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Metal Chelates of Some β,δ-Triketone Homologues. Copper(II) Chelates of 2,6-Diacetyl-4-methylphenol, 2,2′-Dihydroxybenzophenone, 2-Acetoacetylphenol and 2-Acetyl-1,8-dihydroxynaphthalene[*1]

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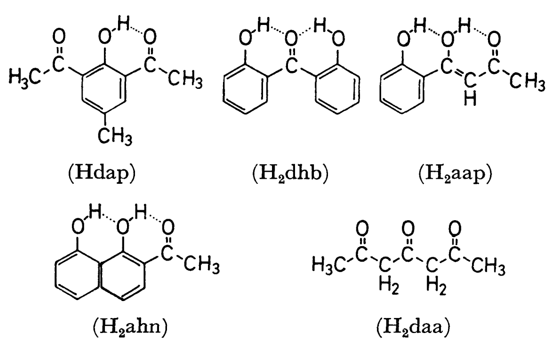
Copper(II) chelates of 2,6-diacetyl-4-methylphenol, 2,2′-dihydroxybenzophenone, 2-acetoacetylphenol and 2-acetyl-1,8-dihydroxynaphthalene were synthesized. The first and last ligands give only a mononuclear chelate of type CuL_2 respectively, whereas the second and third ones give a binuclear complex of type Cu_2L_2 in addition to the mononuclear complex. In the cases of the latter ligands two types of complexes are interconvertible and in a solution phase there exists an equilibrium between them. Higher temperature favors a binuclear form and lower temperature another form. Structures of the complexes are assigned with spectroscopic and thermogravimetric data.

In relation to our work on the metal chelates of 2,4,6-heptanetrione and related compounds,[1] the following four ligands have been synthesized and the properties of copper(II) chelates of the ligands have been investigated. The ligands synthesized are 2,6-diacetyl-4-methylphenol (Hdap), 2,2′-dihydroxybenzophenone (H_2dhb), 2-acetoacetylphenol (H_2aap) and 2-acetyl-1,8-dihydroxynaphthalene (H_2ahn), which are illustrated in Fig. 1. Although the compounds have been reported in literature, no systematic investigation concerning multidentate ligands was reported.


(Hdap) (H_2dhb) (H_2aap)

(H_2ahn) (H_2daa)

Fig. 1. Structure of the ligands.

The coordinating moiety of these ligands resembles that of 2,4,6-heptanetrione. However, features of the ligands are that the mono- or dienol tautomeric structures of the trione is fixed on certain oxygen atoms and that the free rotation of the coordinating site is partly restricted by fused aromatic rings. By analogy with 2,4,6-heptanetrione, the ligands are also expected to behave as bidentate as well as terdentate ligands. Thus, an investigation on the structures and properties of the metal chelates of the ligands may provide us with additional information for understanding 2,4,6-heptanetrione metal chelates.

In the cases of unsymmetrical ligands such as 2-acetoacetylphenol and 2-acetyl-1,8-dihydroxynaphthalene, it is also of interest to study which coordinating sites are preferred for metal chelation if they behave as bidentate ligands.

Experimental

Synthesis of the Ligands. All ligands were synthesized according to the methods given in literature, and were identified by means of their melting points, ultraviolet and infrared absorption spectra, nuclear magnetic resonance spectra and elemental analyses. Melting points and the appearence of the ligands are summarized in Table 1.

Synthesis of the Chelates. Lower temperature favors the mononuclear 1 : 2 chelate formation, while higher temperature favors the binuclear 2 : 2 chelate formation. Thus for preparation of 1 : 2 chelate, procedure A was followed. For preparation of 2 : 2 chelate, procedure B or C was followed.

Procedure A. To a methanolic solution of the ligand (2 mol), an aqueous solution of copper acetate (1 mol) was added with stirring below 15°C. Then pH of the solution was adjusted to 9 with aqueous ammonia. The resulting precipitates were recrystallized from ap-

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1) Fumio Sagara, Hiroshi Kobayashi and Keihei Ueno, This Bulletin, **41**, 266 (1968).

