

## Mono- and Poly-nuclear Complexes of Copper(II) with Linear and Branched Bis- $\beta$ -diketonato Ligands

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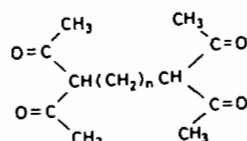
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### Abstract

The coordination of copper(II) with tetradentate bis- $\beta$ -diketonato ligands ( $L^{2-}$ ) has been systematically investigated. Two series of dinegative ligands were considered: one with terminally linked connecting chains,  $CH_3COCHCOCH_2(CH_2)_nCH_2CO-CHCOCH_3$ , (linear ligands;  $n = 4, 6, 8$ ) and the other with centrally linked chains,  $(CH_3CO)_2C-(CH_2)_n-C-(COCH_3)_2$  (branched ligands;  $n = 6, 8, 10, 12$ ). All complexes contained square planar, magnetically dilute  $[CuO_4]$  coordination entities, similar to those formed by mono- $\beta$ -diketonates. In the solid complexes of the linear and short-chain ( $n = 6, 8$ ) branched ligands, the  $[CuO_4]$  entities were linked to form polymeric species, whereas for the longer-chain branched ligands either a monomeric species (for  $n = 12$ ) or a monomer–polymer mixture (for  $n = 10$ ) was obtained.

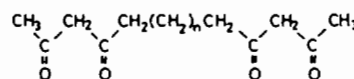
### Introduction

The coordination compounds of copper(II) with the enolates of 2,4-pentanedione and various substituted  $\beta$ -diketonates have been extensively investigated in regard to stability [1–6], structure [7–11], and electronic [12–15] as well as vibrational [16–18] spectra. These investigations have shown that the  $\beta$ -diketonato ligands ( $L^-$ ) coordinate to Cu(II) forming almost exclusively mononuclear, bis-chelate  $[ML_2]$  complexes, the square planar geometry of which is not affected by the presence of substituents on either the central or the terminal C atoms of the chelate systems. Because of the predictably simple geometry and high stability of its  $\beta$ -diketonato complexes, Cu(II) appeared especially suitable to explore the mode of coordination of the tetradentate ligands of types I (linear) and II (branched), in which two  $\beta$ -diketonate moieties are joined together through alkyl chains of varied lengths. In particular, it was of interest to investigate how the tendency of these bis- $\beta$ -diketonates to act as bridging or fused polychelating ('bifurcate') ligands might be influenced by the length and point of attachment of the connecting alkyl chains.



$n = 4, 6, 8$

Type I ligands



$n = 6, 8, 10, 12$

Type II Ligands

### Experimental

#### Starting Materials

The bis- $\beta$ -diketonates were prepared as previously described [19]. Reagent grade Cu(II) acetate and reagent or spectral grade solvents were used as received. Spectral grade pyridine was dried over 4A Linde Molecular Sieves.

#### Measurements

Microanalyses (C,H) were performed by Atlantic Microlab, Atlanta, GA. Mass spectra of selected samples were carried out at the Mass Spectrometry Center, University of Pennsylvania. Thermogravimetric analyses were carried out with a Perkin-Elmer TGS2 Thermogravimetric System. Magnetic Susceptibilities were measured with a Faraday-Cahn balance (at room temperature). Infrared spectra ( $4000-200\text{ cm}^{-1}$ ) were recorded with a Perkin-Elmer 283 Spectrophotometer, using a combination of Nujol and hexachlorobutadiene mulls supported on NaCl, CsBr, or polyethylene disks. Ultraviolet–visible spectra ( $250-800\text{ nm}$ ) were recorded with a Beckman Acta-M-VII spectrophotometer; chloroform was used as the solvent for solution spectra; solids were examined by transmission using Nujol mulls supported on quartz disks with a MgO–Nujol mull as the reference.

### Reaction of Bis- $\beta$ -diketones with Cu(II) Acetate in Ethanol

Finely powdered  $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2$  (0.12 mmol) and the bis- $\beta$ -diketone (0.25 mmol) were each dissolved in 25 ml of hot anhydrous ethanol and mixed slowly with stirring. (The order of addition of the reactants had no effect on the results). The mixture was further stirred with mild heating for *ca.* 10 min. With the linear ligands, a blue-gray flocculent solid formed immediately; with the branched ligands precipitation was slower and often occurred only after the mixture was cooled in a refrigerator. The blue-gray solids were filtered with suction, washed on the filter with ethanol, and dried *in vacuo* over solid KOH at room temperature. Yields were nearly quantitative.

