Copper(II) Chelates of 2,4,6-Heptanetrione and Its Homologues[1]

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Copper(II) chelates of heptane-2,4,6-trione as well as its methylated derivatives such as 3-methylheptane-2,-4,6-trione, 3,5-dimethylheptane-2,4,6-trione, and 2-methoxy-2-heptene-4,6-dione have been synthesized. All the ligands gave 1:2 (metal ion: ligand) chelates. The first two ligands gave in addition binuclear 2:2 chelates. The fact that a 1:2 chelate was relatively easily converted into a 2:2 chelate and the conversion occurred more easily with the chelate of the first ligand than with that of the second one was interpreted by the steric effect of the methyl group. The structures of the 1:2 and 2:2 chelates were discussed on the basis of spectroscopic and other data. Reversible addition of heterocyclic bases to the 2:2 copper chelates was observed, and the coordinating structure of pyridine adduct was found to be of a pentacoordinate square pyramid.

Heptane-2,4,6-trione (H_2daa) or diacetylacetone is a higher homologue of acetylacetone. The ligand exists as a monoanionic ($Hdaa^-$) or dianionic form (daa^{2-}), and can behave as a bidentate as well as a terdentate ligand in complex formation.

Although organic chemistry of this compound and its complexing properties have been studied to some extent,[2-8] no systematic investigation of the compound as a multidentate ligand had been reported before the publication of our communication.[9] Recently, the keto-enol tautomerism as well as the copper(II) chelates of heptane-2,4,6-trione and related triketones have been investigated by Dudley *et al.*[10,11] The characteristics of binuclear copper(II) chelates of the related β,δ-triketone ligands have also been reported by Graddon and Townsend,[12] Toy *et al.*,[13] and Murtha and Lintvedt.[14]

Three oxygen atoms in the β,δ-triketone ligands can be seen to be fixed in the same plane unable to coordinate to the same metal ion simultaneously, and it is of interest to investigate the behavior of the β,δ-triketone ligands as a multidentate ligand upon complex formation. We have investigated the fundamental properties, including keto-enol tautomerism of heptane-2,4,6-trione and its methylated derivatives,[15] the synthesis and structure of the chelates of $[M(HL)_2]$ and $[M_2L_2]$ type of divalent transition metal ions and related β,δ-triketones.[16]

In this paper we present the results of syntheses, structures, and the properties of copper(II) chelates of heptane-2,4,6-trione (H_2daa), as well as its methylated derivatives such as 3-methylheptane-2,4,6-trione (H_2mmd), 3,5-dimethylheptane-2,4,6-trione (H_2dmd), and 2-methoxy-2-heptene-4,6-dione (Hmod).

Experimental

The Ligands. Synthesis and characterization of the ligands have been reported.[15]

Synthesis of the Chelates. 1 : 2 Chelates. Bis(heptane-2,4,6-trionato)copper(II) Dihydrate, $Cu(Hdaa)_2\cdot 2H_2O$. (a): A methanol solution of heptane-2,4,6-trione (1.0 g, 0.0070 mol) was added to an aqueous solution of cupric acetate monohydrate (0.70 g, 0.0035 mol, in 20 m*l* of water) under cooling in an ice-water bath. Blue precipitates were collected and dried in the air. Yield, 0.85 g (63%). Attempts to recrystallize the sample from various organic solvents were unsuccessful, because the compound was easily converted into $Cu_2(daa)_2$ when dissolved in the solvent even at room temperature, mp about 50°C (decompn.). However, it was converted into $Cu_2(daa)_2$ upon heating so easily that no reproducible melting point could be observed. Two moles of water, probably coordinated water, could not be removed even at reduced pressure and lower temperature, without causing rearrangement into $Cu_2(daa)_2$.

(b): Two grams (0.0049 mol) of bis(heptane-2,4,6-trionato)dicopper(II) and 10.0 g (0.070 mol) of heptane-2,4,6-trione were dissolved into 20 m*l* of pyridine containing a small amount of water at 0°C, and the solution was concentrated to about 5 m*l* by evaporating pyridine at reduced pressure at 0°C, to give blue precipitates which were collected and air-dried. Yield, 2.4 g (64%).

