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# Hydroxycarboxylato Complexes of Copper(II): Synthesis and Characterization

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# HYDROXYCARBOXYLATO COMPLEXES OF COPPER(II): SYNTHESIS AND CHARACTERIZATION

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## ABSTRACT

Substitution reactions of anhydrous copper(II) acetate with some higher carboxylic acids and hydroxycarboxylic acids were carried out in toluene under reflux. The isolated products; Cu(OOCR)(OOCR′), Cu(OOCR)(OOCR″) and Cu(OOCR)(OOCR‴) [where R = $C_{13}H_{27}$, $C_{17}H_{35}$ or $C_{21}H_{43}$ and R′ = $C_6H_4OH$, R″ = $C_6H_5CH(OH)$ and R‴ = $(C_6H_5)_2C(OH)$] were characterized by elemental analyses, spectral (infrared and electronic) analyses and conductivity measurements. IR spectra suggest the presence of bidentate–bridging coordination of carboxylate anions in the complexes. Magnetic moment measurement and electron spin resonance spectral data suggest antiferromagnetic coupling between two copper atoms. The dinuclear nature of the complexes was confirmed by molecular weight determinations.

## INTRODUCTION

The chemistry of copper(II) complexes has received considerable attention during the last two decades[1-3]. This is mainly

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because of the variation in the magnetic behaviour of the complexes, the geometries around the $Cu^{2+}$ ion and biochemical applications. Among the large number of copper(II) complexes, carboxylate complexes have attracted major attention[4-6]. Complexes with simple or substituted carboxylic acids are known. Many aliphatic and aromatic hydroxycarboxylic acids are used as coordinating ligands to form complexes with copper(II)[3,7,8]. The literature reveals that no complex of copper(II) is known in which one ligand is a simple carboxylic acid and the other is an hydroxycarboxylic acid. In view of this, some monocarboxylato monohydroxycarboxylato complexes of copper(II) were synthesized by substitution reactions of copper(II) acetate. The structure of the complexes is discussed on the basis of the spectral, magnetic and molecular weight data.

## RESULTS AND DISCUSSION

Substitution reactions of copper(II) acetate with carboxylic acids and hydroxycarboxylic acids were carried out in toluene under reflux. The complexes were formed according to the following reactions:

$$Cu(OOCCH_3)_2 + RCOOH \xrightarrow[reflux]{toluene} Cu(OOCCH_3)(OOCR) + CH_3COOH\uparrow$$

$$Cu(OOCCH_3)(OOCR) + R^*COOH \xrightarrow[reflux]{toluene} Cu(OOCR)(OOCR^*) + CH_3COOH\uparrow$$

where $R = C_{13}H_{27}$, $C_{17}H_{35}$ or $C_{21}H_{43}$ and $R^* = C_6H_4OH$ [R'], $C_6H_5CH(OH)$ [R''] or $(C_6H_5)_2C(OH)$ [R''']

The reaction progress was followed by determining the acetic acid content in the collected azeotrope. The products were soluble in toluene in which copper(II) acetate was insoluble. The complexes are non–volatile coloured solids. The measured molar conductance at $10^{-2}$ – $10^{-4}$ molar concentration in benzene were in the range 0.1 – 1.3 ohm$^{-1}$ cm$^{2}$ mol$^{-1}$. These values show a non–electrolytic nature for all the complexes.

In the infrared spectra of the complexes, no O–H stretching vibrations of free carboxylic acids were found in the region 3600–3250 cm$^{-1}$. The free OH group of hydroxy acids, which has an absorption at 3400 cm$^{-1}$, was shifted to 3200 cm$^{-1}$. This shows the coordination of the hydroxyl group to the $Cu^{2+}$ ion[9]. No bands were found at 1710 cm$^{-1}$ and 935 cm$^{-1}$ which are characteristic vibrations of $\nu$(C=O) and $\delta$(O–H) of the free acids. A new band at 1600 cm$^{-1}$ was assigned to the $\nu$(C=O) stretching vibration ($\nu_8$). In the free acetate ion (in sodium acetate), the asymmetric C–O vibration ($\nu_8$) and symmetric C–O vibration ($\nu_3$) are observed at 1578 cm$^{-1}$ and 1435 cm$^{-1}$, respectively[10]. These bands were shifted to 1600 cm$^{-1}$ ($\nu_8$) and 1450 cm$^{-1}$($\nu_3$) in the IR spectra of the complexes. This shift indicated the presence of bidentate–bridging type of coordination for the carboxylate groups[11,12]. A new band in the complexes around 480 cm$^{-1}$ may be ascribed to Cu–O vibrations[11].

