole groups *cis* to one another, and the other a bis Schiff base adduct containing pyrrole groups *trans* to one another. Further studies of the Cu(II) compounds have indicated that methyl substitution on the imino-nitrogen atom results in bis Schiff base complexation, while larger substituents produce mixed ligand but still square planar products [9].

We now report the synthesis and characterization of several new Cu(II) Schiff base derivatives of 2-acetylpyrrole with various primary amines, and show that the nature of each product is dependent on the size of the amine. Small amines such as ammonia allow *trans* bis Schiff base substitution at room temperature, while bulky amines such as n-butylamine and benzylamine result in mixed-ligand complexes. This chemistry differs markedly from that of pyrrole-2-aldehyde in that

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the steric requirements of the amine alter the stoichiometry of the product rather than its stereochemistry. A mechanistic pathway is proposed to account for this difference. Crystal structures of three new complexes are reported.

Experimental

Elemental analyses (C, H, N) were performed by Galbraith Laboratories. IR and UV spectra were obtained on a Perkin-Elmer 1725X FTIR spectrometer and a Perkin-Elmer Lambda 6 spectrophotometer, respectively.

Preparation of bis{N-[1-(2-pyrrolyl)ethylidene]aminato}copper(II) (**1a**)

Air stable, orange crystals were isolated after several days from an equimolar solution of 2-acetylpyrrole and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 15 M aqueous ammonia, following a procedure similar to that reported previously for $\text{Cu}(\text{C}_7\text{H}_9\text{N}_2)_2$ [9]. *Anal.* Calc. for $\text{Cu}(\text{C}_6\text{H}_7\text{N}_2)_2$: C, 51.9; H, 5.0; N, 20.2. Found: C, 52.1; H, 4.1; N, 20.3%. The IR spectrum of the solid showed a strong $\nu(\text{C}=\text{N})$ band centered at 1558 cm^{-1} .

Preparation of (2-acetylpyrrolato){N-[1-(2-pyrrolyl)ethylidene]n-butylaminato}copper(II)-n-butylamine (**2a**) and (2-acetylpyrrolato){N-[1-(2-pyrrolyl)ethylidene]benzylaminato}copper(II)-benzylamine hydrate (**3a**)

The synthetic procedure was similar to that reported previously for $\text{Cu}(\text{C}_6\text{H}_6\text{NO})(\text{C}_8\text{H}_{11}\text{N}_2)$ [9]. Light blue, needlelike crystals precipitated from an equimolar solution of 2-acetylpyrrole and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in either 50% n-butylamine ($\text{n-BuNH}_2/\text{H}_2\text{O}$) (**2a**) or 50% benzylamine ($\text{BzNH}_2/\text{H}_2\text{O}$) (**3a**). *Anal.* Calc. for $\text{Cu}(\text{C}_6\text{H}_6\text{NO})(\text{C}_{10}\text{H}_{15}\text{N}_2) \cdot \text{C}_4\text{H}_{11}\text{N}$ (**2a**): C, 58.9; H, 7.9; N, 13.7. Found: C, 59.0; H, 7.9; N, 13.8%. *Anal.* Calc. for $\text{Cu}(\text{C}_6\text{H}_6\text{NO})(\text{C}_{13}\text{H}_{13}\text{N}_2) \cdot \text{C}_7\text{H}_9\text{N} \cdot \text{H}_2\text{O}$ (**3a**): C, 63.2; H, 6.1; N, 11.3. Found: C, 63.5; H, 5.9; N, 11.6%. IR spectra of the solids exhibited peaks characteristic of $\nu(\text{N}-\text{H})$ at 3307 and 3252 cm^{-1} (**2a**) and 3315 and 3266 cm^{-1} (**3a**). Strong $\nu(\text{C}=\text{N})$ bands occurred at 1580 cm^{-1} (**2a**) and at 1585 and 1561 cm^{-1} (**3a**).

Preparation of (2-acetylpyrrolato){N-[1-(2-pyrrolyl)ethylidene]n-butylaminato}copper(II) (**2b**)

2a quantitatively converted to brown **2b** after coordinated n-butylamine loss upon heating for 24 h in a vacuum oven at $90\text{ }^\circ\text{C}$, and was subsequently recrystallized from petroleum ether. **3a** also lost coordinated amine at elevated temperature under vacuum, but the resulting brown product was not characterized. *Anal.* Calc. for $\text{Cu}(\text{C}_6\text{H}_6\text{NO})(\text{C}_{10}\text{H}_{15}\text{N}_2)$: C, 57.4; H, 6.3; N, 12.6. Found: C, 57.5; H, 6.3; N, 12.7%. The

IR spectrum of **2b** exhibited $\nu(\text{C}=\text{N})$ peaks at 1586 and 1574 cm^{-1} and a $\nu(\text{C}=\text{O})$ absorbance at 1544 cm^{-1} .

