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Monomer and Dimer Complexes of Copper(II) Acetate with Pyridine and Picolines. Part I. Synthesis and Characterization*

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Synthetic investigations of copper(II) acetate addition compounds with pyridine and picolines have led to the isolation of the 1:2 adducts with pyridine and γ-picoline in addition to the known dimeric 1:1 adducts. The two new compounds have magnetic moments and electronic and epr spectral properties characteristic of monomeric copper complexes. Solutions of the dimeric 1:1 adducts with pyridine, β- and γ-picoline in their respective ligands have spectral and magnetic properties identical to those of the monomers, while traces of the dimer persist in solutions of the α-picoline analog. This is discussed in terms of the steric requirements of the ligands.

The large nmr isotropic shift of the acetate-methyl protons in solutions of the dimeric complexes suggests a greater contribution from superexchange mechanism to the magnetic coupling. Isotropic shifts of coordinated ligands in solutions of the monomeric complexes are analyzed and the contact contributions are discussed in terms of σ- and π-delocalization mechanisms.

Introduction

In addition to the widely known binuclear mono-adducts [1], some copper(II) carboxylates form bis-adducts, $Cu(O_2CCR)_2 \cdot 2L$, with basic ligands [2–5]. Complexes with this stoichiometry display normal magnetic behavior and presumably are monomeric. In complexes for which structural data are available, the coordination at the copper atom is tetragonal with the carboxylate ions acting as bidentate ligands, and the addends are in a *trans* configuration [3, 4]. No clear understanding exists of the factors that influence the adoption of one or another of the two structural types of copper(II) carboxylate adducts nor of the conditions under which one form is favored over the other. Whereas copper(II) acetate, and other alkanoates, tend generally to form the dimeric mono-adducts, copper(II) haloacetates form the monomeric bis-adducts as the most common product. The tendency towards formation of bis-adducts is enhanced with increased halogen substitution, and only a few mono-adducts of copper(II) trihaloacetates are known [1]. The relative instability of the dimeric structure has been attributed to the increased Cu–Cu repulsion in salts of the stronger haloacetic acids. Exceptions to this trend are known and several monomeric bis-adducts of copper(II) salts of relatively weak carboxylic acids have been reported [4].

Although several previous studies of dimeric copper(II) carboxylates have shown that often a small but significant fraction of the copper ions are present as monomers [6], the only known and characterized monomeric bis-adduct of copper(II) acetate (or higher alkanoates) is that with ammonia [7]. In all cases no attempt was made to characterize the monomeric species or to investigate its equilibrium concentration in the mixture. In this paper we report the preparation and characterization of monomeric bis-adducts, as well as the binuclear mono-adducts, of copper(II) acetate with pyridine and picolines, and the results of nmr isotropic shift measurements in their solutions.

Experimental Section

Reagents

Anhydrous copper(II) acetate was obtained by refluxing the hydrate with excess acetic anhydride for several hours. The bluish-green solid was filtered and dried in a vacuum oven at 60 °C overnight. Pyridine and picolines (Aldrich) were distilled from KOH under reduced pressure prior to use. All solvents were Spectral grade and used without further purification.

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Preparation of Complexes

Copper(II) acetate bis-adducts were prepared by the addition of excess ligand to anhydrous copper(II) acetate. In a typical experiment, about 20 ml of freshly distilled pyridine is added to *ca.* 1.5 g of anhydrous copper(II) acetate. The mixture turns blue immediately. The stoppered container is placed in an ice bath and magnetically stirred for about an hour. The blue precipitate formed is filtered in a closed apparatus, washed with small amount of pyridine and stored in a stoppered flask inside a dry box for future use. The yields of all preparations were virtually quantitative. *Anal.* Calcd. for $Cu(CH_3CO_2)_2 \cdot (C_5H_5N)_2$: Cu, 18.7; C, 49.5; H, 4.71; N, 8.25. Found: Cu, 18.5; C, 50.5; H, 4.75; N, 8.79. The color of the γ-picoline complex is purple. *Anal.* Calcd. for $Cu(CH_3CO_2)_2(C_6H_7N)_2$: Cu, 17.3; C, 52.2; H, 5.44; N, 7.62. Found: Cu, 17.5; C, 52.0; H, 6.06; N, 7.61. When exposed to the atmosphere for a while or heated above 60 °C both complexes decompose to the more stable green dimers. The conversion is complete when the complexes are dissolved in most organic solvents. Attempts to prepare the α- and β-picoline analogs have not been successful. The blue solids separated from similar reaction with these ligands begin decomposing at room temperature and their analytical results were not satisfactory, probably due to contamination with the mono-adducts.

