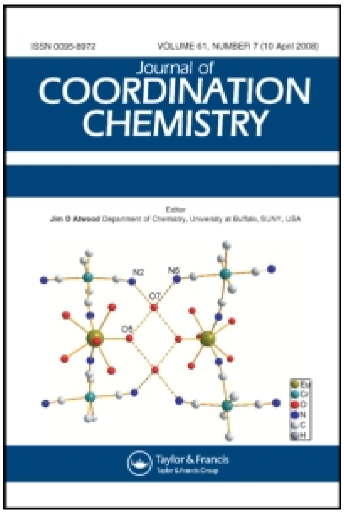

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NOTE: SYNTHESIS OF Cu(II) AND Zn(II) COMPLEXES WITH SCHIFF BASE DERIVATIVES OF 2-ACETYLPYRROLE

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NOTE

SYNTHESIS OF Cu(II) AND Zn(II) COMPLEXES WITH SCHIFF BASE DERIVATIVES OF 2-ACETYLPYRROLE

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Bis chelate complexes of Cu(II) and Zn(II) were synthesized with methylamine and ethylamine Schiff base derivatives of 2-acetylpyrrole. Stable complexes were obtained, with the exception of the Cu(II) ethylamine adduct, which slowly hydrolyzed in air to yield a mixed ligand product containing one ethylamine Schiff base and one 2-acetylpyrrole per metal centre. The instability of the bis Cu(II) ethylamine Schiff base complex with respect to stable Cu(II) methylamine and Zn(II) ethylamine complexes is discussed.

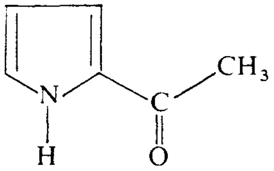
Keywords: Copper, zinc, Schiff base, z-acetylpyrrole, synthesis

INTRODUCTION

Complexes of α-substituted pyrroles with transition metal ions have been studied for many years. Emmert *et al.*,[1,2] reported the synthesis of neutral zinc(II), nickel(II), copper(II), cobalt(II), and iron(II) complexes of various pyrrole derivatives, including those of pyrrole-2-aldehyde. Perry and Weber[3] synthesized and characterized additional metal complexes with bidentate pyrrole ligands, while Davies and Gogan[4] reported on the formation of chromium(III) chelates of some 2-acetylpyrroles. The direct electrochemical synthesis of 2-acetylpyrrole complexes of copper(II), cobalt(III), and chromium(III) has also been reported.[5]

In addition to the direct substitution of 2-acetylpyrrole and pyrrole-2-aldehyde to metal centres, extensive studies have been accomplished on the Schiff base derivatives of these ligands and their resulting metal complexes. For example, Holm, Chakravorty, and Theriot[6] reported on the syntheses, structures, and solution equilibria of bis(pyrrole-2-aldimino)metal(II) complexes with Co, Ni, Pd, Cu, and Zn and with various alkyl groups bonded to the azomethine nitrogen. Yeh and Barker[7] synthesized additional metal chelates of 2-pyrrolealdimines, where the metals employed were Cu, Hg, Pd, and Pt. Crystal structures of several bis(pyrrole-2-aldimino) metal complexes, prepared by the interaction of *tert*-butylamine Schiff base derivatives of pyrrole-2-aldehyde with Zn(II), Cu(II), Ni(II), and Co(II) have also been determined.[8–11]

In the present study, Cu(II) and Zn(II) chelate complexes were synthesized with primary amine Schiff base derivatives of 2-acetylpyrrole (**2Ac**). Stable complexes were realized, with the exception of the Cu(II) ethylamine adduct, which slowly hydrolyzed in air to produce a mixed ligand product containing one ethylamine Schiff base and one 2-acetylpyrrole chelate per metal centre. This complex represents a novel synthetic pathway to the formation of 2-acetylpyrrole chelate complexes of Cu(II), as well as an interesting example of a mixed ligand copper adduct. A comparison of this as well as the other prepared complexes to those reported in the literature is made.



2-acetylpyrrole

EXPERIMENTAL

Preparation of $Cu(C_8H_{11}N_2)(C_6H_6NO)$ *(**Ib**)*

Light blue, needlelike crystals resulted upon the 1/1 reaction of 2-acetylpyrrole with $CuSO_4.5H_2O$ in 35% ethylamine/H_2O. The isolated product was too unstable for satisfactory C.H,N analysis, but a Cu analysis on freshly prepared and air dried product suggested the empirical formula $Cu(C_8H_{11}N_2)_2.H_2O$ (**Ia**). The blue product slowly turned light brown in air (3–5 days), and was subsequently recrystallized from petroleum ether to yield black crystals of $Cu(C_8H_{11}N_2)$ (C_6H_6NO) (**Ib**).

In a like manner, $Cu(C_7H_9N_2)_2$ (**II**) was prepared by reacting $CuSO_4.5H_2O$ with 2-acetylpyrrole in 40% methylamine/H_2O, and $Zn(C_8H_{11}N_2)_2$ (**III**) was formed by the interaction of $ZnCl_2$ with 2-acetylpyrrole in 35% ethylamine/H_2O.

Infrared spectra (KBr discs) were obtained on a Perkin-Elmer 1430 spectrometer. NMR spectra were recorded in $CDCl_3$ on a Varian EM 360A spectrometer using tetramethylsilane as an internal standard. Analytical data are presented in Table I.