Bis(3-methylheptane-2,4,6-trionato)copper(II), $Cu(Hmmd)_2$. A chloroform solution (20 m*l*) of 3-methylheptane-2,4,6-trione (0.50 g, 0.0032 mol) was stirred together with an aqueous solution of cupric acetate monohydrate (0.32 g, 0.0016 mol) at room temperature. The resulting mixture was kept to stand and the chloroform layer formed was evaporated off at room temperature to give blue precipitates which were purified on a silica gel (WAKOGEL Q-23) column. Yield, 0.45 g (75%), mp about 80°C (decompn.). However, the compound converted into $Cu_2(mmd)_2$ by heating so easily

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[1] Contribution No. 209 from the Department of Organic Synthesis, Kyushu University.

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that no reproducible melting point could be observed.

Bis(3,5-dimethylheptane-2,4,6-trionato)copper(II), Cu(Hdmd)$_2$. A similar procedure to the above was carried out using a chloroform solution (50 m*l*) containing 3,5-dimethylheptane-2,4,6-trione (2.00 g, 0.0118 mol) and an aqueous solution (100 m*l*) of cupric acetate monohydrate (1.20 g, 0.0060 mol). The chloroform solution was evaporated to give greenish grey residue, which was purified by elution chromatography on a silica gel column. Yield, 1.42 g (60.1%), mp 162—162.5°C.

Bis(2-methoxy-2-heptene-4,6-dionato)copper(II), Cu(Hmod)$_2$. Heptane-2,4,6-trione (5.0 g, 0.035 mol) was added at 5°C into ether (30 m*l*) containing diazomethane which was prepared from nitrosomethylurea (5.0 g, 0.049 mol) and a 40% potassium hydroxide solution (9.0 m*l*). After being put to stand overnight at room temperature, the ethereal solution was evaporated to give a viscous oil which was dissolved in chloroform (100 m*l*) and treated with an aqueous cupric acetate monohydrate (15.0 g, 0.075 mol). The chloroform layer formed was evaporated to dryness, giving pale blue precipitates, which were recrystallized three times from ethanol. Yield, 2.10 g (32%), mp 160—162°C. The product was assigned to be bis(2-methoxy-2-heptene-4,6-dionato)copper(II).

A chloroform solution of the copper chelate was stirred together with 0.1N hydrochloric acid until the chloroform layer became colorless. The chloroform layer was evaporated to give an oil which was assigned to be heptane-2,4,6-trione by infrared spectral comparison and gas-liquid chromatography. The chloroform solution of the oil was again treated with aqueous cupric acetate. The resulting blue solution was evaporated to give a solid residue which was identified to be $Cu_2(daa)_2$ by infrared spectral comparison.

2:2 Chelates. *Bis(heptane-2,4,6-trionato)dicopper(II), Cu*$_2$*(daa)*$_2$. *(a)*: A methanol solution of heptane-2,4,6-trione (1.0 g, 0.0070 mol) was added portionwise to an aqueous solution of cupric acetate monohydrate (1.4 g, 0.0070 mol) at 30°C with stirring. Resulting green precipitates were insoluble in most organic solvents except for strong coordinating solvents such as pyridine or dimethyl sulfoxide. The precipitates were collected, recrystallized from pyridine and dried under reduced pressure at 65°C for several hours to give green powders, decomposing at about 280°C. Yield, 1.20 g (83%).

(b): A methanol solution (10 m*l*) containing bis(heptane-2,4,6-trionato)copper(II) dihydrate, $Cu(Hdaa)_2 \cdot 2H_2O$, (1.00 g, 0.00262 mol) was heated under reflux for 2 hr. The green precipitates were collected and dried under reduced pressure. The complex was identified to be the above mentioned binuclear chelate by elemental analysis and infrared spectroscopy. Yield 1.02 g (95.3%), mp 280°C (decompn.).

Bis(3-methylheptane-2,4,6-trionato)dicopper(II) Cu$_2$*(mmd)*$_2$. A similar procedure to the above (procedure (b)) was carried out using a methanol solution of bis(3-methylheptane-2,4,6-trionato)copper(II) (1.0 g, 0.0027 mol). The resulting green precipitates were recrystallized from pyridine and dried under reduced pressure at 65°C. Yield, 0.82 g (70%), mp about 280°C (decompn.).