Table 1. Ligands synthesized

Ligand	Mp °C (reported mp)	Solvent for recryst.	Appearance*
Hdap	83.1—83.3 (83)[a]	Ligroin	Y-n
H_2dhb	59.2—59.8 (59—60)[b]	Ligroin	Y-p
H_2aap	88.1—88.8 (90.5—91.5)[c]	Benzene	Cl-n
H_2ahn	97.0—99.8 (101—103)[d]	Chloroform	Y-n unstable in air

a) K. W. Rosemund and W. Schunurr, *Ann. Chem.*, **460**, 85 (1928)

b) R. Richter, *J. prak. Chem.*, **28**, 285 (1883)

c) G. Wittig, *Ann. Chem.*, **446**, 173 (1926)

d) J. C. Overeen, *Rec. Trav. Chim. Pays-Bas*, **83**, 1017 (1964)

* Y: yellow, Cl: colorless, n: needles, p: plates

propriate solvents whenever possible.

Procedure B. Equimolar amounts of the ligand and the metal salt were dissolved in methanol and pH of the solution was adjusted to 9 with aqueous ammonia. The solution was then refluxed for a few hours, until the precipitate of binuclear 2 : 2 chelate came out.

Procedure C. A solution of the mononuclear 1 : 2 chelate in ethanol, chloroform, benzene or pyridine, was refluxed for a few hours, until the precipitates of 2 : 2 chelate came out. If the 1 : 2 chelate was not soluble enough in these solvents, the 1 : 2 chelate was placed in an extraction thimble of a Soxhlet extraction apparatus, and was extracted with hot benzene. The 2 : 2 chelate was precipitated in a refluxing flask.

The results on synthesis of the copper(II) chelates are summarized in Table 2.

Apparatus and Procedure. All melting points are uncorrected. Ultraviolet and visible spectra were measured with a Hitachi 124 recording spectrophotometer. Solid reflectance spectra were measured with a Hitachi EPU-2A spectrophotometer. Infrared absorption spectra and nuclear magnetic resonance spectra were recorded with a JASCO DS-301 spectrophotometer and a Varian A-60 operating at 60 MHz, respectively. Molecular weights were determined with a Mechrolab vapour pressure osmometer. Thermogravimetric analyses on the pyridine 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 a few drops of pyridine was added to it. After the sample was left at room temperature until its weight became constant, the temperature of the furnace was raised at a rate of 5°C per minute under atmospheric pressure, and the weight change was recorded automatically up to 150°C. The results are summarized in Table 3.

Table 3. Thermogravimetric analysis of the pyridine adducts

Starting material		Temp. where elimination occurs	Final-product
Composition	Color		
$Cu(dap)_2\cdot Py$	drak green	34— 54°C	$Cu(dap)_2$
$Cu(Haap)_2\cdot 2Py$	green	26	$Cu(Haap)_2\cdot Py$
		45— 62	$Cu(Haap)_2$
$Cu_2(aap)_2\cdot 3Py$	green	34— 60	$Cu_2(aap)_2\cdot 2Py$
		62—102	$Cu_2(aap)_2\cdot Py$
		102—108	$Cu_2(aap)_2$
$Cu(Hdhb)_2\cdot 2Py$	dark green	34—125	$Cu(Hdhb)_2$
$Cu_2(dhb)_2\cdot 6Py$	dark green	25—72	$Cu_2(dhb)_2\cdot Py$

Table 2. Copper (II) chelates

Chelates	Method of synthesis	Yield %	Molecular formula	Elemental analysis Found (Calcd.)			Appearance[a]
				C%	H%	M%	
$Cu(dap)_2$	A	27	$C_{22}H_{22}O_6Cu$	59.06 (59.25)	4.90 (4.97)	14.35 (14.25)	YO-n (Cl)
$Cu(Hdhb)_2\cdot 1/2\ H_2O$	A	35	$C_{26}H_{18}O_6Cu\cdot 1/2\ H_2O$	62.83 (62.58)	3.81 (3.84)	12.25 (12.74)	YB-pd
$Cu_2(dhb)_2$	B C	45 51	$C_{26}H_{16}O_6Cu_2$	57.27 (56.62)	3.11 (2.92)	21.78 (23.04)	YB-pd M.W. 512 (551)[b]
$Cu(Haap)_2$	A	63	$C_{20}H_8O_6Cu$	57.49 (57.48)	4.50 (4.34)	14.96 (15.21)	YG-n (Et)
$Cu_2(aap)_2\cdot H_2O$	B C	62 26	$C_{20}H_{18}O_6Cu_2\cdot H_2O$	48.01 (48.29)	3.65 (3.65)	24.98 (25.55)	G-n (Th-Lg) M.W. 442 (497)[b]
$Cu(Hahn)_2$[d]	A	38	$C_{24}H_{18}O_6Cu$	61.30 (60.69)	4.01 (4.32)	13.08 (13.38)	YB-pd M.W. 463 (466)[b]
$Cu_2(ahn)_2$[d]	B	35	$C_{24}H_{20}O_9Cu_3$[c]	45.01 (44.82)	3.33 (3.14)	29.93 (29.64)	B-pd

a) Appearance. YO: yellow orange, YB: yellow brown, YG: yellow green, G: green, B: brown, n: needles, pd: powder. Solvent for recrystallization in parentheses. Cl: chloroform, Et: ethanol, Th-Lg: tetrahydrofurane-ligroin mixture.