The products were anhydrous and had analyses corresponding to the empirical formula  $\text{CuL}$ .

Identical products were obtained from other ethanol-soluble Cu(II) salts – e.g. Cu(II) chloride or nitrate – in the presence of sodium acetate with mole ratios 1 Cu: 1 ligand: 2 Na-acetate.

### Thermal Behavior and Solubility of the $\text{CuL}$ Complexes

The  $\text{CuL}$  complexes did not melt upon heating, but gradually decomposed with loss of ligand. When the heating was carried out in a thermobalance with a heating rate of 10 °C/min, under a He flow of 60 ml/min, the average mass loss corresponded to *ca.* 5% of the total ligand at 180 °C and 10–15% of the total ligand at 220 °C; complete decomposition occurred above 250 °C. When heating (120–200 °C) was carried out in a vacuum sublimator, only the parent bis- $\beta$ -diketone (yield, <20%) was found condensed in the cold finger after 24 h.

The complexes of ligand **I-4**, **I-6**, **I-8**, **II-6**, and **II-8** were practically insoluble in all solvents, including water by which they were not decomposed. The complexes of **I-6** and **I-8** did dissolve to a very slight extent upon prolonged boiling in chloroform; however, the solids later isolated from these solutions by evaporation or precipitation with ether were again as insoluble as the original materials. The complex of **II-12** readily dissolved in chloroform, dichloromethane, and benzene, from which it reprecipitated upon dilution with diethylether or ethanol; the reprecipitated solid had solubility identical to the original material. The complex of **II-10** appeared to be a mixture of two analytically and spectrally identical fractions – one readily soluble in chloroform and the other insoluble. When the ‘soluble fraction’ was reprecipitated from chloroform by addition of diethyl ether, the solid obtained again consisted of both a soluble and an insoluble fraction. No ‘completely soluble’ solid was isolated for this compound.

### Preparation of Bis(3-*n*-hexyl-2,4-pentanedionato)copper(II)

The complex was prepared from Cu(II) acetate and the  $\beta$ -diketone in ethanol (mole ratio = 1 Cu: 2 ligands), as described for the bis- $\beta$ -diketone complexes. The compound (gray needles) was very soluble in chloroform and benzene, insoluble in ethanol, ether, hexane, and water.

### Reaction of Linear Bis- $\beta$ -diketones with Cu(II) Acetate in Chloroform

Finely powdered  $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2$  (0.25 mmol) and the linear bis- $\beta$ -diketone (**I-4**, **I-6**, **I-8**; 0.50 mmol) were heated with stirring in chloroform (40 ml), until all Cu(II) acetate had dissolved. From the resulting blue-gray solution no solid separated upon cooling and standing. Partial evaporation of the chloroform or dilution with ether, hexane, or ethanol caused the separation of powdery blue-gray solids identical to those obtained from the reaction in ethanol.

### Reaction of 3-*n*-hexyl-2,4-pentanedione and Branched Bis- $\beta$ -diketones with Cu(II) Acetate in Chloroform

Finely powdered  $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2$  dissolved only in part when heated with a chloroform solution containing a 3-substituted- $\beta$ -diketone (initial mole ratio = 1 Cu: 2 ligands for the mono- $\beta$ -diketone and 1 Cu: 1 ligand for the bis- $\beta$ -diketones). In a typical reaction, approximately 80% of the Cu(II) acetate remained unreacted. No identifiable complexes were obtained from the green chloroform solution, either by evaporation or by precipitation with ether.

## Results and Discussion

### Complexes of Linear Ligands

Copper(II) acetate,  $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2]$ , although nearly insoluble in chloroform alone, readily dissolved in chloroform containing an equimolar quantity of a linear bis- $\beta$ -diketone, **I-4**, **I-6**, or **I-8**. The absorption spectra of the resulting blue-gray solutions were virtually identical to one another and consisted of a relatively weak and broad absorption in the visible region, with partly resolved maxima at 535–540 nm ( $\epsilon = 30$ ) and 650–660 nm ( $\epsilon = 40$ ), together with a very strong and fairly symmetrical band at 298 nm ( $\epsilon = 20,000$ ). This absorption pattern (Fig. 1) closely resembled that of the corresponding 2,4-pentanedionato complex,  $[\text{Cu}(\text{acac})_2]$ , and indicated the presence in solution of square planar Cu(II) species containing two chelating  $\beta$ -diketonato groups. Similar to  $[\text{Cu}(\text{acac})_2]$ , these Cu(II) species exhibited a slight Lewis-acid character. For example, they coordinated pyridine (py) when this was added in very large excess. The electronic spectra of the resulting blue-green solutions were nearly identical (Fig. 2)

