

ADDUCTS OF COPPER(II) ACETATE WITH AMINES IN ETHANOLIC SOLUTION

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ABSTRACT

Copper(II) acetate was calorimetrically titrated with pyridine, 2-, 3- and 4-methylpyridine in absolute ethanol. The enthalpy of reaction and the equilibrium constant were determined for the adduct formation in solution for each ligand. The amines react with copper(II) acetate without breaking the dimeric structure at least in the limit of the concentration ratio $|\text{ligand}|/|(\text{CH}_3\text{CO}_2)_4\text{Cu}_2| < 2$.

INTRODUCTION

A large number of adducts of copper(II) carboxylates exist with stoichiometry $\text{Cu}(\text{RCO}_2)_2 \cdot \text{L}$, where L is a donor molecule such as water or amines. Many of these compounds are better formulated as $\text{Cu}_2(\text{RCO}_2)_4 \cdot \text{L}_2$ with the copper atoms held together by bridging carboxylate groups [1–4].

The value of the effective magnetic moment of copper(II) carboxylate in various solvents has been shown to depend on the solvent. In weaker donor solvents, like ethanol or dioxane, the dimeric structure is preserved while in stronger donor solvents, like pyridine or water, the solvent molecules are capable of breaking the bridging carboxylate group by displacing the metal–carboxylate oxygen bond. The dimeric structure in a particular solvent is maintained as a result of the bond competition between the carboxylate ions and the solvent molecules [5,6].

The addition of ligand L to the terminal position in the copper(II) carboxylate can occur without breaking the structure, even for a moderate coordinating power ligand. Therefore it is of interest to determine the enthalpy of reaction of the ligand at the terminal position. In this work we have examined the reaction of copper(II) acetate with pyridine (py) and the 2-, 3- and 4-methyl derivatives (α -pic, β -pic and γ -pic, respectively) in absolute ethanol. The structures of the solids have also been examined in order to give reasonable support to our structural considerations in solution.

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EXPERIMENTAL

Reagents

Anhydrous copper(II) acetate was prepared by carefully heating pure $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4 \cdot 2\text{H}_2\text{O}$ to about 350 K under high vacuum (10^{-3} mm) and then stored under an atmosphere of nitrogen. Purified absolute ethanol was used as the solvent and freshly distilled pyridine, α -, β - and γ -picoline were used.

The four complexes were also isolated using current methods and the analysis carried out for the metal gave: Cu = 24.3% (expected = 24.4%) in the copper acetate-pyridine complex; Cu = 23.1% (expected = 23.1%) in copper acetate- α -picoline; Cu = 23.1% for copper acetate- β -picoline and Cu = 22.8% for copper acetate- γ -picoline.

Measurements

The LKB 8700-2 precision calorimeter was used for the titrations and the temperature of the system was $25.00 \pm 0.05^\circ\text{C}$. The equipment was calibrated with

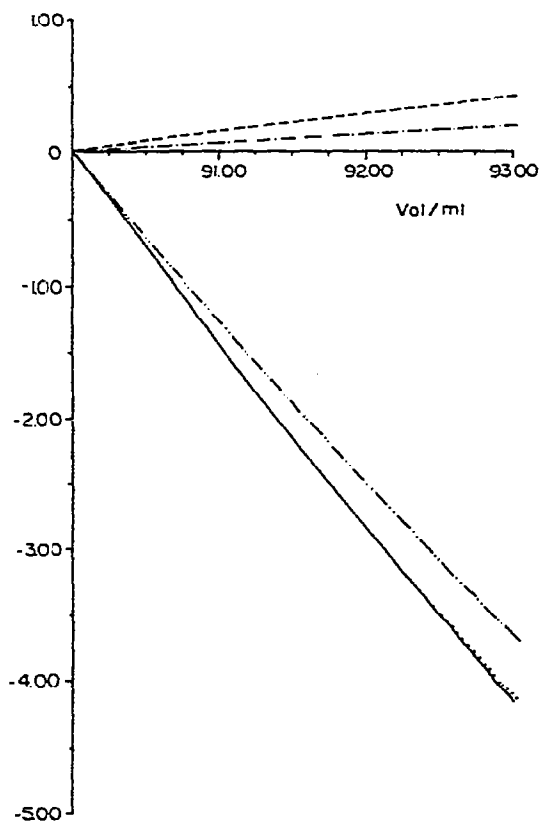


Fig. 1. Calorimetric titration of $(\text{CH}_3\text{CO}_2)_4\text{Cu}_2$ with pyridine in absolute ethanol. (-----) Titration of ethanol with py in ethanol; (-·-·-) titration of copper(II) acetate in ethanol with ethanol; (-·-·-·-) titration of copper(II) acetate in ethanol with py in ethanol; (————) resulting curve; and (·····) calculated curve.