The properties and the results of elemental analyses as well as the conditions of synthesis of the copper chelates investigated are summarized in Table 1.

Base Adducts of 2:2 Chelates. Pyridine or 4-methylpyridine adducts of $Cu_2(daa)_2$ and $Cu_2(mmd)_2$ were prepared by dissolving 1 g of the copper chelate into 50 m*l* of pyridine or 4-methylpyridine, and putting the resulting solution to stand for 1—2 days at 0—15°C. The crystalline precipitates afforded were collected by filtration and air-dried. Yield 0.3—0.6 g (29—43%). The base adducts were dark brown crystals, fairly stable in nonpolar solvents such as hexane or cyclohexane, but readily decomposed in polar solvents such as methanol or water, precipitating green 2:2 chelates.

The amount of base coordinated to the 2:2 chelates and the temperature at which the base began to dissociate were determined by thermogravimetric analysis. The results are summarized in Table 2.

When bis(heptane-2,4,6-trionato)copper(II) dihydrate ($Cu(Hdaa)_2 \cdot 2H_2O$) was treated with concentrated aqueous ammonia, an ammonia adduct was obtained as brown powder. The product was not stable enough to be subjected to thermogravimetric analysis to get reliable results on the number of mole of ammonia added. However, the product was supposed to be the ammonia adduct of $Cu_2(daa)_2$, since the remaining compound after thermal decomposition was found to be $Cu_2(daa)_2$.

Attempts to prepare the solid base adducts of 2:2 chelate with other amine ligands such as ethylamine, diethylamine, triethylamine, aniline, and quinoline were unsuccessful, although adducts were formed in solution as indicated by the color change from green solid to brown solution when the solid 2:2 chelates were dissolved in these amine ligands.

Apparatus and Procedure. All melting points are uncorrected. Visible spectra were measured with a Hitachi

TABLE 1. COPPER CHELATES OF HEPTANE-2,4,6-TRIONE AND ITS METHYLATED DERIVATIVES

Chelate	Reaction condition		Soluble in	Color	Molecular formula	Elemental analysis Found (Calcd)		
	Temp. °C	Solvent				C%	H%	M%
$Cu_2(daa)_2$	30	Methanol or water	Pyridine, THF (ca. 10^{-3}M)	Green	$C_{14}H_{16}O_6Cu_2$	41.41 (41.27)	3.89 (3.93)	31.0 (31.2)
$Cu(Hdaa)_2 \cdot 2H_2O$	0	Methanol or water	Methanol, chloroform, acetone, THF	Blue	$C_{14}H_{22}O_8Cu$	43.75 (43.80)	6.09 (5.81)	16.4 (16.6)
$Cu_2(mmd)_2$	Reflux in methanol (from $Cu(Hmmd)_2$)		Pyridine	Green	$C_{16}H_{20}O_6Cu_2$	44.01 (44.01)	4.42 (4.58)	28.7 (29.2)
$Cu(Hmmd)_2$	Room temp., water		Chloroform	Blue–violet	$C_{16}H_{22}O_6Cu$	51.34 (51.40)	6.12 (5.93)	16.56 (16.99)
$Cu_2(dmd)_2$	Not obtainable		—	—	—	—	—	—
$Cu(Hdmd)_2$	Room temp., water		Chloroform	Blue–violet	$C_{18}H_{26}O_6Cu$	53.47 (53.79)	6.61 (6.52)	15.71 (15.81)
$Cu(Hmod)_2$	Room temp., water		Chloroform	Pale blue	$C_{16}H_{22}O_6Cu$	51.37 (51.40)	5.99 (5.93)	17.06 (16.99)

Table 2. Base adducts of 2: 2 chelates

Chelate	Base	Mole ratio of base/ chelate	Decomposition temp. °C[a]
$Cu_2(daa)_2$	pyridine	2.0	34
	4-methylpyridine	2.1	38
$Cu_2(mmd)_2$	pyridine	2.0	44
	4-methylpyridine	2.0	49

a) The temperature at which the base begins to dissociate.