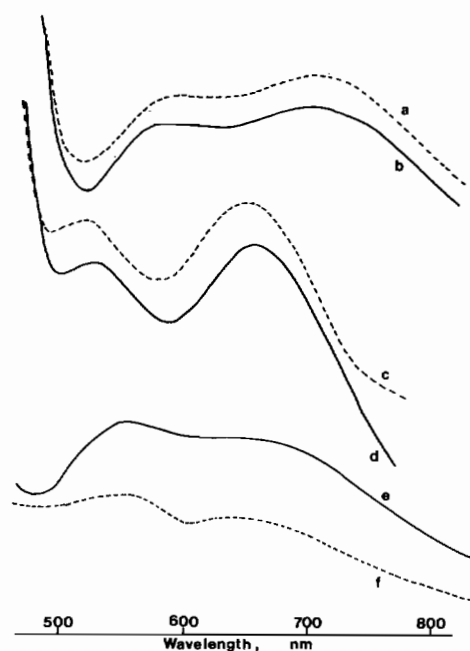


Fig. 1. Electronic absorption spectra in chloroform solution: (a)  $[\text{Cu}(\text{2,4-pentanedionato})_2]$ ; (b)  $[\text{Cu}(\text{I-6})]$ ; (c)  $[\text{Cu}(\text{3-n-hexyl-2,4-pentanedionato})_2]$ ; (d)  $[\text{Cu}(\text{II-12})]$ . Electronic absorption spectra of solid complexes: (e)  $[\text{Cu}(\text{2,4-pentanedionato})_2]$ ; (f)  $[\text{Cu}(\text{I-6})]$ .

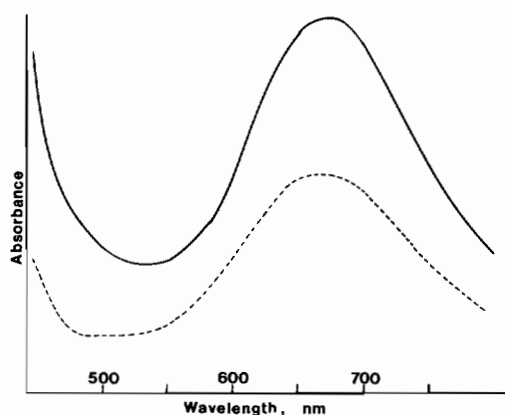


Fig. 2. Electronic absorption spectra of complexes in chloroform solution with added pyridine: (a)  $[\text{Cu}(\text{2,4-pentanedionato})_2]$ ; (b)  $[\text{Cu}(\text{I-6})]$ .

with those of the well-known five-coordinate, square pyramidal  $[\text{Cu}(\text{acac})_2\text{py}]$  complex [20, 21].

Chloroform solutions of the Cu(II)-bis- $\beta$ -diketonato system appeared to be quite stable, in the sense that they showed no spectral changes or tendency to form precipitates over a period of months. However, when the solutions were allowed to evaporate to dryness or were diluted with a 'non-solvent' such as ethanol, diethylether, or hexane, blue-gray powdery products resulted that no longer redissolved in chloroform, or redissolved only in part upon prolonged heating. Identical products resulted when equimolar quantities of Cu(II) acetate and of a

linear bis- $\beta$ -diketonato were allowed to react in hot ethanol solution.

The blue-gray 'insoluble' products thus obtained were analytically pure compounds of general formula  $\text{CuL}$ , where L indicates the dinegative bis- $\beta$ -diketonato ligand. The compounds were not crystalline, appearing as glassy globules under the microscope; however, they were thermally quite stable and began to decompose only at about 200 °C. The mass spectrum of the complex  $\text{Cu}(\text{I-6})$  showed only the ligand and its fragments, with no peak corresponding to a monomeric complex or to low oligomers.