TABLE 1

Vibrational frequencies of $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}_2$ below 400 cm^{-1}

py		α -pic		β -pic		γ -pic		Assignments
IR	R	IR	R	IR	R	IR	R	
352 vs ^a		384 s		354 vs		352 vs		ν_{CuO} E_u
	305 m, p	343 vs		342 vs			304 m, p	ν_{CuO} A_{1g}
264 s		259 vs		257 vs		257 s		ν_{CuO} A_{2u}
240 m		246 s		239 m		235 w		ν_{CuN} A_{2u}
	221 m		223 m		220 m		230 w	ν_{CuN} A_{1g}
186 s		175 m		182 m		186 m		
	100 m		103 s		105 m		100 s	

^a v=Very, s=strong, m=medium, w=weak, p=polarized.

standard tris(hydroxyamino)methane and the protonation heat was $\Delta H^0 = -47.44 \pm 0.23\text{ kJ mole}^{-1}$ (literature value = $-47.61 \pm 0.04\text{ kJ mole}^{-1}$) [7]. The incremental calorimetric titrations [8] were carried out for the three normal steps: (a) copper(II) acetate ($5.00 \times 10^{-3}\text{ M}$; $V = 90.0\text{ ml}$) was titrated with pure ethanol; (b) copper (II) acetate ($5.00 \times 10^{-3}\text{ M}$; $V = 90.0\text{ ml}$) was titrated with an ethanolic solution of an amine (py = 0.248 M ; α -pic = 0.304 M ; β -pic = 0.308 M ; γ -pic = 0.205 M); and (c) pure ethanol ($V = 90.0\text{ ml}$) was titrated with ethanol solution of the amines with concentrations specified above for each. A typical titration curve is shown in Fig. 1. The IR spectra below 400 cm^{-1} were obtained with mulls of the samples in paraffin oil between polyethylene windows. A Perkin-Elmer model 180 spectrophotometer was used. The Raman spectra were obtained with the samples in a rotating cell using the Cary 82 Raman laser spectrophotometer. The 488.0 nm line of an Ar ion laser was used to excite the samples. The vibrational frequencies are presented in Table 1. Visible and UV spectra were obtained in ethanol (complex concentration = 10^{-2} M) using a Zeiss DMR-21 spectrophotometer. The results are presented in Table 2.

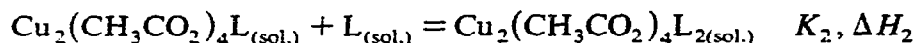
TABLE 2

Electronic spectra of $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}_2$ in absolute ethanol

	λ (nm)	
	Band I	Band II
py	690 ± 5	370 ± 10
α -pic-	695 ± 5	370 ± 10
β -pic-	690 ± 5	370 ± 10
γ -pic-	700 ± 5	370 ± 10

Calculations

The values of K_1 , K_2 and ΔH_1 and ΔH_2 are assigned to the chemical reactions



where

$$K_1 = |\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}| / |\text{Cu}_2(\text{CH}_3\text{CO}_2)_4||\text{L}|$$

$$K_2 = |\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}_2| / |\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}||\text{L}|$$

and ΔH_1 and ΔH_2 are the enthalpy changes of the first and second reactions. The calculations of K and ΔH were carried out using a program which fitted the calculated curve to the experimental one, through a minimization of the function $U(K, H) = \sum [Q_{\text{obsd.}}(i) - Q_{\text{calcd.}}(i)]^2$. $Q_{\text{obsd.}}(i)$ and $Q_{\text{calcd.}}(i)$ are, respectively, the corrected heat and the calculated one (see Fig. 1).

RESULTS AND DISCUSSION

The assignment of the vibrational frequencies of the skeleton $\text{Cu}_2\text{O}_8\text{N}_2$ was made on the basis of a D_{4h} symmetry which has $2A_{1g}(\text{R}) + B_{1g}(\text{R}) + E_g(\text{R}) + 2A_{2u}(\text{IR}) + B_{2u} + E_u(\text{IR})$ stretching vibrations (Table 1). The skeleton is centrosymmetric which is deduced from the noncoincidence of the IR and Raman bands. The two IR active CuO bands appear at ca. 260 and 352 cm^{-1} for py- and γ -pic-complexes but for α -pic- and β -pic-, a splitting of the E_u band is observed. The origin of this splitting is reasonably explained in terms of the lower whole point group symmetry of α -pic- and β -pic-molecules or, in terms of a factor group splitting. The Raman scattering is poor for these compounds and only two bands are assignable as the skeleton stretching vibrations [9], i.e., at ca. 220 and at ca. 300 cm^{-1} . In chloroform solution

TABLE 3

Thermodynamic data ^a for $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}_2$ in absolute ethanol

	py	α -pic	β -pic	γ -pic
$\log K_1^0$	5.37 ± 0.02	4.60 ± 0.05	4.91 ± 0.03	4.35 ± 0.05
$\log K_2^0$	4.35 ± 0.05	4.98 ± 0.03	3.67 ± 0.05	3.31 ± 0.12
ΔH_1^0	-6.0 ± 0.6	-1.4 ± 0.2	-3.8 ± 0.4	-6.5 ± 0.6
ΔH_2^0	-11.0 ± 1.0	-2.5 ± 0.3	-7.5 ± 0.7	-11.5 ± 1.0
ΔG_1^0	-30.6 ± 3.0	-26.3 ± 2.6	-28.1 ± 2.8	-24.6 ± 2.5
ΔG_2^0	-24.9 ± 2.5	-28.4 ± 2.8	-21.0 ± 2.1	-18.9 ± 1.9
ΔS_1^0	82 ± 8	83 ± 8	81 ± 8	60 ± 6
ΔS_2^0	46 ± 5	87 ± 9	45 ± 5	24 ± 3