124 recording spectrophotometer. Solid reflectance spectra were measured with a Hitachi EPU-2A spectrophotometer. Infrared absorption spectra were recorded with a JASCO DS-301 spectrophotometer. Molecular weights were determined with a Mechrolab vapor pressure osmometer. Thermogravimetric analysis on the base adducts were conducted with a Shimadzu automatic recording thermobalance TB-10B. A weighed amount of a chelate (20—100 mg) was placed on a weighing pan of the thermobalance and the temperature of the furnace was raised at a rate of 5°C per minute under atmospheric pressure. The weight change was recorded automatically up to 150°C.

Infrared spectra and visible spectra of some representative copper chelates are shown in Figs. 1 and 2 respectively.

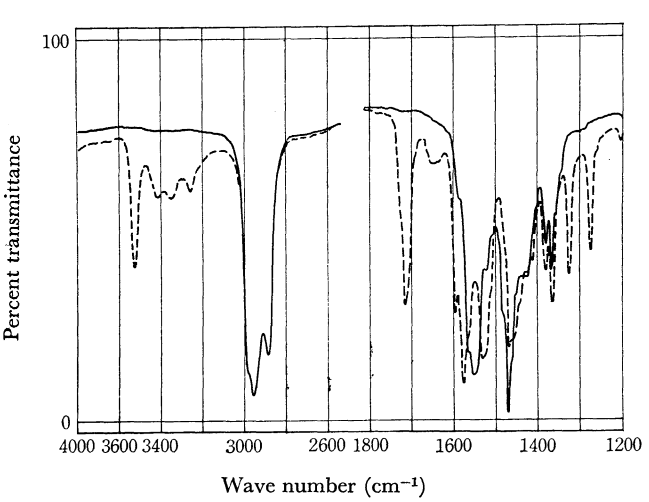


Fig. 1. IR spectra of the copper chelates in Nujol mull. ——: $Cu_2(daa)_2$.------: $Cu(Hdaa)_2 \cdot 2H_2O$

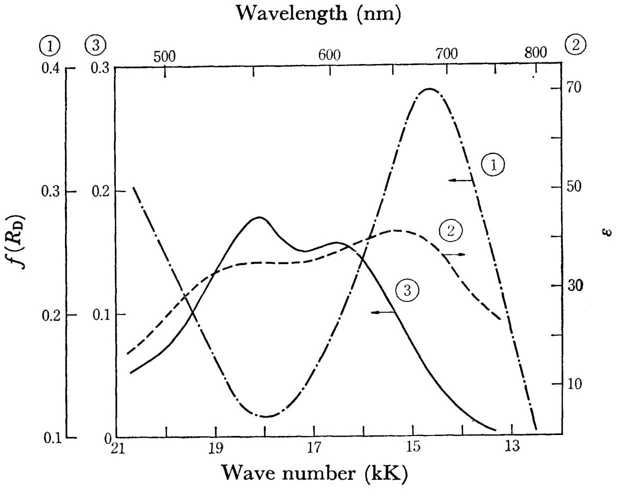


Fig. 2. Visible spectra of the copper chelates and copper acetylacetonate.

1: Powder reflection spectrum of $Cu_2(daa)_2$

2: Absorption spectrum of copper acetylacetonate in chloroform

3: Powder reflection spectrum of $Cu(Hdaa)_2 \cdot 2H_2O$

$f(R_D)$ is calculated according to the Kubelka-Munk equation

Results and discussion

Synthesis of Copper Chelates. Heptane-2,4,6-trione and its homologues can form two types of copper chelates; a mononuclear type, $Cu(HL)_2$, and a binuclear type, Cu_2L_2.[9] As shown in Table 1, heptane-2,4,6-trione and the 3-methyl derivative gave both types of chelates, while the 3,5-dimethyl derivative afforded only the former.