The infrared spectra of the complexes showed the absence of water or hydroxo-impurities and closely resembled the spectrum of  $[\text{Cu}(\text{acac})_2]$ , except for the additional absorptions of the  $-(\text{CH}_2)_n$  chains. In particular, the absorptions of the coordinated  $\beta$ -diketonato groups [22] appeared as two strong, well-resolved absorptions at 1575  $\text{cm}^{-1}$  [ $\nu_{\text{as}}(\text{C}=\text{O})$ ] and 1530  $\text{cm}^{-1}$  [ $\nu(\text{C}=\text{C})$ ]; the Cu(II)-ligand modes appeared at 470 and 280  $\text{cm}^{-1}$ . The electronic spectra of the solid  $\text{CuL}$  complexes were extremely similar to the spectrum of solid  $[\text{Cu}(\text{acac})_2]$  (Fig. 1) and the values of the room-temperature magnetic moments (1.7–1.8 B.M.) further showed the individual Cu(II) units to be magnetically non-coupled.

From these data it may be concluded that the 'insoluble'  $\text{CuL}_n$  species consists of individual square-planar bis( $\beta$ -diketonato) copper(II) entities, linked together through the alkyl chains of bridging ligands to form random-coiled polynuclear chains,  $[\text{CuL}]_n$ . The coordinatively analogous species present in chloroform solution may then be formulated either as monomers involving bifurcate ligands or as ligand-bridged cyclic oligomers. The actual structure of the complexes present in these solutions could not be established by molecular weight measurements via osmometry or tensiometry, because of the accompanying presence of variable quantities of the by-products, acetic acid and water. Attempts to separate the complexes by chromatography on a variety of media resulted in failure, as the complexes gradually became fixed — *i.e.*, they polymerized on the absorbant.

The facile and irreversible formation of the insoluble  $[\text{CuL}]_n$  species shows that these ligand-bridged polymers represent the stable solid form of the Cu(II)-linear-bis- $\beta$ -diketonato systems. Partial depolymerization of the  $[\text{CuL}]_n$  solids occurred upon prolonged heating in chloroform, but only for the longer-chain ligands (the solid complex of ligand I-8 was sufficiently soluble to produce an approximately  $10^{-4}$  M solution). Attempts to depolymerize the  $[\text{CuL}]_n$  solids by vacuum sublimation at temperatures ranging from 120 to 180 °C resulted only in decomposition with gradual loss of the ligand.

### Complexes of Branched Ligands

Chloroform solutions of branched bis- $\beta$ -diketones failed to completely dissolve equimolar quantities of Cu(II) acetate; the same behavior was observed with the mono-chelating 'model branched ligand', 3-n-hexyl-2,4-pentanedione. In each case, only a small fraction of the original Cu(II) salt was extracted into the chloroform-ligand phase and the resulting pale blue-green solution was shown by its d-d electronic spectrum to contain a five-coordinate Cu-oxygen chromophore. An identical spectrum was obtained when a minute quantity of acetic acid was added to a chloroform solution of the Cu(II) complex of 3-n-hexyl-2,4-pentanedionato ligand. It seems reasonable to conclude that the species formed by the direct reaction of Cu(II) acetate with the branched bis- $\beta$ -diketones in chloroform involves coordination of both the acetic acid and the bis- $\beta$ -diketone, with either possibly present in a non-anionic form.

A different behavior was observed in more polar solvents. In hot ethanol solution, the branched ligands reacted rapidly and stoichiometrically with an equimolar quantity of Cu(II) acetate, forming green-gray solutions from which light-gray solids separated either immediately or upon cooling. These light-gray solids had analytical composition corresponding to an empirical formula CuL and their visible-ultraviolet absorption spectra were virtually identical to one another and to the spectrum of the model compound bis(3-n-hexyl-2,4-pentanedionato)copper(II). The infrared spectra were also extremely similar throughout the series, except for the expected variations in the relative intensities of the  $-\text{CH}_2-$  and  $-\text{CH}_3$  modes. It should be noted that for all 3-alkyl-substituted  $\beta$ -diketonato complexes examined in this work, the 1700–1400  $\text{cm}^{-1}$  region of the spectrum differed considerably from that of the complexes of the 2,4-pentanedionato ligand and of its terminally substituted analogs. Specifically, the  $\nu_{\text{a}}(\text{C}=\text{O})$  and  $\nu(\text{C}=\text{C})$  absorptions coalesced into a single strong band at 1575  $\text{cm}^{-1}$  (Fig. 3).