Preparation of bis{N-[1-(2-pyrrolyl)ethylidene]n-butylaminato}copper(II) (**2c**) and bis{N-[1-(2-pyrrolyl)ethylidene]benzylaminato}copper(II) (**3b**)

An equimolar mixture of 2-acetylpyrrole and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in either 50% $\text{n-BuNH}_2/\text{H}_2\text{O}$ or 50% $\text{BzNH}_2/\text{H}_2\text{O}$ was refluxed for 24 h to produce dark blue crystals of **2c** and **3b**, respectively, which were subsequently recrystallized from petroleum ether. *Anal.* Calc. for $\text{Cu}(\text{C}_{10}\text{H}_{15}\text{N}_2)_2$ (**2c**): C, 61.6; H, 7.7; N, 14.4. Found: C, 61.6; H, 7.7; N, 14.4%. *Anal.* Calc. for $\text{Cu}(\text{C}_{13}\text{H}_{13}\text{N}_2)_2$ (**3b**): C, 68.2; H, 5.7; N, 12.2. Found: C, 65.8; H, 5.7; N, 11.7%. The products could also be synthesized by the reflux of **2a**, **2b** or **3a** in water followed by ethanol recrystallization. $\nu(\text{C}=\text{N})$ IR absorbances were observed at 1578 cm^{-1} for **2c** and at 1569 and 1554 cm^{-1} for **3b**.

Preparation of bis(2-acetylpyrrolato)copper(II) (**4a**)

Following the procedure of Perry and Weber [10], an equimolar mixture of basic copper(II) carbonate and 2-acetylpyrrole was refluxed for 30 min in xylene. Upon filtration, the product precipitated from the solution as dark green needles, and was subsequently recrystallized from xylene. *Anal.* Calc. for $\text{Cu}(\text{C}_6\text{H}_6\text{NO})_2$: C, 51.5; H, 4.3; N, 10.0. Found: C, 51.3; H, 4.4; N, 9.9%. **4a** could also be synthesized by the equimolar reaction of 2-acetylpyrrole and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in aqueous solution made slightly basic by either ethylamine or n-butylamine. In addition, preliminary data has been presented which suggest that **4a** may be synthesized by a direct electrochemical method [11]. $\nu(\text{C}=\text{O})$ IR absorbances were observed at 1543 cm^{-1} .

Exchange reactions

A number of ligand exchange and substitution reactions were performed on the various complexes. **4a** was converted to **1a**, $\text{Cu}(\text{C}_7\text{H}_9\text{N}_2)_2$ or $\text{Cu}(\text{C}_6\text{H}_6\text{NO})(\text{C}_8\text{H}_{11}\text{N}_2) \cdot \text{EtNH}_2$ upon stirring at room temperature for 24 h in 15 M aqueous ammonia, 40% methylamine/ H_2O or 35% ethylamine/ H_2O , respectively. In addition, $\text{Cu}(\text{C}_6\text{H}_6\text{NO})(\text{C}_8\text{H}_{11}\text{N}_2)$, when stirred for 24 h at room temperature in 15 M aqueous ammonia, 40% methylamine/ H_2O or 50% n-butylamine/ H_2O , was converted to **1a**, $\text{Cu}(\text{C}_7\text{H}_9\text{N}_2)_2$ or $\text{Cu}(\text{C}_6\text{H}_6\text{NO})(\text{C}_{10}\text{H}_{15}\text{N}_2) \cdot \text{n-BuNH}_2$, respectively.

Studies of metal ion mediation in Schiff base formation

Pyrrole-2-aldehyde readily forms Schiff base derivatives in the presence of primary amines without metal ion mediation [12]. This was clearly observed in solution

as a UV blue shift occurred for pyrrole-2-aldehyde ($\lambda_{\max}=293$ nm, $\epsilon=19\,300$ l mol⁻¹ cm⁻¹) upon ethylamine addition resulting in pyrrolaldethylimine ($\lambda_{\max}=283$ nm, $\epsilon=20\,200$ l mol⁻¹ cm⁻¹). No such reaction occurs for 2-acetylpyrrole in the absence of metal ions.

X-ray structure determinations and refinements

Intensity data for the crystals of **1a**, **3b** and **4a** were measured on an Enraf-Nonius CAD-4 diffractometer equipped with graphite monochromatized Mo K α radiation. Crystallographic data for the three complexes are given in Table 1.