^a Units: K^0 , 1 mole⁻¹; ΔH^0 and ΔG^0 , kJ mole⁻¹; ΔS^0 , J K⁻¹ mole⁻¹.

the last Raman band is polarized and the structure is the same as that observed in the solid state. Unfortunately the lower solubility of the compounds in ethanol made difficult the obtention of the Raman spectra in this solvent. However, although the dielectric constant of ethanol is quite different compared with that of chloroform, they seem to have the same degree of solvent effect [10].

The electronic spectra in ethanol (Table 2) are almost identical with the absorption spectra of other dimeric copper(II) acetate complexes in solid or solution [11]. The main characteristic is the presence of the band at 360 nm, normally called band II, which does not appear for complexes extensively dissociated in solution. The molar conductivity measured for $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{py}_2$ in ethanol (concentration of 1.00×10^{-3} M at 298 K in an atmosphere of nitrogen) gave $\Lambda_M = 1.57 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ while a value of Λ_M between 35–45 $\text{ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ is normally quoted for 1:1 electrolytes in this solvent [12]. It is then quite evident that in solution the structure of the complex is the same as that observed in solid state, i.e., the dimeric structure is present at least in the limit of the concentration ratio $|\text{ligand}|/|\text{Cu}_2(\text{CH}_3\text{CO}_2)_4| < 2$.

The results of the calorimetric titrations are shown in Table 3 and the distribution curve for the titration with py in Fig. 2. The comparison of the calculated titration curve with that of the observed one shows a good superimposition (the typical example is shown in Fig. 1). The value of the function $U(K, \Delta H)$ was between 8×10^{-3} and 2×10^{-4} in every case.

In comparing the $\text{p}K_a$ value of the amines [13] with the calculated ΔH_i^0 and K_i^0 , we did not observe any apparent trend, but it appears that the lower values of $\Delta H_i^0 = -1.4$ and $\Delta H_2^0 = -2.5 \text{ kJ mole}^{-1}$ observed for the α -pic-complex is due to a steric hindrance present in this complex [14].

The observed metal–ligand vibrations are not directly correlated with the basicity

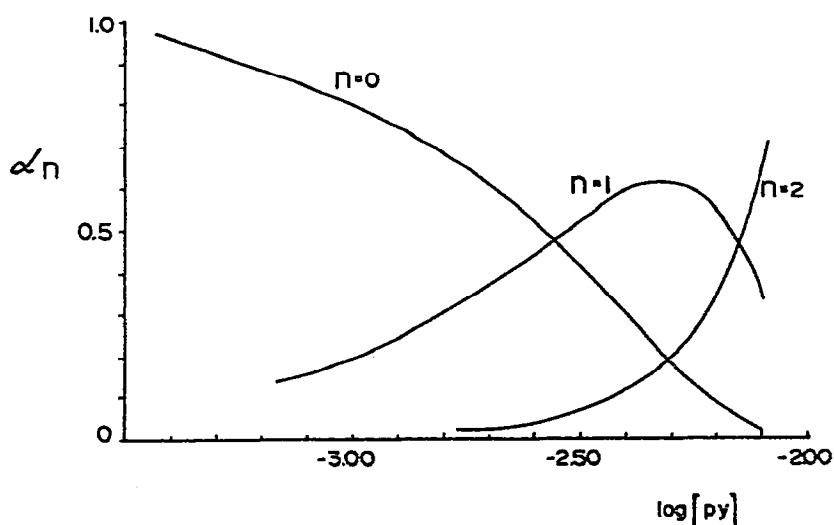


Fig. 2. Curve of distribution of $(\text{CH}_3\text{CO}_2)_4\text{Cu}_2\text{L}_n$ ($n=0, 1$ and 2) where $\alpha_n = |(\text{CH}_3\text{CO}_2)_4\text{Cu}_2\text{L}_n|/C_t$, $\text{L} = \text{pyridine}$, and C_t is the total concentration of copper(II) acetate.

TABLE 4

IR carboxylate stretching frequencies (cm^{-1}) of $\text{Cu}_2(\text{CH}_3\text{CO}_2)_4\text{L}_2$

Anhydrous	H ₂ O	py	α -pic	β -pic	γ -pic
1590 vs	1600 vs	1610 vs 1594 w	1620 vs 1600 w	1620 vs	1625 vs 1612 vs

of the ligand or the calculated enthalpy of reaction since these vibrations are normally highly coupled modes. The carboxylate stretching frequencies (Table 4) show, however, a tendency to shift to higher frequencies as the basicity of the terminal ligand increases. It is reasonable to assume that these frequencies are more pure and are more sensitive to a small change in the stretching force constants.

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