Despite their close spectral similarities, the solid complexes of the branched ligands differed markedly in their solubility: the derivatives of the shorter-chain ligands, **II-6** and **II-8**, were completely insoluble in chloroform; the derivative of **II-12** was very soluble, and that of **II-10** showed an intermediate behavior – in the sense that only a fraction of the solid was soluble. The chloroform solutions thus obtained had visible-ultraviolet spectra similar to those of the corresponding solids and nearly identical to the spectrum of the 3-hexyl-2,4-pentanedionato analog, which was itself extremely soluble in chloroform. Paper chromatography of the chloroform solutions of the **II-12** and 3-hexyl-complexes gave in each case a single clean spot which remained mobile after

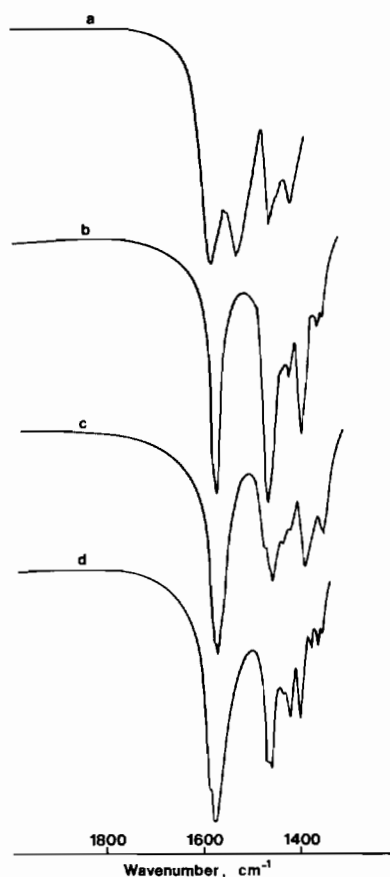


Fig. 3. Infrared absorption spectra of: (a) [Cu(L-8)]; (b) [Cu(II-8)]; (c) [Cu(II-12)]; (d) [Cu(3-hexyl-2,4-pentanedionato)<sub>2</sub>].

drying; the two compounds also had very similar  $R_f$  values. In contrast, chloroform solutions of **II-10** gave non-reproducible long-tailed spots which became fixed on the paper upon drying. On the basis of these observations, it may be concluded that the solid complexes of **II-6** and **II-8** are ligand-bridged polymers, the complex of **II-10** is a polymer-monomer mixture, and that of **II-12** is a bifurcated monomer both in the solid state and in solution. In support of these conclusions, the mass spectrum of the **II-12** complex showed the parent peak of the monomeric form at  $m/e = 428$ , whereas only fragments were observed in the mass spectra of the shorter-chain complexes.

### Conclusions

In evaluating and comparing the coordination of linear and branched bis- $\beta$ -diketonates to copper(II), it is appropriate to distinguish between those factors which are primarily electronic in origin and those which arise from steric or entropic effects. Primarily of electronic origin is the marked decrease in acid strength from the linear to the branched ligands [19], which in turn results in a decreased ability to displace other anionic ligands – specifi-

cally, the acetate ion – from the coordination sphere of Cu(II). Thus, under parallel conditions both 2,4-pentanedione and the linear bis- $\beta$ -diketonates displace the acetate quantitatively, whereas 3-hexyl-2,4-pentanedione and the branched bis- $\beta$ -diketonates do so only to a minimal extent. Also of electronic origin is the difference in Lewis-acid character of the two series of [CuL] complexes, those of the more basic linear ligands exhibiting a much higher degree of coordinative saturation. The choice between polymeric and monomeric (or oligomeric) structure must instead result from a combination of steric and entropic effects. With the very flexible linear ligands, a highly disordered polymeric structure is favored even when the chain connecting the two chelating sites is sufficiently long to span opposite coordination edges in an unstrained loop. For the more rigid and symmetric branched ligands, in contrast, the structure of the complex is determined by the length of the connecting chain – the change from ligand-bridged polymer to bifurcate monomer occurring as the chain increases from  $-(\text{CH}_2)_{10}-$  to  $-(\text{CH}_2)_{12}-$ . A somewhat parallel dependence has been observed for the complexes of square planar  $d^8$  metal ions with ditertiary phosphines; these tend to form *trans*-spanning monomeric species when the connecting chains of the diphosphine exceed  $-(\text{CH}_2)_{10}-$  groups. For the Cu(II) bis- $\beta$ -diketonates, the chain-length requirements are more stringent since the bonds joining the trigonally hybridized  $C_3$ -atom of each chelate ring to the connecting chain point rigidly away from the central metal, in directly opposite directions.

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