Synthetic procedures of these chelates can be classified as follows; For $Cu(HL)_2$ type chelate: Procedure 1. A cold methanol solution of a ligand was added dropwise into half a mole of aqueous cupric acetate at a lower temperature. Procedure 2. A cold chloroform solution of a ligand was stirred with half a mole of aqueous cupric acetate at a lower temperature. Procedure 3. A cold pyridine solution containing a Cu_2L_2 type complex and a large excess of the corresponding ligand was evaporated under reduced pressure at a lower temperature. For Cu_2L_2 type chelate: Procedure 4. An aqueous cupric acetate was added dropwise into a hot methanol solution of an equimolar amount of the ligand. Procedure 5. A methanol solution of $Cu(HL)_2$ type chelate was heated with or without an equimolar amount of cupric acetate as long as necessary.

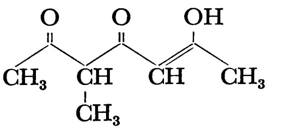
Mononuclear $Cu(HL)_2$ type chelates are not so stable, and tend to convert into binuclear Cu_2L_2 chelates at higher temperatures accompanied by the liberation of free ligand (See Experimental). The maximum temperature below which $Cu(HL)_2$ type complex is stable in methanol, is 0°C for $Cu(Hdaa)_2$ and 30°C for $Cu(Hmmd)_2$. Thus, the reaction temperature in the synthetic procedure 1, 2, and 3 has to be kept below −5°C for the first, and at room temperature for the second, otherwise the mixture of $Cu(HL)_2$ and Cu_2L_2 will be obtained as the reaction product. For the third, there was no indication of conversion into binuclear complex even when heated at refluxing temperature in methanol.

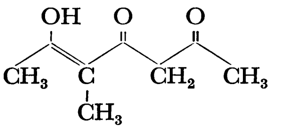
The binuclear chelates can be obtained by either procedure 4 or 5, most easily from heptane-2,4,6-trione and less easily from monomethyl derivative. Thus, $Cu_2(daa)_2$ was obtained by the reaction at room temperature, but $Cu_2(mmd)_2$ was obtained at refluxing temperature in methanol. Attempted syntheses of a binuclear chelate with the dimethyl derivative were unsuccessful under various reaction conditions including those for the above ligands. The *O*-methyl derivative gave only the mononuclear chelate as expected from its bidentate structure.

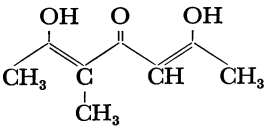
Structure of $Cu(HL)_2$ Chelates. The result of the elemental analysis on 1: 2 chelate of heptane-2,4,6-trione suggests the molecular formula of $Cu(Hdaa)_2 \cdot 2H_2O$. The infrared spectra of 1: 2 chelates from three ligands, $\mathrm{H_2daa}$, $\mathrm{H_2mmd}$, and $\mathrm{H_2dmd}$, showed a free carbonyl band at about 1720 cm^{-1} and multiplet bands in the region of 1600—1500 cm^{-1} due to a coordinated carbonyl and an olefinic group involved in the chelate ring which were not observed in the free ligand (Fig. 1). Broad bands in 1700—1600 cm^{-1} observed in the free ligands disappeared in infrared spectra of the copper chelates. The results suggest that the adjacent two of three carbonyl oxygen atoms are involved in the chelate formation with copper, leaving the side carbonyl oxygen uncoordinated.

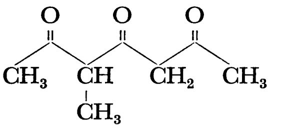
Powder reflection spectrum of $\mathrm{Cu(Hdaa)_2 \cdot 2H_2O}$ shows two broad bands at 16500 and 18100 cm^{-1} which are fairly close to those of bis(acetylacetonato)copper(II) in chloroform (15300, 18200 cm^{-1}). The result indicates that four carbonyl oxygen atoms around copper ion in $\mathrm{Cu(Hdaa)_2 \cdot 2H_2O}$ are of square planar configuration as in the case of bis(acetylacetonato)copper(II), and the coordination of two moles of water to the *z* axis of copper ion is not strong enough to influence the electronic spectra of *d–d* transition.