b) Molecular weight was determined in pyridine. The observed value is followed by the theoretical one in parentheses.

c) A possible structure is discussed in the text.

d) The reaction is carried out under nitrogen stream.

Results and Discussion

Copper(II) chelates of Hdap, H_2dhb, H_2aap and H_2ahn were prepared according to the procedure in Experimental. As in the case of 2,4,6-heptanetrione metal chelates,[2] the chelates of different ratio of metal to ligand were obtained according to the conditions of synthesis

The 1 : 2 chelates are obtained by procedure A, whereas the 2 : 2 chelates are obtained by either procedure B or C. In general, the 1 : 2 chelate is fairly soluble in various organic solvents such as ethanol, chloroform, benzene and pyridine. Thus, in most cases, they can be obtained as crystalline form by recrystallization from such solvents. On the other hand, the 2 : 2 chelates are hardly soluble in organic solvents except pyridine. The only exception is the 2 : 2 chelate of 2-acetoacetylphenol, which can be recrystallized from a mixture of tetrahydrofurane and ligroin. All chelates obtained do not show any definite melting points below 300°C.

As observed in the copper(II) chelates of 2,4,6-heptanetrione, the 1 : 2 chelate of the diprotonic ligands such as H_2dhb, H_2aap and H_2ahn can be converted into 2 : 2 chelates of the respective ligands, as described in the preparation of 2 : 2 chelates by procedure C. Reversely the 2 : 2 chelate can be converted into a 1 : 2 chelate when the solution of the 2 : 2 chelate in pyridine containing an excess of the ligand is kept at a lower temperature. Thus, the equilibrium seems to occur

$$2\mathrm{Cu(HL)_2} \rightleftharpoons \mathrm{Cu_2L_2} + 2\mathrm{L} \text{ (in pyridine)}$$

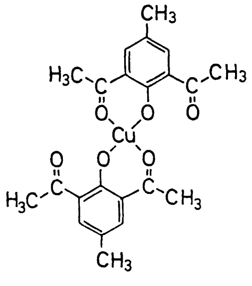
and the higher temperature favors the 2 : 2 chelate and lower temperature the 1 : 2 chelate.

Since the ligands chosen in this investigation are terdentate, there remains the possibility of their affording polymeric forms, especially in the case of the 2 : 2 chelates. The 1 : 2 chelates are, however, so soluble in various organic solvents that they are not likely to be of polymeric form. Moreover, the fairly fast rate of interconversion between the 1 : 2- and 2 : 2 chelates in pyridine suggests that the drastic rearrangement of the chelation is not likely to occur in the process of conversion in a solution phase. The results of the molecular weight determination of the 2 : 2 chelates in pyridine also support the monomeric form. Thus, there is no doubt that the 1 : 2- and 2 : 2 chelates are monomeric at least in a pyridine solution, and this may also be true in solid state. Although there is no positive reason to reject the possibility of affording the polynuclear chelates in solid state, a study with molecular models shows that the polymeric structures can be constructed only with heavy steric hinderance and strain, because free rotation of the coordinating sites is partly restricted by fused aromatic rings.

When the chelates are treated with pyridine, they easily form pyridine adducts, and the number of moles of pyridine per mole of the chelate varies from one to six depending upon the kind of ligand as summarized in Table 3. The reversible pyridine adduct formation is indicative of the vacancy of the coordinating sites of copper(II) on *z* axis. Two copper(II) ions in the chelate can accept at most four moles of pyridine. Thus, in the case of $Cu_2(dhb)_2 \cdot 6Py$, two of the six moles of pyridine are not coordinated to copper ions. It is also noted that the last one mole of pyridine does not dissociate up to 150°C. The stepwise dissociation of pyridine with increasing temperature is clearly observed in the chelates of H_2aap, whereas the pyridine on the rest of the chelates dissociates gradually.