A single broad absorption band was observed in the electronic spectra of all the complexes in the region 14000–15500 cm$^{-1}$. This may be assigned to the $^{2}A_{1g} \rightarrow {}^{2}B_{1g}$ transition. The transition persists both in the solid state (in Nujol mulls) and in benzene solution. This band has a long tail going up to 11000 cm$^{-1}$, which is generally assigned to the $\delta$ bond formed by overlapping of $d_{x^2-y^2}$ orbitals of the two interacting copper atoms[13-15].

The magnetic moments of the complexes were measured at room temperature and the values obtained indicate that all the complexes are diamagnetic. Both unpaired electrons on the two copper atoms interact and are coupled antiferromagnetically to produce a low–lying singlet level which is diamagnetic[16]. The complexes gave no EPR signals which also confirms the antiferromagnetic interactions between two copper atoms.

Molecular weights of the complexes were determined cryoscopically in benzene and the results indicate that all complexes are dinuclear. The proposed dinuclear structure of the diamagnetic mono(carboxylato)mono(hydroxycarboxylato)copper(II) complexes is given in Fig.1. This type of structure has previously been suggested for some dinuclear copper(II) species[17-19].

## EXPERIMENTAL

All reactions were carried out under anhydrous conditions. Copper(II) acetate monohydrate was made anhydrous by boiling under reflux in acetic anhydride and drying *in vacuo*. Benzene and toluene were distilled over sodium. The carboxylic acids were used after distillation under reduced pressure (m.p. myristic acid 55° C, stearic acid 70° C, behenic acid 80° C, mandelic acid 118° C, benzilic acid 150° C and salicylic acid 155° C). Copper was determined as CuSCN. Acetic acid was titrated with standard sodium hydroxide solution using phenolphthalein as indicator.

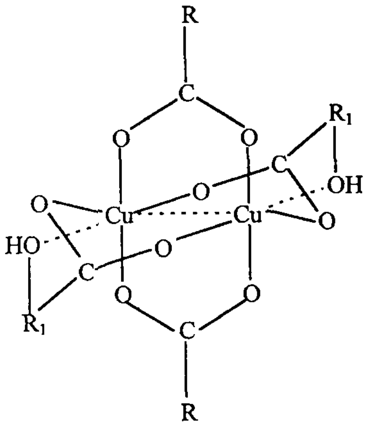

**Fig. 1. Schematic Representation of the Dimeric Cu$^{++}$ Complexes**
**[R = $C_{13}H_{27}$, $C_{17}H_{35}$ or $C_{21}H_{43}$ and $R_1$ = $C_6H_4$–, $C_6H_5CH$– or $(C_6H_5)_2C$– ]**

IR spectra were recorded on a Beckman Acculab–10 spectrophotometer using CsI discs, electronic spectra were recorded on a Hitachi model U–2000 and EPR spectra were recorded on a Varian model–4502 at 11.49 GHz frequency. Magnetic susceptibility measurements were carried out by Gouy's method using $Hg[Co(NCS)_4]$ as a calibrant.

***Synthesis of Complexes***

Myristic acid (8.53 g, 37.3 mmol) was added to a toluene (100 mL) suspension of $Cu(OOCCH_3)_2$ (7.46 g, 37.3 mmol). The contents were refluxed for 12 h with slow and continuous azeotropic fractionation of the liberated acetic acid with toluene (b.p. 106–110° C). The product was soluble in toluene. To this monosubstituted product (2.93 g, 8.3 mmol) mandelic acid (1.27 g,