(C₆H₇N₂)₂Cu (1a)

A thin hexagonal plate-like crystal of orange color, measuring approximately 0.080 × 0.30 × 0.50 mm was mounted on a glass fiber for data collection. Accurate cell dimensions and a crystal orientation matrix were determined by a least-squares refinement of the setting angles of 25 reflections with θ in the range 10–15°. Intensity data were collected by the $\omega/2\theta$ scan method using variable scan speed (1.33–6.67° min⁻¹) and scan width (0.90 + 0.35 tan θ) in the range $2 < \theta < 27^\circ$. Three reflections were monitored every 2 h of exposure time which decayed by 2.6% in a linear fashion; data were corrected by appropriate scaling. The intensities of 1575 reflections were measured, of which 996 had $I > 3\sigma(I)$, where $\sigma^2 I = S + 2B + [0.04(S - B)]^2$, with S = scan count and B = time-averaged background count extended 25% on each side. Data were corrected for Lorentz, polarization and absorption effects [13]; correction range being 0.841–1.295.

With two molecules in the unit cell, space group $P2_1/n$ requires molecules to lie on inversion centers. A Fourier map calculated with copper atom at the origin revealed all the non-hydrogen atoms. Refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms. At an intermediate stage in the refinement, a difference map revealed all H atoms which were included in the subsequent rounds of calculations with isotropic temperature factors. Refinement converged with $R=0.032$ and $R_w=0.030$. In the refinement cycles, weights were derived from the counting statistics. Scattering factors for all three structures were taken from refs. 14 and 15 and allowances were made for anomalous dispersion [16]; no corrections for extinction were needed. A difference map calculated at the conclusion of the refinement had no chemically significant features. Final fractional coordinates are given in Table 2.

(C₁₃H₁₃N₂)₂Cu (3b)

A thin needle-shaped crystal of dark blue color (approximately 0.070 × 0.10 × 0.27 mm) was mounted on a glass fiber. Unit cell constants were obtained from 25 reflections with $10 < \theta < 15^\circ$. Intensity data were collected by the $\omega/2\theta$ scan method using variable scan speed (1.25–6.67° min⁻¹) and scan width (0.80 + 0.35 tan θ) in the range $2 < \theta < 24^\circ$. Three standard reflections were monitored at regular intervals and showed insignificant variations. The intensities of 3951 reflections were collected of which 1503 had $I > 3\sigma(I)$. Data were corrected for Lorentz, polarization and absorption effects; correction range being 0.718–1.302.

TABLE 1. Crystal data for **1a**, **3b** and **4a**

	1a	3b	4a
Empirical formula	C ₁₂ H ₁₄ N ₄ Cu	C ₂₆ H ₂₆ N ₄ Cu	C ₁₂ H ₁₂ N ₂ O ₂ Cu
Formula weight	277.81	458.06	279.78
Space group	$P2_1/n$	$P2_1/c$	$P2_1/a$
a (Å)	11.698(2)	10.647(3)	8.143(2)
b (Å)	5.406(1)	12.737(4)	14.452(3)
c (Å)	10.687(3)	16.371(3)	5.189(1)
β (°)	115.92(1)	90.31(2)	106.82(2)
V (Å ³)	607.8	2220.1	584.5
Z	2	4	2
D_{calc} (Mg m ⁻³)	1.518	1.370	1.590
λ (Mo K α) (Å)	0.71069	0.71069	0.71069
μ (mm ⁻¹)	1.709	0.953	1.783
Temperature (°C)	25	25	25
θ Range (°)	2–27	2–24	2–27
Reflections collected	1575	3951	1463
Reflections used ^a	996	1503	893
R^b	0.032	0.046	0.036
R_w^c	0.030	0.037	0.032
S^d	2.86	1.96	2.64

^a $[I > 3\sigma(I)]$. ^b $R = \sum \|F_o| - |F_c\| / \sum |F_o|$. ^c $R_w = [\sum \Delta^2 / \sum F_o^2]^{1/2}$. ^d $S = [\sum \Delta^2 / (N_o - N_c)]^{1/2}$.

TABLE 2. $(C_6H_7N_2)_2Cu$ (**1a**): final fractional coordinates and equivalent isotropic temperature factors (\AA^2) with e.s.d.s in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ^b
Cu ^a	0.0000	1.0000	0.0000	0.0388(2)
N(1)	0.0743(2)	1.1031(5)	0.1940(2)	0.041(1)
N(2)	-0.0824(3)	0.7506(5)	0.0702(3)	0.049(1)
C(1)	0.1607(3)	1.2636(6)	0.2809(3)	0.048(2)
C(2)	0.1843(3)	1.2168(6)	0.4175(3)	0.051(2)
C(3)	0.1086(3)	1.0163(7)	0.4142(3)	0.048(1)
C(4)	0.0415(3)	0.9488(5)	0.2756(3)	0.041(1)
C(5)	-0.0488(3)	0.7593(6)	0.2022(3)	0.041(1)
C(6)	-0.1002(4)	0.5885(7)	0.2747(4)	0.052(2)

^aCu lies at the origin. ^bEquivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

The structure was solved by the heavy-atom method. Refinement of the structure was by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms. At an intermediate stage in the refinement, a difference map revealed all H atoms which were included in the subsequent cycles at geometrically idealized positions (C–H 0.95 Å) and a fixed isotropic temperature factor. Refinement converged with $R=0.046$ and $R_w=0.037$. In the refinement cycles, weights were derived from the counting statistics. A difference map calculated at the conclusion of the refinement had no chemically significant features. Final fractional coordinates are given in Table 3.