Copper(II) acetate mono-adducts with pyridine and picolines have been prepared previously [8]. The pyridine and γ-picoline mono-adducts were obtained in this work by placing the bis-adduct in a vacuum desiccator for a few hours, and recrystallized from chloroform. The α- and β-picoline analogs are the main products from reaction of the ligands with anhydrous copper(II) acetate and can be recrystallized similarly from chloroform. The light green powders result in deep green crystals. The results of chemical analysis of these complexes were satisfactory. Cu was determined volumetrically and C, H, and N analyses were performed by Chemalytics, Inc. of Tempe, Ariz.

Physical Measurements

Room-temperature magnetic susceptibility measurements of powdered samples were carried out on a Gouy balance at Southern Illinois University, Carbondale, Illinois. Diamagnetic corrections were applied using tabulated values. The effective magnetic moment was calculated from the expression: $\mu_{eff} = 2.84 (\chi'_M \cdot T)^{1/2}$. A Perkin-Elmer R-32 nmr spectrometer was used to record the isotropic shifts and to measure the magnetic moments of complexes in solution by Evans method [9]. TMS was used as internal standard and chloroform, methylene chloride or cyclohexane were used as reference solvents. The effective magnetic moment is related to the reference shift, $\Delta\nu$, at any temperature by the expression: $\mu_{eff} = 2.069 \times 10^{-4} (\Delta\nu \cdot T/c)^{1/2}$, where c is the concentration of the copper complex in mol/ml. Because of instability of the bis-adducts in most organic solvents, the percent of the reference material in the nmr sample is crucial. Reduction in the μ_{eff} values were observed when the amount of reference in solution exceeded 5%. The epr spectra were taken with a Varian E-4 X-band spectrometer on powdered or solution samples sealed under nitrogen. Electronic spectra were obtained in matched 1-cm quartz cells of solutions of the bis-adducts in the respective ligand and of the mono-adducts in chloroform, using a Perkin-Elmer Model 200 spectrophotometer. Instability of the bis-adducts in solvents suitable for molecular weight determination precluded such measurements.

TABLE I. Effective Magnetic Moments, μ_{eff} ± 0.03 B.M., of $[Cu(OAc)_2L]_2$ at Various Temperatures.

Temp., K	Py	α-Pic	β-Pic	γ-Pic
311	1.50	1.50	1.50	1.50
291	1.45	1.45	1.45	1.46
280	1.42	1.41	1.41	1.42
268	1.40	1.38	1.40	1.40
258	1.36	1.36	1.36	1.36
249	1.34	1.33	1.34	1.34
228	1.26	1.26	1.26	1.26

Results and Discussion

Copper(II) Acetate Mono-Adducts

The electronic spectra in the visible region of solutions of the four complexes in chloroform show the two characteristic bands at 700 nm (ϵ = 350) and 370 nm (ϵ = 135 L mol^{-1} (dimer) cm^{-1}). These results are in agreement with previous reports on similar copper(II) systems [10]. However, the molar absorptivities are at variance with the reported low values in benzene [8]. We found these complexes to be sparingly soluble in benzene, but still the ϵ values are comparable to those in chloroform.