TABLE I
Analytical data for the 2-acetylpyrrole Schiff base-metal ion complexes.

	% Calculated			% Found		
Compound	C	H	N	C	H	N
Ib M=Cu	54.81	5.55	13.70	54.49	5.50	13.21
II M=Cu	54.99	5.89	18.33	54.78	6.16	18.09
III M=Zn	57.31	6.57	16.72	57.22	6.64	16.94

RESULTS AND DISCUSSION

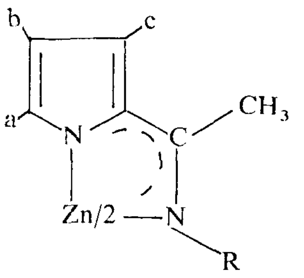
Compound **Ia** exhibits the loss of pyrrole N–H stretching at $3270\,cm^{-1}$, and the appearance of a strong coordinated imine band centred at $1579\,cm^{-1}$.[12] It also shows symmetric and asymmetric primary amine N–H stretching at 3260 and $3315\,cm^{-1}$ respectively, suggesting that hydrolysis and decomposition to **Ib** begins immediately after product isolation; the odour of ethylamine can be detected at this stage. These primary amine bands disappear as **Ia** converts to **Ib** in the atmosphere after several days, and the coodinated imine band at $1578\,cm^{-1}$ is joined by another peak of equal intensity centred at 1542 cm^{-1}, suggesting the presence of a coordinated carbonyl oxygen atom from 2-acetylpyrrole. The shift of carbonyl stretching frequency from 1645 cm^{-1} in free 2-acetylpyrrole to 1542 cm^{-1} in **Ib** is consistent with reported complexes of this type.[4] The mixed ligand product is resistent to further hydrolysis. Cu–N stretching in **Ib** can be tentatively assigned at 344 cm^{-1}; this absorbance, however, could arise from either copper–pyrrole or copper–imine nitrogen as well as copper–carbonyl oxygen, and is not well resolved.

By comparison, compound **II**, in which methylamine is substituted for ethylamine in Schiff base formation, does not hydrolyze to a mixed ligand complex upon standing. It too shows a strong coordinated Cu–imine stretching frequency at 1590 cm^{-1}, but does not exhibit primary amine frequencies in the 3300 cm^{-1} region suggestive of imine decomposition. $Zn(C_8H_{11}N_2)_2$, **III**, exhibits coordinated imine stretching at 1566 cm^{-1}, and is also resistant to the above noted hydrolysis. Table II lists tentative Cu–N and Zn–N stretching assignments for these compounds. The NMR spectrum of the zinc complex (Table III) is consistent with a bis substituted Schiff base compound, and assignments agree with those for Hg and Pd 2-pyrrolealdimino complexes as reported in the literature.[7]

TABLE II
Selected ir frequencies (cm^{-1}) of the metal ion–Schiff base complexes of 2-acetylpyrrole.

Compound	ν(N–H)	ν(C=N)	ν(C=O)	ν(M–N)
2ac	3270 vs		1645 vs	
Ia		1582 vs, 1575 vs		346 m, 323 m
Ib		1582 vs, 1574 vs	1548 vs, 1536 vs	344 m
II		1590 vs		347 m
III		1566 vs		296 m, 287 m

TABLE III
NMR chemical shifts for $Zn(C_8H_{11}N_2)_2$,III (ppm).



					R	
	a	b	c	-CH$_3$	CH$_3$	CH$_2$
R = CH$_2$CH$_3$	6.85	6.34	7.00	2.32	1.05	3.42

Kanters *et al.*,[8] have reported the crystal structure of bis[N-(2-pyrrolemethylene)-*tert*-butylamine]zinc(II), a compound similar to **III** but with tertiary butylamine replacing ethylamine in the Schiff base, as having a distorted tetrahedron for the coordination sphere. Similarly, bis[N-(2-pyrrolemethylene)-*tert*-butylamine]-copper(II) possesses triclinic and tetragonal modifications, with both forms having distorted tetrahedral coordination about the copper atom.[9] However, bis chelate complexes of copper with Schiff base derivatives formed with less bulky amines such as isopropyl and *n*-butylamine have been interpreted to have essentially planar structures.[13,14] In the copper complexes, the size of the R group on the coordinated imine greatly influences the stereochemistry of the molecule.

It is interesting to note that **1b** spontaneously forms from **1a** upon exposure to the atmosphere, while **II**, differing from **1a** only by a methylene group, does not decompose into a mixed ligand complex. Presumably, square planar coordination is present about the copper atom in both derivatives;[13,14] the bulkier ethyl group experiences more non-bonded interactions than the methyl group, and one imine may hydrolyze to relieve this strain and allow the complex to retain a square planar configuration. Only one imine hydrolysis occurs however, and complete conversion to the bis(2-acetylpyrrole)Cu(II) complex does not take place. Hydrolysis does not occur in the corresponding zinc derivative with ethylamine, presumably because it has a tetrahedral structure and therefore the ethyl groups are not as hindered.

Schiff base derivatives of 2-acetylpyrrole complex readily with metal ions. The mixed ligand decomposition product **1b** however is a novel adduct of a type not previously reported in the literature. Work is in progress to determine if bis Schiff base derivatives of other bulky ligands with copper will also result in this sort of conversion.

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