$(C_6H_6NO)_2Cu$ (**4a**)

A blue needle-shaped crystal of approximate size $0.075 \times 0.20 \times 0.40$ mm was mounted on a glass fiber for data collection. Data collection, solution and refinement followed the same procedures as described for **1a**. The intensities of 1463 reflections were measured of which 893 had $I > 3\sigma(I)$; the absorption correction range was 0.738–1.145. At conclusion of the refinement of the structure allowing anisotropic thermal parameters for non-hydrogen atoms and isotropic temperature factors for H atoms; using full-matrix least-squares calculations, R and R_w were 0.036 and 0.032, respectively. Final fractional coordinates are in Table 4.

All computer programs used in this study were part of XTAL2.6 [17] and figures were plotted using ORTEP II [18].

Results and discussion

Previous reports have indicated that Cu(II) forms a bis Schiff base derivative with 2-acetylpyrrole in methylamine, but forms a mixed-ligand product in ethylamine [9]. The present results further illustrate this striking

TABLE 3. $(C_{13}H_{13}N_2)_2Cu$ (**3b**): final fractional coordinates and equivalent isotropic temperature factors (\AA^2) with e.s.d.s in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ^a
Cu	0.2424(1)	0.08365(7)	-0.00122(8)	0.0360(5)
N(1)	0.3204(6)	0.1902(6)	0.0652(4)	0.037(5)
N(2)	0.3564(6)	-0.0124(6)	0.0630(5)	0.035(6)
N(3)	0.1349(6)	-0.0177(6)	-0.0556(5)	0.037(6)
N(4)	0.2108(6)	0.1652(5)	-0.1041(4)	0.038(5)
C(1)	0.3238(8)	0.2946(7)	0.0780(5)	0.044(6)
C(2)	0.4093(8)	0.3215(7)	0.1390(5)	0.052(7)
C(3)	0.4572(7)	0.2280(7)	0.1671(5)	0.048(6)
C(4)	0.4033(7)	0.1486(7)	0.1214(5)	0.032(6)
C(5)	0.4247(8)	0.0376(9)	0.1165(6)	0.043(7)
C(6)	0.5261(8)	-0.0127(7)	0.1689(5)	0.059(7)
C(7)	0.3830(8)	-0.1225(7)	0.0416(5)	0.042(6)
C(8)	0.3293(7)	-0.2074(7)	0.0960(5)	0.035(6)
C(9)	0.3476(8)	-0.3100(8)	0.0740(6)	0.56(7)
C(10)	0.302(1)	-0.3890(8)	0.1207(8)	0.077(9)
C(11)	0.2379(9)	-0.3706(9)	0.1898(8)	0.068(8)
C(12)	0.2206(8)	-0.2690(9)	0.2141(6)	0.063(7)
C(13)	0.2656(8)	-0.1865(7)	0.1672(6)	0.052(7)
C(14)	0.0794(8)	-0.1099(7)	-0.0406(5)	0.042(6)
C(15)	-0.0091(8)	-0.1337(7)	-0.1019(6)	0.051(6)
C(16)	-0.0031(8)	-0.0507(8)	-0.1560(5)	0.054(7)
C(17)	0.0837(8)	0.0222(7)	-0.1272(6)	0.033(6)
C(18)	0.1330(8)	0.1172(7)	-0.1534(5)	0.036(6)
C(19)	0.1000(8)	0.1570(7)	-0.2379(5)	0.060(6)
C(20)	0.2818(7)	0.2553(7)	-0.1330(5)	0.049(6)
C(21)	0.2248(8)	0.3640(7)	-0.1212(5)	0.041(6)
C(22)	0.2993(8)	0.4506(8)	-0.1311(6)	0.065(7)
C(23)	0.253(1)	0.5490(9)	-0.1207(7)	0.077(9)
C(24)	0.130(1)	0.5647(8)	-0.1028(6)	0.070(8)
C(25)	0.0536(8)	0.4808(9)	-0.0937(6)	0.063(7)
C(26)	0.1006(9)	0.3803(7)	-0.1029(6)	0.050(7)

^aEquivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4. $(C_6H_6NO)_2Cu$ (**4a**): final fractional coordinates and equivalent isotropic temperature factors (\AA^2) with e.s.d.s in parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> ^b
Cu ^a	0.0000	0.0000	0.0000	0.0411(3)
O	0.7562(3)	0.9548(2)	-0.0475(5)	0.044(1)
N	1.0524(4)	0.9194(2)	0.3052(5)	0.037(2)
C(1)	1.1808(5)	0.8957(3)	0.5161(8)	0.042(2)
C(2)	1.1224(6)	0.8405(3)	0.6969(8)	0.047(2)
C(3)	0.9498(5)	0.8305(3)	0.5835(8)	0.045(2)
C(4)	0.9051(5)	0.8794(2)	0.3389(7)	0.038(2)
C(5)	0.7519(5)	0.9024(3)	0.1441(7)	0.042(2)
C(6)	0.5826(6)	0.8663(4)	0.1598(10)	0.062(3)

^aCu lies at the origin. ^bEquivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

demarcation in stoichiometry as amine size is varied, with the ammonia derivative **1a** similar to that of methylamine, $Cu(C_7H_9N_2)_2$, while the n-butylamine and benzylamine adducts resemble the chemistry of the

ethylamine complex, $\text{Cu}(\text{C}_6\text{H}_6\text{NO})(\text{C}_8\text{H}_{11}\text{N}_2)$, whose structure has been previously described [7]. The ORTEP drawing of the ammonia derivative (**1a**) is shown in Fig. 1; the molecule is planar with pyrrole groups *trans* to one another, similar to the structure reported for the distorted planar ethylamine derivative, $\text{Cu}(\text{C}_8\text{H}_{11}\text{N}_2)_2$ [8]. Bond distances and angles in **1a** (Table 5) are in agreement with those reported for the planar Cu(II) bis Schiff base derivative of pyrrole-2-aldehyde with ammonia [1]. Figure 2 shows the ORTEP drawing of the benzylamine derivative **3b**. The molecule

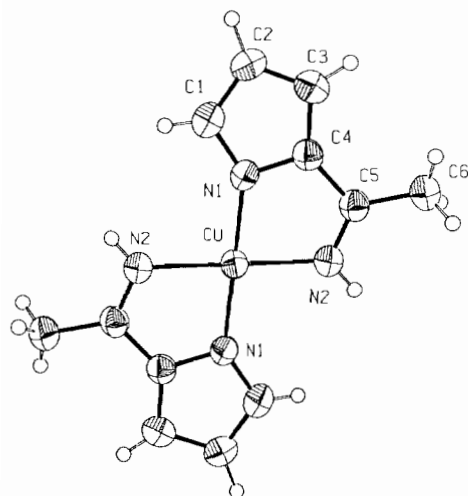


Fig. 1. ORTEP drawing of $(\text{C}_6\text{H}_7\text{N}_2)_2\text{Cu}$ (**1a**).

TABLE 5. $(\text{C}_6\text{H}_7\text{N}_2)_2\text{Cu}$ (**1a**): bond distances (Å) and angles (°)

Bond distances (Å)	
Cu–N(1)	1.947(2)
Cu–N(2)	1.986(3)
N(1)–C(1)	1.348(4)
N(1)–C(4)	1.376(4)
N(2)–C(5)	1.289(4)
C(1)–C(2)	1.385(5)
C(2)–C(3)	1.390(5)
C(3)–C(4)	1.388(4)
C(4)–C(5)	1.434(4)
C(5)–C(6)	1.491(6)
Bond angles (°)	
N(1)–Cu–N(2)	81.7(1)
C(1)–N(1)–C(4)	106.7(2)
C(1)–N(1)–Cu	140.3(3)
C(4)–N(1)–Cu	112.5(2)
C(5)–N(2)–Cu	115.0(2)
N(1)–C(1)–C(2)	110.6(3)
C(1)–C(2)–C(3)	106.5(3)
C(4)–C(3)–C(2)	106.8(3)
N(1)–C(4)–C(3)	109.4(3)
N(1)–C(4)–C(5)	115.4(3)
C(3)–C(4)–C(5)	135.2(3)
N(2)–C(5)–C(4)	115.1(3)
N(2)–C(5)–C(6)	123.1(3)
C(4)–C(5)–C(6)	121.7(3)