**Table I. Analytical and Molecular Weight Data of Complexes**

| Reactants[a] | Product | | Empirical formula | Found (Calcd.) | | | | |
|---|---|---|---|---|---|---|---|---|
| (amounts in g) | Yield (%) | M.p. (° C) | (Formula weight) | $CH_3COOH$ (g) | Cu (%) | C (%) | H (%) | M. Wt |
| $Cu(OOCCH_3)(OOCC_{13}H_{27})$ + R′COOH | $Cu(OOCC_{13}H_{27})(OOCR')$ | | $C_{21}H_{32}O_5Cu$ | 0.50 | 14.71 | 58.1 | 8.1 | 896 |
| (3.01) (1.19) | 86 | 205 | (428.0) | (0.52) | (14.84) | (59.0) | (8.3) | (428) |
| $Cu(OOCCH_3)$ $(OOCC_{13}H_{27})$ + R″COOH | $Cu(OOCC_{13}H_{27})(OOCR'')$ | | $C_{22}H_{34}O_5Cu$ | 0.48 | 14.41 | 58.6 | 7.6 | 916 |
| (2.93) (1.27) | 84 | 192 | (442.1) | (0.50) | (14.37) | (59.8) | (7.8) | (442) |
| $Cu(OOCCH_3)(OOCC_{13}H_{27})$ +R‴COOH | $Cu(OOCC_{13}H_{27})(OOCR''')$ | | $C_{28}H_{38}O_5Cu$ | 0.38 | 12.12 | 64.1 | 7.1 | 1056 |
| (2.12) (1.37) | 82 | 201 | (518.2) | (0.36) | (12.26) | (64.9) | (7.2) | (518) |
| $Cu(OOCCH_3)(OOCC_{17}H_{35})$ + R′COOH | $Cu(OOCC_{17}H_{35})(OOCR')$ | | $C_{25}H_{40}O_5Cu$ | 0.94 | 12.99 | 62.0 | 8.2 | 986 |
| (6.53) (2.21) | 89 | 209 | (484.2) | (0.96) | (13.09) | (62.5) | (8.3) | (485) |
| $Cu(OOCCH_3)(OOCC_{17}H_{35})$ + R″COOH | $Cu(OOCC_{17}H_{35})(OOCR'')$ | | $C_{26}H_{42}O_5Cu$ | 0.88 | 12.75 | 63.1 | 8.5 | 978 |
| (6.54) (2.45) | 83 | 197 | (498.2) | (0.91) | (12.67) | (62.7) | (8.4) | (498) |
| $Cu(OOCCH_3)(OOC$ $C_{17}H_{35})$ + R‴COOH | $Cu(OOCC_{17}H_{35})(OOCR''')$ | | $C_{32}H_{46}O_5Cu$ | 0.90 | 11.11 | 65.8 | 8.2 | 1110 |
| (6.35) (3.53) | 80 | 208 | (574.3) | (0.93) | (11.05) | (66.9) | (8.0) | (575) |
| $Cu(OOCCH_3)(OOCC_{21}H_{43})$ + R′COOH | $Cu(OOCC_{21}H_{43})(OOCR')$ | | $C_{29}H_{48}O_5Cu$ | 0.74 | 11.68 | 63.9 | 9.0 | 1046 |
| (6.13) (1.84) | 82 | 217 | (540.3) | (0.80) | (11.67) | (64.4) | (9.1) | (540) |
| $Cu(OOCCH_3)(OOCC_{21}H_{43})$ + R″COOH | $Cu(OOCC_{21}H_{43})(OOCR'')$ | | $C_{30}H_{50}O_5Cu$ | 0.73 | 11.40 | 64.2 | 9.1 | 1135 |
| (5.97) (1.92) | 88 | 214 | (554.3) | (0.77) | (11.45) | (65.1) | (9.0) | (554) |
| $Cu(OOCCH_3)(OOCC_{21}H_{43})$ + R‴COOH | $Cu(OOCC_{21}H_{43})(OOCR''')$ | | $C_{36}H_{54}O_5Cu$ | 0.80 | 10.13 | 69.4 | 8.4 | 1283 |
| (6.41) (3.16) | 85 | 212 | (630.4) | (0.83) | (10.07) | (68.8) | (8.6) | (630) |

[a] **R′ = $C_6H_4OH$; R″ = $C_6H_5CH(OH)$ and R‴ = $(C_6H_5)_2C(OH)$; Refluxing time = 9 – 12 h.**

8.3 mmol) was added using toluene (100 mL) as a solvent. The mixture was refluxed for 10 h and the acetic acid toluene azeotrope was removed by fractional distillation. The excess of toluene was removed *in vacuo* to give a coloured solid which was recrystallized from benzene–ethanol (1:4) mixture. The same procedure was adopted for other substitutions and the details of analytical results are given in Table I.

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