Effective magnetic moments in chloroform solutions of the four complexes (Table I) vary from about 1.5 to 1.2 B.M. in the temperature range 310 to 230 K. These values are typical of dimeric structure and are comparable to magnetic moment values of powdered samples (1.40 B.M. at 295 K), indicating that the dimeric structure persists in solution. The X-band epr spectra of both powdered samples and chloroform solutions of the four adducts exhibit three absorption lines typical of triplet-state binuclear copper(II) complexes with axial symmetry [11]. A seven-line hyperfine pattern, due to splitting

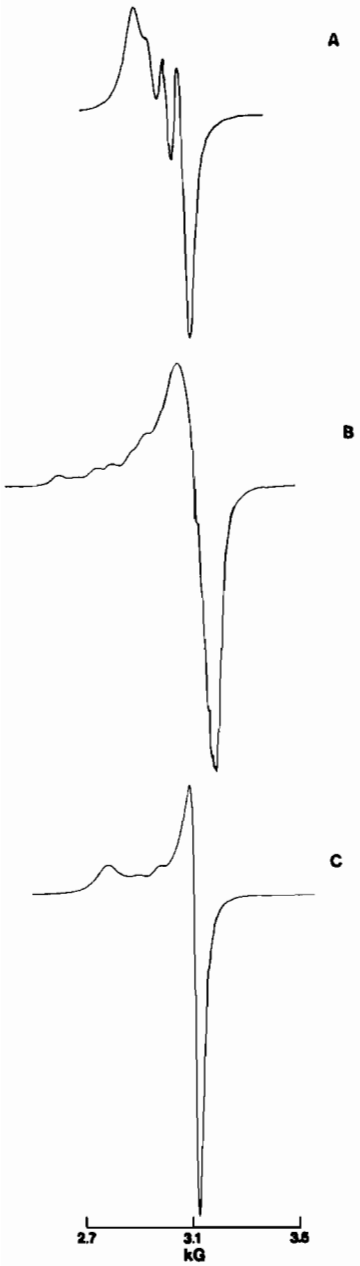

Fig. 1. Representative X-band epr spectra of $Cu(OAc)_2(\gamma\text{-pic})_2$: (A) in γ-picoline solution at room temperature, (B) frozen solution at 103 K, and (C) polycrystalline sample at room temperature.

from the two copper nuclei, on the parallel components is observed in the spectra of frozen solutions. The pyridine adduct has been shown by X-ray measurements [12] to be dimeric and preliminary results of X-ray measurements on the α- and γ-picoline adducts indicate similar structures. The four complexes are almost identical in magnetic and spectral characteristics, and most probably are isostructural.

Copper(II) Acetate Bis-Adducts

The visible spectra of solutions of these complexes in their respective ligands show one broad asymmetric band typical of Cu^{2+} ions in distorted octahedral field. This absorption appears at 650 nm (ϵ = 65) in the spectrum of the pyridine bis-adduct and at 658 nm (ϵ = 84) in that of the γ-picoline analog. The position of the band and the value of its molar absorptivity are in agreement with the results of monomeric copper(II) haloacetate bis-adducts with these ligands [2]. No evidence for the 370 nm band, characteristic of the mono-adducts, was found in the spectra.

The effective magnetic moment, calculated from the magnetic susceptibility of powdered samples of the pyridine bis-adduct at room temperature is (1.85 ± 0.06) B.M. The average value for the effective magnetic moments measured in solutions of these complexes, is (1.93 ± 0.2) B.M. The values remain fairly constant, independent of temperature in the range of 263–310 °K and are within the range of magnetic moments of monomeric Cu^{2+} ion complexes.

Additional evidence for the monomeric structure in the solid, as well as in solution, comes from the epr measurements. Typical epr spectra of γ-picoline bis-adduct in the X-band region are reproduced in Fig. 1. Similar spectra were obtained for the pyridine analog. The solution spectrum at room temperature consists of four lines due to copper nuclear-hyperfine interaction. The spectra of polycrystalline samples and frozen solutions show partially resolved structure with $g_{\parallel} > g_{\perp}$ indicating tetragonally elongated structure [13]. These spectra are characteristic of monomeric copper(II) complexes and show no evidence of contamination with any appreciable amount of the dimer.