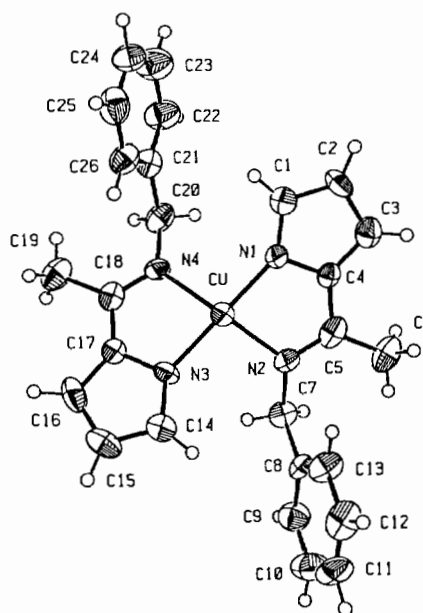


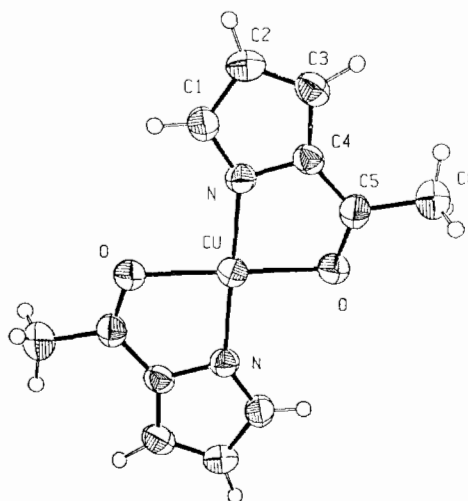
Fig. 2. ORTEP drawing of $(\text{C}_{13}\text{H}_{13}\text{N}_2)_2\text{Cu}$ (**3b**).

of **3b** shows a distorted planar geometry around Cu, with similar bond lengths and angles (Table 6) to those for $\text{Cu}(\text{C}_8\text{H}_{11}\text{N}_2)_2$ [8]. Figure 3 shows the ORTEP drawing of **4a**; the molecule is planar and exhibits similar bond distances and angles (Table 7) to the 2-acetylpyrrole portion of $\text{Cu}(\text{C}_6\text{H}_6\text{NO})(\text{C}_8\text{H}_{11}\text{N}_2)_2$ [7]. The crystal structure data for **1a** and **3b** illustrate that the steric effects of the amine substituent influence the structure of their products. CuN distances for the two compounds **1a** (1.947, 1.986 Å) and **3b** (1.925, 2.015: 1.939, 2.006 Å) are different. As the steric bulk of the imine substituent increases from NH (**1a**) to NCH_2Ph (**3b**) the bond distances between copper and the imine nitrogens increase by about 0.0245 Å which is greater than 3σ . While **1a** and **4a** are planar molecules with CuN_4 (**1a**) and CuN_2O_2 atoms (**4a**) exhibiting no deviation from planarity, the distorted square planar structure of **3b**, caused by bulky imine substituents, results in N(2) and N(4) atoms 0.608 and 0.453 Å, respectively, below the least-squares plane, and N(1) and N(3) atoms 0.198 and 0.220 Å, respectively, above the least-squares plane.

Coordinated C=N and C=O IR stretching frequencies can be assigned on the basis of the structures of compounds **1a** and **4a**, respectively, and are in agreement with reported values [8, 9]. Compounds **2a** and **3a** show evidence of both of these frequencies but the carbonyl region is obscured by NH_2 deformation modes (higher energy symmetric and antisymmetric NH stretching vibrations from the coordinated amines also are present and agree with literature values [19, 20]). Conversion of **2a** into **2b** by the volatilization of the coordinated amine reveals clearly both the coordinated

TABLE 6. $(C_{13}H_{13}N_2)_2Cu$ (**3b**): selected bond distances (Å) and angles (°)