Chelate of 2,6-Diacetyl-4-methylphenol (Hdap). The chelate prepared by procedure A is found to have the formula of $Cu(dap)_2$. As this ligand has only one dissociable proton, the binuclear chelate of type Cu_2L_2 can not be obtained even under the condition of procedure B or C. $Cu(dap)_2$ is obtained as well defined green yellow needles after recrystallization from aqueous methanol, and its formula is confirmed by elemental analysis.

The infrared spectrum of the free ligand is characterized by a broad band of ν_{O-H} at 3000 cm^{-1} and a doublet band of free and hydrogen bonded carbonyl groups at 1669 and 1640 cm^{-1}, respectively. The infrared spectrum of the copper chelate, on the other hand, shows no ν_{O-H} band, but still shows $\nu_{C=O}$ bands at 1670 and 1619 cm^{-1} in addition to the new bands at 1530 and 1520 cm^{-1} which are related to the coordinated carbonyl group.



(I) Structure I

From the results, structure I is proposed for the chelate $Cu(dap)_2$. However, the question remains whether the two ligands take *cis* or *trans* arrangement as regards the central metal ion.

Chelates of 2-Acetoacetylphenol (H_2aap). The free ligand may possibly exist as three tautomeric forms A, B and C. The solid H_2aap, however, seems to exist as form B or C, since a free carbonyl band at 1730 cm^{-1} which is observed in chloroform

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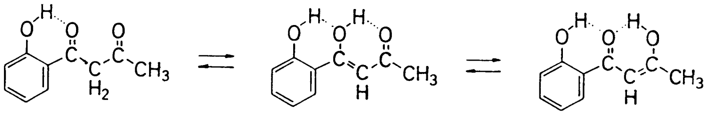
[2] Ref. 1. More details will be published elsewhere.

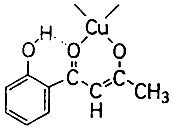


(A) (B) (C)

Scheme 1.

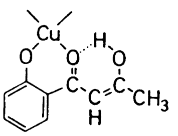
solution, can not be found in the spectrum of a solid sample. In the latter spectrum, absorption bands observed at 1680, 1615 and 1580 cm^{-1} can be assigned to those of the hydrogen bonded carbonyl and the conjugated olefinic groups.

The 1 : 2 chelate, which is obtained as yellow green needles by procedure A, is found to have the formula of Cu(Haap)_2. The infrared spectrum of the 1 : 2 chelate does not show a band due to the free carbonyl group, but shows new bands at 1570 and 1515 cm^{-1} which may be related to the coordinated carbonyl groups. From the above results, either of the following two structures, (II) and (III), can be proposed for the 1 : 2 chelate.



(II)

Structure II



(III)

Stucture III

Of the two structures, the chelating moiety of (II) resembles that of bis(benzoylacetonato)copper(II), and structure (III) resembles that of bis(*o*-hydroxyacetophenonato)copper(II). Comparison of the electronic spectra of Cu(Haap)_2 with those of the above two model compounds suggests the probable chelate structure of this compound. The results of the visible absorption spectra of the pyridine solution and the reflectance spectra of solid samples are summarized in Table 4.

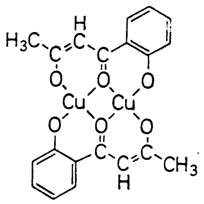
Table 4. Electronic spectra of the copper (II) chelates of 2-acetoacetylphenol, benzoylacetone and *o*-hydroxyacetophenone

Ligand of Cu (II) chelate	Visible absorption spectra in pyridine λ_{max} mμ, (log ε)	Solid reflectance spectra λ_{max} mμ
2-Acetoacetylphenol	680 (1.19), 353 (4.33)	640
Benzoylacetone	664 (1.92), 368 (4.48)	645
o-Hydroxyacetophenone	628 (2.01) 566 (2.14) 362 (3.90)	595

The bands in the range 500—600 mμ can be assigned to the ligand field *d–d* transition band, and the spectrum of Cu(Haap)_2 is more closely similar to that of bis(benzoylacetonato)copper(II) than that of bis(*o*-hydroxyacetophenonato)copper(II) which has two peaks in this region. Thus, it is very likely that the structure of Cu(Haap)_2 is that shown in II.

As to the question of the two ligands taking either *cis* or *trans* arrangement, the *trans* structure is more probable because the *cis* structure may suffer from the steric hinderance of phenolic protons.