Thus, the structure of bis(heptane-2,4,6-trionato)-copper(II) dihydrate is proposed as Structure I. In the case of 3-methylheptane-2,4,6-trione, however, there remains a question as to the site of coordination of the ligand, because the ligand is no more symmetric. Although there is no definite data, NMR study on the keto-enol tautomerism of this ligand in $CDCl_3$ revealed that the fractions of monoenol (A), monoenol (B), bisenol and triketo forms were 76, 9, 12, and 3%, respectively, and these fractions did not change appreciably with temperature.[15]

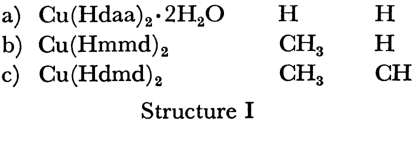

monoenol (A)


monoenol (B)


bisenol


triketo

If one recalls that 1:2 copper chelate of 3-methylheptane-2,4,6-trione was synthesized by contacting the chloroform solution of the ligand with an aqueous solution of cupric acetate, the possible structure of 1:2 copper chelate might be the one in which the methyl group is located on the middle carbon of uncoordinated side as illustrated in structure I.



		R¹	R²
Ia)	$\mathrm{Cu(Hdaa)_2 \cdot 2H_2O}$	H	H
Ib)	$\mathrm{Cu(Hmmd)_2}$	CH_3	H
Ic)	$\mathrm{Cu(Hdmd)_2}$	CH_3	CH_3

Structure I

It is of interest to note that 1:2 chelate of heptane-2,4,6-trione differs from those of the *C*-methylated derivatives with respect to the coordinated water. The former contained two moles of water with a multiplet band at 3530—3260 cm^{-1}, could hardly be removed. Attempted dehydration of the two moles of water under reduced pressure at room temperature resulted in conversion into an anhydrous $\mathrm{Cu_2L_2}$ chelate. Thus, bis(heptane-2,4,6-trionato)copper(II) seems to be stable only in the presence of coordinated water. On the other hand, the 1:2 chelates of 3-methyl- and 3,5-dimethyl derivatives can be obtained as anhydrous chelates respectively. Similarly, replacement of one or both terminal methyl groups with the phenyl group also resulted in anhydrous 1:2 chelates.[11]

A multiplet band at 3530—3260 cm^{-1} observed on bis(heptane-2,4,6-trionato)copper(II) dihydrate may be responsible for ν_{OH} of coordinated water as well as the enolic hydroxyl group. This suggests the partial enolization of the uncoordinated carbonyl group in the chelate. A similar situation was also observed on bis(heptane-2,4,6-trionato)palladium(II) by NMR study.[17]

1:2 Copper chelates of methylated ligands $\mathrm{Cu(Hmmd)_2}$ and $\mathrm{Cu(Hdmd)_2}$ were obtained as anhydrous chelates. No meaningful absorption was observed in 3200—3500 cm^{-1} region. This indicates that the uncoordinated carbonyl group in the chelates of methylated ligands do not enolize appreciably. This can be explained by the steric effect of the methyl group on 3-position. In the case of keto form, the uncoordinated terminal acetyl group can rotate freely, so that there operates little steric repulsion between the methyl groups on terminal- and 3-position. On the other hand, the olefinic double bond of the enol form restricts the free rotation of the terminal group, resulting in the stable configuration. Such steric effect does not exist in bis(heptane-2,4,6-trionato)copper(II), allowing a partial enolization of the uncoordinated carbonyl group.

As to the copper chelate of 2-methoxy-2-heptene-4,6-dione, the result of elemental analysis suggests the molecular formula $\mathrm{Cu(Hmod)_2}$. The reaction of diazomethane with heptane-2,4,6-trione gave only the *O*-methyl derivative ($\mathrm{H_2mod}$) and no *C*-methyl ones ($\mathrm{H_2mmd}$ or $\mathrm{H_2dmd}$). Methylated position of the product should be a side oxygen and not the central one, because the *O*-methyl derivative still showed the ability of chelate formation with beryllium(II) and copper (II) ions to give 1:2 chelate. NMR spectrum of the beryllium chelate indicated the presence of an *O*-methyl group in theligand.[17] The compound, however, could be isolated only in the form of a metal complex, and attempts to liberate the free ligand from the copper chelate were unsuccessful, and resulted in decomposition in an acid medium to give the original heptane-2,4,6-trione even at a lower temperature. This is not surprising because the enol-ether bonding usually degradates rather easily. The process of the decomposition of freed ligand could be traced by gas-liquid chromatography; a chloroform extract immediately after libera-