It should be noted here that epr spectra of dimeric copper(II) acetate mono-adducts with pyridine, β-picoline and γ-picoline in solutions of their respective ligands are all identical and virtually superimposable on the spectra of solutions of the monomeric adducts containing the same copper concentration. The epr spectrum of copper(II) acetate mono-adduct with α-picoline in solutions of the ligand, on the other hand, shows different hyperfine-splitting features of the main signal at about 3100 G and contains additional weak signals at about 600 G and 4600 G, characteristic of the dimer. The results of previously reported epr spectra of solutions of copper(II) propionate mono-adducts with pyridine and α-picoline in the ligands, which were analyzed in terms of dimeric structure [14], may require reexamination in view of these observations. In fact, the major resonance in the epr spectra of copper(II) propionate solutions in these ligands at room temperature is that of the monomer, although signals due to the dimeric form can be discerned.

TABLE II. Average Nmr Molar Shifts, $\Delta\nu/C$ (Hz/M), and Magnetic Moments ($\mu_{eff} \pm 0.02$ B.M.) for $Cu(OAc)_2 \cdot 2L$ in Solution.

Temp., K	Py	γ-Pic	β-Pic	α-Pic
385	227 (1.93)	225 (1.93)	195 (1.80)	185 (1.69)
365	242 (1.94)	235 (1.92)	216 (1.83)	190 (1.69)
345	260 (1.95)	254 (1.94)	230 (1.84)	195 (1.70)
320	280 (1.95)	273 (1.93)	245 (1.83)	205 (1.70)
291	300 (1.93)	295 (1.92)	290 (1.90)	239 (1.72)
268	322 (1.92)		317 (1.91)	246 (1.70)
258	335 (1.92)		330 (1.91)	270 (1.73)

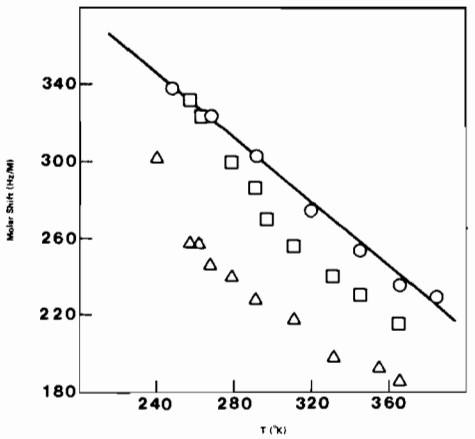

Fig. 2. Variation of the nmr molar shift with temperature in solutions of $Cu(OAc)_2 \cdot L$ complexes in their respective ligands: ○, L = py or γ-pic; □, L = β-pic; △, L = α-pic.

Consistent with these observations are the results of magnetic moment measurements on solutions of dimeric copper(II) acetate mono-adducts in their respective ligands which are summarized in Table II and shown graphically in Fig. 2. Solutions of the pyridine and γ-picoline adducts have magnetic moments and show linear ($\Delta\nu/c$) *vs.* T plots identical to those obtained for solutions of their monomeric bis-adducts, indicating the complete conversion of the binuclear mono-adducts to the monomers. Solutions of the α- and β-picoline analogs, on the other hand, show lower shifts and magnetic moments in the higher temperature region but approach the behavior of a monomer at lower temperatures. While solutions of the β-picoline adduct have magnetic moment values which correspond to a monomer below 20 °C, small amounts of the dimeric complex persist in solutions of the α-picoline analog even below −20 °C.