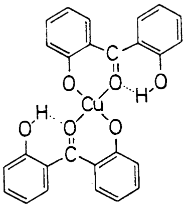
The binuclear chelate $\text{Cu}_2\text{(aap)}_2\cdot\text{H}_2\text{O}$ can be obtained either by procedure B or C as green needles, the yield being higher by procedure B. Molecular weight determined in pyridine solution supports the above formula. No significant difference in infrared spectra is observed between 1 : 2- and 2 : 2 chelates. Thus, it is likely that the structure of $\text{Cu}_2\text{(aap)}_2$ is that shown in IV.



(IV)

Structure IV

Chelates of 2,2′-Dihydroxybenzophenone (H_2dhb). The 1 : 2 copper(II) chelate is obtained as a yellow brown powder by procedure A, and elemental analysis supports the formula $\text{Cu(Hdhb)}_2\cdot 1/2\text{H}_2\text{O}$. The hydrogen bonded carbonyl band of the free ligand at 1630 cm^{-1} disappeared in the infrared spectra of the 1 : 2 chelate, and a new



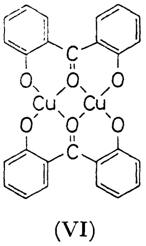
(V)

Structure V

band appearing at 1520 cm^{-1} is assigned to the coordinated carbonyl group. The results suggest structure V for the 1 : 2 chelate. The *trans* form is more probable than the *cis* form because of the steric hindrance of the phenolic protons.

The 2 : 2 copper chelate was obtained as yellow brown powder by procedure B or C, with a slightly higher yield by the latter procedure. The results of elemental analysis and molecular weight determination support the formula $Cu_2(dhb)_2$.

Infrared spectra of the 2 : 2 chelate in 1600—1500 cm^{-1} region differ from those of the 1 : 2 chelate, but structure VI is the most probable for this chelate. It has been reported that the hydrogen atoms at 6- and 6′-positions of the free ligand interfere with each other sterically.[3] Accordingly, the planer structure around copper atoms may be distorted to some extent.

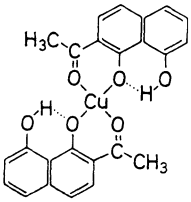


(VI)

Structure VI

Chelates of 2-Acetyl-1,8-dihydroxynaphthalene (H_2ahn). As this ligand is found to be sensitive to atmospheric oxygen, all the procedure with this ligand is carried out in a nitrogen stream.

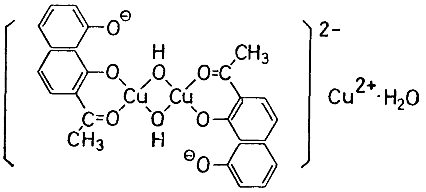
The 1 : 2 copper(II) chelate is obtained as yellow brown powder by procedure A, and elemental analysis as well as molecular weight determination supports the formula of $Cu(Hahn)_2$. Hydrogen bonded carbonyl band of the free ligand at 1640cm^{-1} disappears in the infrared spectrum of the 1 : 2 chelate, and a new band is observed at 1520 cm^{-1} which is assigned to the coordinated carbonyl groups. These results suggest structure VII for the 1 : 2 chelate. The *trans* form is more probable than *cis* form as discussed previously.



(VII)

Structure VII

An attempt to prepare a 2 : 2 chelate of 2-acetyl-1,8-dihydroxynaphthalene by procedure B, results in a chelate of 3 : 2 composition, whose empirical formula is found to be $C_{24}H_{20}O_9Cu_3$. In this procedure, when pH is adjusted to 9, a 3 : 2 chelate is obtained, whereas a 1 : 2 chelate is obtained when the reaction is carried out at pH 6—7. As the infrared spectrum does not show a sharp band at around 3600 cm^{-1}, it is not likely that the chelate contains copper hydroxide. In contrast to the chelates of 2,4,6-heptanetrione, 2-acetoacetylphenol and 2,2′-dihydroxybenzophenone where the interconversion of the 1 : 2- and 2 : 2 chelates is observed, the 3 : 2 chelate of 2-acetyl-1,8-dihydroxynaphthalene can not be converted into a 1 : 2 chelate. Furthermore, the 3 : 2 chelate is hardly soluble in pyridine, whereas 2 : 2 chelates of the other ligands are fairly soluble in pyridine. Thus, the 3 : 2 chelate may possibly be of an ionic complex or a highly polymeric form. One of the possible structures of this chelate may be something like that shown in VIII.



(VIII)

Structure VIII

The authors are grateful to the Ministry of Education for a grant-in-aid for scientific research.

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[3] J. R. Merrill, *J. Phys. Chem.*, **65**, 2023 (1961).