Bond distances (Å)	
Cu–N(1)	1.925(7)
Cu–N(2)	2.015(7)
Cu–N(3)	1.939(7)
Cu–N(4)	2.006(7)
N(1)–C(1)	1.35(1)
N(1)–C(4)	1.38(1)
N(2)–C(5)	1.30(1)
N(2)–C(7)	1.47(1)
N(3)–C(14)	1.34(1)
N(3)–C(17)	1.39(1)
N(4)–C(18)	1.31(1)
N(4)–C(20)	1.45(1)
C(1)–C(2)	1.39(1)
C(2)–C(3)	1.37(1)
C(3)–C(4)	1.38(1)
C(4)–C(5)	1.43(1)
C(5)–C(6)	1.52(1)
C(7)–C(8)	1.52(1)
C(14)–C(15)	1.41(1)
C(15)–C(16)	1.38(1)
C(16)–C(17)	1.39(1)
C(17)–C(18)	1.39(1)
C(18)–C(19)	1.51(1)
C(20)–C(21)	1.52(1)
Bond angles (°)	
N(1)–Cu–N(2)	82.9(3)
N(1)–Cu–N(3)	168.8(3)
N(1)–Cu–N(4)	100.3(3)
N(3)–Cu–N(2)	100.8(3)
N(4)–Cu–N(2)	148.2(3)
N(3)–Cu–N(4)	82.1(3)
C(1)–N(1)–C(4)	105.0(7)
C(1)–N(1)–Cu	142.7(6)
C(4)–N(1)–Cu	112.3(6)
C(5)–N(2)–C(7)	121.2(8)
C(5)–N(2)–Cu	112.8(7)
C(7)–N(2)–Cu	124.8(6)
C(14)–N(3)–C(17)	107.8(7)
C(14)–N(3)–Cu	139.5(6)
C(17)–N(3)–Cu	111.9(6)
C(18)–N(4)–C(20)	119.9(7)
C(18)–N(4)–Cu	112.3(5)
C(20)–N(4)–Cu	126.6(5)
N(1)–C(1)–C(2)	111.8(8)
C(3)–C(2)–C(1)	105.5(8)
C(2)–C(3)–C(4)	107.5(7)
N(1)–C(4)–C(3)	110.0(8)
N(1)–C(4)–C(5)	116.3(8)
C(3)–C(4)–C(5)	133.4(8)
N(2)–C(5)–C(4)	115.5(8)
N(2)–C(5)–C(6)	124.5(9)
C(4)–C(5)–C(6)	119.9(8)
N(2)–C(7)–C(8)	117.8(7)
N(3)–C(14)–C(15)	110.7(8)
C(16)–C(15)–C(14)	105.0(8)
C(15)–C(16)–C(17)	109.1(8)
N(3)–C(17)–C(18)	115.7(8)
N(3)–C(17)–C(16)	107.4(8)
C(18)–C(17)–C(16)	136.8(9)
N(4)–C(18)–C(17)	117.2(8)
N(4)–C(18)–C(19)	123.5(7)
C(17)–C(18)–C(19)	119.2(7)
N(4)–C(20)–C(21)	117.9(7)

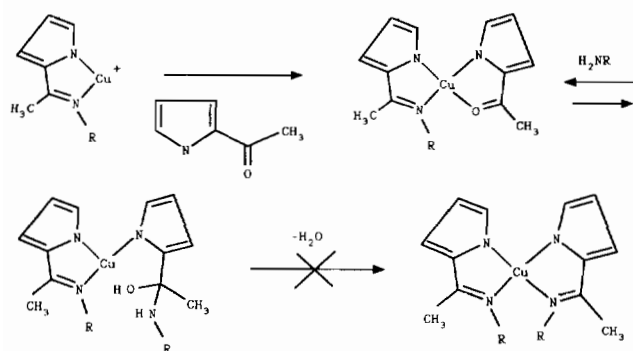
Fig. 3. ORTEP drawing of $(C_6H_6NO)_2Cu$ (**4a**).TABLE 7. $(C_6H_6NO)_2Cu$ (**4a**): bond distances (Å) and angles (°)

Bond distances (Å)	
Cu–N	1.913(3)
Cu–O	2.036(3)
O–C(5)	1.258(5)
N–C(1)	1.321(4)
N–C(4)	1.387(5)
C(1)–C(2)	1.415(6)
C(2)–C(3)	1.365(6)
C(3)–C(4)	1.405(5)
C(4)–C(5)	1.399(5)
C(5)–C(6)	1.498(7)
Bond angles (°)	
N–Cu–O	83.2(1)
C(5)–O–Cu	110.3(2)
C(1)–N–C(4)	107.1(3)
C(1)–N–Cu	141.0(3)
C(4)–N–Cu	111.3(2)
N–C(1)–C(2)	111.0(4)
C(3)–C(2)–C(1)	106.0(3)
C(2)–C(3)–C(4)	107.6(4)
N–C(4)–C(5)	115.7(3)
N–C(4)–C(3)	108.4(3)
C(5)–C(4)–C(3)	135.7(4)
O–C(5)–C(4)	119.4(4)
O–C(5)–C(6)	119.2(4)
C(4)–C(5)–C(6)	121.3(4)

imine and carbonyl bands in the 1600 cm^{-1} region. Finally, *trans* Schiff base derivatives containing *n*-butylamine (**2c**) or benzylamine (**3b**) can be synthesized at elevated temperatures; they exhibit sharp coordinated imine bands similar to that for $Cu(C_8H_{11}N_2)_2$ [8].