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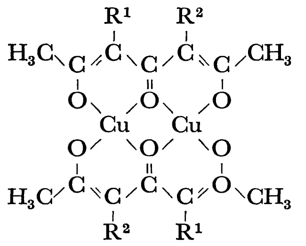
[17] Unpublished results.

tion from the copper chelate with an acid gave a single glc peak at $R_T=1.1$ min, and after about 10 min, glc showed four broad peaks in a shorter R_T range in additon to the original peak. Forty min after the glc again showed a single peak but at $R_T=4.1$ min, which was identical with that of heptane-2,4,6-trione. Additional glc peaks which appeared on the process from the *O*-methyl derivative to heptane-2,4,6-trione were not studied in detail, though they were apparently due to tautomers of the *O*-methyl derivative.

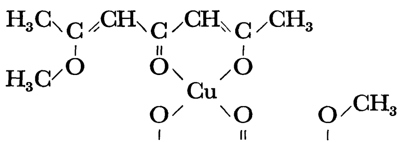
Thus, the coordination with metal ion prevented the cleavage of the enol-ether bonding in 2-methoxy-2-heptene-4,6-dione. Since the enol-ether group does not seem to be directly involved in the coordination with metal ion, the stabilization was presumed to be due to steric hindrance in nucleophilic attack of an anion to a protonated intermediate upon the cleavage of the ether bonding.

Infrared bands in the region 1600—1500 cm^{-1} could be assigned in a similar manner to those of heptane-2,4,-6-trione and its *C*-methyl derivatives. The band at 1635 cm^{-1} was due to an olefinic group connected to oxygen. No positive evidence could be obtained to suggest a macrocyclic chelate ring. The result also indicates that diazomethane attacked a side carbonyl group in heptane-2,4,6-trione and not the central one. Volatility of the copper chelate (130°C /5×10^{-1} mmHg) and solubility in organic solvents such as chloroform, ethanol, and methanol suggested the 1:2 copper chelate to be of a monomeric form containing a six-membered chelate ring as shown in structure III.



		R^1	R^2
IIa)	$Cu_2(daa)_2$	H	H
IIb)	$Cu_2(mmd)_2$	H	CH_3

Structure II



III) Cu(mod)$_3$

Structure III

Structure of Cu_2L_2 Chelates. The results of elemental analysis of the 1:1 heptane-2,4,6-trione chelate suggests the molecular formula Cu(daa). The infrared spectra of 1:1 chelates show multiplet bands in the region 1600—1500 cm^{-1}, which could be assigned to a coordinated carbonyl and an olefinic group involved in the chelate ring as in the case of 1:2 chelates. On the other hand, no characteristic absorption band can be observed in the range 1800—1600 cm^{-1}. This suggests that all the three carbonyl oxygen atoms are involved in coordination. If we consider that the ligand is planar through its conjugated double bond system, and that three carbonyl oxygen atoms eventually can not coordinate to the same metal ion, dimeric structure II becomes the most probable. Although the polymer structure could also be assigned to the chelate, the construction of molecular model gives rise to too great strain to be acceptable. The dimeric structure was also supported by the magnetic moment study down to the liquid helium temperature as well as the ESR study. The strong antiferromagnetism of the copper(II) chelate suggests the dimeric structure. A detailed magnetic study on this system has been recently reported by Baker and others.[11]

The powder reflection spectrum of $Cu_2(daa)_2$ shows one broad band at 14700 cm^{-1}, which suggests a slight distortion from planar structure. The construction of molecular model of $Cu_2(daa)_2$ also needs the displacement of copper ion slightly above or below the plane of ligands.