The thermal instability of six-coordinate monomeric complexes with α- and β-picoline, though stronger bases than pyridine, must be attributed to the steric requirements of these ligands. The scarcity of six-coordinate complexes of α-picoline adducts even with simple salts is well documented [15]. It is generally recognized that steric repulsion between the methyl groups in the *ortho*-position and neighboring ligands is a source of distortion from regular octahedral structure and usually results in complexes of low coordination number [2, 15]. The effect of *ortho*-substituted pyridines on the structural properties of copper(II) carboxylate adducts is quite revealing. The observation has been made that longer Cu–Cu distances have all been found in dimers in which the addend is an *ortho*-substituted pyridine [1]. Furthermore, it should be noted that the only dimeric 1:1 adducts of copper(II) haloacetates result from reaction with these ligands [1]. The tendency to form dimeric complexes may be attributed to the requirement of specific orientation of the axial ligands to minimize steric repulsions with neighboring groups. Because of the close proximity of both ligands to the acetate groups in the bis-adduct, such orientation may not be feasible without major disruption of the Cu-acetate bonding. The prediction is borne out by the results of X-ray structural measurements on the bis-adducts of α-picoline [3] and collidine [16]. Large distortions from ideal geometry are observed in the α-picoline bis-adducts with copper(II) chloro- and dichloroacetate, while the geometry of its binuclear mono-adducts with these salts is normal [17]. The steric repulsion due to the α-methyl groups in the bis-collidine adduct is apparently strong enough to disrupt the acetate group bonding resulting in a four-coordinate square-planar complex. In view of these observations, the relative instability of monomeric bis-adducts with α- and β-picoline can be understood, especially when one considers the lower Lewis acidity of the copper(II) acetate compared to the haloacetate salts.

Nmr Isotropic Shifts

The proton nmr spectra of solutions of the mono-adducts in $CDCl_3$ show broad (300–500 Hz) resonances due to the acetate-methyl protons 900 ± 10 Hz downfield from the corresponding resonance of

zinc acetate. The observed isotropic shift [18] is due to interaction with the fraction of the coupled ions present in the triplet excited state. Corrections for the population distribution and the dipolar shift contribution [19] leads to a negative contact shift of about 1.70×10^3 Hz. The relatively large shift of the acetate group resonance indicates that spin density is delocalized into the molecular orbitals of the bridging groups which is consistent with a greater contribution from the superexchange mechanism to the magnetic coupling between the copper atoms. Isotropic shifts of the methyl protons in the picoline ligands were also downfield from their positions in the free ligands; however, the shifts are small (40–120 Hz) and decrease in the order: α- > β- > α-picoline.

Isotropic shifts of coordinated pyridine and γ-picoline were obtained in solutions of the bis-adducts in their respective ligands over the temperature range of 291 to 385 K. The observed shifts, relative to their positions in the free ligands, are relatively small as compared to analogous Ni(II) and Co(II) complexes [20, 21]. All resonances are broadened to some extent, and the broadening increases with the isotropic shift. The exchange-averaged isotropic shift, $\Delta\nu^{iso}$, for any ligand proton may be calculated from its observed shift, $\Delta\nu^{obs}$, using the relation: $\Delta\nu^{iso} = \Delta\nu^{obs}/Pm$, where Pm is the fraction of ligand coordinated to copper(II) acetate in solution and it is conveniently obtained for each proton from the slope of the linear plot of $\Delta\nu^{obs}$ *vs.* the concentration of the complex. All isotropic shifts show the expected Curie law temperature-dependence. In the pyridine system, all proton shifts are downfield from their respective positions in the free ligand, and the shift increases in the order: $\gamma < \beta \ll \alpha$. Overlap of the β- and γ-proton signals, however, precluded accurate determination of their isotropic shifts. The α- and β-proton isotropic shifts of coordinated γ-picoline are also downfield with a similar trend but are larger in magnitude than those found in pyridine. This is consistent with the thermodynamic values for the formation of these adducts [22] and supports the suggestion [23] that the isotropic shift increases with the increased basicity of the ligand in a related series. The resonance of the methyl protons, on the other hand, is shifted upfield from its position in the free ligand.

The alternating sign of the isotropic shift upon methyl substitution suggests that the major contribution to these shifts is the Fermi contact interaction. A dominant dipolar contribution would require a downfield shift for the γ-methyl proton which has similar geometric factor as the γ-proton in pyridine. Moreover, the results of epr measurements [22] show that the anisotropy in the g factors ($g_\parallel - g_\perp$) in either complex is about 0.2, which makes contribution from the dipolar interaction unimportant. The dipolar contributions to the isotropic shifts were estimated from the geometric factors of these ligands which have been determined previously for analogous axially symmetrical Cu(II) [24] and Ni(II) [18, 20, 21] complexes, and from the measured g values. The results are shown in Table III, from which it can be seen that the dipolar contributions to the isotropic shifts of all protons are indeed very small. The hyperfine coupling constant, An, for each proton is evaluated from the slope of the linear plots of $\Delta\nu^{con}$ *vs.* 1/T, Fig. 3.