The chemistry of 2-acetylpyrrole Schiff base complexes of Cu(II) with NH_3 and CH_3NH_2 differs significantly from that for larger primary amines. Bis Schiff base

adducts form directly in aqueous solutions of ammonia and methylamine at room temperature, while mixed-ligand products result upon reaction in ethylamine, *n*-butylamine and benzylamine. Mechanisms can be proposed which account for the experimental observations. These mechanisms involve metal-mediated Schiff base formation. Proton or Lewis acid catalysis is necessary for Schiff base formation from aryl ketones [21], with Cu(II) serving as the Lewis acid in the present system. In all cases, a deprotonated 2-acetylpyrrole anion initially coordinates with the Cu(II), forming a five-membered chelate ring involving the pyrrole nitrogen and the carbonyl oxygen atoms. Nucleophilic attack by amine on the metal bonded carbonyl occurs, followed by dehydration of the carbinolamine intermediate to yield a coordinated Schiff base [22]. A second coordinated Schiff base forms with pyrrole groups *trans* to one another for smaller amines such as ammonia and methylamine, thereby minimizing adverse steric interactions in the resulting planar molecule. In the case of ethylamine and larger primary amines (Scheme 1), however, after the formation of the first metal mediated Schiff base chelate to the Cu(II) center, the pyrrole ring of the second 2-acetylpyrrole bonds to the metal *cis* to the first ring. Models show that ethyl and larger groups on the already bonded Schiff base imine moiety cause this functionality to possess a larger steric size than a pyrrole group, thereby forcing a new reaction pathway. Metal mediated Schiff base formation cannot now occur on the bonded carbonyl of the second 2-acetylpyrrole chelate if overall complex planarity is preserved, due to steric interference from the large aliphatic group on the first chelate. The second step of the imine formation reaction, the dehydration of the carbinolamine, would bring the N-bonded alkyl groups into close proximity across the copper center. Molecular models indicate that dehydration of the carbinolamine to produce the planar bis imine complex would result in the N-alkyl substituents approaching within bonding distances. These unfavorable non-bonded interactions between N-bonded alkyl groups raise the energy of



Scheme 1.

activation for the dehydration step and thereby favor reversion to the coordinated carbonyl. A coordinated amine molecule remains on the metal center (**2a** and **3a**) in the mixed-ligand product before eventually volatilizing in the atmosphere. The crystal structure of the first compound in this series, Cu(C₆H₆NO)-(C₈H₁₁N₂), has been reported [7], and larger amines form similar complexes as evidenced by elemental analyses and IR spectra. Consideration was given to whether an unstable carbinolamine might be present rather than a coordinated amine in **2a** and **3a**; carbinolamine intermediates have been proposed for products of Schiff bases syntheses [23–25], and at least one crystal structure of a metal coordinated carbinolamine derivative has been obtained [26]. While this unstable intermediate cannot be ruled out for the present complexes without structural analyses, published reports [25, 26] of isolable carbinolamine complexes have involved tetradentate ligands in which formation of the carbinolamine was favored because flexibility of the ligand was increased and thus its coordinating ability enhanced. In the present study, no such driving force can be envisioned for the bidentate ligands. In addition, IR N–H stretching and bending modes are in agreement with those for known amine complexes of Cu(II) [19, 20]. Crystals of **2a** and **3a** are unsuitable for X-ray structural analysis.

At room temperature mixed-ligand complexes form from the reaction of Cu(II), 2-acetylpyrrole, and ethylamine or larger amines; however, at elevated temperatures bis Schiff base derivatives with pyrrole rings *trans* to one another are obtained from these amines (Cu(C₈H₁₁N₂)₂ [**8**], **2c**, **3b**). These results suggest that the thermodynamically stable form for all derivatives is *trans* with two Schiff base chelates per metal center, but that no reaction pathway exists at room temperature to obtain metal mediated formation of bis complexes in ethylamine and larger primary amines due to unfavorable steric interactions. Small differences in reactant size have major effects on product stoichiometry. Pyrrole-2-aldehyde readily forms Schiff base derivatives in the presence of primary amines without metal ion mediation, and these imines in the bulk solution coordinate to the metal center in the most favorable stereochemistry to minimize adverse steric interactions, ranging from square planar to tetrahedral. In contrast, 2-acetylpyrrole requires metal mediation for Schiff base formation, and so the mechanism presented in Scheme 1 explains the resulting mixed-ligand products since Cu(II) maintains a square planar stereochemistry. This study presents a facile synthetic route for the formation of mixed-ligand Schiff base complexes of Cu(II) with 2-acetylpyrrole, and is of potential use for the design of other products with sterically hindered ligands.

Acknowledgement

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Supplementary material

The following are available from the authors on request: Table S-I, crystallographic data collection and structure refinement parameters for **1a**, **3b** and **4a** (6 pages); Table S-II, anisotropic temperature factors (4 pages); Table S-III, parameters of hydrogen atoms (3 pages); Tables S-IV, complete list of bond distances and angles for **3b** (5 pages); Table S-V, bond distances and angles involving H atoms for **1a** and **4a** (2 pages); Table S-VI, mean planes data (7 pages); and Table S-VII, listing of calculated and observed structure factors for **1a**, **3b** and **4a** (49 pages).

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