Interconversion of 1:2 and 2:2 Chelates. The mononuclear and binuclear copper chelates of heptane-2,4,6-trione and its monomethyl derivative are interconvertible, as can be understood from their synthetic procedures. Mononuclear 1:2 chelate can be converted into 2:2 chelate by procedure 5, and 2:2 chelate can be converted into 1:2 chelate by procedure 3. In general, a lower temperature in the presence of excess ligand favors $Cu(HL)_2$ type chelate and a higher temperature Cu_2L_2 type chelate. As no common solvent was found for both types of chelates, equilibrium study on this system was not undertaken. $Cu(Hdaa)_2$ and $Cu(Hmmd)_2$ can be converted into $Cu_2(daa)_2$ and $Cu_2(mmd)_2$ quantitatively by heating methanol solution at 30 and 60°C, respectively.

Facility to form 2:2 chelate of heptane-2,4,6-trione as compared with 3-methyl derivative can be related to the relative enolizability of uncoordinated carbonyl group in 1:2 chelate. Partial enolization of uncoordinated carbonyl group was suggested on bis(heptane-2,4,6-trionato)copper(II), no indication of enolization being observed on bis(3-methylheptane-2,4,6-trionato)-copper(II). Thus, 2:2 chelate of heptane-2,4,6-trione can be obtained at relatively lower temperatures. However, 2:2 chelate of methylated ligand needs a higher temperature to overcome the steric repulsion of methyl groups.

In the case of 3,5-dimethylheptane-2,4,6-trione, NMR study proved that this ligand could not take the *cis*-dienol form, responsible for the 2:2 chelate, because of the steric repulsion of methyl groups.[15] Thus, attempts to synthesize 2:2 chelate of dimethyl derivative have been unsuccessful so far.

Base Adducts of 2:2 Chelates. Chelates of binuclear Cu_2L_2 type are thermally stable. They are not soluble in most organic solvents except for strong coordinating solvents such as pyridine or dimethyl sulfoxide. Green chelates turn brown when they are dissolved in pyridine, from which pyridine adducts can be obtained as brown crystalline precipitates at higher concentration. The thermogravimetric investigation on the pyridine adducts proved that their composition is $Cu_2L_2Py_2$, in other words, each molecule of pyridine added to each copper ion, and that pyridine can be removed by heating the adduct at a relatively low temperature.

Infrared spectra and X-ray diffraction pattern of powdered sample before the addition and after the dissociation of pyridine were found to be identical. The molecular weight of 2: 2 chelates in pyridine determined by a vapor pressure osmometer was found to be 412 (calcd.: 407.4) for $Cu_2(daa)_2$ and 439 (calcd.: 436) for $Cu_2(mmd)_2$.

Visible absorption spectrum of pyridine solution and powder reflection spectrum of pyridine adduct showed a maximum at the same frequency of 13520 cm^{-1}, indicating that the coordinating structure around copper ion in pyridine solution does not differ from that in solid adduct. As regard the infrared spectrum of pyridine adduct, no absorption band due to uncoordinated carbonyl group could be observed, and new bands at 410 cm^{-1} and 386 cm^{-1}, possibly due to the deformation of pyridine ring and the streching mode of N-Cu bond respectively, were observed in addition to the bands observed in the pyridine-free complex.

The results suggest that the dissolution of the 2:2 chelates in pyridine does not destroy the binuclear structure, and that the addition of pyridine is a reversible process. Thus, the structure of pyridine adduct may be of pentacoordinate square pyramid around copper(II) ion, with pyridine molecule coordinating from one side of z-axis of copper ion.

The reversible addition of heterocyclic bases to copper β-diketonates in solution has been investigated extensively.[18] If the adducts were stable, they could be isolated as definite solid adducts. In the case of bis(acetylacetonato)copper(II), mono-4-methylpyridine adduct has been obtained but not with pyridine.[19] In the cases of copper chelates of trifluoro- and hexafluoroacetylacetone, very stable mono- and bis-pyridine adducts were obtained.[20,21] The relative stability in these base adducts can be interpreted by the electron donating property of the heterocyclic nitrogen as well as the electron withdrawing property of β-diketones.

The results of thermogravimetric analysis on pyridine and 4-methylpyridine adducts of the 2: 2 copper(II) chelate, as shown in Table 2, indicates a similar tendency as regards the electronic effect of the methyl group introduced on pyridine or heptane-2,4,6-trione, though the effect was not as great.

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