TABLE III. Isotropic Shift Data (Hz) for $Cu(OAC)_2 \cdot 2L$ at 291 K.

L		$\Delta\nu^{iso}$	$\Delta\nu^{dip}$	$\Delta\nu^{con}$	10^{-5} A_n
Py	α-H	−1083	−138	−945	3.33
γ-Pic	α-H	−1340	−138	−1202	7.05
	β-H	−330	−75	−255	2.04
	γ-CH_3	+382	−44	+426	−2.18

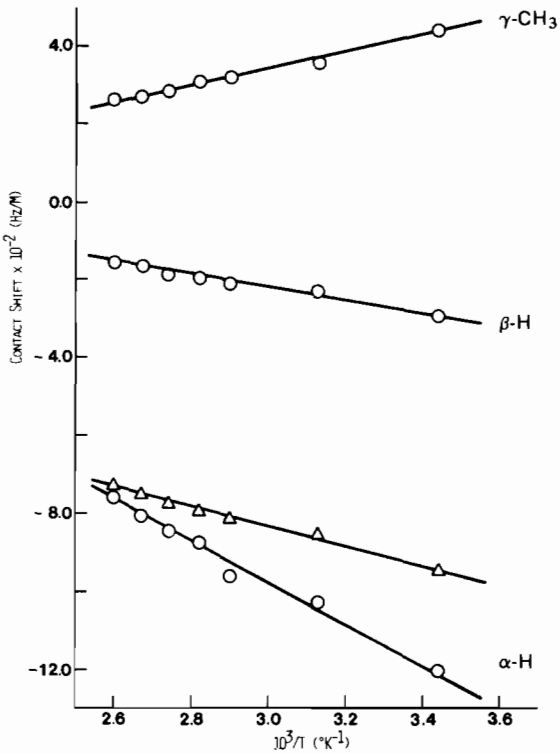

Fig. 3. Temperature dependence of the nmr contact shifts of ligand protons in $Cu(OAc)_2L_2$ solutions: △, L = py; ○, L = γ-pic.

The general pattern of the contact shifts, both in sign and magnitude, for solutions of these adducts is consistent with the well-established contention [21]

that contact shifts in pyridine-type ligands arise predominantly through spin delocalization in the ligand σ molecular orbitals. Copper(II) ion in an octahedral environment has an orbitally non-degenerate ground state with the unpaired electron in a σ-type (e_g) orbital. Sigma metal–ligand interaction places positive spin density on all protons giving rise to the observed downfield shifts. The upfield contact shift of the methyl group proton, on the other hand, has been generally considered to arise from delocalization of unpaired spin in the π orbitals of γ-picoline [21, 23–25]. An extended Huckel MO calculation [25] on $[Ni(\gamma\text{-pic})_6]^{2+}$ shows that the methyl hydrogens "contribute directly to both the π bonding and π antibonding orbitals" of γ-picoline, and the authors concluded that "the π mechanism dominates at the methyl group" in this ligand. Conversely, the isotropic shifts for ^1H and ^{13}C nuclei of pyridine and picolines coordinated to $Ni(acac)_2$ have been accounted for by INDO calculations involving σ-spin delocalization alone [18, 26]. The relatively large contact shift observed for the methyl proton in this study (γ-CH_3/α-H = 0.35 *vs.* 0.092 in $[Ni(\gamma\text{-pic})_6]^{2+}$ and 0.096 in $[Ni(acac)_2(\gamma\text{-pic})_2]$) cannot be accounted for on the basis of a σ delocalization mechanism alone since it requires attenuation of the contact shift with the increased number of intervening bonds. These results may indicate that both direct delocalization of β-spin and spin polarization mechanisms contribute to the contact shift of the methyl proton in γ-picoline coordinated to copper(II) acetate.

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